Tutorial
Room Grand Ballroom H-K - Session TS-SuA
Tutorial Session

Moderators: Prof. Seán Barry, Carleton University, Dr. Scott Clendenning, Intel Corporation

1:00pm **TS-SuA-1 Design Rules for Precursors and Why You Should Break Them*, Seán Barry,*** Carleton University, Canada **INVITED**

1:45pm **TS-SuA-4 A Brief Introduction to Low-Temperature Plasmas: Physics, Diagnostics, and Applications in Atomic Layer Processing*, Mari Napari,*** King's College London, UK **INVITED**

The wide use of plasmas in materials processing is due to two essential features of low-temperature plasma discharges, one is the capability to efficiently generate chemically active species, and the other is the formation of energetic ions, accelerated to energies up to hundreds of electron volts adjacent to the deposition or etching surfaces. Plasma-enhanced (or plasma-assisted) atomic layer deposition and etching (ALD, ALE) are considered to exploit mainly the first of these features, though the role of energetic ions in the processes should not be undermined.

Plasmas are complex environments and the comprehension of both the physical and chemical aspects of the plasma, and the plasma-surface interaction are important. The contribution of the different plasma species (radicals, ions, VUV/UV radiation) on the film growth or etching processes depend significantly on how the plasma is generated, as well as on reactor geometry and vacuum conditions. Therefore it is relevant to understand how these influence the plasma, and how to determine the optimal conditions for your plasma-enhanced atomic layer process, e.g. when high aspect ratio structures or sensitive substrate materials are required.

In this tutorial I will give a brief introduction to fundamental principles of partially ionized, chemically reactive plasma discharges and their applications in atomic layer processing. I will introduce the basic concepts of low-temperature plasmas, such as electron temperature and -density, plasma potential and particle flux across the plasma-surface sheath layer. I will also present a selection of useful plasma diagnostics techniques that can be used directly or indirectly to determine the plasma parameters. In the last part of my talk I will present the different types of plasma sources typically used in ALD/ALE reactors, and discuss their advantages and disadvantages using examples from recent published work on different plasma-enhanced ALD and ALE processes.

2:30pm **TS-SuA-7 The Application of Atomic Layer Deposition for Batteries*, Lei Cheng,*** Argonne National Laboratory **INVITED**

Atomic layer deposition (ALD) has found many applications and emerged as a useful technique for fabricating and improving the performance of energy storage devices, owing to the distinct advantages of the deposition method (conformality, compositional and thickness control, low reaction temperature) and the potential for roll-to-roll manufacturing. ALD has been used to synthesize and fabricate active components of batteries, such as oxide and organic electrodes. More commonly, ALD is used as a powerful surface and interface engineering tool to improve battery material properties. For example, it has been used to create artificial cathode electrolyte interfaces (CEI) to prevent transition metal dissolution from the cathode and prohibit parasitic side reactions resulting from surface electrolyte decomposition. In this tutorial talk, I will discuss examples and strategies for using ALD to improve battery performances in both state-of-the-art Li-ion batteries and next-generation batteries, such as Li-S and solid-state.

3:30pm **TS-SuA-11 Surface Reaction Mechanisms of Thermal and Plasma-Enhanced Atomic Layer Etching (Ale) Processes*, Satoshi Hamaguchi,*** Osaka University, Japan **INVITED**

Atomic layer etching (ALE) is a cyclic process of removing a monolayer or a very thin layer of material in each cycle. As the miniaturization of semiconductor devices approaches the atomic scale, the formation of device structures, especially those in three dimensions, on a material surface poses extreme challenges to manufacturing. ALE is considered to offer one of the most effective solutions to such challenges. ALE can be roughly classified into two categories. One is thermal ALE, where the energy to remove a thin layer in the desorption step is provided by thermal energy. In most cases, thermal ALE offers isotropic etching. The other is plasma-enhanced ALE (PE-ALE), which typically uses ion energy and momentum transfer from plasmas to the surface to remove a thin layer of material in the desorption step. PE-ALE is typically a uni-directional (i.e., anisotropic) etch. A well-known example of the former is the thermal ALE of metals, where organic molecules or organometallic molecules are used to remove metal atoms from the surface by the formation of metal complexes or ligand exchange. The latter examples include PE-ALE of silicon (Si)-based materials such as Si, silicon dioxide, and silicon nitride, by halogen, fluorocarbon, and hydrofluorocarbon plasma irradiation, respectively. Thermal, and therefore anisotropic, ALE of Si-based materials also exists. In this tutorial presentation, I will discuss the surface reaction mechanisms of such processes, referring to recent studies on this subject analyzed with numerical simulations as well as surface reaction experiments.

4:15pm **TS-SuA-14 Surface Functionalization of Powder Materials using Fluidized Bed Reactor ALD*, Se-Hun Kwon,*** Pusan National University, Republic of Korea **INVITED**

Surface functionalization plays an important role in various powder materials with large surface area to volume ratios. And, effective and precise surface functionalization of powder materials are essential for obtaining a desired properties in various industrial and scientific applications. Recently, atomic layer deposition (ALD) has emerged as a powerful technique for surface functionalization of powder materials due to its noteworthy merits such as atomically precise thickness and composition control of ultrathin films with extremely high uniformity. Up to now, various ALD systems using different types of reactors, including a static bed, agitated bed, and fluidized bed, have been developed to deposit coating materials on powder materials. A static bed reactor ALD is typically limited to a small amount of powders because it is difficult for the gas phase precursor to diffuse into the powder bed when a large amount of powder is utilized, leading to non-uniform coatings on the powder surfaces. Therefore, two competitive ALD systems, agitated bed and fluidized bed reactors (FBR)-ALD systems, are considered as more suitable setting for the ALD coating of powder materials. And, this tutorial aims at comprehensively reviewing the fluidized bed reactor (FBR)-ALD techniques. The main advantages of FBR-ALD are including the efficient gas transport for gas-solid interactions and well-mixed solid particles, which can provide precursor reactions with all the surface sites of powder materials and can be used for the production of large quantities of surface functionalized powders. Nevertheless, many challenges are still remaining in the field of FBR-ALD. In this tutorial, therefore, the basics principles of FBR-ALD will be firstly described, and then some technical challenges involved during the FBR-ALD process and recent efforts to overcome them will be discussed. Finally, some promising examples of surface functionalization of powder materials using FBR-ALD will be highlighted.

5:00pm **TS-SuA-17 Atomic Layer Deposition of Active and Passive Films for Electronic Devices*, John Ekerdt,*** University of Texas at Austin **INVITED**

This tutorial will provide the participants with an understanding of the principles that underpin atomic layer deposition (ALD) and will illustrate applications of these principles in the growth of films employed in electronic devices and in key processing steps in device manufacturing.This tutorial is designed to introduce these principles and provide a broad perspective to new workers and researchers to the ever-expanding area of ALD.This talk will cover ALD of dielectric materials, simple (binary) and complex (ternary/quaternary) oxides, and metals.

ALD is a chemical growth process that requires at least two different reactants, whose delivery to the growth surface is done in alternating steps with an intervening evacuation/purge step to restrict the reactions to the growing film surface.This talk will touch on the inorganic, physical, surface and materials chemistry that form the basis for precursor (reactant) selection and the general process approach.In general, the first reactant needs to adsorb in a self-limiting manner up to a monolayer of coverage – a key aspect that allows for conformal thin film deposition over planar surfaces and high aspect ratio 3D structures.The second reactant then reacts with what is adsorbed and converts it chemically into the compound of interest, such as an oxide, nitride, or metal, and presents a surface with reactive groups/sites that enable the first reactant to adsorb.Examples of these reactions and experimental approaches/analytical probes that are used to follow the steps and establish the process parameters (dose/exposure time, evacuation time, temperature) will be presented.ALD processes can be thermal in nature and/or one of the reactants can be plasma activated and examples of both will be discussed.

Atomic Layer Etching
Room Evergreen Ballroom & Foyer - Session ALE-SuP
Atomic Layer Etching Poster Session

ALE-SuP-1 Chemical Approaches to Atomically Controlled Etching of Tertiary Materials and van der Waals Solids*, **Marissa Pina**, M. Whalen, J. Xiao, A. Teplyakov,* University of Delaware

$CrPS_4$ is a 2D van der Waals material with layer-dependent ferromagnetic behavior. While monolayer $CrPS_4$ has a ferromagnetic out-of-plane spin orientation, alternating antiferromagnetic/ferromagnetic behavior was demonstrated for an even vs. odd number of layers. This interesting set of properties makes the material a potentially outstanding candidate for spintronic devices; however, obtaining a specific number of layers on any support surface is currently impossible. Mechanical exfoliation methods can reduce the number of layers to a certain extent, but more controlled methods will be needed to further reduce the thickness of the crystal to the monolayer thickness. Thus, atomically precise methods of etching would be extremely desirable for $CrPS_4$.

The problem with designing atomic layer etching (ALE) approaches for materials containing two or more elements is that the overall chemistry should be equally efficient in removing all the elements simultaneously. We have previously demonstrated that a very efficient method can be applied to etch a tertiary material CoFeB alloy with atomic precision, and it would be expected that for a layered material, such as $CrPS_4$, the van der Waals nature of interlayer interaction would make it easier to design a chemical method to remove the material layer-by-layer. In this work, $CrPS_4$ flakes were exfoliated onto a SiO_2 substrate from a single crystal. Atomic force microscopy was used to determine that the deposited flakes were up to 100 nm thick and several microns wide, with a wide size distribution of shapes and thicknesses. We first used XPS to evaluate the susceptibility of this material to oxidation and then, using an ultra-high vacuum chamber, we heated the sample and exposed it to a specific exposure of acetylacetone in what we define as a cycle. Repeating atomic force microscopy on the flakes, we found an average etch rate of 1.6 nm/cycle. Although the exact etching conditions have to be optimized and chemistry of the etching process has to be determined, these initial experiments promise a successful method for ALE of this material that can also possibly be applied to other van der Waals crystals.

ALE-SuP-2 Electron-Assisted Silicon Etching in an Inductively Coupled CF_4 Plasma via Low-Energy Electron Beam*, **Jiwon Jung**, C. Lim, C. Chung,* Hanyang University, Republic of Korea

Low-energy electron-assisted silicon etching is conducted using an inductively coupled CF4 plasma at a pressure of 4 mTorr. During silicon etching, a low-energy electron beam is generated and controlled by varying the electron acceleration voltage (0-60 V) on grid to assist silicon etching. Silicon etch rate is increased with increasing acceleration voltage, this is because electron beam energy is also increased. By using low-energy electron beam, low-damage etching can be achieved because mass of electron is smaller than that of ion. To observe the damage variation of silicon before and after the low-energy electron-assisted etching process, XPS measurement is conducted.

ALE-SuP-3 Damage-Free Graphene Etching by Ultra-Low Electron Temperature Plasma*, **Junyoung Park**, J. Jung, M. Kim, C. Lim, B. Seo, C. Chung,* Hanyang University, Korea

The effect of ultra-low electron temperature(ULET, T_e < 0.2 eV) on multi-layer graphene etching is investigated. During the etching process using plasma, problems such as substrate damage due to high ion bombardment energy occur, which have a fatal effect on process yield and reliability. In particular, high-strength and high-performance semiconductors are required in recent years, achieving precise etching without damage at the atomic scale is essential. To solve this problem, ULET plasma is generated whose electron temperature is about 20 times lower than that of the conventional inductively coupled plasma(ICP) (T_e ~ 4 eV), and damage-free etching using the ULET plasma is studied. Plasma-induced damage on the wafer is mainly caused by ion bombardment, and the ion bombardment energy is proportional to the sheath voltage. Since the sheath voltage is proportional to the electron temperature, the ion bombardment energy can be minimized by generating ULET plasma. To confirm the damage-free etching effect of ULET plasma, multi-layer graphene is exposed to conventional ICP and ULET plasma, respectively. In the case of graphene exposed to conventional ICP, the crystal structure of graphene is damaged by plasma. On the other hand, when exposed to ULET plasma at the same electron density and time as the conventional ICP, damage does not occur. This confirms that plasma damage due to ion bombardment may be removed using ULET plasma. The removal of the graphene layer was verified by Raman spectroscopy, and T_e was obtained by measuring the electron energy probability function (EEPF).

ALE-SuP-4 Anisotropic Atomic Layer Etching of Molybdenum by Formation of Chloride/Oxychloride*, **Yun Jong Jang**, D. Kim, H. Kwon, H. Gil, G. Kim, D. Kim, G. Yeom,* Sungkyunkwan University (SKKU), Republic of Korea

As the degree of integration of semiconductor devices increases, the line width between patterns of interconnects continues to decrease. In order to solve this challenge, Cu having low resistivity is currently used as an interconnect material with a barrier material in a damascene structure. But, Cu shows a rapid increase of resistivity in a critical dimension (CD) of less than 10 nm due to long mean free path in addition to a limitation in scaling down due to the requirement of a barrier material. Therefore, need for a new material such as Mo, Co, Ru, etc. to replace Cu has been increased to solve this problem. In this study, atomic layer etching (ALE) of Mo has been carried out by using O_2 and Cl_2 as adsorption gases and Ar^+ ion beam for desorption. By using inductively coupled plasma (ICP)-type ion beam for desorption step, it was possible to precisely control the ion energy during ALE. In the adsorption step, the surface of Mo was modified into $MoCl_x$ and MoO_xCl_y using O_2 and Cl_2. In the desorption step, the modified Mo surface was removed using an Ar^+ ion beam. After the process, physical and chemical damage on the surface was analyzed using X-ray photoelectron spectroscopy (XPS), atomic force microscope (AFM), etc.

ALE-SuP-5 New Oxidants for Cu ALE*, **Persi Panariti**, A. Hock,* Illinois Institute of Technology

Atomic Layer Etching of copper is an important challenge when it comes to scaling down electronic devices to sub-10 nm dimensions. ALE of copper is of considerable interest, because copper is widely used an interconnect material for integrated circuits, due to its excellent electrical conductivity, good electromigration resistance and low cost.

ALE of metallic surfaces typically proceeds in two steps, the first being surface activation, followed by the introduction of an organic ligand to yield a volatile metal complex. ---The activation step (oxidation) is especially important for enabling ALE, because metallic Cu surfaces are chemically inert. Another important factor is the ability to control the oxidation *strength* and *reactiondepth* of the oxidizing agent. Several oxidants for metallic Cu surfaces have been reported in the literature, such as ozone, hydrogen peroxide, oxygen plasma etc. These oxidants are aggressive and have numerous issues, such as oxidizing up to several nm of Cu and increasing surface roughness, especially at elevated temperatures. These are undesirable outcomes for ALE, because the oxidized copper surface should remain as uniform as possible after oxidation, so that the etch step yields a smooth and conformal Cu surface. Thickness of greater than a few nm can be incompatible with scaling. Therefore, there is a need for more tunable oxidants, that allow for better control of the oxidation strength and depth of Cu thin films. We have investigated several oxygen atom transfer reagents that formally transfer an oxygen atom to a Cu surface. The oxidation strength of these reagents was probed by *in-situ* X-Ray Absorption Spectroscopy (XAS) on Cu nanoparticles, as well as in real ALE conditions, where the ALE reactions were studied by *in-situ* QCM.

ALE-SuP-6 Atomic Layer Etch Development of Noble Metals Cu and Pt for Mram Technologies*, **Omar Melton**, R. Opila,* University of Delaware

Magnetoresistive random-access-memory (MRAM) is a leading option for non-volatile digital data storage. Due to the combination of the broad range of materials in the device, improving the fabrication methods is challenging. Currently, MRAM technologies mainly rely on epitaxial, atomic layer deposition (ALD), methods to generate the thin layers necessary for ideal performance. Atomic layer etching (ALE), as a time reversed ALD method, has potential for accurately etching nearly all materials, particularly those that cannot be deposited with precision. Herein, we propose the etching of noble transition metals, copper (Cu) and platinum (Pt), and etch stop testing of the tunneling barrier (MgO). The etch is conducted using a thermal approach, rather than commonly used plasma methods, where the film is etched by sequential dosing with to two different chemical moieties, chlorine and acetylacetone (acac). Thus, permitting kinetic factors to overcome thermodynamic limitations, thereby developing a controlled etch driving towards one atomic layer at a time. Results demonstrate that Cu is etched under comparatively mild conditions, whereas Pt requires more aggressive temperatures and pressures to facilitate the etch.Furthermore, MgO exhibited resistance to etching upon exposure to these conditions.

ALE-SuP-7 Layer-by-Layer Etching of 2D Palladium Diselenide, ***Ji Eun Kang****, Y. Ji, S. Choi, G. Yeom,* Sungkyunkwan University (SKKU), Republic of Korea

Recently, there has been a widespread interest in developing high-performance broad band photodetector of 2D materials for sensing, imaging, and spectroscopy. Among them, Palladium diselenide ($PdSe_2$) has emerged as a promising candidate for the future device application due to its large tunable band gap (from 0 eV to 1.3 eV), high electron mobility, and outstanding environmental stability. To obtain mono to multi-layer of $PdSe_2$, various methods such as exfoliation, chemical vapor deposition, and etching can be used. However, in the case of exfoliating or deposition, it is difficult to precisely control the layer, and, in the case of reactive ion etching, it may cause unwanted structural damage in $PdSe_2$ because $PdSe_2$ has a “puckered” structure. In addition, its interlayer coupling is strong, so it can be easily transformed from $PdSe_2$ semiconducting phase to $PdSe_{2-x}$ metallic phase by ion irradiation. In this study, $PdSe_2$ was removed layer-by-layer without damage by applying cyclic isotropic etching through oxidation and organic vapor treatment. And it was confirmed that the etching was performed precisely one layer per one cycle without damaging the $PdSe_2$ puckered structure.

ALE-SuP-8 Cyclic Dry Etch Process of SiO_2 using H/F radicals and Methanol Vapor, ***HaeIn Kwon****, H. Gil, D. Kim, Y. Jang, D. Kim, G. Kim, D. Kim, G. Yeom,* Sungkyunkwan University, Republic of Korea

In the cleaning of deep contact holes, wet etching process is generally used, but there are issues such as inability to etch the bottom of the deep contact holes in nano-size patterns. Therefore, new dry cleaning process is necessary to replace the existing wet etching process for next-generation semiconductor devices. Previously, as dry cleaning processes (or as isotropic etching processes) of SiO_2 for deep contact holes, HF/NH_3 vapor process or the NF_3/NH_3 plasma process has been investigated. However, ammonium salt formed in the process using NH_3 can form solid powders and it may form particles in the process chamber. Therefore, in this study, H/F radicals and Methanol vapor were used for the isotropic cyclic etching of SiO_2 to obtain high selectivity of SiO_2 over Si_3N_4 and Si. HF was formed using a NF_3/H_2 remote plasma and, to remove the F radicals, methanol vapors were injected using shower ring located at the outside the plasma discharge region. Under the optimized conditions, the etching depth per cycle of SiO_2 was about ~13 nm/cycle and the selectivity with Si_3N_4 and Si were over 50 and 20 respectively. Surface chemistry and roughness were investigated at each process step using XPS (X-ray photoelectron spectroscopy), FT-IR (Fourier-Transform Infrared Spectroscopy), and AFM (Atomic Force Microscope).

ALE-SuP-9 Quantum Chemistry Modeling of Plasmaless Anisotropic Etching of Silicon by F2 Molecule, ***Yuri Barsukov****, O. Dwivedi, S. Jubin, I. Kaganovich,* Princeton University Plasma Physics Lab

Anisotropic etching is often used in the semiconductor industry. One of the possible applications is silicon nano-scale texturing for black silicon production. Plasmaless etching can be used for surface texturing if the etch rate depends on the crystal surface orientation and, as a result, the surface is removed faster in one crystal surface direction compared to another. It was experimentally observed that F2 molecules preferentially etch silicon on (100) and (110) faces but very little on (111) at room temperature. We performed quantum chemistry modeling of this process by studying the reaction of F2 dissociative adsorption on fluorinated Si(100), Si(110), and Si(111) surfaces. The reaction probabilities were calculated using DFT (density functional theory) in combination with transition state theory. We established that the energy barrier of F2 dissociation on the Si(111) surface is significantly higher than on Si(100) and Si(110). The reason for high reactivity on Si(100) and Si(110) is that all Si atoms on fluorinated (100) and (110) oriented surfaces are bonded with fluorine atoms. The passivating F atoms attract electrons from Si atoms and, as a result, all Si atoms are positively charged. At the same time, half of the atoms on the fluorinated Si(111) surface are negatively charged, because they have no bonds with the fluorine atoms. The negatively-charged Si atoms on Si(111) create an additional repulsive force with the partly negatively-charged F2 molecule during the dissociation and increase the reaction barrier. Assuming that F2 dissociation is the rate-determining step of the etching process, we compared the calculated rate of F2 dissociation on Si(100) and measured the etch rate of Si(100) by F2. The calculated rate of dissociation matches experimental etch rate well.

ALE-SuP-10 Atomic Layer Etching of Mo with Surface Fluorination and Ion Bombardment, ***Yongjae Kim****, H. Kang, H. Ha, H. Chae,* Sungkyunkwan University (SKKU), Republic of Korea

Resistance of Cu significantly increases in the line width of interconnect below 10 nm due to the electron scattering in the grain boundary and side wall, and the resistance can be reduced by replacing Cu with alternative metals such as Co, Mo, and Ru, which have lower electron mean free path compared to the Cu. [1, 2] Among them, Mo is strong against the electromigration than the Co and Ru due to the highest melting point and cohesive energy. Interconnect metal line based on Mo can be fabricated with reactive ion etching (RIE) due to low boiling point of molybdenum fluoride and ruthenium fluoride compared to the copper fluoride. However, RIE is facing challenges in making nanometer scale patterns in terms of precise etch rate control and surface roughness. Atomic layer etching (ALE) can remove layers with atomic scale precision, low surface roughness, and excellent uniformity compared to the RIE.

In this work, ALE process was developed for Mo in an inductively coupled plasma (ICP) reactor. The Mo surface was fluorinated with C_4F_8 or CHF_3 plasmas, and fluorinated surface was etched by ion bombardment using Ar plasma. The C_4F_8 plasma generates fluorine-rich fluorocarbon layer on the Mo surface compared to the CHF_3 plasma. Etch per cycle (EPC) of Mo was investigated with dependence of ion energy and etching time. ALE window, or constant EPC was observed in the energy range of 100 ~ 225 V for Mo. The EPC of Mo was determined to be 2.8 nm/cycle for C_4F_8 plasma and 0.8 nm/cycle for CHF_3 plasma in the ALE window region. Etch residues and surface roughness were compared with radical etching, RIE, and ALE. Lowest etch residues and surface roughness were confirmed with ALE process compared to the radical etching and RIE.

References

[1] H.-W. Kim, Electronics 11, 2914 (2022)

[2] S. Decoster, E. Camerotto, G. Murdoch, S. Kundu, Q. T. Le, Z. Tőkei, G. Jurczak and F. Lazzarino, J. Vac. Sci. Technol. B 40, 032802 (2022)

Keywords: Plasma atomic layer etching, Molybdenum, ALE window, Etch residues, Surface roughness

ALE-SuP-11 Thermal Atomic Layer Etching of Palladium with Chlorination and Ligand Volatilization, ***Hojin Kang****,* School of Chemical Engineering, Sungkyunkwan University (SKKU), Korea (Democratic People's Republic of)*; Y. Kim,* SKKU Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University (SKKU), Korea (Democratic People's Republic of)*; A. Cho,* Department of Chemical and Biomolecular Engineering Korea Advanced Institute of Science and Technology (KAIST), Korea (Democratic People's Republic of)*; H. Jung,* Department of Chemical and Biomolecular Engineering Korea Advanced Institute of Science and Technology (KAIST) Daejeon, 34141, Republic of Korea3, Korea (Democratic People's Republic of)*; S. Cho, H. Chae,* School of Chemical Engineering, Sungkyunkwan University (SKKU), Korea (Democratic People's Republic of)

Palladium (Pd) hydrogen sensors operate by the change in electrical resistance according to volume expansion [1]. Thinner Pd leads to shorter paths for hydrogen gas molecules, resulting in lower hydrogen concentration and increased sensitivity of the sensor for volume expansion. Conventional wet and dry etch processes face challenges in achieving precise thickness control and uniformity [2]. Atomic layer etching (ALE) processes can remove sub-nanometer layers with precision [3]. In this work, thermal ALE process for Pd was developed with surface chlorination with Cl_2 plasma and ligand volatilization with NH_3 gas in a capacitively coupled plasma (CCP) reactor. In the chlorination step, the Pd surface was converted into $PdCl_2$. The thickness of $PdCl_2$ was increased from 1.0 nm to 2.9 nm as the process temperature increased from 25 to 300 °C, and that of $PdCl_2$ was saturated to 1.6 nm after 30 seconds of Cl_2 plasma time at a process temperature of 150 °C. In the ligand volatilization step, the $PdCl_2$ layer was removed with ligand volatilization using NH_3 gas at the temperatures above 150 °C. The etch per cycle (EPC) of Pd was in the range of 0.8~1.6 nm/cycle with increasing NH_3 gas injection time, and the EPC was saturated to 1.6nm after 30 seconds of NH_3 injection time. The surface roughness increased from 0.3 nm to 0.4 nm after 20 ALE cycle.

ALE-SuP-12 Plasma Enhanced Atomic Layer Etching of Zirconium Oxide using Plasma Fluorination and Ligand Exchange with $TiCl_4$, ***Hyeongwu Lee****, Y. Kim, H. Ha, H. Chae,* Sungkyunkwan University (SKKU), Republic of Korea

Dynamic random access memory (DRAM) capacitor consists of electrodes and dielectric materials, and the dielectric thickness has been continuously reduced to increase capacitance. However, reducing the dielectric dielectric

thickness also increases the leakage current. The leakage current can be decreased by applying thin crystalline ZrO_2 film, which has a high dielectric constant of 39. A thin crystalline ZrO_2 film can be produced by depositing a thick crystalline film and then using atomic layer etching (ALE) to reduce the film thickness. Thermal ALE can precisely control the etch depth at the atomic scale and remove materials in every direction. In this work, a thermal ALE process was developed for ZrO_2 with two steps of plasma fluorination and ligand-exchange with titanium chloride($TiCl_4$). In the fluorination step, ZrO_2 surface was fluorinated with fluorine-containing plasmas to form zirconium oxyfluoride. The formation of Zr-O-F bond was confirmed by X-ray photoelectron spectroscopy analysis. In the ligand exchange step, the fluorinated layer was removed with $TiCl_4$. The etch per cycle of ZrO_2 is saturated at 1.3 Å/cycle after 60 seconds of $TiCl_4$ exposure time. Post plasma treatment was developed to remove fluorocarbon residues on the surface with O_2 and NH_3 plasmas after ALE process. The root mean square (RMS) roughness of ZrO_2 decreased from 0.81 nm after 30cycles of ALE to 0.64 nm after post plasma treatment.

Plenary Session
Room Grand Ballroom A-G - Session PS-MoM

Plenary Session

Moderators: Prof. Seán Barry, Carleton University, Dr. Scott Clendenning, Intel Corporation, Prof. Dr. Steven M. George, University of Colorado at Boulder, Thorsten Lill, Lam Research Corporation

8:45am **PS-MoM-1 ALD Opening Remarks***, S. Barry,* Carleton University, Canada*; S. Clendenning,* Intel

9:00am **PS-MoM-2 ALD Plenary Lecture: Decades of ALD Research – Targets Upside Down***, **Markku Leskela**,* University Helsinki, Finland **INVITED**

ALD (Molecular Layering ML, Atomic Layer Epitaxy, ALE) research has been carried out for decades. The basic principle has been to deposit homogeneous films in a controlled way all around the substrate. The sequential and saturative growth enables the growth of conformal thin films on structured surfaces. The unique properties of ALD have enabled the fast growth of this technology during the last 15 years especially in microelectronics.

Since the early days, many things have changed in ALD research and applications. The main target is not always the deposition of homogeneous, pinhole-free films allover on the substrate. Instead, the aim can be area selective deposition[1], deposition of nanoparticles[2] or reverse ALD, i.e. Atomic Layer Etching (ALE)[3]. The thin film material selection has also expanded from oxides, chalocogenides and nitrides to metals, polymers and inorganic-organic hybrid materials (Molecular Layer Deposition, MLD)[4].

Metal films show often delayed nucleation on oxide surfaces. In platinum group metal case the reason is the oxidative mechanism which utilizes the active oxygen on the metal surface in removal of the organic ligands. This obvious disadvantage in film growth process is successfully applied in fabrication of metal nanoparticle catalysts.

Area selective deposition is coming extremely important when the feature sizes in microelectronics are shrinking. Patterned surfaces contain chemically different areas and area selective ALD (ASD) utilizes these differences to get growth only on the desired areas. Several approaches have been developed for ASD, such as activation of the growth areas, the use of self-assembled monolayers (SAM) or small molecule inhibitors (SMI) to block the growth on unwanted areas. The most attractive ASD process is the inherent selective growth. In that process the precursor molecule selectively adsorbs on the desired areas leaving the other areas bare.

We have recently studied superconformality that is beyond ALD.[5] It is based on capillary/curvature selective vapor deposition, which is able to coat or fill surfaces that have been previously hardest-to-reach in all vapor deposition techniques. It utilizes capillary condensation and targets primarily cracks, narrow interstices, ledges, and even ink-bottle-shaped nanopores.

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2. J.L. Lu, J.W. Elam, P.C. Stair, Surf. Sci. Repts. 71 (2016) 410-472.

3. S.M. George. Acc. Chem. Res. 53 (2020) 1151-1160.

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5. V. Lovikka, Adv. Mater. Interfaces 9 (2022) 2101314.

10:15am **PS-MoM-7 ALE Opening Remarks***,*

10:30am **PS-MoM-8 ALE Plenary Lecture: The Need for Atomic Layer Etching in the Angstrom Era***, **Tristan Tronic**,* Intel Corporation **INVITED**

Atomic layer etching (ALE) processes have been sought by semiconductor manufacturers in order to keep pace with the demands of Moore's Law scaling, because of their promise of atomic-scale control of etching and the possibility of extreme material selectivity. Progress has been made rapidly over the last decade, and pathways now exist for selective etching a range of dielectrics, semiconductors, and conductors at the nanometer scale and below.

In this talk, we will discuss the role that ALE can play in enabling the next era semiconductor scaling. As the semiconductor industry now enters the 'Angstrom Era' of scaling, shrinking device dimensions and increasingly vertical device architectures drive a need for ALE processes that has never been greater. Continued scaling of transistor gate pitch will drive a shift to 'Gate-All-Around' or 'RibbonFET' structures, in which semiconductor nanosheet channels are completely surrounded by gate dielectric and metal contact. RibbonFET structures open the door to further density scaling by stacking monolithically N-MOS and P-MOS vertically.[1] Fabricating such structures will require etch processes with extreme selectivity and nanometer-scale control at increasingly high aspect ratios, strengths of ALE processes.

The next era of scaling will require more than new transistor structures, it will also require new materials to continue to drive performance. These new materials will in term require new etch innovation to enable their integration, and some of these possible materials and opportunities for ALE to meet these requires will be explored in this talk. Transition metal dichalcogenides (TMDs) have been proposed as a path toward continued channel thickness scaling beyond the limits of Si.[2] Controlled etching in the presence of '2D' channel materials of <1 nm thickness will require etch process controlled that ALE is ideally suited to achieve.

[1] S. Datta et al. "Toward attojoule switching energy in logic transistors" *Science* 378, 2022, pp. 733-740

[2] C. J. Dorow et al. "Gate length scaling beyond Si: Mono-layer 2D Channel FETs Robust to Short Channel Effects" *2022 International Electron Devices Meeting (IEDM)*, San Francisco, CA, USA, 2022, pp. 7.5.1-7.5.4

11:15am **PS-MoM-11 ALD 2023 Innovator Awardee Talk: Not Like an Apple - Progress in Understanding Atomic Level Processing at the Atomic Scale***, **Simon Elliott**,* Schrödinger, Ireland **INVITED**

In this talk, we will dip into stories about how simulations have advanced our understanding of the growth mechanisms of ALD, and lately of ALE too. We will also sketch out work on nucleation onto substrates, metal deposition, plasma-surface reactions and precursor design. Building on this, simulations are now showing how to control continuous versus self-limiting processes, and deposition versus etch.

We will emphasize how collaboration has been the main driver of this work, always checking and challenging the relevance of the model results for actual experiments. The wider uptake of atomic-scale modelling as a research tool is confirming its usefulness and impact.

As long as computer power continues to snowball, the future for modelling process chemistry is bright. We are looking forward to finding improved precursors through the semi-autonomous exploration of chemical space. Machine-learning techniques are opening up areas that were out-of-bounds to simulations based on physical laws, such as prediction of complex properties and increased accuracy in interatomic potentials for large systems

11:45am **PS-MoM-13 Sponsor Preview***,*

ALD Fundamentals
Room Grand Ballroom A-G - Session AF-MoA
Precursors and Processes

Moderators: Prof. Seán Barry, Carleton University, Dr. Scott Clendenning, Intel Corporation

4:00pm **AF-MoA-11 Precursors for Photoassisted Area Selective Deposition on Self Assembled Monolayers***, B. Das, R. Singh, C. Brewer,* University of Florida*; R. Holliday, A. Walker,* University of Texas at Dallas*; **Lisa McElwee-White**,* University of Florida **INVITED**

Photoassisted chemical vapor deposition (PACVD), or photochemical CVD, is a technique that can be used for metallization of thermally sensitive substrates such as patterned self-assembled monolayers (SAMs), providing a potential route to area selective deposition (ASD) through different reactivity with the terminal functional groups of the SAM.In this project, photochemical dissociation of the precursor occurs in the gas phase and is dependent upon the photochemical and subsequent thermal reactivity of the precursor.The reactivity is controlled by the excited state properties and bond dissociation energies of the precursor and can be assessed by determining quantum yields for starting material disappearance and appearance of ligand loss products. Screening for the decomposition efficiency of potential precursors for PACVD can be used in a downselection process before deposition experiments begin.

Readily available Ru and Mn compounds, including (η^3-allyl)Ru(CO)$_3$X, (η^4-diene)Ru(CO)$_3$ and RMn(CO)$_5$ complexes, have been assessed for their potential use in ASD by PACVD.Precursor design, electronic structure, and photochemical reactivity of the complexes will be discussed in the context of the results of PACVD of Ru or Mn on functionalized SAMs.

4:30pm **AF-MoA-13 Reductive Thermal ALD of Pd and Au Thin Films***, **Anton Vihervaara**, T. Hatanpää, H. Nieminen, K. Mizohata, M. Chundak, M. Ritala,* University of Helsinki, Finland

Gold and palladium thin films have many potential applications in microelectronics, protective coatings, catalysis and MEMS. Many ALD processes, especially for noble metals, are either highly oxidative or plasma enhanced. While these approaches to the deposition of metal thin films do have their advantages, they also impose challenges. Thus, reductive thermal processes are needed as alternatives. 1,4-bis(trimethylsilyl)-1,4-dihydropyrazine[1] and 1,4-bis(trimethylgermyl)-1,4-dihydropyrazine[2] ((Me$_3$Si)$_2$DHP and (Me$_3$Ge)$_2$DHP) are both relatively novel reducing agents with only few reported ALD processes. In our recent research, we developed a low temperature ALD process for nickel using NiCl$_2$(PEt$_3$)$_2$ and (Me$_3$Ge)$_2$DHP.

In this study, ALD of gold[3] and palladium was realized by combining AuCl(PEt$_3$)with (Me$_3$Ge)$_2$DHP, and PdCl$_2$(PEt$_3$)$_2$with (Me$_3$Si)$_2$DHP. High purity gold films were successfully deposited at 180 °C. Metallic palladium was also deposited at the same temperature. ALD characteristics were confirmed and saturative growth achieved with these processes. While the gold films were extremely pure having less than 0.5 at.% of impurities, Pd films had significantly more of carbon and phosphorus (14 and 5 at.%, respectively). This is likely caused by decomposition of the PEt$_3$ ligands, catalyzed by the Pd surface. However, since neither film had any chlorine, we can conclude efficient reduction of the metal ions. The resistivities of the films correlated with the impurity contents. The gold films had resistivities very close to the bulk value, while the Pd films had much higher resistivities. The gold process had a growth rate of 1.7 Å/cycle, while for the Pd it was 0.4 Å/cycle. When PdCl$_2$(PEt$_3$)$_2$ and (Me$_3$Ge)$_2$DHP were combined, surprisingly, PdGe$_x$ films were obtained.

Based on these and our earlier experiments, we have successfully extended the combination of volatile metal chloride precursors and DHP-type reducing agents, originally demonstrated with (Me$_3$Si)$_2$DHP by prof. Winter and co-workers, as an avenue for reductive, oxygen-free thermal ALD of metals. We have also established the applicability of AuCl(PEt$_3$)and PdCl$_2$(PEt$_3$)$_2$ in ALD processes, both being valuable additions to the slim library of proper ALD precursors for these metals.

(1) Klesko, J. P. et al. *Chem. Mater.***2015**, *27* (14), 4918–4921. https://doi.org/10.1021/acs.chemmater.5b01707.

(2) Vihervaara, A. et al. *Dalt. Trans.***2022**, *51* (29), 10898–10908. https://doi.org/10.1039/D2DT01347A.

(3) Vihervaara, A. et al. *ACS Mater. Au***2023**. https://doi.org/10.1021/acsmaterialsau.2c00075.

4:45pm **AF-MoA-14 Phosphorus Zintl Species as ALD precursors for Metal Phosphide Thin Films***, **Paul Ragogna**, J. Bentley,* Western University, Canada*; E. Goodwin,* Carleton University, Canada*; J. Lomax,* Western University, Canada*; B. Van Ijzendoorn, M. Mehta,* University of Manchester, UK*; S. Barry,* Carleton University, Canada

Atomic Layer Deposition (ALD) is a thin film deposition technique in which precursors sequentially saturate a substrate surface in a self-limiting reaction. This nanoscale process enables the tuning of instrument parameters to synthesize thin films of controlled thickness which results in varied physical and electronic material properties.[1] Metal phosphide thin films can be prepared by vapour deposition techniques using various combinations of metal and phosphorus precursors, and these materials have applications in microelectronics, catalysis, and energy storage.[2,3] Group 13 and 14 materials such as GaP, InP, and GeP possess bandgaps that are amenable to photovoltaic and transistor applications and are derived from PH$_3$, an extremely toxic and pyrophoric reagent requiring specialized facilities. [4] Heptaphosphide (P_7^{3-}) is a relatively easy to prepare Zintl species with various binding modes possible with an electron-deficient metal,[5] and given its structural difference from PH$_3$, a diverse series of metal phosphide film compositions can be produced. In this context, the thermal properties and utility of P$_7$(SiMe$_3$)$_3$ as a phosphorus precursor combined with Group 13 species to produce metal phosphide films were investigated. The P$_7$(SiMe$_3$)$_3$ cluster is sufficiently robust up to ~250 ºC (by DSC) and the precursor also has virtually no residual mass as measured by TGA, and an extrapolated volatilization temperature at 1 torr (T_v) of ~130 ºC. The volatilization and saturative behaviour of the precursor was analyzed by QCM which demonstrated saturation of an Al$_2$O$_3$ crystal to ~16.32 ng/cm^2. As an example of the applicability of P$_7$(SiMe$_3$)$_3$, an ALD processes was performed with P$_7$(SiMe$_3$)$_3$ and AlMe$_3$ with the investigation of other secondary precursors currently on-going. The resulting materials were investigated using quartz crystal microbalance, XPS, ToF-SIMS, AFM and SEM.

[1]Miikkulainen, V. *et al. J Appl. Phys.* **2013**, 113, 021301; [2] Shi, Y. *et al. Chem. Soc. Rev.*, **2016**, *45*(6), 1529–1541; [3] Callejas, J. F. *et al. Chem. Mat.*, **2016**, *28*(17), 6017–6044;[4] Lu. Y. *et al. RSC Adv.*, **2016**, 6, 87188; [5] Turbervill, R. S. P. *et al*. *Chem. Rev.*, **2014**, *114*(21), 10807–10828.

5:00pm **AF-MoA-15 Investigation of Discrete Reactant Feeding for Atomic Layer Deposition of In$_2$O$_3$ Using Novel Liquid Alkyl-Cyclopentadienyl Indium Precursor***, **Hae Lin Yang**, H. Kim,* Hanyang University, Republic of Korea*; T. ONO, S. KAMIMURA, A. EIZAWA, T. TERAMOTO, C. DUSSARRAT,* Air Liquide Laboratories, Japan*; J. Park,* Hanyang University, Republic of Korea

An interest in indium oxide (In$_2$O$_3$)-based metal oxide semiconductors, such as In$_2$O$_3$, indium-gallium oxide (IGO), indium-zinc oxide (IZO), and indium-gallium-zinc oxide (IGZO) for the use of electronic devices has been increased. In particular, In$_2$O$_3$ is spotlighted as a material capable of controlling oxygen vacancies and impurity concentrations to achieve higher carrier mobility[1]. Therefore, an investigation for a novel indium precursor for ALD which is able to obtain a wide process window, superior growth rate, uniformity, and film quality has increased. Nowadays, In$_2$O$_3$ film deposition using metal-organic precursors has been fully investigated but the process of high-temperature region, over 300℃, is not much reported due to the thermal stability. Although the precursors that have cyclopentadienyl (Cp) functional groupare reported stably react over 300℃,[2] InCp is not favorable in the industry because it is a solid phase at room temperature which leads to a particle issue during the process and reported co-oxidant, H$_2$O and O$_2$ plasma show poor conformality on the complex structure. For this reason, our group has evaluated the novel indium alkyl cyclopentadienyl, which has high stability, a broad process window (200-400℃), and a liquid phase at room temperature. In this study, not only the introduction of a new precursor but also the development of the deposition process to obtain an order of double higher growth rate than the conventional method. We adopted a discrete reactant feeding (DRF) to improve the growth rate in this study. This optimized ALD process shows a very high growth rate of 2.0Å/cycle and negligibly low residual carbon impurities around the XPS detection limit. Also, a very wide process temperature range (200-400℃) was obtained and various film analysis methods such as XPS, XRR, XRD, and AFM are used to evaluate the In$_2$O$_3$ film quality. Therefore, the indium precursor having alkyl cyclopentadienyl derivative is one of the promising candidate precursors to form a high-quality In$_2$O$_3$ film for use in the future semiconductor field.

5:15pm **AF-MoA-16 Synthesis and Precursor Property Evaluation of Er Enaminolate Complexes and Deposition of Er_2O_3 Thin Film using Thermal Atomic Layer Deposition (ALD)**, ***Chamod Dharmadasa**, C. Winter, N. Jayakodiarachchi,* Wayne State University*; P. Evans,* University of Wisconsin-Madison*; R. Liu,* University of Wisconsin - Madison

Lanthanide oxide films have many applications in optics, catalysis, and semiconductor devices. Er_2O_3 films have useful properties that arise from its high dielectric constant, a large band gap energy, high refractive index, and thermodynamic stability at high temperatures. These properties have led to the investigation of Er_2O_3 films for possible inclusion in CMOS devices, antireflective and protective coatings on solar cells, and passivation layers for III-V semiconductors. Er_2O_3 films have been grown by many techniques, including PVD, CVD, and ALD. ALD is an important technique since it gives Angstrom-level thickness control and can afford 100% conformal coverage in high aspect ratio features. ALD precursors reported to date for Er_2O_3 films have problems that include low reactivity toward water as a co-reactant, oxidation of substrates when ozone is used as the co-reactant, and variable thermal stabilities. Recently, we described a series of volatile and thermally stable lanthanide(III) complexes that contain enaminolate ligands.[1] We report here detailed synthetic studies of the $Er(L^1)_3$ precursor complex, its ALD precursor properties, and its use in the ALD of Er_2O_3 films using water as the co-reactant. Depending upon the reaction conditions during precursor synthesis the compounds $Er(L^1)_3$, $Er(L^1)_3(L^1H)$, or $K[Er(L^1)_4]$ can be isolated. The reaction conditions can be selected to provide high yields of $Er(L^1)_3$. The volatility and thermal stability characteristics of $Er(L^1)_3$ are favorable for use as precursors for Er_2O_3 and other rare-earth oxides. An ALD window in the growth of Er_2O_3 films using $Er(L^1)_3$ with water as the co-reactant was observed from 150 to 250 °C, with a growth rate of 0.25 Å/cycle. The films were characterized by electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, and atomic force microscopy. Advantages of $Er(L^1)_3$ include its simple synthesis, good volatility and high thermal stability, and high reactivity with water to afford Er_2O_3 films. This class of new ALD precursors has the potential to enable more widespread use of the favorable properties of rare-earth oxide compounds and can be expanded to multi-component complex oxides containing rare earths.

1. N. Jayakodiarachchi, P. G. Evans, C. L. Ward, C. H. Winter, *Organometallics***2021**, *40*, 1270-1283.

5:30pm **AF-MoA-17 Deposition of $CsSnI_3$ Perovskite Thin Films by Atomic Layer Deposition and Pulsed Chemical Vapor Deposition**, ***Alexander Weiß**, M. Terletskaia, G. Popov, M. Leskelä, M. Ritala, M. Kemell,* University of Helsinki, Finland

Cesium tin triiodide ($CsSnI_3$) belongs to the group of halide perovskites, materials with outstanding optoelectronic properties. Halide perovskites gained huge interest in the past decade because they can be used as thin film solar absorbers in perovskite solar cells. This young technology has the potential to deliver low-cost solar energy and has already reached promising power conversion efficiencies above 25 %.

$CsSnI_3$ exhibits a small band gap energy (1.2 – 1.3 eV) and is Pb-free, providing a lower toxicity compared to its Pb-containing analogues, such as $CH_3NH_3PbI_3$ (MAPI) or $CsPbI_3$. Therefore, it is an attractive candidate for an environmentally friendlier and less hazardous absorber layer for perovskite solar cells.

Before perovskite solar cells can become widely commercially available, two problems need to be solved: The lacking scalability to large and/or complex-shaped areas, and the instability impeding the durability of the solar cell. We aim to tackle the scalability issue by employing Atomic Layer Deposition (ALD) as the key method. We believe that developing an ALD-based process for $CsSnI_3$ can also address the stability issue of the perovskite layer. Inorganic perovskites, especially solid-solution perovskites, are reportedly more stable than their organic-inorganic hybrid analogues. Combining an ALD-based $CsSnI_3$ process with our earlier $CsPbI_3$ ALD process[1] or our ALD-based MAPI process[2] would enable the scalable deposition of such solid-solution halide perovskites.

In this work, we report two new ALD-based routes to deposit $CsSnI_3$ thin films. The first route relies on a two-step approach, starting with the deposition of ALD CsI[1] that is subsequently exposed to a new ALD SnI_2 process to convert it to $CsSnI_3$. The ALD SnI_2 process uses $Sn(btsa)_2$ (btsa: bis(trimethylsilyl)amide) and SnI_4 as precursors, works in a narrow temperature range (75 – 90 °C) on CsI and yields phase-pure γ-$CsSnI_3$ films. The second route relies also on the deposition of ALD CsI but in this case it is converted to γ-$CsSnI_3$ by pulsed Chemical Vapor Deposition (pCVD) of SnI_2 using the same precursors. This process works at similar temperatures (160 – 180 °C) as the ALD CsI process, therefore effectively making it a one-step approach that is much faster than the first route. Moreover, exposing the CsI film to the pCVD SnI_2 process at these elevated temperatures ensures that the excess SnI_2 is sublimed, making this process self-limiting with respect of the ternary film composition.

[1] A. Weiß et al., *Chem. Mater.* **2022**, 34, 13, 6087–6097

[2] G. Popov et al., *Chem. Mater.* **2019**, 31, 3, 1101–1109

ALD & ALE
Room Grand Ballroom A-G - Session ALD+ALE-MoA2
Student Awards

Moderators: Simon Elliot, Schrödinger, Inc., Prof. Markku Leskela, University of Helsinki, Finland

1:30pm **ALD+ALE-MoA2-1 Student Award Finalist Talk: Thermal characterization and Area Selective Deposition of NHCs**, ***Eden Goodwin**,* Carleton University, Canada*; J. Lomax,* University of Western Ontario, Canada*; M. Aloisio, C. Crudden,* Queen's University, Canada*; P. Ragogna,* University of Western Ontario, Canada*; S. Barry,* Carleton University, Canada

Nanomanufacturing of integrated circuits requires multiple processes involving sequential deposition, etch, and planarization to create architectures consisting of interconnected metal, semiconductor, and dielectric components built upon a substrate. As the smallest components of these devices begin to reach sub nanometer dimensions, device manufacturers must rely upon area selective atomic layer deposition (AS-ALD) to deposit highly tunable and conformal films on selected regions of the substrate. Conventional AS-ALD employs thiol-based inhibitors with long alkyl groups to deactivate non-growth areas. These thiol-based inhibitors are known to have low surfactant density, and can create electron rich sulphur impurities upon removal, and are of large enough size to become incompatible with shrinking device architectures[1,2].

In this work we explore N-heterocyclic carbenes (NHCs) as area-selective small molecule inhibitors (SMIs) to replace the larger long-chain thiol SAMs. The electronic and steric tunability of NHCs allow flexibility when using them to selectively protect metal surfaces, due to their preferential binding to metal surfaces over dielectric surfaces. In this work we generate carbenes in situ through the controlled thermolysis of benzimidazolium bicarbonate salts, deliver them to non-patterned metal substrates as well as to patterned metal/dielectric substrates. We probe the thermal characteristics of comprehensive library of benzimidazolium bicarbonate salts through thermogravimetric analysis and differential scanning calorimetry. We quantify the growth behavior of various NHC precursors on gold surfaces, using an in-situ quartz crystal microbalance within a home-built tube furnace reactor. Finally, we demonstrate the selectivity of these NHCs through time of flight secondary ion mass spectrometry imaging and X-ray Photoelectron Spectroscopy of plasma-cleaned substrates coated with NHC films using a Picosun R200 plasma-enhanced ALD tool.

References:

1. Yarbrough, J., Shearer, A. B., & Bent, S. F. (2021). Next generation nanopatterning using small molecule inhibitors for area-selective atomic layer deposition. Journal of Vacuum Science & Technology A, 39(2), 021002. https://doi.org/10.1116/6.0000840
2. Yasmeen, S., Ryu, S. W., Lee, S. H., & Lee, H. B. R. (2022). Atomic Layer Deposition Beyond Thin Film Deposition Technology. In Advanced Materials Technologies. John Wiley and Sons Inc. https://doi.org/10.1002/admt.202200876

1:45pm **ALD+ALE-MoA2-2 Student Award Finalist Talk: Reaction Mechanism on ALD Process of Ru and Pt**, ***Heta-Elisa Nieminen**, M. Putkonen, M. Ritala,* University of Helsinki, Finland

Detailed reaction mechanism studies help to understand ALD processes and advance the technology through the increased knowledge. As the film growth is dictated by reactions between the precursors on the substrate surface, many ALD processes can be designed around analogous reaction chemistry. One such group of processes is deposition of noble metals by using organometallic precursors together with O_2 as a counter reactant. The reaction pathway for the processes is mainly known, but not all mechanistic details have been confirmed directly in ALD conditions. For example the nature of the dissociated surface oxygen, adsorption of the organometallic

precursor, completeness of the reactions and the nucleation of the metallic film require detailed investigation. This work aims to enlighten the mechanisms overall by studying metallic Ru and Pt processes with a set of *in situ* and *in vacuo* techniques.

Deposition of noble metals requires reduction of the metal cation of the precursor molecule to its elemental state. Hence, it is somewhat counterintuitive to use oxygen as the second reactant. The idea is that the organometallic ligands of the metal precursor itself act as the reducing agents in combustion reactions with O_2 that produce gaseous CO_2 and H_2O byproducts. Earlier reaction mechanism studies have revealed that in addition to combusting the ligands, the O_2 molecules dissociate onto the noble metal surface. This way the combustion reactions occur during both precursor pulses. The O_2 dissociation has suggested to be dependent on the deposition temperature as well as on the noble metal in question. For ruthenium, for example, substantial amount of O_2 is suggested to temporarily adsorb into the subsurface region of the film.

In this work reaction mechanisms are studied by investigating the film surface with *in vacuo* XPS and TPD together with monitoring the film growth with *in situ* QCM. The depositions are done in a commercial flow type ALD reactor using $RuCp_2$ and $MeCpPtMe_3$ for metallic Ru and Pt, respectively, together with O_2 as the counter reactant. The assumptions regarding the main reaction pathway are confirmed in our measurements. In addition, detailed analysis is performed to compare these two processes that represent nominally similar reaction chemistry.

2:00pm **ALD+ALE-MoA2-3 Student Award Finalist Talk: Thermal Atomic Layer Etching of Gold Using Sulfuryl Chloride for Chlorination and Triethylphosphine for Ligand Addition***, **Jonathan Partridge**, J. Murdzek, S. George,* University of Colorado at Boulder

Gold (Au) is one of the most revered metals with many uses including as a conductor in electronics. Nanostructured gold is also important in plasmonics and photonics. Au ALE could be used in the fabrication of gold nanostructures. In this study, Au thermal ALE was demonstrated using sequential chlorination and ligand-addition reactions. Sulfuryl chloride (SO 2 Cl 2) was used for chlorination and triethylphosphine (P(Et) 3) was used for ligand addition. Sulfuryl chloride is believed to chlorinate the gold surface and form AuCl. Triethylphophine ligand addition then adds to AuCl and produces volatile AuClP(Et) 3 etch products. This demonstration of Au ALE employed a custom quadrupole mass spectrometer (QMS) reactor to identify the etch products. High sensitivity detection is achieved when the etch products exit an aperture and form a molecular beam with line-of-sight to the ionizer. Gold nanopowders were used to maximize the surface area for the ALE reactions. Additional measurements of etch rates during Au ALE were performed using quartz crystal microbalance (QCM) studies. The QMS experiments were performed at 150 ?C at partial pressures of 2 Torr for sulfuryl chloride and triethylphosphine. During SO 2 Cl 2 exposures, the time-resolved QMS ion intensities for SO 2 + relative to the parent SO 2 Cl 2 + were consistent with the self-limiting chlorination of the gold surface. During PEt 3 exposures, AuCl(PEt 3) + ion intensity at m/z 350 was observed as the major etch product. Corresponding experiments at 150 °C on Au-coated QCM crystals observed a mass gain for SO 2 Cl 2 exposures during chlorination and a mass loss for PEt 3 exposures during ligand addition. The mass changes were consistent with an etch rate for Au ALE of 0.63 Å/cycle at 150 °C.

Sequential SO 2 Cl 2 and P(Et) 3 exposures were also observed to etch Cu and Ni nanopowders. The etch product during Cu ALE was observed at m/z 432 and assigned to Cu 2 Cl 2 (PEt 3) 2 + . The etch product during Ni ALE was observed at m/z 366 and assigned to NiCl 2 (PEt 3) 2 + . Additional QCM experiments on Cu-coated QCM crystals confirmed Cu ALE at 100 °C. This mechanism of chlorination and ligand addition should be useful for the ALE of many metals that form stable metal chlorides.

2:15pm **ALD+ALE-MoA2-4 Student Award Finalist Talk: Conformality of Atmospheric-Pressure Plasma-Enhanced Spatial Atomic Layer Deposition of SiO--$_2$ and TiO$_2$***, **Mike van de Poll**,* Eindhoven University of Technology, Netherlands*; H. Jain,* TNO-Holst Centre & Eindhoven University of Technology, The Netherlands*; B. Macco, P. Poodt, E. Kessels,* Eindhoven University of Technology, Netherlands

ALD is the thin-film method of choice for applications involving 3D structured surfaces. This includes, e.g., high aspect ratio structures in DRAM and NAND but also nanostructured optics and particle-based cathodes of Li-ion batteries. The conformal deposition of films can be achieved by sufficiently high precursor doses and co-reactant exposures. Challenges can arise, however, when using spatial ALD configurations for high throughput processing. Moreover, when a plasma is used as co-reactant, the situation can become even more challenging due to the potential loss of reactive plasma species by recombination at surfaces. Here, we present the first systematic study of the conformality of atmospheric-pressure plasma-enhanced spatial ALD (PE-s-ALD) complementing our earlier work on temporal PE-ALD at low pressures [1].

Employing the lateral high-aspect-ratio (LHAR) method (enabled by PillarHall™ LHAR test chips by Chipmetrics Ltd), we demonstrate that PE-s-ALD is capable of depositing conformal SiO_2 and TiO_2 films in 3D structures. The films were deposited using an atmospheric-pressure s-ALD tool equipped with a DBD plasma source operated on O_2/N_2. Using plasma exposure times as short as 0.7 s per cycle, aspect-ratios up to 80 and 210 could be conformally coated with SiO_2 and TiO_2, respectively. The penetration depth in the structures was found to be recombination-limited. In order to determine the recombination probability of the O-radicals present in the plasma, the experimental data was analyzed by a reaction-diffusion model. From this model, a relation was obtained between the penetration depth of O-radicals and their recombination probability. The extracted recombination probabilities at atmospheric pressure (i.e., 5.0×10^{-4} for SiO_2 and 3.4×10^{-5} for TiO_2) are comparable to those found in previous work at low pressure.[1] Differently shaped thickness profiles were observed for SiO_2 and TiO_2, showcasing the influence of various side-effects on the conformality of PE-s-ALD. Furthermore, estimations for the plasma time required for reaction-limited growth were made for substrates with various aspect ratios. For low aspect ratios (<60 for SiO_2), this time was found to be even lower than for low-pressure PE-ALD due to shorter saturation times at atmospheric pressure. These results demonstrate the potential of PE-s-ALD as a method for scaling up ALD for high-volume manufacturing.

[1]Arts, K.; Utriainen, M.; Puurunen, R. L.; Kessels, W. M. M.; Knoops, H. C. M. *J. Phys. Chem. C* **2019**, 123, 27030−27035.

2:30pm **ALD+ALE-MoA2-5 Student Award Finalist Talk: “Inverted ASD” with High Selectivity: Polymer on SiO$_2$ vs. Si-H and Polymer on Si-OH vs. SiO$_2$***, **Nicholas Carroll**, H. Margavio, G. Parsons,* North Carolina State University

Area-selective deposition (ASD) is of considerable interest to augment lithographic patterning, but new strategies are needed to leverage its usefulness. An important target of ASD is control over surface selectivity, including selectivity inversion of a deposition reaction to manipulate two arbitrary patterned surfaces to display either growth or non-growth behavior. However, to our knowledge, work to date is limited to ASD processes with pre-defined growth and non-growth surfaces. Achieving “inverted ASD,” where the patterned growth and non-growth surfaces could be selected arbitrarily, for example by precursor choice, surface preconditioning, or other treatments, would provide new capability for ASD process integration, particularly if high selectivity could be attained in either configuration. In this work, we report an inverted ASD process where poly(3,4-ethylenedioxythipohene) (PEDOT) conjugated polymer is deposited with high selectivity on Si-OH vs. SiO_2, or on SiO_2 vs. Si-H, where inversion is achieved by selective modification of the substrate surface energy via treatments with dilute hydrofluoric acid (DHF), (Dimethylamino)trimethylsilane (DMATMS), and water. PEDOT was selected as a case study due to its rapid deposition rate and known selectivity on SiO_2 vs. Si-H [1]. On Si/SiO_2 line structures with chemical oxide from piranha cleaning on the Si region, PEDOT grows uniformly on all surfaces (Figure 1a). However, after removing the oxide layer in 5% DHF for 5 seconds, the PEDOT shows a strong nucleation delay on Si-H (Figure 1b). If the HF-treated Si/SiO_2 is exposed to vapor-phase DMATMS under vacuum conditions, we find that DMATMS selectively passivates the SiO_2, inducing a delay in PEDOT nucleation, and the PEDOT grows only at the boundary region between the Si-H and passivated SiO_2, likely due to passivation defects in this region (Figure 1c). When the passivated Si/SiO_2 pattern is briefly submerged in water, the Si-H becomes hydroxyl terminated without changing the surface state of the SiO_2-TMS, leading to inverted selectivity (Figure 1d-f). Versatile control over selectivity configurations during ASD has implications for deposition of lateral control layers to reduce over-growth defects, blocking layers for non-selective deposition steps, and sacrificial layers for recently reported simultaneous deposition and etching processes [2]. Extension of these surface energy treatment strategies to other materials will provide additional opportunities for selectivity inversion, leading to flexible applications for ASD in manufacturing settings.

[1] J.-S. Kim et al., *Chem. Mater.***33**, 23(2021)

[2] S. K. Song et al., *ACS Nano*. **15**, 7(2021)

2:45pm **ALD+ALE-MoA2-6 Student Award Finalist Talk: Plasma Isotropic ALE of GaN Using SF_6 Plasma and TMA**, ***Nicholas Chittock**, W. Kessels,* Eindhoven University of Technology, The Netherlands*; H. Knoops,* Oxford Instruments Plasma Technology, Netherlands*; S. Elliott,* Schrödinger, Ireland*; A. Mackus,* Eindhoven University of Technology, The Netherlands

GaN is an enabling material for advanced radio frequency (RF) and power semiconductor devices due to its improved material properties compared to Si.[1] Typically, reactive ion etching (RIE) is used in GaN device fabrication which can result in a thick contamination layer and rough etch front that degrades device performance. In this work, an isotropic plasma ALE process using SF6 plasma and TMA has been developed for GaN, allowing accurate film thickness control, removal of O and C contamination, and surface smoothing.

From density functional theory (DFT) studies performed with the Schrödinger Materials Science Suite it was determined that the SF6 plasma/TMA chemistry was likely to result in ALE behavior. Natarajan-Elliott analysis revealed the fluorination reaction is in the preferred self-limiting regime, which suggests it is a suitable modification step. Additionally, the predicted ligand-exchange reaction between GaF3 and TMA was found to be energetically favorable, with higher temperatures resulting in a more negative free energy change.

Experimental results support the observations from DFT: saturation curves of both half-cycles at 150 ℃ and 300 ℃ give etch rates of 0.31 ± 0.01 and 0.40 ± 0.02 nm/cycle, respectively. Soft-saturation behavior of the SF6 step suggests that the process follows a diffusion-driven fluorination mechanism, similar to ALE of Al2O3.[2] A relatively thick (~10 nm) partially oxidized surface layer was present on the GaN surface before etching due to the oxyphilic nature of GaN. After ALE, the C and O content were significantly reduced, with only a small increase in F content detected by XPS, demonstrating that this process can remove film contamination. Evaluation of the EPC as a function of temperature reveals an ALE temperature window between 150-300 ℃. Below 150 ℃ the EPC decreases rapidly and no etching is observed at 100 ℃. Compared to thermal isotropic ALE of GaN reported in literature,[3] a higher EPC is achieved, highlighting a benefit of plasma isotropic ALE. AFM studies show smoothing of the GaN film post ALE, with a reduction of the RMS roughness from 2.6 ± 0.1 nm to 1.9 ± 0.1 nm after 25 nm of ALE.

The ability to accurately control GaN film thickness, while simultaneously smoothing and removing contaminants, makes isotropic plasma ALE a good candidate for post RIE surface cleaning. Consequently, isotropic ALE will be a valuable technique for the fabrication of future 3D GaN-based RF and power semiconductor devices.[1]

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3:00pm **ALD+ALE-MoA2-7 Student Award Finalist Talk: Competition between Deposition and Etching Reactions in ALD of Indium Gallium Zinc Oxide (IGZO)**, ***Iaan Cho,*** Hongik University, Republic of Korea*; J. Cho, J. Jeong,* Hanyang University, Republic of Korea*; B. Shong,* Hongik University, Republic of Korea

Indium gallium zinc oxide (IGZO) is considered as active material for thin-film transistors (TFTs) and NAND flash memory devices due to its high charge carrier mobility, low off-currents, and long-term stability. Along with the recent trend of miniaturization and structural complication of electronic and optoelectronic devices, atomic layer deposition (ALD) method is becoming essential. Especially, the elemental composition and the resulting material properties of multicomponent thin films can be precisely modulated with the ALD method. IGZO thin films with controllable composition can be manufactured using supercycle ALD by controlling the injection sequence and ratio of each elemental precursors [1]. However, in ALD of multicomponent materials, the atomic composition of the deposited films is often different from the ratio of the precursors injected during the deposition process. Such deviation in the composition of the multicomponent thin films versus the ALD recipe may originate from etching of an element in the substrate by another precursor during the deposition process [2]. In this study, the deposition and etching reactions between In-Ga-Zn elements during ALD is evaluated through density functional theory (DFT) calculations. Trimethylindium (TMI), trimethylgallium (TMG), and diethylzinc (DEZ) were considered as precursors; indium oxide (In_2O_3), gallium oxide (Ga_2O_3), and zinc oxide (ZnO) were used as substrate materials. It was found that DEZn has the highest reactivity, so that the etching of In or Ga by Zn would be the most preferrable, possibly resulting in decrease of In and Ga and increased Zn content in the deposited films. Our results show good correspondence with experimentally observed dependency of the compositions of IGZO on the sequence of the supercycle ALD.

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3:15pm **ALD+ALE-MoA2-8 Student Award Finalist Talk: Atomic Layer Deposition of Semimetallic TiS2 Contact Layer on MoS2-based Thin Film Transistor for Contact Resistance Reduction**, ***Jeongwoo Seo**, H. Yoon, S. Lee, J. Yoo,* Yonsei University, Korea*; Y. Nam, J. Lim,* Samsung Display Co., Ltd., Republic of Korea*; S. Chung, H. Kim,* Yonsei University, Korea

Two-dimensional transition metal dichalcogenides (2D TMDCs) have been researched as promising materials for electronic devices owing to their outstanding electrical and mechanical properties. Among 2D TMDCs, molybdenum disulfide (MoS_2) has been considered as an ideal semiconducting material for thin film transistor (TFT) with high mobility, on/off ratio, and drain current level. However, high contact resistance at the interface between the metal and MoS_2 channel remains as a main challenge to be overcome for high performance MoS_2-based TFT.

High contact resistance at the interface originates from the high Schottky barrier height (SBH). Among various factors, metal-induced gap state (MIGS) causes Fermi level pinning, resulting in high SBH. Since MIGS occurs due to the unwanted gap states under the metal contact, semimetallic material as additional contact layer between the metal and semiconductor can be a solution to suppress the MIGS and further reduce the contact resistance.

In this study, ALD TiS_2 was used as semimetallic contact layer for the improvement in the contact between the channel and metal for MoS_2-based TFT. ALD TiS_2 (~10 nm) was directly deposited on the CVD-grown MoS_2, followed by Ti/Au evaporation for the metal deposition. Owing to the low temperature (~100°C) process of ALD TiS_2, smooth semimetallic TiS_2 can be deposited as contact layer without introducing defects in MoS_2 channel. Compared to the contact without TiS_2 contact layer, it showed significant improvement in electrical properties. Drain current has been increased about 100 times, owing to the semimetallic nature of TiS_2. In addition, threshold voltage, mobility, and subthreshold swing have been improved as well. These results suggest that ALD TiS_2 can be used as an appropriate contact layer for the high performance MoS_2-based TFT with low contact resistance.

Acknowledgement

This research was supported by Samsung Display Co., LTD..

Atomic Layer Etching
Room Grand Ballroom H-K - Session ALE-MoA
Metal ALE

Moderators: Dr. Thorsten Lill, Lam Research Corporation, Dr. Tristan Tronic, Intel Corporation

4:00pm **ALE-MoA-11 Wet Atomic Layer Etching of Metals**, ***Paul Abel,*** Tokyo Electron America, Inc. **INVITED**

Here we present a new strategy for implementing atomic layer etching (ALE) of metals using wet chemistry at room temperature. Unlike plasma- and thermal-ALE, material removal in wet ALE is achieved through dissolution of the self-limiting passivation layer rather than volatilization. This relaxes the temperature requirements of thermal ALE, and the sputter threshold requirements for plasma ALE. Solubility is strongly dependent on solvent species, so solvent exchange can be used as the trigger for release of the self-limiting passivation layer as an alternative to ligand exchange. In the first half of the etch cycle, a self-limiting metal-ligand surface complex is formed on exposure to the first etch solution. The surface layer must be insoluble in this solution, but readily soluble in the second etch solution in order to complete the ALE cycle. Additionally, the second solution must be unreactive with the freshly exposed metal surface. Sequential exposure to both etchants is required for material removal. A diagram of this wet ALE process is shown in Figure 1.

Most transition metal complexes form around oxidized metal centers, so formation of the surface complex is governed by solution redox chemistry in the presence of appropriate ligands. Solubilization of this complex can be achieved in one of several ways. Solvent exchange can be used to dissolve the layer in an appropriate solvent. Ligand exchange in a non-redox active solution can be used to alter the solubility of the surface complex without changing the solvent or reacting with the underlying substrate. And lastly, ion exchange can be used if the surface complex is a coordination compound containing both a ligand-bound complex ion and a counterion.

In this talk, we apply these strategies to the wet ALE of copper and cobalt. These metals easily form thick native oxide layers. The thickness of this layer, as well as the ease with which it forms makes it inappropriate to use as the modified layer for wet ALE. Exposure to an appropriate ligand-containing solution, however, forms a monolayer of metal-ligand complex on the native oxide surface. This metal-ligand complex is a much more appropriate modified layer, and the etch amount per cycle is strongly dependent on ligand chemistry. Both ligand surface packing density and ligand binding strength influence the metal removal rate. Selective removal can then be accomplished through either a solvent exchange to directly dissolve the modified layer or a ligand exchange to form a more soluble compound through reactive dissolution.

4:30pm **ALE-MoA-13 Thermal Atomic Layer Etching of Molybdenum Based on Sequential Oxidation and Chlorination Reactions**, ***Taewook Nam**, J. Partridge, S. George,* University of Colorado at Boulder

Previous pathways for thermal ALE of metals, such as Cu and Co, have employed either oxidation or chlorination reactions for surface modification followed by either ligand-substitution or ligand-addition reactions for volatile release. This study introduces another mechanism for the thermal ALE of metals using sequential oxidation and chlorination reactions. This mechanism relies on the metal having volatile oxychloride complexes. The thermal ALE of Mo was studied using quartz crystal microbalance (QCM), x-ray reflectivity (XRR), and quadrupole mass spectrometry (QMS) measurements. Mo films were first deposited on quartz crystals or silicon coupons using sputtering. The mass or thickness changes were then measured versus sequential oxidation and chlorination reactions using O_3/O_2 and $SOCl_2$ as the reactants.

The QCM measurements observed very digital mass changes during the sequential O_3/O_2 and $SOCl_2$ exposures. QCM results showed pronounced mass gains during O_3/O_2 exposures and distinct mass losses during $SOCl_2$ exposures. QCM measurements for three cycles of Mo ALE at 175°C are displayed in Figure 1. The mass changes were also self-limiting versus O_3/O_2 and $SOCl_2$ reactant exposure. The mass loss per Mo ALE cycle was -1,600 ng/cm^2 or 15.7 Å/cycle under the saturation reaction conditions at 175°C. The Mo ALE etch rate was studied from 100°C to 250°C and larger etch rates were observed at higher temperatures.

Mo ALE is dependent on the release of volatile oxychloride etch products. For under-saturation reaction conditions, the mass changes during the O_3/O_2 exposures could either be negative or positive. Lower O_3/O_2 exposures led to negative mass changes and higher O_3/O_2 exposures led to positive mass changes. This behavior can be explained based on the volatile oxychloride etch product during Mo thermal ALE. There is chlorine on the surface after the $SOCl_2$ exposure. Initial O_3/O_2 exposures remove the chlorine as a volatile Mo oxychloride product and produce a mass loss. As the chlorine is removed, larger O_3/O_2 exposures can then proceed to oxidize the Mo surface and produce a mass gain.

QMS experiments were performed to identify the etch products. To improve the detection sensitivity, these experiments utilized various powder samples to model the Mo surface after the O_3/O_2 or $SOCl_2$ exposures. The main Mo oxychloride species detected was MoO_2Cl_2. Figure 2 shows the observation of MoO_2Cl_2 during $SOCl_2$ exposure on MoO_3 after a previous O_3/O_2 exposure. The parent $MoO_2Cl_2^+$ ion intensities are observed in a cluster of peaks around m/z 200. All of the main ion intensities are explained by the natural isotopic abundances of Mo and Cl in MoO_2Cl_2.

4:45pm **ALE-MoA-14 Non-Halogen Plasma for Selective Removal of Titanium Compounds Applied in Advanced Atomic Layer Etching**, ***Thi-Thuy-Nga Nguyen,*** Nagoya University, Japan*; K. Shinoda,* Hitachi, Ltd., Japan*; S. Hsiao,* Nagoya University, Japan*; H. Hamamura,* Hitachi, Ltd., Japan*; K. Maeda, K. Yokogawa, M. Izawa,* Hitachi High-Tech Corp., Japan*; K. Ishikawa, M. Hori,* Nagoya University, Japan

Selective removal of metal gate materials such as TiC, TiAlC, TiN, or TiAl is required in the fabrication of next generation field effect transistor (FET) of logic semiconductor devices. In our development of advanced etching methods, we have proposed wet-dry etching or wet-like plasma etching that combines the advantages of wet etching (high isotropy and selectivity) and dry etching (high controllability). For atomic layer etching (ALE) processes, surface modification reduces surface energy of sample surface in the first step, and the modified layer is removed in the next step.

Surface modification of metal carbide TiAlC using floating wire-assisted non-halogen vapor plasma, that can generate a high-density plasma at medium pressure, has been demonstrated in our recent study, indicating a potential of isotropic and selective etching of TiAlC by using chemistries containing NH, H, and OH. In this study, the N-H-O containing plasmas can selectively remove TiAlC over TiN. Film thickness change of titanium compounds was measured by an *in situ* ellipsometer, and surface chemical bonding during the processing was analyzed by an *in situ* attenuated total reflectance-Fourier transform infrared spectrometer. Optical emission spectra of NH and OH molecular lines from plasmas were detected by a high-resolution optical emission spectrometer. The sample surface was analyzed before and after the plasma treatment by X-ray photoelectron spectroscopy.

By controlling the surface reactions, selective removal of TiAlC over TiN can be achieved by its reaction with N-H-O plasma to form volatile products, as firstly proposed here. We emphasized that this non-halogen etching method can be applied for highly selective etching of metal carbide, nitride, or oxide.

5:00pm **ALE-MoA-15 Leveraging Surface Nitridation to Enable Plasma-Thermal Atomic Layer Etching of Ni Based Metals**, ***Taylor Smith**, J. Chang,* University of California, Los Angeles

Metals are of increasing importance in modern electronics. For example, Ni and Ni-based alloys have been used for extreme ultraviolet lithography (EUVL) absorber layers and as components in composite multiferroics for magnetoelectric devices. In this work, we present an atomic layer etching (ALE) technique to etch Ni that relies on plasma nitridation to modify the Ni surface and organic vapor exposure to remove the modified layer. Theoretical study by density functional theory has shown that ALE of metals including Ni is possible through nitridation and formic acid (FA) exposure, through the formation of dimeric $Ni_2(HCOO)_4$ and NH_3 as reaction products.[1] Since surface nitridation is not a spontaneous reaction like oxidation upon exposure to ambient air (e.g., moisture), this process can be analyzed more definitively without the convolution of native oxide formation.[2] In this work, we experimentally examined this new method using a remote nitrogen plasma and a custom vapor chamber to modify and etch nickel and nickel based alloys.

A pure nitrogen plasma in a custom planar geometry ICP reactor was used to form the nickel nitride.The thickness of the nitridized layer is controlled by modifying the power, pressure, and exposure time of the plasma and quantified by a combination of spectroscopic ellipsometry (SE) and scanning electron microscopy (SEM).To alleviate the complication in SE analysis by the fact that the optical constants of thin metal films can vary depending on deposition method and thickness, SE measurements of samples that have undergone similar numbers of ALE cycles are fit simultaneously assuming that the optical constants over a narrow thickness range are the same. This improves the thickness measurement accuracy, as corroborated by SEM analysis. FA in the solution phase and vapor phase are both examined as a means of removing the nitridized Ni layer, with X-ray photoelectron spectroscopy (XPS) showing both phases completely removing the N 1s peak that forms after plasma nitridation. The etch rate of Ni by nitridation and FA solution is 6.1 nm/cycle.For the case of a Ni ALE cycle involving plasma nitridation and FA vapor exposure at 80°C, the etch rate was about 1 nm/cycle, indicating a relatively controllable process. For the Ni_xAl_y alloy, both solution phase and vapor phase FA at 80°C removed the nitridized surface layer. However, this led to Al surface enrichment, suggesting the ALE cycle preferentially etched Ni over Al. The selectivity to common hardmasks was also tested.

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5:15pm **ALE-MoA-16 Plasma Atomic Layer Etching of Ruthenium with Surface Fluorination and Ion Bombardment for Next-generation Interconnect Metal**, ***Yongjae Kim,** H. Kang, M. Choi, H. Ha, H. Chae,* Sungkyunkwan University (SKKU), Republic of Korea

Cu is widely used for interconnect metal in semiconductor devices, but the resistance of Cu increases significantly as the interconnect width decreases

below 10 nm due to electron scattering at grain boundary and surface. Ruthenium is one of the candidate materials to replace Cu as the interconnect metal because resistivity of Ru is lower than that of Cu when the interconnect width is less than 10 nm. [1] Reactive ion etching (RIE) is used for direct patterning of metals, but controlling atomic-level film thickness in nanopatterning processes is challenging. Atomic layer etching (ALE) is suggested as an alternative to RIE because ALE can remove layers with atomic scale precision, excellent uniformity, and low surface roughness. [2]

In this work, plasma ALE process was performed for Ru in an inductively coupled plasma (ICP) reactor. The ALE process consists of two steps: surface fluorination with CHF_3, C_4F_8 or CF_4 plasmas and ion bombardment with Ar plasma. The CHF_3 and C_4F_8 plasmas generate fluorocarbon layer on the Ru surface and the CF_4 plasma converts the Ru surface to RuF_x. The C_4F_8 plasma produces fluorine-rich fluorocarbon layer on the Ru surface compared to the CHF_3 plasma. Etch per cycle (EPC) of Ru was investigated according to ion energy and etching time. ALE window of Ru was observed in the ion energy range of 150 ~ 200 V for CHF_3 and C_4F_8 plasmas and 100 ~ 200 V for CF_4 plasma. The EPC of Ru was determined to be 0.6 nm/cycle for CHF_3 plasma, 1.5 nm/cycle for C_4F_8 plasma, and 0.3 nm/cycle for CF_4 plasma in the ALE window region. Chemical sputtering threshold energy of Ru was determined to be 100 V for CHF_3 plasma, 50 V for C_4F_8 and CF_4 plasmas. The EPC of Ru was increased with increasing Ar plasma time and exhibits self-limiting properties at 180 seconds for CHF_3 plasma and at 300 seconds for C_4F_8 and CF_4 plasmas. Surface roughness and etch residues of Ru were compared with RIE and ALE.

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Keywords: Atomic layer etching, Ruthenium etching, Fluorine-contained plasma, Surface roughness, Etch residues

5:30pm **ALE-MoA-17 Comparison of Ruthenium ALE based on ICP and Ion Beam***, D. Kim, H. Kwon, Y. Jang, H. Gil, D. Kim, G. Kim,* ***Geun Young Yeom****,* Sungkyunkwan University, Republic of Korea

In this study, using etching tools based on both ICP system and ICP-ion beam system, Ru ALEs have been carried out and their etch characteristics were compared. For Ru ALE based on ICP system, RuO_x was formed on the surface using direct O_2 plasma in the ICP system and then RuO_x was removed from the surface using Ar plasma by biasing the substrate. For Ru ALE based on ICP-ion beam system, and where, plasma source and the substrate were separated by grids on the ICP-ion beam source, only O radicals were supplied to the Ru surface using remote plasma to form RuO_x, and then RuO_x was removed using an Ar^+ ion beam. Using both Ru ALE techniques, surface oxidation characteristics according to direct plasma and remote plasma were compared, and desorption methods for realizing ideal atomic layer etching were investigated. In addition, physical and chemical changes occurring on the Ru surface during adsorption and desorption steps were evaluated, and the etching mechanisms were compared.

Nanostructure Synthesis and Fabrication
Room Regency Ballroom A-C - Session NS-MoA

2D Growth

Moderators: Prof. Dr. John Conley, Oregon State University, Prof. Xiangbo Meng, University of Arkansas

4:00pm **NS-MoA-11 A Modified ALD-like Approach to Demonstrate Exceptionally Thin Dielectric Layer Growth on 2D Materials***,* ***Daire Cott****, S. Sergeant, R. Rennen, G. Benjamin,* IMEC Belgium*; D. Lin,* IMEC, Belgium*; X. Wu,* IMEC Belgium*; Z. Lin,* IMEC Belgium,, Belgium*; T. Schram, Q. Smets, I. Asselberghs, P. Morin,* IMEC Belgium **INVITED**

Uniform deposition of extremely thin dielectrics on 2D materials is sought after to exploit the potential of 2D materials in future nano-electronic devices. To that end, significant challenges must be overcome. The surface of thin layers of pristine 2D materials can be seen as fully passivated where all covalent bonding is located parallel to the plane and layers are bound together by Van der Waals forces. To form an effective interface between the 2D material surface and an oxide covering layer a lowering of the overall surface energy must be achieved. Interestingly, 2D materials already possess an extremely low surface energy (~40 mJ/m^2)[1] indicating that wetting is a significant challenge. Additionally, when considering ALD - the method of choice to form scaled high-k dielectric layers on Si device technology - which relies on the ability to form a uniform covalently bound atomic layer as the starting surface to nucleate subsequent layers. Conversely, to maximize 2D materials electronic potential the pristine nature of the 2D material should be maintained without damaging the in-plane covalent bonding of the system. This excludes many well-established physical deposition techniques such as PVD sputtering or even plasma enhanced ALD techniques where damage to the 2D layer can be created, inducing defects that although will enhance the nucleation of oxides will simultaneously degrade the electrical performance in nanoscale devices.

In this presentation, a method to overcome the inert nature of 2D materials to support oxide formation without inducing defects into the 2D material will be discussed. Insights into the formation mechanism of thin Aluminum oxide based layers on 2D materials will be outlined with particular focus on two types of transition metal dichalcogenides namely, WS_2 and MoS_2. Combining our method with 5nm HfO_2 to form the top oxide in lab based dual gated MOSFETs a low equivalent oxide thickness (EOT) of 2.1nm was demonstrated [2], Additionally, the upscaling of this approach to large area 300mm 2D material covered substrates will be also discussed [3]

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4:30pm **NS-MoA-13 Water-free SbO_x-ALD-process for Coating Bi_2Te_3-particles***,* ***Sebastian Lehmann****, F. Mitzscherling, S. He, J. Yang, M. Hantusch, A. Bahrami, K. Nielsch,* Leibniz Institute for Solid State and Materials Research, Germany

We developed a water-free Atomic Layer Deposition (ALD) process to homogeneously deposit SbO_x using $SbCl_5$ and Sb-Ethoxide as precursors reported for the first time. The coating is applied on Bi_2Te_3 particles which were synthesized via the solvothermal route to enhance the thermoelectric properties (i.e. Seebeck coefficient, thermal and electrical conductivity) via interface engineering. The amorphous character of the coating was shown by the missing reflexes on the XRD diffractograms. A shift from the oxidation state +III to +V of the Sb-species was observed towards increasing SbO_x-coating layer thickness using XPS. Additionally, a peak shift of the Sb $3d_{5/2}$ + O 1s peak indicating increased n-type doping of the material. Electrical measurements of spark plasma sintered bulk samples confirmed the doping effect by a decreased specific resistivity with increasing SbO_x-layer thickness. The Seebeck coefficient was improved for the coated samples compared to the uncoated reference sample while the total thermal conductivity remained almost constant resulting in an enhancement of the Power factor and the zT. The results distinctly show that surface engineering via Powder ALD is an effective tool to improve key properties of thermoelectric materials.

4:45pm **NS-MoA-14 2D FeS_X Nanosheets by ALD: Electrocatalytic Properties Towards Hydrogen Evolution Reaction***,* ***Raul Zazpe****, J. Rodriguez Pereira, S. Thalluri, L. Hromadko,* University of Pardubice, Czechia*; D. Pavliňák, E. Kolíbalová,* Brno University of Technology, Czechia*; H. Sopha, J. Macak,* University of Pardubice, Czechia

In the last years, the search of novel and cost-effective catalysts to replace costly and scarce noble metals drove to explore a wide range of materials, such as transition metal dichalcogenides (TMDCs), phosphides, carbides, nitrides among others.[1] Inspired by the first experimental evidences reported on the catalytic activity of MoS_2 edge sites,[2] an intense researching work has been devoted in exploring the catalytic properties of other 2-dimensional (2D) TMDCs, e.g. WS_2, $MoSe_2$, and $MoTe_2$.[3–6] 2D materials offer unique structural, optical and electronic properties as compared to the bulk counterparts. In addition, they show significant prospects as catalyst mainly due to the flake-like morphology with minimal thickness, high surface-to-volume ratio, and capability of surface functionalization and tuning the catalytically active edges sites.[7] Among the TMDCs materials, the catalytic properties of iron sulfide and its different phases, namely FeS_2, Fe_3S_4 and FeS, have been largely overlooked and barely explored compared to other TMDCs, despite the relative low cost and toxicity and the high natural abundance of iron and sulfur.

Herein, we present 2-dimensional (2D) FeS_x nanosheets of different sizes as an electrocatalyst towards hydrogen evolution reaction (HER) in alkaline media. The 2D FeS_x nanosheets were synthesized by applying different numbers of Atomic Layer Deposition (ALD) cycles on TiO_2 nanotube layers

and graphite sheets as active supporting materials. The electrochemical results confirmed the electrocatalytic activity with an excellent long-term stability and an enhanced catalytic activity reflected by a noteworthy drop of the HER overpotential. Using a range of characterization techniques, it was unveiled that the origin of the enhanced catalytic activity was caused by the synergistic interplay between in situ morphological and composition changes experienced by the 2D FeS_x nanosheets during HER. Under the application of a cathodic potential in alkaline media, it was observed that the original 2D FeS_x nanosheets transformed to iron oxyhydroxide-iron oxysulfide core-shell nanoparticles, which exhibited a higher active catalytic surface and newly created Fe-based HER catalytic sites. [8]

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5:00pm **NS-MoA-15 300 mm Wafer-Scale and Self-limiting Layer Synthesis of 2D $MoSe_2$ by Atomic Layer Deposition***, A. Zacatzi, M. Miller, R. Kanjolia,* ***Thong Ngo,*** EMD Electronics

2D Transition metal dichalcogenide (TMD) materials have opened a route to continue the down-scaling trend of semiconductor technology. As part of the TMD materials library, $MoSe_2$ has demonstrated itself to be a very promising candidate as a channel material for transistor devices, achieving field-effect mobilities up to ~ 150 - 200 $cm^2/(V\ s)$. [1]

The synthesis of high quality 2D $MoSe_2$ is required to unlock the potential application of this material in electronic devices. However, to date, there are limited reports on $MoSe_2$ synthesis in comparison to the variety of techniques used to obtain MoS_2 in the literature. A previous approach describes a two-step $MoSe_2$ deposition, where MoO_3 is first deposited by atomic layer deposition (ALD) onto a substrate followed by a selenization process performed at 900°C [2]. While this route produced 2D $MoSe_2$, a single, lower temperature process would be preferred to better meet the high-volume manufacturing demands in the semiconductor industry. In this work, we developed a process to synthesize uniform, 300 mm wafer-scale 2D $MoSe_2$ films using conventional ALD. A detailed study of the $MoSe_2$ ALD process window, from 425 °C - 600 °C, correlated with the composition and structural properties of the $MoSe_2$ film will be presented. The resulting $MoSe_2$ films from the optimized process are stoichiometric and present a 2H phase. Furthermore, this novel optimized ALD process exhibited a self-limiting layer synthesis-like behavior [3], allowing the precise control over the $MoSe_2$ thickness.

The proposed ALD approach presented in this work contributes to the efforts in developing high-quality 2D materials for the realization of atomically thin channel materials.

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5:15pm **NS-MoA-16 Wafer-Scale Controlled Growth of Two-Dimensional Metal Dichalcogenides Through Atomic Layer Deposition and Top-Bottom Epitaxy***,* ***Chanyoung Yoo,*** *W. Choi, J. Jeon, B. Park, G. Jeon, S. Jeon, C. Hwang,* Department of Materials Science and Engineering and Inter-University Semiconductor Research Center, Seoul National University, Republic of Korea

Two-dimensional (2D) metal dichalcogenides (MDCs) are a class of MX_2 compounds that exhibit unique electrical, optical, and mechanical properties due to their 2D van der Waals (vdW) structures[1]. Among them, Sb_2Te_3 is a p-type semiconductor with a narrow direct bandgap that has the potential for applications in a topological insulator[2], thermoelectric[3], and optoelectronic. Sb_2Te_3 is also utilized in phase-change memories, where the pseudobinary GeTe-Sb_2Te_3 tie line compositions are the primary materials[4]. To utilize the unique properties of Sb_2Te_3 and for other 2D MDCs, continuous films with ultrathin thicknesses (<< ~10 nm) must be formed on substrates. However, depositing 2D MDCs such as Sb_2Te_3 with ultrathin thickness is challenging due to their tendency to grow in an island-type non-uniform manner, exhibiting prominent plate-shaped morphologies.

In this study, a novel atomic layer deposition (ALD) method utilizing amorphous (a-) GeTe as a buffer layer was developed to change the island-type growth of Sb_2Te_3 film to layer-by-layer growth, enabling precise control of film thickness with high uniformity, as shown in Figure 1. The Ge atoms in the buffer layer act as anchoring sites where the Sb-precursors can adhere uniformly. After forming a uniform Sb_2Te_3 layer, the growth was self-terminated by the inert vdW surface (Figure 2a), and the substitutional reaction of Ge atoms with the Sb-precursors dominated the growth. The replacement of Sb atoms formed crystalline (c-) GeSbTe and further Sb_2Te_3 cycles transformed the c-GeSbTe layer into a pure Sb_2Te_3 film (Figure 2b). The self-terminated thickness of the Sb_2Te_3 film was determined by the thickness of the a-GeTe buffer layer (Figure 2c). This new ALD method, referred to as top-to-bottom epitaxial growth, involved depositing the Sb_2Te_3 film through the displacement and diffusion of Sb atoms from the surface to the substrate (see the overall illustrations in Figure 2d). This approach resulted in conformal c-axis-oriented Sb_2Te_3 films with ideal layer-by-layer growth. Furthermore, layer-by-layer growth was maintained on contact hole structures (compare Figure 3a-c and 3d-f), exhibiting c-axis orientation along the curvature without any protruding plates, as evidenced by the characteristic vdW gaps of Sb_2Te_3 parallel to the curved corner. This new ALD method utilizing an amorphous buffer layer holds great potential for application to other 2D MDCs and provides a versatile and scalable platform for their growth.

References

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ALD Fundamentals
Room Evergreen Ballroom & Foyer - Session AF-MoP
ALD Fundamentals Poster Session

AF-MoP-2 Atomic Layer Deposition of hfo2 Thin Film Using a Novel Heteroleptic Ethylenediamine Based Hf Precursor*, **Choel Wan Park**, E. Shin, E. Cho, H. Kim, K. Mun, K. Lee, J. Park,* Hansol Chemical Co., Ltd., Republic of Korea

Group 4 metal oxide materials such as ZrO_2, TiO_2, and HfO_2 have attracted considerable attention for dielectric materials for microelectronic devices. HfO2 film has an outstanding high-dielectric constant (κ ~ 20-25, t-HfO2) , large band gap Energy (E_g, ~ 6.0 ev) and good thermal stability. For these reason, the HfO_2 thin film applicate microelectronic devices such as the dynamic random access memory (DRAM) capacitors and central processing memory (CPU) gate dielectric application.

In this study, we propose a novel heteroleptic ethylendiamine based Hf precursor namely HEA. The physical characteristic of HEA was investigated by NMR Spectroscopy. Also, we measure the properties of the HfO_2 thin film of HEA against usually usedCpTDMAH by thermal atomic layer deposition (TALD).

The evaporation characteristics of HEA and CpTDMAH were carried out in a thermogravimetric analysis (TGA). The amount of residue was about < 0.45 % for HEA, which had a less residue compared to CpTDMAH (< 0.98 %). For both precursors HEA and CpTDMAH, the characteristic self-limiting ALD growth mode was confirmed. The growth rate of HEA was 1.19 Å/cycle with ozone as a reactant gas and showed a Low temperature ALD window in a range of 150–250℃.

HfO_2 thin film properties were investigated by SIMS depth profile and Transmission electron microscope (TEM). The deposited film of HEA represented better step coverage and improved carbon impurity compared to that of CpTDMAH. From this study, The HEA is expected to be advantageous precursor for low temperature thin film deposition technique.

AF-MoP-4 Al Precursor with Low Growth Rate for Conformal Al_2O_3 Thin Film*, **Kyuhyun Yeom**, H. Lee, K. Mun, D. Ryu, J. Seok,* Hansol chemical, Republic of Korea

Al2O3 thin film is variously used for an encapsulation layers of display, blocking layers of NAND, and capacitor dielectric of dynamic random access memory(DRAM).

Trimethylaluminium(TMA) that highly reactive is usually used to make Al_2O_3 thin film. Howerver, TMA has pyrophoric which leads to difficult handling and non-safety.

In addition, it has a high growth per cycle(GPC), which is not pappropriate to the micro process such as the $ZrO_2/Al_2O_3/ZrO_2$(ZAZ) process of DRAM dielectric need to precise controllable deposition.

We designed an Al precursor that has non-pyrophoric and a low GPC compared to TMA. Al_2O_3 was deposited on SiO_2, and ozone was used as a reactant gas.

The source and reactant gas showed self-saturation, respectively, and a wide and flat ALD range of 100-340°C was shown.

GPC had about 65-70% of TMA. In addition, Al_2O_3 thin film properties we examined such as XPS, XRR, and TEM.

AF-MoP-5 Low-Temperature HfO_2 Gate Dielectric for Topological Insulator Devices*, P. Shekhar, S. Shamim, V. Hock,* Physikalisches Institut (EP3) and Institute for Topological Insulators, Universität Würzburg, Germany*; H. Buhmann, **Johannes Kleinlein**,* Physikalisches Institut and Institute for Topological Insulators, Universität Würzburg, Germany*; L. Molenkamp,* Physikalisches Institut (EP3) and Institute for Topological Insulators, Universität Würzburg, Germany

On this poster, we present details of our low-temperature (30 **°**C) hafnium oxide atomic layer deposition (ALD) process **[1].** We apply the layers as gate dielectrics in devices of the thermally sensitive topological insulator HgTe **[2,3]**. The gate structures are used to tune the charge carrier density in the HgTe quantum well. For the hafnium oxide deposition, we utilize a home-made reactor and TDMAH and water as precursor and reactant, respectively. Due to the low deposition temperature, the films can be patterned by lift-off processes. Here, we present the layout of our home-made reactor and a schematic of the complete ALD system. Furthermore, we show results of our investigations on the homogeneity of the hafnium oxide layer thickness over the whole sample stage area, as well as on long-term reproducibility. We provide details of our gate fabrication process, following a self-aligned lift-off process: Both the dielectric and the electrode are deposited successively using a single resist mask. We use standard photoresist technology for device dimensions in the micrometer range, and PMMA and electron beam lithography for nanostructure devices. Finally, we exemplary show applications of low-temperature hafnium oxide gate insulators in micro- and nanostructure devices, such as quantum spin hall effect devices **[4]**, HgTe-based superconducting devices **[5]**, and quantum point contact devices **[6]**. We analyze the gate performance in these devices, as well as leakage currents and gate hysteresis.

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AF-MoP-6 Silicon Nitride ALD Process Using High Purity Hydrazine for Low Temperature Deposition*, **Hayato Murata**, Y. Koda, Y. Wada, T. Kameoka,* Taiyo Nippon Sanso Corporation, Japan*; J. Spiegelman,* RASIRC*; N. Tomita,* Taiyo Nippon Sanso Corporation, Japan

High quality ALD silicon nitride (SiN) at low temperature is required for advanced device structure complexity. High purity hydrazine (N_2H_4) is a promising nitrogen source for low temperature ALD nitride process due to its high reactivity. We have reported various advantages of N_2H_4 for titanium nitride (TiN) film ALD process over the conventional ammonia (NH_3) process [1-2]. In this study, we found that N_2H_4, comparing to NH_3, was capable to have high quality SiN film at 550°C by ALD processing with dichlorosilane (DCS, SiH_2Cl_2). This result shows N_2H_4 instead of NH_3 has potential to be new nitrogen source for state-of-the-art devices.

In such low temperature region, purity of source is very sensitive for film quality. We used N_2H_4 of BRUTE Hydrazine (RASIRC, Inc.) which enabled safe delivery of high-purity N_2H_4 gas. SiN ALD process was experimentally evaluated by delivering DCS/N_2H_4 or DCS/NH_3 to a hot-wall tubular reactor. ALD SiN films using DCS/N_2H_4 were formed at 550-650°C.

GPCs (growth per cycle) in DCS/N_2H_4 ALD were found to be 0.49-1.27 Å/cycle while those in DCS/NH_3 ALD were 0.10-1.02 Å/cycle at 550-650°C. These results indicate that N_2H_4 could be available to further enhancement in throughput. In addition, refractive index (R.I.) of DCS/N_2H_4 film was about 1.90 at 550°C while R.I. of typical SiN was about 1.9-2.1. In contrast, R.I. of DCS/NH_3 film formed at 550°C was under 1.50 likely due to the formation of silicon oxide whose R.I. is around 1.45. Moreover, WER in dilute hydrofluoric acid (100:1 HF) of DCS/N_2H_4 film was 14.1 Å/cycle at 550°C. On the other hand, WER of DCS/NH_3 film formed at 550°C was twenty times higher (303.7 Å/cycle) compared with that of DCS/N_2H_4. These results indicate that N_2H_4 as higher reactive nitrogen source has an effect on SiN film quality at lower temperature.

In order to investigate reactivity of N_2H_4, activation energies (Ea) for nitriding reaction to the DCS chemisorption surface structure were calculated. The quantum chemical calculation was performed by B3LYP density functional with cc-pVDZ basis set. The Ea of N_2H_4 reaction with the DCS chemisorption structure was 31 kJ/mol while that of NH_3 reaction was 60 kJ/mol. These results indicate N_2H_4 is a higher reactive nitrogen source for surface than NH_3.

Thus, we concluded that N_2H_4 is very promising nitrogen source for ALD with high reactivity at low temperature and that N_2H_4 is practical option for ALD process development to be satisfied with both throughput and SiN film quality.

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AF-MoP-7 ALD Precursor Design for Post-Transition Metal Films*, **Atsushi Sakurai**, N. Yamada, T. Yoshino, A. Nishida, M. Hatase, M. Enzu, A. Yamashita, Y. Ooe, C. Mitsui,* ADEKA CORPORATION, Japan

This presentation will share the basic chemistry of potential ALD precursors in relation to the post-transition metals such as Zn, Ga, In, Sn, Pb, Sb and Bi. Most of those metals take p-block configurations and prefer low oxidation state from 2+ to 4+. Consequently, their ALD precursor and process design should be different from the early and late transition metals which have been very well investigated. For example, many organometallic compounds (with metal-carbon bonds) with post-transition metals could be isolated, stable and volatile even with simple and small ligand design, whereas early

and late transition metal (d-block) ones do not have enough thermal stability for ALD use. Also, we need to recognize that some of those compounds are pyrophoric (e.g. trimethylgallium, diethylzinc) and environmentally restricted due to adverse influence on human body (e.g. tetraethyllead). However, we can also say that metal amides (metal-nitrogen bond) with post-transition metals are not always stable. Zn bis(dialkylamide), In tris(dialkylamide), Pb bis(trimethylsilylamide) and Bi tris(dialkylamide) are thermally very unstable, whereas Ga tris(dimethylamide), Sn tetrakis(dialkylamide) and Sb tris(dialkylamide) are reasonably stable so as to be considered as ALD precursor candidates.

We will summarize the basic precursor data (TGA, DSC, etc.) of post-transition metal ALD precursors and will discuss the chemistry driving ligand selection leading to attractive vapor pressure, thermal stability and ALD reactivity.

AF-MoP-8 Correlating In-Situ Photoluminescence and Ellipsometry: A Novel approach to Analyze and Optimize ALD Materials for Photovoltaic Applications*, N. HARADA, A. LEVTCHENKO,* IPVF, France*; D. COUTANCIER,* CNRS, France*; F. DONSANTI,* IPVF, France*; J. GUILLEMOLES,* CNRS, France*; D. SUCHET,* Ecole Polytechnique - CNRS, France*; G. DELPORT,* ***Nathanaelle SCHNEIDER****,* CNRS, France

For the last decades, Atomic Layer Deposition (ALD) has undoubtedly become a key technique to deposit thin films in various research fields. As the deposition is sequential and self-limited, a high control over the films' thickness can be reached together with a high conformality. Moreover, the deposition can be done at low temperatures (below 100 °C) and allows the growth of a large panel of materials on different substrates. In the field of PV, ALD films are already used at an industrial scale (for instance in PERC solar cells) but their use also extends to buffer layers for CIGS cells, transparent conductive oxides (TCO), passivation or charge transport layers (ETL & HTL) for perovskite solar cells … [1]

In-situ ellipsometry together with photoluminescence (PL) were considered as relevant techniques to correlate film's growth properties and its functionalization. Indeed, by acquiring Spectroscopic Ellipsometry (SE) data, the film's thickness and optical constants are addressed during the growth [2], while its function is determined by analysing PL spectra or PL decays (by Time Resolved Photoluminescence TRPL) [3]. While in-situ SE is commonly used during ALD growth, only one example of in-situ PL has been developed to our knowledge and none combines the two techniques [4], making our approach original. In-situ characterizations would also be very useful for pre-industrialization, by reducing the number of samples required to totally take advantages of ALD specificities and generate highly performant devices. This presentation will introduce our experimental set-up in more details, as well as some first analysis results on the growth of ALD thin films on solar cells correlating SE and PL measurements (Fig. 1).

6. "Atomic Layer Deposition (ALD). Principes Généraux, matériaux et applications" *Ouvrage spécial desTechniques de l'Ingénieur : Principes et applications de la technique ALD (Atomic Layer Deposition)*
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AF-MoP-9 Chemistry of Boronic Acids on Semiconductor Surfaces: Pathways to Organic Monolayer Resists and Single Molecule Inhibitors for AS-ALD*,* ***Dhamelyz Silva Quinones****, A. Teplyakov,* University of Delaware

As the size of the components in electronic devices is shrinking, new approaches and chemical modification schemes are needed to produce nanometer-size features with bottom-up manufacturing.

Organic monolayers can be used as effective resists to block the growth of materials on non-growth substrates in area-selective deposition methods, particularly in AS-ALD. At the same time, same or similar organic molecules can act as small molecule inhibitors (SMIs) introduced during the ALD process.

This study aims at investigating the chemistry of boronic acids that can be used to make such resists on oxide and elemental semiconductors. We use 4-fluorophenylboronic acid (FPBA) as a model to investigate the reaction of boronic functionality with surfaces of TiO_2 and Al_2O_3 nanomaterials and with a functionalized Si(100) surface. On oxides surfaces, the reaction involves a condensation between a boronic acid functionality and the surface hydroxyl groups. On a Si(100) surface, the reaction is determined by surface termination. We use Cl-terminated Si(100) surface as an example to follow the reaction. The coverage of boronic acid attached to all these materials is the key to evaluate its potential as a blocking resist for ALD. Microscopy (AFM) and spectroscopy (ToF-SIMS, XPS, IR, and solid-state NMR) methods, together with cluster model DFT calculations are used to understand the chemical nature and surface bonding of FPBA on all these model surfaces. A commercial thermal ALD of TiO_2 based on TDMAT and water is used to test the reactivity of functionalized silicon surfaces and the potential of FPBA to be used as a non-growth resist. A possibility to use boronic acids as SMIs is also discussed.

AF-MoP-10 Trench Coverage Properties of Oxide Films Deposited at Low Temperature by Pure Ozone ALD*, N. Kameda, T. Hagiwara,* ***Soichiro Motoda****,* MEIDEN NANOPROCESS INNOVATIONS, INC., Japan*; K. Nakamura, H. Nonaka,* AIST, Japan

We report improvement of trench coverage of Al_2O_3 and SiO_2 films deposited by ALD using a pure ozone gas (PO-ALD) at low temperatures.

Pure ozone gas has a higher concentration of O_3 gas(≥99 vol%) than in the conventional ozone gas (<10 vol%).In this gas, high purity is achieved, while NO_x and heavy metal contaminants are 3-4 orders of magnitude lower compared to the conventional ozone gas. Thus, it is an effective oxidation source for producing high-quality oxide films at low temperatures. For example, Al_2O_3 film using PO-ALD with TMA precursor has low carbon content below detection limit by XPS at 150°C [1].

Another feature of an ozone molecule in the gas phase at the pressure range (up to 1000 Pa) during the PO-ALD process is its long half-life time, which is calculated from rate constant of its chemical reaction to be over 1000 seconds at 150°C. This half-life time is far longer than exposure time to the oxidant gas within each ALD cycle (< 100 seconds). Therefore, improvement in productivity during batch processing and improvement in trench coverage can be expected by supplying ozone without any decomposition to the inner part of trenches with high aspect ratios.

To confirm this expectation, Al_2O_3 film was deposited by PO-ALD with TMA for the trench with an aspect ratio of 55 (width 2.4um and depth 134um). The coverage, defined as the ratio of oxide thickness at the trench bottom to that at the trench top, was 0.52 and 0.98 at deposition temperatures of 100 and 300°C, respectively. At an ALD window temperature of 300°C, where TMA can be uniformly adsorbed to the bottom of the trench, PO-ALD can be formed on the bottom of the trench as well as on the top. On the other hand, at 100°C, which is lower than the ALD window, the amount of TMA adsorption was different between the top and the bottom of the trench, leading to the decrease in the coverage. However, if we compare each of GPC at the bottom of trench (GPC_{bottom}), the GPC_{bottom} of PO-ALD at 100°C was 0.076 nm/cycle, which is still larger than that of ALD using H_2O and O_2 plasma (0.064 and 0.056 nm/cycle) under the same condition for supplying the precursor gas. These results indicate that PO-ALD is so effective as to more homogeneous oxidation inside the trench structure with its higher reactivity even at the trench bottom compared to other oxidant gases.

We will also report and discuss trench coverage with a higher aspect ratio such as that over 100 and the case with SiO_2 films.

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AF-MoP-11 Novel Volatile and Liquid Sc Precursors for Electronic Applications*, M. Kapitein, S. Herritsch, M. Balmer, T. Hepp, E. Schlathoelter,* ***Oliver Briel****, J. Koch,* Dockweiler Chemicals, Germany

Scandium (Sc) based materials are gaining increased attention in research labs evaluating devices for electronic applications. The continuous down-scaling of transistors demands new materials that meet the stringent requirements of semiconductor devices. Sc-based oxides are discussed to replace HfO2 as dielectric in metal gate and additionally, these oxides show good etch properties[1]. A new field of research is (Al,Sc)N MOCVD, which could disrupt power and rf signal processing device performance if successful[2]. However, conventional Cp3Sc is a solid-state precursor with relatively low vapor pressure, hampering the application of Sc-based materials. Other alternatives show complicated synthesis routes or may contain species that are unfavorable for a certain process.

Here we present a series of newly developed Sc-based precursors for CVD and ALD applications. Compared to commonly known Cp3Sc, the Sc

precursors are liquid showing an increased vapor pressure, therefore improving vapor formation under process conditions. Molecule structures and thermogravimetric data are discussed.

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AF-MoP-12 PEALD Growth of Doped Indium Oxide Films with Control Over the Film Composition and Properties by Supercycle Approach Implementation*, M. Zered, **Valentina Korchnoy**, K. Weinfeld, G. Frey, M. Eizenberg,* Technion - Israel Institute of Technology, Israel

This investigation explored composition and physical properties of doped In_2O_3 films deposited on glass or thermal oxide substrates at temperature 220°C in an Ultratech Fiji G2 PEALD System. Sn, Ti and Mo were examined as potential dopants for In_2O_3.Doping was performed using supercycle of In precursor and dopant precursor. In precursor was delivered in multipulse mode by a sequence of two consecutive pulses in a quick succession, to extend precursor residence time. Doping level was controlled by varying dopant cycles to In cycles ratio. A schematic diagram of the process is shown in Fig1. Growth per cycle rates for doped materials (ITO, ITiO and IMoO) and pure materials depending on the cycle ratio are presented in Tables1,2. Doped materials growth rates are in good agreement with ones calculated using Rule of Mixtures. Fig2,3 show Sn/In and Ti/In atomic ratio extracted from XPS depth profile for 1:12 and 1:20 films deposited on SiO_2. For ITO, the deposited atomic ratio is very close to Sn:In cycle ratio used in the process and is in good agreement with Rule of Mixtures. For ITiO, extracted from XPS Ti atomic ratio is higher than its ratio in the supercycle recipe and deviates from Rule of Mixtures.

Electrical measurements Fig4, show that introducing dopants to In_2O_3 films causes resistivity changes: for ITO resistivity drops by~ an order of magnitude. For ITiO resistivity rises for heavily doped films and decreases along with decrease of Ti cycle ratio. Optimal conductivity was reported for 2-3% of Ti

Thermal annealing of deposited films was carried out in N_2 atmosphere, at temperature 400°C, for 10 minutes. Thermal treatment has greatly lowered resistivity by 1-3 orders of magnitude for all films, Fig4. Lowest resistivity achieved for Sn-doped, Ti-doped, and Mo-doped were $2.8\cdot10^{-4}\Omega cm$, $4.2\cdot10^{-4}\Omega cm$ and $6.1\cdot10^{-4}\Omega cm$ respectively. The drop in the film resistivity for undoped In_2O_3 film can be explained by generation of O vacancies, which effectively increase carrier concentration. Optical changes were measured by transmission spectrophotometry, Fig5. Transmission decrease in IR region after annealing is attributed to free charge carrier absorption in conduction band due to dopant activation. Absorption edge shift towards lower wavelengths (Moss-Burstein effect), related to the filling of conduction band states, is observed for the annealed films. Mo-doped and Ti-doped films exhibit superior IR transparency over the conventional Sn-doped films

Supercycle approach based on indium and dopant cycle ratios was successfully employed to produce doped In_2O_3 films with control over the films composition and properties

AF-MoP-13 Using Glow-Discharge Optical Emission Spectroscopy to Characterize Polymers Treated Through Vapor Phase Infiltration*, **Seancarlos Gonzalez**, Y. Choe, D. Bergsman,* University of Washington

Vapor phase infiltration (VPI) is a variation of atomic layer deposition (ALD) which takes advantage of long hold times to allow reactants to diffuse into a porous substrate. Recently, VPI has been used for the post-synthesis modification of polymers by infusing metal oxides into the polymer matrix to improve crucial membrane properties such as solvent stability and separation performance. However, characterizing polymers modified by infiltration, such as the depth and concentration of infiltrated reactants, can be challenging. Ellipsometry can be used to characterize surface thickness, but it cannot determine the depth to which the infiltration is successful or the elemental composition as a function of thickness. Cross-sectional scanning electron microscopy (SEM) can determine elemental composition, but its resolution for certain elements is limited to only very thick layers. X-ray photoelectron spectroscopy (XPS) can depth profile to determine elemental composition, but this technique is extraordinarily time and cost intensive.

In this work, we examine the use of glow-discharge optical emission spectroscopy (GD-OES) to characterize polymer membranes treated by infiltration. This technique uses plasma to sputter a crater into a sample, and then measure the atomic emissions of the sputtered elements. Signals are produced for each element as a function of time, which can yield quantitative data of elemental composition as a function of depth when calibrated to a standard. We demonstrate the use of GD-OES to explore the effectiveness of VPI on thin polymers by determining the depth to which infiltration was successful and comparing the elemental compositions of polymers infiltrated under different conditions.

AF-MoP-14 New Approaches for the Thermal Atomic Layer Deposition of Elemental Antimony Thin Films*, **Daniel Beh**,* Wayne State University*; Z. Devereaux, T. Knisley,* Applied Materials*; C. Winter,* Wayne State University

Elemental antimony (Sb) thin films have applications in phase change memory, doping of semiconductors, and as precursors to Sb-containing materials. Atomic layer deposition is an important thin film growth technique that can afford Angstrom-level thickness control and perfect conformality in high aspect ratio features. Many applications of Sb films require growth in substrates with nanoscale features where perfect thickness uniformity and conformal coverage are required. Accordingly, the growth of Sb films by ALD is an important research goal. Elemental Sb films have been previously grown by thermal ALD using $SbCl_3$ and $Sb(SiEt_3)_3$[1] and $Sb(SiMe_3)_3$ and $SbCl_3$.[2] We have previously reported the use of 2-methyl-1,4-bis(trimethylsilyl)-2,5-cyclohexadiene (**1**) or 1,4-bis(trimethylsily)-1,4-dihydropyrazine (**2**) as reducing co-reactants in ALD.[3] Herein, we describe the thermal ALD of elemental Sb films using $SbCl_3$ and **1** or **2** as the co-reactants. Most deposition experiments were conducted using **2** as the co-reactant, since it is more reactive than **1**. Sb films were deposited at substrate temperatures between 75 and 150 ºC using $SbCl_3$ and **2** as precursors. At a substrate temperature of 75 ºC, a growth rate of 0.58 Å/cycle was observed on Si-H substrates. The X-ray diffraction pattern of a 28 nm thick film on an Si-H substrate matched the reference pattern for elemental Sb. X-ray photoelectron spectroscopy of a 28 nm thick film on Si-H afforded a composition of 98.5% elemental Sb after 20 minutes of argon ion sputtering. Other properties of the Sb films will also be described. Finally, we will present alternative halogen-free Sb precursors and nitrogen-based co-reactants that also afford elemental Sb films in thermal ALD processes.

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AF-MoP-15 Electron Beam Generation and Precise Control of Beam Energy for Large Area Electron Enhanced Atomic Layer Deposition*, **MINSEOK KIM**, J. Jung, J. Park, C. Lim, B. Seo, C. Chung,* Hanyang University, Republic of Korea

A large-area electron beam is generated, and the electron beam energy is precisely controlled using several DC grids. As the electron beam source's electron temperature is lowered (T_e =2.43 eV to 0.8 eV), the electron beam's energy spread is reduced from 7.8 V to 2.7 V. This is because the low electron temperature plasma has a narrow electron energy distribution, which makes the energy spread of the generated electron beam smaller. Through precise control of the electron beam energy, the generation of N and F radicals according to the beam energy is observed in Ar/N2 and Ar/CF4 plasmas. It is expected that a precursor decomposition and ligand formation can be selectively made in the electron-enhanced ALD process through precise control of the large-area electron beam.

AF-MoP-16 Development of Piezo Controlled Vapour Delivery System for Ru ALD Application*, **Hiroshi Nishizato**,* HORIBA STEC, Co., Ltd., Japan*; G. Krunal,* HORIBA STEC, Co., Ltd., India*; T. Moriyama,* HORIBA STEC, Co., Ltd., Japan*; K. Uesugi,* Hiroshima University, Japan*; G. Rahman,* Hiroshima University, Bangladesh*; P. Lowery, T. Freeman,* HORIBA Reno Technology Center*; Y. Amemiya, A. Teramoto,* Hiroshima University, Japan

Atomic layer processes, such as atomic layer deposition (ALD) use precursors. Some of the Metal ALD process uses rare metal such as Ru for metal connection.This kind of metal organic chemical vapor used in ALD processes has to be delivered at a constant volume, and concentration per pulse, without wasting unused precursor through the vent lines during

purge cycles. In the present study, the newly developed fast response flow-controlled vapor delivery system using a piezoelectric actuated electromechanical valve (EMV) was developed and implemented for this ALD application. This valve shows a response time of <1ms for ON/OFF pulsing and <10ms for the flow control with the ability of programable waveform control. Ruthenium film formation has been confirmed from Ru precursor and Oxygen on the oxidised Si surface by using this piezo actuated electromechanical valve (EMV).Fig. 1 shows a Tool configuration and setting of Ru ALD. In the configuration shown, no ruthenium precursor vent lines are used and ruthenium precursor dosing goes directly to the reactor in the ALD cycle.

AF-MoP-17 Realization of Conductive Electrodes for Solar Cells by Spatial ALD Using New Coinage Metal Precursors*, N. Boysen,* Ruhr University Bochum, Germany*; T. Hasselmann, B. Misimi,* University of Wuppertal, Germany*; M. Karppinen,* Aalto University, Finland*; T. Riedl,* University of Wuppertal, Germany*; **Anjana Devi**,* Ruhr University Bochum, Germany

The realization of conducting and transparent ultra-thin metallic films by ALD remains a major challenge due to a pronounced Volmer-Weber type island growth on different substrates. Several applications that are relying on thin metallic films, such as transparent electrodes for solar cells, might not be easily accessible by ALD, as precursors with suitable characteristics are missing. Especially for the deposition of metallic silver films by ALD, a precursor possessing high thermal stability, volatility and reactivity is still sought after. Based on our iterative efforts in terms of ligand engineering, new copper and silver precursors were developed and their successful application in low-temperature plasma-assisted spatial ALD processes at atmospheric pressure (APP-ALD) was demonstrated.[1] Introducing the stabilizing N-heterocyclic carbene ligand (NHC), combined with reactive anionic counterparts such as hexamethyldisilazides (hmds) or *β*-diketonates (acac), copper and silver precursors and their respective processes for metallic thin films could be established.[2] The new silver precursor [Ag(NHC)(hmds)] provides a significantly enhanced reactivity compared to its commercially available counterpart [Ag(fod)(PEt_3)] (fod: 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate), which enables spatial ALD processes with H_2/Ar plasma at a record-low deposition temperature of 60 °C. This not only significantly reduces the total thickness of the layers needed for percolated and thus conductive silver films, but also enables an application of the silver films as conductive electrodes in organic solar cells.[3] Furthermore, new ALD processes based on the NHC-stabilized copper precursors, namely [Cu(NHC)(hmds)] and [Cu(NHC)(acac)] were established. Using [Cu(NHC)(hmds)] and H_2/Ar plasma, pure and conductive copper films were deposited at a low deposition temperature of 100 °C by APP-ALD.[4] Also, in a thermally-driven ALD process with [Cu(NHC)(acac)] and hydroquinone, nanoparticulate metallic copper deposits could be obtained at remarkably low deposition temperatures of 145 °C to 160 °C. These new findings reiterates that deposition of conductive copper or silver thin films at low temperatures can only be realized by a rational design of highly reactive precursors that are tailor-made for such demanding processes.[5] This contribution summarizes the main findings of precursor and process development at RUB, BUW and Aalto University over the last years and presents ideas on how to further strengthen the precursor and process characteristics for different applications.

AF-MoP-19 Comparative Study of the Surface Reactivity and PEALD of Monoaminosilanes and Cyclic Azasilanes*, **Chad Brick**, T. Ogata, J. Collins,* Gelest, Inc

In this work, we report the physical properties, surface reactivity and plasma-enhanced atomic layer deposition (PEALD) of a series of monoaminosilanes and cyclic azasilanes, with a focus on the relationship between chemical structure and properties such as vapor pressure, pulse times required to reach surface saturation, practical material consumption rates in a production-like tool, and water contact angle. Additionally, the conversion of these chemical structures to SiO_2 using oxygen plasma PEALD will be discussed in terms of growth per cycle, the required temperature and plasma pulse times for conversion to oxide, and the resulting film composition and properties.

AF-MoP-20 Atomic Layer Deposition of Strontium Oxide on Different Materials*, **Marek Eliáš**,* CEITEC, Brno University of Technology, Czechia*; A. Harumningtyas,* Osaka University, Japan*; D. Nečas, L. Janů, E. Dvořáková,* CEITEC, Czechia*; T. Ito, P. Vinchon, S. Hamaguchi,* Osaka University, Japan*; L. Zajíčková,* CEITEC BUT & Masaryk University, Czechia

Atomic layer deposition (ALD) on different substrates is challenging because of its extreme surface-chemistry sensitivity given by the targeted ALD self-limiting nature. In this study, we investigated the growth of strontium oxide from bis(tri-isopropylcyclopentadienyl) strontium $Sr(iPr_3Cp)_2$(98%, Strem, Massachusetts, USA) using either H_2O oxidation step in thermal ALD or oxygen plasma step in plasma-enhanced ALD. The primary motivation was to prepare strontium-containing films for spinal implants. Strontium has a dual effect of stimulating osteoblast function and inhibiting osteoclast function and can be used for osteoporosis treatment. In combination with TiO_2, a typical biocompatible material, it can enhance the bioactivity of coated implants. The combination of SrO with TiO_2 is also advantageous in other applications. The ternary strontium titanate $SrTiO_3$ is of significant interest for high-density metal–insulator–metal (MIM) capacitors. $SrTiO_3$ perovskite applications span from electronics to energy. Thus, it is essential to understand how ALD of SrO works on different materials either because of the need to fine-tune the composition of ternary oxides or create thin-film heterostructures. Polymer substrate brings an additional challenge to the ALD processes. We studied the ALD of SrO on Si, Ti, TiO_2, and polyetheretherketone (PEEK) with different surface treatments. The selection of the PEEK substrate was motivated by applications for spinal implants because its elastic modulus is similar to the human cortical bone.

AF-MoP-22 Effects of Silicon Surface Termination on the Initial Stages of TiO_2 Deposition by ALD*, **Tyler Parke**, A. Teplyakov,* University of Delaware

As atomic layer deposition (ALD) emerges as a method to fabricate architectures with atomic precision, emphasis is placed on understanding surface reactions and nucleation mechanisms. ALD of titanium dioxide with $TiCl_4$ and water has been used to investigate deposition processes in general, but the effect of surface termination on the initial TiO_2 nucleation lacks needed mechanistic insights. Further, a wider toolkit of terminations, which promote or inhibit nucleation, may allow for more elaborate deposition schemes involving the same overall deposition chemistry. This work examines the adsorption of $TiCl_4$ on Cl-, H-, and -OH terminated silicon single crystal surfaces to elucidate the general role of different surface structures and defect types in manipulating surface reactivity of growth and non-growth substrates. Other surface terminations derived from these starting points, specifically additional modification step with primary amines, were also tested. The surface sites and their role in the initial stages of deposition are examined by X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). Density functional theory (DFT) computations of the local functionalized silicon surfaces suggest oxygen-containing defects are primary drivers of selectivity loss on most of these surfaces.

AF-MoP-24 Deposition Characteristics Evaluation of New In Precursor for IGZO TFT*, **Yong Hee Kwone**, S. Jeon, S. Lee, T. Byun, Y. Im, S. Lee,* DNF Co. LTD., Republic of Korea

In accordance with the high resolution/high integration of the display market, the required performance of the driving element required for the back-plane is increasing in order to secure uniform performance in a large area.

Accordingly, various studies on materials and processing methods of TFT devices are being conducted. In particular, as a material for TFT, IGZO based on In_2O_3, which has the advantages of relatively high mobility compared to amorphous silicon, excellent uniformity compared to polycrystalline silicon, and a simple manufacturing process, has been actively studied. However, conventional indium precursors have disadvantages of high price as well as low vapor pressure and low deposition rate.

In this study, the deposition characteristics of In_2O_3 were evaluated using the newly developed Indium precursor (DIP-4) for the purpose of dramatically improving the disadvantages of the existing Indium precursor (Fig 1). In addition, it was compared with DADI((3-Dimethylaminopropyl)dimethylindium), a currently commercialized indium precursor.

The deposition process used the PEALD process, which is easy to control the composition and excellent in thickness uniformity in the deposition of a multi-component thin film with a multi-layer structure. As a result of evaluating the basic ALD characteristics (Saturation, Window, etc.) of the DIP-4 and DADI, In_2O_3 deposited with each Precursor showed similar characteristics (Composition, Density, Crystal Structure). However, the deposition rate of the DIP-4 was about 35% higher than that of DADI(Fig 2).Through this, the high productivity of the DIP-4 was confirmed.

In addition, the DIP-4 is advantageous in terms of unit price because it can be obtained with simplified synthesis and high yield by distillation.

For the formation of multi-layered IGZO thin films, the incubation time, deposition rate, and interface characteristics of In_2O_3 deposited with the DIP-4 were evaluated according to the surface (Ga_2O_3, ZnO).

AF-MoP-27 Atomistic Study of Amorphous Si-O-X Networks for Plasma Enhanced Atomic Layer Deposition-Produced SiO_2 Films: Illuminating the Structure-Composition-Mechanical and Electrical Property Connections, *A. Dernov,* University of Minnesota, USA*; P. Agarwal, R. Kumar,* Lam Research Corporation*; **Traian Dumitrica**,* University of Minnesota, USA

Using self-consistent density functional tight-binding simulations it is shown that Aluminum (Al) content in amorphous silica (*a*-SiO2) changes its ideal microscopic structure in a manner compatible with densification. Similar to the structure of pressure-densified *a*-SiO2, the Al-modified *a*-SiO2 comprises a network of Silicon (Si)-centered tetrahedra as well as unquenchable pentahedra and, to a smaller extent, hexahedra coordination defects. Al itself acts not only as a network former, with fourfold coordination but also as a center for fivefold and sixfold coordination defects. Al content promotes densification since it shifts the potential energy minima at densities larger than in their pristine counterpart. Calculations uncover that Young's modulus (*Y*) and static dielectric constants ($\varepsilon 0$) can be effectively doubled through densification. Oxygen starvation promotes network polymerization, which further increases *Y* and $\varepsilon 0$. However, the small ring formation through Si–Si bonding and the presence of undercoordinated Si introduce electronic states in the electronic band gap. The results provide guidance for the bottom-up design of amorphous silica with tunable microscopic structure and properties desirable for advancing electronic applications.

AF-MoP-28 Surface Modification of 2,6 Diamino-Pyrazine-1-Oxide by Atomic Layer Deposition of Al_2O_3, ***John Miller**, R. Reeves,* Lawrence Livermore National Laboratory

Inkjet additive manufacturing utilizes a stream of solid particles embedded in a cross-linking fluid which is ejected from a nozzle and stacked layer by layer to make custom shapes with tunable properties. The properties of the printed components are highly dependent on the solid content capable of being loaded into the inks. Atomic layer deposition (ALD) provides a means to modify the surface of particles to reduce their surface energy and thus cohesivity in inkjet solutions, allowing for increased solids loading. This work investigates the effects of ALD Al_2O_3- on the surface of dry 2,6 Diamino-Pyrazine-1-Oxide (DAPO) particles, which can be used as a solid filler in ink solutions. In bulk quantities, powder rheometry was utilized to measure the basic flowability energy of coated DAPO as a function of ALD cycles. Results show that increasing the number of coating cycles increases the basic flowability energy, indicating a decrease in overall powder cohesivity. Small samples of uncoated and coated DAPO were also measured by Inverse Gas Chromatography to directly measure changes in surface energy before and after coating. Results showed that surface coatings reduce the surface energy at low gas coverage corresponding to saturation of high energy sites on the surface of the DAPO.

AF-MoP-29 Precise Interface Engineering for High Thermoelectric Performance in CuNi Alloys Using Powder ALD, *S. He,* Leibniz Institute for Solid State and Materials Research, Germany*; A. Bahrami,* Helmholtzstraße 20, Germany*; S. Lehmann, **Kornelius Nielsch**,* Leibniz Institute for Solid State and Materials Research, Germany

In thermoelectric materials, interfaces of phase boundaries play a critical role in carrier/phonon transport. Herein, we present a strategy for designing a sandwich coating structure based on powder atomic layer deposition (pALD) to precisely control and modify the phase boundaries of CuNi alloys, and thus decouple thermoelectric parameters. Ultrathin interlayers of ZnO and Al2O3 oxides are uniformly deposited on the phase boundary of CuNi alloys to demonstrate the effectiveness of this strategy. The hierarchical deposition of ZnO and Al2O3 layers contribute to the creation of an energy barrier, that augments the Seebeck coefficient significantly. Despite a slight decrease in the electrical conductivity, the enhanced Seebeck coefficients for 50 cycles ZnO coated samples compensated for the loss, resulting in a ~45% increase in power factor over the uncoated sample. Thereupon, the sandwich-like multiple layers structure ($ZnO/Al_2O_3/ZnO$) was built to enhance electrical resistance at phase boundaries. Beyond 50 ALD cycles, the multiple-layered structure sustained the increased power factor while notably reducing thermal conductivity. In the sample with 44 cycles ZnO/11 cycles Al_2O_3/ 44 cycles ZnO cycles multi-layer structure, a maximum figure of merit (*zT*) of 0.22 was achieved at 673 K. Due to the decoupling of thermoelectric parameters by ALD, the *zT* value increased 144% when compared to pristine CuNi and is nearly as high as previously reported values. The ALD-based approach to decoupling thermoelectric parameters is easily applicable to other thermoelectric materials, resulting in the development of high-performance materials.

AF-MoP-30 High-Throughput SiO_2 PEALD Using a Novel Si Precursor, ***Jin Sik Kim**, B. Kim, J. Choi, W. Koh,* UP Chemical Co., Ltd., Republic of Korea

A newly developed Si precursor can enhance SiO_2 PEALD throughput greatly. A notable application of SiO_2 PEALD is double patterning, for which SiO_2 film is deposited over photoresist at low temperature between room temperature and 150°C.The PEALD growth-per-cycle using the novel Si precursor is 2.3 times larger than bis(diethylamino)silane (BDEAS) and 1.7 times larger than diisopropylaminosilane (DIPAS) using O_2 plasma at 125°C. It may enhance productivity of PEALD double patterning process 2.3 or 1.7 times compared to using BDEAS or DIPAS. PEALD deposition characteristics and SiO_2 film properties including film step coverage, thickness uniformity, wet etch rate, carbon content, etc. deposited from the novel precursor and conventional ones such as BDEAS, DIPAS and BTBAS are presented and compared. The novel Si precursor shows the same or better characteristics.

AF-MoP-31 Oxidation Mechanism of Atomic Layer Deposition of HfO_2 Using O_3, ***Soo Hyun Lee**, B. Shong,* Hongik University, Republic of Korea

As the size of semiconductor device is shrinking down to the ultimate limit, there have been needs for deposition techniques that can control the thin films at atomic scale. Atomic layer deposition (ALD) is a powerful deposition technique that can fabricate thin film in excellent conformality even on substrates with high aspect ratio geometries. Hafnium oxide (HfO_2) is a representative thin film material that is often deposited via ALD due to its high k value and superior properties as dielectric. For ALD of HfO_2, commercialized Hf precursors containing amido ligands such as TEMAH (tetrakis(ethylmethylamino) Hf) and CpHf (tris(dimethylamido)cyclopentadienyl Hf) are often used. While TEMAH or other homoleptic amido precursors allow ALD using either water (H_2O) or ozone (O_3) as counter-reactants, the heteroleptic CpHf require oxidants stronger than H_2O such as O_3 in order to reduce carbon impurities [1,2]. Regardless of popular adaptation of O_3 as oxidant in oxide ALD processes, however, the chemical mechanism for the reaction of O_3 during HfO_2 ALD has not been elucidated yet. In this study, the oxidation mechanism of surface-adsorbed Hf precursors by O_3 is analyzed using density functional theory (DFT) calculations. Multiple possible oxidation reaction pathway which successfully removes remaining amido ligand on Hf are considered. Reaction of O_3 are expected to occur through multiple elementary steps, finally forming -OH moieties and remove C/H/N via liberation of several byproducts. Overall these reactions are found to be highly exothermic, possibly due to high reactivity of O_3.

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AF-MoP-32 Eggshell-Type Catalysts by Atomic Layer Deposition: Distribution of Zinc Oxide Within Mesoporous Alumina Spheres, ***Jihong Yim**,* Aalto University, Finland*; N. Heikkinen,* VTT Technical Research Centre of Finland*; E. Haimi, C. Gonsalves, A. Chahal, J. Velasco, R. Karinen,* Aalto University, Finland*; J. Lehtonen,* VTT Technical Research Centre of Finland*; R. Puurunen,* Aalto University, Finland

Atomic layer deposition (ALD) is an intriguing method for preparing heterogeneous catalysts with well-defined surface structures.[1,2] A recent study by Arandia et al.,[3] related to this work, demonstrated the potential of zinc acetylacetonate [$Zn(acac)_2$] as an ALD reactant for tuning the surface properties of mesoporous zirconia-supported copper. In this work, we aim (i) to prepare a uniform coating of zinc oxide (ZnO) on mesoporous alumina (Al_2O_3) in a fixed bed flow type ALD reactor and (ii) to control the penetration depth of ZnO coatings on Al_2O_3 spheres by adjusting the dose of $Zn(acac)_2$.

ZnO was added on porous Al_2O_3 with an irregular shape (particle size ca. 0.1 mm) and Al_2O_3 spheres (particle sizes 1.0, 1.8 and 2.5 mm) in F-120 ALD reactor. The $Zn(acac)_2$ (vaporized at 120 ℃) was chemisorbed on calcined supports at 200 ℃ for 3 h in the ALD reactor. The leftover ligands after the chemisorption were oxidatively removed in synthetic air in a tube furnace at 600 ℃. Information on ZnO ALD on Al_2O_3 was obtained by inductively coupled plasma-optical emission spectrometry (ICP-OES), scanning electron microscopy (SEM) with energy-dispersive X-ray spectrometry (EDS), and in-situ diffuse reflectance infrared Fourier transform spectroscopy-mass spectrometry (DRIFTS-MS). By EDS analysis, a uniform zinc signal was observed throughout the 0.1 mm Al_2O_3 particle (Fig. 1 of supporting information). Zinc loading was ca. 3.1 wt% (1.8 Zn/nm^2). Meanwhile, zinc was observed near the outer surface of the Al_2O_3 spheres (Fig. 2). The penetration depth of the ZnO and the zinc loading increased (highest ca. 2.5 wt%) while increasing the dose of $Zn(acac)_2$ was directed through the support bed. These results indicate that the reaction of $Zn(acac)_2$ on Al_2O_3 spheres did not reach saturation yet. DRIFTS-MS showed that acac ligands adsorbed on Al_2O_3 were removed as CO_2 up to 550 ℃. The surface coverage

profile of zinc coating on sphere support was simulated by a diffusion-reaction model fitted for various exposures, comparing well with experimental data (Fig. 3). We believe that the ALD process can be used to prepare eggshell-type heterogeneous catalysts.

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AF-MoP-33 Numerical Simulation of Surface Reactions During Plasma-Enhanced Atomic-Layer Deposition (PE-ALD) of Silicon Nitride (SiN), *J. Tercero,* Osaka University, Japan; *M. Krstić,* Karlsruhe Institute of Technology (KIT), Germany; *A. Jaber, E. Tinacba, N. Mauchamp, M. Isobe, T. Ito, K. Karahashi,* ***Satoshi Hamaguchi,*** Osaka University, Japan

Fabrication methods of high-performance semiconductor devices have reached a stage where precise processes with atomic-scale accuracy are required. As such, plasma-based surface processing techniques such as plasma-enhanced atomic layer deposition (PE-ALD) have been widely employed to deposit highly conformal thin films on surfaces with complex geometries. Each cycle of PEALD typically consists of self-limiting adsorption and desorption steps.[1] For example, in the case of silicon nitride (SiN) PE-ALE[2], chlorosilanes are adsorbed on the SiN surface at an elevated temperature. This study first analyzed the desorption process of chlorosilanes (SiH_xCl_{4-x}) on the Si(100):2´1 surface, using density-functional-theory (DFT) simulation, evaluating the adsorption and activation energies of chlorosilanes. It is observed that most chlorosilanes are dissociatively adsorbed on the surface barrierlessly even at zero surface temperature. We also performed classical molecular dynamics (MD) simulations to evaluate the adsorption reaction (sticking) probabilities of chlorosilanes on Si and SiN surfaces. Molecular dynamics simulation was also performed to study the nitridation step where the surface is exposed to nitrogen/hydrogen or ammonia plasmas. It was found that hydrogen radicals play an important role in removing excess chlorine (Cl) atoms from the surface.

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AF-MoP-34 Effect of Precursor Temperature of 1,4-Phenylene Diisocyanate (PPDI) on the Growth Rate of Polyurea Using Molecular Layer Deposition (MLD), ***Jae Seok Lee,*** *S. Song, B. Choi,* Korea University, Republic of Korea

For molecular layer deposition (MLD), it is important to find a saturated pulse, purge time at a specific temperature. In the case of a precursor in a solid state at room temperature, the vapor pressure is lower than that in a liquid or gaseous state, and thus a longer pulse, purge time is required. Since the vapor pressure of the precursor is proportional to the temperature, heating precursor during deposition can reduce the cycle time. However, for certain molecules, intermolecular dimerization occurring at temperatures above the melting temperature (T_m) may affect the growth rate of the thin film. Therefore, it is necessary to consider this and determine the appropriate precursor temperature.

In this study, MLD was used to synthesize a polyurea thin film using 1,4-phenylene diisocyanate (PPDI) and ethylenediamine (EDA) as precursors. 70℃, 120℃, and 180℃ are selected as precursor temperature based on T_m of PPDI which is approximately 99℃. Polyurea thin film was deposited on Si wafer at a room temperature. Growth per cycle (GPC) for each condition was measured using X-ray reflectometry (XRR) and Fourier transform infrared spectroscopy (FTIR) to evaluate the effect of PPDI temperature on the growth rate and structure of the thin film. In addition, to verify the dimerization of PPDI, heat treatment was performed at 70℃, 120℃ and 180℃ for a week using dry oven. Transition of PPDI molecular structure and physical properties were analyzed using differential scanning calorimetry (DSC) and FT-IR.

As a result, dimerization was identified at 120℃ and 180℃, which is the cause of the increasing melting point. Through XRR data, there is clear tendency of decrease in GPC with 120℃ and 180℃ cases while 70℃ does not. IR peak analysis is for double checking the results from PPDI. In conclusion, the precursor temperature must be decided considering both the reactivity and thermal stability of substances.

AF-MoP-35 Multicomponent $RuTiO_x$ Thin Films through Atomic Layer Modulation, *N. Trinh, C. Nguyen, B. Gu, H. Lee,* ***Mingyu Lee,*** Incheon National University, Republic of Korea

Recently, atomic layer deposition (ALD) has become a key technique for fabrication of multicomponent films in nanoscale devices. Conventionally, the supercycle method consisting of two or more ALD processes has been used, and the compositional ratio of the films can be controlled by cyclic ratio of two ALD processes. However, the compositional ratio often is not consistent with the theoretical calculation due to different surface reactions on each surface. Furthermore, the supercycle method requires a certain film thickness to maintain a compositional ratio, so it can't be used in a few nanometers thickness films. Based on understanding of surface reactions mechanism in atomic layer deposition (ALD), we have studied the concept of atomic layer modulation (ALM) for fabrication of the multicomponent thin film with atomic-scale control. The main key idea of ALM is that the compositional ratio is determined by the physical steric hindrance and the chemical reactivity of two precursors on the surface which can be predicted by theoretical calculations. We successfully fabricated a $RuTiO_x$ multicomponent thin film which have the potential applications for interconnects materials. The $RuTiO_x$ thin film was deposited with controllable dopant ratio using a Ru precursor, dicarbonyl-bis(5-methyl-2,4-hexane-diketonato)Ru(II) (Carish), and a Ti precursor, titanium tetraisopropoxide (TTIP). Due to the steric hindrance effect, the component ratio of $RuTiO_x$ thin films is determined by the exposure sequence of precursors. Theoretical calculations were employed using Monte Carlo (MC) and density functional theory (DFT) to study physical and chemical reaction mechanisms, respectively. The results are consistent with the experimental results analyzed by X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). With the ability to control doping concentrations even at atomic scale, not only the ALM method could be contributed to expand the possibility of fabricating multicomponent oxides materials, but also improving the quality of the deposited films.

AF-MoP-36 Fine-Tuning of Low Surface Energy Substrate Functionality to Lower the Nucleation Delay Inherent for ALD of Noble Metals, *S. Thalluri, R. Zazpe, J. Rodriguez-Pereira, H. Sopha,* ***Jan Macak,*** University of Pardubice, Czechia

Platinum group metals such as Pt, Ru, Pd, Ir, etc., have superior performance for various catalytic applications[1]. Due to their scarcity, efforts were being made to reduce or replace these noble metals. Atomic Layer Deposition (ALD) is one among the best technique to facilitate lowering of loading mass on a support of interest[2],[3]. Furthermore, ALD is the most suitable technology that can decorate high aspect ratio and high surface area substrate architectures[4]. Due to the governing surface energy variations between noble metals and support surfaces, the growth initiates as nanoparticles (NP) and with a further increase in ALD cycles the agglomeration among NP's dominates over the individual NP size increase, thus developing thin films of relatively higher thickness. These variations are also known to increase the nucleation delay of noble metals especially for Ru considerably. In this regard our efforts were laid to improve the functionality with pretreatments on carbon paper (CP) supports which were shown promising to reduce the nucleation delay of ALD deposited Ru.

For electrocatalytic applications, it is important to choose the right substrates. Among available substrates, CP and titania nanotube (TNT) layers are best choices considering their physio-chemical properties, availability, vast literature, and low costs incurred using these as support substrates in electrocatalysis and photocatalysis. Several surface modifications for CP's and variations on morphological aspects of TNT layers had received a great attention form applied fields due to their improved surface area, conductivity and stability[5]–[8]. Uniformly decorating these CP's and TNT layers by NPs or thin films of catalysts proved to be highly efficient with no boundaries on applications[9].

The presentation will introduce and describe the synthesis of different noble metal NPs by our ALD tool (Beneq TFS 200) on various aspect ratio TNT layers and CP substrates. It will also include the corresponding physical and electrochemical characterization and encouraging results obtained in electrocatalysis.

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AF-MoP-37 Growth Behaviors and Structural Characterization of PEALD In_2O_3 thin films using Amide-based and Alkyl-Based Novel Indium Precursors*, **Gyeong Min Jeong**, Y. Kim, H. Yang,* Hanyang University, Republic of Korea*; M. Kim, S. Lee, Y. Kwone, S. Jeon, Y. Im,* DNF, Republic of Korea*; J. Park,* Hanyang University, Republic of Korea

Oxide semiconductors are attracting attention as active channel materials due to their advantages like high field effect mobility, low off current, and low process temperature. Indium-based oxides, such as In-Ga-Zn-O (IGZO), In-Ga-Sn-O (IGTO), In-Ga-O (IGO), have been mainly studied for high electrical characteristic. Indium oxide is critical source in electron properties because it has very low electron formation energy that can easily generate electron. Indium provides carrier transport path through overlap from the large size of their 5s orbital. As the device scaling down according to Moore's law need nanoscale controlling in process, the atomic layer deposition (ALD) is powerful method which can control film thickness in atomic scale and can control chemical composition. Since ALD process is based on self-limiting reaction nature, choice of precursor has significant influence on the properties of thin film. Many indium precursors ($InCl_3$, TMIn, InCp, DADI, In-CA-1, etc.) for ALD have been developed. Especially, (3-Dimethylaminopropyl) dimethylindium (DADI) is mostly used precursor in developing oxide semiconductor. The DADI precursor which is liquid phase has moderate GPC because amine ligand has high reactivity, but it is expensive and has low vapor pressure. In contrast, TMIn is inexpensive and high vapor pressure precursor than DADI, but it is a solid phase material that make low growth rate properties. So that, researching the cheaper precursor that have high reactivity and high growth rate is needed. In this study, we newly synthesized two indium precursors of DIP-3 and DIP-4 based on structure of DADI and TMIn, respectively. DIP-3 is liquid phase precursor based on DADI that have structure that is consist of amine ligand and coordination bond. On the other hand, DIP-4 is Alkyl based liquid phase material like TMIn. DIP-4 has not only higher vapor pressure compared to DIP-3 but also advantage in price. We made indium oxide film using DIP-3, DIP-4 and O_2 plasma in setting temperature 100 ~ 300°C. As a result, indium oxide layer using DIP-4 precursor has higher GPC (~1 Å/cycle) than DIP-3 (~0.6 Å/cycle). In addition, enlarged grains that help to enhance electrical properties are found from sample using DIP-4 due to smaller precursor size. We explain the origin of difference through analysis of film and DFT calculation. Therefore, it is useful method to get enhanced GPC and enlarged grain size that changing structure of precursor.

AF-MoP-38 Evaluation of a Zr Precursor and Hf Precursor with Higher Thermal Stability for the Atomic Layer Deposition of ZrO_2 and HfO_2 Films*, **Randall Higuchi**,* EMD Electronics*; R. Waldman, P. Arab, C. Chen, D. Lee,* EMD Electronics, USA

For DRAM applications the crystallinity of the dielectric film is critical to obtaining the correct dielectric constant. Precursors that allow higher temperature deposition could lead to crystalline as-deposited films and the thermal stability could lead to better step coverage. A Zr precursor and a Hf precursor were used to deposit ZrO2 and HfO2 films, respectively, in order to examine their deposition properties, electrical properties, and step coverage. These precursors have similar vapor pressure but improved thermal stability and can be deposited above 350C with no decomposition. Use of the Zr precursor with ozone shows a deposition rate of 0.65A.cyc from 250-350C. Use of the Hf precursor with ozone shows deposition rate of 0.65A/cyc from 300-350C. We looked at the leakage and EOT of the resulting ZrO2 and HfO2 films and showed comparable or better electrical performance to films deposited from other precursors. Crystallinity of the films was confirmed to correlate with the electrical performance. We also tested step coverage and the better thermal stability of the precursors led to improved step coverage. The current study covers the process window and electrical results for the investigated precursors.

AF-MoP-39 Hybrid PEALD/PEVCD Reactor Design for Depositing Thick GaN Films on Si*, **Birol Kuyel**, A. Alphonse, J. Marshall,* NANO-MASTER, Inc.

Depositing thick GaN on Si wafer using PECVD or CVD will require a thin buffer layer on sapphire wafers. We have presented results showingALD deposited GaN on Si wafer could possibly be a buffer layer for growing thick GaN layer on Si because of Si/GaN interlayer mixing* during ALD deposition. Now we want to show results of depositing a thick GaN film in a PECVD system on a Si wafer having ALD GaN. Furthermore we will show that our new "Hybrid PEALD/PECVD reactor"** can deposit both thin ALD buffer layer and thick PECVD GaN on Si wafer in same chamber without changing the hardware and breaking the vacuum.

*Deposition of GaN using $GaCl_3$ with N_2 plasma using PAALD, 44th ICMCTF conference at San Diego, Apr 2015.

**Patent US11087959B2

AF-MoP-41 ALD Infilling of Macroscopic Nanoporous Solids: Expanding Beyond Al_2O_3*, **Benjamin Greenberg**, K. Anderson, A. Jacobs, J. Wollmershauser, B. Feigelson,* U.S. Naval Research Laboratory

ALD of Al_2O_3 from trimethylaluminum (TMA) and water has many advantages as an infill process for macroscopic nanoporous solids. Both TMA and H_2O are relatively small molecules that diffuse relatively quickly through nanopores, and their excellent stability at ALD temperatures prevents decomposition during infiltration, which for macroscopic substrates can take several minutes regardless of molecule size. Additionally, the production of approximately 1.5 moles of methane for every mole of TMA consumed enables relatively straightforward monitoring of deposition progress with the ALD chamber pressure gauge. Many potential nanocomposite applications, however, require infills other than Al_2O_3 with specific optical, electronic, or chemical properties. In this work, we infill macroscopic (>1 mm thickness) nanoparticle networks (e.g., ~100 nm Al_2O_3 nanoparticles) with ZnO using diethylzinc (DEZ) and water or with SiO_2 using bis(t-butylamino)silane (BTBAS) and ozone, and we compare our results to those obtained from Al_2O_3 infilling. We explore strategies for achieving uniform and pure infills despite larger and less stable precursor molecules as well as methods for confirming infill completeness in the absence of obvious reaction/saturation signals in the chamber pressure readings. We determine infill uniformity and composition via analysis of nanocomposite mass and color as well as electron microscopy, energy-dispersive X-ray spectroscopy, X-ray diffraction, and electrical conductivity measurements.

AF-MoP-42 Properties of VHF PEALD Silicon Nitride Film Deposited by Precursors with Different Amino Ligands*, **Seung Yup Choi**, Y. Ji, H. Kim, J. Kang,* Sungkyunkwan University, Republic of Korea*; A. Ellingboe,* dublin City University, Ireland*; H. Chandra,* EMD Electronics*; C. Lee,* EMD Electronics, Republic of Korea*; G. Yeom,* sungkyunkwan University, Republic of Korea

Silicon nitride film is widely used in semiconductor and display industry as gate spacer and encapsulation layer, etc. Among various deposition methods, plasma enhanced atomic layer deposition (PEALD) methods using Si precursor with nitrogen plasma are attracting attention due to advantage of low temperature deposition in addition to excellent thickness control, conformality, etc. as the ALD method. Among different Si precursors for silicon nitride PEALD, chlorosilane precursors commonly used in PEALD processes have corrosive reactants and particle issues for their byproducts. Amino silane precursors, compared to chlorosilane, can be used for lower temperature deposition but film conformality using aminosilane with N_2 plasma is known to be one of the biggest challenges. In this study, to overcome such challenge, two amino silane precursors with different types of ligands were studied for SiN x thin film properties deposited by PEALD using N_2 plasma excited by very high frequency (VHF, 162MHz). Compared to BTBAS having two amino ligands, DSBAS having one amino ligand showed prominent film properties. Silicon nitride thin film grown by DSBAS showed smoother surface, higher density, higher breakdown field, lower wet etch rate and higher growth per cycle (GPC) than BTBAS due to its structural feature. Furthermore, the fact that DSBAS films at 300℃ has less impurities such as carbon was revealed through XPS analysis. Also, DSBAS exhibited remarkable step coverage when deposited on high aspect ratio (30:1) trench pattern at 300℃.

AF-MoP-43 Influence of Metal Precursors on the Low-Temperature Crystalline Vanadium Oxide Synthesis Using Oxygen Plasmas, *A. Mohammad, K. Joshi, D. Rana, S. Ilhom, B. Wells, B. Sinkovic,* University of Connecticut*; A. Okyay,* Stanford University*; **Necmi Biyikli**,* University of Connecticut

Vanadium oxide shows phase-change behaviors at different stoichiometries including the metal-insulator transition (MIT) for VO_2around 70 °C shifting between monoclinic to tetragonal rutile structure phase. Such materials have the potential to be used in low power opto-electrical switches and in memory devices. The ALD reports in the literature show VO_x growth mainly via thermal atomic layer deposition (ALD) using TEMAV and VTIP metal precursors and water vapor or ozone as co-reactant and the as-grown VO_x films are mostly amorphous. Post-deposition thermal annealing at comparatively elevated temperature (typically higher than 500 °C) is performed to transform the as-grown amorphous films to different crystalline structures. However, no significant report is yet noticed on low-temperature as-grown crystalline VO_x films grown by thermal or plasma-ALD.

Our aim in this work is to demonstrate as-grown crystalline VO_x films using a hollow-cathode plasma HCP-ALD reactor at substrate temperatures 150 °C and to further improve the crystalline quality and transform the phase structure of the deposited VO_x film into the desired VO_2 stoichiometry. We have grown crystalline V_2O_5 thin films at 150 °C using TEMAV as the vanadium precursor and O_2 plasma as the oxygen co-reactant. The recipe for the plasma-ALD experiments was as the following: 0.250 s of TEMAV pulse with 10 sccm of N_2-carrier flow, 50 sccm Ar-purge for 10 sec, 50 sccm O_2 plasma for 10 s, plasma power 50- 300 W, followed by another 10 s of Ar purge. The TEMAV precursor cylinder is heated at 115 °C to provide enough TEMAV precursor in the reactor. The resulting films are crystalline V_2O_5 with a growth per cycle (GPC) value reaching ~2 Å and a refractive index of 2.45. The corresponding growth process has been real-time monitored with *in-situ* ellipsometry depicting the individual chemisorption and ligand exchange surface reactions.

We have also experimented the VTIP precursor grown vanadium oxide thin films via HCP-ALD process (with 0.09 s dose and heated at 60 °C) under the same plasma parameters and substrate temperature. The as-grown film is still V_2O_5 with a refractive index ~2.55. While comparing the VO_x films grown by TEMAV and VTIP precursor, it was noticed that TEMAV experiments resulted in higher GPC compared to the VTIP experiments. We have performed post-deposition thermal annealing and were able to obtain VO_2 phase at 500 °C.

We will present a detailed optical, structural, and electrical characterizations to explore both the similarities and differences between the TEMAV and VTIP metal organic precursor grown VO_x thin films.

AF-MoP-47 Characterizing TEMAZ and TBTEMT for ALD*, **Marjorie Sarad**, J. Daubert, K. Cheatham, T. Adam, J. Kelliher,* Northrop Grumman

In this work, we studied the atomic layer deposition of ZrO2 and Ta2O5 using Tetrakis(ethylmethylamino)Zirconium (IV) (TEMAZr) and (tert-butylimido) tris(ethylmethylamido) Tantalum (V) (TBTEMTa) respectively with water as an alternative to Tetrakis(dimethylamido)zirconium(IV) (TDMAZr)and Tris(diethylamido)(tert-butylimido)tantalum(V) (TBTDETa). The new precursors were evaluated because they offer higher thermal stability than the existing precursors. These precursors offer a lower vapor pressure which produce films properties that were similar. We explored the deposition rate of ALD ZrO2 and Ta2O5 in the temperature range of 80℃ - 200℃ which produced amorphous films. We report on the film properties of deposited and annealed films as measured by ellipsometry, X-ray diffractometer and Toho 2320-S stress gauge. The films were annealed to determine a change in roughness and establish temperature the film changes to polycrystalline. We investigated the wet etch rate for both BOE and HF, and how those changes with annealing. Metal Insulator Metal capacitors (MIMCAPs) were built to measure the films' electrical properties in terms of capacitance, leakage, and breakdown voltage were measured and evaluated after forming gas anneal for a 300 Å film. The dielectric constant was calculated from the capacitance-voltage measurement.

The ZrO2 film deposited by wither precursor TEMAZ or TDMAZ behaves similar, both crystallizes at 300℃ and neither deposited film etches with HF. The ZrO2 film, however, does etch with BOE and a linear decrease on the etch rate is measured when deposited at higher temperature. Films deposited at 80℃ and 120℃ had no change in stress after annealing, but the stress of the 200℃ deposited film became twice as tensile after annealing.

The TBTEMTa precursor achieved enough vapor pressure at 125℃ for uniform deposition from 80℃ to 200℃. The TBTDETa precursor needed the boost system to get sufficient vapor pressure at 120℃ for a uniform film. Both old and new precursor did not show any film removal with BOE. At lower processing temperature, Ta2O5 easily etches with HF. However once furnace annealed at 750℃ for an hour, the etch rate decreases by 30% and we report on the WER and stress. The films deposited at 80℃ had a density change after a 750℃ anneal for an hour, and the stress becomes more tensile after further annealing of the film. The Ta2O5 films deposited at 120℃ and 200℃ deposition had no change in density even after 5hr at 750℃, but the stress becomes more compressive. We will compare the effects of rapid thermal annealing (RTA) with shorter time against diffusion furnace anneal.

AF-MoP-48 ALD Film Closure and Thickness by Low Energy Ion Scattering*, R. ter Veen, **Karsten Lamann**, M. Fartmann, B. Hagenhoff,* Tascon, Germany

The applications of ALD have continuously been expanding. Whereas this deposition technique was initially focusing on the manufacturing of thin films for semiconductor applications on flat samples, currently ALD is used in a variety of fields, with many different substrate topologies. ALD has been used amongst others to manufacture pillar structures, to deposit metals on catalyst supports with high specific surface area, and in the application of coatings to protect cathode materials in Li ion batteries.

When the applications of ALD are expanding, characterization techniques need to follow this trend. Low Energy Ion Scattering (LEIS) does this. LEIS is a chemical analysis technique that is specific to the outermost atomic layer on a sample, making it the most surface specific chemical analysis technique in existence. This makes it particularly suited to determine film closure. The one monolayer specificity gives LEIS a distinct advantage in the determination of film closure over other techniques (e.g. ellipsometry, XRF). These other techniques can determine how much is deposited, but cannot tell the difference between one closed layer and a half closed double layer.

The presentation will first reporton LEIS applications to thin films deposited on flat samples (the nucleation behavior of GaSb films on SiO_x, figure 1). The second part of the presentation will focus on expanding the applicational range of LEIS to thin films on rough materials and particles with a chemically more complex composition. Samples are taken from cathode material for Li ion batteries, in particular, AlO_x films deposited on $LiMnNiCoO_x$ (figure 2).

AF-MoP-49 Development of HF-Free YF3 ALD Process and Its Dry Etch Resistance*, **Sunao Kamimura**, T. Teramoto,* Air Liquide Laboratories, Japan*; T. Ono,* Air Liquide Advanced Materials*; C. Dussarrat,* Air Liquide Laboratories, Japan*; N. Blasco,* Air Liquide Advanced Materials, France*; N. Gosset,* Air Liquide Laboratories, Japan*; G. Nikiforov,* Air Liquide Advanced Materials

Aluminum-based ceramics have been extensively used in semiconductor plasma processing equipment as plasma-facing materials. However, these materials are eroded by corrosive fluorocarbon plasmas, resulting in the production of contaminant particles on the wafer. In order to solve this problem, yttrium oxide (Y_2O_3) and yttrium fluoride (YF_3) coatings have recently attracted substantial attention due to their high resistance to erosion in plasma, especially plasma etch, avoiding the generation of fluoride particles from the chamber wall surface, thereby reducing particulate contamination.

Atomic layer deposition (ALD) is a thin film coating method that enables conformal dense and pinhole-free film deposition even for the complex structures like showerheads. However, the formation of YF_3 thin films by ALD has been challenging since common fluorine sources such as HF are generally dangerous and corrosive, hence could lead to permanent damage to the chamber of semiconductor plasma processing equipment.

We have carried out the screening of several types of organometallic yttrium precursors for ALD, and have succeeded in depositing an ALD YF_3 film using a novel F containing yttrium organometallic precursor called Ybeta-prime in combination with O_3 as the co-reactant. These precursors are introduced sequentially, leading to a HF-free YF_3 thin film coating process. The YF_3 thin film growth was confirmed by XPS measurements, and it revealed that growth per cycle (GPC) increases as reactor temperature increases. The refractive index of deposited YF3 thin film was constant with the deposition temperature, its value being consistent with bulk YF_3 value. Dense, uniform, conformal hydrophobic (WCA > 90 degrees) films are obtained at the range of temperature between 225°C and 300°C. SEM was used to measure step coverage of the ALD YF_3 film deposited at 275°C in a 1:6.25 aspect ratio structure. The SEM image shows excellent step coverage (top: 22 nm/bottom: 22 nm), opening interesting perspectives for industrial

applications requiring high conformality. This contrasts with YF_3 films obtained through CVD processes.

The erosion behavior of YF_3 coupon was analyzed under representative plasma etching conditions, using the same bias power and processing gases (CF_4 and O_2) where high density CF_4/O_2 plasma are produced (RF source power: 1300 W. RF bias power: 200 W). Etch rates of YF_3 thin film was one order of magnitude lower than Al_2O_3 thin film. Furthermore, Y_2O_3 thin film prepared using an ALD technique was used to compare the surface erosion behaviors with YF_3 film.

We are uncovering a new class of HF-free metal fluoride processes that go well beyond yttrium.

AF-MoP-50 Role of Ga Doping in IZO Films Grown by Atomic Layer Deposition, ***Ae-Rim Choi**, I. Oh, Y. Jeong, D. Lim,* Ajou University, Republic of Korea*; S. Kim, S. Ryu, D. Kim,* SK Hynix, Korea

Recently, DRAM devices have faced physical limitations of scaling down, involving inhigh leakage current. Thin film transistor (TFT) with a indium-based multi-component oxide semiconductor has been suggested to replace conventional 1T1C DRAM structure. For example, InZnO (IZO) films have high field-effect mobility, optical transparency, high conductivity, andhigh mobility.[1,3] Further,Ga doping into IZO films improves electrical properties.[4] Ga–O bonds, which are stronger than Zn–Oand In–O bonds, improve the controllability of carrierdensities in the nearly degenerate state.[5] However,in spite of its technical importance, the role of Ga doping has not been clearly unveiled. It would be because the lack of a proper fabrication method. Since doping concentration significantly affects electrical properties,4] the study of Ga-doped IZO films with deposition technique for precise controlling of chemical composition needs more attention.

Because of excellent conformality and thickness control, atomic layer deposition (ALD) is suitable for thin film deposition on complex nanostructures. In this work, we investigate ALD IZO films with gradual change of Ga contents, to elucidate the role of Ga doping. For the fabrication of Ga-doped IZO films, we employ super cycles consisting of multiple sequential steps of In_2O_3, Ga_2O_3, and ZnO, by $(CH_3)_2In(CH_2)_3N(CH_3)_2$, $Ga(CH_3)$, and $(C_2H_5)_2Zn$ precursors, respectively. The chemical composition is investigated by X-ray photoelectron spectroscopy (XPS). Grazing incidence X-ray diffraction (GI-XRD) is performed to study the crystallinity. Transmission electron microscopy (TEM) is also performed for interfacial analysis between gate insulator and channel layer and between channel layer and metal. TFT devices are fabricated by photolithography and the electrical properties of I_d-V_g curves are measured using B1500A semiconductor analyzer. We compare the performance of ALD IZO TFT devices with gradual increase of Ga doping and discuss the availability for next generation 3D DRAM devices.

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AF-MoP-51 The Effects of in-situ Atomic Layer Annealing on Thermal Atomic Layer Deposited Silicon Nitride, *D. Le, S. Hwang, J. Kim,* University of Texas at Dallas*; J. Spiegelman,* RASIRC*; J. Kim,* University of Texas at Dallas*; M. Benham,* RASIRC*; **Si-Un Song**,* University of Texas at Dallas*; R. Choi,* Inha University, Republic of Korea

We demonstrated the deposition of thermal ALD SiNx over a wide range of deposition temperatures using anhydrous hydrazine (N2H4) as the nitrogen source.1 Although the N2H4–based process was able to deliver highly conformal thin films with an enhanced growth rate and improved film properties compared to ammonia (NH3), the wet etch resistance was still undesirable.

Herein, we examined the impact of the in-situ atomic layer annealing (ALA) process utilizing Ar plasma on thermal ALD silicon nitride (SiNx) thin films. The growth characteristics, wet-etch rate (WER), bonding information, and conformality over different aspect ratio (AR) nanotreches of the SiNx with in-situ plasma cycles were carefully investigated and compared to the reference process (thermal ALD only).

When the in-situ plasma treatment was introduced in the thermal ALD process, the growth rate of SiNx was reduced by ~45% compared to the standard procedure. While SiNx deposited via the standard ALD process exhibited a growth rate of ~0.05 nm/ cycle, the ALD/ALA process delivered thin films with a growth per cycle (GPC) of ~0.022 nm/ cycle between 320–480 °C. Despite the decrease in growth rate, the addition of in-situ ALA treatment resulted in notable enhancements in the deposited SiNx thin film properties, such as improved reflective index (RI), lower wet etch rate (WER,) and increase in film density. At 410 °C, the RI increased from 1.80 to 2.00, suggesting thin films achieved with ALD/ALA process would be more Si-rich than thermal-ALD. Furthermore, while the WER of SiNx decreased from 12.9 nm/ min to 0.69 nm/min (evaluated in diluted HF 200:1), the film density increased from 2.61 to 2.80 g/ cm3. Ex-situ FTIR was employed to further investigate the effects of in-situ atomic layer annealing on embedded –NHx (x=1,2) bonds within the deposited thin films. Compared to the reference sample, the thin films that deposited with the additional plasma cycles showed a slightly lower –NHx bond density. Furthermore, the conformality of ALD/ALA SiNx thin films was also evaluated using ~6:1 AR trench structures. The TEM cross-sectional images showed >80% conformality of SiNx thin film could be achieved when incorporating the in-situ plasma treatment into the ALD process. The experimental details and results will be presented.

We would like to express our gratitude to RASIRC Inc. for their financial support and for providing BRUTE hydrazine source.

[1] ALD 2021, Paper Number: 69751.

AF-MoP-52 Low Toxicity Electron Transport Layer of Atomic Layer Deposited TiO_2 and SnO_2 for Sb_2S_3 Thin Film Solar Cells, *Y. Kim, P. Pawar, **Jaeyoung Heo**,* Chonnam National University, Republic of Korea

In antimony sulfide (Sb_2S_3) thin-film solar cells (TFSCs), the hole transport layer (HTL) is an important parameter to minimize interface defects at the Sb_2S_3/metal interface, thus providing better charge carrier extraction. However, HTL materials are highly expensive and toxic and demand a controlled atmosphere. In addition, they are susceptible to the humid environment, thus resulting in reduced performance. Recently, the application of double buffer layers has been proven to be a beneficial approach for the enhancement of the power conversion efficiency (PCE) of Sb_2S_3 TFSCs. Herein, atomic-layer-deposited (ALD) SnO_2 and TiO_2 ETLs were applied as a double buffer layer with CdS for Sb_2S_3 TFSCs. The Sb_2S_3 absorber was deposited using a facile hydrothermal method. The TFSC devices were fabricated based on $FTO/SnO_2/CdS/Sb_2S_3/Au$ or $FTO/TiO_2/CdS/Sb_2S_3/Au$ structure without HTLs. Experimental analysis revealed the reduction of the surface roughness of ETLs and decreased unfavorable (hk0) orientation of the Sb_2S_3 absorber after utilizing double buffer layers. Initially, incomplete nucleation of Sb_2S_3 was observed on SnO_2 and TiO_2 ETLs, which resulted in the formation of a shunting path. Conversely, complete nucleation of Sb_2S_3 was observed on CdS and double buffer layers. The highest PCEs of 3.98% and 4.23% were obtained for SnO_2/CdS and TiO_2/CdS double-buffer-layer-based cells with improvements exceeding 1% compared with the reference CdS buffer layer. Additionally, improvements in open-circuit voltage (V_{OC}) of the order of ~25 mV and ~45 mV were respectively observed for SnO_2/CdS (V_{OC} = 0.676 V) and TiO_2/CdS (V_{OC} = 0.696 V) double-buffer-layer-based devices compared with the reference CdS buffer layer (V_{OC} = 0.648 V). The enhanced device properties are mainly attributed to the improved charge carrier collection and formation of suitable band offset at the absorber and ETLs interfaces.

AF-MoP-53 Growth and Crystallization of Conductive srruo3 Films by Atomic Layer Deposition Depending on the Substrates, ***Youngsin Kim**, C. Hwang,* Seoul National University, South Korea

This study reported the properties of SrRuO3 (SRO) thin films used as bottom electrodes of SrTiO3 (STO) dielectric films. The SRO has a close lattice match with the STO, making it a suitable electrode for STO crystallization.[1] The SRO films were grown via atomic layer deposition of SrO and RuO2 using Sr(iPr3Cp)2 and Rudense® as precursors, respectively, on different substrates. It was confirmed that the growth rate of RuO2 using the Rudense® precursor is relatively lower during the SRO deposition process compared to the conventional RuO2 deposition with the pulsed chemical vapor method using the ToRuS as the precursor.[2] Unlike the SRO films grown with ToRuS, which showed excessive RuO2 growth due to the catalytic characteristic of the intermediate metallic Ru, the SRO films grown with the Rudense® precursor did not show undesirable excessive growth since the catalytic effect was not involved.

The SRO films were crystallized with rapid thermal annealing (RTA) at 650oC in an O2 atmosphere after deposition. TiN, Pt, Si, and Al2O3 substrates were used to deposit the SRO. The atomic force microscopy (AFM) analysis (Figure 1) revealed that the surface roughness was highest and lowest when TiN and Al2O3, respectively, were used as the substrate. The SRO films deposited on the TiN substrate showed cracks on the surface when observed by the scanning electron microscope (SEM). In addition, the sheet resistance of the SRO sample deposited on the TiN substrate, measured by the 4-point probe, was about 100 times higher than samples using other substrates. The SRO peak was not observed with the grazing incidence X-ray diffraction (GIXRD) when Pt was used as the substrate. The SRO peak was only observed by GIXRD when the oxygen partial pressure was increased by more than 7 times. The transmission electron microscope (TEM) of the SRO film deposited on the Pt substrate revealed that the film was amorphous, although the aggregation characteristics were observed. It is presumed that the Pt crystal trapped the oxygen needed for the SRO growth, which suppressed the formation of the crystallized SRO.

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AF-MoP-54 In-Situ Gas Monitoring of ALD Processes Using Remote Optical Emission Spectroscopy, ***Nessima Kaabeche,*** Gencoa, UK*; C. Guerra,* Swiss Cluster, Switzerland*; J. Brindley, D. Monaghan,* Gencoa, UK

Effective and robust monitoring of individual gas concentrations during the ALD processes offer a unique insight into the process behaviour as well as being an important step in the eventual wide-spread industrialisation of the ALD technique.

Conventional quadrupole residual gas analysers have difficulty monitoring ALD processes due to the high process pressures and the presence of contaminating hydrocarbons contained within many ALD precursors. For these reasons monitoring of precursor gas concentrations during the ALD process is not often undertaken, especially at the production stage.

An alternative gas sensing technique that operates directly at pressures above 10^{-4} mbar has been built around remote plasma emission monitoring. This technique involves the generation of a small, remote plasma using an inverted magnetron placed within the ALD vacuum system. Consequently, species that are present within the vacuum become excited in the sensor’s plasma, emitting a spectrum of light, which can then be used to identify and monitor the emitting species. Importantly, this plasma, generated inside the sensor, has a sole function as a gas detector and does not affect the ALD process itself.

This work will demonstrate that the sensing method is robust when exposed to the ALD processing environment. Previous work had demonstrated the usefulness of this technique, but limitations were encountered when using a DC voltage to generate the sensor’s plasma as contamination and reduced sensitivity developed when used with certain precursors. This work will describe a novel method of generating the detector plasma using a high peak power, low duty cycle pulsed voltage. It will be demonstrated that the pulsed power technique is more effective than DC in preventing contamination of the sensor’s electrodes as well as improving the detection sensitivity of common ALD precursors and their reaction by-products.

Examples of this sensing technique’s practical uses for Al_2O_3 processes are discussed; this includes detection of contaminants, optimising purge cycle length and monitoring the reaction dynamics in terms of precursor gas consumption and reaction by-products.

AF-MoP-55 The Application of Rare-Earth Metals as ALD Precursors, ***Yu-Chieh Pao,*** Industrial Technology Research Institute, Taiwan*; B. Lee,* Industrial Technology Research Insitute, Taiwan

Rare-earth metal compounds have exquisitely unique electronic and magnetic properties that make them irreplaceable in the field of semiconductor, manufacturing, chemical industry, etc. As the technology trend is focused towards downscaling the size of transistors, rare earth oxides are becoming increasingly important in the field of microelectronics due to large band gaps, high dielectric constants, and good thermodynamic stability on silicon. Therefore, rare-earth metal oxides such as La2O3 can be utilized as the gate dielectric layer in field effect transistors.

The advantages of atomic layer deposition (ALD) such as high conformality, high uniformity, and precise thickness control, are all important when trying to downscale the size of transistors. As a result, the development of ALD precursors HAS attracted much attention. From a molecular design point of view, by selecting the appropriate type of ligand and modifying the substituent group of ligands, properties such as thermal stability, vaporization rate, reactivity and purity of resulting thin film can be readily adjusted. The design and application of rare-earth element-related ALD precursors will be introduced in this paper.

AF-MoP-57 Characterization of Snox Thin Films Deposited by Atomic Layer Deposition, ***Taekjib Choi,*** *S. Lee, J. Yun,* Sejong University, Republic of Korea*; I. Choi, B. Cho, J. Yang,* TES Co., Ltd., Republic of Korea

Metal oxide photoresists are currently being considered as alternatives to chemically amplified resists. They consist of a metal oxide core surrounded by ligands that tune solubility, crosslinking and other properties and provide high etch resistance. In particular, organotin compounds are highly sensitive to extreme ultraviolet (EUV), enabling high-resolution patterning. The strength and dissociation mechanism of C-Sn bonds are factors that can be related to EUV photosensitivity. And SnO_x photoresists are presented as EUV resist with high absorptivity and etch resistance. SnO_x thin films deposited by TALD and PEALD were compared under different deposition temperatures. We analyzed the optical, chemical, and electrical properties of the SnOx thin films under various deposition conditions, focusing on the influence of the carbon ratio. Additionally, we will evaluate and discuss their etch properties.

AF-MoP-58 Laser Diagnostics of Plasma Surface Interactions, ***Mruthunjaya Uddi,*** Advanced Cooling Technologies*; A. Dogariu,* Texas A&M University*; E. Kudlanov,* Advanced Cooling Technologies*; G. Urdaneta,* texas A&M University*; Y. Xiao, D. Jensen, C. Chen,* Advanced Cooling Technologies

Plasma surface interaction has been a critical area of research for many applications such as Plasma-Enhanced Atomic Layer Deposition (PEALD). To meet the demanding needs of more advanced atomically controlled microfabrication methods, the physics of PEALD needs to be better understood to enable high quality, repeatable and controllable deposition process. Several challenges that need to be addressed regarding PEALD include damage to the substrate from highly energetic species and UV radiation, need for precise amorphous/crystalline modulated selective layer deposition, conformality in coating non-uniform substrates, achieving an aspect ratio of >100, repeatability and controllability of the finish. To address these challenges, we are developing laser diagnostics methods to measure species over substrates by advanced laser diagnostics such as femtosecond- Two-Photon Absorption Laser Induced Fluorescence (fs-TALIF) to image N atoms over substrates. Here we present measurements of N atom densities over a substrate with high spatial (< 10 microns) and time resolution (<1 ns) using fs-TALIF at pressures of 5-150 mTorr.

AF-MoP-59 Density-Functional Theory Modeling for Thermal Atomic Layer Etching of Cobalt with Hexafluoroacetylacetone Chelation, *S. Chae,* ***Sangheon Lee,*** Ewha Womans University, Republic of Korea

In this study, a thermal atomic layer etching process for Co comprising two steps—plasma chlorination and chelation with hexafluoroacetylacetone (Hhfac)—was developed. We investigated the thermodynamics associated with the adsorption of Hhfac on chlorinated Co surfaces, and the subsequent removal of these surfaces based on the disk-like $CoCl_2$ models. We employed a disk-like chlorinated Co surface model and identified thermodynamically favorable reaction pathways and governing factors controlling the overall etching process. We found that thermodynamically the most favorable reaction pathway proceeded via the adsorption of hfac on a low-coordinated surface Co site followed by the desorption of $CoCl_2$hfac cluster; the adsorption and desorption steps were thermodynamically uphill and downhill, respectively. We also found that

the kinetic energy barrier for the Hhfac adsorption step tended to be noticeably greater than that for the $CoCl_x(hfac)_y$ desorption step. These calculation results suggest that the Hhfac adsorption step is the rate-determining-step in the chelation process of chlorinated cobalt surfaces. Finally, we suggest that the strong tendency of the hfac-induced sp^3 hybridization of Co is a governing factor in the thermodynamics of etching the chlorinated Co layer with Hhfac as an etching gas.

AF-MoP-60 Study on Phase and Chemical Bonding of Molybdenum Film Grown by Atomic Layer Deposition, ***So Young Kim**, C. Jo, H. Shin,* Yonsei University, Republic of Korea*; M. Cheon, K. Lee, D. Seo, J. Choi,* Hanwha Corporation, Republic of Korea*; H. Park,* BIO-IT Micro Fab Center, Republic of Korea*; D. Ko,* Yonsei University, Republic of Korea

As the semiconductor integration has advanced, there have been limitations in selecting candidates for interconnect metals because of the exponential increase in metal resistivity at scaled pitches. Tungsten and copper are the most widely used materials for back-end contact vias and metal lines. However, their resistivity increases up to ~19[1)] and ~22 μΩcm[2)] at 10 nm thick film while their bulk resistivity are as low as 5.28 and 1.67 μΩcm, respectively. Therefore, there are needs for finding metals with lower resistivity for contact and back-end metal at tight pitch, which has led to the emergence of molybdenum, cobalt, and ruthenium as promising alternatives over traditional metals. Among those next generation metals, molybdenum has the lowest product of electrical resistance and electron mean free path(ρ0×λ)[3)]; it has a merit of having low resistivity, compared to copper and tungsten, as thickness reduces.

Since molybdenum film grown by atomic layer deposition(ALD) has not yet been actively studied, we investigated the phase and chemical bonding states of molybdenum film at different thickness. We also examined the feasibility of molybdenum nitride as the diffusion barrier of molybdenum against silicon oxide. Molybdenum films and molybdenum nitride films were deposited by thermal ALD equipment, manufactured by Hanwha Corporation, using MoO_2Cl_2 precursor as molybdenum source and H_2 and NH_3 as reducing agent.

The phases of molybdenum were observed by grazing incidence x-ray diffraction(GIXRD) and the morphology and surface roughness of the thin films were observed by atomic force microscope(AFM). X-ray Photoelectron Spectroscopy(XPS) showed the Mo concentration and binding energy of the film. The sheet resistance obtained by 4-point-probe(4PP) and the thickness measured by X-Ray Reflectometry(XRR) were used to calculate the resistivity of the Mo film. The phase and binding energies were analyzed via GIXRD and XPS to confirm the successful growth of pure Mo film. As-deposited 10 nm-thick Mo film showed standard XRD peaks for polycrystalline-Mo phase. In addition, ALD-grown Mo films showed low resistivity of ~13 μΩcm with 10 nm thickness while it increases up to ~30 μΩcm when the film thickness become as low as 6 nm.

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AF-MoP-61 Area-Selective Atomic Layer Deposition of Silicon Nitride for Nand Flash Memory with a Very High-Frequency Plasma Source, ***Min-Jeong Rhee**,* Ajou University, Republic of Korea*; W. Lee,* Pukyong National University, Republic of Korea*; I. Oh,* Ajou University, Republic of Korea*; G. Yoo,* Soongsil University, Seoul, Republic of Korea*; J. Heo,* Ajou University, Suwon, Republic of Korea

Silicon nitride (SiN_x) thin film has been used as a charge trap layer (CTL) in 3D NAND flash memory devices. Because thermal atomic layer deposition (ALD) demands a relatively high temperature, SiN_x is mostly deposited via the plasma enhanced-ALD (PE-ALD) technique for low impurity contents. However, due to energetic radicals in plasma, PE-ALD usually produces low step coverage and bottom layer damage. In NAND flash memory, damage to the SiN_x of the bottom layer can lead to tunnel oxide degradation and a reliability problem. Therefore, the development of a SiN_x process with high step coverage and low damage to the bottom substrate while maintaining the advantages of a low deposition temperature is required. In addition, in scaled 3D NAND flash devices, the isolation of each CTLs is required for device reliability by reducing cell-to-cell interference. However, the conventional top-down photolithography cannot achieve topological the formation of patterns or selective growth of thin films, where patterned films should be grown vertically separated on the tunnel oxides.

In this study, we develop the area selective ALD (AS-ALD) process of SiN_x films through very high frequency (VHF) plasma. We used bis-diethylamino silane ($H_2Si((N(C_2H_5)_2)_2)$) as a precursor and N_2 plasma as a reactant. The process using radio frequency (RF, 13.56 MHz) will be comparatively discussed with that using VHF, 60 MHz by chemical composition, step coverage, and damage of the thin film through X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). For AS-ALD, the inhibitors are sequentially deposited prior to each PE-ALD cycle, and the selectivity of each cycle was calculated. For a more accurate selectivity analysis, the selectivity between the metal substrate and the oxide substrate was analyzed through TEM. This comparative research and the AS-ALD process of SiN_x show the applicability of VHF PE-ALD in NAND flash memory, which requires high step coverage, low damage, and high capacity.

AF-MoP-62 Growth Mechanism of Ge-Sb-Te Thin Films by Supercycles of ALD GeTe and Sb_2Te_3, ***Okhyeon Kim**, Y. Kim,* Sejong University, Republic of Korea*; H. Kim,* sejong University, Republic of Korea*; C. Park, D. Ahn, B. Kuh,* Samsung Electronics Co., Ltd., Republic of Korea*; W. Lee,* Sejong University, Republic of Korea

Recently, a three-dimensional vertical architecture has been proposed to increase the integration and productivity of phase-change random-access memory (PCRAM) devices. Atomic layer deposition (ALD)technology is essential to prepare memory and switching materials on a high-aspect-ratio hole pattern with uniform thickness and composition. Since the ALD of Ge-Sb-Te (GST) film was reported by supercycles of ALD of GeTe and Sb_2Te_3 using an alkylsilyl Te compound [1], various ALD supercycle processes were reported using alkylsilyl Te compounds. In the ALD supercycle process of GST, GeTe thin films should be grown on Sb_2Te_3 thin films, and Sb_2Te_3 thin films should be deposited on GeTe, which is significantly different from the case of continuous growth of GeTe or Sb_2Te_3 film [2]. Therefore, in this study, we investigated the growth behaviors of ALD GeTe and Sb_2Te_3 during the supercycle process. The in-situ quartz crystal microbalance (QCM) analysis expected a Ge-rich, Te-deficient composition of the $GeTe_{1-x}$ thin film grown on Sb_2Te_3 films. To produce a stoichiometric $Ge_2Sb_2Te_5$ thin film by supercycle process, we controlled the ratio of $GeTe_{1-x}$ and Sb_2Te_3 subcycles and then annealed the deposited film in a Te ambient. As a result, a high-density stoichiometric $Ge_2Sb_2Te_5$ thin film was produced on a high-aspect-ratio pattern with a uniform thickness and composition.

ALD for Manufacturing
Room Evergreen Ballroom & Foyer - Session AM-MoP
ALD for Manufacturing Poster Session

AM-MoP-1 Numerical Analysis on Gas Flow Field for a Sustainable ALD Process Chamber, ***Kyung-Hoon Yoo**,* Korea Institute of Industrial Technology (KITECH), Republic of Korea*; G. Song,* KUMYOUNG ENG Inc., Republic of Korea*; C. Kim,* TNG Inc., Republic of Korea*; J. Hwang, H. Lee, S. Lee,* Korea Institute of Industrial Technology, Republic of Korea*; K. Lee,* SAMSUNG DISPLAY, Republic of Korea

In order to develop a sustainable ALD processing cluster tool for 300 mm wafers, it is necessary to establish a manufacturing technology for a high-productivity, high-efficiency ALD process chamber that reduces the intrinsic excessive consumption of energy and materials.[1] In the present study, as the part of countermeasure to the excessive consumption, a micro-gap ALD process chamber is considered for the optimized design with the process space volume decreased. The changes in the flow field of nitrogen in the process space of the process chamber with the gap sizes of 1 mm and 10 mm respectively are observed at 200 °C, utilizing computational fluid CFD numerical analysis. For the present nitrogen flow field with a base pressure of 1 Torr and a temperature of 200 °C, the Knudsen number Kn<0.1 and Reynolds number Re<<2300 are evaluated, and consequently the continuity and momentum equations of a steady-state compressible laminar flow field are considered.[2,3]

Acknowledgment

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AM-MoP-2 Atomic Layer Deposition Reactor for Fixed-Bed Powder Processing with Inert Sample Transfer*, S. Andsten, J. Velasco, S. Larkiala,* Aalto University, Finland*; K. Salonen,* Elabs Oy engineering, Finland*; C. Gonsalves, J. Rask, J. Stang, V. Miikkulainen, S. Jääskeläinen,* ***Riikka Puurunen****,* Aalto University, Finland

Processing atomic layer deposition (ALD) coatings on porous high-surface-area particles is of increasing interest related to applications as heterogeneous catalysts. ALD on particles can be made in various reactor configurations such as fixed powder bed, fluidized bed, and rotating drum. Also reactors meant for thin film processing are used for porous particles, by placing the particles on a tray and allowing the gasses to flow over the bed and diffuse into the bed.

Although the fundamental ALD mechanisms are the same irrespective of the geometry of the substrate material, specialized particle coating reactors differ significantly from mainstream thin-film ALD reactors. Most important is to take into account the much larger reactant doses needed to saturate the surface with the adsorbed species. One gram of a high-surface-area often contains ~100 to 1000 m^2, compared to ~0.1 m^2 of a typical silicon wafer. The required amount of reactant scales directly with the surface area to be coated. Furthermore, porous high-surface-area materials can be estimated to have extremely high aspect ratios (HAR): mesopores with 5 nm diameter and particle size of 1 mm give an aspect ratio of ~100 000. Coating HAR substrates requires longer reactant exposures, allowing the reactant to diffuse into the structure. Of the various specialized particle coating reactors, the fixed bed reactors are the most simple to construct, and oldest in use: both historical development branches of ALD - atomic layer epitaxy (ALE) and molecular layering (ML) - employed such reactors.

In this work, we present a new ALD reactor design for coating porous high-surface-area particles in a fixed bed. The reactor reported in this work is aimed for fundamental laboratory-scale studies, allowing the coating of a few grams of porous high-surface-area material at a time. Loading and unloading of the sample inertly is possible, enabling the processing of air-sensitive substrates and the investigation of the adsorbed species without air contact. Pre-treatment can be made at temperatures up to 800°C under controlled gas flow. ALD reactants are loaded in sources which can be heated up to about 200°C. Gaseous sources are included. The reactor is equipped with an afterburner and condenser for treating the unreacted reactant. Port for gas analysis e.g. via mass spectroscopy is foreseen.

AM-MoP-3 Reverse Templating Effects of Low-Resistivity Ru Ald on Sputtered Ru*,* ***Chenghsuan Kuo****,* UCSD, Taiwan*; V. Wang,* UCSD*; R. Kanjolia,* EMD Electronics, USA*; M. Moinpour,* EMD Electronics*; J. Woodruff,* EMD Electronics, USA*; H. Simka,* Samsung Electronics*; A. Kummel,* UCSD

Ruthenium is a promising candidate to replace Cu as an interconnect metal due to its low resistivity in narrow vias and resistance to electromigration. In previous work, a Ru Atomic Layer Deposition (ALD) process using $Ru(CpEt)_2$ and O_2 was developed to produce films with bulk-like resistivities. However, the ALD exhibits poor initial nucleation with variable initial nucleation delay causing thickness control to be difficult and high surface roughness. In this work, the effects of depositing low resistivity ALD Ru on 2 and 10-nm sputtered Ru films are investigated to eliminate the initial poor nucleation while retaining low overall film resistivity.

AM-MoP-4 Thermal Evaporation Enhanced Atomic Layer Deposition for Far Ultraviolet Mirror Coatings*,* ***Robin Rodríguez****, J. Hennessy,* Jet Propulsion Laboratory (NASA/JPL)

UV instruments on NASA space missions such as Hubble Space Telescope (HST), the Far Ultraviolet Spectroscopic Explorer (FUSE), and the Galaxy Evolution Explorer (GALEX) have made groundbreaking astrophysical discoveries in areas as diverse as galaxy evolution, star formation, and molecular cloud chemistry. These spectrometers have all benefited from the use of Al mirrors that are highly reflective in the ultraviolet (UV). Aluminum is the only reflective metal that offers broad ultraviolet/visible/near-infrared response, making it highly relevant for use in all far ultraviolet (FUV, 90-200 nm) instruments. However, aluminum is very reactive and susceptible to oxidation, which can limit its reflective performance in the FUV. Ultra-thin coatings of metal-fluorides such as AlF_3, MgF_2, and LiF can be used to protect the Al surface while preserving its high reflectance in the FUV. Atomic layer deposition (ALD) provides unparalleled uniformity and thickness control, making it the ideal process for coating these curved mirrors and shaped optics. However, the Al mirrors are typically fabricated via a separate physical vapor deposition (PVD) process, requiring the mirror to move between one vacuum system to another and exposing it to air, which results in the immediate formation of the native oxide on the Al surface. Therefore, it is necessary to coat the Al surface with the metal-fluoride before exposing it to air.

Herein lies the need to have both processes, PVD and ALD, occur within the same vacuum environment. We report on the development of a custom, in-house built, thin film deposition reactor that is capable of doing thermal evaporation of Al and ALD of metal-fluorides within the same vacuum chamber. Sequentially combining both deposition techniques without breaking vacuum has the potential to enhance the performance of UV aluminum mirrors. It also has the potential to enable the fabrication of metal-dielectric bandpass filters with deeper FUV transmission bands. In this presentation we will describe our thermal evaporation enhanced ALD (TE-ALD) reactor and present preliminary characterization results of FUV mirrors and bandpass filters fabricated using this reactor.

AM-MoP-6 Technical Analysis and Solution of Critical Electrostatic Chuck Problem in High Temperature CVD Process through Estimation Model of the Johnsen-Rahbek Chucking Force*,* ***Youngbok Lee****, S. Han, S. Cho,* Samsung Electronics, Republic of Korea*; Y. Kim,* Samsung Electronics

In the state-of-the-art semiconductor manufacturing process, the deposition layer becomes thicker and contains higher stress, which requires higher chucking force and leads to various wafer chucking problems on Electrostatic chuck (ESC). ESC is the device utilized to fix the wafer by attractive force (chucking force) during the semiconductor manufacturing process such as chemical vapor deposition (CVD), etching and ion implantation. There are technical problems with the ESC during the processes such as Amorphous Carbon Layer (ACL) and mold CVD where excessively high voltage is currently required for increasing chucking force, which can lead to arcing problems and damages on wafers. Also recently, wafer backside defect problems such as cracks and scratches marks are arising during the CVD processes which is caused by excessive chucking pressure.

To prevent such issues in the ESC, it is helpful to estimate the chucking force at the various conditions. Therefore, we have established a rigorous estimation model of chucking force based on Johnsen-Rahbek type ESC. The proposed model reflects the emboss structure and dielectric coating on the ESC, and various layers of the wafer. The effect of the ESC geometry such as diameter, height and number of the emboss on the chucking force is adequately reflected on. Also, the model predicts the trend of change in chucking force with respect to the thickness/material of the ESC coating and layers on the wafer.

Based on the model, it is possible to verify how the chucking force changes according to the various conditions. Several technical proposals, such as changing the material of the ESC coating and wafer layers, are suggested in this research to increase the chucking force. Also, a strategy to relax the chucking pressure while maintaining the total chucking force same was suggested. Therefore, this proposed model can contribute to solve the chucking problems by giving the suggestions to increase the chucking force without the excessive chucking voltage. Moreover, the proposed methodology and analysis can be easily adapted to other processes and equipment that require extreme chucking performance in high temperature and thick layer condition.

AM-MoP-10 Multi Cycle and Material Deposition for Spatial Atomic Layer Deposition Process*,* ***Atilla Varga****, M. Carnoy, M. Funding la Cour, M. Plakhotnyuk, I. Kundrata,* ATLANT 3D, Denmark*; J. Bachmann,* Friedrich-Alexander Universität, Germany

Spatial Atomic Layer Deposition (sALD) offers a unique opportunity for localized deposition due to its physical separation and isolation of precursor and co-reagent dosing.[1] While simple in theory, due to well-developed examples of sALD, in practice miniaturization of sALD requires substantial effort into the creation of suitable micro-nozzles.[1] Uniquely, ATLANT 3D has developed proprietary sALD micronozzles, called microreactor Direct Atomic Layer Processing - µDALP™.

The µDALP™ process undergoes the same cyclic ALD process but is only done in a spatially localized area.[2] The microreactor or micronozzle confines the flows of gases used for ALD within a defined µm-scale centric

area on the substrate, to deposit the desired material. Similarly, to spatial ALD, the creation of this monolayer then hinges on the movement of the substrate.[1,2]

Since sALD and the µDALP™ process are based on physical separation, it is theoretically compatible with any ALD material process however requires development as ALD processes are highly tool dependent.[3] As such, the material capabilities can match traditional ALD and exceed other patterning techniques, such as lithography, which can be costly and time-consuming, especially for rapid prototyping required for innovation.[4,5]

sALD using the µDALP™ technology also vastly increases the efficiency and innovation potential of material and precursor development. Using a small amount of precursor (due to low flow rates required) multiple film thicknesses can be deposited onto a single wafer used to calculate a processes growth rate within only a few hours, compared to days for a traditional ALD process (**Fig 1**). Multiple depositions can also be performed at varying temperatures for the calculation of temperature dependent growth rate (for "ALD window"), and film characteristics all within a few hours on a single sample. The µDALP™ process has also been used to demonstrate the selective deposition of different materials on the same substrate without the need for masking shown in **Fig 2.** By facilitating the more efficient development of ALD processes, µDALP™ sALD can help to enable continued and more efficient growth of the ALD industry and the development of new and innovative technologies. Multi-material sALD also enables unseen potential for versatile patterning and complex geometry formation, applicable to efficient, iterative, and low-cost device and sensor development.

AM-MoP-11 Hike Furnace HCD SiN Matching TEL Furnace HCD SiN*, Yuan Hsiao Su,* Taiwan Semiconductor Manufacturing Company, Taiwan

In this work, we describe how Hitachi Kokusai (HiKE) vertical furnaces developed the novel thin film formation method, to provide the second tool type of FinFET hard mask silicon nitride (HM SiN) process that widely used in tsmc very large scale integrated (VLSI) devices fabrication line, The background is the first tool type Tokyo Electron (TEL) not able to provide formula furnace with end of maintenance (EOM).

We develop an innovation HiKE low-temperature 500C process with good film property control of silicon nitride (SiN) formed by low-pressure atom layer deposition (LPALD), and it has been developed by using hexachlorodisilane (HCD, Si2Cl6). The potential scope of application to lead the advanced production line extend from the conventional low-pressure vapor deposition (LPCVD) technique performed at 600C and produced by TEL formula vertical furnaces. The film formed by HiKE furnace shows excellent uniformity with the same refractive index 2.28 and silicon-nitride ratio (Si:N ratio), to lead the same performances of film properties and is advantageous for thermal budget and cost reduction.

In this study, HCD-SiN deposition characteristics, temperature dependence of the film composition and film properties under VLSI fabrication processes are reported, and the differences with the conventional LPCVD HCD-SiN are discussed.

Emerging Materials
Room Evergreen Ballroom & Foyer - Session EM-MoP
Emerging Materials Poster Session

EM-MoP-1 Conformal ALD of Ferromagnetic ε-Fe2O3 Thin Films*, T. Jussila,* Aalto University, Finland*; **Anish Philip**, J. Kinnunen, M. Utriainen,* Chipmetrics Oy, Finland*; M. Karppinen,* Aalto University, Finland

Magnetic and multiferroic thin films are vital for next-generation electronic and spintronic devices. For instance, strong room-temperature ferromagnets are required for high-density magnetic data storage while multiferroic materials could enable ultra-fast electrical writing and non-destructive magnetic reading of memory devices. However, the state-of-the-art magnetic and multiferroic materials typically have complex chemical composition including critical elements and their functional properties do not meet the requirements of the next-generation applications. Fortunately, there is a highly promising material, ε-Fe_2O_3, which possess a unique combination of multiferroic properties including ultra-hard room-temperature ferromagnetism and magnetoelectric coupling of the ferromagnetic and ferroelectric properties.[1] Moreover, this simple iron oxide is composed of Earth-abundant, low cost, and biocompatible elements. The only drawback is metastability of the ε–Fe_2O_3 polymorph; it is easily transformed to more stable α-Fe_2O_3 and γ-Fe_2O_3 polymorphs. Therefore, the synthesis of phase-pure ε-Fe_2O_3 has been notoriously challenging which has hindered its potential for practical applications. Excitingly, atomic layer deposition (ALD) has turned out to be superiorly suited for the deposition of in-situ crystalline and amazingly stable ε–Fe_2O_3 thin films from simple precursors ($FeCl_3$ and H_2O) in the temperature range of 260 – 300 °C.[2]Here we show the high quality of our ALD-grown ε–Fe_2O_3 thin films through ^{57}Fe Mössbauer spectroscopy, magnetic and crystallographic analyses.[3] Then, most inspiringly, we demonstrate excellent suitability of the robust ε–Fe_2O_3 ALD process for high-aspect ratio substrates using PillarHall LHAR4 structures.[4] The conformality is shown using various methods such as optical microscopy, SEM, and Line scan optical reflectometry. Deposition of ε–Fe_2O_3 over complex surfaces creates exciting possibilities in terms of nanostructuring (magnetic 3D nanodevices) and modification of the fine magnetic properties through dimensional effects.

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EM-MoP-3 In-situ FTIR Analysis of Molecular Atomic Layer Deposited Hybrid Thin Films for EUV Resist Applications*, **Dan Le**, S. Hwang, J. Veyan, T. Park, J. Kim,* University of Texas at Dallas*; R. Choi,* Inha University, Republic of Korea*; W. Lee, A. Subramanian,* Stony Brook University*; N. Tiwale, C. Nam,* Brookhaven National Laboratory*; J. Kim,* University of Texas at Dallas

The progression of lithography technology has enabled the downscaling of device feature size, prolonging Moore's law over decades. However, this has also necessitated the development of novel photoresist systems to keep pace with advancements in patterning technology. Thus, the lack of appropriate photoresist materials for EUV (λ=13.5 nm) lithography is still a pressing challenge in the current race toward the 1 nm node. In recent years, molecular atomic layer deposition (MALD) has emerged as an innovative route to synthesize highly homogenous hybrid inorganic-organic photoresist systems with the ability to control the material thickness at the atomic-scaled level. However, as these photoresist systems have only recently been proposed, there is a gap in our fundamental understanding of the chemical reactions induced by EUV exposure.

Herein, we demonstrate a unique methodology to examine the chemical reactions that occur within MALD inorganic-organic hybrid thin films composed of trimethylaluminum (TMA) and hydroquinone (HQ) under EUV-like exposure conditions. Specifically, we have employed an in-situ Fourier-transform infrared (FTIR) spectroscopy system equipped with an electron flood gun to examine various crosslinking mechanisms of MALD TMA/HQ hybrid thin film. Since various reported studies suggested the generation of secondary electrons during EUV exposures,[1] this study focuses on the interaction between electrons with energy ≤80 eV and the hybrid thin films. In addition, a residual gas analyzer (RGA) was also used to monitor the byproducts produced during the low-energy electron exposures. The obtained RGA and IR absorbance spectra revealed the role of low energy electrons in the crosslinking mechanisms responsible for the solubility switching of the MALD TMA/HQ hybrid thin films in the developer solution. Furthermore, we also studied the effects of thermal annealing on the MALD hybrid thin films before and after low-energy electron exposures. While pre-exposure baking showed no effectiveness, the post-exposure baking process demonstrated an improvement in pattern quality in terms of thickness contrast as well as edge roughness. The detailed experimental procedure and results will be discussed.

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EM-MoP-4 Exploring the Benefits of Reduced Cycle Time in Molecular Layer Deposition (MLD) of Metal-linked 7-(trioxysilyl)heptanoeate (M-TOSH)*, Jesse Kalliomäki*, *J. Binte Mariam, R. Ritasalo, T. Sarnet,* Applied Materials, Finland

Molecular layer deposition (MLD) is being increasingly adopted by industries, like organic electronic manufacturing and medical technology. Increased interest is driven by the versatility MLD adds to he more established sister technique, Atomic Layer Deposition (ALD). Similarly with ALD, after the adoption to industrial process flow, effort must shift to increase its performance, which is measured with metrics such as throughput (wafers per hour). The principal way to increase throughput in the atomic layer processing family is to either increase the growth per cycle (GPC) or decrease cycle time. For high-GPC MLD processes, such as M-TOSH, decreasing the cycle time is an obvious low hanging fruit.

For the M-TOSH process, the literature values for cycle times in a research environment ranges from in excess of one minute [1] up to 416 s (7min) [2]. Our previously reported values in batch ALD chamber were 205 s [3].For this work, we have studied the effect of cycle time optimization on different varieties of M-TOSH (Al, Hf, Ti) films deposited in Picosun R&P-series tools on 200 mm wafers at 90°C. The impact of decreased cycle time was studied using a range of measurement tools, including XPS, FTIR, DSA, ellipsometer.

As a result, we found out that several key process steps could be decreased by >95%. Specifically in the case of O_3, reduction was found to be beneficial. Overexposure to the oxidant lead to decreased C-content, lower GPC and compromised moisture barrier properties. By adopting the reduced cycle time, M-TOSH growth rate (Å/min) was increased more than 200% and uniformity (1σ WiW) improved by almost 50%

This work aims to strengthen the general perception of MLD as an industrially viable deposition method and signal MLD's graduation from a research to a useful tightly optimized nanostructure engineering tool beside putting it more closely on par with other thin film deposition methods.

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EM-MoP-5 Low-Temperature Atomic Layer Annealing Deposition of Crystallized Gallium Nitride on Oxide-Free Si (111)*, SeongUk Yun*, *A. Kummel, P. Lee, A. Mcleod, J. Fammels, J. Watson, H. Kashyap,* University of California at San Diego*; J. Spiegelman,* RASIRC*; W. Aigner, T. Metzger,* Qualcomm Germany RFFE GmbH, Germany

Gallium nitride (GaN) has gained interest due to its wide band gap 3.39 eV and as a buffer layer for other III-V deposition with applications in power electronics operated at high voltage and high temperature [1]. Ueda et al. and Shih et al. showed that atomic layer annealing (ALA) improved the crystallinity of the epitaxy layers of III-V compounds (aluminum nitride) at low temperatures as compared to the conventional thermal ALD [3,4]. Rouf et al. reported that the ionized NH_3 or N_2 could deposit GaN epitaxial layers below 250°C by using typical plasma-enhanced ALD [5]. 100 nm of SiO_2 and sapphire substrates were reported to deposit the crystallized GaN ALA films using krypton by UCSD. However, crystallized GaN ALA films have not been widely studied to deposit on inert, oxide-free Si (111) due to the lattice mismatch (~16%) and coefficient of thermal expansion mismatch (~54 %) between Si and GaN [2].

Thermal ALD and ALA processes were investigated for the low-temperature GaN ALD films on oxide-free Si (111). The native Si oxide was removed by dipping in 2 wt.% HF solution. The self-limiting ALD growth was achieved at 800 ms of N_2H_4 (Rasirc), 100 ms of TDMAGa (EMD), and 400°C (Figure 1a-c). However, a significant CVD process was observed at 150 ms of TDMGa and 430°C. Lower O contents (below 3.3 at.%) were observed in four GaN ALA films on Si (111) as compared to the GaN thermal ALD film (4.6 at.%) (Fig 2a). The higher N/Ga atomic ratio in the GaN ALA films than those in the thermal ALD suggested the ALA process improved the quality of GaN thin films. It is noted the low N/Ga ratio is an artifact of the AES sensitivity factors and ex-situ XPS confirmed a nearly stoichiometric N/Ga ratio.

The intensity of GaN (200) XRD pattern in GaN ALD films on Si was increased with the pulse length of Ar plasma up to 15-20 s (Figure 2b), suggesting the ALA process could improve the crystallinity of GaN epi-layers. The excess ALA plasma (30 s) could damage the crystallized GaN epi-layers. Smooth surface morphologies were observed in the GaN ALD films (RMS = 0.6~1.0 nm) regardless of Ar plasma pulse length (not shown). The Ga-N species in both spectra of Ga $2p_{3/2}$ (Figure 3a) and N 1s (Figure 3b) were dominant after 10 min Ar sputtering and oxide species disappeared after 20 min Ar sputtering, suggesting the formation of good-quality GaN film without Ga-O bonds. These observations suggested that high-quality crystallized GaN ALD thin films with a smooth surface were successfully deposited on oxide-free Si (111) using 15 s of the ALA process at a low temperature (275°C) using TDMAGa and N_2H_4 precursors.

EM-MoP-6 Vapor Deposited MOFs as Low-K Dielectrics for Logic and RF*, J. Watson, **Dohyun Go**, A. Kummel,* UCSD

The present work investigates metal-organic frameworks (MOFs) as low-k dielectrics used to fill the gaps between vias or interconnects in the semidamascence process. An ALD grown ZnO layer is converted to the MOF ZIF-8 by dosing the ZnO in an organic linker gas at elevated temperature. The present study determined the key factors in maximizing the 12x volumetric expansion which is critical to gap fill: The volumetric expansion is a function of the crystallinity of the ZnO film, which depends on the substrate temperature of the ALD process. Three different MOF reaction processes were compared: sealed isothermal, sealed temperature differential, and unsealed temperature differential which were all in atmosphere. The sealed isothermal method provided materials at least as good as the more complex methods.

Three substrate temperatures for the ALD ZnO process were examined to investigate the effect on crystallinity of the ZnO film and subsequent MOF layer thickness. XRD measurements demonstrate that crystallinity decreases with decreasing ALD temperature (Fig 1a). These films were converted to MOF using the same sealed isothermal process. The volumetric expansions as determined by ellipsometry for the three films in order of lowest to highest ALD temperature was 11.2x, 7.5x, and 7.7x (Fig 1b). It is concluded that low-temperature deposited ZnO has higher MOF conversion due to lower crystallinity.

Incorporating a temperature differential into the MOF conversion reaction with a sealed container resulted in the build-up of organic linker vapor near the cold substrate which caused organic linker crystals to condense on the ZnO.Shown in Figure 2, incorporating the temperature differential with an unsealed container showed equivalent results to that of the sealed isothermal container, with roughly 12.2x conversion after two hours. Since the unsealed temperature differential set-up is less reproducible, it is concluded that running the MOF reaction isothermally in sealed conditions is superior. Running the MOF reaction under vacuum will be investigated. It is also noted that the RMS roughness of the initial ZnO layer was roughly 6% of the ZnO thickness, while the MOF layer's RMS roughness was roughly 20% of the MOF layer thickness. Finally, to demonstrate the gap filling ability of the MOF conversion process, the 0 nm 4patterned trenches will be filled which have a 5:1 aspect ratio (Fig 3).

EM-MoP-8 Towards Sequentially Infiltrated Two-Photon Polymerized 3d Photonic Crystals for Mid-IR Spectroscopic Applications*, A. Singhal,* University of Illinois - Chicago*; **Ralu Divan**,* Argonne National Laboratory*; A. Dalmiya, P. Lynch,* University of Illinois - Chicago*; L. Stan,* Argonne National Laboratory*; I. Paprotny,* University of Illinois - Chicago

Photonic crystals (PhCs) can slow the group velocity of light for enhanced light-matter interaction, enabling applications in mid-infrared (MIR) spectroscopic sensing systems [1]. The photonic bandgap (PBG) is a group of wavelengths that are forbidden to pass through the PhCs. Over planar microfabrication techniques, two-photon polymerization (2PP) allows rapid fabrication of 3D-PhCs. But 2PP materials have a low refractive index, which leads to only partial PBGs. The process of sequential infiltration synthesis (SIS), derived from atomic layer deposition (ALD) [2], allows precursor gases to infiltrate and react deep within the polymer [3], resulting in increased refractive index.

In this work, we present 2PP-fabricated IP-Dip resin-based 3D PhCs and use SIS to achieve broad PBG. The partial PBG was confirmed by Fourier transform infrared spectroscopy (FTIR) analysis. For infiltration testing, 100 µm cubes were fabricated at a 700 nm hatching distance and ZnO SIS was performed. The ZnO-infiltrated cube was focused ion beam (FIB) half-milled, and energy dispersive spectroscopy (EDS) was performed on the milled structure, showing counts of Zn L-shell, confirming infiltration. SIS is further used on 2PP-fabricated PhCs to achieve increased refractive index, making PhCs suitable for applications in MIR spectroscopic sensing.

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ALD Applications
Room Grand Ballroom H-K - Session AA1-TuM
ALD for Batteries

Moderators: Prof. Dr. Hyeontag Jeon, Hanyang University, Prof. Markku Leskela, University of Helsinki, Finland

8:00am **AA1-TuM-1 Nanoscale Surface Engineering for Battery Electrode and Solid Ionic Electrolytes**, ***Chunmei Ban,*** CU Boulder **INVITED**

This presentation will discuss the effects of using atomic/molecular layer deposition (ALD/MLD) in stabilizing surface/interface of battery electrode materials and facilitating ion diffusion at the surface of ionic conducting materials. ALD and MLD have proven themselves to be the best methods to grow continues, conformal and pinhole-free ultrathin films for high-aspect-ratio microstructures and nanomaterials. Thus, ultrathin oxides layers (<5nm) have been used to protect surface of electrode materials from liquid electrolytes, leading to the greatly improved battery cycling performance of lithium-ion electrodes. In addition, surface coatings via ALD/MLD have been recently applied to ionic conducting materials to increase wettability and electrochemical stability. This talk will summarize recent studies on surface modification using ALD/MLD for electrodes and solid-state electrolytes, to correlate the electrochemical properties of the coated electrochemical materials with chemistry of coating materials. Electrochemical analysis will be used to study how the modified surfaces alter charge transfer and electrochemical reactions at the electrode surface or at the electrode-electrolyte interface. Furthermore, we will combine electrochemical diagnosis with spectroscopic studies to investigate the structural and morphology evolution of the coating materials during electrochemical processes, present insights in design of surface coatings and their applications in solid-state batteries.

8:30am **AA1-TuM-3 Enabling Fast Charging of Lithium-ion Batteries by Coating of Graphite with ALD**, *E. Kazyak, K. Chen, Y. Chen, T. Cho,* ***Neil P. Dasgupta,*** University of Michigan, Ann Arbor

Increasing the achievable charging rate of lithium-ion batteries (LIBs) is critical to the widespread commercialization of electric vehicles (EVs). The primary factor limiting the fast-charge ability of state-of-the-art LIBs is the propensity for Li metal to plate out on the graphite surface during charging.[1] The poor reversibility of Li metal in LIB electrolytes leads to rapid capacity fade, consumption of the electrolyte (cell drying), and possibly even short-circuit from dendrites penetrating the separator. This problem is exacerbated in high-energy density cells with thicker electrodes, leading to energy-power tradeoffs.

To prevent/mitigate these effects, in this study[2] we implement an atomic layer deposition (ALD) surface coating on calendered graphite anodes. We demonstrate that this artificial solid electrolyte interphase (a-SEI) that outperforms the natural SEI in fast-charging ability. The large majority of the previous ALD coatings that have been investigated as electrode coatings for LIBs have been binary metal oxides that have very low ionic conductivity. In contrast, the ALD coating used here is a lithium borate-carbonate (LBCO) solid electrolyte. This ALD single-ion conductor has previously been shown to exhibit ionic conductivities above $2*10^{-6}$ S/cm and excellent electrochemical stability, including with Li metal.[3]

Here we demonstrate that in comparison to uncoated control electrodes, the LBCO a-SEI coating: 1) eliminates natural SEI formation during formation cycles, 2) decreases interphase resistance by >75% compared to that of the natural SEI, and 3) extends cycle life under 4C-charging conditions, enabling retention of 80% capacity after 500 cycles (compared to 12 cycles in the uncoated control) in pouch cells with >3 mAh-cm^{-2} loading. Not only is this a promising approach to enable fast-charging of LIBs, but it also challenges the prevailing thinking that mass-transport limitations in the liquid electrolyte must be addressed to enable fast charging. In the future, this opens up new possibilities for engineering of LIB interfaces for performance enhancements beyond improved stability and cycle life.

References

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3. E. Kazyak, K.-H. Chen, A. L. Davis, S. Yu, A. J. Sanchez, J. Lasso, A. R. Bielinski, T. Thompson, J. Sakamoto, D. J. Siegel, and N. P. Dasgupta, *J. Mater. Chem. A* **6**, 19425 (2018)

8:45am **AA1-TuM-4 Aluminum Doping of Lithium Phosphate using Atomic Layer Deposition**, ***Daniela Fontecha****, K. Gregorczyk, A. Kozen, G. Rubloff,* University of Maryland, College Park

Metal phosphate glasses developed by ALD have been used for a variety of applications in microelectronics. Lithium phosphate deposited by ALD is relevant in solid-state battery (SSB) applications as a Li-ion conducting thin film that is compatible with many Li-ion battery chemistries, enabling the passivation of reactive interfaces between solid-state cathode and electrolyte films. It has also been shown that lithium aluminum phosphate (LAP) is a promising protection layer for cathode materials in SSBs. This work explores the impact of Al-doping of lithium phosphate in terms of its structural, chemical, and Li^+ ion conducting properties with a new ALD synthesis method for thin film applications.

The constituent ALD process for crystalline Li_3PO_4 (LPO) utilizes lithium tert-butoxide (LiO^tBu), water, and trimethyl phosphate (TMP) at 300 °C with a growth rate of 0.8 Å/cycle and ionic conductivity of $1.3x10^{-9}$ S/cm. Trimethyl aluminum (TMA) and water are then used to insert aluminum into the LPOfilm by cycling between 1 cycle of TMA + water and **[n]** cycles of LPO (n = 30-120) to produce a film with Al content between 1-4 %. This work shows that the ionic conductivity of LAPincreases to $4.0x10^{-8}$ S/cm – one order of magnitude higher than that of LPO– due to the role aluminum plays in cross-linking phosphate groups even at these low Al concentrations. Deposition temperatures ranging from 250 – 300 °C show growth rates from 0.8 to 0.9 Å/cycle, respectively. The TMA + water pulse appears to have a minimal effect on the overall growth rate, which indicates compatible precursor chemistry between hydroxylated TMA and LiO^tBu.XPS O 1s high resolution spectra of LAP films show an increase in bridging oxygen content with a shift in the bridging oxygen peak to lower binding energies suggesting the increase of Al-O-P bonding. The presence of P-O-P and Al-O-P binding states as well as GIXRD results showing some loss of crystallinity in as-deposited LAP compared to LPO suggest that there is cross-linking between phosphate groups at low Al-doping levels. We find that deposition temperature is a critical factor in controlling resultant film morphology with films deposited at 300 °C exhibiting an additional peak at 28.3° 2θ. This peak lies between crystalline Li_3PO_4 and $AlPO_4$ peaks seen in literature, suggesting that at higher deposition temperatures, a mixture of crystalline LPO and $AlPO_4$ phases develops. In this talk, thin film processing of LAP is discussed along with materials characterization of a new Li-ion conducting thin film by ALD.

9:00am **AA1-TuM-5 Developing High-Performance Nickel-Rich Cathodes of Lithium-ion Batteries via Atomic Layer Deposition**, ***Xiangbo Meng****, X. Wang, K. Velasquez Carballo, A. Shao,* University of Arkansas; *Y. Liu, H. Zhou,* Argonne National Laboratory; *X. Xiao,* Brookhaven National Laboratory

$LiNi_xMn_yCo_zO$ (NMCs, x + y + z =1) are promising for next-generation lithium-ion batteries (LIBs) and emerging lithium metal batteries (LMBs), featuring their higher capacity and lower cost than those of $LiCoO_2$. In particular, the advantages of NMCs in capacity and cost become more evident with increased Ni content. In other words, the higher the Ni content is, the higher the capacity is and the lower the cost is. With the increasing Ni content, however, the issues of NMCs become more challenging, exhibited as performance fading and safety risk. The issues include residual lithium compounds, irreversible phase transition, oxygen release, transition metal dissolution, and microcracking. They can further cause interface problems and electrolyte degradation and eventually lead to cell failure. This is particularly evident for Ni-rich NMCs (x ≥ 0.6).

In searching for solutions to these issues, surface coating remains as an important technical strategy and has proven effectiveness. In the past decade, atomic layer deposition (ALD) has emerged as a new surface coating process and has been attracting an ever-increasing attention for addressing issues of various battery systems.[1-4] Its advantages lie in multiple aspects: (1) uniform and conformal coating, (2) moderate process temperature, and (3) the only capable technique enabling coatings over either prefabricated electrodes or battery powders. In addressing the issues of Ni-rich NMCs, we have been intensively investigating various surface coatings via ALD, including binary oxides, ternary Li-containing oxides, binary sulfides, and ternary Li-containing sulfides.[5-8] Our efforts revealed that these coatings commonly could inhibit interface reactions, mitigate microcracking, and suppress irreversible phase transition. Among them, Li-containing compounds could enable better ionic conductivity while sulfide coatings could offer some unique protective effects through scavenging oxygen released from NMC lattices. Our original discovery on sulfide coatings is particularly significant, for it opens a new research direction on

surface coatings of rechargeable batteries and paves a novel technical avenue for achieving high performance of NMCs and the like in LIBs and LMBs.

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8. Wang, X., *et al.*, *Journal of Energy Chemistry* (2022) **69**, 531

9:15am **AA1-TuM-6 Molecular-Layer-Deposited Zincone Films Induce the Formation of LiF-Rich Interphase for Lithium Metal Anodes*, Wei-Min Li,*** Jiangsu Leadmicro Nano-Technology Co., Ltd., China*; S. Chang, A. Li,* Nanjing University, China

Lithium (Li) metal has been recognized as the promising anode material for rechargeable batteries because of its high theoretical capacity of 3,860 mAh g^{-1} and the lowest electrode potential (−3.04 V v.s. the standard hydrogen electrode (SHE)). However, Li metal usually forms a fragile solid electrolyte interphase (SEI), which is not sufficiently dense to passivate the surface of Li metal. During stripping and plating, the SEI cannot suppress the side reaction between Li metal and electrolyte. The poor SEI may also induce the heterogeneous deposition of Li, leading to the formation of notorious dendrites. The uncontrolled Li dendrites not only consume cyclable Li but also accumulate irreversible "dead lithium" owing to the loss of electric connection. Coulombic efficiency (CE) is then dramatically reduced. At a fixed loading, the deliverable capacity decays rapidly. In addition, Li dendrites may cause safety issues such as short circuits and catastrophic cell failures, which hinders the practical application of Li metal batteries.

In this work, we report a zincone (ZnHQ) MLD technology and its application for induced LiF-rich SEI on a copper nanowire (CuNW) anode. Zincone is a zinc-based hydroquinone (HQ) where Zn replaces hydrogen of HQ. As shown in **Figure 1a**, the hydroxyl (-OH) modified Cu is grafted with HQ during the MLD. Diethylzinc further reacts with the hydroxyl groups of grafted HQ to yield ZnHQ. HQ is selected as the backbone molecule because it is relatively stable upon lithiation and a single chain of ZnHQ has a terminal oxygen, which can serve as the nucleophilic group to attack Li bistrifluoromethanesulfonimide (LiTFSI) upon negative polarization. The resultant LiF-rich SEI (**Figure 1b, c**) can facilitate Li ion diffusion and suppress the dendritic Li growth that is usually induced on a pristine Cu (**Figure 1d, e**). More importantly, zinc atoms can facilitate the deposition of Li metal owing to the lithiophilicity.

Furthermore, the high surface area of porous scaffold and CuNWs reduces the local current density and prolongs the Sand's time. As a result, the CuNW@ZnHQ electrode demonstrates superior cyclability for over 7000 h at a capacity of 1 mAh cm^{-2} and can maintain more than 300 h at a high loading capacity (15 mAh cm^{-2}). In addition, CuNW@ZnHQ is paired with NCM523 at a capacity of 3.2 mAh cm^{-2} with excellent cyclability of 90% capacity retention for 1000 cycles. This work provides an alternative approach to developing nanoscale interfacial coatings for Li metal and demonstrates that the zincone MLD strategy may serve as a potential technology for next-generation high-energy Li metal anodes.

9:30am **AA1-TuM-7 Deconvoluting the Impacts of Lithium Morphology and SEI Stability on Battery Cyclability Using ALD-Grown Thin Films*, Sanzeeda Baig Shuchi,*** *S. Oyakhire, Y. Cui, S. Bent,* Stanford University

The establishment of a fossil-fuel-free world strongly depends on electrification. The Li-ion battery, a universal mode of electrochemical energy storage, is reaching the theoretical limit, creating an urgency to produce more efficient batteries for next-generation applications. A more energy-dense battery configuration is the anode-free Li metal battery (LMB), in which Li is directly plated on and stripped from the Cu current collector (CC).

Electrodeposited Li morphology and solid electrolyte interphase (SEI) are the two most crucial performance modulators in LMBs. The literature has shown that low surface area morphology and anion-derived SEIs are desired for improved performance. However, it is difficult to deconvolute the individual impact of low surface area morphology and anionic SEI species on performance as they coexist and are correlated. We demonstrate a novel interface engineering approach to deconvolve the effects of Li morphology and SEI stability using atomic layer deposition (ALD). First, we modify the Cu CC surface using two thin films with distinct characteristics: resistive, acidic HfO_2; and conductive, acidic ZnO, using TDMAHf-H_2O and DEZ-H_2O precursors.

We leverage ALD to precisely vary the thickness of the nanofilms and establish that increasing the film resistance results in improved performance due to resistance-derived Li morphology. In addition, the HfO_2-modified CCs performed better than the ZnO-modified CCs, consistent with their relative resistivities. To decouple the impact of SEI species from morphology, we preform the SEI before cycling using a simple potential hold step for these two acidic metal oxide films, each of which has different electric properties. We find that with increasing film thickness, the preformed SEI has more anionic species due to the surface acidity of the thin films. Despite being anion-rich, the preformed SEI does not improve performance, which we attribute to its evolution into an organic-rich SEI during plating. Moreover, the impact of the preformed SEI was statistically insignificant during long-term cycling while the role of resistance became more evident.

In conclusion, the results indicate that morphological control is more successful for improved battery cyclability due to the inherent challenges with preformed SEI preservation. Correspondingly, the results suggest that resistance of the ALD-grown thin films is more important than surface acidity for CC modification. We show this resistance-derived Li morphology and performance enhancement in three different electrolytes with at least a twofold increase in cycle life along with improved capacity retention in practical anode-free pouch cells.

ALD Applications
Room Grand Ballroom H-K - Session AA2-TuM
MEMS, Actuators, Hard Films

Moderators: Prof. Anjana Devi, Ruhr University Bochum, Viljami Pore, ASM

10:45am **AA2-TuM-12 ALD for MEMS Sensors and Actuators*, Luca Lamagna,*** STMicroelectronics, Italy **INVITED**

Atomic layer deposition (ALD) has undoubtfully become one of the leading technologies employed for the deposition of nanometer-scale films at an industrial level. ALD allows for the deposition of conformal ultra-thin layers with an extremely precise thickness control. Moreover, ALD processes have been scaled on large area substrates, making this technique very promising for the industrial high throughput need. With ALD it is possible to develop and optimize the growth of novel ultra-thin dielectric, metal, and complex ternary compounds films.

Microelectromechanical systems (MEMS) have been attracted since the very beginning by ALD as a deposition technology that can address with its outstanding conformality the deposition on 3D complex structures. ALD turned out to be also a powerful approach to significantly increase the material selection available for MEMS processing. Simultaneously, ALD came up with the potentiality to offer layers with functional and tunable properties for the more disparate applications. Indeed, ALD is also able to realize thin functional layers that can be employed for specific surface engineering.

We will review the relationship between ALD processes and MEMS technology in terms of equipment and processes and we will provide an outlook for the future applications of ALD on advanced MEMS sensors and actuators.

11:15am **AA2-TuM-14 Applications of Piezoelectric, Ferroelectric, and Antiferroelectric Thin Films Grown by Atomic Layer Deposition*, Nicholas Strnad,*** DEVCOM Army Research Laboratory*; G. Fox,* Fox Materials Consulting, LLC*; T. Tharpe,* Oak Ridge Associated Universities*; R. Knight, R. Rudy, J. Pulskamp,* DEVCOM Army Research Laboratory

Piezoelectric materials offer efficient transduction of electrical and mechanical forces and have been implemented in many commercial products including medical ultrasound transducers, ink-jet print heads, atomic force microscope cantilever drives, and radio-frequency filters (thin-film bulk acoustic resonators, or FBARs). Actuators for microelectromechanical systems (MEMS) that utilize piezoelectric thin films offer larger forces and displacements compared to electrostatic actuators, and higher operating frequencies compared to thermal actuators. Despite the performance advantages offered by piezoelectric thin films, there are few reported ALD processes that have yielded viable piezoelectric

properties. This presentation addresses several knowledge gaps in the field of ALD piezoelectric thin films. First, we present ALD processes for some of the most commercially relevant piezoelectric and ferroelectric thin films, including aluminum nitride (AlN), lead zirconate-titanate (PZT), additional Pb-containing perovskites (lead hafnate-titanate or PHT, lead hafnate or PHO), and $Hf_{1-x}Zr_xO_2$ (HZO). Second, we present methods of characterizing the effective transverse piezoelectric coefficient ($e_{31,f}$) which is critical for actuators but is underreported in the literature compared to the effective longitudinal piezoelectric strain constant ($d_{33,f}$). Third, we present new MEMS actuator concepts and initial fabrication results that leverage 3D, conformal ALD piezoelectric thin films that will lead to greater performance (up to 200x larger piezoelectric energy density) compared to traditional planar piezoelectric-enabled MEMS actuators. These new actuator concepts require aggressive aspect ratio scaling, sidewall-selective depositions, and 3D patterning, which presents new challenges and opportunities for atomic layer processing technologies.

11:30am **AA2-TuM-15 Effect of RF Substrate Biasing in Tuning the Tribological Properties of Plasma Enhanced Atomic Layer Deposited Titanium Vanadium Nitride Thin Films*, Md Istiaque Chowdhury,*** Lehigh University*; M. Sowa,* Veeco Instruments Inc.*; K. Van Meter,* Florida International University*; A. Kozen,* University of Maryland, College Park*; S. Lazarte, B. Krick,* Florida International University*; N. Strandwitz,* Lehigh University

Ultra-low wear rates, approaching those of diamond, have recently been reported for transition metal nitride thin films deposited by plasma enhanced atomic layer deposition (PEALD). Apart from low wear, these films exhibit low electrical resistivities (~100 μΩ cm) comparable to metals (1-100 μΩ cm) and high chemical stability, which opens them up for applications in MEMs, NEMs, as electrodes, etc. Our aim is to understand the synthesis-structure-property relationships of these films by introducing substrate bias during deposition. The substrate bias helps regulate the energy distribution of the incoming plasma ions, which plays a vital role in modifying the resultant structure of the film and ultimately influence the functional properties. Researchers are using substrate biasing to modulate the ion-surface interaction in PEALD films but the correlation between the bias and the resultant structure and properties are not linear.

In this study, the magnitude of RF substrate bias, $|V_{bias}|$, was varied from 0 to 40 V during PEALD growth of ternary $Ti_xV_{(1-x)}N$ thin films to observe how $|V_{bias}|$ correlates with structure and tribological properties. Tetrakis (dimethylamido) titanium, tetrakis(dimethylamido) vanadium, and N_2 plasma were used as precursors. The growth rate per metal precursor exposure was 0.5-0.6 Å/cycle. The film densities approached 95% of the theoretical density as estimated by X-ray reflectivity. The electrical resistivity was evaluated to be 130-170 μΩ cm by four-point probe measurements. X-ray diffraction measurements revealed that the films have a cubic rocksalt crystal structure formed by a solid solution of TiN and VN. The crystal quality, indicated by the Bragg peak intensity, changed non-monotonically with $|V_{bias}|$. The (200) peak had the highest intensity for $|V_{bias}|$=20 V which was reflected in the minimum wear rate (10^{-8} mm^3/Nm) observed at this $|V_{bias}|$. The distribution of ion energies of the bombarding plasma was modified by $|V_{bias}|$, which provides an additional boost of energy to the adatoms promoting the crystal growth up to $|V_{bias}|$=20 V. Beyond 20 V, the additional energy from the bias causes continuous re-nucleation resulting in poor crystal quality, thus increasing the wear rate. The impact of $|V_{bias}|$ on tuning tribological properties of PEALD films have not been extensively studied, but it has been demonstrated that the residual stress of PEALD nitride films can be switched from compressive to tensile with $|V_{bias}|$. Substrate biasing can be a very useful tool to tune the tribological properties of PEALD nitride films and potentially create ultra-low wear materials.

11:45am **AA2-TuM-16 Towards ALD of hard AlTiN coatings*, Pamburayi Mpofu,*** Linköping University, Sweden*; J. Lauridsen, O. Alm, T. Larsson,* Seco Tools AB, Sweden*; H. Högberg, H. Pedersen,* Linköping University, Sweden

AlN has a wide bandgap (6.2 eV), high dielectric constant (k ∼ 9), high electrical resistivity (ρ ∼ 1011–1013 Ω cm), and a very good thermal conductivity (2.85W/K cm)[1] making it interesting for microelectronics and optoelectronics. AlN is also used in microelectromechanical systems (MEMS devices) because of its piezoelectric properties. As AlN has good miscibility with other nitrides, it also has the potential to be used in ternary materials with e.g., Ga, In, Ti, or Hf, increasing the range of its possible applications. One such material is meta-stable $Al_xTi_{1-x}N$ where the cubic rock salt structure of TiN is preserved even with x = 0.9. $Al_xTi_{1-x}N$ primarily finds use as hard material in protective coatings, often on cemented carbide tools. While ALD of AlN has been reported several times, reports on ALD of ternary materials comprising AlN are scarce. $Al_xTi_{1-x}N$ has only three entries in the Atomic Limits database[2], for semiconductor-related applications. Our aim is to explore the possibility of using ALD, for the first time, to deposit hard protective coatings of $Al_xTi_{1-x}N$. We aim to explore both an ABC-type ALD cycle with $AlMe_3$, $Ti(NMe_2)_4$, and NH_3, and an AB-type ALD cycle with co-evaporation of $Al(NMe_2)_3$ and $Ti(NMe_2)_4$.

We will present an ALD comparison study of AlN, from a hard coating perspective. We compare $Al(NMe_2)_3$ and $AlMe_3$ as Al precursors and NH_3 with and without plasma activation as the N precursor. In addition to standard Si (100) substrates, we also deposit on cemented carbide, i.e., tungsten carbide particles sintered in a cobalt matrix, with and without a TiN coating. We studied the AlN ALD process in the temperature range from 100 to 400 °C with the aim to optimize the process for crystalline quality rather than electronic properties. Polycrystalline, stoichiometric, and high-purity AlN films have been obtained when using $AlMe_3$ (both plasma and thermal) but with varying thicknesses, growths per cycle, saturation times, nucleation delays, and temperature windows. Films prepared via the plasma route exhibit improved properties concerning the growth rate per cycle, total cycle duration, and homogeneity. By comparing our experimental results to recent modeling results from density functional theory methods, we can show strong evidence for the surface chemical mechanism of TMA on an NH_2-terminated AlN surface.

We will also describe our initial results from depositions of $Al_xTi_{1-x}N$ using the ALD approaches outlined above.

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2. https://www.atomiclimits.com/alddatabase/

ALD Fundamentals
Room Grand Ballroom E-G - Session AF1-TuM
Precursors and Processes I

Moderator: Prof. Dr. Charles H. Winter, Wayne State University

8:00am **AF1-TuM-1 Precursor Design Enabling Angstrom Era Semiconductor Manufacturing*, Charles Mokhtarzadeh,*** *E. Mattson, S. Lee, S. Clendenning, P. Theofanis,* Intel Corporation **INVITED**

The ever more challenging dimensions and architectural complexity of nanofabricated structures in the semiconductor industry and beyond are often combined with the need for new materials. This drives the need for the chemist and the thin films deposition engineer to innovate across the periodic table. For example, recent advances in the Gate All Around (GAA) RibbonFET transistor technology characteristic of the Angstrom Era of semiconductor manufacturing necessitate the use of atomic layer deposition in high aspect ratio complex spaces and are also creating opportunities for atomic layer etch and selective deposition. At the heart of this is a need for new precursor and thin films chemistry. Taking a survey of well-established ALD precursors as a starting point, we will consider new ligand scaffolds and the synthesis of derived precursors and thin films. Approaching thin films from an etch point of view, we will look at how non-traditional ligands can be used for the ALE of industry relevant films. Lastly, some perspective will be provided on precursor design and synthesis as key elements in meeting future manufacturing needs

8:30am **AF1-TuM-3 Atomic Layer Deposition of Silver Halides***, **Georgi Popov**, T. Hatanpää, A. Weiß, M. Chundak, M. Ritala, M. Kemell,* University of Helsinki, Finland

Although AgCl, AgBr and AgI have unique attractive properties, our primary motivation for developing ALD processes for these materials is the deposition of silver halide perovskites. Silver halides are IR-transparent and antiseptic, which has enabled their use in niche optical and medical applications. Silver halides are also light-sensitive, which we believe can be exploited for patterning applications. Most importantly, silver halides are components of double perovskites, such as $Cs_2AgBiBr_6$.

Halide perovskites are a major topic in materials science and are associated with Pb compounds, photovoltaics, and challenges with scalability, stability, and toxicity. However, one-third of the publications on perovskites are unrelated to photovoltaics. The largest and fastest growing non-photovoltaic applications of perovskites are light-emitting diodes, sensors, and microelectronic components. In these applications, it is possible to use Pb-free alternatives like double perovskites. Silver and bismuth double perovskites, like $Cs_2AgBiBr_6$, are stable and nontoxic, eliminating two of the three challenges.[1] Depositing double perovskites with ALD could address the remaining scalability challenge.

The development of ALD processes for ternary and quaternary compounds begins with the processes for the corresponding binary compounds. From our previous work[2] we know how to deposit cesium halides, but no processes for silver and bismuth halides are known. This work focuses on silver halide processes using $Ag(fod)(PEt_3)$, a silver precursor well established in the ALD and CVD of metallic silver.

Our metal-halide ALD processes employ volatile metal halides, like SnI_4, as halide precursors. In our previous work, we discovered that the choice of the volatile metal halide makes or breaks the process.[3] The byproducts generated by the volatile metal halide can be benign or detrimental by being able to etch the film material or by being nonvolatile, which results in the incorporation of impurities and poor crystallinity. Therefore, we screened the candidates to identify suitable pairs. The candidates are the corresponding halides of titanium, gallium and tin.

For example, $Ag(fod)(PEt_3)$ and SnI_4 are one such pair. These precursors produce crystalline β-AgI films in the 100 – 200 °C temperature range with the largest GPC of 0.9 Å at 140 °C. The films were smooth, uniform, and contained a negligible amount of impurities. We continue our process studies on suitable precursor pairs for the other silver halides.

[1] Lei et al., *Adv. Funct. Mater.* **2021**, 31, 2105898.

[2] Weiß et al., *Chem. Mater.* **2022**, *34*, 6087.

[3] Popov et al., *Dalt. Trans.* **2022**, *51*, 15142.

8:45am **AF1-TuM-4 Novel Metal Fluoride ALD Processes***, **Elisa Atosuo**, M. Mäntymäki, M. Heikkilä, K. Mizohata, M. Leskelä, M. Ritala,* University of Helsinki, Finland

The number of ALD processes for metal fluorides has been limited, especially when compared to ALD processes for metal oxides, nitrides, and sulfides. Recently, however, interest towards ALD of metal fluorides has increased. The applications for metal fluoride films range from optical coatings to lithium-ion batteries (LIB) and luminescence devices. This work summarizes recent studies on ALD of metal fluorides at University of Helsinki.

New ALD processes for rare earth and transition metal fluorides are presented. Of the rare earth metal fluorides, we have included an ALD process for ScF_3, which is a negative thermal expansion (NTE) material. To our knowledge, this is the first wide-temperature range NTE material deposited by ALD. The films are close to the stoichiometric, and, e.g., in films deposited at 300 °C the total impurity content (O, C, and H) is only ~2.6 at-% as measured by ToF-ERDA. In addition, an ALD process for GdF_3 and its *in-situ* conversion to $NaGdF_4$ by Nathd (thd=2,2,6,6-tetramethyl-3,5-heptanedione) are presented. GdF_3 is an important material for antireflection coatings, whereas $NaGdF_4$ is a potential host material for luminescence centers, especially for medical applications. Of the transition metal fluorides, an ALD process is presented for CoF_2 that is a potential LIB cathode material.

In addition to the new metal fluoride ALD processes, we introduce a new fluoride source, NbF_5, the use of which has been inspired by the successful use of TiF_4 and TaF_5 as fluoride sources in ALD. In this work NbF_5 was combined with $Ho(thd)_3$ to deposit HoF_3. In HoF_3 films, Nb impurity content as low as 0.2 at-% was obtained.

We aim to give a comprehensive overview of ALD of metal fluorides. Therefore, also future research directions will be discussed.

9:00am **AF1-TuM-5 Halide-free, Low Melting, Volatile, Thermally Stable Mo(0) Precursors for ALD of Mo films***, C. Barik, A. Leoncini,* Applied Materials – National University of Singapore Corporate Lab, Singapore*; F. Liu,* Applied Materials, Inc.*; J. Tang, J. Sudijono,* Applied Materials – National University of Singapore Corporate Lab, Singapore*; M. Saly,* Applied Materials, Inc.*; **Chandan Das**,* Applied Materials, Inc., Singapore

State-of-the-art devices require surrounding Cu interconnects with a layer of tantalum (Ta liner) and a layer of tantalum-nitride (TaN barrier) to prevent diffusion of Cu atoms into the surrounding dielectric, which is detrimental to the lifetime of the IC. Downscaling of integrated circuits (ICs) faces significant challenges because the resistivity of Cu features increases at smaller dimensions according to the product $\lambda \times \rho_0$, and further thinning of the Ta/TaN layers would result in increased resistivity and poorer performance. Among metals with lower $\lambda \times \rho_0$ values, cobalt (Co) requires a barrier film and ruthenium (Ru) is difficult to process during CMP. Molybdenum (Mo), which does not require a barrier and is CMP processable, is a suitable alternative for Co and Ru and the entire Cu/Ta/TaN interconnect. Current commercial processes use solid halide-based precursors ($MoCl_5$ and MoO_2Cl_2). As device integration becomes more complex with each node generation, halide-free deposition processes are necessary. We designed and successfully synthesized a halide free Mo precursor with small ligands, which is low melting and has high volatility. We studied its thermal stability, volatility and chemical properties. Our precursor consists of a) Mo at zero oxidation state, b) neutral halide-free ligands – easier to detach from metal thermally during deposition.

We synthesized and characterized our precursor by ^{1}H-, ^{13}C- and ^{31}P- NMR spectroscopy, and its molecular structure has been confirmed by x-ray crystallography. Its low-melting point (35 °C) makes it easy to handle and enables liquid delivery. Thermogravimetric analysis shows good volatility, with $T_{1/2}$ 173 °C and low residual mass. The thermal stress analysis showed that it is stable at 200 °C for at least 7 days (Figure 1b). The clean TGA profile with ~1% residue after annealing indicates its thermal stability. Moreover, the isothermal TGA at 100 °C indicates that the chemical is volatile and deliverable to the reaction chamber (Figure 1c). The precursor was also employed for ALD and CVD deposition of Mo-rich films, and we investigated how the film composition responded to different deposition conditions.

9:15am **AF1-TuM-6 Thermal Atomic Layer Deposition of MoC Thin Films***, **Paloma Ruiz Kärkkäinen**, T. Hatanpää, M. Heikkilä, K. Mizohata, M. Chundak, M. Putkonen, M. Ritala,* University of Helsinki, Finland

Transition metal carbides (TMCs) are widely used in catalytic and wear resistance applications. They exhibit excellent chemical and thermal stabilities, exceptional hardnesses, and low resistivities. Additionally, TMCs typically have good electromigration resistances. These properties make them relatively good conductors for metal wires when the dimensions shrink to the sub-10 nm range. Development of TMC ALD processes opens the possibility to use carbides in semiconductor applications. Molybdenum carbides (MoC_x) have the potential to improve the performance, efficiency, and reliability of semiconductor devices. Recently, they have emerged as potential candidates for diffusion barriers, interconnects, and gate electrodes.[1–3] The ALD of metal carbides is, however, still in its infancy, and current challenges include a lack of thermal ALD processes, high process temperatures, and low growth rates.

In this work, we report a novel thermal ALD process for MoC with $MoCl_5$ and bis(trimethylgermyl)-1,4-dihydropyrazine ($(Me_3Ge)_2DHP$) as precursors. $(Me_3Ge)_2DHP$ has previously been used as a reducing agent in ALD of nickel and gold.[4,5] In the current process, $(Me_3Ge)_2DHP$ acts as both the reducing agent and carbon source for the first time. The process was investigated at temperatures between 200 and 300 °C. At 275 °C, high growth rates of 1 Å/cycle were observed. The films are very smooth with XRR roughnesses of approximately 0.25 nm. The growth rate is strongly affected by the $MoCl_5$ pulse length, and we observed a small etching component by $MoCl_5$ in all depositions. Remarkably, according to XPS the MoC films do not contain any metallic Mo. The resistivities of the moderately crystalline films are ~200 μΩcm at a film thickness of ~100 nm, which is slightly higher than those for bulk MoC_x. No change in the crystallinity was observed after annealing up to 1000 °C under N_2 atmosphere. The influence of process parameters on the MoC film properties as well as the mechanism of the process is discussed in detail.

[1] Tripathi, C. C., *et al. Appl. Surf. Sci.* **255**, 3518–3522 (2009). https://doi.org/10.1016/j.apsusc.2008.09.076.

[2] Leroy, W. P., *et al. J. Appl. Phys.* **99**, 063704 (2006). https://doi.org/10.1063/1.2180436.

[3] Ha, M.-J. *et al. Chem. Mater.* **34**, 2576–2584 (2022). https://doi.org/10.1021/acs.chemmater.1c03607.

[4] Vihervaara, A. *et al. Dalt. Trans.* **51**, 10898–10908 (2022). https://doi.org/10.1039/D2DT01347A.

[5] Vihervaara, A. *et al. ACS Mater. Au* (2023). https://doi.org/10.1021/acsmaterialsau.2c00075.

9:30am **AF1-TuM-7 Precursors and Processes for the Atomic Layer Deposition of Bismuth Metal Thin Films***, **Daniel Beh,*** Wayne State University*; Z. Devereaux, T. Knisley,* Applied Materials*; C. Winter,* Wayne State University

The element bismuth (Bi) is an important component of materials ranging from insulators to superconductors. For many applications, thin films containing Bi need to be grown in high aspect ratio features with perfect conformality and Angstrom-level thickness control. Atomic layer deposition (ALD) is a film growth method that can afford uniform thickness films, even in narrow and deep nanoscale features. While Bi ALD precursors have been reported for materials such as oxides,[1] there have been no reports to date of the ALD growth of Bi metal films. Herein, we will describe a family of thermal ALD processes for Bi metal thin films. Bi precursors used in this work include $BiCl_3$, $BiPh_3$, and $Bi(NMe_2)_3$. Reducing co-reactants fall into two general classes. Processes with $BiCl_3$ and 2-methyl-1,4-bis(trimethylsilyl)-2,5-cyclohexadiene (**1**) or 1,4-bis(trimethylsily)-1,4-dihydropyrazine (**2**)[2] afforded Bi metal films at substrate temperatures ranging from 50 to 175 ºC. Here, **1** and **2** serve as the reducing agents, with elimination of Me_3SiCl and toluene (**1**) or pyrazine (**2**). ALD processes were also developed using $BiCl_3$, $BiPh_3$, or $Bi(NMe_2)_3$ in combination with nitrogen sources such as ammonia, hydrazine, alkyl hydrazines, or alkyl amines. The processes with nitrogen-based co-reactants are proposed to proceed via the formation of unstable "BiN", which decomposes to afford Bi metal films. All of these processes afforded crystalline Bi metal films, as determined by X-ray diffraction. X-ray photoelectron spectroscopy demonstrated that the films were >94% pure Bi metal after argon ion sputtering to remove adventitious surface impurities.

1. For example, see: Hatanpää, T.; Vehkamäki, M.; Ritala, M.; Leskelä, M. *Dalton Trans.***2010**, *39*, 3219-3226.

2. Klesko, J. P. Thrush, C. M.; Winter, C. H. *Chem. Mater.***2015**, *27*, 14, 4918–4921.

9:45am **AF1-TuM-8 Atomic Layer Deposition of Tin Oxide Thin Films Using a New Liquid Precursor Bis(ethylcyclopentadienyl) Tin***, **Makoto Mizui,** N. Takahashi, F. Mizutani,* Kojundo Chemical Laboratory Co., Ltd., Japan*; T. Nabatame,* National Institute for Materials Science, Japan

Transparent conductive oxide thin films, including SnO, SnO_2, In-Sn-O (ITO), Zn-Sn-O (ZTO), and In-Zn-Sn-O (IZTO) films, have recently attracted much attention for various applications such as flat-panel displays, gas sensors, and solar cells. We have reported the atomic layer deposition (ALD) of In_2O_3 and ZnO thin films using cyclopentadienyl-based precursors [1, 2]. In order to deposit such transparent conductive oxide thin films by using ALD, ALD-Sn precursor is essential. This time, we report ALD of tin oxide (SnO_x) thin films using a new liquid cyclopentadienyl-based precursor.

As a new ALD-Sn precursor, bis(ethylcyclopentadienyl) tin, $Sn(EtCp)_2$, was synthesized. $Sn(EtCp)_2$ is a liquid precursor at room temperature. Differential scanning calorimetry (DSC) was conducted to measure its thermal decomposition temperature. The decomposition temperature was estimated approximately 230 °C, so the deposition temperature was set to 200 °C, which is the same temperature in the case of ALD of In_2O_3 and ZnO thin films [1, 2]. The vapor pressure of $Sn(EtCp)_2$ was determined by directly measuring the equilibrium vapor pressures at several points. From the Clausius-Clapeyron plot for $Sn(EtCp)_2$, the precursor temperature was set to 70 °C, which corresponds to the vapor pressure of approximately 0.8 Torr.

SnO_x thin films were deposited on 150 mm Si wafers with native oxide films. ALD process was conducted by using $Sn(EtCp)_2$ as a precursor and O_2 plasma as an oxidant. Saturation of reaction was confirmed when 14 s of $Sn(EtCp)_2$ and 45 s of O_2 plasma pulse times were applied. At this condition, linear growth of SnO_x thin film was observed. The growth per cycle (GPC) was approximately 0.18 nm/cycle with this ALD condition. This growth rate was relatively fast compared with a previous experiment using tetrakis(dimethylamino)tin (TDMASn) as a precursor and O_2 plasma as an oxidant (~0.13 nm/cycle) [3]. On the contrary, by applying H_2O for 30 s in the place of O_2 plasma, the thickness of SnO_x films scarcely increased by increasing the number of ALD cycles.

SnO_x thin films were deposited by ALD using a new cyclopentadienyl-based precursor $Sn(EtCp)_2$, and linear growth of SnO_x thin film was confirmed.

References

[1] F. Mizutani, S. Higashi, M. Inoue, and T. Nabatame, AIP Advances **9,** 045019 (2019).

[2] F. Mizutani, M. Mizui, N. Takahashi, M. Inoue, and T. Nabatame, ALD2021, AF1-10 (2021).

[3] M. A. Martínez-Puente, J. Tirado, F. Jaramillo, R. Garza-Hernández, P. Horley, L. G. S. Vidaurri, F. S. Aguirre-Tostado, and E. Martínez-Guerra, ACS Appl. Energy Mater. **4,** 10896 (2021).

ALD Fundamentals
Room Grand Ballroom E-G - Session AF2-TuM
Precursors and Processes II

Moderators: Dr. Paul Poodt, Holst Centre / TNO, Dr. Paul J. Ragogna, University of Western Ontario, Canada

11:00am **AF2-TuM-13 Influence of Plasma Species on the Growth Kinetics, Morphology, and Crystalline Properties of Epitaxial InN Films Grown by Plasma-Enhanced Atomic Layer Deposition***, **Jeffrey Woodward,** D. Boris,* U.S. Naval Research Laboratory*; M. Johnson,* Huntington Ingalls Industries*; S. Walton, J. Hite, M. Mastro,* U.S. Naval Research Laboratory

The controlled co-delivery of reactive and energetic plasma species during plasma-enhanced atomic layer deposition (PEALD) enables the growth of epitaxial layers at significantly reduced temperatures which are prohibitive to other methods. However, this capability is challenged by the complexity which arises from the reliance on plasma-surface interactions, and it is thus necessary to understand the influence of the plasma properties on the growth kinetics and resultant film properties. Among the III-nitride binary compounds, indium nitride (InN) is particularly well-suited for the investigation of the roles of reactive and energetic plasma species, as high-quality crystalline films can be achieved using trimethylindium (TMI) and a relatively simple N_2/Ar plasma rather than $N_2/Ar/H_2$ or NH_3/Ar plasmas which generate greater varieties of species. This was explored in recent studies of InN PEALD on gallium nitride (GaN) using *in situ* synchrotron x-ray scattering, which revealed that the growth mode is correlated with the relative density of atomic N, while coarsening behavior is influenced by ion flux.[1]

In this work, epitaxial InN films are grown by PEALD on GaN (0001) at approximately 320 °C using TMI and N_2/Ar plasma within various regimes of plasma species generation in order to investigate the influence on the resultant film structural properties. Optical emission spectroscopy and Langmuir probe measurements are used to correlate the production of atomic N and ions with the N_2 and Ar gas flows into the inductively coupled plasma source. The InN films are characterized by atomic force microscopy (AFM), x-ray reflectivity (XRR), high-resolution x-ray diffraction (HRXRD), in-plane grazing incidence diffraction (IP-GID), and synchrotron grazing incidence wide-angle x-ray scattering (GIWAXS). The films are found to exhibit wurtzite phase and sixfold rotational symmetry with a clear epitaxial relationship to the GaN. Low fluxes of atomic N are found to promote larger domains, increased crystalline order, and smoother morphology compared to films grown with high atomic N fluxes. For the high atomic N flux condition, increasing ion flux is found to promote a very rough morphology containing large cluster-like features and decreased in-plane crystalline order, but increased out-of-plane crystalline order and a reduction in mosaic twist.

[1] J. M. Woodward *et al*., J. Vac. Sci. Technol. A **40**, 062405 (2022)

11:15am **AF2-TuM-14 Towards Self-Limiting III-Nitride Epitaxy via Hollow-Cathode Nitrogen Plasmas***, N. Ibrahimli, S. Ilhom, A. Mohammad, J. Grasso, B. Willis,* University of Connecticut*; A. Okyay,* Stanford University*; **Necmi Biyikli,*** University of Connecticut

Research efforts on low-temperature synthesis of crystalline GaN thin films using plasma-assisted ALD utilized various reactor configurations featuring different plasma sources. While our early GaN growth experiments using quartz-based ICP sources resulted in nanocrystalline/amorphous films with elevated oxygen impurities, stainless-steel based hollow-cathode plasma (HCP) sources revealed highly (002) oriented polycrystalline GaN films on Si(100) substrates. Upon further modification of the hollow-cathode plasma

source and reactor chamber design, in this study, monocrystalline GaN films on sapphire substrates was achieved at temperatures as low as 240 ℃. In this presentation we share our experimental findings on the epitaxial growth efforts of the entire wide bandgap III-nitride binary compounds including GaN, AlN, InN, and BN using self-limiting HCP-ALD.

The films were deposited using metal-alkyl precursors (triethylgallium, trimethylaluminum, trimethylindium, and triethylboron) and various nitrogen plasmas (N_2/H_2, N_2-only, N_2/Ar, and N_2/H_2/Ar) as metal precursor and nitrogen co-reactant, respectively. Growth experiments have been performed within 200 – 250 °C temperature and 100 – 200 W rf-power range. *In-situ* Ar-plasma annealing cycles were also employed to enhance the surface crystallization process. *In-situ* ellipsometry and optical emission spectroscopy (OES) were employed to monitor the surface ligand-exchange reactions, plasma surface interactions, and reaction byproducts in real-time. *Ex-situ* spectroscopic ellipsometry measurements revealed the film thickness, growth-per-cycle (GPC), and optical properties of the films. When compared to reference films grown on Si(100) substrates, GPC values obtained for III-nitride films on sapphire substrates showed a notable increase.

For GaN samples, grazing-incidence XRD (GIXRD) measurements revealed single-phase hexagonal polycrystalline films on Si(100) substrates while GaN/sapphire samples exhibited no crystal peaks at all. Rocking curve XRD scans displayed a strong single (002) peak, confirming the monocrystalline character of the GaN films on sapphire substrates. We attribute this improvement in crystal quality to the synergistic impact of customized HCP-ALD reactor, large-diameter hollow-cathode plasma source, and optimized growth conditions (plasma gas mixture, rf-power, chamber pressure). Among the binary III-nitride compounds, InN and BN films showed highest and lowest GPC values, respectively. With further improvement in film properties, we aim to achieve device quality electrical properties that can be used for back-end-of-the-line (BEOL) transistor channel layers.

11:30am **AF2-TuM-15 Thermal Atomic Layer Deposition of Gallium Nitride at 150 - 300°C using Tris(dimethylamido)gallium Precursor and Hydrazine***,* ***Adam Bertuch,*** Veeco Instruments*; J. Casamento, J. Maria,* Pennsylvania State University

Gallium nitride (GaN) and its alloys with aluminum nitride (AlN) have established themselves as leaders in electronic and photonic devices for high frequency, high voltage, and harsh environment applications.[1] This is due to their ultra-wide bandgaps, heterojunction polarization induced free carriers with high mobility in the absence of chemical doping, large thermal conductivity, and high temperature stability.The promising physical properties of this material system are generally realized by plasma assisted techniques such as molecular beam epitaxy (MBE) or high temperature metal organic chemical vapor deposition (MOCVD) processes. Accordingly, there are significant opportunities for new device functionalities and heterogeneous integration in batch processing if crystalline GaN with low impurity (e.g., oxygen and carbon) concentrations can be realized in a low temperature, plasma free process.

In this work, GaN thin films were deposited using Tris(dimethylamido)gallium (CAS 57731-40-5) and hydrazine (N_2H_4) at temperatures from 150°C to 300°C using thermal Atomic Layer Deposition (ALD). At these temperatures the process is self-limiting, exhibiting ALD behavior and a uniform growth per cycle (GPC) throughout the process chamber. For compositional analysis, the GaN films were capped *in-situ* using ALD deposited AlN with Trimethylaluminum (TMA) and Hydrazine. The ALD deposition rate for the GaN film is large, ranging from 1.2 to 1.4 Å/cycle, while the AlN growth rate is determined to be 0.30 to 0.75 Å/cycle, as a function of increasing temperature.

Compositional analysis by Auger emission spectroscopy (AES) revealed oxygen and carbon concentrations less than 5 atomic % at 300°C deposition for both the GaN and AlN film stack; among the best reported values for deposition temperatures less than 400°C.[2] Initial findings with scanning electron microscopy (SEM) show smooth continuous surface morphologies for the deposition on silicon substrates. Composition, crystallinity via X-Ray Diffraction (XRD), and RMS roughness via X-Ray Reflectivity (XRR) will be analyzed as a function of growth temperature. These results present a promising step towards the development of low temperature, plasma-free GaN based thin films.

References

[1]*High-Frequency GaN Electronic Devices,* edited by P. Fay, D. Jena, and P. Maki (Springer, 2019).

[2] S. Banerjee et al. J. Phys. Chem. C **123**, 23214 (2019).

11:45am **AF2-TuM-16 Crystalline Gallium Nitride Deposition on SiO_2/Si by RF-Biased Atomic Layer Annealing***,* ***Ping-che Lee****, A. Mcleod,* Univ. of Cal., San Diego*; S. Ueda,* Materials Science and Engineering Program, Univ. of Cal., San Diego*; J. Spiegelman,* Rasirc*; R. Kanjolia, M. Moinpou,* EMD Electronics*; A. Kummel,* Department of Chemistry and Biochemistry, Univ. of Cal., San Diego

High-quality GaN deposition on Si substrates attracts attention due to its high heat capacity, and thermal conductivity [1]. However, a major problem of current GaN on Si techniques is that thermal shrinkage causing microcracks during >700 ℃ MOCVD process. Here, polycrystalline GaN with 40 nm thickness on Si substrates at 275 ℃ was deposited by using an atomic layer annealing (ALA) process. Inert gas plasma was directed by an RF substrate biasing to bombard the growth surface of the ALD-grown GaN. Surface defects were healed through either atom displacement or a collision cascade[2, 3]. This GaN film was transferred to a sputter chamber and employed as a template for AlN for heat spreaders. The record high thermal conductivity AlN sputtered film (1 um thick) obtained in this work benefited from this ALA GaN layer, which improved the crystallinity and decreased the phonon-defect scattering at the interface. Other film deposition techniques could also be integrated into this novel ALA GaN layer to design a promising heat spreader.

The GI-XRD measurements (Fig. 1(a)) were preformed to investigate the film crystallinity. In the non-substrate-biased ALA, a diffraction peak at 34.5 ˚ showed that even gentle ion bombardment at the end of each cycle mobilized the surface adatoms. All of the RF-biased conditions demonstrated narrower FWHM values (0.65 ˚, 0.58 ˚, and 0.51 ˚, respectively), meaning that ions with comparatively higher momentum more effectively crystallized the films; this was further confirmed by an increase in film density observed by XRR in Table. 1.

Sputtered AlN was deposited on ALA GaN film to increase the total film thickness for thermal conductivity measurements. Grain boundary analysis (Fig. 1(b)) indicated that both the template GaN layer and sputter AlN layer had an identical bamboo grain structure. Moreover, the nanobeam electron diffraction in (Fig. 1(c) and(d)) showed that the (0002) axis of bottom GaN coincided with the top sputter AlN, which further confirmed that polycrystalline GaN layer pinned the growth direction of sputtered AlN. The larger thermal conductivity measured by time-domain thermoreflectance (TDTR) confirmed the effectiveness of this low-temperature buffer layer to achieve a record high thermal conductivity AlN (120 W/m*K) with a thickness of 1 um (Fig. 2). This local domain epitaxy relationship at the interface played a crucial role in ensuring that phonon delivering heat along (0002) axis would be relative uninterrupted by phonon-defect scattering.

[1] J. Leitner et al., Thermo. Acta, 401, 2003, 169-173,

[2] W.H. Lee et al., Appl. Surf. Sci. 525, 2020, 146615

[3] S.T Ueda et al., J. Mater. Chem. C, 10, 2022, 5707

ALD & ALE
Room Grand Ballroom A-C - Session ALD+ALE-TuM

ALD/ALE Session

Moderators: Prof. Dr. Steven M. George, University of Colorado at Boulder, Dr. Anil Mane, Argonne National Laboratory

8:00am **ALD+ALE-TuM-1 Intensified Atomic Layer Deposition and Atomic Layer Etching***,* ***Greg Parsons,*** North Carolina State University **INVITED**

Atomic layer deposition (ALD) and atomic layer etching (ALE) are arguably two of the most precise chemical reaction methods currently used in manufacturing.To fabricate electronic devices, deposition and etching steps are generally performed as discrete processes in dedicated reaction chambers.However, new problems are arising that demand better control, precision and flexibility of deposition and etching processes. In large-scale manufacturing of fine chemicals, significant advances are being made by adopting the principles of “Process Intensification” defined, in part, as the intimate coupling of two distinct processes to improve cost, reduce environmental impact, or improve product quality. A 2022 Consensus Study Report: “New Directions for Chemical Engineering” from the National Academies of Science, Engineering and Medicine states: “*Research investments in materials should be directed to… discovery and design of new reaction schemes… with a steady focus on process intensification, especially for applications in electronic materials.*” However, to date, there are few, if any, reports addressing process intensification in semiconductor manufacturing.

This talk will introduce the concept of "Intensified Atomic Scale Processing", where combining thermally-driven ALD, ALE, and other dep/etch processes can lead to improved or unexpected outcomes.It is well established that ALD can involve both deposition and etching reactions. For example, during ALD of NbN and AlZnO, the reactants or gas-phase products can act in parallel to etch the surface, leading to unusual trends in growth per cycle.

Our research group is exploring how deposition and etching reactions can couple and interact, particularly to enable area-selective deposition, ASD. Several groups have shown that by introducing etching cycles into an ALD sequence, unwanted nuclei can be removed to improve selectivity. Furthermore, we have discovered that for some combinations of reactants and solid materials, deposition and etching of two different materials can proceed simultaneously on different regions of a patterned substrate, enabling multimaterial "orthogonal ASD". Other groups are also discovering how combined dep/etch using thermal and/or plasma processing can help control film crystallinity, improve surface roughness, and achieve other improved properties. We believe that these examples constitute the beginnings of "Intensified" ALD and ALE processing of electronic materials, and it is likely that further attention will lead to additional helpful and potentially surprising outcomes.

8:30am **ALD+ALE-TuM-3 Mass Changes During and After $Al(CH_3)_3$ Exposures for Thermal Al_2O_3 ALE at Low TemperaturesUsing HF and $Al(CH_3)_3$ as Reactants***, Andrew S. Cavanagh, S. George,* University of Colorado at Boulder

For thermal ALE at high temperatures, the surface reactions take place quickly and obscure the underlying adsorption and desorption processes.By lowering the temperature, the surface reactions can be slowed to reveal details during reactant adsorption and etch product desorption.This study explored thermal Al_2O_3 ALE using sequential HF and $Al(CH_3)_3$ (trimethylaluminum, TMA) exposures.In situ quartz crystal microbalance (QCM) investigations examined the mass changes during and after TMA exposures.The results illustrate the complex nature of the adsorption and desorption reactions and provide insight to the competition between Al_2O_3 ALE and AlF_3 ALD.

For thermal Al_2O_3 ALE at low temperatures, HF coverage is known to reside on the AlF_3 surface after the fluorination of Al_2O_3 to AlF_3.This adsorbed HF plays a key role in defining the temperature-dependent Al_2O_3 ALE etch rate.If TMA reacts with this adsorbed HF, various $Al_xF_y(CH_3)_z$ species can be formed that may either desorb or lead to AlF_3 deposition.If the $Al_xF_y(CH_3)_z$ species are desorbed, then the TMA can undergo ligand exchange with AlF_3 to produce Al_2O_3 ALE.To unravel this competition, a series of TMA mini-doses were exposed to a fluorinated Al_2O_3 surface at 225°C using 3 s mini-doses and 30 s purges.The in situ QCM results are shown in Figure 1.

The first TMA mini-dose resulted in a large, transient mass gain.This mass increase is attributed to the reaction between TMA and HF on the AlF_3 surface.The intermediates formed by this reaction then desorb from the surface.Additional intermediates continue to desorb after the end of the TMA mini-dose.The mass change from the first TMA mini-dose is -13.6 $ng \cdot cm^{-2}$.This mass loss does not offset the mass gain of the fluorination reaction, +30.1 $ng \cdot cm^{-2}$.If the surface were not exposed to additional TMA mini-doses, then these reaction conditions would produce deposition.

The subsequent 2nd through 10th TMA mini-doses lead to additional mass loss during the TMA mini-dose and after the TMA mini-dose.This mass loss is attributed to ligand exchange and subsequent desorption of $Al_xF_y(CH_3)_z$ species.The next 11th through 15th TMA mini-doses then display a slight mass gain during the TMA mini-dose and then a mass loss corresponding with desorption of $Al_xF_y(CH_3)_z$ species after the TMA mini-dose.The cumulative mass loss for the 15 mini-doses is shown in Figure 2.The successive TMA mini-doses continue to remove mass with diminishing returns.The competition between Al_2O_3 ALE and AlF_3 ALD is dependent on the total TMA exposure and purge time.The transition between deposition and etching occurs at > 2 TMA mini-doses under these conditions.

8:45am **ALD+ALE-TuM-4 Crystallinity of Sacrificial Etch Layer Influences Resulting Structure During Simultaneous Deposition and Etching***, Hannah R. M. Margavio, L. Keller,* North Carolina State University*; N. Arellano, R. Wojtecki,* IBM Almaden Research Center*; G. Parsons,* North Carolina State University

Integrated atomic layer deposition (ALD) and etching for area selective deposition (ASD) provides a tunable approach for bottom-up metal patterning during semiconductor device fabrication. Previous work has shown that different device structures are possible by adjusting the processing temperature during integrated deposition and etching. In this work, we study the effects of starting substrate crystallinity on the relative deposition and etching rates during ASD via simultaneous tungsten deposition and TiO_2 etching. Sequential $SiH_{4(g)}$ and $WF_{6(g)}$ exposures onto a pre-patterned TiO_2/Si substrate at 220°C results in W growth on Si and TiO_2 removal by chemical vapor etching (CVE). Here, we expose 2 different sources of TiO_2 patterns to 10 W ASD cycles: i) 100 nm thick TiO_2 lines on Si with 250 nm half-pitch size; and ii) 85 nm thick micron sized TiO_2 pads on Si. Fig. 1a shows a cross-sectional SEM image of starting substrate (i), and Fig. 1c shows a bright field TEM cross section of starting substrate (ii). 200 kV HAADF STEM imaging and STEM EDS elemental mapping shows that after 10 W ASD cycles, < 5 nm of TiO_2 was removed from substrate (i) (Fig. 1b), and ~ 75-80 nm of TiO_2 was removed from substrate (ii) (Fig. 1d). Despite the drastic difference in TiO_2 etching rates on the two starting patterns, the rate of W deposition is nearly identical. High-resolution TEM imaging and XRD show differences in the crystallinity of the starting TiO_2 patterns. Particularly, a broad feature centered around 23° is shown in the XRD spectrum for substrate (i) and not in that for substrate (ii). This x-ray peak is attributed to the a-TiO_2 (100) reflection. Differences in starting substrate crystallinity affect the relative rates of deposition and etching during integrated ALD/CVE and allow various nano-architectures to be fabricated by the same chemical process.

9:00am **ALD+ALE-TuM-5 There's no Place like a Surface: How Deposition and Etch Chemistry Depend on the Nature of the Surface***, Michael Nolan,* Tyndall National Institute, University College Cork, Ireland **INVITED**

In Atomic Layer Deposition (ALD) and Thermal Atomic Layer Etch (tALE), the key chemistry takes place at surfaces. This includes nucleation at the initial surface, metal precursor adsorption, co-reactant adsorption, fluorination, conversion and ligand exchange. This surface driven chemistry is supposed to be the origin of the self-limiting chemistry of ALD and tALE and can be elucidated using state of the art first principles simulations, primarily with density functional theory (DFT). In many studies of ALD and tALE, DFT simulations use lowest energy surface facets of crystalline materials and tend to consider ideal or simplified surface terminations. While this yields results that allow for prediction and understanding of ALD and tALE chemistry, it is important to recognise that surfaces show much more complexity than this; the catalysis community has been evolving in this direction in recent years. This increased complexity includes: amorphous surfaces, surfaces with point defects, surfaces with a range of non-bulk and non-perfect terminations, higher energy surface facets, among many possibilities.

In this talk, I will discuss how the chemistry of some selected ALD and tALE processes depends on the nature of the surface. For metal deposition, we show that (001) and (100) surfaces of Co and Ru display rather different chemistry in both the stability of the surface post-H2/NH3 plasma step and the interaction with M(Cp)2 precursors. The role of surface structure is important in promoting particular chemistries. For Ru deposition on TaN, we show how different TaN terminations with H/NH/NH2 promote different reactivity with Ru(Cp)2 and RuO4 precursors. The impact of amorphous *vs.* crystalline surfaces is exemplified through a comparison of the thermodynamics of fluorination in tALE of high-k dielectrics, where a higher etch rate is observed for the amorphous oxides. The role of hydroxyl groups that are generally present on these oxide surfaces will be discussed. Finally we present a brief analysis of the impact of different Si and SiO2 surface termination on the chemistry of plasma ALD of Co.

This work shows how the nature of the surface that may be present during an ALD or tALE process can strongly influence the resulting chemistry of the process and needs to be considered when designing new ALD and tALE processes.

9:30am **ALD+ALE-TuM-7 Substrate Dependent HfO_2 Atomic Layer Etch Rate Evolution Observed by In-situ Quartz Crystal Microbalance during Integrated ALD+ALE***, Landon Keller, G. Parsons,* North Carolina State University

Hafnium oxide (HfO_2) is highly desirable for high-κ dielectric and ferroelectric memory applications in transistors and advanced FERAM devices. As devices transition to complex 3D architectures, precise and isotropic methods of depositing and etching materials are needed beyond conventional deposition processes. Despite the growing demand for HfO_2 in nanoscale devices, few studies report compatible HfO_2 ALD and ALE processes suitable for modern applications.

In this work, we report ALE of HfO_2 using WF_6 and BCl_3 at 275°C where ALE is performed sequentially within integrated ALD+ALE super-cycles, and the etch reaction is monitored *in-situ* using quartz crystal microbalance (QCM) using various super-cycle recipes. ALD is performed using TDMAHf and H_2O. This process was tested on various surfaces including cobalt with a native

oxide (Co) and aluminum oxide (Al_2O_3). Within the ultrathin film regime, extremely close to the substrate, we find that the amount of HfO_2 removed per ALE cycle changes as etching proceeds, and the extent of change depends on the substrate on which HfO_2 is deposited.

Figure 1 shows QCM mass loading during integrated HfO_2 ALD+ALE at 275°C on two coated crystals, one with Co deposited *ex-situ* by electron beam evaporation and one with Al_2O_3 deposited *in-situ* by ALD. The deposition behavior is similar on both surfaces, but the etching behavior is significantly different. On Al_2O_3, the etch rate slows down slightly during the etch step, and subsequent etch steps are able to remove all mass gained during the deposition step. On Co, the etching slows down significantly to the point of no additional mass removal, and even results in mass gain during the latter ALE cycles. This behavior is present during subsequent etch steps on Co, but the etch slowdown and mass gain is less pronounced. Figure 2 shows QCM mass loading during integrated HfO_2 ALD+ALE at 275°C on Co coated crystals at different super-cycle recipes. For 20xALD, the etch rate approaches 0 ng/cm^2 after 10 cycles during each etch step, but this phenomenon does not occur until cycle 15 for 30xALD. 40xALD shows no evidence of decreasing etch rate or approaching 0 ng/cm^2, indicating the absence of a surface selective ALE mechanism as the HfO_2 film grows away from the Co surface.

These results demonstrate varied ALE behavior during integrated ALD+ALE throughout the course of the etch step and subsequent etch steps depending on the underlying surface that can result in area selective ALE. We believe these findings provide valuable insight on ALE of ultrathin HfO_2 films and the impact of the underlying substrate on the evolution of the etch rate.

9:45am **ALD+ALE-TuM-8 Al Mirror Passivation with Atomic Layer Etching of Native Oxide and in-Situ Passivation with Atomic Layer Deposition of AlF_3 or MgF_2**, ***Hoon Kim**, J. Du, J. Wang, D. Allen, E. Pierce, M. Huang, N. Borgharkar, K. Woo,* Corning Research and Development Corporation

Al mirror is a key component of vacuum ultraviolet (VUV) or Far UV optics due to its high reflectance for short wavelength (100~200 nm). However, oxidation of Al surface immediately happens by contact with air which resulting in major reflectance drop (90 to 30%) by even 2 nm of native Al_2O_3 on surface. Thus, the passivation of Al surface from oxidation is a major challenge for Al mirror for these applications. PVD MgF_2 or AlF_3 are employed for this passivation layer following PVD Al. However, PVD film has pinholes which may cause oxidation of the Al mirror. To address this issue, atomic layer deposition (ALD) is proposed which has high conformality and pinhole free passivation. Atomic layer etching (ALE) of native oxide of PVD Al and in-situ ALD AlF_3 passivation was successfully demonstrated. However, HF is used for ALE and ALD which has safety concern in handling and residue in the reactor. Thus, safer fluorine source should be considered for industrial use. In this study, SF_6 remote plasma is used for ALE and ALD for AlF_3 and MgF_2. ALD MgF_2 is firstly evaluated as passivation layer because it is known as better oxidation resistance than that of AlF_3.

Hot wall batch ALD reactor with remote plasma source was employed in this study. Fluorine radical was generated by using SF_6 flow through Inducted coupled plasma (ICP) source.Trimethyl-Al (TMA) precursor is used for ALE of native oxide on Al surface and ALD of AlF_3. $(EtCp)_2Mg$ is used as Mg precursor and deposition condition is same as last year publication in ALD conference. PVD Al is deposited using an electron-beam evaporation method. It was exposed to air prior to introducing to the ALD reactor. ALE and ALD AlF_3 are done at the same temperature. Right after ALE, ALD AlF_3 is deposited in-situ to passivate the oxide free Al surface. Single layer of 28 nm AlF_3 and hybrid bi-layer of combining 5 nm AlF_3 and 23 nm MgF_2 are evaluated as passivation layers on the Al surface. The reflectance of VUV range (100~160 nm) was measured by a spectrophotometer. Impurities of the films and at the interfaces were measured by SIMS.

ALE using SF_6 remote plasma and TMA has effectively removed the native oxide of PVD Al surface that is confirmed by SIMS depth profile. Compared to AlF_3 single layer passivation, AlF_3/MgF_2 bi-layer shows higher reflectance for the VUV range (120~160 nm) because lower carbon impurity level and higher transmittance of the MgF_2. The ALE and ALD AlF_3/MgF_2 bi-layer passivation shows 92% of reflectance at 120 nm and maintained >85% up to 200 nm wavelength.

Atomic Layer Etching
Room Grand Ballroom A-C - Session ALE-TuM
Modeling of ALE

Moderators: Prof. Dr. Michael Nolan, University College Cork, Dr. Thomas Tillocher, GREMI CNRS/Orleans University

11:15am **ALE-TuM-14 Plasma Oxidation of Copper: Molecular Dynamics Study with Neural Network Potentials**, ***Yantao Xia,*** University of California at Los Angeles; *S. Philippe,* University of California, Los Angeles

The formation of thin oxide films is of significant scientific and practical interest. In particular, the semiconductor industry is interested in developing a plasma atomic layer etching process to pattern copper, replacing the dual Damascene process. Using a nonthermal oxygen plasma to convert the metallic copper into copper oxide, followed by a formic acid organometallic reaction to etch the copper oxide, this process has shown great promise. However, the current process is not optimal because the plasma oxidation step is not self-limiting, hampering the degree of thickness control. In the present study, a neural network potential for the binary interaction between copper and oxygen is developed and validated against first principles calculations. This potential covers the entire range of potential energy surfaces of metallic copper, copper oxides, atomic oxygen, and molecular oxygen. The usable kinetic energy ranges from 0 - 20 eV. Using this potential, the plasma oxidation of copper surfaces was studied with large-scale molecular dynamics at atomic resolution, with an accuracy approaching that of the first principle calculations. An amorphous layer of CuO is formed on Cu, with thicknesses reaching 2.5 nm. Plasma is found to create an intense local heating effect that rapidly dissipates across the thickness of the film. The range of this heating effect depends on the kinetic energy of the ions. A higher ion energy leads to a longer range, which sustains faster-than-thermal rates for longer periods of time for the oxide growth. Beyond the range of this agitation, the growth is expected to be limited to the thermally activated rate. High-frequency, repeated ion impacts result in a microannealing effect that leads to a quasicrystalline oxide beneath the amorphized layer. The crystalline layer slows down oxide growth. Growth rate is fitted to the temperature gradient due to ion-induced thermal agitations, to obtain an apparent activation energy of 1.0 eV. A strategy of lowering the substrate temperature and increasing plasma power is proposed as being favorable for more self-limited oxidation.

11:30am **ALE-TuM-15 Multi-scale Simulation Study for the Role of High C/F ratio Plasma on Etch Selectivity of SiO_2 and Si_3N_4 in q-ALE**, ***Hojin Kim**, D. Zhang, T. Hisamatsu, A. Ko,* TEL Technology Center, America, LLC, USA

Using multi-scale simulation techniques, we studied how C/F ratio in plasma affected the etch selectivity between Si_3N_4 and SiO_2 with a formed thin FC film on each surface during a q-ALE process. In SAC etching for via or contact holes into oxide to make a contact, nitride also can be etched, resulting in the yield issue. Thus, we need to reduce the nitride loss effectively. However, as the device becomes smaller, it is hard to control to obtain enough selectivity.Previous experiments with various C_xF_y gases showed the enhancement of etch selectivity between Si_3N_4 and SiO_2 with high x/y ratio gas. However, the understanding of the underlying behavior has been not clear. First, we revealed the relationship between intrinsic C/F ratio neutral and species fluxes by using the plasma simulation, observing that high C/F ratio gas could create high C/F ratio radicals. With atomistic Molecular Dynamics (MD) simulation and DFT calculation, we also studied the possible role of C/F ratio on FC film formation on both substrates and following an ion bombardment. MD simulation results showed that with higher C/F ratio plasma, harder and denser FC film could be formed on Si_3N_4 by significantly increasing absorbed carbon (C), Si-C, and C-C bonds. In the SiO_2 case, we could observe many O-C bonds that cause to weaken the formed FC film by converting it to highly volatile materials (i.e., CO_2). The highest C/F ratio gas case showed that significant O-C bonds on SiO_2 were generated. Following the ion bombardment step with both modified substrates, we observed that the highest C/F ratio case exhibited less loss of total atoms and regenerated Si-C bonds, probably a dangling bond behavior. In Si_3N_4, N-C bonds were generated more to protect the substrate but not in SiO_2; O-C bonds were lost during the ion bombardment. We confirmed the surface reaction with DFT calculation. It showed that both Si and N removal was difficult without F, while O removal was possible even without F. Thus, we determined that Si_3N_4 etching was more F-limited than Ox, indicating that selectivity at high C/F ratio gas would be improved. Based on all findings, We concluded that using the plasma with high C/F ratio radical helped to increase selectivity by protecting Si_3N_4 more with denser and harder FC film but not on SiO_2 due to the O-C bonds in formed

FC film. This study will help to understand the fundamental behavior of the dielectric selectivity with various C/F ratio plasmas during the q-ALE process and ultimately provide the guideline for the experiment.

11:45am **ALE-TuM-16 Selecting a Method for ALE Modeling**, *Y. Barsukov, S. Jubin, S. Ethier,* ***Igor Kaganovich,*** Princeton University Plasma Physics Lab

Several methods can be used for modeling dry etch processes, such as transition state theory (TST), classical and ab-initio molecular dynamics (MD), and density functional based tight binding (DFTB) approaches. The combination of TST and quantum chemistry methods, usually DFT (density function theory), enables the calculation of rate constants for the elementary steps of gas-surface reactions during the etching process. This allows insight into the etching mechanism, and we can then perform chemical kinetics modeling to predict the etch rate as a function of gas phase species fluxes and surface temperature. One limitation of the TST approach is the evolution of the structure and composition of the surface during the etching process, which results in a change in the rate constants. The purpose of chemical kinetics modeling is to find the rate-limiting step in surface reactions that determines the overall rate of the whole etching process. Here we present simulation results explaining the orientation dependence of silicon surface etching by F2 molecules using the TST approach. Namely, we show that the Si etching in the (111) direction is much slower than in the (100) and (110) directions; therefore, F2 can be used for the anisotropic etching process to produce black silicon. Moreover, this approach allows us to propose a new reactant to etch silicon with higher anisotropy. Among the other methods, classical and ab-initio MD simulations enable the study of surface transformation during the etching process, as well as the dynamics predicting surface composition and structure. However, great care must be taken when choosing the interatomic potentials for classical MD and the semi-empirical parameters for DFTB in order to correctly represent the surface reactions and their rates. Our simulations showed that bond order MD potentials unrealistically described boron adsorption on a graphene sheet, and available DFTB parameters sets were unable to predict the existence of NH4F and NH5F2 salts, which are broadly used for SiO2 and Si3N4 etching. The ab-initio MD method completely avoids these issues but is so time-consuming that simulating surface reactions proceeding through significant barriers can become prohibitively long. Nevertheless, it can be successfully used for studying barrier-free reactions or reactions with low barriers, such as SiO2 and Si3N4 etching by NH4F and NH5F2 salts. Thus, the selection of suitable modeling methods allows our group to simulate etching and identify key processes. These methods can be used for optimization of process parameters in designing new etchants.

Area Selective ALD
Room Regency Ballroom A-C - Session AS1-TuM
Surfaces and ASD

Moderators: Dr. Jeffrey W. Elam, Argonne National Laboratory, Dr. Adrie Mackus, Eindhoven University, Netherlands

8:00am **AS1-TuM-1 Advances in the Industrial Adoption of Selective ALD Processes**, ***David Thompson,*** Applied Materials, Inc. **INVITED**

Since the initial adoption of atomic layer deposition in capacitor dielectrics for DRAM, and for gate dielectrics in logic at 45 nm, ALD has played a transformative role in enabling a wide variety of integration, without which the industry would have been unable to scale.However, over the last 15 year the number of steps required to process a chip has dramatically increased and integration has become increasingly complicated.

Selective deposition can offer enabling and/or simplified integration approaches, and while there has been strong adoption of some selective processes (e.g. selective epitaxy of Si and selective capping of copper with CVD Co), there remains a tremendous opportunity for the industry to solve many integration problems with selective ALD processes.

This talk will focus on several high value problems that can be addressed by selective ALD, and the additional steps required to enable these selective processes.A specific case study on leveraging selective ALD to enable higher chip speeds through reducing RC delays by leveraging an integration scheme enabling selective ALD TaN will be examined.In this particular case, the selective barrier can reduce via resistance by >50% with no reliability degradation.

Finally, the lessons learned in enabling the selective ALD TaN process will be highlighted as they relate to enabling the many other selective ALD applications that promise to continue enabling device manufacturers roadmaps.

8:30am **AS1-TuM-3 Control of Silanol Density in Silicon Oxide Surfaces via Gas-Phase Treatments to Control Metal Atomic Layer Deposition**, ***Mohammed Alam,*** University of California at Riverside; *F. Zaera,* University of California - Riverside

Controlling the deposition of metal films grown on oxides by atomic layer deposition (ALD) requires stringent control over the surface nucleation sites, typically hydroxyl groups. The hypothesis driving this project is that preliminary surface modification steps may be used to alter the hydroxyl surface density and with that, the properties of the ALD metal films. In the case of area-selective ALD, for example, the use of surface modifiers such as silylation agents has been implemented to deactivate all silanol sites on the non-growth surface in order to spatially direct film deposition onto the growth surface. The extent of silylation may also be controlled to tune the ALD in terms of the film density. Partial silylation can help deposit metal nanoparticles of varying sizes by immobilizing them thereby preventing their aggregation and sintering at high temperatures.

The medium in which surface modification reactions, such as silylation, are carried out in is vital to achieve control over the efficiency of the process of blocking nucleation sites. A liquid-phase environment affords little control over the surface modification process and may result in the formation of defects within the organosilane layer. These drawbacks may be eliminated by conducting the modification step in the gas phase, as was tested in this work.

In our XPS study, Si-OH sites in silica surfaces were blocked in a controlled fashion via gas-phase silylation using *N,N*-dimethyltrimethylsilylamine. The silylation efficacy was assessed by evaluating the kinetics of metal oxide ALD on the resulting substrates. The results from gas-phase silylation were compared to a set of experiments in which the modification step was performed in the liquid-phase. In both cases, the SiO_x/Si(100) surface becomes fairly unreactive during the initial stages of TiO_2 or HfO_2 ALD and remains passivated up to 5 TiO_2 cycles; the passivation is less effective with HfO_2. Nucleation sites are eventually re-activated with increasing cycles, but partial surface passivation is maintained up to 50 cycles. These results suggest that the metal precursor can eventually chemisorb onto defect sites in the silylated layer after sufficient interaction with the surface, propagating film growth. Moreover, as the results obtained with gas- vs. liquid-phase silylation are comparable in terms of ALD passivation, it is concluded that there is an intrinsic limitation to the degree of passivation achievable using this surface modification scheme. Finally, preliminary NMR results with porous silica indicate that the extent of silylation can be tuned to modify the ratio of free vs. capped nucleation sites.

8:45am **AS1-TuM-4 Inherently Area-Selective Atomic Layer Deposition of Device-Quality $Hf_{1-x}Zr_xO_2$ Thin Films through Catalytic Local Activation**, ***Hyo-Bae Kim,*** *J. Lee, W. Kim, J. Ahn,* Hanyang University, Korea

Area-selective atomic layer deposition (AS-ALD) has attracted tremendous interest as an alternative bottom-up patterning process to implement versatile fabrication of selectively formed thin films in both vertical and lateral direction in extremely downscaled 3D semiconductor devices. In this study, we report a methodology for achieving inherently selective deposition of $Hf_{1-x}Zr_xO_2$(HZO) thin films by catalytic local activation not only on noble metal surfaces like Ru and Pt, but also on the TiN surfaces. For achieving selective deposition on metal surfaces, O_2 gas was utilized as a mildly oxidizing co-reactant and cyclopentadienyl-tris(dimethylamido)hafnium(zirconium) precursors ($Hf(Zr)[Cp(NMe_2)_3]$) which require strong oxidizing agents were used to deposit HZO thin films. As a results of catalytic dissociation of O_2 molecules, we successfully achieved inherent selectivity greater than ~7 nm on both blanket Ru substrate and Pt/Si patterned substrates. Furthermore, it was demonstrated that the anti-ferroelectric HZO thin films with high dielectric constants of 31 and 34 can be fabricated selectively on TiN and Ru substrate, respectively, through the inherent AS-ALD method using catalytic local activation and ozone post-treatment. It should be noted that this intriguing approach for achieving inherent selectivity expands the potential utility of bottom-up nanopatterning processes for next-generation nanoelectric applications.

9:00am **AS1-TuM-5 Targeted Dehydration as a Route to Site-Selective Atomic Layer Deposition at TiO_2 Defects**, ***Jessica Jones***, *E. Kamphaus, A. Martinson,* Argonne National Laboratory

Distinct reactivity of unique atomic arrangements (i.e. defects) on material surfaces allows for selective surface chemistry exclusively at those sites. We

present an atomic layer deposition (ALD)-based technique of site-selective ALD (SS-ALD) targeting undesirable defect sites. Defects on the TiO_2 and other oxidized surfaces affect the electronic properties, interfaces, and performance of devices utilizing those interfaces. We present first principles calculations to predict the difference in hydration/hydroxylation of pristine TiO_2 terraces and minority atomic configurations including step edges and oxygen vacancies. In situ ellipsometry reveals the nucleation behavior of SS-ALD at process conditions precisely tuned for selective hydroxylation of surface defects. An island growth model for nucleation and atomic force microscopy (AFM) imaging are consistent with a site-selective growth mechanism that depends on defect density.

9:15am **AS1-TuM-6 Inhibitor-Free Area Selective Atomic Layer Deposition based on Atomic Layer Nucleation Engineering and Surface Recovery with a Feature Size of Nearly 10 nm***, **Yu-Tung Yin**, C. Chou,* National Taiwan University, Taiwan*; W. Lee, C. Chuu,* TSMC, Taiwan*; C. Hou,* Academia Sinica, Taiwan*; T. Wang,* National Taiwan University, Taiwan*; J. Shyue,* Academia Sinica, Taiwan*; M. Chen,* National Taiwan University, Taiwan

While conventional photolithography faces more and more challenges to follow the progress of aggressive semiconductor scaling, area-selective atomic layer deposition (AS-ALD) has become a promising technique that can directly reduce the number of lithography and etching processes. In this study, novel concepts including the “atomic layer nucleation engineering (ALNE)” and “surface recovery (SR)” techniques, were proposed for the realization of AS-ALD without using any inhibitors. The AS-ALD process based on ALNE and SR results in nearly 100% selectivity of the oxide (Al_2O_3) and nitride (AlN) deposition between the dielectric (SiO_2) and the metal (Pt or W). For ALNE, by directly introducing the radio-frequency (RF) substrate bias after the exposure and purging of precursors in each ALD cycle, the difference in the binding energy of the precursor adsorbed on dielectric and metal surfaces give rise to the selectivity of film deposition. The relatively lower binding energy of the precursor on the metal surface, as compared with that on the dielectric surface, opens a processing window for the local substrate plasma to remove the precursor adsorbed on metal, which contributes to the inhibitor-free AS-ALD between SiO_2 and Pt. Furthermore, for those metals that are easily oxidized during the oxide deposition, the SR technique (i.e., by introducing the RF substrate bias again) is subsequently applied to dispose of the oxidized layer on the metal surface. Accordingly, the ALNE method achieves the high-selectivity AS-ALD over 100 ALD cycles for Al_2O_3 and AlN between the SiO_2 and Pt surfaces. For tungsten (W) which is easily oxidized during the exposure of oxidant in the ALD process, the AS-ALD of Al2O3 without any selectivity loss over 100 ALD cycles is realized between the SiO2 and W surfaces. In addition, the AS-ALD process based on the ALNE and SR treatments has been further demonstrated on the SiO_2/W patterned substrates with the scaling of the feature size from 75 µm to ~10 nm. In conclusion, the concept of ALNE and SR has realized the inhibitor-free AS-ALD with high selectivity, which is substantially beneficial to further extension of Moore’s Law.

9:30am **AS1-TuM-7 Dopant-selective Choreography of Metal Deposition for Bottom-up Nanoelectronics***, **Nishant Deshmukh**, D. Aziz, A. Brummer, S. Kurup,* Georgia Institute of Technology, USA*; M. Filler,* Georgia Institute of Technology

The entirely bottom-up fabrication of nanoelectronic devices promises an unprecedented combination of performance and scalability. While current bottom-up methods can create suitable semiconductor structures, creating semiconductor-metal contacts or the gate stack of a transistor still require top-down processes. For example, contacting Si nanowire pn diodes grown with the vapor-liquid-solid (VLS) mechanism usually employs e-beam lithography, deposition, and lift-off. Here, we report a fully bottom-up approach that combines dopant-modulated surfaces, dopant-selective attachment of a self-assembled monolayer (SAM), and area-selective atomic layer deposition (AS-ALD) to direct the deposition of Pt contacts on Si. Briefly, a bifunctional undecylenic acid SAM is first blanket attached to the Si surface. Exposure to KOH removes it from heavily-doped (~10^{20} cm^{-3}) Si surfaces while it remains on lightly-doped (~10^{14} cm^{-3}) Si surfaces. Subsequent Pt ALD yields deposition primarily on the heavily-doped Si, with selectivity ratios as high as 100. X-ray photoelectron spectroscopy (XPS) studies of undecylenic acid and its monofunctional derivatives show that undecylenic acid attaches primarily through the alkene on lightly-doped Si surface. In situ oxidation of the heavily-doped Si surfaces leads undecylenic acid to bond via the carboxylic acid. This difference in attachment allows facile undecylenic acid removal from the heavily-doped surface but not the lightly-doped surface upon exposure to aqueous KOH. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) studies as a function of ALD cycle number reveal Pt film morphologies consistent with classic Pt nucleation and growth. The contact resistance of the resulting Pt contacts will also be presented. This work shows a method for the dopant-selective deposition of metal contacts on semiconductors, with potential use in the fully bottom-up fabrication of semiconductor devices such as diodes and transistors for hyper-scalable nanoelectronics.

9:45am **AS1-TuM-8 Effect of Surface Pretreatment to reduce the Incubation Period of Iridium Thin Film grown by ALD on the Oxide Surface***, **Myung-Jin Jung**, J. Baek, S. Lee, S. Kwon,* Pusan National University, Republic of Korea

Iridium (Ir) has low figure of merit ($\rho_0\lambda$) and high melting temperature properties, so it has been recently spotlighted as a very important copper (Cu) alternative interconnect material in next-generation semiconductor devices. In particular, in the case of depositing a thin film using atomic layer deposition (ALD) technology, it can be expected to deposit extremely thin film with conformal, uniform and excellent step coverage characteristics even in a very complex structure or a trench structure of several nm dimension due to the inherent self-limiting characteristic of ALD. In this regard, ALD-Ir is considered as one of the most suitable metallization process for the application of advanced semiconductor interconnects. Therefore, considerable efforts have been conducted to develop a reliable ALD-Ir process having improved film qualities. And, ALD-Ir process with excellent thin film properties such as low electrical resistivity and negligible oxygen impurities was recently reported using Tricarbonyl (1,2,3-η)-1,2,3-tri(tert-butyl)-cyclopropenyl iridium ($C_{18}H_{27}IrO_3$, TICP) precursor and oxygen [1]. However, in the case of this TICP precursor, it was difficult to deposit extremely thin and continuous Ir films on the hydroxyl-terminated oxide layer due to its long incubation delay.

Therefore, in this study, a method for depositing a very thin, uniform and continuous ALD-Ir thin film with low resistivity even on oxide materials was explored by reducing the incubation period and promoting nucleation using various surface pretreatment conditions. In addition, the nucleation behavior as well as film properties of ALD-Ir on the oxide material were systemically compared and analyzed according to the surface pretreatment conditions, and finally, ALD-Ir thin film with excellent properties on the oxide surface was obtained.

References

10. Park, Na-Yeon, et al. Chemistry of Materials 34.4 (2022): 1533-1543.

Area Selective ALD
Room Regency Ballroom A-C - Session AS2-TuM
Inhibitors and ASD

Moderator: Prof. Dr. Stacey Bent, Stanford University

10:45am **AS2-TuM-12 Consequences of Random Sequential Adsorption of Inhibitor Molecules for Loss of Selectivity During ALD***, **Joost Maas**,* Eindhoven University of Technology, Netherlands*; I. Tezsevin,* Eindhoven University of Technology, Turkey*; M. Merkx, E. Kessels,* Eindhoven University of Technology, Netherlands*; T. Sandoval,* Universidad Tecnica Federico Santa Maria, Chile*; A. Mackus,* Eindhoven University of Technology, Netherlands

For achieving area-selective atomic layer deposition (ALD), vapor-phase dosing of small molecule inhibitors (SMIs) is currently being explored, motivated by its compatibility with industrial processing. During vapor-phase dosing, SMIs typically arrive one-by-one at random sites, leaving relatively large gaps in between the inhibitor molecules where a precursor can potentially interact with the surface. This so-called random sequential adsorption (RSA) mechanism results in partial packing (i.e., deviating from close packing) of inhibitor molecules on the non-growth area, serving as the main challenge for the development of highly-selective processes using SMIs. In this work, RSA simulations are performed to emulate the vapor-phase dosing of various di-ketone (e.g. Hacac, Hthd) and aromatic (e.g. benzene, aniline) inhibitor molecules during an ALD process.[1] The understanding of the coverage and the inhibitor packing obtained by RSA simulations gives insights into the selectivity loss during area-selective ALD processes.

To carry out the RSA simulations, density functional theory (DFT) simulations are used to determine the 2D footprint of favorable binding configurations. A surface functionalized with inhibitor molecules is simulated by placing molecules one-by-one at random sites until the

surface is saturated. Simulations were performed for different di-ketones to investigate the influence of the inhibitor size on the packing. It was found that the size of the inhibitor plays a critical role in achieving a high packing density, with the bulky 2,2,6,6,-Tetramethyl-3,5-heptanedione (Hthd) inhibitor giving a lower packing density but a higher covered area as compared to acetylacetone (Hacac). Furthermore, the surface structure of the non-growth area influences the density of inhibitor molecules. For example, benzene packs with a relatively high density on Ru because it matches the lattice constant. The distribution of the available sites for ALD precursor adsorption are estimated as a measure for precursor blocking, allowing for a comparison to experimental ellipsometry and infrared spectroscopy data on area-selective ALD of SiO_2 and TiN.[2, 3] Based on this analysis, insight is also obtained into the influence of the precursor choice on the selectivity loss, illustrating that area-selective ALD with high selectivity requires a complementary set of inhibitor and precursor molecules.

[1] Li *et al., J. Vac. Sci. Technol. A***40**, 062409 (2022)

[2] Merkx *et al.*, *J. Phys. Chem. C*, **126**, 4845 (2022)

[3] Merkx *et al.*, *Chem. Mater.*, **32**, 7788 (2020)

11:00am **AS2-TuM-13 In-Situ Formation of Inhibitor Species Through Catalytic Surface Reactions During Area-Selective Tan ALD***, **Marc Merkx**, T. Janssen, I. Tezsevin, R. Heinemans, R. Lengers,* Eindhoven University of Technology, Netherlands*; J. Chen, C. Jezewski, S. Clendenning,* Intel*; E. Kessels,* Eindhoven University of Technology, Netherlands*; T. Sandoval,* Universidad Técnica Federico Santa Mariá, Chile*; A. Mackus,* Eindhoven University of Technology, Netherlands

Recently, small molecule inhibitors (SMIs) have been gaining attention, as an alternative to self-assembled monolayers (SAMs), for achieving area-selective atomic layer deposition (ALD) due to their compatibility with vapor-phase processes and plasma-assisted ALD. However, in contrast to SAMs, vapor-phase application of SMIs typically results in a disordered inhibitor layer, and therefore a lower inhibitor coverage.[1] This lower coverage makes it more challenging to achieve a high selectivity. In previous work, aniline was found to be an excellent inhibitor molecule for enabling area-selective ALD of TiN and TaN with metal/dielectric selectivity.[2] In this contribution, the precursor blocking mechanisms by aniline inhibitor molecules are studied using in-situ reflection adsorption IR spectroscopy (RAIRS) to understand what makes aniline an effective inhibitor.

The RAIRS spectra show that aniline undergoes catalytic surface reactions for substrate temperatures above 250 °C. These reactions turn the adsorbed aniline into C_6H_x adsorbate species, while NH_3 and potentially H_2 desorb from the surface. For the same temperatures (>250°C), a much higher selectivity was observed for area-selective TaN ALD using aniline as inhibitor, with respect to lower substrate temperatures. These observations suggest that the catalytic surface reactions play an important role in improving precursor blocking by the aniline inhibitor layer. The improvement in the selectivity is likely caused by the formation of a more carbon-rich inhibitor layer. Such carbon-rich layers have been shown to be effective at blocking ALD precursor adsorption.[3,4] More importantly, the catalytic surface reactions chemically alter the dosed inhibitor on the surface, i.e. new inhibitor species are formed in-situ during area-selective ALD. These reactions therefore provide a new strategy for forming inhibitor layers, enabling the use of inhibitor species that are otherwise more challenging or impossible to dose in vapor-phase.

[1] Li et al., J. Vac. Sci. Tech. A 40, 062409 (2022)

[2] Merkx et al., Chem. Matter. 32, 7788 (2020).

[3] Stevens et al., Chem. Matter. 30, 3223 (2018)

[4] Vervuurt et al., Adv. Mater. Interfaces 4, 1700232 (2017)

11:15am **AS2-TuM-14 Area Selective Atomic Layer Deposition of Ru and W Using W Precursor Inhibitor***, **Mingyu Lee**, T. Nguyen Chi, L. Trinh Ngoc, B. Gu, H. Lee,* Incheon National University, Republic of Korea

Area Selective Atomic Layer Deposition (AS-ALD) is a method which can inhibit or promote the following growth by changing surface property. AS-ALD has been considered as an approach to overcome the current challenges in nanofabrication for 3D Si devices which can't be achieved by the conventional photolithography and etching processes. For AS-ALD, self-assembled monolayers (SAMs) have been widely used to control surface property for inhibition and promotion. However, the thermally unstable organic ligand and the size of SAMs are the main obstacles to commercialize AS-ALD using SAMs. Precursor inhibitor (PI) can be an alternative material to SAMs for this purpose since the size of precursors are usually smaller than those of SAMs and the precursors are already used for the commercialized fabrication process. In this study, $EtCpW(CO)_3H$ precursor is utilized as an inhibitor to block following Ru and W ALD on a W surface. Density functional theory (DFT) calculation results indicated that the W PI can adsorb on the W surface and has unfavorable energy to the following precursors and reactants adsorptions. Monte Carlo (MC) simulation was used to calculate the surface coverage and physical interactions between the metal precursors and the W PI. The physical steric hindrance effect played an important role of the W PI adsorptions, the MC simulation showed that surface coverage can be improved by multiple exposure of the PI divided by nitrogen purging step. These results showed high consistent with the experiments analyzed by water contact angle (WCA) and transmission electron microscopy (TEM). By combining the theoretical and experimental results, the blocking mechanism of the W PI against Ru and W could be explained. We believe that the conceptof PI for AS-ALD could be applied to overcome various challenges in the patterning process of Si device fabrication.

11:30am **AS2-TuM-15 Partial Surface Passivation for Controlled Growth and Conformality Improvement on High Aspect Ratio Features Using Small Molecule Inhibitors***, **Kok Chew Tan**, C. Yeon,* Soulbrain, Republic of Korea*; J. Kim,* Hongik University, Republic of Korea*; J. Jung, S. Lee, T. Park, Y. Park,* Soulbrain, Republic of Korea*; B. Shong,* Hongik University, Republic of Korea

The motivation to keep semiconductor industry scaling has seen devices such as DRAM and VNAND continue to move vertically. Unlike 2D features, deposition of excellent film properties using atomic layer deposition (ALD) is increasingly challenging on high aspect ratio (HAR) 3D features. Various small molecule inhibitors and new deposition strategies with a particular emphasis on achieving conformal thin films are actively being investigated.

In this work, we have identified potential small molecule inhibitors suitable for application in different types of ALD films (e.g. oxide, nitride and metal films). Surface passivation using these inhibitors could overcome the limitations of conventional ALD in 3D nanofabrication such as poor conformality, seam formation and edge placement error in top-down approach nanofabrication. These inhibitors are introduced into the deposition chamber prior to every precursor feed step to modulate surface reactivity on the top region of the trench. The blockage of top reactive sites by the inhibitors allow more diffusion-limited (precursor) deposition reaction at the bottom trench, leading to improved film conformality on HAR features. Effective in-situ removal of the adsorbed inhibitors in each reactant feed step is another merit of this work that could prevent impurity incorporation.

Our work using these small molecule inhibitors has demonstrated lower growth per cycle, signifying growth inhibition and visible conformality improvement in nitride and oxide films, achieving conformality of more than 90% on HAR features **[1, 2]**. These experiment results were further elucidated by density functional theory (DFT) calculations with a focus on the roles of inhibitor on SiN_x surface and its reaction with reactant, NH_3**[3]**. The inhibition ability of the inhibitor was evidenced by the DFT results in term of activation energy. These DFT results also showed feasible reaction of NH_3 with the adsorbed inhibitors on the surface, consequently removing unwanted impurity contamination and regenerating the $–NH_2$ functional groups on the surface.

References:

11. C. Yeon, J. Jung, H. Byun, K.C. Tan, T. Song, S. Kim, J.H. Kim, S.J. Lee and Y. Park, AIP Advances 11, 015218 (2021).
12. K.C. Tan, J. Jung, S. Kim, J. Kim, S.J. Lee and Y. Park, AIP Advances 11, 075008 (2021).
13. J. Kim et. al. (2022, Oct 26-28). Mechanism for Partial Passivation of Silicon Nitride Surface with t-Butyl Chloride. Fall Conference of the Korean Institute of Metals and Materials, Jeju Island, Republic of Korea

11:45am **AS2-TuM-16 Fundamental Surface Chemistry Considerations for Selecting Small Molecule Inhibitors for AS-ALD***, A. Mameli,* TNO Science and Industry, the Netherlands*; **Andrew Teplyakov**,* University of Delaware

Current atomically-precise processing methods, specifically area-selective atomic layer deposition (AS-ALD), are firmly dependent on the difference in reactivity between growth and non-growth surfaces. However, this selectivity is always lost after certain number of ALD cycles, and etch-back and/or passivation of the surface reactive sites or defect sites with small molecule inhibitors (SMI) is required.

This talk will focus on a connection between surface chemistry of potential SMI on target (mostly oxide) materials and the selection criteria for using these organic molecules in realistic processes on realistic surfaces. Many of the concepts of the classical surface chemistry that had been developed over several decades can now be applied to design such SMIs. We will consider the roles of selectivity, chemical stability of a molecule on a specific surface; volatility, fast attachment reaction kinetics, steric hindrance, geometry and packing strength of adsorption as detailed by interdisplacement to determine the most stable SMI, minimal number of various binding modes, precursor of choice for material deposition. We then describe how to down-select appropriate SMI based on their properties. We will specifically focus on various acids, alcohols, and diketones and consider several materials, including ZnO and TiO_2.

ALD Applications
Room Grand Ballroom H-K - Session AA1-TuA
Energy: Catalysis and Fuel Cells

Moderator: Dr. Chang-Yong Nam, Brookhaven National Laboratory

1:30pm **AA1-TuA-1 Surface Texture Design of Pt/C Catalyst to Enhance Oxygen Reduction Reaction by FBR-ALD***, J. Baek, M. Jung, S. Lee, S. Kwon, **MinJi Kim**,* Pusan National University, Republic of Korea

Proton exchange membrane fuel cell (PEMFC) is an efficient electrochemical energy conversion device that directly generates electricity from the chemical energy of fuels without the emission of greenhouse gases. The most reliable catalyst in PEMFC is Platinum (Pt) metal nanoparticles (NPs) that exhibit excellent electrochemical activity and stability compared to other catalysts. However, using of Pt catalyst is limited due to its very high cost and low abundance on Earth. Therefore, it is important to use Pt catalyst efficiently for making the PEMFC economically viable. In this regard, several synthesis techniques have been developed to reduce the loading and uniform distribution of Pt NPs on carbon support with high electrochemically active surface area (ECSA).One of the most efficient techniques to uniformly deposit Pt NPs with a controllable size on carbon support is to use a fluidized bed reactor (FBR) atomic layer deposition (ALD). Our group recently demonstrated that FBR-ALD Pt/C catalysts can exhibit high fuel cell performance and high endurance even with low Pt NPs loading by optimizing the surface of carbon supports combined with proper ALD process parameters [1]. However, it is still challenging to further improve the fuel cell performance by rational designing the Pt NPs surfaces in order to make FBR-ALD into a viable commercial production.

In this study, a unique way to improve the fuel cell performance was suggested to design and optimize atomic scale surface textures of Pt NPs. During the FBR-ALD of Pt NPs, in-situ surface modulation of Pt NPs was applied via a proper protective oxide deposition and etching. A careful surface studies was performed to analyze the surface morphology, distribution and uniformity of Pt NPs. Electrochemical performances were evaluated and optimized by measuring cyclic voltammetry (CV) and oxygen reduction reaction (ORR).

References

14. W.-J. Lee, S. Bera, H.-C. Shin, W.-P. Hong, S.-J. Oh, Z. wan, S.-H. Kwon, *Adv. Mater. Interfaces* 6, 1901210 (2019).

1:45pm **AA1-TuA-2 Stabilization of ALD-grown Iridium Species for the OER Activity***, **Muhammad Hamid Raza**,* Humboldt-Universität zu Berlin, 2-Helmholtz-Zentrum Berlin für Materialien und Energie GmbH (HZB), Germany*; M. Frisch, R. Kraehnert,* Department of Chemistry, Technische Universität Berlin, Germany*; N. Pinna,* Institut für Chemie and IRIS Adlershof, Humboldt-Universität zu Berlin, Germany

Water-splitting electrocatalysts are vital because of the growing demand for renewable energy and the concurrent depletion of fossil fuels. Different types of catalytically active oxides are used as electrode materials for electrochemical water splitting. The catalytic performance of those materials depends on the surface composition and morphology of the active species. Increasing the number of potentially active sites on electrode surfaces leads to enhancing the catalytic efficiency of such electrodes. Iridium (Ir) / iridium oxides (IrO_x) are currently one of the most promising candidates for competent oxygen evolution reaction (OER) in acidic media. So far, the very high costs for Ir impede the large-scale production of hydrogen (H_2). Atomic layer deposition (ALD) has been researched to maximize the utilization of Ir-based electrocatalysts. However, the stability of the system with an ultra-thin film of electrocatalytically active species is challenging especially in acidic media. We report an electrode coating concept with template-controlled mesoporosity surfaces modified with Ir species. A temperature-controlled ALD process of Ir/IrO_x films grown has been studied and the resulting films have been examined structurally and in terms of their electrocatalytic activities. Ir/ IrO_x films are successfully grown using 1-Ethylcyclopentadienyl-1,3-cyclohexadieneiridium(I) and ozone between 160 and 120 °C. Metallic Iridium can be deposited at higher temperatures. However, a pseudo amorphous Iridium oxide film is deposited at a lower temperature that not only provides a remarkable catalytic performance but also stabilizes the overall system by conformally covering the carrier's surfaces. With our ALD process at low temperatures, we can achieve an outstanding mass-specific OER activity of the order of 3000mA mg_{Ir}^{-1} at 1.60 V vs. RHE at 25°C and 0.5 m H_2SO_4. This shows great promise for the development of highly efficient (electro-)catalysts. The peculiarities of ALD not only make this a technique of choice to synthesize optimized electrocatalysts, but also provide the possibility to verify fundamental theories and develop a clear structure−property relationship will be discussed.

2:00pm **AA1-TuA-3 Atomic Layer Deposited Nickel Sulfide as a (Pre)Catalyst for Oxygen Evolution Reaction***, **Miika Mattinen**, T. Hatanpää, K. Mizohata,* University of Helsinki, Finland*; S. Bent,* Stanford University*; M. Ritala,* University of Helsinki, Finland

Hydrogen gas (H_2) is currently one of the most important feedstocks of the chemical industry. In the future, H_2 is foreseen to play a major role in decarbonizing society, for example by acting as a clean fuel and replacing carbon in steelmaking. These uses require replacement of the current fossil fuel based H_2 production with cleaner alternatives, such as electrochemical water splitting. Of its two simultaneously occurring half-reactions, the oxygen evolution reaction (OER) is limiting the efficiency of water splitting. Thus, development of highly active, stable, and affordable OER catalysts is critical.

Nickel sulfides (NiS_x) have been identified as highly active OER electrocatalysts. It has been shown that at least the surface of NiS_x may transform to oxyhydroxide under the highly oxidizing OER conditions.[1] Therefore, NiS_x electrocatalysts may best be described as precatalysts for the actual catalyst. However, factors such as the extent and rate of the catalyst transformation process and ultimately the catalytically active species remain poorly understood. Well-defined thin films catalysts prepared by ALD are ideal for obtaining such insights.

We began by developing a new ALD process for NiS_x using a low-cost, easily synthesized $NiCl_2$(TMPDA) precursor[2] (TMPDA = *N,N,N′,N′*-tetramethyl-1,3-propanediamine) with H_2S. The process exhibits saturating growth behavior and deposits highly conducting films on a range of different substrates at 165–225 °C. The deposited films are highly pure (<3% total H, C, N, O, and Cl impurities) and consist of a mixture of β-NiS and Ni_9S_8 phases.

For the OER electrocatalysts, we deposited NiS_x films on SnO_2:F coated glass and studied them under alkaline conditions. X-ray photoelectron spectroscopy measurements indicate that the NiS_x films lose the vast majority of S under the OER conditions and transform to (oxy)hydroxide-like material. Electrochemical measurements and electron microscopy show that this transformation is accompanied by an increase in surface area due to the films becoming porous. We propose that the porosity enables the nickel atoms inside the films to participate in OER, thus increasing the electrocatalyst activity. Additional studies examine the transformation process in more detail as well as the long-term stability of catalysts formed from NiS_x. In order to tailor the porosity and surface area of nickel-based electrocatalysts, we are also working on expanding the family of thiolate hybrid materials[3] to nickel.

1 Wygant et al., *ACS Energy Lett.*, 2018, **3**, 2956

2 Väyrynen, Ritala et al., *Adv. Mater. Interfaces*, 2018, **3**, 1801291

3 Shi, Bent et al., *JVSTA*, 2022, **40**, 012402

2:15pm **AA1-TuA-4 Novel Phosphite Doping into ALD SiO_2 to Improve H^+ and H_2 Permeability in Water Electrolyzers***, **Sara Harris**, M. Weimer,* Forge Nano*; K. Yim, L. Cohen, D. Esposito,* Colombia University*; A. Dameron,* Forge Nano

H2 is a carbon-free and versatile energy carrier, anticipated to be an integral part of the clean energy future. Hydrogen fuel has significant relevance today; currently comprising roughly 1.5% of global energy use. Unfortunately, over 95% of H2 production comes from highly polluting, oil and coal, or grey (methane) sources. Currently, the cost of green H2 from electrolysis is not competitive with fossil fuel sources.[i] One pathway to drive down cost is by increasing the efficiency of polymer electrolyte membrane (PEM) electrolyzes by reducing the ohmic overpotential required by the cell. In this work, the path to ohmic overpotential reduction, which is partially dictated by the membrane thickness [ii] and the H^+ conductivity, will be explored by replacing Nafion with an ultra-thin proton-conducting oxide membrane (POM) deposited by ALD. Specifically, an SiO2 ALD film deposited with a unique catalytic process has been explored over a range of temperatures and thickness to measure the H^+ conductivity and gas permeation (H2). To address the inherently low H^+ permeability of baseline SiO2 films, phosphorous-based dopants were explored to increase H^+ permeability without sacrificing other requirements. Phosphate, $PO4^{-3}$ species were doped into an SiO2 ALD film

using two novel ALD precursors.[iii] Both precursors were found to incorporate into the growing SiO2 film, as measured by X-ray photoemission spectroscopy (XPS), but not grow a P2O3 or P2O5 monolith with H2O, O2 or O3. The largest $PO4^{-3}$ percent incorporation was observed in an ABC-type ALD sequence, where the $PO4^{-3}$ precursor did not see a separate oxidant, shown in Figure 1 below. All POx:SiO2 films also showed a decrease in refractive index. Critically, H^+ permeability improved with $PO4^{-3}$ addition. An ABC-type ALD processes showed the largest improvement of ~8.5x in acidic solution with a rotating disk electrode. Unexpectedly, the addition of $PO4^{-3}$ also decreased H2 gas permeability across all samples by up to 12x. Importantly, ALD POM films have the potential to directly coat membranes onto high surface area porous transport or gas diffusion layers for integration into current PEM electrolyzer cells, further improving efficiency. This work is the first step in building full electrolyzers that employ a novel ultra-thin ceramic membrane with the potential to enable a competitive green H2 market.

[i] https://hub.globalccsinstitute.com/ and https://www.mckinsey.com/industries/oil-and-gas/our-insights/global-energy-perspective-2022

[ii] Han, et al., Int. J. Hydrogen Energy, 40, 2015

[iii] Henderick, L., et al., Appl. Phys. Rev. 9, 011310, 2022

2:30pm **AA1-TuA-5 Atomic Layer Deposition of Copper Catalysts for Electrochemical Recycling of Carbon Dioxide***, J. Lenef, S. Lee, K. Fuelling, K. Rivera Cruz,* University of Michigan, Ann Arbor*; A. Prajapati, C. Hahn,* Lawrence Livermore National Laboratory*; C. McCrory,* ***Neil P. Dasgupta,*** University of Michigan, Ann Arbor

Electrochemical recycling of carbon dioxide into value-added products is a promising strategy to mitigate climate change as the CO_2 reduction reaction (CO_2RR) can be driven using renewable electricity (i.e. wind, solar). So far, copper metal is the only known single element catalyst to form multi-carbon products, such as ethylene and ethanol, from CO_2RR. Numerous synthesis strategies have been employed to deposit copper-based catalysts including sputtering, evaporation, electrodeposition, and solution processing; however, they do not enable atomically precise control of film thickness and particle size and have limited conformality on 3D substrates such as carbon gas diffusion electrodes. To address this knowledge gap, we fabricate Cu catalysts using plasma-enhanced atomic layer deposition (PE-ALD) with varied PE-ALD cycle numbers on 3D carbon electrodes to achieve precise control of catalyst loading. A polycrystalline Cu metal layer was confirmed by grazing incidence X-ray diffraction. The catalyst surface morphology was probed by scanning electron microscopy and atomic force microscopy, highlighting the island-growth mode of the metal catalyst.

We demonstrate that Cu surfaces prepared by PE-ALD can reduce CO_2, forming value-added products such as carbon monoxide, methane, and ethylene. Parasitic hydrogen evolution was minimized to Faradaic efficiencies of ~10%, as quantified using *in situ* gas chromatography measurements. We further demonstrate a selectivity over 40% Faradaic efficiency for ethylene production, which is among the highest values reported to date in an H-cell geometry. Compared to evaporated Cu catalysts, we show significant methane suppression for the PE-ALD Cu. Finally, we demonstrated stability for up to 15 h for CO_2 reduction products with minimum loss in the ethylene production rate. In summary, we demonstrate CO_2RR using PE-ALD of Cu catalysts with high selectivity and stability, which provides a pathway to conformal deposition on 3D substrates with precise control of particle size and catalyst loading.

2:45pm **AA1-TuA-6 Stability of Molecular Layer Deposited (MLD) Alucone in Acetonitrile for Photoelectrochemical CO_2 Reduction Applications***,* ***Hyuenwoo Yang,*** North Carolina State University, Republic of Korea*; H. Margavio, L. Keller, G. Parsons,* North Carolina State University

In this work, we study an organic-inorganic hybrid metalcone material deposited by molecular layer deposition (MLD) for applications in solar-energy driven CO_2 reduction to liquid fuel.In the field of photoelectrochemical CO_2 reduction reaction (CO_2RR), controlling the selective absorption of CO_2 on silicon-bound molecular catalysts for photo-electron driven reduction ischallenging to avoid the hydrogen evolution reaction (HER) that proceeds during the competitive reduction of available protons.Recently, researchers have shown that for some geometries, organic encapsulation layers can improve the stability of the catalysts and at the same time increase the selectivity of CO_2 conversion.To date, however, organic layers formed by MLD have not been significantly studied for this application. Advantages of metalcones have great potential as an encapsulation layer for inducing selective catalytic reactions.

Here, we demonstrate photoelectrochemical compatibility of alucone thin films on Si photoelectrode in acetonitrile electrolyte. Alucone layer was deposited with trimethylaluminum (TMA) and ethylene glycol (EG) in low temperature (< 100°C). Alucone showed outstanding stability in acetonitrile (0.1 M Tetrabutylammonium hexafluorophosphate, $TBAPF_6$) electrolytes under 1 sun illumination and applied potential of -1.8 to 0.7 V versus $Ag/AgNO_3$ reference electrode. In contrast, the thickness of alucone shrank by 94% within an hour in water based electrolyte (0.1 M potassium chloride, KCl) under -1.5 to 0 V versus Ag/AgCl reference electrode. This result matches with the previous research that vapor absorption changes the thickness of metalcone. This results supports the photoelectrochemical stability of alucone to acetonitrile which has high solubility of CO_2.

Our study opened the new possibility of applying MLD metalcone thin films to CO_2RR fields through its excellent transparency, molecular permeability and CO_2 selectivity. MLD alucone layer is expected to be feasible as an encapsulation layer for Si photoelectrodes and surface modification layer to form favorable CO_2 microenvironment with its permeability, transparency and hydrophobicity.

3:00pm **AA1-TuA-7 Enhanced Green Hydrogen Production Using ALD-based Catalysts for Ammonia Decomposition***,* ***Yu-Jin Lee****, H. Sohn, H. Jeong, S. Nam,* Korea Institute of Science and Technology (KIST), Republic of Korea*; J. Park,* Seoul National University, Republic of Korea*; Y. Kim,* Korea Institute of Science and Technology (KIST), Republic of Korea

Ammonia-based hydrogen value chains are emerging as one of the most promising ways for achieving a carbon-neutral hydrogen economy. In order to expedite the development, it is essential to develop highly efficient and scalable catalysts for ammonia decomposition. In this study, we demonstrate the use of atomic layer deposition (ALD) to fabricate highly efficient Ru/TiO_2-ALD/γ-Al_2O_3 bead catalysts for ammonia decomposition. By utilizing the ALD technique to introduce an ultrathin TiO_2 layer between Ru nanoparticles and the γ-Al_2O_3, followed by high-temperature alloying, we were able tochange the electronic structure of the Ru and shift the nitrogen binding energy to lower, resulting in an enhancement of catalytic activity. One of the most intriguing aspects of this study is the use of ALD technology to overcome the limitations of reducible oxides in high-temperature reducing atmospheres, such as particle encapsulation or consolidation that can diminish the catalytic activity of nanoparticles. Compared to state-of-the-art Ru-based catalysts with rare-earth metal oxides such as Y_2O_3 and La_2O_3, the Ru/ALD-TiO_2/γ-Al_2O_3 catalysts developed in this study demonstrated superior catalytic performance as well as cost competitiveness due to minimized utilization of functional oxide. The promising results of this study indicate that the use of ALD technology catalysts has the potential to significantly advance the establishment of ammonia-based hydrogen value chains, leading to enhanced efficiency in the hydrogen reconversion process and ultimately reducing the levelized cost of hydrogen.

3:15pm **AA1-TuA-8 Atomic Layer Depositied Silver Catalysts for Anion Exchange Membrane Fuel Cells***,* ***Gwon Deok Han,*** *H. Han, F. Prinz,* Stanford University*; J. Shim,* Korea University, Republic of Korea

In the automotive industry, the paradigm shift from internal combustion engine vehicle to electric vehicle is accelerating to respond to the global climate crisis. Fuel cell electric vehicles (FCEVs) powered by hydrogen are one of the zero-emission means of transportation, and its advantages are long mileage and fast charging time. However, proton exchange membrane fuel cell (PEMFC), which is the propulsion system of FCEVs, requires the use of precious metal catalysts such as Pt. This is a decisive factor hindering the popularization of FCEVs in terms of economic feasibility. Anion exchange membrane fuel cell (AEMFC) is receiving considerable attention as a next-generation technology due to its unique advantage of operating in an alkaline environment that allows the use of Pt-free catalysts. In this study, a high-performance AEMFC cathode containing carbon nanotubes surface-modified with Ag particulates was fabricated using plasma-enhanced atomic layer deposition (PEALD). HEMFC cathode coated with ALD Ag particulates delivers a maximum power density of 2,154 $mW\cdot mg_{Ag}^{-1}$ in an alkaline environment. The AEMFC cathode decorated with ALD Ag contributed to reducing the polarization energy loss by improving the cathodic oxygen reduction reaction. Through the application of PEALD, it was successfully demonstrated that an optimized microstructure design is possible while minimizing the load of the Ag catalyst at the cathode. This study is significant in that it successfully demonstrated the potential applicability of ALD in the manufacture of high-performance AEMFC cathodes.

ALD Applications
Room Grand Ballroom H-K - Session AA2-TuA

Emerging Materials

Moderators: Joel Molina Reyes, Instituto Nacional de Astrofísica, Óptica y Electrónica (INAOE), Tero Pilvi, Picosun Oy

4:00pm **AA2-TuA-11 Unfolding the Challenges to Prepare Epitaxial Complex Oxide Membranes by Chemical Methods***, **Mariona Coll**, P. Salles,* ICMAB-CSIC, Spain **INVITED**

Epitaxial transition metal complex oxides have raised enormous interest to be integrated in next-generation electronic devices envisaging distinct and novel properties that can deliver unprecedented performance improvement compared to traditional semiconductors. However, this step demands for ease heterointegration in mature semiconductor device technology including bendable, wearable and light-weight devices. The possibility to fabricate free-standing single crystal complex oxides has revolutionized this field stimulating new research from synthetic procedures and uncommon combination of materials to fundamental physics, foreseeing an even broader spectrum of applications.[1]

Motivated by the use of cost-effective chemical deposition approaches to prepare high quality complex oxide epitaxial films and investigate the influence of defects on its properties, here it is presented our most recent studies towards the fabrication of epitaxial complex oxide membranes using the sacrificial layer approach. First, it will be introduced a facile chemical route to prepare $Sr_3Al_2O_6$ (SAO) sacrificial layers [2] and how to overcome its instability in air. Then, it will be discussed the preparation of bendable and magnetic $CoFe_2O_4$ [3] and $La_{0.7}Sr_{0.3}MnO_3$ membranes with special focus on the influence of the sacrificial layer composition on the membrane crystallinity and physical properties. Advanced X-ray diffraction analysis (XRD), reflection high energy electron diffraction (RHEED) and scanning transmission electron microscopy combined with electron energy loss spectroscopy (STEM-EELS) are used to unfold and start solving the challenges to prepare free-standing epitaxial membranes by chemical methods. This approach here presented offers a new opportunity to work with crystalline oxide membranes, easy manipulate them and fabricate new artificial heterostructures allowing future investigations of novel physical phenomena that can bring new opportunities for high-performance oxide electronic devices.

[1]*Synthesis of freestanding single-crystal perovskite films and heterostructures by etching of sacrificial water-soluble layers*, Di Lu, Harold Y Hwang et al. **Nature Materials**, 15, 11255-1260 **(2016)**

[2] *Facile Chemical Route to Prepare Water Soluble Epitaxial $Sr_3Al_2O_6$ Sacrificial Layers for Free-Standing Oxides* Pol Salles, Ivan Caño, Roger Guzman, Wu Zhou, Mariona Coll* et al.**Advanced Materials Interfaces**, 8, 2001643 **(2021)**

[3]*Bendable Polycrystalline and Magnetic $CoFe_2O_4$ Membranes by Chemical Methods P*ol Salles, Roger Guzmán, David Zanders, Anjana Devi, Mariona Coll* et al. **ACS Applied Materials Interfaces***.* 14,10 12845-12854**(2022).**

4:30pm **AA2-TuA-13 Tailoring Lattice Match by Cation Substitution in a Functional Ternary Oxide***, M. Rogowska, L. Rykkje,* ***Henrik Sønsteby,*** University of Oslo, Norway

Integration of functional complex oxide thin films can push the boundaries of electronic device performance. Functionality can be enhanced by implementing materials with tailored properties, or completely new functionality may be achieved by *e.g.* making use of ferroic characteristics. Model systems have been predicted, designed, and found to be interesting, but their realization often comes to a halt due to the difficulty of preparing samples under conditions feasible for ICT industry.

One example is the integration of $SrTiO_3$ (STO) as a high-κ material in transistor architectures. The dielectric constant of defect-free STO is among the highest known, but integration of the material very often leads to structural defects that hamper its functionality. High-quality STO can be deposited by high-temperature techniques, but these are seldom compatible with device manufacturing. Furthermore, the properties of STO are sensitive to strain and the quality of epitaxy at the interface, which is often hard to control when applying a high thermal budget. A functional template layer deposited under industrially relevant conditions, that can mitigate strain effects while working as an electronic conductor, would be a significant step towards harnessing the attractive properties of STO.

One such material could be $LaNiO_3$ (LNO). LNO is structurally similar to STO while being a metallic conductor and ALD epitaxy has already been shown. Unfortunately, LNO imposes a 1.7 % strain on STO, which again hampers the dielectric properties by inducing structural defects and pinholes.

In this work, we use the unique strengths of ALD to deposit a lattice matched and conductive material that may act as a template for implementation of STO. The material is based on $LaNiO_3$, but utilizes substitution of Sc on B-site to increase the lattice size to match STO. We show that the lattice parameters can be continuously tailored from those of $LaNiO_3$ to $LaScO_3$, albeit exhibiting a critical substitution level at which the metallic properties of are lost. Luckily, at lattice matched substitution levels (a_{pc} = 3.905 Å), low resistivity is maintained. We show that direct epitaxial integration of this quarternary compounds is achievable by ALD, and that the interfacial quality towards STO is of high quality. We also pinpoint a crucial advantage of the low thermal budget of ALD: The mixed compound seems to be metastable and decomposes into binary/ternary constituents at higher temperatures.

We believe this is a large step towards integration of functional complex oxides in future ICT, while at the same time showcasing the fantastic opportunities of using ALD to deposit complex oxides.

4:45pm **AA2-TuA-14 *In situ* Atomic Layer Doping of Epitaxially Grown β-Ga_2O_3 Films via Plasma-enhanced ALD at 240 ℃***, S. Ilhom,* Univerisity of Connecticut*; A. Mohammad, N. Ibrahimli, J. Grasso, B. Willis,* University of Connecticut*;* ***Ali Okyay,*** Stanford University*; N. Biyikli,* University of Connecticut

Wide and ultrawide bandgap (WBG/UWBG) semiconductors make the backbone of high-power high-frequency electronics, used in electric vehicles, 5G and beyond wireless communication systems, and smart power grids. However, the relatively complex growth reactors and typical growth temperatures around 1000 °C lead to increased production costs and limited application space. Gallium oxide (Ga_2O_3) is an emerging UWBG semiconductor showing superior material properties particularly ideal for harsh environments (high temperature, high-energy radiation, corrosion) applications. Reducing the growth and doping process temperatures for Ga_2O_3 would potentially enable a wider integration platform towards post-CMOS integration and flexible electronics.

Hence, we report on the low-temperature as-grown crystalline β-Ga_2O_3films on Si, glass, and sapphire via hollow-cathode plasma-enhanced atomic layer deposition (HCPA-ALD). The films were deposited using triethylgallium (TEG) and Ar/O_2 plasma as metal precursor and oxygen co-reactant, respectively. Additionally, we have employed in situ atomic layer doping to n-type dope β-Ga_2O_3films where tris-dimethylaminosilane (TDMAS) and tetrakis-dimethylaminotin(IV) (TDMASn) were utilized as the dopant precursors. Growth experiments have been performed at 240 °C under 50 W rf-power. The doping process was carried out via both supercycle (ABC-type ALD-cycle) and co-dosing methods. Additionally, eachunit ALD-cycle was followed by an *in situ* Ar-plasma annealing treatment, which consisted of Ar-plasma exposure for 20 seconds at 250 W rf-power. Both in-situ and ex-situ ellipsometry were employed to measure the thickness and optical properties of the films. X-ray diffraction (XRD) of the sample on sapphire revealed epitaxial Ga_2O_3 films with monoclinic β-phase. On the other hand, GIXRD of the samples grown on Si and glass displayed polycrystalline β-Ga_2O_3 films. HR-STEM imaging and EDX elemental analysis confirmed the epitaxial relationship of the β-Ga_2O_3films grown on sapphire substrates and displayed successful incorporation of dopant elements. Preliminary electrical conductivity measurements showed highly resistive samples. Therefore, *ex situ* thermal annealing studies are ongoing to explore possible dopant activation. Further studies from our XPS characterizations will provide additional insight about the chemical bonding states of the dopant species. A significant effort will be devoted for the comparison of Si and Sn-doping strategies and potential suggestions will be provided to overcome the challenges in achieving device quality undoped and doped β-Ga_2O_3 layers at low growth temperatures.

5:00pm **AA2-TuA-15 Plasma Enhanced Atomic Layer Deposition of Niobium Nitride for Scalable Quantum Device Fabrication**, ***Yi Shu,*** Oxford Instruments Plasma Technology, UK*; C. Lennon,* University of Glasgow, UK*; Z. Ren,* Oxford Instruments Plasma Technology, UK*; H. Knoops,* Oxford Instruments Plasma Technology, UK, Eindhoven University of Technology, Netherlands*; F. Morini, A. Kurek, T. Hemakumara,* Oxford Instruments Plasma Technology, UK*; R. Hadfield,* University of Glasgow, UK

Superconducting niobium nitride (NbN) thin film has gained extensive attention in quantum computing and quantum communication applications[1,2] due to its high transition temperature (T_c) and high critical current. Highly uniform NbN films over whole processed wafers are essential to improve device scalability and fabrication yield. Moreover, superconducting through silicon vias (TSV) is one of the key technologies enabling 3D quantum integration where highly conformal NbN liners inside TSVs are required for interconnection between quantum and control/readout circuits[3]. Plasma enhanced atomic layer deposition (PEALD) of superconducting NbN is a promising option to meet all these requirements.

In this work, we firstly present PEALD NbN films grown at 250 ºC on 200 mm Si wafers, utilizing (t-butylimido)-tris(diethylamido) niobium (TBTDEN) and H_2/Ar plasma, carried out on an Oxford Instruments Plasma Technology FlexAL ALD tool equipped with an independent-controlled RF-biased electrode table (13.56 MHz, substrate biasing up to 100 W power, -350 V resulting DC bias voltage). By optimizing the substrate bias used in plasma steps, NbN films were produced at much faster speed (plasma exposure time in each ALD cycle was reduced from 60 s[4] to 5 s) with excellent film quality and uniformity. Characterization of T_c with a series thickness of NbN thin films (5 nm, 8 nm, 15 nm, 20 nm, and 30 nm) has demonstrated excellent film quality: T_c was as high as 10.2 K with the ultrathin 5 nm film and approached 13.5 K with the 30 nm film, as illustrated in Figure 1. Also, uniformity of the 8 nm NbN film was explored by investigating the thickness and superconducting properties spread up to a wafer size of 200 mm. Unparalleled uniformity over the whole 200 mm wafer was observed for both film thickness (±2.8%) and transition temperature T_c (±3.1%), as illustrated in Figure 2 and 3. A comparison of our parameter spread with literature data[4] is summarized in Table I.

In addition, superconducting TSV with conformal NbN coating was also explored by respectively depositing 50 nm PEALD NbN films on frontside and backside of a perforated TSV sample. Preliminary tests on such sample have revealed superconducting interconnections between the frontside and backside NbN films, provided by the NbN coated TSVs at ~10.7 K.

15. Yan et al., Supercond. Sci. Technol. 35, 065004 (2022)
16. Taylor et al., Appl. Phys. Lett. 118, 191106 (2021)
17. Yost et al., npj Quantum Inf 6, 59 (2020)
18. Knehr. et al., J. Vac. Sci. Technol. A 39, 052401 (2021)

5:15pm **AA2-TuA-16 Superconducting NbN Thin Films Deposited by Plasma Enhanced Atomic Layer Deposition**, ***Jakob Zessin,*** SENTECH Instruments GmbH, Germany*; M. Hagel, T. Reindl, L. Freund,* SF Nanostructuring Lab, Max Planck Institute for Solid State Research, Germany*; P. Plate,* SENTECH Instruments GmbH, Germany*; J. Weis,* SF Nanostructuring Lab, Max Planck Institute for Solid State Research, Germany

Niobium nitride (NbN) is a superconductor with a critical temperature up to 16 K[1]. The application of NbN as a superconductor has already been demonstrated in superconducting nanowire single-photon detectors in the near infrared range[2] and resonators[3].

Atomic layer deposition (ALD) is an advanced technique used to deposit thin films with precisely controlled thickness in the sub-nanometer range, high conformality on complex 3D structures and the possibility of uniform deposition for large area fabrication.

With the Nanostructuring Lab of the Max-Planck-Institute for Solid State Research Stuttgart, we developed a plasma-enhanced ALD (PEALD) process of NbN. The depositions have been carried out in a SENTECH PEALD tool. Tris(diethylamido)(tert-butylimido)niobium(V) (TBTDEN) was used as a precursor and H_2 and Ar as plasma gas mixture. The influence of the most critical process parameters, such as temperature and plasma exposure time on room temperature resistance and critical temperature will be discussed. The highest achieved critical temperature was 9.6 K.

[1]Hazra et al. *Supercond. Sci. Technol.***2016**, 29, 105011.

[2]Cheng et al. *Appl. Phys. Lett.***2019**, 115, 241101.

[3]Sheagren et al. *J. Low Temp. Phys.***2020**, 199, 875.

5:30pm **AA2-TuA-17 Work-Function Modulation using Atomic Layer Deposited TaN and Ternary TaAlN Metal Gate**, ***Moonsuk Choi,*** *B. Ku, S. Kim, C. Chung, C. Choi,* Hanyang University, Republic of Korea

With the disruptive scaling in semiconductor technology, high-k/metal gate (HKMG) stacks have been introduced to overcome direct tunneling in gate leakage current and reliability issues associated the conventional poly-Si/SiO_2 stacks. To implement a wide range of threshold voltage (V_{TH}) in MOS devices, work-function modulation is required. There are several factors that govern V_{TH}, which is significantly influenced by metal gate. The selection of suitable metal electrodes to modulate their work function remains still a challenging task. Considering 3D structure in FinFET and Gate-all-around FET (GAAFET) with the narrow dimensional margin, atomic layer deposition (ALD) is the promising process to form the advanced gate electrodes due to the excellent thickness control, outstanding film quality, and applicable complex structure with high aspect ratio.

In this study, we characterized ALD TaN and TaAlN and their relevant work functions were investigated. The different metal precursors were used such as metal-organic (tertbutylimide tris-diethylamido tantalum, TBTDET) and metal-halide (tantalum(V) chloride, $TaCl_5$) precursors as Ta source and tri-methylaluminium (TMA) as Al source, respectively, with reacting ammonia (NH_3) gas and deposition temperature was 350 °C. The chemical structures of the metallic precursors as well as the specific sequence in the ALD process are illustrated in Figure 1 (a)-(b). After the deposition process, the films were treated by forming gas annealing (FGA) treatment to confirm the effects of the thermal budget. Figure 2 (a)-(b) shows the resistivity of these metal gates. Their low values are a promising feature even at the thinner thickness as well as the increased amounts of Al element. MOS devices in the structure of p-Si/HfO_2/metal gate electrodes (TaN and TaAlN)/capping metal (either W or Al) were fabricated. The capacitance-voltage (C-V) characteristics are estimated in Figure 3 (a)-(b). The increase of sub-cycle ratios and pulse time of TMA in ALD induces the positive flat band voltage (V_{FB}) shift with enhancing Al incorporation into TaN films. In figure 4 (a)-(b), the work function of both films was summarized V_{FB} as a function of parameters. The effect of Al incorporation into TaN can provides the modulation of the work function from the mid-gap to the valence band of Si. The FGA process presents another option for tuning the work function in both thin films by reducing the amounts of carbon under a hydrogen ambient. These results can contribute to a better understanding to a feasible application for HKMG stacks with improved electrical properties such as engineering of the work function as well as multiple V_{TH}.

ALD Fundamentals
Room Grand Ballroom E-G - Session AF1-TuA
Plasma ALD I

Moderators: Erwin Kessels, Eindhoven University of Technology, Netherlands, Prof. Christophe Vallee, SUNY POLY, Albany

1:30pm **AF1-TuA-1 Plasma Enhanced Atomic Layer Deposition of Silicon Carbonitride**, *S. Johnson, T. Yang,* University of Texas at Austin*; J. Zhao, T. Iwao, C. Schlechte, J. Carroll, G. Blankemeyer, P. Ventzek,* Tokyo Electron America Inc.,*; J. Resasco, G. Hwang,* ***John Ekerdt,*** University of Texas at Austin

Conformal deposition of dielectrics is necessary for many applications, including as spacers for self-aligned multiple patterning and as charge trap layers in NAND memory features. Plasma enhanced atomic layer deposition (PEALD) of silicon nitride is promising for these applications. However, silicon nitride films deposited with this technique typically have low HF acid wet etch resistance, limiting its applications. Incorporating carbon into silicon nitride to form silicon carbonitride (SiCN) films can overcome this shortcoming by increasing wet etch resistance, but it also increases leakage currents. By incorporating small amounts of carbon to form silicon carbonitride films, a large increase in etch resistance can be achieved with only a small increase in leakage current. Finding a process that delivers a ternary component film with specific material properties is inherently complex as both stoichiometry and bonding nature need to be controlled through surface reactions. Managing the carbon content and nature of bonding within SiCN films is the focus of this talk.

We use PEALD to deposit silicon carbonitride by alternating a thermal exposure of a silicon derived single source precursor containing Si-N, Si-C, and N-C bonds at 100 °C and a plasma step as a model system for SiCN deposition. The precursor contains all the film components (Si:C:N). A

plasma step creates a surface on which the precursor can chemisorb leading to ideal film formation. An experimental capacitively coupled RF plasma source is used to survey how different plasmas, including ammonia, hydrogen, nitrogen, and pure argon impact of the nature of chemisorption and film nature. Films were characterized using *in situ* Fourier transform infrared spectroscopy (FTIR) and *in situ* X-ray photoelectron spectroscopy (XPS).First principles simulations are used to assess the fundamental mechanisms at play.

FTIR measurements show the plasma type has a large effect on the carbon bonding (C-C, C-N, C=N, C≡N, and C-Si) and the carbon content.XPS measurements reveal ammonia plasma results in no carbon being incorporated into the films; however, hydrogen plasmas result in significant carbon incorporation. Nitrogen plasma assisted processes are characterized by high growth per cycle and very high concentrations of C≡N and C=N bonds. Multiplexing different plasma treatment steps allows the film stoichiometry and bonding nature to be tuned. The fundamental mechanism associated with surface/film chemistry control is discussed in terms of the role of plasma species removal and addition of important nitrogen and carbon containing ligands.

1:45pm **AF1-TuA-2 Boron-Carbon Thin Films Deposited via PE-ALD***, **Neil Richard Innis**, C. Marichy, C. Bousige, C. Journet,* Laboratoire des Multimatériaux et Interfaces, UMR CNRS 5615, France

Boron carbide (B_xC) finds diverse applications due to its superior hardness, high neutron absorption, and semiconducting nature. The band gap for boron-rich B_xC films is known to increase with an increasing B:C ratio. Magnetron sputtering[1], and high temperature (≥ 1000 °C) chemical vapor deposition (CVD) are the conventional processes to obtain boron carbide thin films. CVD involves boron hydrides[1] or halides[2] as precursors along with dihydrogen or simple hydrocarbons. Such precursors come with challenges such as high toxicity and/or corrosive by-products. Furthermore, conformality and thickness control of these films is still a challenge. To overcome it, atomic layer deposition (ALD) appears as a technique of choice, however, B_xC has never been synthesized by this technique so far.

From triethylborane (TEB) and hydrogen gas (H_2) as precursors, amorphous B_xC thin films with atomic-level thickness control on Si 100 substrate using plasma-enhanced atomic layer deposition (PE-ALD) are successfully obtained. The use of hydrogen plasma to remove ethyl groups of TEB to deposit $B_xC$films at low substrate temperatures (≤ 200 °C) is demonstrated. It should be noted that in this process the expected by-products are non-toxic and non-corrosive.

Here, the influence of the deposition parameters on the film growth rate, composition and structure will be discussed. The ALD reaction temperature is being investigated between 150 °C and 250 °C alongside spectroscopic ellipsometry. Additionally, the pulse/purge of precursors is optimized to ensure a saturated self-limited surface reaction, and the role of H_2 concentration and plasma power in the composition and growth of the deposit is being explored.

In-situ optical emission spectrometry (OES) is also performed to detect and compare the intensity of hydrogen lines, and to look at species responsible for etching and deposition during the ALD cycle. The impact of plasma-activated hydrogen species (as a function of plasma power and H_2 concentration) on the morphology and B:C ratio of the deposits is preliminarily assessed via secondary electron microscopy (SEM) and energy dispersive spectroscopy (EDS), respectively. Moreover, surface-sensitive quantification and bonding information are obtained via time-of-flight secondary-ion mass spectrometry (ToF-SIMS) and ex-situ x-ray photoelectron spectroscopy (XPS).

References:

19. Pascual et al., *Diamond and Related Materials***8**, 402–405 (1999).

20. Byun et al., *Nanostructured Materials***5**, 465–471 (1995).

21. Buzhinskij et al., *Fusion Engineering and Design***45**, 343–360 (1999).

2:00pm **AF1-TuA-3 SiO_2 Electron-Enhanced Atomic Layer Deposition (EE-ALD) at Low Temperature Using Disilane and Ozone or Water as Reactants***, J. Gertsch, Z. Sobell, A. Cavanagh,* University of Colorado Boulder*; H. Simka,* Samsung Semiconductor, Inc.*; **Steven George**,* University of Colorado Boulder

Electrons can enhance SiO_2 atomic layer deposition (ALD) at low temperature using disilane (Si_2H_6) and either ozone (O_3/O_2) or water (H_2O) as the reactants.SiO_2 electron-enhanced ALD (EE-ALD) was demonstrated at 35°C by exposing the sample to sequential electron, oxygen reactant, and Si_2H_6 exposures (see Figure 1). The reaction sequence was electron beam exposure for 3 s, purge for 5 s, O_3/O_2 or H_2O exposure at 0.5-1.0 Torr for 3 s, purge for 10 s, Si_2H_6 exposure at 100 mTorr for 1 s, and purge for 15 s. The electron exposure was an electron current of ~150 mA for 3 s. The electrons were produced by a hollow cathode plasma electron source operating with a grid bias of ~-300 V. These electrons could irradiate a sample area of ~2 cm x 2 cm.

In situ spectroscopic ellipsometry measurements determined that the SiO_2 EE-ALD films nucleated rapidly and deposited linearly versus number of EE-ALD cycles on silicon wafers (see Figure 2). The SiO_2 EE-ALD growth rate at 35°C was 0.89 Å/cycle using O_3 and 0.88 Å/cycle using H_2O. The SiO_2 growth rate was also self-limiting at higher electron and Si_2H_6 exposures. The SiO_2 EE-ALD films could be grown on conducting silicon wafers or insulating SiO_2 films. SiO_2 EE-ALD is believed to be possible on insulating SiO_2 films because the secondary electron yield for SiO_2 at electron energies of ~100-300 eV is greater than unity. Under these conditions, the SiO_2 film charges positive during electron exposure and then pulls back secondary electrons to maintain charge neutrality.

The SiO_2 EE-ALD films had properties that were comparable with thermal SiO_2 oxides. The refractive indices of the SiO_2 EE-ALD films were n = 1.44 ± 0.02 and equivalent to the refractive index of a wet thermal SiO_2 oxide film. Depth-profile x-ray photoelectron spectroscopy (XPS) revealed that the SiO_2 EE-ALD films were high quality with carbon atomic percent below the detection limit. Grazing incidence x-ray diffraction (GI-XRD) analysis determined that the SiO_2 EE-ALD films were amorphous. In addition, the SiO_2 EE-ALD films yielded etch rates in dilute buffered oxide etch solutions that were only slightly higher than the etch rate of a wet thermal SiO_2 oxide film. SiO_2 EE-ALD should be useful to deposit high quality SiO_2 films on insulating and conducting substrates for various applications at low temperatures.

2:15pm **AF1-TuA-4 ALD of Transition Metal Chalcogenide TaS_X Using TBTDMT Precursor and H_2S Plasma***, **Sanne Deijkers**, H. Thepass,* Eindhoven University of Technology, The Netherlands*; H. Sprey, J. Maes,* ASM Belgium*; E. Kessels, A. Mackus,* Eindhoven University of Technology, The Netherlands

Tantalum sulfide (TaS_x) is a transition metal chalcogenide (TMC) with applications ranging from optical switches and Cu diffusion barriers to quantum dots [1–3]. Currently, synthesis of TaS_x is done by mechanical exfoliation, chemical vapor deposition, or sulfurization processes. These processes lack control over the growth, are performed at relatively high temperatures, and/or are not suitable for large-scale processing, in contrast to the synthesis method of atomic layer deposition (ALD).

In this study, we have developed a plasma-enhanced ALD process of TaS_x using tert-butyliminotrisdimethylaminotantalum (TBTDMT) as Ta precursor and an H_2S plasma as co-reactant. Our ALD process of TaS_x is the first to be reported in literature. Films of TaS_x were grown on thermal SiO_2 in an Oxford Instruments FlexALreactor equipped with a remote inductively coupled plasma source. Growth of the TaS_x films has been monitored with in situ spectroscopic ellipsometry and shows a linear growth at the temperature range 150-300°C. Evaluation of the precursor dose shows slight soft-saturating behavior, requiring relatively long precursor dose times (20 s). Furthermore, the plasma dose saturates after 10 s. The resulting growth per cycle (GPC) at 300°C is 1.2 Å.

The TaS_x films have been investigated by x-ray photoelectron spectroscopy (XPS), and the results show that ALD TaS_x films contain minor carbon contamination (< 2%), are only slightly oxidized and have a Ta:S ratio of 1:2.9. Furthermore, the films have been investigated by Raman spectroscopy, x-ray diffraction and scanning electron microscopy.

22. Perfetti, L. *et al.* Time evolution of the electronic structure of 1T-TaS2 through the insulator-metal transition. *Phys. Rev. Lett.***97**, 1–4 (2006).
23. Lo, C. L. *et al.* Enhancing Interconnect Reliability and Performance by Converting Tantalum to 2D Layered Tantalum Sulfide at Low Temperature. *Adv. Mater.***31**, 1–10 (2019).

24. Zhou, L. *et al.* Tantalum disulfide quantum dots: preparation, structure, and properties. *Nanoscale Res. Lett.* **15**, 1–8 (2020).

2:30pm **AF1-TuA-5 High Deposition Rate NbN and TiN for Superconducting Resonators for Quantum Devices by PEALD***, **Louise Bailey**, D. Besprozvannyy,* Oxford Instruments Plasma Technology, UK*; R. Renzas,* Oxford Instruments Plasma Technology*; H. Knoops,* Oxford Instruments Plasma Technology, Netherlands*; M. Powell,* Oxford Instruments Plasma Technology, UK

In recent years, plasma ALD has become a relevant technique in the field of nanoscale fabrication, including high-volume manufacturing, due to its self-limiting precursor behaviour and low temperature operation regimes. ALD is often limited to ultra-thin films, however, due to slow deposition rates. High-rate ALD is a practical necessity for the widespread adoption of ALD for many applications where film thicknesses in the 50-200 nm range are required. Superconducting quantum devices are one of these applications. These devices are comprised of superconducting resonators coupled to qubits. The operational frequency of the resonator is set by its geometry, but can be shifted undesirably by kinetic inductance effects, which depend on thickness. It is necessary to ensure that the superconducting resonator is thick enough to minimize the effect of kinetic inductance - typically by depositing 50-100 nm of material. Presently, these resonators are typically fabricated by sputtering, but sputtering has failed to meet other device needs, such as low loss at the superconductor-air interface and reproducibility of challenging nitrides. The challenge is to deliver fast processes while maintaining the desired film properties.

Here, we will share our recent development of high-quality superconducting NbN and TiN for quantum applications, such as resonators and interconnects, deposited at rates > 25 nm/hour, which is approximately 3x faster than previously reported. The RF-driven remote plasma source design and chamber of our ALD system are optimized to enable this high deposition rate.

The quality of the deposited films was demonstrated to be excellent, as measured by four-point probe electrical resistivity, conformality, and superconducting transition temperature (T_c). Good superconductive properties of the film were demonstrated by SQUID measurement. Thickness uniformity of < ±5% across a 150 mm Si wafer was achieved with good repeatability. We will also show how stress can be tuned as a function of process parameters.

Emerging quantum technologies based on superconducting nitride materials are showing great promise and will benefit not only from the uniformity of the deposition, conformality and film quality, but also from the speed and control provided by this ALD process.

2:45pm **AF1-TuA-6 Black TiO_2 Synthesized using Plasma-Enhanced Atomic Layer Deposition (PEALD)***, S. Berriel, **Terrick McNealy-James**, B. Butkus, T. Currie, C. Chen, L. Shultz, C. Feit, K. Davis, T. Jurca, P. Banerjee,* University of Central Florida

Black TiO_2 is a name given to TiO_2 in its heavily reduced state. This unique form of TiO_2 is characterized by its black color and optical absorbance from UV to infrared spectrum. Accordingly, black TiO_2 has been used as a light absorbing layer in solar cells, catalyst for H_2 generation and for the removal of environmental contamination. To date, black TiO_2 has been synthesized in various form factors such as single-phase nanoparticles using hydrogen thermal treatment, core-shell nanoparticles using high-pressure hydrogen treatment, and thin films using ambient hydrogen-nitrogen treatment of TiO_2 films. However, very little has been reported on ALD of black TiO_2 till date.

In this paper, we report on the synthesis of black TiO_2 using plasma enhanced atomic layer deposition (PEALD) deposited using alternate pulses of titanium tetraisopropoxide (TTIP) and Ar/H_2 plasma. The PEALD process was conducted at 200°C with a remote plasma and a TTIP temperature of 80°C. The films were characterized using *in situ* spectroscopic ellipsometry, four-point probe resistivity, UV-vis spectrometry, x-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM).

Our data shows a higher growth rate for this PEALD process than for thermal ALD using TTIP, ~0.2 Å/cy and ~0.12 Å/cy respectively. Further, we find that black TiO_2 produced via PEALD is a conducting film. The utility of these films is assessed i) as carrier-selective contacts in Si solar cells and, ii) as photocatalysts for studying model dye degradation.

3:00pm **AF1-TuA-7 Optimizing for the Neutral Radicals in Plasma Enhanced ALD***, **Lauren Otto**,* Laminera

ALD has long been an enabler of cutting edge silicon technologies but is not without its issues. Ammonia used in thermal ALD of TiN causes leakage issues with DRAM capacitors. Thermal ALD films have higher impurities and high resistivities, and thermal ALD requires processing at high wafer temperatures (≥400ºC). PEALD was developed to reduce processing temperatures, but ions in PEALD are aggressive reactants and often damaging during film growth like in 3D NAND gate formation with ALD TiN and CVD/ALD W. Plasma damage from ions, electrons, and photons can be an issue in traditional capacitively coupled plasmas (CCPs) as well as inductively coupled plasmas (ICPs) and can cause unwanted local electric fields, charge traps, surface roughening, contamination, and further issues. Neutral radical species are "gentler" reactants than their ionic counterparts and can mitigate issues in traditional ALD and PEALD while maintaining lower temperature deposition. At Laminera, we have worked with a neutral radical source (Mantis Deposition MATS30) to mitigate issues from plasma damage and developed a novel ALD vacuum system designed specifically for working with the mean free path limited (as they are likely to recombine upon close approach) neutral radicals. This talk will cover the science behind working with and designing for the neutral radicals, designing and commissioning a vacuum system for ALD with neutral radicals, initial characterization of TiN deposited using the neutral radical source, and next steps for further technology development and improvement.

ALD Fundamentals
Room Grand Ballroom E-G - Session AF2-TuA
Novel ALD Processing

Moderators: Agnieszka Kurek, Oxford Instruments Plasma Technology, Netherlands, Dr. Matthias Minjauw, Ghent University, Belgium

4:00pm **AF2-TuA-11 Electron-Enhanced ALD and CVD at Low Temperature Using Reactive Background Gas***, Z. Sobell, S. George, **Andrew S. Cavanagh**,* University of Colorado at Boulder

Electron-enhanced atomic layer deposition (EE-ALD) was utilized for the growth of TiN, TiO_2, and TiCN films at T < 70 °C. EE-ALD was employed with a reactive background gas (RBG) present concurrently during the EE-ALD process (Figure 1). Three Ti-based films were all grown using sequential exposures of tetrakis(dimethylamido) titanium (TDMAT) precursor and electrons together with the continuous presence of RBG. The three RBGs utilized to tune the film composition were ammonia (NH_3), oxygen (O_2), and methane (CH_4).

TiN EE-ALD was performed at T < 70°C using TDMAT together with an NH_3 RBG at a pressure of ~1 mTorr. NH_3 is believed to interact with the electron beam and liberate •H and •NH_x radicals. The •NH_x radicals may facilitate Ti nitridation and C removal from the film. The TiN films nucleated rapidly and displayed purities of > 96% and ultralow resistivities of < 120 µΩ-cm. These films may be useful as diffusion barriers in backend interconnects.

TiO_2 EE-ALD was performed at T < 70 °C using TDMAT together with an O_2 RBG at ~1 mTorr. O_2 is believed to interact with the low energy electron beam, creating •O radicals which add oxygen to form TiO_2 and remove any N and C from the TDMAT precursor. XPS showed no detectable C or N in the TiO_2 films and a slightly O-rich stoichiometry. Oxygen-rich TiO_2 films may be more photochemically active due to bandgap narrowing and may be useful in photocatalysis. TiCN EE-ALD was also deposited at T < 70 °C using TDMAT together with a CH_4 RBG at a pressure of ~0.2 mTorr. The TiCN films were C-rich, with a stoichiometry of $Ti_{1.6}N_1C_{4.3}$ as measured by XPS after surface sputtering. TiCN is a promising amorphous diffusion barrier for back-end interconnects.

Electron-Enhanced chemical vapor deposition (EE-CVD) was also used to deposit WN and SiC films at T < 100 °C. EE-CVD films were grown by pulsing the precursor with the electrons and RBG present continuously during the deposition (Figure 2). EE-CVD offers enhanced growth rates for some systems compared with EE-ALD. WN EE-CVD was performed at T< 100 °C using $W(CO)_6$ with NH_3 RBG present at a pressure of ~1 mTorr. The WN films were free from C and O by XPS after surface sputtering. The WN EE-CVD films also displayed a low resistivity of 468 µΩ-cm as measured by spectroscopic ellipsometry. In addition, SiC EE-CVD was demonstrated at T < 100 °C using Si_2H_6 with CH_4 RBG present at a pressure of ~0.45 mTorr. The SiC films were stoichiometric as measured by XPS after surface sputtering with a small (<3%) oxygen signal likely from atmospheric oxidation.

4:15pm **AF2-TuA-12 ALD of Multicomponent Films Using Precursor Co-Dosing**, ***Paul Poodt,*** Eindhoven University of Technology, The Netherlands

A growing number of ALD applications require the deposition of ternary or quarternary compounds. Examples include doped films (e.g. ZnO:Al), mixed oxides to tune dielectric properties (e.g. HfZrO), tunable bandgap materials for solar cells (e.g. ZnOS-) or opto-electronic materials (e.g. InGaN), and high mobility oxide semiconductors (e.g. InGaZnO). A common method to deposit multicomponent films in ALD is the supercycle approach [1], where sub-cycles of different binary compounds are combined to deposit films where the resulting net composition is determined by the cycle ratio of the individual sub-cycles. A drawback of the supercycle method is that essentially multilayer stacks are deposited instead of true alloys and the film composition varies out-of-plane, potentially impacting film properties.

An alternative method is to use precursor co-dosing, where two or more precursors are simultaneously dosed and co-adsorb during a half-reaction. The resulting film composition is then determined by the ratio of the partial pressures of the individual precursors during the precursor dose. As each ALD cycle deposits a true alloy, it results in excellent out-of-plane compositional uniformity. The co-dosing method has first been reported in the late 1980's to deposit ternary and quarternary III-V compounds [2] and has been used since for a wide range of materials. In the last decade it has become the method of choice for depositing multicomponent materials with Spatial ALD.

A proper understanding of the relation between film composition and precursor partial pressure during co-dosing is essential for accurate control of the film composition. This is not straightforward, as the surface chemistry of co-dosing can be quite complex, involving competitive adsorption, heterogeneity of reactive sites, exchange reactions and more. We willdiscuss how the surface chemistry of precursor co-dosing determines the film composition. In analogy to the IUPAC classification of adsorption isotherms for single adsorbents [3], we will introduce a similar classification of adsorption isotherms for multiple absorbing precursors which we will use to review and explain results reported in literature. Finally, we will discuss some interesting new opportunities for co-dosing, such as the deposition of gradient composition films and the use of co-dosing for area-selective deposition.

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[3]: M. Thommes et al, Pure & Appl. Chem. 87 (2015) 87

4:30pm **AF2-TuA-13 Controlling the Nucleation and Growth in Atomic Layer Deposition of Ruthenium: The Role of Surface Diffusion**, ***Amnon Rothman,*** *A. Werbrouck, S. Bent,* Stanford University

Atomic layer deposition (ALD) of noble metals has gained significant attention due to its potential uses in areas such as microelectronics, catalysis, and nanotechnology applications. Ruthenium is an attractive noble metal due to its beneficial physical properties, including low bulk resistivity and high work function, making it suitable for catalysis and integrated-circuit applications such as capacitor electrodes for dynamic random-access memories (DRAM). However, due to an island growth mechanism and nanoparticle formation, forming continuous and pinhole-free layers from Ru metal ALD on oxide surfaces can be difficult, leading to poor-quality films. These nonidealities are mainly due to the poor wettability of these low-surface energy surfaces and the lack of nucleation sites on the oxide substrate. In order to maximize the potential of ALD, it is important to fully understand the nucleation and growth mechanism of the ALD process and to develop ways by which nucleation can be enhanced.

In this work, we study the nucleation enhancement of ALD ruthenium layers on silicon substrates by using single organometallic monolayers, with and without H_2O exposure, prior to deposition. The resulting nucleation and growth mechanism is studied using scanning electron microscopy (SEM), ellipsometry, and X-ray photoelectron spectroscopy (XPS) on the treated and untreated substrates. Ru ALD nucleation enhancement is observed after the different types of pre-treatments. Unlike previous studies that relate the enhancement mechanism to a ligand exchange reaction between the chemisorbed organometallic molecules and the gaseous metal precursor, the current study relates the enhancement to other atomistic processes such as surface-diffusion of adatom and nanoparticle nucleation, diffusion, and coalescence. A model based on the Avrami nucleation and growth equation is fitted to the experimental results, pointing to the possible growth enhancement mechanism, which we hypothesize to be an increase in the surface diffusivity of nanoparticles/adatoms on the pretreated surface. Understanding the enhancement mechanism by pretreatment with organometallic molecules introduces a potential route to achieve improved nucleation and growth of ultrathin films.

4:45pm **AF2-TuA-14 Combining Atomic Layer Deposition Routes and Solvothermal Conversion: Towards Access to Layer Stacking of Porphyrin-Based Mofs**, *B. Gikonyo,* ***Catherine Marichy,*** *S. Forel, A. Fateeva,* Laboratoire des Multimatériaux et Interfaces, CNRS/Université Claude Bernard Lyon 1, France

Metal-organic frameworks (MOFs) have received much attention as promising porous materials with wide range of applications, such as gas storage or separation, catalysis, drug delivery, or electrochemistry. In the latter field, porphyrin-based MOFs are attractive as for fuel cells, and electrocatalysis.[1] For real breakthroughs, fine-tuning of their structure and thus physico-chemical properties with high precision is required. In particular, incorporating metals into the tetrapyrrolic core has proven effective to impart new functionality such as optical properties and electrocatalytic activity. Besides, to integrate these hybrid materials into microelectronic devices, thin films are needed. In these regards, atomic layer deposition (ALD) based approaches are highly promising. Combining ALD of metal oxide with its solvothermal conversion into MOF has proven to be an efficient route that allows fabricating MOF layers on various substrates.[2,3] Furthermore, vapor phase infiltration (VPI) is an elegant post-synthesis modification path for tuning MOF properties while preserving the network structure. VPI has been demonstrated enabling the insertion of metal cation into mesoporous and microporous MOFs.[4,5,6] Herein, ALD and VPI along with solution-based synthesis are implemented to fabricate functionalized porphyrin-based MOF films on FTO and Si substrates. Particular attention is given to the fabrication of layer stacking of MOFs. Briefly, Al-PMOF[7] thin films are first fabricated by the solvothermal conversion of an ALD grown Al_2O_3 seed layer, as previously reported.[2] Then, using a single precursor, isolated metallic entities are installed by VPI in the porphyrinic core, modifying the optical properties of the MOF thin film. A second metal oxide deposition and conversion step leads to a stacking of porphyrinic MOF films with different composition and optical properties. The obtained Al-PMOF, modified-Al PMOF layers and bilayers are characterized in terms of morphology, composition, structure and optical properties. In particular, UV-Visible and photoluminescence spectroscopies permit monitoring the different fabrication steps. By adjusting the ligand and the metal inserted into the MOF core, tunable stacking of various porphyrin-based MOFs is expected accessible.

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5:00pm **AF2-TuA-15 Crystal Phase Transition of Atomic Layer Deposited Antimony Telluride Thin Films with Thickness and Substrate-Dependent Orientations**, ***Sangyoon Lee,*** *J. Seo, I. Sohn,* Yonsei University, Korea; *Y. Kang, C. Lee, W. Yang,* Samsung Advanced Institute of Technology, Republic of Korea; *S. Chung, H. Kim,* Yonsei University, Korea

With the advances for the vertical-NAND flash memories, phase-change memory (PCM) has attracted enormous interests as one of the next-generation storage-class memory, combined with ALD technologies.[1] In general, the PCMs are composed of complex chalcogenide alloys which can be tuned by ternary or quaternary alloys such as Ge-Sb-Te (GST).[2] Among chalcogenides for PCMs, antimony telluride (Sb_2Te_3) has been considered as a candidate with a high crystallization speed. While it is the basic component of the GST, Sb_2Te_3 has received relatively less attention due to its low thermal stability and electrical resistivity. However, in recent years, the stacking and forming heterostructures composed of chalcogenides including Sb_2Te_3 has been found to have huge potential as PCM.[3] Since the out-of-plane orientations of heterostructured layers is important, the atomic-scale observation of film growth and crystallinity formation of Sb_2Te_3 is required, including substrate dependency. Though, most of studies have focused on the formation of GST alloys, not the growth of ALD Sb_2Te_3 itself. Herein, we aimed to investigate the atomic-scale thin film growth and phase transition of ALD Sb_2Te_3 thin films. Comparatively, thin film growth modes of ALD Sb_2Te_3 on amorphous and crystalline substrates were studied by observing transformation of crystal structures. On SiO_2, predominant amorphous phases at initial growth stage were observed, followed by

polycrystalline island growth with randomly oriented grains. However, on crystalline W, the highly out-of-plane (00l) orientations and layer-by-layer growth was found. Furthermore, the consequent changes in electrical resistivity of ALD Sb_2Te_3 were observed to examine the correlations with substrate-dependent film orientations. We anticipate that this work can contribute to understanding of atomic-scale growth of ALD Sb_2Te_3 thin films, which will be utilized in a wide range of applications.

Acknowledgement

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5:15pm **AF2-TuA-16 Molecular Layer Deposition as a Strategy to Direct Polymer Adsorption and Crystallization***, **Maurice Brogly**, S. Bistac, D. Bindel,* Université de Haute Alsace, France

Deposition of dedicated organic molecules on a substrate appears as an efficient strategy to control its surface properties of the substrate such as wettability or surface reactivity. These modified surfaces have many applications in polymer coatings, hybrid or composite materials as they contribute to improve polymer adsorption and adhesion onto the modified substrate. Thiol or silane based organic molecules are good candidate as they self-assemble after deposition from solution. An understanding of the mechanisms governing the growth and structure of this thin organic layer is a major step forward for optimal performance of the resulting coating, hybrid or composite material. This study focuses on the adsorption and grafting from solution of such self-assembling monolayer (SAM) on various substrates (Au, Al). Main objectives are to understand how SAM molecules absorb and bond to metallic substrates, how they organize to form SAM, and how their tail functional group direct polymer adsorption and crystallization. The characterization techniques used were wettability to access surface energy of the substrates before and after grafting, atomic force microscopy (AFM) to characterize the morphology of the organic thin layer formed, and polarization modulation infrared spectroscopy in reflection mode (PM-IRRAS) to access the molecular orientation of the adsorbed molecules. This study contributes first to understand the mechanisms that govern adsorption, growth, and structuration of these molecular layer on metal substrates. As an example, it's shown that the tilt angle of the grafted molecule depends on the nature of the substrate, but mainly on the nature of the anchoring group functionalities. In a second step homopolymers and copolymers were spin-coated on these modified metal substrates. The influence of the surface chemistry of the substrate on the organization and structuration of homopolymers and copolymers of different compositions was then studied. Chains orientations and conformations as well as surface morphologies were thus characterized in order to understand the competition between polymer/polymer and polymer/substrate interactions, which will have a direct effect on the crystallization. This was explained by changes in the balance of polymer/polymer vs polymer/substrate interactions as the surface chemistry of the substrate drives the balance between these interactions.

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5:30pm **AF2-TuA-17 Optical Monitoring of $MoCl_5$ Delivery for Atomic Layer Deposition Applications***, **Berc Kalanyan**, E. Jahrman, J. Maslar,* National Institute of Standards and Technology

Vapor phase deposition of molybdenum films using fluorine-free precursors is desirable for fabrication of interconnects in transistor and flash memory structures. ALD is well-suited to this task due to its low thermal budget and high conformality, enabling its integration into back-end processing. The reduction of molybdenum pentachloride ($MoCl_5$) with hydrogen is one of several known methods to deposit metallic Mo films[1,2]. While $MoCl_5$ is attractive for deposition applications, it is a low-volatility solid under typical delivery conditions and readily forms volatile oxychlorides upon exposure to trace moisture. The challenges associated with achieving sufficient $MoCl_5$ flux are reflected in the literature by a wide range of vessel temperatures used for nominally the same deposition chemistry (e.g., 70 °C to 210 °C for MoS_2 ALD[3,4]). Further, the potential existence of oxychlorides in the vapor phase is problematic because those species are reactive toward surfaces and can serve as precursors for film deposition[2,5]. An additional complexity is the tendency of $MoCl_5$ to etch Mo and Mo-containing films[6]. Therefore, a detailed understanding of $MoCl_5$ deposition behavior requires *in situ* measurement of the partial pressures of $MoCl_5$ and reactive impurities such as $MoOCl_4$.

To address this need, we employed direct absorption measurements to monitor the partial pressure and delivery rates of $MoCl_5$ as a function of operating conditions typical for ALD. We first measured quantitative vapor phase spectra of neat $MoCl_5$, $MoOCl_4$, and MoO_2Cl_2 using an ultraviolet-visible (UV-vis) spectrometer under static conditions. We evaluated the stability of the compounds in the optical cell and in the ampoule headspace using a large number of replicate measurements and peak fitting. We used spectral fingerprints for $MoCl_5$ and $MoOCl_4$ to design in-line non-dispersive gas analyzers with selectivity toward each species. Gas analyzers consisted of a broadband source, filters for wavelength selection, and avalanche photodiodes. Using results from these measurements, we will present on the reproducibility of $MoCl_5$ delivery rates, sensitivity to $MoOCl_4$ contamination, and precursor aging. Potential implications for deposition applications will also be discussed.

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Atomic Layer Etching
Room Grand Ballroom A-C - Session ALE1-TuA

Plasma and Energy-Enhanced ALE

Moderators: Paul Abel, Tokyo Electron America, Inc., Dr. Dmitry Suyatin, Lund University

1:30pm **ALE1-TuA-1 In-Situ Analysis of Surface Reactions on Thin Films in Plasma-Assisted Thermal-Cyclic Atomic Layer Etching***, **Kazunori Shinoda**, N. Miyoshi, H. Kobayashi,* Hitachi, Ltd., Japan*; M. Izawa,* Hitachi High-Tech Corp., Japan*; K. Ishikawa, M. Hori,* Nagoya University, Japan **INVITED**

Isotropic atomic layer etching (ALE) is a conformal etching technique based on the sequential reactions of surface modification and desorption of the modified surface. Isotropic ALE may play a significant role in the manufacturing of next-generation 3D devices such as lateral gate-all-around (LGAA) FETs. Significant efforts are currently underway to develop and commercialize isotropic ALE for various thin-film materials utilized in semiconductor device manufacturing. The authors have developed a new approach for isotropic ALE called plasma-assisted thermal-cyclic ALE, which is based on the cycles of plasma exposure for surface modification and infrared heating for fast desorption of the modified surface. This approach offers a high degree of controllability in material selectivity because it uses two different temperatures for the modification step and desorption step. For example, the selectivity of W and TiN can be changed from highly selective to nonselective by tuning the infrared heating time, since heating at low temperature results in desorption of only the modified surface of W while heating at high temperature results in the desorption of the modified layers of both W and TiN. The two key reactions of plasma-assisted thermal-cyclic ALE are the formation and desorption of ammonium salt-based modified layers on nitride films. Conformal selective ALE of Si_3N_4 and TiN has been demonstrated by utilizing the ammonium salt-based reactions with hydrofluorocarbon-based plasmas. Highly selective ALE of nitride films over other films such as SiO_2 and poly-Si can be obtained because ammonium salt-based modified layers form only on nitride films. Selective ALE of SiGe over Ge was also demonstrated by using nitrogen-containing hydrofluorocarbon-based plasmas. One possible mechanism of the ALE of SiGe is the formation of an ammonium salt-based modified layer on SiGe. A new 300-mm etching tool, dry chemical removal (DCR), that features an inductively coupled plasma (ICP) source and infrared lamps, has been

developed to enable rapid thermal-cyclic reactions. Selective ALE of a variety of materials including Si_3N_4, SiO_2, TiN, W, Co, and SiGe is possible using the DCR tool. This paper reviews the development of plasma-assisted thermal-cyclic ALE, places this development in the historical context, provides detailed information on surface reactions during ALE by *in-situ* x-ray photoelectron spectroscopy, clarifies the effects of surface oxides on surface reactions, and reports the latest results for atomic layer reactions on TaN.

2:00pm **ALE1-TuA-3 Isotropic Atomic Layer Etching Process for HfO_2 Film**, *J. Kwon, C. Kim,* ***Byung Chul Cho****, J. Park, S. Park, J. Chun,* Semiconductor R&D Center, WONIK IPS Co., Ltd., Republic of Korea

The atomic layer etching (ALE) process is a sub-nanometer scale removal technique base on sequential, self-limiting surface reactions.[1,2] In this study, we developed a cyclic isotropic plasma ALE process that involves fluorination with NF3 plasma and ligand exchange with dimethylaluminumchloride (DMAC) for hafnium oxide (HfO_2). The HfO_2 surface is converted to HfOFx by NF3 remote plasma in the fluorination step, and the fluorinated layer is removed by a ligand exchange reaction with DMAC in the removal step. The ALE process was analyzed by ellipsometry, atomic force microscopy, dynamic secondary ion mass spectrometry, transmission electron microscopy, x-ray diffraction. Etching was not observed at 200 °C and was increased from 1.41 Å/cycle to 2.22 Å/cycle as the process temperature increased from 250°C to 300°C. Isotropic removal of HfO2 thin films was observed on the trench patterns with an aspect ratio of >15. In addition, the ALE process decreased the surface roughness of the HfO2 thin films.

2:15pm **ALE1-TuA-4 Thermal Atomic Layer Etching of CoO by an "Oxidation-Reduction" Mechanism Using Sequential Reactions of Ozone and Acetylacetone**, ***Aziz Abdulagatov****, J. Partridge,* University of Colorado at Boulder*; V. Sharma,* ASM Microchemistry Ltd., Finland*; J. Murdzek, A. Cavanagh, S. George,* University of Colorado at Boulder

Thermal atomic layer etching (ALE) of CoO was demonstrated using sequential exposures of ozone (O_3) and acetylacetone ($CH_3COCH_2COCH_3$, Hacac). Hacac can form volatile $Co(acac)_2$ complexes. Ozone was employed to remove carbon residue resulting from Hacac adsorption. *In situ* spectroscopic ellipsometry (SE) observed a linear decrease in CoO film thickness versus O_3 and Hacac exposures with etch rates of 0.09 and 0.43 Å/cycle at 200 and 250 °C, respectively. The O_3 and Hacac surface reactions were also found to be self-limiting.

The sequential O_3 and Hacac exposures were also observed to cause changes in oxidation state and crystal structure. X-ray diffraction (XRD) analysis of the as-deposited CoO thin films showed mostly hexagonal crystal structure. After O_3 exposures, XRD studies observed that hexagonal CoO was oxidized to cubic Co_3O_4. After ALE ending with Hacac exposure, XRD analysis also showed that the film was converted to cubic CoO. These XRD results indicate that Hacac can reduce Co_3O_4 back to CoO. In agreement with the thin film studies, XRD studies on Co_3O_4 powder observed the reduction of cubic Co_3O_4 to cubic CoO after Hacac exposures. X-ray photoelectron spectroscopy (XPS) analysis was also consistent with oxidation of CoO to Co_3O_4 by O_3 and the reduction of Co_3O_4 back to CoO by Hacac.

Quadrupole mass spectrometry (QMS) measurements observed $Co(acac)_2$ etch products during the Hacac exposures on CoO or Co_3O_4 powder. The observation of combustion products, such as CO_2 and H_2O, during Hacac exposures on Co_3O_4 powder was also consistent with the reduction of Co_3O_4 to CoO. The XRD, XPS and QMS results reveal alternating oxidation and reduction reactions during the O_3 and Hacac exposures that define this CoO thermal ALE process. The sequential reactant exposures that result in volatile release of $Co(acac)_2$ etch products occur concurrently with changes in the oxidation state and crystal structure of the underlying cobalt oxide.

2:30pm **ALE1-TuA-5 Surface Modification with Neutral Gas Cluster Beams and Its Application to Atomic Layer Etching**, ***Noriaki Toyoda****, H. Tanaka, M. Takeuchi,* University of Hyogo, Japan

We have reported that halogen-free ALE can be performed on various metal films at room temperature using gas cluster ion beams (GCIB) and organic acids. However, GCIB system requires large vacuum pumps and high voltage power supplies. Even worse, throughput of GCIBs is relatively low, which limits the variety of applications.

We investigated the possibility of ALE using neutral cluster beams. Neutral cluster beams have a simple apparatus configuration and can be expected to enhance surface reactions by directional energy beams (total energy of about several hundred eV). In this study, the surface condition after neutral cluster beam irradiation was evaluated by XPS, and the etching depth after pseudo-ALE was investigated.

First, Ni film surface was cleaned by 500 eV Ar^+ irradiation, and then the substrate was irradiated with a neutral O_2 cluster beam for 300 s at a substrate temperature of 150 °C. After irradiation, the results were evaluated by XPS. NiO peak appeared around 860 eV in the Ni film on the O_2 cluster beam axis. On the other hand, NiO is not formed in the Ni film not irradiated by O_2 cluster beam, and Ni oxidation does not occur with residual oxygen. This indicates that the Ni oxide film can be formed by neutral O_2 cluster beam irradiation at a temperature where oxidation by the residual oxygen gas not occur.

Quasi-ALEs were performed by repeating O_2 neutral cluster beam irradiation on Ni films at 150°C and subsequent oxide film removal with acetic acid. At the on-axis position of O_2 neutral cluster beam, EPC was 1.6 nm. On the other hand, there was no measurable etching depth for the Ni film located at off-axis position. These results indicates that neutral cluster beam irradiation can be used for novel method for directional ALE.

2:45pm **ALE1-TuA-6 Development Plasma-Based Atomic Layer Etching of Zinc Oxide by Using Tetrafluoromethane Plasma and Dimethylaluminum Chloride**, ***Chien-Wei Chen****, C. Chang,* Taiwan Instrument Research Institute, National Applied Research Laboratories, Taiwan*; Y. Jhang,* Taiwan Instrument Research Institute, National Applied Research Laboratories, Hsinchu, Taiwan

In recent years, atomic layer etching (ALE) has been proposed to be introduced into advanced semiconductor processes, especially in gate-all-around (GAA) or nano-sheet FET structures, due to its precision control and high selective ratio etching characteristics. Therefore, ALE processes for various thin-film materials are being developed with great enthusiasm. In this study, we achieved plasma ALE verification of ZnO thin films using tetrafluoromethane (CF_4) plasma and dimethylaluminum chloride (DMAC) as the precursors. The entire ALE reaction was performed on a 6" cluster ALE system (Fig.1) developed by Taiwan Instrument Research Institute (TIRI). We first deposited about 87 nm thick polycrystalline ZnO films with ALD at 200°C, and then performed a total of 50 fluorinations of the ZnO films with a remote CF_4 plasma at a frequency of 10 s/cycle, and then performed *in-situ* XPS analysis. From Fig. 2a, it can be seen that the peak of Zn 2p 3/2 shifts from 1023.8 eV (Zn-O) to the stronger binding energy of 1024.4 eV (Zn-F) on the surface of the ZnO film after treated with CF_4 plasma, and a significant F1s signal appears (Fig. 2b). After confirming that the CF_4 plasma could achieve the ZnO surface fluorination modification, we added DMAC for the fluoride removal half-reaction. The complete process sequence was first to pass CF_4 gas to stabilize the chamber pressure at 0.5 Torr, then 50 W RF power was applying to trigger CF_4 plasma for 10 s, followed by passing LN_2 to remove the residual CF_4 gas, and then passing DMAC to remove the fluoride on the surface of ZnO film. DMAC is then passed through the chamber to purge the residual CF_4 gas, followed by DMAC pulsing for 0.1 s and soaking for 1 s to remove the volatile fluoride formed on the ZnO surface, and finally LN_2 is passed through to remove the residual DMAC to complete a complete ALE cycle. We also established the etching curve of ZnO ALE in Fig. 3, and it can be estimated that the etching per cycle (EPC) of ZnO ALE at 400°C is about 5.5 Å. In addition, we also observed in the subsequent TEM image analysis that the etched polycrystalline ZnO films in this ALE method will form porous ZnO films after a certain number of ALE cycles, which is presumed to be related to the crystal boundary of ZnO, and we will conduct more research on this characteristic in the future.

3:00pm **ALE1-TuA-7 Resistive Capillary Array Calorimetry Method for ALD and ALE Processes**, ***Anil Mane****, J. Elam,* Argonne National Laboratory, USA **INVITED**

Calorimetry is an essential analytical technique for determining the thermodynamics of chemical reactions. In-situ calorimetry during atomic layer deposition and etching (ALD/ALE) processes would be a valuable tool to probe the surface chemical reactions that yield self-terminating growth and removal of material at the atomic scale. Besides this, in-situ calorimetry would reveal the partitioning of chemical energy between the individual half-reactions that constitute the ALD or ALE cycle. Here we present a calorimetry strategy that utilizes the temperature-induced resistance changes in ALD thin films. Our calorimetry approach utilizes an ALD nanocomposite resistive thin film deposited conformally on the inner surfaces of microcapillary array substrates. These substrates are fabricated using borosilicate glass capillaries, 3D-printing, or through-substrate interposers. The ALD nanocomposite layer has a high resistivity and a well-defined thermal coefficient of resistance (TCR), both of which can be fine-

tuned by adjusting the nanocomposite layer composition via ALD process parameters.

In practice, the resistive capillary array (RCA) calorimeter is installed in the ALD system and electrically biased to produce a current that is recorded in real time. During the ALD/ALE surface reactions, heat exchanged with the coating produces transient current features due to the non-zero TCR of the nanocomposite resistive layer. These transient features are highly reproducible and can be used to calculate the reaction enthalpies of the individual surface reactions based on the TCR value and the thermo-physical properties of the capillary array substrates.

To demonstrate the RCA calorimetry method, we performed in-situ calorimetry measurements for a range of ALD processes including Al_2O_3, AlF_3, $Al_xO_yF_z$, ZnO, MgO, TiO_2, and ZrO_2 as well as ALE processes including Al_2O_3, TiO_2, MoS_2, and HfO_2. We also studied the nucleation behavior when transitioning between ALD processes and from ALD to ALE processes. We find good agreement between reported enthalpy changes for ALD reactions and the values measured by in-situ RCA calorimetry. We believe that RCA calorimetry is a versatile in situ method to study the thermodynamics of ALD/ALE surface reactions and a convenient diagnostic for real-time ALD/ALE process monitoring in a manufacturing environment. Briefly, we will also discuss the challenges and limitations of RCA calorimetry method.

Atomic Layer Etching
Room Grand Ballroom A-C - Session ALE2-TuA

Low-Temperature and SiN ALE

Moderator: Dr. Kazunori Shinoda, Hitachi, Ltd.

4:00pm **ALE2-TuA-11 Atomic Layer Etching at Cryogenic Temperature***, **Thomas Tillocher**, G. Antoun, J. Nos,* GREMI CNRS/Orleans University, France*; C. Cardinaud, A. Girard,* IMN CNRS/Nantes University, France*; P. Lefaucheux, R. Dussart,* GREMI CNRS/Orleans University, France **INVITED**

Atomic Layer Etching (ALE) has been extensively studied for various materials these last years for microelectronic processes where high precision is required. Since cryogenic etching processes show interesting features, such as reduced reactor wall contamination, damage-free etching, enhanced surface residence time, ALE can benefit from cooling the substrate to cryogenic temperature (“Cryo-ALE”). Two approaches for Cryo-ALE have been developed and studied at GREMI for SiO_2, Si and Si_3N_4 and are presented in this paper.

Typically, ALE of SiO_2 is performed at room temperature and involves a C_4F_8 plasma in the modification step, which leads to some fluorocarbon deposition on the reactor walls, and eventually to process drifts. This can be addressed by flowing C_4F_8 in gas phase above the SiO_2 substrate cooled at cryogenic temperature. Under such conditions, species are physisorbed only at the cooled surface and therefore, wall pollution is suppressed. It is shown that repeating cycles of a C_4F_8 physisorption step followed by an Ar plasma with low energy ion bombardment, each separated by a purge step, makes it possible to sequentially etch SiO_2. Cryo-ALE of SiO_2 using C_4F_8 has proved successful results at -120°C and 3 Pa. However, no etching is observed at -110°C, since C_4F_8 does not significantly physisorb at such a temperature. In this paper, the role of the surface temperature on physisorption and the surface residence time is discussed by means of quasi in-situ XPS, mass spectrometry and in-situ ellipsometry.

In the second process presented in this paper, C_4F_8 physisorption is replaced by a SiF_4/O_2 plasma, with the substrate still cooled at low temperature. A SiO_xF_y layer is deposited at each cycle and acts as a fluorine reservoir used to etch the substrate when exposed to a low energy ion bombardment in an Ar plasma. It is shown that the process switches from a deposition regime at room temperature to an etching regime at low temperature. The threshold temperature, which is material dependent (-65°C for Si_3N_4 and -100°C for Si), is related to the deposition of a much thicker and more fluorinated SiO_xF_y layer. Therefore, there is a narrow temperature window in which it is possible to etch Si_3N_4 selectively to Si by ALE. This will be further discussed with in-situ ellipsometry measurements and quasi in-situ XPS analyses.

Acknowledgments: The authors thank K. Maekawa, K. Yamazaki, N. Sato, S. Tahara from TEL for financial support and helpful discussions. This work was also supported by CERTeM platform, which provides most of the equipment, and the CNRS-Réseau des Plasmas Froids for giving access to the Optimist platform.

4:30pm **ALE2-TuA-13 SiO_2 ALE based on High Boiling Point Fluorocarbon Physisorption***, **Dain Sung**, G. Yeom, H. Tak, D. Kim,* Sungkyunkwan University, Republic of Korea

SiO_2 atomic layer etching (ALE) using fluorocarbon plasmas as adsorption process is currently investigated to etch silicon dioxide for self-aligned contact (SAC) etch process of logic devices due to various benefits such as high etch selectivity over silicon nitride, low aspect ratio dependent etching (ARDE), low surface damage, controlled etching, etc.However, for conventional SiO_2 ALE utilizing fluorocarbon plasmas, a drift in etch process through cycles could be induced by chamber contamination caused by dissociated fluorocarbon radicals during the plasma generation. To avoid chamber contamination by fluorocarbon radicals, adsorption of fluorocarbon gases instead of generation of fluorocarbon plasmas by using cryo etching technique is also currently investigated, however, it requires extremely low substrate temperature facilities, etc. To overcome these challenges, ALE based on high boiling point PFC physisorption in low substrate temperature as the fluorocarbon adsorption is proposed as an alternative process. In this study, 100nm Si_3N_4 line masked SiO_2 was etched in an ICP etch system and high boiling point (HBP) PFC was used as a precursor during the physisorption step. When the substrate was cooled at 0°C and -10°C, HBP PFC molecules were adsorbed on SiO_2 and Si_3N_4 because it has boiling point higher than room temperature. After purging step, the etching step is achieved by using Ar plasma with a low energy ion bombardment. After the ALE process, ellipsometry and field emission scanning electron microscopy (FE-SEM) were used to analyze the etch properties such as etch rate, etch selectivity, and etch profiles of SiO_2. Compared to C_4F_8 plasma ALE, physisorption ALE using HBP PFC exhibited higher SiO_2 etch selectivity over Si_3N_4 in addition to no contamination of chamber walls.

4:45pm **ALE2-TuA-14 Cryogenically Cooled, Saturating Quasi-ALE of Silicon Nitride***, **Frank Greer**, D. Shanks, R. Ahmed, J. Femi-Oyetoro, A. Beyer,* Jet Propulsion Laboratory (NASA/JPL)

Silicon Nitride is one of the most important materials used in photonic integrated circuits. Anisotropic Plasma Atomic Layer Etching (ALE) is well known for its inherent advantages of uniform, precise, and smooth etching of materials. These features may make the technique attractive for waveguide etching to reduce sidewall losses. However, there are some important limitations of a truly atomic layer-by-atomic layer etching approach. Waveguides can be ~800nm thick, making sub-nanometer etch rates per cycle (EPC) substantially slower than conventional ICP and RIE etching processes. Although there are reported approaches that enable higher EPC, the process conditions cited are difficult to repeat in a standard ICP etching chamber due to the high process pressures utilized.[1] Additionally, some materials, like silicon nitride, do not have plasma chemistry that naturally divides into saturating reaction and desorption steps with high ALE synergy.[2]

In this work, we have leveraged cryogenic substrate temperatures to dramatically enhance the ALE synergy of silicon nitride etching for films from two different LPCVD silicon nitride deposition recipes. Our cyclic Cryo-ALE process utilizes a simple gas chemistry involving H2, SF6, and Ar where a biased hydrogen implantation dose step creates a chemically modified damage layer, that is removed by a gentle SF6/Ar ICP etch step. ALE synergy dramatically improves as substrate temperature is reduced because cryogenic temperatures largely quench the spontaneous etching caused by fluorine radicals. At 10C, ALE synergy is ~30%, but increases to as high at 70% at -50C. As expected, saturating behavior for EPC is improved in the SF6 step at low temperature. Additionally, cryo-temperatures are accompanied by smoother etched surfaces. As with the previous report for quasi-ALE of silicon nitride, our cryo-ALE process EPC can be controlled precising by tuning the bias voltage of the hydrogen implantation step. Surprisingly, however, despite the high degree of ALE synergy and the nearly identical silicon to nitrogen ratio of the two LPCVD films, the etch profile was very different, showing that the hydrogen content of the as-deposited film and/or the density also plays a role.

These results suggest that the combination of creating a chemically modified damage layer with cryogenic etching temperatures may be a general approach to simultaneously increase EPC and ALE synergy for fluorine-based etching of materials. Opportunities to generalize this approach and silicon nitride device data will also be discussed.

1 Sonam D. Sherpa *and* Alok Ranjan JVST A **35**, 01A102 (2017)

2 Akiko Hirata *et al* 2022 *Jpn. J. Appl. Phys.***61** 066002

5:00pm **ALE2-TuA-15 High Throughput SiN ALE and Its Damage Control***, **Akiko Hirata,*** Sony Semiconductor Solutions Corporation, Japan **INVITED**

The miniaturization of semiconductor devices has almost come to an end, but the combination of 3D devices / 3D structures, miniaturization, and new materials continues to meet market demands. Dry etching technology using plasma is one of the most important processes in achieving this performance improvement. In particular, processing technology at the atomic/molecular level is required to realize device shrinkage and dimensional control of several nm is indispensable for manufacturing cutting-edge devices. Atomic Layer Etching (ALE) can realize high-precision etching, however, has the issue of long processing time. In the conventional ALE (conv.-ALE), the low ion energy is used to realize the self-limited reaction at the atomic level. Self-limiting process means the extremely high-selective etching of a modified layer over the pristine substrate. One ALE cycle consisted of a surface modification step and a removal step of the modified layer. In the modification step, the binding energy in the surface reactive layer is weakened so that it is easier to remove than the bulk. ALE was performed by irradiating Ar ion for a long time.

In this study, we focused on SiN ALE [1]. We verified the feasibility of high-throughput ALE (HT-ALE). To reduce the time, we performed HT-ALE with high ion energy and evaluated the amount of etched SiN. SiN HT-ALE for short time with high ion energy exhibited a quasi-self-limited reaction, which is a characteristic of ALE, and the processing time could be reduced by 1/5th. To further analyze HT-ALE with varying energy in the desorption step, the energy required to remove the reaction layer was calculated. The amount of etching in the reaction layer was determined by the number of Ar ions, incident energy considering IEDF, energy loss in the polymer, and process time. Next, the interface trap density values after conv.-ALE and HT-ALE were performed for damage evaluation. However, HT-ALE using CH_3F in the adsorption step exhibited signs of increased damage due to ion injection with high energy. The HT-ALE has a deeper H penetration depth and a deeper Si damage layer than the conv.-ALE from the surface analysis. Thus, C_4F_8 that does not contain H can significantly reduce the damage, even in HT-ALE conditions. Damage is generated by the knock-on effect of H, which has a small atomic weight. H-less HT-ALE achieves both damage-less and high throughput. To alleviate the issue of long ALE processes, it is important to precisely control the ion energy/flux, process time, and damages.

[1]Hirata, A., Fukasawa, M., Kugimiya, K., Karahashi, K., Hamaguchi, S., Hagimoto, Y., and Iwamoto, H.,*Japanese Journal of Applied Physics* **61**, SI1003 (2022).

5:30pm **ALE2-TuA-17 The Atomic Layer Etching Database: A Valuable Crowd-Sourced Platform for the Community***, N. Chittock, A. Mackus, H. Knoops, B. Macco,* ***Erwin Kessels,*** Eindhoven University of Technology, The Netherlands

In this contribution, we will introduce the ALE database (DOI:10.6100/aledatabase [https://www.atomiclimits.com/aledatabase/]) which is free of charge available on the AtomicLimit.com blog site. It was established after launching the ALD database (DOI: 0.6100/alddatabase [https://www.atomiclimits.com/alddatabase/]) in 2019. The latter has become very popular in academia and in industry and it has appeared in many presentations and publications in recent years. It has also been used as a starting point in review papers, for example by applying data analytics. We hope that a similar thing will happen to the ALE database in order to serve the ALE community.

The ALE database displays all ALE process reported in the literature in the format of the periodic table. It distinguishes between anisotropic ALE processes and isotropic ALE processes. By clicking on an element in the periodic table, a list of materials containing that element is displayed as etched by an ALE process. The etchants species are listed per ALE process and there is also a direct link to the publications in the literature. The ALE database been compiled from the data in the literature and new processes can be added by visitors of the website. This means that it stays up to date by crowd-sourcing. Authors of ALE papers are stimulated to add their ALE processes to the database.

In the presentation, the features of the ALE database will be highlighted and also some scientific trends will be discussed as can be inferred from the data in the ALE database. Also the possibilities for data mining will be addressed and potential future extensions (relying on contributions from the community) will be discussed. The intention is to make the ALE database an even more valuable platform for the ALE community.

Area Selective ALD
Room Regency Ballroom A-C - Session AS1-TuA

Polymers

Moderator: Prof. Han-Bo-Ram Lee, Incheon National University

1:30pm **AS1-TuA-1 The Role of Co-Reactant Reactivity and Surface Passivation During Cu-Doping of NiO ALD***,* ***Matthias Minjauw,*** Ghent University, Belgium*; B. Vermeulen,* Ferroelectric Memory Company, Germany*; A. Illiberi,* ASM, Belgium*; V. Sharma,* ASM Microchemistry Ltd., Finland*; M. Givens,* ASM, Belgium*; J. Dendooven, C. Detavernier,* Ghent University, Belgium

P-type transparent conducting oxides are of high interest for applications in electrocatalysis, optoelectronics, and sensing. Nickel oxide is a viable candidate owing to its chemical stability, wide band gap and excellent transparency in the visual spectrum. However, as for most applications the hole conductivity of NiO is too low, it needs to be increased by doping the NiO with metal cations such as Al, Cu, Co or Zn.[1,2] ALD has proven to be a suitable method for the growth of ultra-thin, precisely doped transition-metal-oxide films on nanostructured devices.
In this work we demonstrate ALD growth of Cu-doped NiO, using the bis(N,N'-di-t-butylacetamidinato)nickel(II) and bis(dimethylamino-2-propoxy)copper(II) precursors. For the $Ni(tBuAMD)_2$-precursor, NiO ALD growth has been demonstrated with H_2O as a co-reactant at 150°C.[2] For the $Cu(dmap)_2$-precursor, using H_2O as the co-reactant at 150°C leads to Cu_2O growth, while using O_3 leads to CuO growth at temperatures of 110°C-175°C.[3] Cu-doped NiO ALD was attempted by combining the two water-based processes in a super-cycle approach. Although the individual NiO and Cu_2O processes display growth rates compatible with literature reports (0.028 and 0.019 nm/cycle resp.), combining both processes in a super-cycle decreases the growth rate significantly (Fig. 1). In vacuo XPS experiments revealed that NiO growth is inhibited on an ALD Cu_2O surface, with negligible deposition even after 145 NiO ALD cycles (Fig. 2). By exposing the Cu_2O to ozone, NiO growth can be initiated from the initial ALD cycles. The effect of this O_3-exposure is two-fold: the Cu_2O is oxidized to CuO, and persistent carbon and nitrogen species are removed from the surface. As exposure of the O_3-treated CuO surface to a single pulse of $Cu(dmap)_2$ blocks NiO growth, but doesn't change the oxidation state of the CuO surface, it must be the $Cu(dmap)_2$ surface ligands themselves that cause the NiO growth inhibition. This is backed up by the fact that there are no ALD NiO literature reports combining $Ni(dmap)_2$ with H_2O. Finally, we demonstrate that Cu-doped NiO ALD growth can be achieved by combining the O_3-based processes in a super-cycle approach, with a growth rate comparable to the growth rates of the unit processes (Fig. 1).

1:45pm **AS1-TuA-2 Elucidating the Role of Functional Groups of Ligands for Selective Metal Blocking via Vapor-Phase Sam Deposition***,* ***Chandan Das,*** Applied Materials Inc., Singapore*; B. Bhuyan,* Applied Materials Inc.*; Z. Li, J. Wu,* National University of Singapore*; J. Sudijono,* Applied Materials Inc., Singapore*; M. Saly,* Applied Materials Inc.

One of the key areas of area-selective atomic layer deposition (AS-ALD) that the industry is looking for, is the development of fully self-aligned vias (FSAV) for BEOL applications in the advanced nodes. The current study demonstrates the development of ligands possessing suitable volatility for vapor phase SAM growth, additionally being selective to the metals and not on dielectrics. While considering selectivity to the metals by specific azide-, and organophosphorus-based head groups, the tail length and head functional groups have been carefully modified as shown in Fig 1 and 2 (ESI), for delivering the ligands to the chamber for vapor phase SAM growth. Out of various ligands, L_n has shown promising selectivity (WCA ~104°) on metals compared to the SiO_2/Si (WCA ~65°) at 200 °C growth temperature [Fig 3, ESI]. The SAM grown samples have further been annealed up to 300 °C in the presence of organometallic precursors to check the stability under deposition conditions. No loss in the WCA indicates promising stability of Ln SAM, which would be a potential candidate for selective deposition at a relatively higher temperature.

2:00pm **AS1-TuA-3 Integrating Area-Selective Ald with Electrohydrodynamic-Jet Printing to Enable Additive Nanomanufacturing***,* ***Tae Cho,*** *N. Farjam, T. Newsom, C. Allemang, R. Peterson, K. Barton, N. Dasgupta,* University of Michigan, Ann Arbor

The demand for customizable micro/nanoscale patterning of functional materials has led to a strong interest in bottom-up manufacturing of electronics. The current state-of-the-art in fabricating functional devices includes multiple deposition and etching steps in a resource-intensive

cleanroom environment. There is yet no universal manufacturing technique that can enable low-cost, high-resolution/quality, and high-throughput additive nanomanufacturing. In this work, we demonstrate the versatility of area-selective ALD with electrohydrodynamic jet (EHD) printing to pattern functional materials and manufacture fully functional devices without the traditional lithographic process.

EHD printing is an additive manufacturing technique which has been previously used to deposit functional materials with solution inks. The printing is performed at atmospheric conditions, and provides an unparalleled combination of high spatial resolution (sub-micron), fast printing speeds, and low cost. However, the materials that can be printed are limited by the solution inks, which are mostly used to print polymers. In this work, we combine EHD printing with ALD in three different manufacturing methods to pattern functional materials: additive and subtractive area-selective ALD (AS-ALD), and acid-based subtractive printing of ALD films. As shown in Scheme 1, ALD films are selectively grown by EHD printing of inhibitors on the surface. We printed polyvinylpyrrolidone (PVP) ink to "passivate" the surface and N-methyl-pyrrolidone (NMP) solvent ink to "activate" the surface towards ALD growth. This enabled additive and subtractive printing with an average linewidth of 312 nm and 9 µm, respectively.

In addition to directly patterning the polymer inhibitors, we also introduce a new subtractive printing process using acid-based inks to directly pattern the metal oxide films deposited by ALD. For this work, we patterned 50 nm thick ZnO ALD by EHD printing acid-based ink to achieve sub-10 µm resolution [2]. Various ink compositions were tested to study the etch and evaporation rates. The printed ALD ZnO features were examined using scanning electron microscopy and atomic force microscopy. Using these integrated techniques, a bottom-gate thin-film transistor (TFT) with an ALD zinc-tin-oxide (ZTO) channel was fabricated without any lithography process [1,3]. This new additive micro/nanomanufacturing platform can enable flexible and customizable patterning of metal oxides without the need for traditional lithography.

2:15pm **AS1-TuA-4 Enhanced ALD Nucleation on Polymeric Separator for Improved Li Batteries***, **Giulio D'Acunto**, S. Shuchi, M. Mattinen, S. Bent,* Stanford University

Lithium batteries are the preferred choice of power sources for portable devices, electric vehicles, and energy storage due to their high energy density. However, despite their widespread use, Li batteries still have several limitations: low thermal stability, limited cycle life, and capacity decay, to name a few. To improve the efficiency of the Li batteries, ongoing research is conducted in several areas, such as battery design and active modification of well-established components. One specific area of focus is the separator, a critical element of all batteries. Its role is to separate the positive and negative electrodes while allowing ion transport.

In this study, separators, which have drawn attention due to their crucial impact on safety and good electrochemical performance, are modified by ALD Al_2O_3 to enhance thermal stability and increase the cycle life of batteries. After optimizing the surface pre-treatment, Al_2O_3 deposition is performed with trimethylaluminum (TMA) and water at 80 ^oC, below the shrinkage temperature of the separator, with a long exposure time and on a custom-made reaction bed, allowing uniform and conformal deposition all around the separator.

A Celgard 2325 separator - polypropylene (PP)/polyethylene (PE)/PP - is modified using different exposure times of UV ozone (UVO) to functionalize the inert carboxyl group. X-ray photoelectron spectroscopy (XPS), water contact angle (WCA), and scanning electron microscopy are used to characterize the membranes and test the effectiveness of the UVO functionalization as well as its role in the nucleation of Al_2O_3. Moreover, electrochemical measurements, such as Li-ion conductivity and long-term cycling tests on Li|Cu half-cells, are performed.

The more hydrophilic nature of the membrane after ozone treatment, which saturates after 4.5±1.0 min of exposure to UVO, is confirmed by XPS and WCA. The thickness of ALD Al_2O_3, with 20% $Al(OH)_3$, strongly correlates to the oxygen content present on the membrane after UVO exposure. The deposition on the polymeric separator also leads to a notably lower growth rate (0.8±0.2 Å/cycle), in contrast to the well-established 1.1 Å/cycle determined on SiO_2.

Overall, we show how a controlled UVO pre-treatment can enhance the growth of ALD Al_2O_3 on the separator. We also show that adding ALD Al_2O_3 can improve battery cycle life. The resistive Al_2O_3 overlayer does not affect the Li-ion conductivity of the separator but improves its thermal stability. This work shows how a readily-accessible treatment can enhance the nucleation and control the deposition of a metal oxide by ALD, opening new possibilities to develop better Li batteries.

2:30pm **AS1-TuA-5 Improved Metal Selectivity via Inherent Orthogonal ASD: Polymer ASD Improves Nucleation Inhibition for Metal ASD***, **Hwan Oh,*** North Carolina State University, Republic of Korea*; H. Margavio,* North Carolina State University*; H. Yang,* North Carolina State University, Republic of Korea*; G. Parsons,* North Carolina State University

Despite recent achievements in area-selective deposition (ASD), the current focus on ASD is limited to single-material ASD. The integration of discrete ASD processes into a sequential process, *i.e.,* multi-material ASD has great potential to provide additional leeway in fabricating semiconductor devices.[1] Specifically, combining organic and inorganic ASD processes in an orthogonal sequence, in which the organic ASD layer can act as a sacrificial layer, can extend the functionalities of individual ASD processes. In this work, we demonstrate a multi-material ASD using individual inherent ASD processes in an orthogonal sequence: 1) poly(3,4-ethylenedioxythiophene) (PEDOT) ASD on SiO_2*vs.* Si-H [2] *via* oxidative chemical vapor deposition (oCVD) using 3,4-ethylenedioxythiophene (EDOT) as a monomer and antimony pentachloride ($SbCl_5$) as an oxidant, and 2) W ASD on Si-H *vs.* SiO_2 [3] *via* atomic layer deposition (ALD) using tungsten hexafluoride (WF_6) and highly diluted silane (2 wt% SiH_4 in Ar). Herein, PEDOT ASD on SiO_2 (*vs.* Si-H) serves as a potential sacrificial layer to inhibit undesired nucleation of W on SiO_2. The cross-sectional scanning transmission electron microscopy (STEM) and energy-dispersive X-ray spectroscopy (EDX) analyses show that without a pre-deposited PEDOT layer on SiO_2, 10 cycles of W ALD result in ~ 7.7 nm of W ASD on Si-H with growth per cycle (GPC) of 7.7 Å/cy, but the formation of undesired W nuclei (*i.e.,* selectivity loss) is also observed on SiO_2 (Figure 1a and 1b). On the other hand, with a pre-deposited PEDOT layer on SiO_2, the same W ALD process leads to similar growth of W ASD on Si-H, but no growth of W is confirmed on SiO_2 (Figure 1c and 1d). This result indicates that pre-deposited PEDOT (first ASD) can improve the selectivity window of W (second ASD) by inhibiting unwanted nucleation of W. This study can be extended to other material pairs or other multi-material configurations. For example, a polymer ASD can be achieved on metal (*vs.* dielectric) for another subsequent ASD of interest, such as low-k ASD on dielectric (*vs.* metal). Overall, weanticipate that multi-material orthogonal ASD canbring a new paradigm to future microelectronics manufacturing beyond sing-material ASD processes.

2:45pm **AS1-TuA-6 Self-Aligned Patterning by Area-Selective Etching of Polymers and ALD***, V. Lasonen, C. Zhang, M. Vehkamäki, A. Vihervaara,* University of Helsinki, Finland*; L. Mester,* attocube systems AG, Germany*; M. Karimi,* AlixLabs AB, Sweden*; Y. Ilarinova,* AlixLabs, Sweden*; R. Jafari Jam, J. Sundqvist,* AlixLabs AB, Sweden*; **Mikko Ritala,*** University of Helsinki, Finland

We have recently presented area-selective etching of polymers as a new approach for self-aligned thin film patterning [1]. The area-selective etching is based on different catalytic properties of surfaces under the polymer film being patterned. When annealed at a proper temperature in presence of a proper etching gas, the polymer is decomposed away from catalytically active surfaces whereas on catalytically inactive surfaces the polymer remains. The process is made possible by the small etching gas molecules (O_2 and H_2) being able to diffuse through the polymer layer and become activated by the catalytic surface. With some catalyst - polymer combinations no etching gas is needed as the polymer decomposition occurs by catalytic thermal cracking.After the self-aligned patterning of the polymer, it may remain as part of the device or, more likely, used as the growth directing template in various deposition processes, such as area-selective ALD and CVD, and line-of-sight PVD followed by lift-off.

A critical question is how accurate line edges can be made with the area-selective etching process. An obvious concern is that spill-over of activated etching gas atoms or polymer flow can blur the interface between the decomposed and non-decomposed polymer area. In this research we have explored the capabilities of the method by using about 100 nm diameter metal dots as the starting pattern. These dots were made by a lift-off process using Talbot displacement lithography and electron beam evaporation. Polyimide deposited by molecular layer deposition and poly(methyl methacrylate) (PMMA) deposited by spin coating were used as polymers. Nano-FTIR spectroscopy verified accurately defined selective removal of PMMA from Pt. After the area-selective removal of the polymers from the Pt dots, ALD Ir and Ni processes were conducted. In the

case of Ir, perfect area-selective deposition was achieved, while the nickel process resulted in some scattered deposition also on the polymer but these nuclei were removed upon removal of the polymer.

Reference

25. C. Zhang, M. Leskelä and M. Ritala, Coatings, **11**, 1124 (2021).

Nanostructure Synthesis and Fabrication
Room Regency Ballroom A-C - Session NS-TuA
Nanostructures and Membranes

Moderators: Christian Dussarat, Air Liquide Laboratories, Michelle Paquette, University of Missouri-Kansas City

4:00pm **NS-TuA-11 Chemical Vapor Functionalization of Polymer Membranes for Water Treatment**, ***Jeffrey Elam**, A. Mane, R. Pathak, R. Shevate, V. Rozyyev,* Argonne National Laboratory

Polymer membranes are used extensively in water purification to filter and remove particulate and molecular contaminants. Ideally, these membranes should exhibit high permeance, selectivity, and fouling resistance, but these attributes are rarely achieved simultaneously. One approach to improve membrane performance is to modify the polymer using reactive chemical vapors to impart the desired physiochemical properties. In this presentation, I will describe recent work at Argonne using atomic layer deposition (ALD), sequential infiltration synthesis (SIS), and vapor-phase grafting to modify polymer membranes used for ultra- and nano-filtration in water treatment. These techniques rely on self-limiting chemical reactions between gaseous precursors and a solid surface to grow material in an atomically controlled fashion. We have used ALD to produce ultrathin and conformal inorganic layers allowing the membrane pore size and pore wall composition to be precisely tuned, SIS for the bulk modification of polymers by creating an organic-inorganic hybrid material, and vapor-phase grafting of small molecules to achieve additional control over the membrane surface properties. Our studies employ a suite of in-situ and in-operando measurements to elucidate the surface chemistry for these processes and extensive ex-situ characterization and testing to understand the effects of chemical vapor treatment on polymers and how they impact membrane performance.

4:15pm **NS-TuA-12 The Molecular Structure of Desalination Polyamides Made by Molecular Layer Deposition**, ***Brian Welch**,* Technion, Israel; *E. Antonio, T. Chaney, O. McIntee,* University of Colorado at Boulder; *J. Strzalka,* Argonne National Laboratory; *V. Bright, A. Greenberg, M. Toney,* University of Colorado at Boulder; *T. Segal-Peretz,* Technion, Israel; *S. George,* University of Colorado at Boulder

The leading method for creating thin, selective polymer films for desalination membranes is interfacial polymerization (IP). Notwithstanding, IP is challenging to control, and isolated films are difficult to develop and study. Molecular layer deposition (MLD), on the other hand, provides a means to synthesize and study polyamide films, and it serves as a promising direct route for membrane fabrication. This work probes the molecular structure of two prominent desalination polyamides synthesized by spatial MLD. Comparisons between the MLD and IP synthesized films shed light on the role of polyamide molecular structure on membrane performance and on the formation of crosslinked polymers via MLD.

MLD with m-phenylenediamine and trimesoyl chloride produced a crosslinked, aromatic polyamide which is prevalent in commercial reverse osmosis membranes, while MLD of piperazine and trimesoyl chloride formed polypiperazine amide, commonly used in nanofiltration membranes. Growth rates were 2.9 and 1.5 Å per cycle at 115°C, respectively. Grazing-incidence x-ray scattering showed oriented molecular spacing features of 3.8 Å in the reverse osmosis polyamide, and larger, isotropic spacing features of 4.6 Å in the nanofiltration films. These orientation and size differences, rather than the crosslink density, correlate to membrane water passage and solute retention.

From ellipsometry and x-ray reflectivity results, we posit that the surface of crosslinked organic MLD films is comprised of polymer tails up to two monomers in length which are connected to a crosslinked bulk layer. These segments are short in comparison to un-crosslinked MLD chemistries whose long segments experience thermal motion which make double reactions more probable with increasing temperature. The structure and surface of MLD and IP polyamide films were compared using x-ray photoelectron spectroscopy, infrared spectroscopy and atomic force microscopy. The MLD films presented properties which are favorable for salt rejection, water flux and fouling resistance: compared to IP, MLD films were dense, highly crosslinked, smooth and homogenous in molecular structure. These results contribute to understanding MLD behavior as well as the synthesis and performance of reverse osmosis and nanofiltration membranes.

4:30pm **NS-TuA-13 Deposition of an Atomic Layer Inside Microfluidic Channel**, ***Albert Santoso**, J. van Ommen, V. van Steijn, M. David, Y. Hounat, R. Zheng, N. Wijers, J. de Roeck,* TU Delft, Netherlands

Since its introduction in the field of microfluidics in 1998, polydimethylsiloxane (PDMS) has seen a rapid increase in its use as a material to construct microfluidic devices. However, its broad application is limited by the absence of its surface anchoring groups and its incompatibility with common organic solvents. Current strategies to address these shortcomings include altering PDMS throughout leading to unwanted changes to the bulk properties or modifying its surface often leading to relatively thick layers.

We present a novel strategy to deposit an atomic layer of metal oxides (TiO_x and SiO_x) on the inside of PDMS microfluidic channels using atmospheric pressure atomic layer deposition (AP-ALD). We alternatingly flow nitrogen carrier gas convectively containing the precursors (TDMAT, $SiCl_4$, ozone, or water) through the microchannels (aspect ratio of 30-200). Infiltration of the porous PDMS walls results in a unique surface-subsurface layer, providing a robust hydrophilic barrier that prevents swelling of PDMS upon contact with organic solvents (Santoso et al. Chemical Communications, 2022). Additionally, little to no changes are observed in the transparency and mechanical property of PDMS. We then studied the use of this coated channel for various applications such as isotope extraction involving common organic solvents. Using the coated chip, we managed to extract 98%±2% natural Ga isotope. As a comparison, the non-coated microfluidic chip leaked and it was difficult to even establish a fluid flow. Using the same set-up, we also deposited TiOx – gold nanoparticle and performed photocatalytic Rhodamine B dye reduction. After 1 minute of contact time, we achieved 30% reduction with comparable kinetic behaviour with previously reported value (Hashemi et.al., Nanoscale, 2020). This study demonstrates ALD as a tool to broaden the application of PDMS devices. This enables the use of PDMS microfluidic system in various high-end applications, positively contributing to the emerging fields involving precision and better contact area such as bioassays and photo-based micro-reaction.

4:45pm **NS-TuA-14 Tunable and Scalable Synthesis of ZnO Nanostructures using ALD Seed Layers**, ***Alondra M. Ortiz-Ortiz**, A. Gayle, J. Wang, D. Delgado, D. Penley, H. Faustyn, K. Fuelling,* University of Michigan, Ann Arbor; *A. Bielinski,* Argonne National Laboratory; *C. Sherwood, N. Dasgupta,* University of Michigan, Ann Arbor

There has been significant advancement in the synthesis of nanostructured materials for use in biological, environmental, and energy fields in recent decades, with many novel processes demonstrated at the laboratory scale. Nevertheless, challenges remain at the nanomanufacturing frontier, where it is necessary to maintain tunable material structure and properties using high-volume, high-throughput, and low-cost processes. One of the most facile techniques for the tunable and scalable synthesis of nanostructured materials is atmospheric-pressure hydrothermal synthesis of ZnO, which occurs under mild conditions. We have previously demonstrated that by using Atomic Layer Deposition (ALD) to deposit tunable "seed layers" with sub-monolayer precision in composition and structure, we can programmably tune geometric parameters (spacing, length) of the resulting ZnO nanostructures [1]. We refer to this process as "surface directed assembly", which has been used to enable applications ranging from photocatalysis to anti-biofouling surfaces [2,3].

In this study, we explore a third dimension of programmable control: using ALD seed layers to tune the ZnO nanostructure shape. Specifically, we demonstrate synthesis of Al-Zn-O nanosheets (NSs) using the surface directed assembly process by depositing a seed layer of Al_2O_3. The formation of a zinc-aluminum layered double hydroxide phase occurs from the interactions between the Al and Zn^{2+} ions during the hydrothermal synthesis, as confirmed by X-ray Diffraction (XRD). We demonstrate that the density of the ZnO NSs can be controlled by the number of cycles of Al_2O_3. Furthermore, Scanning Electron Microscopy (SEM) analysis shows that a transition from NS to nanowires (NWs) occurs after extended growth time. To rationalize this behavior, we propose a "phase diagram" for surface

directed assembly of nanostructures using ALD. Additionally, we demonstrate the ability to scale-up this surface-directed assembly process onto non-planar, large (cm-scale) surfaces facilitated by the design of a customized flow reactor. This work provides a new pathway to scalable nanomanufacturing enabled by the precise interfacial tunability of ALD for macroscopic applications, including medical devices and marine sensors.

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5:00pm **NS-TuA-15 Block Copolymer Templated HfOx Nanowires – From Fundamental Understanding to Rational Design***, **Ruoke Cai**, T. Segal-peretz,* Technion, Israel

Hafnium oxide (HfO_2) is an attractive material for optoelectronic applications and high-κ dielectrics in semiconductor devices due to its advantageous properties- high dielectric constant, wide band gap, and high stability. However, hafnium oxide nanostructure fabrication currently relies on complex nanofabrication processes. Sequential infiltration synthesis (SIS)- a method derived from atomic layer deposition (ALD), in which vapor phase precursors diffuse into polymers and react with them to form hybrid material, can provide a simple and cost-effective alternative for these processes.

In this study, we demonstrated the formation of hafnium oxide nanostructures- vertical and horizontal nanowires,usingblock copolymers (BCPs) templates. BCPs were self-assembled into highly ordered and periodic nanostructures, followed by hafnium oxide SIS process. In SIS, selective interactions between the hafnium organometallic precursor and the polar block of the BCP resulted in selective growth within the polar block domains. Following the growth, the BCP template was removed to yield hafnium nanowirestemplated by the BCP morphology. We first explored the precursor-polymer interactions in various homopolymers using *in-situ*quartz crystal microbalance (QCM) microgravimetric measurements. This fundamental understanding was further applied in finding a suitable BCP for templating HfO_2 inorganic nanostructure. We probed the formation of vertical and horizontal nanowires from the BCP templates using high-resolution TEM, EDS, and XPS. This research demonstrates the rational design of the HfO_2 nanostructure via template morphology tuning and control over HfO_2 growth.

5:15pm **NS-TuA-16 Compressible Polymer Sponge Electrodes via oMLD of PEDOT onto Polyurethane Sponge Supports***, **Mahya Mehregan**, G. Luebbert, K. Brathwaite, Q. Wyatt, E. Throm, D. Stalla, M. Young,* University of Missouri

The formation of compressible porous sponge electrodes is appealing to overcome liquid phase diffusion limitations in applications including electrochemical energy storage, electrochemical water desalination, and electrocatalysis. Previous work has employed wet chemical synthesis to deliver conductive materials into porous polymer sponge supports, but these approaches struggle to produce functional electrodes due to (1) poor electrical connectivity of the conductive network and (2) mechanical rigidity of the foam after coating. In this work we employ oxidative molecular layer deposition (oMLD) via sequential gas-phase exposures of 3,4 ethylenedioxythiophene (EDOT) and molybdenum pentachloride ($MoCl_5$) oxidant to imbibe polyurethane sponges with electrically-conductive and redox-active poly(3,4 ethylenedioxythiophene) (PEDOT) coatings. We analyze the oMLD deposition on compressive polyurethane sponges and modify the reaction conditions to obtain mechanically compressible and electrically conductive sponges. We specifically identify the importance $MoCl_5$ dose time to enhance the conductivity of the sponges and the importance of EDOT purge time to preserve the mechanical properties of the sponges. This approach produces an electrically conductive PEDOT network within the sponge support with minimal impact on the sponge's mechanical properties, offering advantages over wet-chemical synthesis approaches. The compressible, conductive sponges we generate have the potential to be used as compressible electrodes for water desalination, energy storage, and electrocatalysis.

5:30pm **NS-TuA-17 Low Cost, Large Area Sers Substrates by All Ald Deposited 3d Porous Filter Papers***, **Feng Niu**,* Raytum Photonics

Surface enhanced Raman scattering (SERS) has emerged as a promising spectroscopic tool for ultrasensitive trace detection of target molecules in the vicinity of nanostructured noble metal surfaces. Researchers have developed many techniques to create SERS substrates with most of them falling into three categories: metal nanoparticles by colloidal chemistry, nano-patterned surfaces, physical and chemical vapor deposition or a combination of them. However, all these techniques have limitations to coating hotspots directly inside 3D SERS substrates. On one hand there is high demand for super-enhancement, and ultra-sensitivity SERS substrates, on the other hand it is still challenging due to lack of stability, reproducibility, and reusability for such SERS active substrates to enter the realms of real, practical applications. Thus, new concepts, new techniques for simple, larger area, cost-effective fabrication techniques for SERS substrates are still in demand. Atomic layer deposition (ALD) has shown great performance in various fields such as semiconductor development, catalysis, energy and environmental applications. Due to its unique characteristics of super conformity, large area uniformity, easy layer thickness/composition control with precision in atomic scale, low cost and easy scale-up, if designed rationally it is an excellent technique for the bottom-up fabrication of nano-scaled materials and devices. Thus since 2010 ALD has also been investigated for the fabrication of SERS active substrates including Au or Ag nanoparticles (NP), ultra-thin films, conformal coatings of 3D scaffolds, high aspect ratio nanostructures, core-shell nanostructures, tunable nanogaps and high-density hot spots on nanostructured scaffold, etc.

We successfully developed ALD process for making Ag nanoparticles on 3D porous glass fiber filter paper and investigated evolution of Ag NPs with some key process parameters. By fine tuning Ag nanostructures and controlling cycle numbers we were able to obtain high density isolated Ag NPs without formation of agglomerates and continuous Ag films. We demonstrated the presence of strong localized surface plasmon resonance (LSPR) peaks and discovered multiple LSPR peaks associated with multiple scale NP size distributions. We also demonstrated the presence of the SERS signals on these ALD Ag coated glass fiber filter substrates using pyridine as the test analyte. Our results demonstrate that ALD is not only a very promising technique for the rational design as compared to other existing techniques but also has great potential for the fabrication of large area, low-cost nanostructured substrates for commercial applications.

ALD Applications
Room Evergreen Ballroom & Foyer - Session AA-TuP
ALD Applications Poster Session

AA-TuP-1 Improved Properties of the $SrRuO_3$ Electrode by Controlling Annealing Conditions and Adopting Al-doping, ***Junil Lim**, C. Hwang,* Seoul National University, Republic of Korea

This study reports on the properties of $SrRuO_3$ (SRO) thin films used as a bottom electrode of $SrTiO_3$ (STO) dielectric film with a good lattice match[1]. SRO film was grown via atomic layer deposition of SrO and pulsed-chemical vapor deposition of RuO_2 using the $Sr(^iPr_3Cp)_2$ ($^iPr_3Cp$ means 1,2,4-trisisopropyl-cyclopentadienyl) and RuO_4 (product name ToRuS) precursors, respectively. Because oxygen-deficient SRO film was deposited, annealing in an O_2 atmosphere was necessary for its crystallization. During annealing, the Ru of SRO film reacted with oxygen to form the volatile RuO_4 (gas). In addition, many voids formed during the annealing by the agglomeration hindered its use as a bottom electrode. Al was doped in the SRO films to improve these properties, of which the optimal annealing conditions were searched. The effects of Al on the formation of the volatile RuO_4 were experimentally and theoretically investigated. The theoretical calculation confirmed that the Al substituted with Ru (Al_{Ru}) in the SRO film improved the crystallinity of cubic-SRO. Thus, Al-doped SRO (ASRO) film had a larger grain size, higher crystallinity, and improved surface morphology. Furthermore, surface morphology improvements improved resistance properties (~ 1000 $\mu\Omega\cdot$cm at a thickness of 25 nm).

Figure 1. (a) Resistivity of SRO and ASRO films after PDA as a function of thickness. (b) The internal energy (E) differences between crystalline (*xtal*) and amorphous (am) structures in pure, Al_{Ru}, and $2Al_{Ru}$ + oxygen vacancy (V_O) SRO.

Acknowledgments This work was supported by the National Research Foundation of Korea (2020R1A3B2079882).

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AA-TuP-2 Yttrium-doping in TiO_2 Films for DRAM Capacitor Applications, ***Tae Kyun Kim**, C. Hwang,* Seoul National University, South Korea

This work reports on the electrical and structural behavior of Yttrium-doped TiO_2 (YTO) thin film as a dielectric layer for a capacitor of dynamic random-access memory. Yttrium (Y) is one of the well-known doping elements for dielectric materials such as ZrO_2 [1] and $SrTiO_3$ [2] for improving their electrical performances. It could be anticipated that the doped Y ions in TiO_2 thin films might reduce leakage current density by forming acceptor defects, as the doped Al in TiO_2 did [3]. However, the doping effect of Y in TiO_2 thin films appeared differently depending on the amount of dopant in one Y atomic layer deposited cycle. The doping concentration of Y ions was controlled by decreasing Y-source feeding time (Y F.T.) from its saturated feeding time (10 s) during the atomic layer deposition (ALD). Among different Y F.T.s, the best electric performance was observed when Y F.T. is 4s achieving equivalent oxide thickness (EOT) of 0.5 nm at physical oxide thickness (POT) of 8 nm (Fig. 1a) on the Ru bottom electrode. Moreover, the dielectric constant of YTO films increased when Y F.T. is 2s compared to TiO_2 films. This effect was ascribed to the relaxation of lateral tensile strain in the TiO_2 layer, induced by different thermal expansion coefficients of the TiO_2 ($8\text{-}11\times10^{-6}$/K) and Si substrate (2.6×10^{-6}/K). The size of Y^{3+} (Ionic radius: 104 pm) is larger than that of Ti^{4+} (74.5 pm), so tensile strain can be relaxed when the Ti ions are substituted with Y ions. However, Y_2O_3 particles were formed after 2s of Y. F.T. due to the low solubility of Y in TiO_2, which decreased the dielectric constant (Fig. 1b). The relaxation of strain and Y_2O_3 formation can be supported by the change in the position of rutile TiO_2 peaks from XRD data (Fig. 1c). These results indicated that the highly doped Y ions did not diffuse into the TiO_2 layer well but formed Y_2O_3 particles, which limited the diffusion and increased EOT. Therefore, careful control of Y-doping concentration and profile is necessary to optimize the capacitor dielectric performance.

AA-TuP-3 Non-Diffusive Phenomenon of Al and Y Doping in the ZrO_2/Al_2O_3 and ZrO_2/Y_2O_3 Bilayer Thin-Films and Its Influence on the Field-Induced Ferroelectric Properties, ***Haengha Seo**, J. Shin, J. Lim, T. Kim, H. Paik, C. Hwang,* Seoul National University, Republic of Korea

The emergence of the ferroelectric phase in the non-polar ZrO_2 or doped-ZrO_2 (e.g., $Hf_xZr_{1-x}O_2$) thin films under a sufficiently large electric field, which corresponds to the field-induced ferroelectric (FFE) transition, has led to a promising breakthrough to the future dynamic random access memory (DRAM) capacitor. A large extra charge can be stored reversibly in the DRAM capacitive layer by carefully manipulating the FFE materials. However, the leakage current control for such a thin film (sub-10 nm) must be a bottleneck for using the FFE material in mass production. Therefore, inserting layer or p-type doping (e.g., Al_2O_3) technique has been introduced for leakage current suppression. However, there is a lack of research on how the FFE characteristic of the ZrO_2 film would change in the presence of those aliovalent dopants.

It was reported that when the inserted Al_2O_3 layer was thicker than 0.3 nm (~monolayer) in the atomic-layer-deposited $ZrO_2/Al_2O_3/ZrO_2$ stack, the Al ions no longer diffused into the ZrO_2 lattice but formed a separated Al_2O_3 layer.[1] On the other hand, Y_2O_3 layer insertion in the ZrO_2 resulted in the full Zr-Y inter-diffusion even up to ~ 1 nm of the Y_2O_3 layer.

However, recent research showed that when the thin insertion layer was located on top of the ZrO_2 (i.e., bilayer system), diffusion of the dopant did not occur regardless of the doping element. Furthermore, it was found that only a small amount of diffusion occurred in the ZrO_2/Y_2O_3 case when the underlying ZrO_2 was extremely thin (~ 4 nm). This finding is interesting because even a low density of Al or Y ions could stabilize the tetragonal-ZrO_2 phase, thus eliminating the film's FFE hysteresis loop at a given electric field. Indeed, introducing a thin Al_2O_3 or Y_2O_3 layer in the middle region of the ZrO_2 film removed the FFE hysteresis loop of the film completely within the breakdown voltage range. On the contrary, both the ZrO_2/Al_2O_3 and ZrO_2/Y_2O_3 bilayer stacks showed the hysteresis loop with its magnitude of which the shape corresponds to the pristine ZrO_2 layer of the same thickness.

Therefore, introducing a thin capping layer on the ZrO_2 film rather than adding it in the middle should be a promising technique for controlling the leakage current issue while maintaining the FFE performance. The non-diffusive phenomenon also occurred when the layer was present underneath the ZrO_2 layer. However, this bottom-layer structure did not guarantee the thickness or quality of the crystalline structure of the ZrO_2 due to its different growth behavior on the insertion layer.

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AA-TuP-4 Promoted Crystallization of $SrTiO_3$ Thin Film for DRAM Capacitor by Inserting GeO_x Buffer Layer in $Ru/SrTiO_3/RuO_2$ Capacitor, ***Heewon Paik**, C. Hwang,* Seoul National University, Korea

$SrTiO_3$ (STO) is a perovskite material with an ultra-high dielectric constant(~300)[1]. However, STO has relatively low bandgap energy(3.2eV)[1] and is vulnerable to the formation of micro-crack during annealing at high temperatures, which could lead to high leakage current[2]. Therefore, carefully controlling the leakage current while securing high capacitance is necessary for STO to be used as a dynamic random access memory (DRAM) capacitor layer. This study presents the enhanced crystallization behavior of the STO thin film by inserting GeO_x buffer layer between the STO and the underlying Ru bottom electrode. The STO film and GeO_x buffer layer were deposited via atomic layer deposition (ALD) at 350℃, using $Sr(^iPr_3Cp)_2$, $Ti(CpMe_5)(OMe)_3$, $Ge(NMePh)(NMe_2)_3$ as Sr-, Ti-, and Ge- precursors, respectively. Post-deposition annealing at 475~650℃ was conducted to form a perovskite crystal structure.

The crystallization of STO was initiated at a lower temperature (475℃) with the aid of GeO_x buffer layer. As a result, the STO film with GeO_x buffer layer (b-Ge-STO) crystallized at 575℃ with a *k* value of ~159. In contrast, STO without the buffer layer showed a mixed structure of amorphous and crystalline phase(*k*~71.7), which required a higher annealing temperature of 650℃ for better crystallization (*k*~129.5). As the leakage path formation mainly occurs during high-temperature annealing[2], the lowered annealing temperature could efficiently suppress the leakage current without any degradation of crystallinity. However, when GeO_x buffer layer was inserted in the middle of the STO film (m-Ge-STO), it separated the upper and lower STO layers, and only the upper STO layer crystallized well at 575℃. As a result, the minimum equivalent oxide thickness values of b-Ge-STO annealed at 575℃ were 0.43nm, which could meet the leakage criteria for DRAM capacitor($<10^{-7}$A/cm^2 at a capacitor voltage of 0.8V). The significance of this study is that GeO_x buffer layer enabled controlling leakage current of STO without the conventional 2-step process involving the thin STO seed layer[2].

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AA-TuP-5 Laterally Resolved LEIS for Surface Coverage Analysis in Porous Materials, ***Thomas Grehl***, *P. Brüner,* IONTOF GmbH, Germany; *S. Saedy,* Chemical Engineering Department, Delft University of Technology, Netherlands; *J. Järvilehto, C. Gonsalves, J. Velasco,* Department of Chemical and Metallurgical Engineering, Aalto University, Finland; *J. van Ommen,* Chemical Engineering Department, Delft University of Technology, Netherlands; *R. Puurunen,* Department of Chemical and Metallurgical Engineering, Aalto University, Finland

One of the essential advantages of ALD is in many applications of minor importance – its ability to deposit on rough and porous materials far beyond the classical semiconductor applications. This is already exploited for heterogeneous catalysts and similar material systems. However, the characterization is challenging for many of the analytical techniques when it comes to judging the surface coverage and film thickness on internal surfaces. Still the coverage, nucleation behaviour/dispersion, thickness distribution etc. need to be assessed even inside the pores, much like for the planar surfaces in classical thin film deposition.

The surface sensitivity of Low Energy Ion Scattering (LEIS) is key to determining these properties on planar films. The same properties can be determined also on rough and insulating surfaces like catalyst supports, which are often porous oxides. In combination with cross-sectioning of these support materials and laterally resolved LEIS analysis, essential information is gained.

In this contribution, we will illustrate the approach by reporting results from cross-section analysis of mesoporous γ-alumina spheres which were impregnated with Pt in an ALD process. Depending on the conditions, the deposition extends more or less deep into the sphere. LEIS can quantify the surface coverage of the Pt, which is the active phase of many catalysts, in a laterally resolved way and therefore allows to study the precursor exposure inside the porous material.

Another application of this approach is the analysis of deposition on PillarHall^{TM} chips, which are used as a vehicle to study the precursor transport and exposure in general. Also here, not only the deposited amount of material, but more precisely the coverage and thickness of the (incomplete) film is evaluated as a function of diffusion length.

AA-TuP-6 Group III-Nitride Semiconductor Materials Made by Plasma Atomic Layer Deposition, ***Noureddine Adjeroud,*** Luxembourg Institute of Science and Technology (LIST), Luxembourg

III-N semiconductors are largely present in the industry, through chemical vapor deposition (CVD) techniques such as Metalorganic vapour-phase epitaxy (MOVPE). Those deposition techniques use conventionally the reaction of ammonia (NH3) with industrially relevant precursors such as trimethylaluminum (TMA), trimethylgallium (TMG) or trimethylindium (TMI) at high temperatures (750-900 °C) [1]. Plasma-assisted Atomic Layer Deposition (PA ALD) is becoming a trustworthy alternative to the standard CVD deposition techniques, and it appears as a solution for highly conformal coating and low temperature processing as two important assets to tackle growth temperatures of the nitride films not interfering with CMOS circuitry.

This work is based on the optimization and engineering of the plasma ALD of c-axis highly oriented aluminium nitride (AlN) films we proposed [2]. The pathway was further extended to facilitate low temperature (<450 °C) deposition of other III-N materials, such as GaN and InN semiconductors with wide and small bandgap respectively. In this work we utilized a gas mixture of H2/Ar/N2 as nitrogen precursor for nitride thin films initiated by a plasma source. The mix of Ar and H2 allows both to stabilize the plasma phase and to induce an optimized reducing of the ligands of the organometallic precursors reducing the carbon contaminants measured in the materials. We observed by XPS stoichiometric III-N films with no detectable carbon contaminants and also a low level (<5%) of oxygen contaminants in the nitride films. The XRD and TEM analysis confirm privileged hexagonal crystalline structure of the thin film below 100 nm thickness.

Insights on the ALD set-up and specific sequence of the deposition process will be presented for the growth of aluminium nitride (AlN), gallium nitride (GaN), indium nitride (InN), and ternary III-N films.

Those results have the potential to pave a way for both buffer-oriented seed films for post-growth, and also films with tailor made electronics properties for the next-generation of III-Nitride/CMOS components and functional coatings with piezoelectric and semiconducting properties for MEMS applications with transducing capabilities.

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AA-TuP-7 High-Temperature High-GPC SiO_2 Gap-Filling by Thermal ALD Using Novel Si Precursors, ***Wonyong Koh***, *J. Kim, B. Kim, J. Choi,* UP Chemical Co., Ltd., Republic of Korea

SiO_2 gap-filling by high-temperature ALD are used for semiconductor device manufacturing, especially for 3D-NAND Flash memory devices. Excellent step coverage is necessary to fill gaps with very high aspect ratio. Stress control and other requirements necessitate high deposition temperatures over 600°C. Newly developed Si precursors show high ALD growth-per-cycle (GPC), which is stable over wide temperature range between 600 and 800°C. It is in contrast of ALD using tris(dimethylamino)silane (3DMAS), of which GPC is smaller and the GPC is not maintained at temperatures higher than 750°C. Novel Si precursors show better step coverage than 3DMAS despite of more than twice larger GPC than 3DMAS. SiO_2 ALD films from novel precursors also show the same or better film characteristics such as wet etch rate, shrinkage, density, etc. compared against SiO_2 ALD films from 3DMAS at same temperatures using tube furnace type ALD reactor with O_3. Experimental results are presented and compared against those of 3DMAS.

AA-TuP-9 Molecular Layer Deposition of Lithium-Containing Polymeric Coatings for Superior Lithium Metal Batteries, *X. Wang,* ***Xiangbo Meng,*** University of Arkansas

Lithium (Li) metal is currently among the most attractive anodes of rechargeable batteries, ascribed to its extremely high capacity of 3860 mAh/g and the lowest negative electrochemical potential (-3.04 V versus the standard hydrogen electrode).[1] However, the dendritic growth and continuous formation of solid electrolyte interphase (SEI) have prohibited Li metal from commercialization. Surface coating remains as a facile and effective route to secure stable Li metal anodes. Recently, we for the first time designed and developed a novel cross-linked lithium-containing polymeric coating (LiGL, GL = glycerol) via molecular layer deposition (MLD), enabling excellent protection effects over Li metal anodes.[1] MLD features its controllable film growth with excellent uniformity and conformality.[2] Our results revealed that the Li anodes coated by this MLD-LiGL polymeric layer can achieve a superior cycling stability, accounting for an extremely long cyclability up to ten thousands of Li stripping/plating cycles without failures in Li/Li symmetric cells.[1] Not limited to LiGL, we have been developing other new polymeric coatings via MLD, which have shown promising applications in lithium metal batteries. The excellent protection over Li anodes by these MLD coatings are commonly ascribed to their exceptional ionic conductivity, flexibility, and chemical stability. They are representing a new pathway to address the issues of lithium metal batteries.

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AA-TuP-10 Suppression of Interfacial Layer Formation in ZrO_2-Based Capacitors with TiN Electrode by Adopting MgO Thin Films as an Oxygen Diffusion Barrier, ***Seungwoo Lee,*** *D. Han, H. Seol, M. Nam,* Kyung Hee University, Republic of Korea; *D. Kim, H. Oh, H. Kim, Y. Park,* SK Trichem, Republic of Korea; *W. Jeon,* Kyung Hee University, Republic of Korea

ZrO_2-based capacitors with TiN electrodes are typical high-*k* materials applied to dynamic random-access memory capacitors. However, when ZrO_2 is grown on the TiN electrode by atomic layer deposition (ALD) using ozone as a reactant, it forms an undesirable TiO_xN_y interfacial layer due to the high reactivity of the TiN bottom electrode (BE). [1] This TiO_xN_y interfacial layer may have been formed by oxygen diffusion toward TiN BE during ZrO_2 ALD and the subsequent annealing process. It accompanies the formation of an oxygen-deficient ZrO_2 phase and creates oxygen vacancy-related defects, which influence the electrical properties degradation of the metal-insulator-metal capacitor. [2] Also, TiO_xN_y interfacial layer can decrease the capacitance density by increasing the thickness of the dielectric film. These interfacial properties can be improved by inserting an oxygen diffusion barrier such as Al_2O_3. [3] However, the crystallinity of

tetragonal ZrO_2 deposited on the amorphous Al_2O_3 may deteriorate. Therefore, in this presentation, we investigated the effect of adopting MgO thin films as an oxygen diffusion barrier on TiO_xN_y interfacial layer formation. MgO thin films were used as oxygen diffusion barriers due to high chemical and thermal stability and did not show oxygen scavenging effects when interfaced with TiN. [4, 5] In addition, MgO has a larger bandgap (~7.8 eV) and higher dielectric constant (~10) than Al_2O_3 (~8) and does not degrade ZrO_2 crystallinity due to a low lattice constant mismatch with tetragonal ZrO_2. We fabricated ZrO_2/MgO capacitors with TiN using ALD and evaluated their electrical properties to analyze the effect of MgO insertion. The insertion of MgO significantly reduced leakage current density and improved C-V nonlinearity and frequency-dependent capacitance degradation. The capacitance density decreased because of the lower dielectric constant of MgO. However, for a specific MgO thickness, it was similar to the equivalent oxide thickness of a ZrO_2 single layer. The results of chemical state analysis by X-ray photoelectron spectroscopy showed that MgO suppresses the formation of an interfacial layer by preventing oxygen diffusion.

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AA-TuP-11 Improvement in Dielectric Properties of ZrO_2 Thin Film by Employing Thermal Stability Enhanced Zr Precursor in High-Temperature Atomic Layer Deposition*, **Yoona Choi**, A. Lee,* Kyunghee univ., Republic of Korea*; H. Oh, Y. Park,* SK trichem, Republic of Korea*; W. Jeon,* Kyunghee univ., Republic of Korea

Currently, ZrO_2 film is deposited by the atomic layer deposition (ALD) method, it can be used as the dynamic random-access memory (DRAM) capacitor material with a high dielectric constant (high-*k*) and excellent film quality [1]. However, as a size scaling down of the DRAM device is continued, a thinner dielectric film with high-*k* and low leakage current is required. To improve the electrical properties as described, a high-temperature atomic layer deposition is considered. And a precursor with high thermal stability is also required to withstand high deposition temperatures.

The ZrO_2 thin film deposited at a high temperature can produce more nuclei before the annealing process. Because the film contains many nuclei, the grain size is smaller than a film that is deposited at a low temperature after post-deposition annealing (PDA) treatment. The thin film with a small grain size has a long leakage path, so it can contribute to a decrease in the leakage current [2]. Also, at a high deposition temperature, it can reduce impurities by increasing the reactivity of the precursor. And it can improve electrical properties such as a dielectric constant through an increase in crystallinity [3]. In this study, using thermal stability enhanced Zr precursor, it is deposited a ZrO_2 film by ALD at a wide range of temperatures (270–400 °C) on a TiN substrate. Compared to Cp-Zr, the representative Zr precursor, the differences in electrical properties and crystallization were confirmed at a high deposition temperature. And it discussed the advantage of the dielectric film using the high-temperature ALD method.

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AA-TuP-12 Enhancing the Electrical Characteristics of ZrO_2-TiSiN Based MIM Capacitor by Introducing Y_2O_3 Inserting Layer*, **JongHwan Jeong**, A. Lee, W. Jeon,* Kyung Hee University, Republic of Korea

Dynamic Random Access Memory (DRAM) is one of the representative semiconductor memory devices and is used importantly in various industries due to its wide application range. In the process of scaling to improve DRAM performance, it is required to have a smaller area and a thinner thickness. So, a high aspect ratio structure was formed. However, collapse of the pattern occurred in the high aspect ratio structure because of the weak mechanical strength. [1] Therefore, to solve this problem, this study attempted to introduce TiSiN as a bottom electrode of DRAM capacitor, which has a good mechanical property and is considered advantageous to endure a structure with the high aspect ratio. But, when ZrO_2 films deposited on Si, the interfacial layer that contained a Zr-silicate phase and/or a SiO_x phase was formed. [2] Interfacial layer degrades the electrical properties. So, it was concerned that the degradation of electrical properties of TiSiN because of Si doping. To prevent this concern, this study introduced Y_2O_3 inserting layer. To compare with to the electrical properties of the pristine sample, Y_2O_3 inserting layer having various thicknesses was deposited. After analyzing the electrical properties according to thickness of Y_2O_3 inserting layer, additional analysis of electrical properties was performed by changing other variables. By using these results, the advantages of Y_2O_3 inserting layer were discussed.

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AA-TuP-13 Atomic Layer Deposited Vanadium Oxides with Various Crystallinity for Uncooled IR Sensor Application*, **Hyeon Ho Seol**,* Kyung Hee University, Republic of Korea*; S. Lee, W. Jeon,* Kyung Hee university, Republic of Korea

Vanadium oxide has been studied as a material used for the microbolometer of uncooled infrared sensors.In the previous study, vanadium oxide is known to exhibit high reactivity through the high temperature coefficient of resistance (TCR) value at room temperature.[1] Vanadium dioxides have various crystallinity, which includes monoclinic phase, brookite phase, and rutile phase.[2] The most stable phase in vanadium dioxide is a monoclinic phase, where semiconductor to metal transition occurs by mott transition at 67 ℃, which is not suitable for use as an infrared detection layer for microbolometers in a wide temperature range.[2] However, brookite phase which is metastable phase and amorphous state vanadium oxides can be alternative. Because, in the case of brookite phase and amorphous state, mott transition does not occur in a wide range of room temperature, so it is suitable for use as an infrared detection sensor.

In this study, we suppressed the expression of monoclinic phase so that vanadium oxides had a uniform TCR value over a wide temperature range. Vanadium oxides was deposited by atomic layer deposition (ALD)with TEMAV as a precursor and ozone as a reactant. The deposition process temperatures was 140 °C, 200 °C, and 250 °C. We evaluated the vanadium oxides thin film through XRD, XPS, and XRF.TCR evaluation was conducted through resistance measurement for each temperature from 30 ℃ to 100 ℃.

It was confirmed that the brookite phase was dominantly expressed at high temperature deposition. At low temperature deposition, the amorphous state was maintained even when the annealing process was conducted. The XPS and XRD data supported the result. TCR values were measured from -1.5 to -2 %/K in the case of brookite phase, and from -2 to -2.5 %/K in the case of amorphous state.

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AA-TuP-14 Self-Isolation Electrode Formation by Selective Deposition Behavior of MoO_2/MoO_3 Thin Films by Atomic Layer Deposition*, **Yewon Kim**, J. Park,* Kyunghee university, Korea*; S. Moon, T. Youn, Y. Jung, E. Han, Y. Jang, M. Lee,* SK Hynix, Korea*; W. Jeon,* Kyunghee university, Korea

For the DRAM capacitor application, a metal–insulator–metal (MIM) capacitor should meet the requirements of a sufficiently high capacitance density as well as a low enough leakage current to ensure robust device operation.[1] Especially, MoO_2 has been proposed as a conductive oxide electrode for TiO_2-based MIM capacitors. Owing to the highly crystallized MoO_2 structure, deposited TiO_2 films also exhibited high rutile crystallinity. By employing MoO_2, a rutile TiO_2 thin film exhibiting a dielectric constant value as high as 150 was obtained. And high work function of MoO_2 was also attributed to leakage current suppression in the MIM capacitor. The minimum equivalent oxide thickness of 0.35 nm, the lowest ever reported, was achieved.[2]

Thus, MoO_2 is the most promising capacitor electrode for further improving electronic applications. To apply actual DRAM application, it is important to have different deposition behavior depending on the substrate. Because, in

the real devices, oxide layers exist between the electrodes to separate each electrode. Molybdenum oxide thin films have various stoichiometries of MoO_x($2 \le x \le 3$). MoO_2 is conductive oxide, but MoO_3 is insulator. MoO_x thin films should be deposited MoO_2 on the electrode and MoO_3 on the oxide layer.

In this study, we examined selectively growing of MoO_x thin film as the electrode application for demonstrating the MoO_2 electrode implicated DRAM capacitor. The characteristic crystallization behavior of MoO_2 on the TiN resulted in self-isolation between bottom electrodes by the formation of MoO_3 on the mold oxide. To confirm the selective formation of MoO_x in the DRAM capacitor structure, various analyses methods were employed. Therefore, the proposed MoO_2 ALD is applicable to developing next-generation DRAM devices.

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AA-TuP-15 Formation of Mo Thin Film from ALD-Mo_2N Using Subsequent Reduction Process with Introducing a Mechanical Strain Applying Layer*,* ***Jeong Hyeon Park**, Y. Kim, W. Jeon,* Kyunghee university, Republic of Korea

It is necessary that the metal interconnects has low resistivity to connect devices to devices by acting as current-carrying. However, the resistivity of the interconnects are gradually incresasing as intergrated circuits were downscaling by the design rule. The resistivity increase as the size of interconnects decreased to nano-scale because scattering increase at the interface and grain boundary. Therefore total resistivity is proportional to ρ_o (bulk resistivity) × λ (mean free path), which is called resistivity size effect. Mean free path of Cu and Mo are 39 nm and 17 nm, respectively. So we can use Mo metal instead of Cu as a new interconnect material [1]. Mo has a benefit that is has a lower ρ_o x λ and thermal expansion coefficient (α = 4.8×10^{-6} K^{-1}). Among the Mo compounds, molybdenum carbide and molybdenum nitride also have low resistivity, but Mo metal has the lowest resistivity, so it is most suitable as interconnect material [2], [3].

Mo metal is deposited mainly by sputtering. However, the film deposited through the sputtering method is limited to use on nano-scale or 3D structrures because the step coverage is poor. If the roughness of the film deposited by sputtering is poor [4], the resistivity and capacitance of the metal increase and RC delay occurs [5]. Therefore, it is neccesary to deposit conformal metal by atomic layer deposition (ALD).

In this study, we deposit Mo metal by plasma enhaced atomic layer deposition (PE-ALD) for interconnect.

Because Mo film is not possible to directly deposit Mo metal by ALD, it was deposited molybdenum nitride and then reduced to metal film. However, in this process, agglomeration occurs, resulting in morphology degradation. Therefore, in order to suppress agglomeration, we suppress agglomeration with capping layer through applying mechanical strain.

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AA-TuP-16 Novel Cyclopentadienyl-Based Yttrium Precursor for Atomic Layer Deposition of Y_2O_3 Thin Films*,* ***Han Sol Oh**, H. Kim,* SK Trichem Co. Ltd, Republic of Korea*; S. Lee, Y. Ryu, W. jeon,* Kyung Hee University, Republic of Korea*; Y. Park,* SK Trichem co. ltd, Republic of Korea

The high dielectric constant (high-*k*) materials has been attracted a lot of attentions for improving the operation characteristics of various electronic applications, such as gate dielectric in metal oxide semiconductor field effect transistors, and insulator of metal-insulator-metal capacitors. However, the intrinsic property of high-*k* materials, a trade-off relationship between *k* value and bandgap, induces the leakage current problem, inevitably.

Among the various high-*k* materials, yttrium oxide (Y_2O_3) has been investigated one of the candidate for the gate dielectric and the insulator applications due to its relatively high *k* value (~12) with large intrinsic bandgap (5.5 - 5.8 eV). In this regard, various yttrium precursor complexes have been developed, but most of these compounds have solid phases[1-2] or liquid phases, which have high viscosity[3], making them difficult to apply to the actual atomic layer deposition (ALD) process.

Herein, we developed a novel cyclopentadienyl-based yttrium precursor with very low viscosity, good volatility, and thermal stability for demonstrating a reproducible thermal ALD process of Y_2O_3 thin film. By employing the newly designed yttrium precursor and ozone, the typical saturation behavior was obtained within an ALD window of 180 to 320 °C on SiO_2 substrate and a growth per cycle (GPC) up to 0.081 nm/cycle at 320 °C. The deposited Y_2O_3 films exhibited a cubic phase crystalline structure without any carbon and nitrogen contamination.We fabricated a metal-insulator-metal capacitors with Y_2O_3 and TiN electrode using ALD and evaluated their electrical properties such as dielectric constant and leakage current.

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AA-TuP-17 Novel Amidinate-Based Yttrium Precursor for Atomic Layer Deposition of Y_2O_3 Thin Films*,* ***Hanbyul Kim**, H. Oh,* SK Trichem Co. Ltd., Republic of Korea*; S. Lee, Y. Ryu, W. jeon,* Kyung Hee University, Republic of Korea*; Y. Park,* SK Trichem Co. Ltd., Republic of Korea

Yttrium oxide (Y_2O_3) thin film is one of the strong high dielectric constant (high-*k*) candidates for various electronic applications, such as a gate dielectric in metal oxide semiconductor field effect transistor or an insulator in the metal-insulator-metal capacitor, because of its valuable dielectric properties of the dielectric constant of around 12 with a relatively large intrinsic bandgap (Eg = 5.5-5.8 eV).

Therefore, various yttrium compounds for the precursor application in the thin film deposition process have been reported. Most of the reported compounds had a solid phase or highly viscous liquid phase, which was induced to obtain certain thermal stability.[1] However, these phases are not favorable as the precursor application, because they would result in difficulties in the actual deposition process, such as too low vapor pressure or low reactivities.[2]

Herein, we developed a novel amidinate-based yttrium precursor with low viscosity, excellent thermal stability, and high vapor pressure for the thermal atomic layer deposition process (ALD) application. The ALD process of Y_2O_3 thin film deposition utilizing newly designed amidinate-based yttrium compound and ozone was investigated. The ALD process exhibited a typical saturation growth behavior with a growth per cycle of 0.099 nm/cycle at 300 °C on SiO_2 substrate. Moreover, the high vapor pressure and low viscosity allowed for achieving a robust and reproducible ALD process of Y_2O_3 thin film. Finally, the crystallinity and dielectric properties of the Y_2O_3 thin film deposited on TiN electrode were examined.

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AA-TuP-18 Tailoring the Surfaces of Atomic Layer Deposited Metal Oxides for Metal Ion Removal from Aqueous Solutions*,* ***Vepa Rozyyev**, R. Pathak, R. Shevate, A. Mane, J. Elam,* Argonne National Laboratory, USA

The quality of water has worsened due to a wide range of contaminants from industrial waste, pesticides, and pharmaceuticals. These contaminants, including heavy metal ions and organic pollutants, can have adverse effects on human health even at low concentrations. Here we developed a method for functionalizing the surfaces of porous and flat adsorbents for enhanced metal ion removal from aqueous solutions. Atomic layer deposition (ALD) of metal oxides is utilized for the uniform and conformal coating of flat and porous substrates followed by vapor phase grafting of functional silanes. Here, we investigated the monolayer grafting of six different silanes with amine, thiol, nitrile, and ester functionalities. It is demonstrated that the density of reacted silanes and surface hydrophobicity varies depending on the reaction temperature and

functional groups on the silane agents. Next, we extended the study onto porous substrates by coating mesoporous silica with ALD metal oxide thin films followed by grafting with monolayer functional silanes. We then studied the adsorption properties of surface-functionalized mesoporous silica to evaluate the removal of metal ions from aqueous solutions. The functionalized surfaces exhibited enhanced selective adsorptive removal efficiency towards a wide range of metal ions.

AA-TuP-20 ALD for Lead-Free Microchannel Plate Fabrication: Optimization of the Thermal Coefficient of Resistance by Modification of the Resistive Layer*, **Stefan Cwik**, M. Aviles, S. Clarke, M. Foley, C. Hamel, A. Lyashenko, M. Popecki, D. Mensah, S. Shin, M. Stochaj,* Incom Inc.*; A. Mane, J. Elam,* Argonne National Laboratory, USA*; A. Tremsin, O. Siegmund,* UC Berkeley*; M. Minot,* Incom Inc.

Microchannel plates (MCPs) have a negative thermal coefficient of resistance (TCR) which leads to challenges in non-temperature-controlled environments. Rising device temperatures lead to thermal runaway, while the increased resistance under cooling results in reduced detection performance including gain depletion. In contrast to conventional hydrogen-fired lead glass MCPs, the ALD-GCA-MCP technology from Incom Inc allows the optimization of the resistive properties independently of other performance characteristics like gain. The TCR improvements are expected to have a high impact on in-field and space flight applications of MCP based photodetectors as the temperature related resistance changes become less prominent.

The glass capillary array (GCA) substrate is comprised of a physically and chemically robust silicate glass with high resistance which enables large area MCP fabrication. For the functionalization, a resistive nanocomposite and an emissive layer are deposited on the electroded GCA via ALD. The tunability of the resistive layer is based on the nanocomposite mixing of metallic and insulating components. For improved thermal performance stability, the ratio of both components in our baseline resistive material (Chem1) is optimized to yield an improved TCR of ALD-GCA-MCPs on level with conventional MCPs. However, on large area (up to 400 cm^2) MCPs the large number of parallel conductors requires a higher resistivity on the layer limiting the tunability. This motivated the development and implementation of new resistive nanocomposites in the pilot scale production environment to achieve even lower TCR values for a given resistivity.

Herein, we present the performance characteristics of our TCR optimized Chem1 MCPs fabricated with our baseline resistive technology that are the foundation of our Large Area and High Rate / Resolution Picosecond Photodetectors (LAPPD and HRPPD). Moreover, the performance of low TCR resistive layers developed together with colleagues at Argonne National Laboratory (ANL) is discussed in prospect of integrating the technological advance in the ALD-GCA-MCPs production process. Implementation and commercialization of these developments to large area ALD-MCPs and Incom MCP based picosecond photodetectors will be discussed.

AA-TuP-21 New Secondary Electron Emissive Technologies for MCP-PMTS: Optimization of Water and CO_2 Adsorption on Microchannel Plate Surfaces*, **Melvin Aviles**, S. Clarke,* Incom, Inc*; S. Cwik, M. Foley, C. Hamel, A. Lyashenko, M. Popecki, D. Mensah, S. Shin, M. Stochaj,* Incom, Inc.*; A. Mane, J. Elam,* Argonne National Laboratory, USA*; M. Minot,* Incom, Inc.

Incom's ALD-GCA-MCP technology for the fabrication of large area microchannel plates (MCP) relies on the performance of the ALD secondary electron emissive (SEE) film. This technology provides MCP functionality by combining resistive and emissive films with glass microchannel substrates. The use of glass and films makes possible mechanically robust MCPs, of any shape and resistance required by the application. MgO is the state-of the-art SEE coating for open MCP instruments and UHV sealed microchannel plate photomultiplier tubes (MCP-PMT), due to high gain and long-term performance stability. Earlier studied alternative SEE layers, including Al_2O_3, offered initially high secondary electron yield (SEY) but suffered from declining gain as adsorbed water was scrubbed out of the channels. This effect reduces detection efficiency with extracted charge, potentially to an unacceptably low level.

However, the strong adsorption of water and CO_2 on the air-exposed MgO surface makes the integration of MCPs into photodetectors challenging, since residual adsorbed species contribute to ion afterpulsing. Such afterpulsing leads to the degeneration of the photocathode, therefore reducing the detection efficiency, and leading ultimately to device failure. Additionally, applications requiring open-MCP instrumentation, where the MCP chamber gets routinely vented, also have to consider the reversable adsorptions of moisture and CO_2, Thes adsorptions then require extended evacuation and may create gain variations.

A series of ALD thin films have been evaluated and optimized by Incom and colleagues from the Argonne National Laboratory to develop application tailored SEE coatings with acceptable gain and gain stability, together with reduced gas adsorption. We will report SEE based MCP performance demonstrating the relation between the material selection, film thickness and gain. While lower SEY can be deemed sufficient for the respective application, declining gain during operation renders a huge drawback for our customers. Therefore, the gain stability after extracted charge and the afterpulsing level are key parameters for newly developed and upcoming SEE technologies. The gain and afterpulsing performance of the new films will be evaluated and discussed as a function of extracted charge and deliberate exposures of water and CO_2.

AA-TuP-23 ALD-based Catalysts with TiO_2 Interlayer for Ammonia Decomposition and LOHC Dehydrogenation Reactions*, **Yu-Jin Lee**,* Korea Institute of Science and Technology (KIST), Republic of Korea*; Y. Kwak,* University of Delaware*; S. Moon,* Ecole Politechnique Fédérale de Lausanne, Switzerland*; H. Sohn, H. Jeong, S. Nam, Y. Kim,* Korea Institute of Science and Technology (KIST), Republic of Korea

In this work, we demonstrate the use of atomic layer deposition (ALD) to fabricate catalysts that can accelerate the production of green hydrogen through ammonia decomposition and liquid organic hydrogen carrier (LOHC) dehydrogenation reactions. The ALD-based catalysts were designed with tailored surface properties, including the deposition of a TiO_2 interlayer, to enhance the catalytic activity, selectivity, and stability for these reactions. We tested the catalysts in a series of experiments and observed a significant improvement in the reaction rate and lower activation energy for ammonia decomposition and LOHC dehydrogenation, compared to conventional wet chemistry-based catalysts. Our study demonstrated significant improvements in catalytic activity for both ammonia decomposition and LOHC dehydrogenation reactions. These improvements can be attributed to the efficient modification of the electron structure of metal nanoparticles, which was facilitated by the uniform TiO_2 interlayer introduced onto a 3D-shaped substrate using the ALD technique. Our results suggest that ALD with TiO_2 interlayer is a promising technique for developing efficient catalysts for green hydrogen production, which can help accelerate the transition to a sustainable energy future.

AA-TuP-24 A Co-Design Approach to Optimize Neuromorphic Architectures for High Temperature Computing Integrating Novel ALD Materials*, **Angel Yanguas-Gil**, S. Madireddy, J. Elam, A. Mane,* Argonne National Laboratory

There is a need to broaden the temperature range of microelectronics. For applications such as enhanced geothermal systems, relevant downwell temperatures can exceed 300℃, which is well above the limits of VLSI and even high temperature Silicon on Insulator technology. In this work we demonstrate an application-driven codesign methodology that leverages machine learning techniques to identify optimal materials that maximizes the performance of architectures for an application-relevant task.

In particular, we have explored the integration of ALD materials based on metal/metal oxide nanolaminates for threshold logic-inspired architectures. An advantage of threshold logic approaches is that they minimize the number of transistors required to carry out complex operations, something relevant for high temperature computing, where the footprint of a transistor can be four orders of magnitude larger than the leading edges. Our approach integrates two different approaches: first, we cast the threshold logic circuits as models in deep learning frameworks such as pytorch or tensorflow. This allows us to use stochastic gradient descent approaches to identify the optimal values of the resistive elements in our architecture. We then use an asynchronous model-based search algorithm to explore and find optimal configurations in terms of accuracy and other criteria such as power consumption. Finally, we apply quantization approaches to minimize the number of processing steps required to realize the proposed architecture and identify the right ALD processes.

In addition to demonstrating the performance on baseline machine learning tasks such as MNIST, FashionMNIST, and KMNIST, we have explored the robustness of the proposed approach to process variability, noise, and shifts on the threshold voltage. Finally, we provide a realistic exemplar case where we use this approach to implement convolutional kernels for image processing applications.

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AA-TuP-25 Forming Voltage-Free Memristive Hafnium Oxide Devices for Non-Polar Switching Applications*, **Minjong Lee**, Y. Hong, J. Kim, H. Hernandez-Arriaga,* University of Texas at Dallas*; R. Choi,* Inha University, Republic of Korea*; J. Kim,* University of Texas at Dallas

Resistive memory-devices, the memristors, have received great amount of attentions for future memory applications. Among memristor devices, a resistive random-access memory (ReRAM) has been widely studied with its high on/off current ratio and applicable for compute-in memory applications. However, conventional ReRAM based on a filamentary switching mechanism requires electrochemical formation of filaments which causes reliability issues in ReRAM. This challenge issue must be addressed to achieve an advanced memory behavior.[1] In this regard, C. A. Paz de Araujo *et al*. reported the universal non-polar switching behavior in carbon-doped transition metal oxide (TMO) films deposited by spin-on fabrication, in which reliable operation and immunity from forming voltage were observed.[2]

In this work, we demonstrate the forming voltage-free memristive hafnium oxide (HfO_x) devices based using the conventional low-temperature atomic layer deposition (ALD) technique, which is high compatible for 3D structure and back-end-of-line (BEOL) process. For the ALD process, tetrakis(dimethylamino) Hf (TDMA-Hf) and carbonated hydroperoxide (H_2O_2) were utilized as the Hf and oxygen precursors, respectively. For activating the conductive carbon bond states, rapid thermal annealing (RTA) at 450 °C for 1 min was performed. By adopting the carbon composited HfO_2 films, the switching and memory behaviors were observed without any high forming voltage. It is noted that the first reset operation of the demonstrated devices is different from ReRAM forming in terms of the magnitude of switching voltage and current level. Although the high-resistance states are quite low due to the carbon composition, the set and reset voltages are reliable respectively as ~1.6 and ~0.6 V with similar high- and low-resistance states (HRS and LRS) in cycle-to-cycle variation. In addition, the intriguing operation in the carbon composited HfO_2 devices is non-polar switching behavior, showing programmable HRS and LRS regardless the polarities of operation voltage. These phenomena enable the devices to exhibit both unipolar and bipolar operation, which would be highly compatible for the further circuit applications. Detailed experimental procedure and results will be discussed.

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AA-TuP-26 Impact of Oxygen Source and Cocktail Precursor on Ferroelectricity of ALD $Hf_xZr_{1-x}O_2$ Thin Films*, **Jin-Hyun Kim**, Y. Jung, M. Lee, D. Le, S. Lee,* University of Texas at Dallas*; J. Spiegelman, M. Benham,* RASIRC*; S. Kim,* Kangwon University, Republic of Korea*; R. Choi,* Inha University, Republic of Korea*; J. Kim,* University of Texas at Dallas

The ferroelectricity in Zr-doped HfO_2 (HZO) film has attracted great interest for memory applications. Generally, HZO thin films can be deposited by super-cycle process with Hf and Zr precursors (e.g., TEMA-Hf/Zr and TDMA-Hf/Zr) via thermal atomic layer deposition (tALD) technique.[1]

In this work, we demonstrated the ferroelectricity of ALD HZO thin films without using a super-cycle process, in which TEMA-Hf/Zr cocktail precursor was employed. The great merit of the cocktail precursor is to achieve a higher throughput based on their simple ALD cycles. To comprehensively understand the proposed precursor, the effects of different oxidants (O_3, H_2O, H_2O_2) and deposition temperature on the growth characteristics and film properties were investigated. At 250 °C, the deposited HZO thin films using different oxygen sources exhibited ALD saturated growth characteristics. Although H_2O_2-based thin films exhibited higher growth per cycle (GPC) compared to other oxidants, HZO deposited with O_3 showed the lowest nonuniformity percentage. Unlike H_2O- and H_2O_2-based processes, the growth rate of O_3-based HZO remained constant between the deposition temperature of 200–300 °C. Furthermore, the etch resistance of deposited thin films was evaluated using 200:1 HF diluted solution. While exhibiting higher GPC than H_2O-based HZO, the films deposited with H_2O_2 showed a similar wet etch rate compared to H_2O process (~0.99 nm/ min). Interestingly, O_3-based HZO showed the lowest wet etch resistance. The observed results indicated that H-₂O and H_2O_2 delivered HZO thin films with higher density compared to O-₃-based process. To extend our studies to device applications, the TiN/HZO/TiN capacitors are fabricated by ALD at 250 °C with various oxygen precursors. The device fabrication flows were similar to our previous studies,[1] except using TEMA-Hf/Zr cocktail precursor. As a result, the H_2O_2-based devices exhibit a higher remanent polarization (P_r) and higher dielectric constant than those with H_2O- and O_3-based processes, due to the higher density of H_2O_2-based process. Overall, we thus believe that the combination of TEMA-Hf/Zr cocktail precursor and H_2O_2 would deliver HZO thin films with improved growth characteristics, film properties, and enhanced electrical performance.

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AA-TuP-29 Multifunctional Carbon Textile Prepared by Carbothermic Reduction for Energy Materials*, D. Lam, J. Kim, **Seung-Mo Lee**,* Korea Institute of Machinery and Materials (KIMM), Republic of Korea

Carbothermic reduction in the chemistry of metal extraction (MO(s) + C(s) → M(s) + CO(g)) using carbon as a sacrificial agent has been used to smelt metals from diverse oxide ores since ancient times. Here, we paid attention to a new aspect of carbothermic reduction that remained unnoticed till now to prepare activated carbon textiles for high-performance energy materials. Based on the thermodynamic reducibility of metal oxides reported by Ellingham, we employed not carbon, but metal oxide as a sacrificial agent to prepare activated carbon textile. We conformally coated ZnO on bare cotton textile using atomic layer deposition (ALD), followed by pyrolysis at high temperature (C(s) + ZnO(s) → C′(s) + Zn(g) + CO(g)). We figured out that it leads to concurrent carbonization and activation in a chemical as well as mechanical way. Particularly, the combined effects of mechanical buckling and opening-mode fracture that occurred between ZnO and cotton turned out to play an important role in carbonizing and activating cotton textiles. This effect significantly increased surface area (nearly 10 times) compared with the cotton textile prepared without ZnO. The battery and supercapacitor using the carbon textiles prepared by carbothermic reduction as an electrode showed impressive combination properties of high power and energy densities (over 20 times increase) together with high cyclic stability.

AA-TuP-31 Comparison between Doped and Undoped Ferroelectric HfO_2*, **Liliane Alrifai**, E. Skopin, N. Guillaume, P. Gonon, A. Bsiesy,* Univ. Grenoble Alpes, CNRS, LTM, France

The recent discovery of ferroelectric behavior of doped hafnium oxide (HfO_2) has led to a renewed interest in this material for its potential use in CMOS technology, such as integrated FeRAM ferroelectric non-volatile memory. Indeed, since HfO_2 was used in CMOS as an insulating layer, its elaboration process, physical and chemical properties are largely mastered even at ultrathin layers. Following the HfO_2 ferroelectric discovery, much effort has been devoted to the understanding of the role of doping. Different dopants have been investigated since it is widely believed that doping allows the stabilization of HfO_2 non-centrosymmetric orthorhombic phase which is the origin of the HfO_2 ferroelectric behavior. However, a number of reports showed experimental evidence of ferroelectricity in HfO_2 undoped layers. These results cast the light on the origin of the ferroelectric behavior and the role of doping in stabilizing it.

In this work, the ferroelectric properties and crystalline structure of doped [1] and undoped HfO_2 layers in TiN/HfO_2/TiN stacks were studied as a function of the layer thickness. For high conformity, precise thickness control and deposition at low temperatures, HfO_2 (or doped HfO_2) layers

and TiN contacts were deposited by Plasma Enhanced Atomic Layer Deposition (PEALD) in the same chamber without getting exposed to air.

To clarify the role of doping, the crystalline and electric properties of undoped HfO_2 layers were compared to that of doped layers. For doped and undoped ultrathin HfO_2 layers, the increase of ferroelectric crystalline phase as well as the ferroelectric behavior were found to be similar. Indeed, the remnant polarization was linearly increasing as a function of thickness but this trend started splitting at 6.5nm. Above this thickness, a slight increase of the monoclinic phase was noticed in undoped layers until it dominated and led to a drop in the remnant polarization above 14nm thick layer. In contrast, for doped samples, the remnant polarization kept increasing linearly with thickness. These results were analyzed in the light of possible role of mechanical stress in stabilizing the ferroelectric phase in ultrathin HfO_2 layers.

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AA-TuP-32 Control of the Electrical Resistivity and Stress of ALD W for 3d Nand Word Line Applications*, **Donguk Kim**, C. Suh, I. Sung, W. Choi, S. Jin, C. Kim,* SK Hynix, Korea (Democratic People's Republic of)

Since 3D NAND products were mass-produced, the number of stacking layers with W word lines has been increasing to achieve higher cell density. The total height of 3D NAND is also increasing with the increased number of W word lines, causing technical challenges such as channel-hole etch with a high aspect ratio and a high wafer warpage. As one of the solutions to overcome these technical challenges, the vertical pitch of the word line has been scaled down. However, in the aspect of W metallization, the gap fill at a reduced WL pitch becomes more challenging. Therefore excellent properties of W thin film with very low electrical resistivity and high step-coverage are required. Also, extremely low mechanical stress of W thin film is one of the important requirements because the word line W, which occupies more than 30% volume of the 3D NAND structure, causes a high wafer warpage.

ALD W process has been applied to the word line metallization of 3D NAND to meet the process requirements. Based on sequential alternating gas precursors with self-limiting reactions, ALD W film has excellent step-coverage on high-aspect ratio structures of 3D NAND. In addition, ALD W film generally has an electrical resistivity and mechanical stress of 50% or less compared to CVD W films. The most practical use of ALD W is that it is easy to control thin film properties with various process factors.

In this study, the effect of W nucleation layer on the electrical resistivity and stress of ALD W thin film is investigated. W nucleation layer using sequential pulses of B_2H_6 and WF_6 gases affects the bulk growth of ALD W, resulting in lower resistivity at higher nucleation thickness. In addition, the surface condition of TiN substrate affects the surface coverage of W nucleation on it. This leads to changes in the thin film properties of ALD such as electrical resistivity and stress. The effect of the surface condition of TiN substrate on W nucleation and ALD W films and their growth mechanism will be presented.

AA-TuP-33 Low-Temperature Atomic Layer Deposition of Indium Oxide and Tin Doped Indium Oxide using Ozone*, **Huazhi Li**, D. Gorelikov,* Arradiance LLC.*; A. Agrawal, W. Zhu,* NIST

Indium oxide (In_2O_3) and tin-doped indium oxide (ITO) are well known transparent conducting oxides (TCO). Due to their high optical transmittance and excellent electrical conductivity, they are used in various optical, electrical and photo-electric device technologies such as heat mirrors, antistatic coatings, electrochromic devices, flat panel displays, light-emitting diodes and solar cells. For optimal performance and utilization of the expensive indium, most of the above-mentioned applications need precise control over the conductive film thickness and composition. In addition, many applications require the ability to deposit thin In_2O_3 or ITO layers onto very high aspect ratio structures or high surface area materials. That makes atomic layer deposition (ALD) more advantageous over other deposition techniques such as chemical vapor deposition and physical vapor deposition. 100 °C temperature or below growth of In_2O_3 or ITO ALD films [1,2,3] recently gained more attention due to the need of using low temperature budget sensitive substrates like halide perovskites and polymers.

Arradiance desired to provide industry a low-cost solution for conformal In_2O_3 or ITO ALD films over substrates at or below 100 °C utilizing the GEMStar™ platform. In this work, we studied the growth kinetics, crystalline structure, resistivity, and purity of ITO and In_2O_3 thin films as grown using O_3 as the primary reactant gas in combination with the most cost efficient In and Sn ALD precursors on the chemical market: trimethylindium (TMIn) and tetrakisdimethylaminotin (TDMASn). Electrical measurements were performed using a four-point probe, and optical measurements (for growth rate and non-uniformity) using spectroscopic ellipsometry (SE). We found both films conductive at 100 °C growth temperature with the conductivity in tens mOhm range. Our findings prove that low-temperature ALD processing of ITO and In_2O_3 is feasible and scaleable utilizing existing ALD and supporting hardware solutions on the market like that from Arradiance.

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AA-TuP-34 Thin Titanium Oxynitride Film as Alternative to ITO for Optoelectronic Devices*, **Clemence Badie**,* Eindhoven University of Technology, The Netherlands*; V. Astie, J. Decams,* Annealsys SAS, France*; B. Sciacca, O. Margeat, L. Santinacci,* Aix-Marseille University, France

Transparent and conductive films (TCF) are critical parts of current and future optoelectronic devices (e. g. solar cells or displays). The most commonly used is In-doped SnO_2 (ITO) that exhibits satisfying transparency and conductivity. Due to indium scarcity, it is necessary to propose alternative TCFs. Another approach consisting of turning into transparent a conductive material by decreasing its thickness to nanometric scale should be highlighted and developed. It can extend significantly the variety of promising material available. Therefore, atomic layer deposited (ALD) titanium nitride as a metal-like material is an interesting candidate. However, from literature and our previous studies, as-grown ALD TiN films contain an oxynitride contribution[1,2]. The obtained films present a rather high resistivity for a metal but remains in TCFs range (10^{-4} Ω·cm). Depositions from 10 to over 100 nm have been performed to assess their optical and electrical properties.

TiO_xN_y layers are grown on fused silica by thermal and plasma-enhanced ALD using TDMAT (tetrakis(dimethylamido)titanium) and two different N-sources (NH_3, N_2). This enables to investigate their impact on the layer characteristics. Highest transmittance measured for thermal and N_2-plasma routes are highly satisfactory for 10 nm-thick films (87%) while NH_3-plasma one is slightly lower (83 %). Those values are compared to commercial ITO used as benchmark[3]. In visible range, the transmittances are very closed while, in the IR region, TiO_xN_y layers remain transparent and ITO exhibits a non-negligible absorption. Since numerous photons of the solar radiation are emitted in this region, the use of TiO_xN_y can result in a huge enhancement in photocurrent and then a better photoconversion yield of photovoltaic cells. The resistivity depends as well on the thickness, down to 1608 and 578 10^{-4} Ω.cm for both plasma routes (100 nm) while it remains stable for the thermal process around 550 10^{-4} Ω.cm. In the case of NH_3-plasma, after a thermal treatment at 700°C in nitriding atmosphere, the resistivity drops to 137 10^{-4} Ω.cm (10 nm) while the transmittance remains at 80%. Additional investigations are currently carried out to characterize the roughness and the crystallinity of the TCFs but current results are already very interesting. In addition, ALD can be used to conformally coat structured substrates that could be highly suitable for antireflective coatings and metasurfaces.

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AA-TuP-36 Advanced $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ Cathodes by Sulfide Coating via Atomic Layer Deposition*, **Xin Wang**, X. Meng,* University of Arkansas

Layer-structured $LiNi_xMn_yCo_{1-x-y}O_2$ (NMCs, 0< x, y <1) cathodes are among the promising cathodes for next-generation lithium-ion batteries (LIBs). However, these cathodes suffer from severe issues, which hinder them from commercialization, mainly in two aspects: performance degradation and safety hazard. They are reflected as cation mixing, oxygen evolution, phase transition, transition metal ion dissolution, and microcracking. In tackling these interrelated issues, surface coating has been proved being a facile and effective strategy. In recent years, atomic layer deposition (ALD) has emerged as an accurate tool to apply uniform and conformal coatings

over NMCs at the atomic level, which have shown remarkable effects on battery performance improvement.[1-4] Recently, we for the first time discovered that lithium sulfide as surface coating via ALD could remarkably improve the performance of NMC811[5]. The ALD sulfide coating has dramatically enhanced the cyclability and rate capability of NMC811 cathodes. In exploring the protective mechanism of the ALD coating, we utilized a suite of characterization tools including X-ray diffraction, scanning electron microscopy, high resolution transmission electron microscopy, and synchrotron-based transmission X-ray microscopy. Our results revealed that the ALD sulfide coating has evidently helped sustain the NMC structure during cycling and thereby significantly mitigated the formation of cracks. More importantly, X-ray photoelectron spectroscopy measurements have further revealed that the sulfide coating has experienced some transformations to sulfite or/and sulfate. Such transformations could remove oxygen released from NMC811 during cycling, protect electrolytes from oxidation and further degradation, and thereby contribute to the battery's improved performance. This work is significant, for it paves a new technical avenue for addressing the issues of NMCs and the like and has some important implication on other sulfide coatings in LIBs and beyond.

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AA-TuP-37 Improved Performance of Li||Nmc Batteries by a Novel Polymeric Coating via Molecular Layer Deposition*, Kevin Velasquez Carballo, X. Wang, X. Meng,* University of Arkansas

Abstract:

Lithium-metal batteries (LMBs) have received considerable attention for their great potential to achieve much higher energy densities than those of lithium-ion batteries (LIBs). [1-3] Among them, Li||NMC LMBs are very promising and could realize an energy density up to 500 Wh/kg, in which Li is the lithium metal anode and NMC is one variant of $LiNi_xMn_yCo_zO_2$ (x + y + z = 1) as the cathode. Although promising, they suffer from a series of issues, which hinder them from commercialization and are rooted in the Li anode and NMC cathode. Aimed at addressing these issues of Li||NMC LMBs, recently we developed a novel polymeric film, LiGL (GL = glycerol) via molecular layer deposition.[1] We revealed that LiGL as a surface coating could produce exceptional effects on the Li anode in Li||Li symmetric cells and enabled long-term cyclability. Inspired by this discovery, we adopted LiGL-coated Li chips (i.e., LiGL-Li) to couple with $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NMC811) cathodes. We prepared NMC811 cathodes with different mass loadings, varying from 2 to 14 mg/cm^2. Compared to bare Li||NMC811 cells, in all the cases, LiGL-Li||NMC811 cells enabled much better performance, in terms of sustainable capacity and rate capability. We ascribed the improvements of LiGL-Li||NMC811 cells to the excellent protection effects of the polymeric LiGL coating, i.e., inhibiting SEI formation and mitigating Li dendritic growth. All these results are encouraging, for they clearly indicate that MLD could be an effective pathway for us to address the issues of Li||NMC LMBs rooted in the Li anode. This study also clearly revealed that it is critical to address the issues rooted in both the Li anode and NMC cathode simultaneously for ultimately commercializing Li||NMC LMBs.

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AA-TuP-39 Resistivity Engineering of Atomic Layer Deposited Tungsten Carbonitride Thin films *via* Carbon Concentration Control for 3D VXP Electrodes Applications*, Seunggyu Na, T. Kim, S. Park,* Yonsei University, Korea*; M. Kim,* SK Hynix, Korea*; S. Chung, H. Kim,* Yonsei University, Korea

As a demand for data storage and processing has been exponentially increased, phase change memory (PCM) with fast speed and non-volatility is attracting huge attention. In particular, three-dimensional (3D) vertical cross-point (VXP) array architecture is one of the most promising technologies for fabricating PCM with increased integration density due to its cost-effective vertical structure with narrow holes realized by atomic layer deposition (ALD) compared to the conventional planar memory structures. This 3D VXP structure requires selectors to suppress undesirable sneak current from unselected cells, such as ovonic threshold switching selector (OTS). However, the switching behavior of OTS selector depends heavily on electrodes, which are essential part of the OTS device, depending on the electrode material and interface. Thus, detailed engineering of electrode material is required to obtain desirable properties for 3D VXP. Electrodes for 3D VXP require moderate resistivity because of the trade-off between thermal efficiency and power consumption. As a matter of fact, resistivity of film can be shifted by carbon incorporation. Even though ALD is essential technique for depositing conformal film on sidewalls in 3D VXP structure, studies on ALD process and resistivity control for electrodes applications are insufficient. Tungsten nitride is mainly used as an electrode due to its high thermal stability and conductivity.

Herein, we developed thermal ALD tungsten carbonitride process with intentional carbon control in films for effective tuning of film properties including resistivity by changing process parameters, such as deposition temperature, purge gas flow rate, and reactant flow rate. Subsequently, various ALD process parameters of tungsten carbonitride were controlled to observe changes in growth characteristics and film characteristics to investigate the effect of carbon concentrations in films. This opened the possibility of tuning the characteristics of the electrodes in detail, which will eventually help control the electrical characteristics of the devices.

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AA-TuP-40 Broadband Anti-Reflective Coatings on Plastic Optics Using Graded Refractive Index Alumina by Atomic Layer Deposition*, Philip Klement, L. Gümbel, I. Müller, J. Schörmann, S. Chatterjee,* Justus Liebig University Giessen, Germany

Plastic optics from acrylic glass or polycarbonate find widespread applications in eyeglasses, cell phone cameras, windows and displays as they are lightweight, cheap and easy to manufacture. All these applications require broadband, omni-directional and durable anti-reflective (AR) coatings which are difficult to achieve for plastics using conventional deposition methods. Typical problems are the low limit in process temperatures, modifications of the surface through the process plasma or the lack of rigid chemical bonding between the coating and the plastic.

Here, we present nanoporous alumina on plastic optics with a graded refractive index to produce broadband, omni-directional and durable AR-coatings. Atomic Layer Deposition (ALD) of alumina on poly (methyl methacrylate) or polycarbonate and the subsequent immersion in hot water forms grass-like alumina. Using this approach, we achieve an excellent AR-performance with a reduction of the residual reflectance to 0.4% in the visible range (400–900 nm) for a single-sided coating. Angular spectral reflectance (0–70°) confirms the omni-directional characteristic of the AR-coating with a minimal residual reflectance under all angles of incidence. Further, infiltration of the polymer substrate with inorganic precursors during ALD forms rigid chemical bonds and allows for durable coatings. The combination of excellent AR-performance, facile processing with strong adhesion to many relevant optical plastics and compatibility with commercial deposition systems should enable a multitude of practical use for this AR-technology.

AA-TuP-41 Revelation of Ferroelectricity of ALD ZrO_2 Thin Films through a Trace of Ge Incorporation*, Seonyeong Park, S. Na,* Yonsei University, Korea*; W. Choi, B. Kim, C. Jung, H. Lim,* Samsung Electronics Co., Inc., Republic of Korea*; S. Chung, H. Kim,* Yonsei University, Korea

Since the research on ferroelectricity of doped HfO_2 was first announced in 2011, a lot of research on $Hf_{1-x}Zr_xO_2$ (HZO) has been conducted due to its low crystallization temperature and high remanent polarization. However, HZO has problems such as high intrinsic coercive fields and electric fields cycling instability, and La doping has become a promising solution to improve ferroelectric behavior of HZO films. Recently, ferroelectricity of

ZrO_2 is highly promising because of its compatibility with CMOS technology. Although undoped ZrO_2 thin film is generally known to have antiferroelectricity, it exhibits ferroelectricity in very thin films of 2 nm. However, as the film becomes thinner, there is a possibility that device characteristics may be deteriorated due to inter-cell interference. In order to exhibit ferroelectric properties in ZrO_2 thin films of 10 nm or more, lattice distortion is required. According to the DFT calculation result, crystallinity can be improved when doping an element with a small atomic radius in the HfO_2 thin film. Therefore, we selected Ge as a doping element, which has smaller atomic radius than Zr and has good compatibility with Si.

In this study, super-cycle ALD method was used to incorporate Ge. Controlling the number of ALD GeO_X process cycle, we varied the proportion of Ge from 0.1 % to 2.7 %, which was examined by XPS analysis. In particular, through XRD analysis, it was found that the crystallinity of the ZrO_2 thin film significantly increased when Ge was doped at less than 1%. It was also confirmed that ferroelectricity appeared in about 13 nm thin film with only 0.1 % doping, and it is predicted that the increased crystallinity affected the revelation of ferroelectricity. If further research is conducted, it is expected that this film can be applied to real industry.

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AA-TuP-43 Atomic Layer Deposited TiN Capping Electrode for sub-10 nm $Hf_{0.5}Zr_{0.5}O_2$ Gate Oxide in Ferroelectric Transistors with 8 nm Gate Length Defined by Helium Ion Beam Lithography, ***Yu-Sen Jiang**, C. Wang, T. Chang, Z. Huang, M. Chen,* National Taiwan University, Taiwan

Since the discovery of ferroelectricity in $Hf_{0.5}Zr_{0.5}O_2$ (HZO) thin films, they have attracted considerable interest in a variety of devices including ferroelectric field effect transistors, ferroelectric random-access memory, ferroelectric tunneling junctions, and neuromorphic computing. The scaling of the HZO thickness down to the sub-10 nm region, along with a low thermal budget while maintaining pronounced ferroelectric (FE) properties, is of significant importance in practical applications. In this study, the TiN capping electrode deposited by atomic layer deposition (ALD) is used to enhance the ferroelectric properties of sub-10 nm $Hf_{0.5}Zr_{0.5}O_2$ (HZO) thin films. Compared with the TiN prepared by sputtering, the ALD TiN facilitates the crystallization into the orthorhombic phase in HZO without any post-annealing treatment. With the ALD TiN capping electrode, high remnant polarization ($2P_r$), low thermal budget (<300°C), low operation voltage, and high endurance are demonstrated in the ferroelectric HZO thin films with the thickness scaling from 10 to 3 nm. A maximum $2P_r$ as high as ~50 $\mu C/cm^2$ is reached in the 6 nm HZO, and the ferroelectricity still remains robust with a good $2P_r$ of 21.6 $\mu C/cm^2$ in HZO with a thickness of only 3 nm. The wake-up effect is almost negligible when the HZO thickness is above 5 nm, which could be attributed to the dependence of the stability between tetragonal and orthorhombic phases on the film thickness. On the other hand, high endurance (10^{11} cycles) is achieved in the 3 nm HZO thin film due to the increasing dielectric breakdown strength with the decreasing thickness. The distinguished ferroelectric properties can be ascribed to the formation of the TiO_xN_y mixed phase and a large in-plane tensile strain in HZO by the ALD TiN capping electrode. Finally, a Si junctionless transistor with a short gate length (~8 nm) and 6 nm HZO gate oxide is also demonstrated by using helium ion beam lithography based on the hydrogen silsesquioxane (HSQ) resist. Owing to the ferroelectric negative capacitance effect, the HZO gate oxide contributes to the suppression of the off-state current by around two orders of magnitude and the reduction in the subthreshold swing to ~33 mV/dec. All the results demonstrate the enhancement of ferroelectricity and the alleviation of short-channel effects in nanoscale transistors by the ferroelectric HZO thin films capped with a TiN top electrode deposited by ALD.

AA-TuP-45 Metal Oxide ALD Overlayers Enhance Thermal Stability and Activity of Platinum Catalysts in Propene Oxidation Reaction, ***Bang T. Nhan**, S. Bent,* Stanford University

The transportation sector is a major contributor to greenhouse gas emissions in the U.S. In the efforts to reduce the amount of toxic pollutants found in exhaust gas that is released into the atmosphere, many diesel and gasoline-powered vehicles are equipped with catalytic converters comprised of platinum-based catalysts. These catalysts contain platinum-group nanoparticles (NPs) dispersed on metal oxides such as alumina that have been shown to be highly effective at oxidizing harmful exhaust emissions containing CO, NO, and hydrocarbons. However, under harsh conditions (high temperature, oxidizing environment, steam), these NPs often sinter to form large particles, leading to a reduction in active surface area and, consequently, decreased catalytic activity.

One way to prevent particle sintering is to encapsulate the metal NPs within porous oxide layers. The oxide layers act as a cage around the NPs, reducing their mobility at elevated temperatures and thus limiting particle migration and coalescence. Encapsulation techniques such as chemical vapor deposition (CVD) and sol-gel chemistry have successfully formed stable core-shell particles. However, these techniques often lead to a stability-activity tradeoff where catalytic activity is compromised by mass transfer resistance of gaseous emissions associated with the tens of nanometer-thick protective layers. Atomic layer deposition (ALD) can meet the needs for growing uniform thin films on metal nanoparticles with angstrom-level thickness control over surface composition, which allows for a better understanding of the catalyst surface for fine-tuning purposes.

In this work, we investigated how the stability and activity of catalysts comprised of Pt supported on Al_2O_3 that was nanocasted from polymer organic framework (POF) (Pt/Al_2O_3) materials changed with both TiO_2 and CeO_2 overlayers. These metal oxides were selected as overlayers due to their prominence as supports in heterogeneous catalysis. We found that Pt/Al_2O_3 catalysts modified by TiO_2 ALD showed improved stability and retained activity after aging at 800 ºC in propene oxidation reaction conditions compared to the unmodified Pt/Al_2O_3 catalyst control. Particle size analysis of the aged samples showed a significant reduction in NP size as the number of TiO_2 ALD cycles increased, suggesting less sintering. We also explore Pt/Al_2O_3 encapsulated in CeO_2 ALD layers. As a catalyst support, CeO_2 is known to be much more active compared to TiO_2 due to its unique surface chemistry. A comparison of the activity and stability for CeO_2 encapsulated Pt/Al_2O_3 catalysts with both the TiO_2-modified and unmodified Pt/Al_2O_3 catalysts will be presented.

AA-TuP-46 ALD for Spatial Control of Redox Reaction Selectivity, ***Wilson McNeary**,* National Renewable Energy Laboratory; *W. Stinson, D. Esposito,* Columbia University; *K. Hurst,* National Renewable Energy Laboratory

Photocatalytic water splitting holds great potential in the pursuit of the U.S. Department of Energy's Hydrogen Shot initiative to bring the cost of H_2 to $1/kg by 2031. A key challenge in the development of photocatalysts is increasing their overall solar-to-hydrogen efficiency by enhancing charge separation yields and redox selectivity. In this work, we use area selective ALD of oxide films to develop tunable interphase layers for selective oxidation and reduction reactions on a single substrate. This presentation details initial synthesis and characterization of Pt- and Au-based planar thin film electrodes in which Au regions were deactivated towards ALD growth through self-assembled thiol monolayers. The suppression of TiO_2 ALD selectivity of thiols was assessed through ellipsometry, X-ray photoelectron spectroscopy (XPS), and cyclic voltammetry. A patterned planar sample comprised of interdigitated arrays of Au and Pt, used as a surrogate for a photocatalyst particle containing two different co-catalysts, was exposed to ALD growth and removal of the inhibitor species. Scanning electrochemical microscopy (SECM) was used then to probe the local activity of different regions of the patterned surface towards the hydrogen evolution reaction (HER) and iron oxidation and correlated with the ionic and e^- blocking effects of the area selective ALD coating. We will also detail the application of these findings to the ongoing development of 3D, particle-based photocatalysts.

AA-TuP-47 Influence of Oxygen Source on Ferroelectricity of ALD-$Hf_{0.5}Zr_{0.5}O_2$ Thin Films With and Without Capping Layer, ***Hye Ryeon Park**,* Kangwon National University, Republic of Korea; *S. Park,* Kangwon National university, Republic of Korea; *J. Kang,* Kangwon National University, Republic of Korea; *J. Kim, Y. Jung, J. Kim,* The University of Texas at Dallas; *S. Kim,* Kangwon National University, Republic of Korea

Ferroelectric $Hf_{0.5}Zr_{0.5}O_2$ (HZO) thin films have recently gained great attention in the semiconductor industry due to their high compatibility with standard CMOS processes, high dielectric constant, and high scalability.[1] Specifically, HZO thin films not only pave the way to overcome the scaling limitations that have been a chronic problem of conventional perovskite films, but also provide low thermal budget and availability of atomic layer deposition (ALD) processes. Since ALD is a chemical vapor deposition method that uses self-limiting and sequential surface reactions, the type of oxygen source used during the process can affect residues (e.g., carbon impurities or hydroxyl groups) in the deposited film.[2,3] Meanwhile, it is known that the ferroelectric properties of HZO originate from the non-centrosymmetric polar orthorhombic phase (o-phase).[1] In order to promote the formation of the o-phase in HZO, the films must undergo additional

stress during crystallization process. One representative approach for inducing mechanical stress in the film involves the use of a capping layer, commonly referred to as the "capping layer effect". Therefore, in this study, we comprehensively investigated the effect of an oxygen source on the ferroelectric properties of ALD-HZO thin films with and without a capping layer. 10-nm-thick HZO films were deposited on the TiN bottom electrodes by ALD using TDMA-Hf and TDMA-Zr as the Hf and Zr precursors and O_3 or H_2O or D_2O as the oxygen source. O_3-, H_2O-, and D_2O-based HZO samples were annealed in N_2 atmosphere at 400°C for 60 s by rapid thermal annealing before or after deposition of the TiN top electrode, respectively. As a result, the HZO samples annealed with the capping layer showed excellent ferroelectric properties regardless of the type of oxygen source, and the largest ferroelectric polarization was confirmed in the O_3-based HZO film. On the other hand, samples annealed without a capping layer showed ferroelectric properties only in H_2O- and D_2O-based HZO films, whereas O_3-based HZO film showed linear dielectrics properties. These results suggest that different types of oxygen sources should be used depending on the presence or absence of a capping layer in order to obtain and enhance the ferroelectric properties.

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AA-TuP-48 The Optimizing Mobility-stability Trade-off by Vertically Stacked IGZO/GZO TFT with Controlling of Indium-free GZO Layer via PEALD*, H. Oh, Y. Kim,* ***Jin-Seong Park,*** Hanyang University, Korea

Oxide semiconductor-based TFTs have already been commercialized for display backplane circuits based on advantages such as high mobility, large-area uniformity, low temperature processability, and low production cost[1,2]. In addition, oxide semiconductors, which have the advantage of low off-current (≤10^{-18} A/μm), are drawing attention in recent application fields in ultra-high resolution display, AMOLED, DRAM, 3D-NAND and CMOS image sensors. However, mobility-stability trade-off is observed in oxide semiconductors, and it is important to find an appropriate compromise to apply them to various commercial applications.

In this study, we fabricated an PEALD IGZO/GZO TFT with a stacked indium-free GZO layer on the front channel to solve the mobility-stability trade off relationship. We focused that control of the cation composition of the GZO layer via PEALD enables (1) interface engineering through defect density control and (2) band alignment modulation. In addition, it was confirmed that these effects greatly affect the improvement of the electrical performance and stability of the IGZO/GZO TFT. As a result, the optimized IGZO/GZO TFT has high electrical characteristics with mobility (μ_{FE}) of 31.86±0.74 cm^2/Vs, threshold voltage (V_{th}) of -0.14±0.12 V, and subthreshold swing (S.S.) of 0.20±0.01 V/decade. In addition, it has excellent stability compared to IGZO TFT with ΔV_{th} = 0.00 V and -3.46 V under PBTS (60 ℃, 2 MV / cm stress) and NBIS (1000 lux, -2 MV / cm stress) conditions, respectively. Our study shows that the electrical performance and stability of TFTs can be effectively enhanced by applying an In-free GZO layer with an appropriate composition to the interface between GI and active by PEALD.

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AA-TuP-50 Interface Engineering of Porous Cathodes by Spatial ALD for Improved Cycle Retention in Liquid Electrolyte*,* ***Diana Chaykina****, N. Huijssen, W. Manders, F. van den Bruele, A. Kronemeijer, M. Ameen,* TNO/Holst Center, Netherlands

Lithium ion batteries are an important component to the energy transition, enabling widespread deployment of e.g. electric vehicles. To achieve societal targets for performance and sustainability, research has been focused towards finding cobalt-less (NMC), and nickel-less (LMNO) cathode chemistries. In addition, some of these cathode materials are considered "high-voltage" cathodes (e.g., NMC811), leading to a higher cell voltage, and ultimately, energy density[1]. However, these new cathode chemistries are often incompatible with the currently used liquid electrolytes, resulting in electrolyte oxidation/degradation and a number of parasitic side reactions during battery operation[2]. These unfavorable interactions between the cathode and electrolyte ultimately lead to capacity fade and cell death.

To mitigate this, we engineer the interface between the high voltage cathode and liquid electrolyte by depositing an ultrathin (<2 nm) passivation layer on the porous cathode by spatial atomic layer deposition (sALD)[3]. With this technique, we can deposit thin conformal coatings with atomic control of many different materials (e.g., metal oxides) at atmospheric pressure and at a high growth rate (throughput), which renders sALD a scalable manufacturing process for integration in the battery manufacturing process flow.

We assessed the effect of different deposition parameters/conditions, such as precursor dose, oxidator nature and purge times, on the electrochemical performance of battery cells using NMC811. As well, we studied the impact of the sALD process on the full electrode stack and investigated, among other aspects, the penetration depth of the coating throughout the thick porous cathode. Combining the device performance with physical analysis, we optimized the cathode passivation and showed that the use of an sALD barrier is beneficial for capacity retention.

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AA-TuP-51 Study of Nb_2O_5 high-k Dielectric Material Deposited by Atomic Layer Deposition for Metal-Insulator-Metal Capacitor*,* ***Kou Ihara****, C. Labbé, J. Cardin, C. Frilay, M. Philippe,* CIMAP Normandie Université, France*; M. Leménager,* Murata Integrated Passive Solutions, France

The application of new high-k materials can help improve the properties of modern capacitors such as capacitance density. However, it is necessary to understand the deposition conditions of both electrode and dielectric materials in order to master the dielectric properties in future capacitors. One potentially interesting high-k material is Nb_2O_5 deposited by Atomic Layer Deposition (ALD) using NEO as niobium precursor and H_2O as reaction agent and oxygen source. Nb_2O_5 films are deposited directly on a silicon (Si) substrate or on a titanium nitride (deposited by ALD on Si substrate). Their structural properties are characterized by spectroscopic ellipsometry, scanning electron microscopy and atomic force microscope. Subsequently, a MIM structure (Ti/Nb_2O_5/TiN) is produced by adding a second titanium layer deposited on a Nb_2O_5/TiN/Si stack by the sputtering method. The electrical properties of Nb_2O_5 dielectric layer such as dielectric constant, breakdown field and leakage current at possible user voltage are measured on this last structure. These measurements indicate that the electrical properties of the Nb_2O_5 material produced by ALD with specific settings are promising for the application in capacitors. These results provide new insight into our understanding of the application of Nb_2O_5 realized by ALD for the MIM capacitor.

AA-TuP-52 Cathode Electrolyte Interphase Development and Residual Lithium Compound Removal via Chemical Vapor Treatment on Nickel-Rich Cathode*,* ***Rajesh Pathak****, V. Rozyyev, A. Mane, J. Elam,* Argonne National Laboratory, USA

The cycling performance of lithium-ion batteries depends greatly on the interface between the cathode and the liquid electrolyte.With the industry shifting towards higher capacity nickel-rich cathode materials, methods are needed to remove residual lithium compounds (RLCs) from the nickel-rich cathode surface and create a robust cathode electrolyte interphase (CEI). In this study, we utilized an ALD-like process, chemical vapor treatment (CVT), to remove RLCs such as LiOH and Li_2CO_3 from the surface of NMC811 cathode powders. We investigated the process using in situ Fourier transform infrared (FTIR) spectroscopy and ex situ X-ray photoelectron spectroscopy (XPS) and nuclear magnetic resonance (NMR) measurements.These measurements revealed the conversion of LiOH and Li_2CO_3 surface contaminants into Li_3PO_4 via self-limiting surface chemical reactions. Following the CVT, the NMC811 powders were integrated into coin cells to evaluate the effect of the Li_3PO_4 coating on the cycling performance.We found that the removal of the RLCs maintained the cathode structural integrity and improved the Li-ion transport. In addition, the Li_3PO_4 CEI not only acts as a physical barrier between the cathode and liquid electrolyte but also provides strong covalent bonding of the PO_4^- group enabling high thermal stability. As a result, CVT Li_3PO_4 on NMC811

yielded more stable cycling, lower voltage hysteresis, and higher-rate capability compared to the bare NMC811 during electrochemical cycling.

AA-TuP-53 Pt-Al2O3 Metamaterial with Tunable Resistivity, ***Ritwik Bhatia***, Veeco Instruments Inc.

Films of intermediate resistivity in between semiconductors and insulators are needed to prevent static build up while minimizing/controlling current discharge. Atomic layer deposition (ALD) has been used to create such materials using a blend of transition oxide semiconductors and insulators [1,2]. This approach is problematic due to lack of stability of these materials [2]. An alternate approach with ALD of molybdenum or tungsten nano-dots in an Al2O3 matrix has been developed in the context of micro channel plates [3] and has also been applied to electro-optical MEMS devices [4].

Deposition of Mo (MoF6+Si2H6) or W (WF6 + S2H6) requires a high level of engineered safety since S2H6 (disilane) is a highly flammable gas and the reaction produces hydrogen fluoride as a byproduct. In this work, we have replaced Mo/W with platinum as the material in the nano-dots. Platinum is deposited using the metal organic precursor MeCpPtMe3 with molecular oxygen as the co-reactant. Managing environmental health and safety for platinum deposition is much easier than for molybdenum or tungsten. Further the low growth per cycle (GPC) of Pt (~ 0.05nm/cycle) allows finer control of the resistivity compared to Mo or W (GPC ~ 0.5nm/cycle)

We show that resistivity can be varied by several orders of magnitude by either changing the size of nanodots (holding the ALD Al2O3 cycles constant and varying the number of Pt cycles) or by changing the spacing between the nanodots (holding the number of Pt cycles constants and varying the number of Al2O3 cycles). The resistivity range accessed to date is 1e3 to 1e10 ohm.cm. We also discuss stability of the material in response to electrical and thermal stresses and the thermal coefficient of resistance.

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AA-TuP-54 Effect of Ar Purge Step Condition on PEALD-TiN Film Properties, ***Ju Eun Kang***, *S. An, S. Hong,* Myongji University, Republic of Korea

The role of the metal diffusion barrier become more crucial for the low power consumption and high reliability in the metallization process. TiN thin film has been a conventionally preferable material for Cu diffusion barrier using atomic deposition layer (ALD). Despite of the purge steps in time-divided cyclic ALD, undesired residues of precursor and reactants remained inside the process chamber may turns into unexpected particles in the film which can jeopardize the film quality. Extending purge time can avoid the presence of the particle, but it also decreases the manufacturing throughputs due to the extended process time. Therefore, we investigated the relationship between purge time and characteristics of the TiN thin film quality. The TiN films deposited in 6-inch PEALD system with varyied purge conditions was inversigated with repect to the thickness, sheet resistance, and surface composition with ellipsometry, a 4-point probe, and X-ray photoelectron spectroscopy, respectively. The by-product production, with respect to the flow rate of the purge gas and flow time, was also investigated using Employing Chemkin simulation study.

As the longer Ar flow time, the N 1s peak of 300 sccm as the Ar flow rate and thickness decrease because the screening effect increases and it means that residual Ar atoms are intervened between the adsorbents to block the adsorption of the precursors and reactants. As shown in Fig. 1, through chemical reaction simulations, we found that the production rate of hydrocarbon increased as the Ar flow rate increased because Ar as inert gas increases the collision between chemical species in the chamber, making the production rate increase. We found that when the Ar flow rate increased, the reaction between the desorbed ligands increased to form an unstable compound (CH_3), and as the material was formed, the carbon component increased. Especially, in low Ar flow rate, the C_3H_6 production rate increased. Carbon 1s peak decreased at a lower Ar flow rate because the stable compound (C_3H_6) is easily removed from the chamber by the pump. Thus, we concluded that inducing the generation of these compounds can reduce the removal of the incorporation of materials into the thin film surface. In the past ALD process cycle optimization research, the focus has been on optimizing the flow time of precursors and by-products rather than purging. However, in this study, the effect of the purge condition on the characteristics of the TiN thin film was confirmed was proposed. This can be a novel approach to prevent by-product incorporation through purge conditions in terms of controlling the surface composition of thin films.

AA-TuP-55 Probing the Structural and Chemical Evolution of Interfacial SiO_x Layers Formed During ALD and Post-Deposition Processing, ***Ben M. Garland***, *N. Strandwitz,* Lehigh University

Atomic layer deposited (ALD) aluminum oxide (AlO_y) has been investigated to increase silicon solar cell efficiency by decreasing carrier recombination as a passivating interfacial tunneling layer, as well as a non-tunneling active layer in passivating emitter and rear contact (PERC) cells. When subjected to post-ALD annealing, a negative fixed charge forms at the interface with silicon oxide (SiO_x) to provide field-effect passivation. Post-ALD annealing also promotes chemical passivation of dangling bonds near the interface from the diffusion of residual hydrogen left over from the ALD process. The interfacial SiO_x chemistry is impacted by the Si surface preparation, ALD growth parameters, and post-preparation or post-deposition annealing. Previous work in x-ray photoelectron spectroscopy (XPS) and computational studies has indicated that the suboxides of SiO_x, where x=1-3, exist at interfaces and in ultrathin layers along with the dominant SiO_2. These suboxides could promote trap-assisted carrier tunneling in layers < 3 nanometers thick and/or change passivation characteristics.

In this work, we investigated the thickness and composition of interfacial SiO_x layers using XPS in Si|SiO_x and Si|SiO_x|ALD AlO_y structures to provide a comprehensive understanding of the interface. Hydrogen-termination, oxide grown with the Radio Corporation of America (RCA) process, ultraviolet ozone-grown oxide, and nitric acid-grown oxide were explored as silicon preparations often used in industry processing. The annealing condition (425°C in N_2 for 20 minutes) was chosen since it is in the range often used to promote passivation by ALD AlO_y. The Si 2p core level location associated with the primary SiO_x component was observed to shift to lower binding energy after AlO_y deposition, implying a change in the chemical structure that was examined through peak fitting. The Al 2p core level position and relative intensity to Si 2p was also studied, H-terminated silicon having the smallest intensity of Al 2p due to inhibited initial nucleation of ALD AlO_y. 2-bin and 5-bin peak fitting models were used to quantify the SiO_x layer thickness and composition. Between the two models, a ~0.2-0.3 nm difference in SiO_x thickness was seen depending on processing conditions; for example, with Si|nitric acid-grown SiO_x|ALD AlO_y, the SiO_x thickness was 0.9 nm in the 2-bin model and 1.1 nm in the 5-bin model. Silicon preparation, the presence of AlO_y, and post-preparation/deposition annealing influenced the SiO_x thickness and composition. Our findings may shed light on the SiO_x conditions that arise from processing and yield knowledge useful in silicon device manufacturing.

AA-TuP-57 Ultraviolet Bandpass and Wedge Filter ALD Coatings for Astrophysics Instruments, ***John Hennessy***, *R. Rodriguez, A. Jewell,* Jet Propulsion Laboratory (NASA/JPL)

We report on the use of atomic layer deposition (ALD) for the development of metal-dielectric bandpass filters that can be integrated directly onto back-illuminated imaging sensors for operation at far ultraviolet wavelengths (FUV, 90-200 nm). These coatings utilize previous developments in ALD metal fluoride processes for materials like MgF_2 and AlF_3, which are then combined with evaporated aluminum layers in multilayer structures. Planar coatings can produce an FUV bandpass response that allows broadband silicon CCD or CMOS imaging sensors to operate with visible and solar blindness, this enhances the utility of these devices for use in astrophysics sensing applications. We describe the fabrication and optical characterization of these coatings, and describe the development of detectors integrating these coatings that are planned to be delivered to upcoming NASA CubeSat and Explorers Missions.

We also report on the extension of this concept to include graded thickness dielectric layers deposited by ALD. We show that a graded lateral thickness can be engineered in a variety of thermal ALD processes by depositing into a shallow horizontal cavity. Process parameters like delivered dose, and background pressure can influence the lateral extent of the grading effect and therefore allow the slope of the graded thin film to be tailored without the need for moving parts inside the vacuum chamber. This allows for the fabrication of detector-integrated filter coatings with a spatially-varying response that can be matched to the spectral dispersion of spectrometer instruments. At visible and near infrared wavelengths this is used to produce graded dielectric anti-reflection coatings on silicon with R<1% over

a wavelength range of 300–1000 nm. Metal-dielectric variants provide order-sorting and long-wavelength rejection for FUV applications. Prototype graded coatings are demonstrated over areas up to 4 x 4 cm, and characterized for optical performance and environmental stability.

AA-TuP-58 Internal Photoemission (IPE) Spectroscopy Measurement of Interfacial Barriers in Fatigued ALD Ferroelectric Hafnium Zirconium Oxide MFM Devices*, **Jessica L. Peterson**,* Oregon State University*; T. Mimura, J. Ihlefeld,* University of Virginia*; J. Conley,* Oregon State University

Ferroelectric $Hf_xZr_{1-x}O_2$ (HZO) is under intense investigation for its potential ease of integration into advanced CMOS memory and logic applications. Atomic layer deposition (ALD) is the preferred method of depositing HZO. Inducing ferroelectric behavior in HZO typically requires "wake-up" – repeated voltage cycling above the coercive field.[1] Once woken, there is a period of stable behavior. Eventually, additional voltage sweeps fatigue the HZO, degrading ferroelectric performance.[2] Here we study the impact of cycling fatigue on metal/HZO band offsets and IPE yield in metal/ferroelectric/metal (MFM) devices.

20 nm of ~$Hf_{0.5}Zr_{0.5}O_2$ was deposited on TaN/Si substrates at 150 °C via ALD in an Ultratech S100 using 102 1:1 supercycles of TDMAH / H_2O and TDMAZ / H_2O. Next, 20 nm of sacrificial TaN was sputtered and the structure was annealed at 600 °C for 30 seconds. Following the anneal, the top TaN was stripped and replaced by an optically transparent 5 nm TaN/5 nm Pd top electrode. The completed MFM devices were "woken" using 5k cycles of a 10 kHz +/- 5 V square wave and then stressed at increasing intervals of cycles up to 500 k cycles. Band offsets and photoemission yield were measured using a lab-built IPE system.[3] Voltage applied to the bottom electrode was swept from -1.5 to 1.5V in 0.1 V steps. Simultaneously, monochromatic light focused onto the top electrode was swept from 1.7 to 5.5 eV. IPE thresholds were extracted at each voltage from plots of the square root IPE yield vs. photon energy. Zero field HZO/electrode zHHZOband offsets were extracted from plots of IPE thresholds vs. square root electric field.

Compared to pristine devices, the initial 5k waking cycles had little impact on band offsets but slightly reduced yield. An additional 5k cycles (total 10k) (i) reduced band offsets from 2.6/2.9 eV to 2.2/2.3 eV for top/bottom electrodes, respectively, with no further significant change up to 100k cycles, and (ii) reduced yield for both electrodes. Continued cycling up to 40k total did not significantly impact yield, indicating a regime of stable operation. Beyond 40k cycles, decreasing photon yield and increased leakage with increasing cycles was observed, consistent with fatigue. At 500k cycles, the devices were no longer functional. The decrease in yield, especially between 4-5 eV, accompanied by increased leakage is consistent with fatigue related to oxygen vacancy generation and movement.[4]

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AA-TuP-59 Understanding the Reactions of ALD Precursors on Lithium Metal and Its Application to Lithium Metal Batteries*, **Donghyeon Kang**, A. Mane, J. Elam,* Argonne National Laboratory

Trimethylaluminum (TMA) is a widely utilized aluminum precursor for atomic layer deposition (ALD) in various aluminum-based coatings. For example, TMA produces Al_2O_3 with H_2O,[1] AlF_3 with HF-pyridine,[2] and Al_2S_3 with H_2S [3] by well-defined ALD mechanisms. These ALD processes have been widely applied into various substrates to introduce ultra-thin Al-based coating layers, including energy storage materials such as battery cathodes, anodes, and solid electrolytes. Our group demonstrated that the Al_2O_3 ALD process using TMA can be used for Li-metal anode coating to improve electrochemical stability and reduce Li-dendrite formation during battery cycling.[4]

Although many studies about ALD on Li metal anodes have been reported using TMA, most of them focus on Li-metal battery performance, instead of ALD chemistry. During deep investigation on ALD chemistry of TMA, we recently discovered an interesting chemistry between TMA and reactive metal substrate (i.e., Li metal). Based on our observation, TMA reacts with Li-metal during ALD cycles then producing a carbon composite layer on the top of Li metal, not following conventional ALD mechanisms. It may come from highly reactive nature both of TMA and Li metal. Despite of wide use of TMA, this phenomenon has not been reported to date because Li metal is passivated by several layers such as Li_2CO_3, LiOH and Li_2O even stored in glovebox environment. In this presentation, we will discuss the chemistry between TMA and Li metal found by in-situ QCM, high-resolution XPS, SEM, and Raman studies. Then we will also demonstrate how this unexpected 'side reaction' can be utilized in Li-metal battery applications using liquid and solid electrolytes.

AA-TuP-61 Magnesium-doping in TiO_2 Dielectric Films for DRAM Capacitor Applications*, **YU-KYUNG PARK**, C. Hwang,* Seoul National University, South Korea

This work reports the electrical and structural behavior of Mg-doped TiO_2 (MTO) thin film as a dielectric layer for a dynamic random-access memory capacitor. As a successor of the current ZrO_2-based high-k (k ~ 40) capacitor dielectric thin film, rutile-structure TiO_2 film with a k-value > 100 draws great attention [1]. However, its low band gap (~3.1 eV) incurs concerns about the leakage current. Al-doping decreased the leakage current significantly by the acceptor-doping effect [1]. However, Al-doping degrades the -k-value of the TiO_2 film to 70 - 90, depending on its concentration. This work exploits another acceptor-type dopant, Mg, as an alternative to Al to decrease the leakage current while minimizing the k-value degradation. Figure 1(a) shows the variations in the equivalent oxide thickness (EOT), which is the physical thickness of the film multiplied by 3.9/k, grown on the Ru substrates. The bulk k-values of the TiO_2 film and MTO can be calculated from the slopes of the linear fit graphs and are ~113 and ~90 for the films, respectively. MTO exhibits a higher k-value than ATO, which is known to be ~80. This effect was ascribed to the relaxation of oxygen sublattice caused by oxygen vacancies, and the reduction of Mg^{2+} ions can promote the rutile phase transformation of TiO_2. When Mg^{2+} ions are doped into TiO_2, they are successfully incorporated at the substitutional site of Ti^{4+}, and one oxygen vacancy is formed [2]. Furthermore, because the ionic radius of Mg^{2+} (86 pm) is larger than that of Al^{3+} (67.5 pm), tensile strain can be relaxed when the Ti^{4+} (74.5 pm) ions are substituted with Mg ions. In contrast, the inhibition of the phase transformation by Al doping is known due to the lattice constraint effect [3]. The best electric performance of MTO was observed at an equivalent oxide thickness (EOT) of 0.44 nm and a physical oxide thickness (POT) of 8 nm with a J value of 6.7×10^{-8} A/cm^2 at +0.8V. Figure 1(b) compares the J-V curves of 20-nm-thick MTO and ATO samples in both the positive and negative bias regions. The MTO sample shows lower leakage current than the ATO sample at +0.8V, with a remarkable difference of nearly two orders of magnitude, is observed in the high-voltage region. The shift in band offsets caused by Mg doping may be more effective than that induced by Al doping due to the lower number of valence electrons of Mg ions than Al ions. Therefore, Mg doping in the TiO_2 film is a promising approach to improve the capacitor dielectric performance.

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AA-TuP-62 Electrical Characteristics Modification of Dual Gate Oxide Semiconductor Thin-film Transistor*, **Sehun Jeong**, S. Park,* Korea Advanced Institute of Science and Technology, Republic of Korea

Thin film transistors (TFTs) are a critical element in the development of next-generation displays, and oxide semiconductor TFTs have garnered considerable attention due to their advanced electrical properties. Specifically, oxide semiconductors have high electron mobility, low leakage current, and remarkable electrical stability, making them suitable for use as active channel materials in TFTs.[1] To further control the electrical characteristics of oxide semiconductor TFTs, we propose using dual gate structures, which offer controllable subthreshold swing and rapid hard saturation. Our research has shown that the capacitance ratio between the top gate insulator and the bottom gate insulator in dual gate structured oxide semiconductor TFTs can be used to control the subthreshold swing and that the voltages needed to switch between the on and off states can be adjusted by changing the subthreshold swing.[2] Furthermore, we have demonstrated that hard saturation, a crucial characteristic for TFTs used in display applications, can be achieved by applying voltage bias to both gates.[2] In addition to their electrical advantages, dual gate structures also offer structural benefits, such as the ability to block external light from both the top and bottom gates. Our findings suggest that by tuning the gate insulators in dual gate structured oxide semiconductor TFTs, we can achieve ultra-rapid switching properties with hard saturation, making them a promising candidate for advanced TFTs in next-generation displays. Overall, our work highlights the potential of dual gate structured oxide semiconductor TFTs as a new and exciting avenue for the development of advanced displays.

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AA-TuP-63 Control of Hydrogen Content via Super-Cycle ALD Deposited Al_2O_3 Gate Insulator*, **Hwayoung Kim**, S. Park,* Korea Advanced Institute of Science and Technology, Republic of Korea

Oxide thin film transistors (TFTs) have gained much attention in the display market due to their outstanding properties such as high mobility and low off-current. Of the various types of oxide semiconductors, InGaZnO (IGZO) and InSnZnO (ITZO) deposited through atomic layer deposition (ALD) are being actively studied. Because ALD can precisely control the film thickness and enables conformal deposition, it is one of the best methods for depositing oxide semiconductors that are sensitive to the number of carriers, and even it can form complex structures. In addition, multi-component oxide semiconductors can be deposited through the super-cycle method.

In oxide TFT, carrier concentration is a major factor determining device characteristic; and hydrogen, of which content is difficult to control, greatly affects the carrier concentration. The hydrogen diffused into the semiconductor can act as a donor, but it can also act as a defect passivator. Therefore, it is important to optimize the interface between semiconductor and gate insulate layer, where the hydrogen diffusion occurs a lot. For the gate insulate layer, ALD-deposited Al_2O_3 with a high dielectric constant and excellent barrier properties for moisture and air, was used. The Al_2O_3 layer can be grown by plasma-enhanced ALD (PE-ALD) and thermal ALD (T-ALD) that uses O_2 plasma and H_2O as an oxygen reactant respectively. Therefore, it results in distinct hydrogen content and characteristics[1]. In studies so far, the ALD super-cycle method has been used only for active layers to control the carrier concentration. In this study, the hydrogen content in gate insulator was controlled through the super-cycle of PE-ALD and T-ALD. One super-cycle consisted of n cycles of T-ALD and m cycles of PE-ALD, and the ratio (n:m) was varied between 0:1, 1:1, 1:4, and 1:8. As the number of T-ALD cycle in super-cycle increases, the mobility gradually increases by 100 cm^2/Vs. Furthermore, damage on semiconductor during the gate insulator deposition was reduced as the PE-ALD cycle ratio decreases. Since the carrier concentration differs depending on the oxide semiconductor, it would be possible to fabricate a TFT with an appropriate number of carriers by finding an optimized super-cycle ratio for each type of semiconductors.

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AA-TuP-64 Atomic Layer Deposited ZnO and Al_2O_3 on Nonwoven Fibre Materials – Improving Antimicrobial Properties and Moisture Resistance*, **Laura Keskiväli**,* VTT Technical Research Centre of Finland*; P. Porri,* University of Helsinki, Finland*; S. Salo, K. Heinonen, A. Harlin,* VTT Technical Research Centre of Finland

Atomic layer deposition (ALD) is an excellent technique to produce different inorganic-organic hybrid materials. Self-terminating nature of ALD cycles helps attaining reliable coverage of the complex nonwoven fibre structures. Low-temperature deposition of metal oxides can be used to improve antimicrobial properties of the hybrid materials and to enable effective decontamination and moisture resistance.[1,2] These properties are beneficial in personal protective equipment, such as technical masks.

In this study we deposited zinc oxide (ZnO) and aluminum oxide (Al_2O_3) on nonwoven viscose (Lyocell) and foam-formed cellulose fibres (JKL, from VTT Jyväskylä pilot plant).[3]The 75-400 cycles of ALD ZnO were produced with Picosun R-200 ALD reactor from diethyl zinc (DEZ) and H_2O at 80 °C. Furthermore, additional 7 cycles of Al_2O_3 (TMA, trimethylaluminium + H_2O) on ZnO coatings were studied. The visual appearance and distribution of ZnO was analysed by SEM-EDS. Hydrophobicity (contact angle measurement) was tested with deionized water. Furthermore, antimicrobial properties, filtration efficiency and particle shedding were studied. For antimicrobial properties, modified ISO 22196, MS2 virus and S.Aureus bacteria were used.

According to the contact angle measurements, Lyocell with 150 c and 300 c of ZnO and additional 7 c of Al_2O_3 were hydrophobic. With JKL cellulose samples no proper hydrophobicity was reached. ALD coatings did not affect on filtration efficiency, even though the ZnO coating penetrated throughout the fibre sample sheets and the amount of ZnO was equivalent on both sides according to SEM-EDS results. Particle shedding results revealed the differences in stability of the ZnO and Al_2O_3 treatments between the two fibre substrates. In the case of Lyocell, the ALD coating seems to be firmly attached and prevents the fibre particle shedding as well. In the case of JKL samples, the number of shedded particles exceeds the reference sample with 150 cycles or more of ZnO ALD, indicating the shedding of the ALD coating material. Antimicrobial efficiency was notable since both fibre types performed well already with 75 cycles of ZnO. All samples were microbicidal for both bacterial and viruses, and many of the samples exceeded the microbicidal impact of 3 log cfu/sampe, which is considered as an excellent effectiveness (Figure 1). ZnO ALD coating seems to have stronger microbicidal impact when deposited on foam-formed cellulose (JKL) compared to viscose material (Lyocell).

AA-TuP-65 Evaluation of Encapsulation Characteristics of $Si_xSn_yO_z$ Thin Film for OLED*, S. Jeon, Y. Kwone, S. Lee, T. Byun, Y. Im, **Sang Ick Lee**,* DNF Co. LTD., Republic of Korea

The current display market is led by OLED(Organic Light Emitting Diodes), and mass production of QNED(Quantum Nano-Emitting Diode) and Micro LED is being attempted. Since these display devices are vulnerable to moisture and oxygen, encapsulation is essential. A low WVTR(Water Vapor Transmissiion Rate) is required for the encapsulation film, and an appropriate refractive index is required to increase light extraction efficiency.

In this paper, in order to confirm that WVTR characteristics can be improved by doping Sn into SiO_2 and the refractive index can be controlled according to the Sn concentration, a $Si_xSn_yO_z$ thin film was deposited through PEALD process and its properties as an encapsulation film were evaluated.

For Si and Sn precursors, NSi-01 and DTP-01 developed by DNF were used(Table 1), and N_2O was used as the reaction gas. After depositing the $Si_xSn_yO_z$ thin film by controlling the vapor pressure of each precursor, the basic characteristics were analyzed(Fig 1a). As a result, it was confirmed that the refractive index and concentration can be controlled by adjusting the vapor pressure(input amount) of each precursor(Fig 1b). Through TEM mapping analysis, there were confirmed that Si and Sn were evenly distributed(Fig 2). As a result of analyzing the stress and film density according to the Sn concentration, it was confirmed that as the Sn concentration increased, the stress changed from compressive stress to tensile stress and the film density increased.(Fig 3) For transmittance and WVTR analysis, $Si_xSn_yO_z$ was deposited on PEN (Poly Ethylene Naphthalate) film. The transmittance measured by UV-Vis. was close to 100%. The WVTR of the $Si_xSn_yO_z$ film measured using MOCON's AQUATRAN 2 equipment showed excellent characteristics compared to SiO_2 of the same thickness(Fig 4).

Through this, the possibility of encapsulation application of $Si_xSn_yO_z$, which can control the refractive index and has excellent properties as an encapsulation film, was confirmed.

Area Selective ALD
Room Evergreen Ballroom & Foyer - Session AS-TuP
Area Selective ALD Poster Session

AS-TuP-1 iCVD Polymer as Inhibiting Layer for the Area-Selective ALD of Transparent Conducting Oxide Thin Films*, R. Feougier, C. Guerin, **Vincent Jousseaume**,* Univ. Grenoble Alpes, CEA, LETI, France

Transparent semiconductor oxides and transparent conducting oxides (TCO) are of critical importance for the development of thin-film transistors. TCO are also used as transparent electrodes for optoelectronic devices and microdisplays. In order to facilitate the integration of TCO that are difficult to pattern with standard lithography and etching processes, area selective deposition (ASD) is investigated. One approach consists in using self-assembled monolayers or polymeric films that can act as ALD inhibiting layers and prevent deposition in certain areas. For the introduction of this process in the microelectronic industry, one of the challenges is to deposit a sufficiently dense and stable inhibiting layer, preferably by a vacuum-based process.

In this work, polymeric thin films deposited by initiated chemical vapor deposition (iCVD) were evaluated as potential inhibiting layers for the AS-

ALD growth of transparent conducting oxides such as ZnO and SnO_2. iCVD is a vacuum-based deposition technique that allows a very good control of polymer thickness (down to nanometer) with low roughness, on large substrates. TCO films were deposited on different polymer layers by low-temperature ALD, and the film growth and material structure were analyzed with several characterization techniques including ellipsometry, X-ray reflectometry, atomic force microscopy and time-of-flight secondary ion mass spectrometry. It is shown that poly(neopentyl methacrylate) (P(npMA)) is a very good inhibiting layer for ALD growth of zinc oxide deposited from diethylzinc and water. For example, 12 nm of P(npMA) allows to inhibit up to 100 nm of ZnO. This work shows that the same iCVD polymer can also inhibit ALD growth of SnO_2 deposited from tetrakis(dimethylamino)tin and H_2O_2. The need for a minimum polymer thickness due to the possible diffusion of the precursor in the polymer layer is also highlighted. This solution appears to be a promising alternative to self-assembled monolayers and constitutes a new path toward the implementation of ASD for the fabrication of innovative thin-film transistors, for TCO-based channels as well as for electrodes.

AS-TuP-2 Direct Patterning of ZnO Deposition by Atomic-Layer Additive Manufacturing Using a Safe and Economical Precursor*, S. Stefanovic, N. Geshlaghi,* Chemistry of Thin Film Materials, Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany*; D. Zanders,* Inorganic Materials Chemistry, Ruhr University Bochum, Germany*; I. Kundrata,* ATLANT 3D Nanosystems, Denmark*; **Anjana Devi,*** Inorganic Materials Chemistry, Ruhr University Bochum, Germany*; J. Bachmann,* Chemistry of Thin Film Materials, Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany

Area-selective deposition (ASD) enables bottom-up nanofabrication with individual atoms as building blocks, exploiting chemical control to deliver self-aligned fabrication without dedicated lithographic steps. However, the need for (lithographically) pre-patterned substrates, which is inherent to ASD, the generation of defects outside of the desired growth area resulting from imperfect selectivity, and the limited selection of substrate materials represent limitations to applications of ASD.

To overcome these limitations, we have invented atomic-layer additive manufacturing (ALAM): a direct-patterning atomic layer 3D-printing method based on a microfluidic nozzle design which deposits lines and arbitrary patterns of materials with atomic precision using the underlying chemical principles of ALD. With respect to methods reliant on lithography, ALAM increases flexibility, reduces manufacturing cost and time, while delivering atomic resolution (on the vertical axis). The deposition chemistry of ALAM is similar to conventional ALD and all the commercially available gaseous precursors which have been used in g-ALD are compatible with ALAM. Additionally, the minimized precursor consumption of ALAM allows us to explore new reactions with precursors which are typically less preferred in ALD because of their low vapor pressure or limited reactivity.

Here, we establish ZnO ALAM using as precursors water and $Zn(DMP)_2$ (DMP = dimethylaminopropyl), which differs from the well-studied diethylzinc ($ZnEt_2$) by its lower vapor pressure and lower reactivity. Lines and patterns of ZnO deposited by ALAM are continuous, display sharp edges, and offer residual-free surfaces. The solid is crystalline and the crystallites can be either isotropically or preferentially oriented depending on the application, as chosen based on the growth conditions. The growth rate is 1.0 Å per pass at 200°C. We demonstrate the reliability and applicability of ZnO ALAM direct patterning by fabricating a metal oxide transistor and characterizing the device performance. Taken together, these results highlight how ALAM can be more flexible and facile than ASD on lithographically defined patterns, and simultaneously more economical and safer than classical ALD.

AS-TuP-3 Density Functional Theory Study on the Passivation of Oxides Surfaces by Inhibitor*, R. Hidayat,* Sejong University, Republic of Korea*; T. Mayangsari,* Universitas Pertamina, Indonesia*; **Khabib Khumaini,** H. Kim, W. Lee,* Sejong University, Republic of Korea

Small molecule inhibitor (SMI) has been studied extensively for area-selective deposition and seamless gapfill processes. Acetylacetone (Hacac) passivates the aluminum oxide (Al_2O_3) surface to inhibit the growth of silicon oxide (SiO_2) by plasma-enhanced atomic layer deposition (PEALD) [1]. On the other hand, ethanol (EtOH) partially passivates the Al_2O_3 surface, resulting in a decrease of growth per cycle of the ALD Al_2O_3 process by almost half [2]. However, no theoretical study compared Hacac and EtOH as SMI. Also, there has been no report on basic compounds as an SMI. In addition, there is no theoretical study to compare oxide surfaces with different acidities. In this study, we investigated the chemisorption of three types of inhibitors, alcohol, amine, and acetone, on different oxide surfaces. EtOH, diethyl amine (Et_2NH), and Hacac were selected as the SMIs. We considered three kinds of surface, SiO_2, titanium oxide (TiO_2), and zirconium oxide (ZrO_2), due to their different acidities. The density functional theory (DFT) calculations were used to study the inhibitor chemisorption, and all possible pathways were considered to understand the mechanism. We constructed and optimized the hydroxyl groups on oxide surfaces for the simulation. The reaction and activation energies of each pathway were calculated to compare the reactivity of different inhibitors. The results can provide fundamental insights into a better selection of the SMI for seamless or area-selective ALD processes. Details of the calculation results will be presented.

AS-TuP-4 Selective Deposition on Next-Generation Patterned Carbon/SiO_2 Materials*, **Maggy Harake,*** Stanford University*; I. Oh,* Ajou University, Korea (Democratic People's Republic of)*; S. Bent,* Stanford University

The semiconductor industry continues to display increased interest in manufacturing smaller and more complex chips, but current top-down processing technology has proven to be challenging for these next generation devices. The versatility and sequential, self-limiting nature of atomic layer deposition (ALD) can address some of these fabrication challenges. A useful extension of ALD is area-selective ALD (AS-ALD), which can be performed using several tunable strategies including inherent selectivity and surface inhibition to provide spatial control over thin-film deposition. One such strategy is the protection of the non-growth surface using self-assembled monolayers (SAMs), which are long-chained organic molecules that chemically adsorb onto a surface to create a well-packed and dense inhibiting layer, resulting in restricted ALD growth wherever the SAM is present.

This work reports on a HfO_2 AS-ALD process on C/SiO_2 patterns using two different SAMs: octadecyltrichlorosilane (ODTS) and octadecyltrimethoxysilane (OTMS). Properties of ALD-grown dielectric materials can be exploited on carbon materials and have the potential to be used in hard mask applications. The ALD precursors used for HfO_2 ALD were tetrakis(dimethylamido)hafnium and water. Plasma-enhanced chemical vapor deposition (PE-CVD) carbon, photoresist (PR), and spin-on carbon were explored as the growth surfaces. SiO_2 was studied as a non-growth surface. The two different SAMs were compared to identify if better inhibition on SiO_2 could be achieved by exploiting the differences in the siloxane head group of the SAM molecule.

Due to the subtle variability in surface chemistries of the carbon materials, results show that in addition to adsorbing on the non-growth (SiO_2) surface, the SAMs also adsorb to varying extents onto the carbon growth surface, as detected by water contact goniometer measurements. Minimizing SAM deposition on the carbon growth regions was achieved by optimizing a cleaning procedure that works for all three carbon substrates investigated. After performing 25 cycles of HfO_2 ALD (equivalent to 2.5 nm of HfO_2), selectivities approaching 100% for all three carbon materials were retained, as confirmed by x-ray photoelectron spectroscopy. Upon increasing ALD cycles, selectivities decrease, falling below 20% after 75 cycles of HfO_2 ALD on all carbon substrates. C/SiO_2 patterns are used in combination with OTMS, and the results show that AS-ALD can be achieved in feature sizes at the submicron scale. Finally, the use of UV-ozone treatment before ALD and the selection of different ALD precursors as potential avenues to improve selectivity will be described.

AS-TuP-6 Thermal Assisted Atomic Layer Deposition of Ruthenium by Ru Precursor and O_2 as a Reactant*, **Gagi Tauhidur Rahman,*** Graduate School of Advanced Science and Engineering, Hiroshima University, Japan*; Y. Amamiya, K. Uesugi, A. Teramoto,* Research Institute for Nanodevices, Hiroshima University, Japan

Area-Selective Deposition (ASD) has the potential to enable self-aligned patterning schemes. Ruthenium is a promising material for next generation interconnect and so on, due to the advantages of low bulk resistivity and large work function.A study of Ru deposition on different surfaces to determine the suitable deposition conditions, which enables the demonstration of ASD of Ru film.

Fig. 1 shows a schematic time sequence of Ru ALD. The chemical name of Ru precursor is Tricarbonyl (η^4 4 -2-methylene -1,3-propanediyl) ruthenium (II) and the chemical formula is $C_7H_6O_3Ru$. The temperatures of the Ru precursor tank and the susceptor of the ALD equipment are 60 ℃ and 250 ℃, respectively. We investigated three types different surfaces; the surfaces SPM (H_2SO_4/H_2O_2 solution) and diluted HF solution, and SiO_2 film by CVD method using Tetraethoxysilane.

Fig. 2 shows Ru film thicknesses on three surfaces, where the thicknesses are converted from XRF measurement using the calibration curve. It is evident that films on SPM (-OH terminated) and SiO_2 (-O terminated) surfaces are almost the similar however the films on HF (-H terminated) are different from the previous two films. Ru thicknesses on SPMand SiO_2 surfaces are larger than that on HF surface.

In SPM/SiO_2 cases, the terminated molecules are Si and O, and O is more electronegative than Si, so these surfaces exhibit polarization. The electronegativities of H, O and Si are 2.1, 3.5 and 1.9, respectively. However, in HF case, the terminated molecules are Si and H, and they have small differences in electronegativity. The surface shows neutral characteristics. The catalytic character is also higher in HF surface rather than SPM/SiO_2 surface. We expect more deposition on HF surface than SPM/ SiO_2 surfaces. However, HF surface showed lower deposition.For those reasons we need to investigate that on HF surface less absorption occurs or the gaseous molecules go desorption after absorption. Parallelly, we have to change the deposition condition to find the fact.

We conclude this research. ALD deposition on SPM, HF and SiO_2 surfaces were successfully completed.SPM and SiO_2 surfaces showed satisfactory deposition regarding thickness while HF surface did not exhibit due to surface neutrality. The deposited Ru was ~0.13 nm per cycle.

[Acknowledgement]

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AS-TuP-7 Enhanced Deposition Selectivity of High-k Dielectrics by Vapor-Dosed Phosphonic Acid Inhibitors Combined with Selective Lift-Off*, **Jeong-Min Lee**, W. Kim,* Hanyang University, Republic of Korea

In modern technologies, misalignment issues of multi-level pattern structures arising from conventional lithographic steps have limited further device downscaling. Accordingly, area-selective atomic layer deposition (AS-ALD) has emerged as a game-changing bottom-up patterning method, which can not only eliminate such misalignment issues but provide selective deposition on desired areas with atomic-level accuracy by virtue of chemo-selective adsorption of inhibitory molecules. Concurrently, high-*k* materials are vital for nanoelectronic fabrication, among them, ZrO_2 has been considered as an ideal candidate due to its relatively high dielectric constant and wide band gap, as well as excellent thermal and chemical stability. Therefore, we report a methodology for achieving selective deposition of ZrO_2 films by surface modification through vapor-phase functionalization of octadecylphosphonic acid (ODPA) inhibitor molecules accompanied by post-surface treatment. In this work, comparative evaluation of deposition selectivity and electrical properties of ZrO_2 thin films deposited with O_3 versus O_2 reactants was performed on SiO_2, TiN, and W substrates. Through surface modification of vapor-dosed ODPA molecules, significant growth retardation against the ZrO_2 ALD process was selectively found on TiN and W, in contrast to SiO_2 substrates. With applying chemo-selectively inhibitory characteristics, we successfully demonstrate AS-ALD of ZrO_2 films on a metal/dielectric-patterned substrate. We anticipate that this approach will advance AS-ALD of high-*k* dielectrics toward the upcoming bottom-up 3D nanofabrication.

AS-TuP-10 Area-Selective Atomic Layer Deposition of Ru Thin Films Using Phosphonic Acid Self-Assembled Monolayers for Metal/Dielectic Seletivity*, **Seo-Hyun Lee**, J. Lee, W. Kim,* Hanyang University, Korea

Area selective atomic layer deposition (AS-ALD) is a promising technique for 3D nanofabrication and emerging device architectures. AS-ALD offers numerous advantages over conventioanl top-down patterning processes. This technique exploits a bottom-up additive process that selectively binds to pre-defined areas through chemo-selective interations between the substrate and molecules. In this study, we investigated the efficacy of different phosphonic aicd (PA) self-assembled monolayers (SAMs), including octadecylphosphonic acid (ODPA), octylphosphonic acid (OPA), ethylphophonic acid (EPA), and phenylphosphonic acid (PPA), for their ability to selectively block metal/dielectirc surfaces, specifically TiN and W versus SiO2. This effectiveness of the SAM-treated surfaces was evaluated using Ru ALD as a model process for metal/dielectirc selectivity. Our results demonstrate that the PA SAMs exhibit chemo-selective adsorption on TiN and W, but their blocking quality improves with increasing alkyl chain lengths due to strong van der Waals interactions between adjacent SAMs. Notably, the ODPA SAMs showed the highest efficacy, enabling area selective ALD (AS-ALD) of Ru thin films over 15 nm on patterned TiN/SiO2surfaces.

AS-TuP-11 Area-Selective Atomic Layer Deposition on Dielectric Substrates via Selective Adsorption of Small Molecule Inhibitors*, **Jieun Oh**, H. Park, J. Lee, W. Kim,* Hanyang University, Korea

Area-selective atomic layer deposition (AS-ALD), surface-determined patterning of bottom-up approaches, is a key technical element compatible with the manufacture of 3D nanoelectronics. It is possible to solve the misalignment issues that occur during the lithography step through accurate pattern placement onto the desired area (referred to as the growth area). The current dominant method for AS-ALD involves using self-assembled monolayers (SAMs) to deactivate certain surface areas. However, SAMs have some drawbacks that prevent their use for sub-10 nm device applications due to their large size, making it difficult for them to be deposited on substrates by vapor phase delivery. To overcome the limitations of using SAMs, a possible alternative is to use small molecule inhibitors (SMIs) that can be delivered in the vapor phase due to their high volatility. In this work, we have demonstrated AS-ALD on dielectric substrates based on the chemo-selective adsorption of small molecule inhibitors. This work employed molecules containing a new silane as a vapor-phase surface moderator to prevent film growth during the subsequent ALD process.The chemical adsorption of inhibitors was confirmed by exploring SiO_2 as a growth area and SiN and SiON substrates as a non-growth area. Ru ALD was carried out to check the blocking capability of the inhibitor on surfaces. It is worth noting that this approach would be applicable to advance the bottom-up nanofabrication to oxide and nitride patterns for next-generation nanoelectronics.

AS-TuP-12 Inline Metrology to Characterize and Improve Process Control of Area Selective Deposition*, **Ganesh Vanamu**, W. Lee,* Nova Metrology Instruments*; R. Koret, J. Hung,* Nova Measuring Instruments, Israel*; J. Watkins, T. Stoll,* Nova Measuring Instruments

As the semiconductors industry transitions more rapidly towards integration of nanoscale three-dimensional electronic devices, the need for Area Selective Deposition (ASD) increases because self-aligned patterning with selective Atomic Layer Deposition is advantageous over conventional patterning with lithography. The selectivity in ASD is usually achieved by changing the surface chemistry in the area where film growth is either desired or not desired. ALD techniques have proven effective in controlling the adsorption of precursor molecules in specific areas on the substrate. Area-selective ALD faces challenges such as the loss of selectivity after only a few nm thick films are deposited and the extremely long-time intervals necessary to coat defect-free self-assembled monolayers. To overcome these challenges, ASD processes have recently been developed to combine selective modification deposition and selective etching. During the first deposition process, material imperfections such as different composition films are being simultaneously deposited on different material surfaces.

During device fabrication, atomic composition and thickness of the film in the desired locations - as well as unwanted residual material left over in the un-desired locations - need to be precisely monitored after the selective etch processes. This paper explores the use of Nova VERAFLEX®, an industry standard in-line X-ray Photo Spectroscopy (XPS) system measuring materials thickness and composition including bonding states in critical HVM deposition steps. VERAFLEX® measures ultra-thin films with Angstrom level resolution and sensitivity and is used for advance process control of the deposition process. XPS with automated feed forward capability, provides a precise thickness and composition of multi-layers without being affected by the properties of the underlying complex films. Compared to optical metrology solutions such as ellipsometers, XPS holds the advantage of directly detecting and analyzing atom-specific signals without the need to deconvolve optical properties from film thicknesses. For this particular ASD process, we measure the different surfaces where the ALD occurs prior to the deposition and then measure the film after the selective etch to determine the thickness and composition of the desired and unwanted materials on each of the surfaces. With fully automated inline capability on 300mm wafers, VERAFLEX® enables quick turnaround of XPS measurements, thus accelerating the development of ASD process development and help solve critical device challenges by provide better process control.

Nanostructure Synthesis and Fabrication
Room Evergreen Ballroom & Foyer - Session NS-TuP
Nanostructures Synthesis and Fabrication Poster Session

NS-TuP-1 Membrane Property Modification for Energy-efficient Membrane Separations via Vapor Phase Infiltration, ***Yuri Choe**, M. Ong, D. Bergsman,* University of Washington

Vapor phase infiltration (VPI) is an emerging method synthesize inorganic materials within polymers using vapor-phase reactants. The incorporation of a secondary molecular species within the polymer via VPI can be used to control the mechanical properties, chemical stability, and thermal resistance of these polymers, making this VPI process applicable to many technologies. For example, VPI has been shown to make commercial membrane filters more stable to organic solvents and high temperatures, potentially enabling their use for emerging separation areas. However, only a handful of VPI process chemistries have been explored. To further expand the properties that can be produced using this technique, more diverse reactants need to be tested. This project focuses on testing organic VPI reactants, such as diethylzinc (DEZ) with ethylene glycol (EG) to synthesize zincones (Zn-organic hybrid material). We expose polyethersulfone (PES) membranes to these reactants, measuring diffusion of reactants and the possible successful reaction of these reactants, along with any changes in the mechanical, thermal, and chemical stability of the resulting hybrid membranes. X-ray photoelectron spectroscopy (XPS) is used to measure any reaction products, while scanning electron microscopy (SEM) along with energy dispersive X-ray (EDX) is used for depth profiling of elemental compositions Ultimately, this project focuses on producing hybrid organic-inorganic membranes with greater stabilities at high temperatures and with various chemicals, in the hope that these membranes could be used to separate materials previously inaccessible to polymer membranes, such as organic solvents.

NS-TuP-2 Stacking 2D Chalcogenides Utilizing ALD, *D. Shin, J. Yang, F. Krahl, **Sebastian Lehmann**, K. Nielsch,* Leibniz Institute for Solid State and Materials Research, Germany

Chalcogenides, especially transition metal dichalcogenides (TDMCs, but also some other chalcogenides like SnS_2 and Sb_2Se_3) have a layered structure similar to graphene, but instead of being a semimetal they offer a wide variety from semiconducting to conducting materials that are interesting for efficient, fast (and possibly flexible) electronics. Their electronic behavior can be strongly influenced by the thickness of the material (e.g. how many sheets are stacked on top of each other) [1].

With atomic layer deposition (ALD) the layer stacking and individual layer thickness can be precisely controlled in the nm scale and several 2D materials have already been deposited with ALD [2], [3]. ALD is also scalable, unlike other methods for the synthesis of 2D materials e.g. exfoliation.

We utilize ALD to deposit superlattice stacks of 2D materials with “spacing” materials in between to examine their electrical properties. An example is our fabrication of a superlattice consisting of SnS_2 and Sb_2S_3 via ALD but results on other systems including TiS_2, PbS and other sulfides will be presented as well.

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NS-TuP-3 Stepwise Growth of Crystalline MoS_2 in Atomic Layer Deposition, *A. Cho, S. Ryu, **Seong Keun Kim**,* Korea Institute of Science and Technology, Republic of Korea

Atomic layer deposition (ALD) is considered a promising growth technique for transition metal dichalcogenides (TMDCs) because it ensures uniformity and homogeneity of the TMDC grains. However, the poor crystallinity of ALD-grown TMDCs remains a critical challenge. Although crystallinity depends on the growth mechanism, the growth behavior of crystalline TMDCs in ALD is unclear. We investigated the growth behavior of highly crystallized molybdenum disulfide (MoS_2) by ALD at 650 C with an extra pulse of remote H_2 plasma. Growth at high temperatures using the activated species aided surface diffusion of the adsorbates. The ALD process facilitates repeated growth and saturation of MoS_2, unlike the normal ALD of 3D bulk materials, where the film thickness monotonically increases with the number of ALD cycles. This unique behavior resulted from the evolution of the basal plane without dangling bonds. On the basal plane, MoS_2 lateral growth dominates vertical growth, and prolonged incubation is required for nucleation on the basal plane. The grain size is small (up to two monolayers) because of the limited mobility on SiO_2, and the grains of the third layer grow to a few hundred nanometers. These findings provide insights into the development of ALD technology for application to high-quality TMDCs.

NS-TuP-4 Electrical Properties of ZnO Nanostructures Derived from Sequential Infiltration Synthesis in Self-Assembled Block Copolymer Patterns: Effects of Alumina Priming, ***Won-Il Lee**, A. Subramanian,* Stony Brook University/Brookhaven National Laboratory*; N. Tiwale, K. Kisslinger,* Brookhaven National Laboratory*; C. Nam,* Brookhaven National Laboratory and State University of New York at Stony Brook

Self-assembled block copolymers (BCPs) are promising for the bottom-up, low-cost lithography of functional nanoarchitectures. Especially, BCP thin films can be directly converted into inorganic replicas by sequential infiltration synthesis (SIS), an organic-inorganic hybridization method derived from atomic layer deposition (ALD), which can selectively infiltrate target inorganic materials into one of the polymer blocks in vapor phase. For the high-fidelity infiltration of target materials, alumina is often first infiltrated (“alumina priming”) to overcome weak binding of the precursors of target inorganic materials with BCP templates. However, the effects of priming alumina–an electrical insulator–on the electrical properties of the final inorganic nanostructures have been rarely studied. In this work, we investigate the effects of alumina priming on the structural and electrical properties of ZnO nanowire fingerprint patterns fabricated by SIS using diethylzinc (DEZ) and water vapor on the lamellar pattern of self-assembled poly(styrene-b-methyl methacrylate) (PS-b-PMMA) BCP thin film as a function of the amount of infiltrated AlOx contents controlled by trimethylaluminum (TMA) exposure time during a single alumina priming cycle. We find that the characteristic dimension, chemical composition, and electrical conductivity of synthesized ZnO nanostructures could be fine-tuned by controlling TMA exposure duration. Specifically, increasing TMA exposure time naturally led to improved ZnO infiltration/structural fidelity and increasing feature dimensions (width and height of nanowires), accompanied by elevating Al contents. Counterintuitively, the electrical resistivity of ZnO nanostructure, extracted via transmission line method (TLM) from the two-terminal current-voltage characteristics, was initially decreasing with increasing TMA exposure time, down to 14.3 kΩ·cm, with corresponding Al concentration of 5.3 at.%., while a further increased TMA exposure duration beyond rendered the resistivity up to two orders of magnitude higher. The observed enhancement in ZnO electrical conductivity by alumina priming could be understood from the well-known case of Al-doped ZnO (AZO), where optimal Al doping in a similar concentration range as in the current study maximizes the ZnO conductivity. The results show that the alumina priming condition typically used for SIS in the field would generally improve the conductivity of infiltration-synthesized ZnO nanostructures, along with their infiltration and structural fidelities.

NS-TuP-5 *in-Situ* XPS Analysis for Wo_3 Sulfurization Process, *C. Chang, B. Liu,* Taiwan Instrument Research Institute, NARlabs, Taiwan*; **Yang-Yu Jhang**,* Taiwan Instrument Research Institute, NARLabs, Taiwan

TMDs are layered materials that can exhibit semiconducting, metallic and even superconducting behavior. In the bulk formula, the semiconducting phases have an indirect band gap. Recently, these layered systems have attracted a great deal of attention mainly due to their complementary electronic properties when compared to other 2D materials. However, these bulk properties could be significantly modified when the system becomes monolayer; the indirect band gap becomes direct. Such changes in the band structure when reducing the thickness have important implications for the development of novel applications, such as high photoluminescence (PL) quantum yield, excellent flexibility, and thermal stability.

Previous studies have demonstrated direct sulfurization of the metal precursor as an effective route to produce large-area TMDs. In this paper,

we have produced WS_2/SiO_2 by depositing WO_x thin films directly onto Si wafer followed by sulfurization to produce WS_2/SiO_2 heterostructures. However, ALD technique is well known for its thickness controllability, reproducibility, wafer-level thickness uniformity and high conformality. Here, we grew WO_x films by ALD method, and the synthesized WS_2 layer retained the inherent benefits of the ALD process. The overall experiments and measurement were carried out on our homemade 6" cluster systems, which include ALD, RTP, and XPS modules. The sample transfer inside were under $5x10^{-6}$ torr to avoid air pollution. WO_x films were deposited on Si wafer at ALD moduleat ~230°C. After that, sulfurization process were progressed at RTP module, which connected the sulfurization equipment. This unit heats TAA powder at ~130°C and results H_2S gas. Lastly, XPS measurements revealed binding energy shift of $W4f_{5/2, 7/2}$, indicating mostly WO_x converse to WS_2 during the process.

NS-TuP-7 Reversible Electronic Phase Transition in VO_2 Thin Films and Nanostructures*, **Jun Peng**, D. Hensel,* Center for Hybrid Nanostructures, Universität Hamburg, Germany*; L. Maragno, N. James,* Integrated Materials Systems Group, Institute of Advanced Ceramics, Hamburg University of Technology, Germany*; C. Heyn,* Center for Hybrid Nanostructures, Universität Hamburg, Germany*; K. Furlan,* Integrated Materials Systems Group, Institute of Advanced Ceramics, Hamburg University of Technology, Germany*; R. Blick, R. Zierold,* Center for Hybrid Nanostructures, Universität Hamburg, Germany

High-quality vanadium dioxide (VO_2) reveals a phase transition from a dielectric to a metallic state at around 340 K. Despite ongoing discussions regarding the underlying cause of this transition. It has been demonstrated that the complex coupling among lattice, charge, spin, and orbital results in an electronic transition that alters the sample's electrical, thermal, and optical properties at the phase transition. This unique property has led to its utilization exploration in various electronic and optoelectronic applications, including high-temperature thermoelectric materials, thin-film resistors, and optical modulators.

We will present the synthesis and characterization of tailor-made VO_2 thin films (2D), nanotubes (1D), and inverse opals (3D) prepared through a combination of thermal atomic layer deposition (ALD, from TDMAV plus water in a custom-built reactor) and subsequent thermal annealing. Temperature-dependent electrical measurements, Raman spectroscopy, and UV-Vis-NIR characterization comprehensively evaluate the electronic phase transition. First, the report will discuss the impact of various parameters during preparation on the thin film quality and the insulator-to-metal transition (IMT), including substrates, ALD parameters, and annealing conditions. Afterward, the fabrication of VO_2 nanostructured electrical devices will be highlighted, based on the optimized recipe for synthesizing VO_2 thin films with a phase transition temperature of around 335 K, a hysteresis width of approximately 10 K, and a remarkable resistance change of about three orders of magnitude. Specifically, the phase transition in electrically contacted, individual core-shell (Si-VO_2) nanowires is shown. Moreover, we show that the applied voltage can trigger the IMT in such an ALD-based one-dimensional VO_2 device. Finally, we will outline the preparation route for switchable photonic crystals based on inverse VO_2 opals.

Based on the reported results, it can be concluded that ALD of VO_2 holds significant promise for the development of functional, switchable materials in 1D (elongated structures), 2D (thin films), and 3D (inverse opals or bulk-like samples) laying a solid basis for future large-scale applications. Exemplarily, energy-efficient, next-generation nanostructured smart windows are conceivable that can dynamically alter their transmission properties in response to external stimuli, such as temperature, voltage, and current.

NS-TuP-8 Fabrication of 2D-SnS_2 Film Using Atomic Layer Deposition and Hydrogen Sulfide Gas Annealing*, **Yeonsik Choi**, S. Song, J. Kim, D. Lee, J. Bae, Y. Lee, H. Jeon,* Hanyang University, Korea

2D-tin disulfide (SnS_2) is a material with unique physical, optical, and electrical characteristics that can be used in various optoelectronic devices. In addition, it is possible to fabricate a 2D-SnS_2 material forming a two-dimensional layered structure with precise thickness control using atomic layer deposition (ALD). Since 2D-SnS_2 deposited through ALD is based on a low-temperature process, it has the advantage of being applicable not only to silicon substrates but also to flexible substrates such as polyimide (PI) and polyethylene terephthalate (PET). However, since the process is performed at a low temperature, the crystallinity of the material is low and the film quality is relatively poor compared to other processing methods. Therefore, various post-annealing processes that improve the crystallinity of SnS_2 material have been studied, and various aspects such as the crystallinity improvement or the phase transitions were shown depending on the post-annealing atmospheres and temperatures. In this work, we analyzed the crystallinity and grain sizes of 2D-SnS_2 deposited by ALD according to the concentration of hydrogen sulfide (H_2S) in a H_2S gas atmosphere at 4.00 and 99.99% and the high crystallinity was shown at 350°C with a high concentration of 99.99% H_2S gas. Carrier concentration was also measured and more than 10^{18} cm^{-3} was measured at 350°C in the 99.99% concentration of H_2S atmosphere. Comparing to 4.00% concentration of H_2S, pure tetravalent positive states of Sn (Sn^{4+}) were confirmed through binding energy analysis in the post-annealing in the H_2S atmosphere of 99.99% concentration. In addition, as a result of the post-annealing process after deposition on a 4-inch large-area substrate, a high film uniformity and high step coverage (> 98%) on a trench structure wafer were achieved confirming the possibility of future application to the semiconductor industry.

NS-TuP-11 Phase Control of Two-Dimensional Tin Sulfide Compounds Deposited by Atomic Layer Deposition*, **Dong Geun Kim**, J. Lee, J. Choi, J. Ahn,* Hanyang University, Korea

Two-dimensional (2D) metal chalcogenides have received great attention because of their unique properties, which are different from bulk materials. Among 2D metal chalcogenides, tin sulfide compounds (SnS_x) including tin monosulfide (SnS) and tin disulfide (SnS_2) have excellent optoelectronic properties, low melting point, thermal stability, and hydrolytic stability compared to the other representative 2D materials such as MoS_2 and WS_2. Because the electrical property of SnS_x is highly dependent on its phase, phase-selective deposition has been required. It has been reported that high-quality SnS_x flakes can be synthesized for chemical vapor deposition (CVD) and sulfurization of metals or metal oxides. However, there is a limitation of applying for next-generation semiconductor devices because of a high process temperature and poor uniformity. Meanwhile, the ALD method based on the self-limiting reaction enables large-area uniformity and conformality over complex-shaped substrates with low growth temperatures. In addition, since the properties of 2D materials are strongly affected by their thickness, the ALD with atomic level thickness control is a suitable deposition technique for 2D materials. In this study, we investigated the phase transition tendency of SnS_x thin films according to deposition temperature and post-annealing atmosphere. SnS_2 phases were dominated at H_2S ambient annealing of relatively low annealing temperature regardless of deposition temperature, according to the increased annealing temperature, the phase transition for SnS_2 to SnS occurred. These phase transitions from SnS_2 to SnS phase were observed at forming ambient gas annealing. In addition, as the annealing pressure decreased regardless of ambient gas, the phase transitions occurred at a lower temperature. Finally, the electrical properties were evaluated by fabricating thin film transistors (TFTs) using optimized conditions of SnS_2 and SnS thin films.

NS-TuP-12 Area-Selective Deposition of 2D-MoS_2 using Self-Assembled Monolayer*, **Jeong-hun Choi**, D. Kim, S. Lee, J. Ahn,* Hanyang University, Korea

Layered two-dimensional molybdenum sulfide (MoS_2) has attracted great interest for a promising candidate material for opto-electronics and photo sensors applications due to its unique characteristics such as tunable bandgap, high electron mobility and high current on/off ratio. Significant efforts have been placed to apply MoS_2 in industrial fields, leading to significant progress in the deposition method of MoS_2. [1],[2] However, patterning technology for MoS_2 remains a challenge. In particular, 2D materials like MoS_2 have extremely thin and weak interlayer bonding due to the absence of dangling bonds, making it difficult to apply traditional top-down patterning approach. Therefore, we demonstrated a new area-selective deposition method for MoS_2 using self-assembled monolayer (SAM). To prevent the degradation of SAM, the deposition of MoS_2 was carried out using a pulsed metal-organic chemical vapor deposition (MOCVD) method, which allowed for the synthesis of high-quality MoS_2 at a low temperature. The growth of MoS_2 was effectively prevented by the SAM patterned using photolithography processes. The selectivity for MoS_2 according to the length of the SAM backbone was investigated using X-ray Fluorescence spectroscopy and Raman measurement. Additionally, the influence of the SAM coating process on the crystallinity and impurity concentration of the MoS_2 film was confirmed using X-ray diffraction and X-ray photoelectron spectroscopy. Furthermore, the potential of area-selective deposition of MoS_2 using SAM was demonstrated by fabricating a MoS_2 gas sensor.

ALD Applications
Room Grand Ballroom H-K - Session AA1-WeM
Memory RRAM, Neuromorphic, NVM

Moderator: Dr. Robert Clark, TEL Technology Center, America, LLC

8:00am **AA1-WeM-1 3D Integrated Device Applications of ALD-Grown Ferroelectric and Oxide-Semiconductor Materials***, **Masaharu Kobayashi**,* University of Tokyo, Japan **INVITED**

Ferroelectric memory is a candidate for lower power memory device. HfO_2-based ferroelectric (FE-HfO_2) has been recently discovered [1], which drives ALD-based ferroelectric (FE) material and opens pathway to high-capacity memory. Oxide semiconductor (OS) such as IGZO is now getting attention for BEOL-compatible transistor channel material [2]. 3D integrated device application requires ALD growth of OS. These two ALD-based materials have been intensively explored in R&D of LSI community as key enablers for energy-efficient computing devices. In this presentation, I will discuss challenge and opportunity of ALD process for 3D integrated device applications based on our recent research progress.

(1) Monolithic 3D integration of OS FET and $HfZrO_2$ FE-capacitor

HfO_2-based FE-capacitor can be formed at BEOL because of its low thermal budget. Monolithic integration of embedded FeRAM can be realized by FE-HfO_2 and OS FET, which enables high density and high bandwidth nonvolatile memory for xPU. High quality $HfZrO_2$ can be grown by ALD, where HfO_2 and ZrO_2 are alternatively grown layer by layer. After crystallization anneal, $HfZrO_2$ becomes orthorhombic phase and shows ferroelectricity. We found that OS capping layer helps to reduce anneal temperature and improves memory reliability. We demonstrated 1T1C FeRAM cell operation by Sn-doped IGZO (IGZTO) access transistor and HZO FE-capacitor with just 400℃ thermal budget [3].

(2) 3D vertical channel FeFET for high-density and low power FE storage memory.

Ferroelectric FET (FeFET) is an one-transistor memory device with FE gate insulator. Depending on its polarization, FET can be set as high V_{th} state or low V_{th} state. Similar to NAND flash memory, FeFET can also have 3D vertical channel architecture. We are interested in OS channel material instead of conventional poly-silicon channel for 3D FeFET because of its high mobility, low thermal budget, and potentially high reliability. We developed ALD growth process of InOx and applied it to 3D vertical channel FeFET integration process. We demonstrated memory operation of 3D vertical channel FeFET with 5nm-thick InOx [4].

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8:30am **AA1-WeM-3 Cross-Point Metal-Ferroelectric-Metal Capacitors Array for Compute-in-Memory Applications***, **Minjong Lee**, H. Hernandez-Arriaga, J. Kim, J. Kim,* University of Texas at Dallas

Rapid advancement of electronic technology has been a driving force towards the development of high-density and low-power processors, from a classical von-Neumann computing architecture to an interesting compute-in-memory (CIM) configuration. With the adoption of ferroelectric (FE) materials for CIM applications, most researchers have focused on the FE field-effect-transistors based vector-matrix multiplication (VMM) operation which can realize the analog conductance states;[1] however, the studies for metal-FE-metal (MFM) structure are rare to see.

In this work, we demonstrate a 2×2 pattern recognition system using a 4×2 cross-point array configuration of $Hf_{0.5}Zr_{0.5}O_2$ (HZO) MFM capacitors. TiN/HZO/TiN MFM capacitors were fabricated following our previous work.[2] However, the finger shaped TiN top and bottom electrodes (TEs and BEs) were patterned by the photolithography and ICP metal etching, and the thicker TEs were adopted to reduce series resistance components in TE lines. Since the polarization-change in MFM capacitors induces the different amounts of stored charges, the current signal can allow binarized states, generally called as switching and non-switching currents. It should be noted that the feature of HZO MFM capacitors is particularly similar to a polarization-induced synaptic charge behavior unlike conventional resistance/capacitance ones. Furthermore, the devices enable an excellent VMM operation, eligible for the neuromorphic computing with binary weight, by implementing the readout of maximum current value. For the pattern recognition, we followed the experimentally demonstration-method of 2×2 pattern recognition, introduced in a previous report.[3] Each cell of 2×2 pattern was applied to the TiN TEs, in which the white pattern is regarded as positive polarization state by 2.5 V set-pulse while the black pattern implies a negative polarization state by –2.5 V set-pulse. The tested patterns are all occurrences in 2×2 patterns (total 16 patterns). As the pattern recognition results, the current readout has the recognition accuracy of 81.3%, which is comparable results with the previous report,[3] thus highlighting the promise of the simple MFM capacitors towards the neuromorphic computing applications. The detailed results will be presented.

This work is supported by GRC-NMP program (#3001.001) of SRCUT Dallas' Texas Analog Center of Excellence (TxACE). The ozone generator used in this work was provided by TMEIC.

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8:45am **AA1-WeM-4 Using ALD to Precisely Place Multiple Transition Metal Impurities to Defect Engineer MIM Diode Performance***, **Shane Witsell**, J. Conley,* Oregon State University

Metal/insulator/metal (MIM) diodes promise ultra-fast rectification for applications in THz energy harvesting and detection but simultaneously require low turn on voltage (V_{ON}), low zero bias resistance (ZBR), and reasonable current-voltage (*I-V*) asymmetry (f_{asym}). Methods for improving these parameters beyond the standard use of different work function metal electrodes ($\Delta\Phi_M$), include multiple insulators (MIIM, MIIIM) to promote resonant or "step" tunneling, geometric field enhancements (using, e.g., carbon nanotubes), and *intrinsic* defects to promote defect-enhanced conduction [1]. Recently, we applied atomic layer deposition (ALD) to precisely insert transition metals into the Al_2O_3 tunnel barrier of dissimilar electrode MIM diodes. These metals introduce *extrinsic* defect levels that enable conduction pathways not present in undoped Al_2O_3 [2]. Ni (D_{Ni}) defects placed nearer the smaller Φ_M electrode, improved f_{asym}, but increased V_{ON}, likely due to negative charge trapped at defect levels lying energetically near or below the equilibrium Fermi level ($E_{F,equil}$) of the electrodes [3]. On the other hand, Ti (D_{Ti}) defects placed near the larger Φ_M electrode reduced V_{ON} due to positive charge trapped in levels above $E_{F,equil}$, but slightly increased f_{asym}. Results were consistent with asymmetric trap assisted tunneling (TAT). In this work, both Ni and Ti impurity defect layers were inserted at specific positions within the Al_2O_3 insulator thickness to allow for defect levels to align at specific applied voltages to promote asymmetric dual defect assisted tunneling.

ALD was performed using TMA/H_2O, $Ni(tBu_2DAD)_2/O_3$, and TTIP/H_2O. Two versions of doped structures were created: (i) "Dual Doped" in which the two ALD cycle Ni defect layer was positioned within the Al_2O_3 closer to the smaller Φ_M electrode and the two ALD cycle Ti layer inserted near the higher Φ_M electrode, and (ii) "Reverse Doped" in which the positions of the Ni and Ti layers were swapped. Electrode pairs with varying work functions were tested to investigate defect alignment. The Dual Doped Pt/Al_2O_3/Al produced the largest increase in low voltage asymmetry over undoped MIM devices, while the Reverse Doped Pt/Al_2O_3/Al device produced higher breakdown voltages and high voltage asymmetry. Both devices show lower ZBR. Additional results will be presented at the meeting including capacitance-voltage measurements on MIM and metal/oxide/semiconductor (MOS) devices. This work shows that ALD can be an effective tool for engineering device behavior.

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9:00am **AA1-WeM-5 The Impact of Oxygen Source on the Formation of TiN Interface at the Initial Stage ALD process of Hafnia-based Ferroelectrics: An *in-situ* Analysis***, **Jin-Hyun Kim**, S. Kim, D. Le, Y. Jung, S. Hwang, H. Hernandez-Arriaga, M. Lee, A. Khosravi, K. Tan,* University of Texas at Dallas*; J. Spiegelman, M. Benham,* RASIRC*; S. Kim,* Kangwon University, Republic of Korea*; J. Kim,* University of Texas at Dallas

Ferroelectricity in doped hafnia is widely studied with its promising capability for memory applications. However, despite the mature HfO2 ALD technology, hafnia-based ferroelectrics still have major reliability issues such as relaxation, imprint, fatigue, and breakdown.1 These reliability properties are deeply related to the interface condition between the ferroelectric film and the electrodes. Thus, many reports suggested ways to improve reliability and enhance ferroelectricity by modifying the interface states of the metal-ferroelectric-metal (MFM) capacitors.2 Furthermore, the interface becomes a bigger issue for the ferroelectric layer scaled down thinner than 5 nm due to series capacitance and difficulties in crystallization

due to high surface energy.3 Therefore, it is crucial to understand the interface formation and the properties more carefully to further improve the reliability and scalability of the hafnia-based ferroelectric materials.

Herein, we investigated the effects of various oxidants on the interface layer using in-situ reflectance absorption infrared spectroscopy (RAIRS) and X-ray photoelectron spectroscopy (XPS). With these techniques, we monitored the surface reactions and interface formation in Hf0.5Zr0.5O2 (HZO) ALD process with TDMA-Hf/Zr and three different oxidants sources (H2O, O¬3, and anhydrous H2O2) on TiN substrate at 250 °C. As determined with in-situ IR absorbance spectra, all three oxidants effectively oxidized the TiN surface with just 1 exposure cycle. With additional pulses of O3, the intensity and peak area of features related to Ti–O and TiN–O continuously increased. However, in the case of H2O and H2O2, limited formation of oxygen bonds was observed on TiN surface. Interestingly, contrasting to H2O, H2O2 formed self-limiting peroxyl groups on the TiN surface with a minimum interface formation, resulting in superior film properties and robust reliability of H2O2-based HZO capacitors.

Moreover, the in-situ XPS data using H2O showed the formation of Ti–O bonds after the initial cycle more clearly, which strongly supports the RAIRS result. Extensive in-situ XPS analysis will be conducted to confirm these observations in the IR spectra.

We thank YEST and KEIT for supporting the project through ISTD Program (No.20010806). This work is also supported by GRC-LMD program (task#3001.001) through SRC. The BRUTE hydrogen peroxide was provided by RASIRC and the ozone generator was from TMEIC.

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9:15am **AA1-WeM-6 Performance Enhancement in HZO Based Ferroelectric Memory Devices**, ***Ranjith K. Ramachandran**, L. Lukose,* ASM Belgium*; A. Leonhardt, M. Surman,* ASM Microchemistry Ltd., Finland*; V. Koladi Mootheri,* ASM Belgium*; M. Ioana Popovici,* IMEC, Belgium*; M. Givens, A. Illiberi,* ASM Belgium

HfO_2 based ferroelectric (FE) materials have gained tremendous attention as a potential candidate for memory applications such as FeFET and FeRAM. Since its first demonstration as a FE material [1], immense research has been done to circumvent the challenges such as scalability, increasing the remnant polarization (Pr), and improving endurance. Among others, Zr-doped HfO_2, hafnium zirconate (HZO) is being intensively studied due to its compatibility with complementary metal oxide semiconductor (CMOS) processing and excellent scalability.

The ferroelectricity in HZO films is believed to originate from the presence of polar metastable orthorhombic phase (o-phase: Pca21). Several methods have been explored to stabilize o-phase in the films, such as annealing, doping, and interface engineering. This, in turn, depended on the advent of synthesis methods that offer atomic level control over the thickness, composition, and interface, i.e., Atomic Layer Deposition (ALD). In this report, using ALD, we demonstrate three different methods such as 1) precursor selection 2) doping, and 3) interface engineering to improve the FE performance of HZO. ALD of HZO and La:HZO films was performed in a 300mm, industrial scale, EmerALD ALD reactor at a substrate temperature of 275°C. Both halide and MO-based precursors were used as the metal source with H_2O/O_3 as a co-reactant and their FE performances were compared via remanent polarization (2Pr) and endurance measurements.

First, the influence of ALD precursor and co-reactant on the performance of HZO devices is demonstrated. Halide-based precursor shows initially high 2Pr compared to the MO (with O_3 as co-reactant). However, the onset of fatigue is at $1x10^5$ cycles due to the presence of possible Cl impurities. In the case of MO precursor, there is an observed wakeup effect which can be attributed to the transition from the tetragonal-orthorhombic phase (t-o phase) to the stable o-phase with increased cycling. The stable o-phase leads to higher 2Pr with the number of cycles and better endurance (fatigue at $3.5x10^7$ cycles) compared to the halide-based precursor (**Fig. 1**). Together with low coercive field (2Ec) and high 2Pr, this MO-based process has useful applications in Fe-RAM. In addition, ozone as co-reactant shows improved 2Pr compared to water.

Furthermore, La doping on HZO was carried out to improve wake-up, max 2Pr, and endurance (Table 1). Subsequently, interface engineering with La-doped HZO resulted in record-high 2Pr (63 µC/cm^2), with high endurance and lower wake-up (**Table 1**) [2].

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9:30am **AA1-WeM-7 Stabilization of Tetragonal Phase of Ti-doped ZrO_2 Deposited by ALD**, ***Seokhwi Song**, Y. Choi, E. Kim, K. Kim, H. Jeon,* Hanyang University, Korea

Manufacturing metal-insulator-metal (MIM) capacitors with high capacitance and low leakage current for dynamic random access memory (DRAM) has become a challenge as electronic devices rapidly decrease in size and distances between devices increase. Therefore, in this study, Ti-doped ZrO2 was investigated as a high-k material for DRAM capacitors. ZrO2 film has been widely studied as a high-k material for DRAM capacitors due to its high permittivity and wide bandgap. ZrO2 has monoclinic, cubic and tetragonal crystal phases. The dielectric constant of ZrO2 is highly dependent on the crystal structure (monoclinic: 19.7, cubic: 36.8, tetragonal: 46.6). However, a material with a higher permittivity than common ZrO2 was required, and a method of changing the crystal structure of ZrO2 through doping was studied. The same tetravalent element as Zr can stabilize the cubic/tetragonal phase of ZrO2 without introducing oxygen vacancies into the thin film. When the tetravalent dopant is replaced by a Zr atom, the distance between the dopant and the O atom is different from that of the Zr-O atom, so it is converted into a cubic or tetragonal phase. Among them, Ti dopant is a promising stabilizer to replace Zr atoms.

Atomic Layer Deposition (ALD) is an optimal deposition method for Ti-doped ZrO2 at a desired Ti dopant concentration. The concentration of Ti may be controlled through a super cycle ALD process in which n ALD cycles for the host material ZrO2 and 1 ALD cycle for the dopant material Ti are repeated. Through this ALD process, Ti-doped ZrO2 having a desired doping concentration can be deposited to a desired thickness. Ozone with high oxidizing power is essential to improve crystallinity. Since the crystallinity varies not only with the dopant concentration but also with the ozone concentration, Ti-doped ZrO2 is deposited at various ozone concentrations of 100 to 400g/m3 to check the crystallinity change.

In this study, Cyclopentadienyl Tris(dimethylamino)zirconium (CpZr(NMe2)3) was used as a precursor and titanium isopropoxide (TTIP) was used as a dopant. And ozone was used as a reactant. You want to deposit Ti doped ZrO2 and analyze the film with a supercycle ALD process. The core of this study is to confirm the change in the crystallinity of the thin film and the change in the physical properties of the thin film according to the Ti doping concentration.

9:45am **AA1-WeM-8 Three Terminal Synaptic Devices Employing ALD Grown Dual Dielectrics and Their Linear Learning Process**, ***Jung Wook Lim**,* Electronics and Telecommunications Research Institute, Republic of Korea*; J. Kim,* ETRI, Republic of Korea

To overcome the limitation of the von-neumann architecture, synaptic devices has been widely researched to emulate synaptic functions[1-2]. For this, synaptic devices with high stability and CMOS compatibility are required to overcome the barrier of commercial entry. Three terminal inorganic oxide transistors may be most suitable to satisfy these requirements. In our group, three terminal synaptic transistors employing ALD grown the TiO_2 channel layer and dual gate dielectrics were fabricated on Si n^{++} wafers (used as bottom gate electrodes) and the vertical structure is shown in Fig. 1. The synaptic behavior is performed by storing or capturing charges, and for this purpose, the interface trap sites were formed at the interface between channels and dielectrics by in-situ ALD process. We have used selectively deep traps among traps at different levels in the energy bandgap for capturing holes, resulting in negative shift of threshold voltages[3-4]. As a synapse device in which learning is performed by an electrical signal, a phenomenon in which the transfer curve moves in a negative direction by hole traps was observed after supplying an electrical pulse. Interestingly, when a voltage pulse of 10 V or higher is applied for 0.5 s, the conductivity increases abruptly and the metallic behavior was observed and the result is shown in Fig. 2. For confirming synaptic performance, paired pulse facilitation (PPF) curves were obtained, in which 0.4 s and 11.11 s of life times were obtained for the pulse times of 5 ms and 0.5 s (10 V), respectively. With electrical pulses

of 10 V and 3 ms of short-term plasticity condition derived from PPF curves, long term plasticity was obtained with repeated pulses and the results are shown in Fig. 3. The 1024 conduction states (10 bit) was obtained with high linearity, which implies the high accuracy of recognition. The dual dielectrics are composed of ALD grown SiOx and AlOx films. The deep trap sites were formed at the interface of SiOx and TiO_2 channel layer, hence indicating that the in-situ plasma treatment is very important during the ALD growth. The AlOx films confirms the stability of devices and enhances the performance of transistors. In the further study, synaptic devices will implement the forgetting curves of human brains and their various phenomena.

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ALD Applications
Room Grand Ballroom H-K - Session AA2-WeM

Memory DRAM

Moderator: Prof. Parag Banerjee, University of Central Florida

10:45am **AA2-WeM-12 Opportunity of Atomic Scaled Materials in Revolutionary Memory Technologies*, Seiyon Kim,*** SK Hynix, Republic of Korea **INVITED**

The ALD technology has been widely utilized in modern nanometer scaled electronic due to the excellent uniformity, conformality, and thickness controllability.

The unique advantage of ALD is the “tune-ability” of the materials thanks to the freedom of changing concentration of elements and crystalline states. It makesALD films as versatile functional and structural materials with the capability to optimize electrical and physical properties for multiple applications spanning from logic to memory.

In DRAM storage node capacitor, without ALD technique, the metal electrode and the dielectric material cannot be deposited uniformly, considering the height of DRAM capacitor is more than 1µm, while the top opening of capacitor is just a few tens of nanometers. The aspect ratio of 3D NAND is even more severe than DRAM capacitor. Very conformal deposition with good uniformity is required in several critical steps, such as O-N-O charge trapping layer formation inside plug and thin metal deposition in replacement word line gates. In logic technology, Hf-based high K dielectric layer paired with ALD deposited work function metal has still been used for gate stacks since it revolutionized the transistor performance two decades ago. The low-k but robust SiOC film is key element of enabling gate pitch scaling and epi SD formation of Finfet devices.

As DRAM and NAND reaches sub-10nm node and 1000 layers respectively, many industries are afraid that the evolutionary approaches to extend the scaling would not work anymore. Therefore, revolutionary path technology such as stacked DRAM is taking more attention more than ever. The new revolutionary platform will require new devices, new integration schemes, and new materials. The requirement for new materials is expected to be very challenging, and more importantly, may require very different properties never asked in the past.

In this talk, I would like to illuminate how ALD materials have been utilized in ultra-scaled electrical devices, especially for DRAM and NAND. Then I will introduce emerging revolutionary memory technologies on the horizon. I also discuss about the requirement of structural and functional ALD materials to enable the future memory devices.

11:15am **AA2-WeM-14 Ultra High-k $HfZrO_4$ Thin Films Grown by Atomic Layer Deposition using Metal-Organic and Brute HOOH Precursors*, Harshil Kashyap,*** *A. Kummel,* University of California San Diego*; J. Spiegelman, M. Benham,* RASIRC

Lower leakage at low EOT is a requirement for DRAM application. Ferroelectric/antiferroelectric $HfZrO_4$ films have shown high-k at 10 nm but as the films are scaled, the dielectric properties of the films decrease[2,3]. The key to low EOT is to find a material with high-k at 5 nm or sub-5nm thickness with low leakage.

Metal-Insulator-Metal capacitors were[MB1] [#_msocom_1][HK2] [#_msocom_2] fabricated with $HfZrO_4$ thin films. 5nm $HfZrO_4$ was grown by ALD on sputtered TiN and W substrates at 275 °C using tetrakis(dimethylamino)hafnium (TDMAH), tetrakis(dimethylamino)zirconium (TDMAZ) (STREM) and H_2O_2 (Rasirc). $HfZrO_4$ thickness was determined by cross-sectional TEM and were between 5.0 and 5.5 nm. TiN and W electrodes were deposited by magnetron sputtering. Top electrodes were patterned by photolithography. Samples were annealed in N_2 at 600°C for 2 minutes. Control samples with H_2O were also fabricated for comparison with TiN and W electrodes.

C-V measurements were performed for $HfZrO_4$ films deposited with HOOH (Fig 1). Control samples made with H_2O were used for comparison. For $HfZrO_4$ using HOOH with TiN electrodes, there are 4 switching peaks in the C-V consistent with presence of the AFE phase (Fig. 1a). HZO with 1:1 Hf:Zr ratio is known to show FE switching; however, use of HOOH precursor may lead to Ti diffusion from TiN substrate into the HZO film. Small amounts of Ti are known to stabilize the AFE phase in HZO[4]. To study the impact of metal electrodes, samples with sputtered W electrodes were fabricated since W is known to show enhanced FE/AFE switching in HZO films. Undoped HZO with 1:1 Hf:Zr and W electrodes grown with HOOH (Fig 1b) shows only FE switching and no AFE switching.

When using HOOH, both the samples with TiN and W electrodes show record high capacitance for 5 nm films (> 10 mF/cm^2). Extrinsic contributions to k value from domain walls play an important role. A higher vol% of domain walls may be key to the extremely high-k observed in films fabricated using HOOH vs H_2O. A heuristic model of domain walls show surpassed polarization which are very susceptible to eternal stimuli and thus show high permittivity (Fig 2).

For DRAM application, it essential to have high-k near 0V. Both capacitors fabricated using HOOH show record high-k at (~58 with TiN, ~88 with W) 5 nm thickness which results in ultra-low EOT of ~3.5 A with TiN and ~2.5 A with W (Fig 3 a). The sample with W electrodes shows higher leakage in comparison with samples with TiN electrodes (Fig 4). This may be in part due to higher crystallinity in $HfZrO_4$ imparted by the W electrodes since major leakage pathway in crystalline $HfZrO_4$ thin films is grain boundaries.

11:30am **AA2-WeM-15 Achieving Ultra-High Mobility and Reliability of ALD-IGZO TFTs via Selective N2O Plasma Reactant for BEOL Applications*, Dong-Gyu Kim,*** Hanyang University, Republic of Korea*; H. Choi,* Chungnam National University, Republic of Korea*; Y. Kim, D. Lee, H. Oh,* Hanyang University, Republic of Korea*; J. Lee,* Chungnam National University, Republic of Korea*; J. Kim,* Ulsan National Institute of Science and Technology, Republic of Korea*; S. Lee, B. Kuh, T. Kim,* Samsung Electronics, Republic of Korea*; H. Kim,* Chungnam National University, Republic of Korea*; J. Park,* Hanyang University, Republic of Korea

The semiconductor industry is expanding toward artificial intelligence (AI), cloud data centers, and high-bandwidth memory processing in memory (HBM-PIM). In these fields, atomic layer deposition (ALD) is indispensable for adjusting thickness control and high step coverage. The design of high-performance field-effect transistors (FETs) with low-voltage operation, high field-effect mobility (μ_{FE}), and low leakage current have propelled the development of relevant fields. Oxide-based thin-film transistors (TFTs) are garnering increased attention owing to their steep sub-threshold swing (SS) and extremely low leakage current. Although oxide-based TFTs are known to restrict μ_{FE} (~30 cm^2/(V·s)), numerous research groups have demonstrated exceptional μ_{FE} values exceeding 100 cm^2/(V·s). However, the high stability of oxide-based TFTs is another prerequisite for their widespread application. Achieving high mobility and stability is challenging as the overall properties of oxide-based TFTs are compromised. Doping at oxide semiconductors with anions may resolve the issue of uniformity. Previous studies have confirmed that nitrogen (N) doping is promising for regulating oxygen vacancy (V_O) defect concentration. Because the atomic radius of N is comparable to that of oxygen (O), doped N is a suitable replacement for V_O defect sites.

In this work, we deposited plasma-enhanced ALD (PEALD)-IGZO TFT with O_2 plasma reactant using the super-cycle method at a set temperature of 200°C. For the In_2O_3, Ga_2O_3, and ZnO deposition, (3-dimethylaminopropyl)dimethylindium (DADI), trimethylgallium (TMGa), and diethylzinc (DEZ) precursors were utilized. To gain insight into N dopants for each cation of PEALD-IGZO, a nitrous oxide (N_2O) plasma reactant was selectively applied for each PEALD cation cycle. Our strategy here, the N_2O plasma reactant, is completely different from plasma treatment in that it participates in chemical reactions during the ALD process. Using a combinatorial study of experimental analysis and theoretical interpretation,

the N-doping mechanism and the associated enhancement in the performance and stability of PEALD-synthesized IGZO TFTs were investigated. Based on these insights, high-performance with stable PEALD-IGZO TFTs could be obtained with minimal V_{TH} shifts of 0.35 V in difficult PBTS environments (temperature stress: 95℃, field stress: 2 MV/cm) despite a high μ_{FE} of 106.5 ± 2.7 $cm^2/(V{\cdot}s)$. Our results provide insights into the atomic precision optimization of the performance and stability of IGZO TFTs.

11:45am **AA2-WeM-16 Ultrathin and Highly Crystalline Indium Oxide Thin Films Using Novel Liquid In Precursor as a New Channel Material*, Su-Hwan Choi, R. Seong-Hwan,*** Hanyang University, Korea*; C. Yeon, J. Jung, Y. Park,* Soulbrain, Republic of Korea*; J. Park,* Hanyang University, Korea

Oxide semiconductors containing indium oxides (InOx), such as IGZO, IGTO, and ITO, have been attracting attention for various applications, such as field effect transistors (FETs), catalysts, and active layers of memory devices because of their outstanding properties, such as high mobility, low off-current, and excellent uniformity. Among the oxide semiconductors, indium oxide is crucial because the electron carrier transport path mainly consists of In 5 s orbitals. The study of crystalline mechanisms and preferred crystal orientation of indium oxide were widely conducted because the characteristics of indium oxide, such as electrical and optical properties and reliability, are affected by InOx film crystallinity. Mengwei Si et al. reported an InOx channel FET with a thickness of 0.7 nm that can be applied to extended devices such as monolithic three-dimensional (3D) integration and dynamic random access memory (DRAM)[1]. However, the electrical properties of FETs were inferior because of the amorphous properties of 0.7nm thick InOx thin film. Since a constant thickness is required to crystallize the InOx film, the study of the critical thickness of crystallization is needed for further applications of InOx[2].

In this study, we developed a new liquid indium precursor with an ALD window from 200 to 350℃. To the best of our knowledge, this 350 ℃ is the highest ALD InOx deposition temperature using ozone as a reactant without impurities such as carbon and nitrogen. According to various analysis methods such as XRD and GIWAXS, 3 nm is the critical thickness of crystalline InOx films deposited by the ALD method using the SBIP-03 precursor. The authors studied the crystallinity effect of InOx in terms of thickness, deposition temperature, and post-annealing process. The crystallized 3 nm thick InOx film is adopted as the channel layer of FET. The FET has excellent transistor characteristics in terms of field-effect mobility (39.3 cm^2/Vs), threshold voltage (-0.7 V), subthreshold swing (310 mV/dec), and on-off current ratio (3.3x10^7).

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ALD Fundamentals
Room Grand Ballroom E-G - Session AF1-WeM
In Situ Measurement
Moderator: Prof. Mikko Ritala, University of Helsinki

8:00am **AF1-WeM-1 Measuring the Time-Resolved Heat of ALD Surface Reactions*, Ashley Bielinski,*** *E. Kamphaus, L. Cheng, A. Martinson,* Argonne National Laboratory **INVITED**

Our understanding of ALD reactions is often limited to simplified and idealized models. Developing a mechanistic understanding of ALD surface reactions is beneficial in a wide range of applications such as optimizing film properties, interface engineering, and area- or site-selective ALD. *In situ* measurement techniques such as ellipsometry and IR spectroscopy are increasingly used to investigate ALD processes, but they primarily probe the ALD film between surface reaction steps. Pyroelectric calorimetry provides new insight into ALD processes by enabling quantitative and time-resolved measurement of the heat evolved in ALD surface reactions.

We report the total heat generation and heat generation rates for the ALD reactions between trimethylaluminum (TMA) and water to form Al_2O_3 as well as the ALD reactions between tetrakis(dimethylamino)zirconium (TDMAZr) and water to form ZrO_2 at different temperatures. The calorimetric data was combined with *in situ* spectroscopic ellipsometry and Rutherford backscattering spectrometry analysis of optical growth rates and composition. The total heat generation of each reaction was compared with the theoretical reaction enthalpy and first-principles computational models to investigate the reaction mechanisms and thermodynamics. While the calorimetric measurements of ALD reaction heat agree well with the calculated standard reaction enthalpies, there is significant spread in how the first-principles computational results compare to the experimental values. This enables evaluation of proposed models and mechanisms while providing a benchmark for future models. Additionally, the heat generation rate provides information on reaction kinetics. For example, the water reaction for ZrO_2 was found to proceed approximately 100× faster than the water reaction for Al_2O_3 and the TDMAZr heat generation rate suggests a kinetically resolved two-step reaction.

Pyroelectric calorimetry provides unprecedented measurements of ALD reaction heat with resolution down to 50ns and 0.1 $\mu J/cm^2$. This provides a unique opportunity to investigate how ALD surface reactions proceed to deepen our understanding of what drives and limits these processes.

8:30am **AF1-WeM-3 HfO_2 ALD on Si(111) - A Mechanistic in-Situ Study through Time-resolved APXPS*, Rosemary Jones,*** Lund University, Sweden*; G. D'Acunto,* Stanford University*; P. Shayesteh,* Lund University, Sweden*; J. Gallet, F. Bournel, F. Rochet,* Sorbonne Universite, France*; I. Pinsard,* Lund University, Sweden*; A. Head,* Brookhaven National Laboratory*; J. Schnadt,* Lund University, Sweden

The introduction of atomic layer deposition, ALD, to the microelectronics industry has introduced a large number of new possible materials, able to be deposited in layers with atomic thickness control. One such material is the high-κ oxide HfO_2; thermally stable and ultrathin HfO_2 films deposited by ALD are a significant contender to replace SiO_2 as the gate oxide in capacitor applications. In such a device the typical support remains Si, and thus the HfO_2 gate oxide/Si interface is an integral part of the device. The characteristics of this interface can dramatically affect the overall performance of the device itself. We present a mechanistic study of the first deposition cycle of HfO_2 on the Si(111) surface using tetrakis(dimethylamido) hafnium (TDMA-Hf) and water as precursors using operando ambient pressure x-ray photoelectron spectroscopy (APXPS). This methodology allows us to observe the chemical reactions in a time-resolved manner, giving details of mechanism and kinetics of the reaction. It is found that even low levels of moisture contamination at the 1×10^{-7} mbar level can dramatically affect the substrate and therefore the initial ALD cycle. Here, we show that the hydroxylation of the clean Si(111) surface by residual water vapour, resulting in a 0.3 monolayer coverage of hydroxyls, leads to instantaneous full surface coverage of TDMA-Hf. The change in the atomic ratio of Hf to C/N found during the first deposition half-cycle, however, does not match the assumed immediate ligand loss through reaction with surface hydroxyls. One would expect an immediate loss of ligands, indicated by a Hf:N ratio of approx. 1:3 as TDMA-Hf deposits onto the surface. However, a Hf:N ratio of 1:4 is seen until 2 minutes after exposure. In addition, there is no evidence that any removed ligands remain on the surface, skewing the Hf:N ratio. The ligand exchange mechanism proceeds a lot slower than expected with a possible initial physisorption step – in the order of minutes rather than seconds. The slower reaction kinetics have many implications in terms of the quality of the interface when conditions are compared to industrial ALD reactors. Industrial reactors work on much faster timescales and at higher pressures than observed in this study which could result with intact precursor left physiosorbed to the substrate unreacted. In addition, the moisture contamination observed in this study would be unavoidable at more standard ALD reactor pressures, which implies that residual water needs to be an important consideration for the ALD performance and eventual interface quality.

8:45am **AF1-WeM-4 In Situ Reflection High Energy Electron Diffraction Investigations of Epitaxial Growth and Crystallization of Gallium Oxide Thin Films*, Alexandra Howzen,*** *N. Strandwitz,* Lehigh University

The precursor decomposition temperature sets the maximum growth temperature of the “ALD window” which often limits the structural perfection and crystallinity of the resulting films. Intermittent annealing in between precursor chemical exposures during ALD film growth has been explored previously and shown to increase density and improve the electrical properties of ALD films[1]. However, without direct monitoring of one or more of the physical properties of the films, it can be difficult to determine the nuances of film transformation, such as crystallization temperature, crystallographic texture, surface roughening, and dependence on gas ambient.

In this work we utilize a home-built thermal ALD system with integrated reflection high energy electron diffraction (RHEED) for *in-situ* monitoring of both the deposition of direct epitaxial films and the transformation of

amorphous ultrathin films during *in-situ* post-deposition annealing. RHEED is a surface sensitive diffraction technique that utilizes high energy (> 10 keV) electrons at a glancing angle, and is most commonly utilized in molecular beam epitaxy and pulsed laser deposition systems. Gallium oxide thin films were grown at several temperatures using trimethyl gallium/Ozone precursors and monitored with RHEED during deposition and post-deposition annealing. Films grown at low temperature were amorphous and films grown at higher temperatures resulted in epitaxial growth of β-Ga_2O_3 on sapphire. The initial phases of a direct epitaxial β-Ga_2O_3 film on sapphire revealed RHEED streaks that were coincident with spots in the zero order Laue zone of the sapphire substrate's diffraction pattern within as few as 5 ALD cycles. Conversely, the blurring-out of the sapphire substrate's diffraction pattern is seen in RHEED during the growth of an amorphous Ga_2O_3 film. *In-situ* RHEED is then used to monitor the structural evolution of the films during an immediate post-deposition, high temperature anneal. Our unique setup allows us to closely monitor the structural evolution of the direct epitaxial and thermally transformed films. It also allows us to determine the conditions in which the metastable polymorphs of Ga_2O_3 form in epitaxial systems. The integration of RHEED with ALD offers a slow-motion picture of traditional epitaxial growth techniques by decoupling the deposition and crystallization steps with simultaneous monitoring of the surface structure.

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9:00am **AF1-WeM-5 Surface and Film Stress during ALD of Al_2O_3 and ZnO: *In Situ* Measurements Using Wafer Curvature Techniques*, Ryan B. Vanfleet*,** *E. Sorinto, A. Cavanagh, V. Bright, S. George,* University of Colorado at Boulder

In situ surface and film stress were measured during atomic layer deposition (ALD) using wafer curvature techniques in a new custom reactor. Aluminum oxide (Al_2O_3) ALD using trimethylaluminum (TMA) and H_2O as the reactants was used as a model system to test this new apparatus. Al_2O_3 ALD was explored at different deposition temperatures ranging from 130 to 285°C. The *in situ* measured film stress during Al_2O_3 ALD is a tensile stress of 450 MPa at 130°C (Figure 1). The tensile stress decreases with increasing deposition temperature. These *in situ* temperature-dependent Al_2O_3 ALD film stresses are in good agreement with *ex situ* film stress measurements for Al_2O_3 ALD films reported in the literature [1].

High sensitivity wafer curvature measurements are also able to measure the surface stress from individual surface reactions (Figure 2). These *in situ* measurements revealed that the TMA exposure results in a compressive surface stress. This compressive stress is attributed to repulsion between surface methyl species. In addition, the H_2O exposure removes surface methyl species and releases the compressive stress. The compressive surface stress resulting from the TMA exposure grows from 0.4 N/m at 150°C to 0.75 N/m at 285°C. This increase in the compressive surface stress from the TMA exposure can be attributed to the greater relative change in methyl coverage at higher deposition temperatures.

Additional *in situ* measurements explored the surface and film stresses during zinc oxide (ZnO) ALD using diethyl zinc (DEZ) and H_2O as the reactants. ZnO ALD showed interesting stress evolution with an initial compressive stress that evolves to tensile stress, then returns to compressive stress (Figure 1). The initial compressive and tensile stress is attributed to the nucleation and coalescence of islands during ZnO film growth. The largest steady-state compressive film stress measured during ZnO ALD was -150 MPa. ZnO ALD shows opposite surface stress behavior compared with Al_2O_3 ALD. The H_2O exposure results in a compressive stress, while the DEZ exposure yields a tensile stress. The magnitude of surface stresses from the DEZ and H_2O surface reactions range between 0.2 N/m to 0.4 N/m and may depend on the dominant crystal orientation at the film surface.

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9:15am **AF1-WeM-6 Chemisorption Mechanisms of Aminosilane Precursors during ALD of SiO_2: *in situ* Characterization and ab initio Study*, Khabib Khumaini*,** *H. Son, H. Roh, O. Kim, R. Hidayat, H. Kim, W. Lee,* Sejong University, Republic of Korea

The ALD of SiO_2 thin films using aminosilane-type precursors, such as DIPAS ($SiH_3(N^iPr_2)$), BDEAS ($SiH_2(NEt_2)_2$), or TDMAS ($SiH(NMe_2)_3$), is being used in dielectric deposition and multiple patterning processes. The chemisorption of silicon precursors during the ALD of SiO_2 can be studied by density functional theory (DFT) calculation and in situ characterization techniques [1]. DFT studies assumed that dialkylamino ligands of silicon precursors combine with H atoms of surface hydroxyl groups to form amine molecules as the byproduct. However, there was a lack of reports considering the type and distance of the hydroxyl groups on the surface. In addition, in situ characterization for comparative studies of precursors with different numbers of dialkylamino ligands is also lacking. Therefore, in this study, we compared the chemisorption of aminosilane-type precursors on different OH-terminated SiO_2 surfaces modeled with different hydroxyl types and distances by DFT simulation. We also compared the chemisorption reactions of DIPAS and BDEAS, the precursors having different numbers of dialkylamino ligands. Reaction energies were calculated for all possible reaction pathways, and then the activation energies were obtained for exothermic pathways. Finally, we compared the number of released ligands (*n*) from the DFT simulation result with the experimental results from *in-situ* quartz crystal microbalance (QCM). For DIPAS, the DFT predicted that the chemisorbed species would be $–SiH_3*$, which agrees with QCM and FTIR observation. DFT predicted that chemisorbed species of BDEAS would be $–SiH_2(NEt)*$ and $–SiH_2*$ depending on the type of hydroxyl group, which is consistent *n* ~ 1.5 ligands calculated from QCM. Therefore, the surface species predicted by DFT simulation well explains the experimental results from in-situ quartz crystal microbalance (QCM) and Fourier-transform infrared (FTIR) spectroscopy.

9:30am **AF1-WeM-7 Seeing It Happen: Insights Into the Surface Chemistry of HfO_2 and TiO_2 ALD from *Operando* Ambient Pressure X-ray Photoelectron Spectroscopy*, Joachim Schnadt,*** Lund University, Sweden **INVITED**

The development of ALD processes is based on a number of different considerations and factors. One consideration is the envisaged ALD surface chemistry, which has to match not only the desired process outcome and processing conditions, but also the reaction properties of both the precursor and the surface. For many precursors, their surface chemistry is assumed to follow general reaction schemes. For example, the thermal ALD of transition metal oxides from amido complex and water precursors is typically assumed to follow a ligand exchange mechanism. The wide spread of such general reaction schemes results from that they often provide a sufficiently successful prediction of the ALD process outcome, but also because experimental tools are lacking that allow direct insight into reaction mechanisms. Indeed, it has been noted that surface chemistries can be both more complex and varied than general reaction schemes make believe [1,2].

Methods that allow the time-resolved monitoring of ALD processes, such as quartz crystal microbalance measurements, quadrupole mass spectrometry, pyroelectric calorimetry and ellipsometry provide deepened insight into ALD surface reaction mechanisms. More recently, these methods have been joined by two chemically sensitive techniques for the time-resolved characterisation of ALD processes, namely infrared spectroscopy [3] and ambient pressure x-ray photoelectron spectroscopy (APXPS) (cf., e.g., [4,5]). These two methods are capable of following the ALD surface chemistry in real time and at processing pressures equal or similar to those in an ALD reactor.

Using the metal amido complex- and water-based ALD of HfO_2 and TiO_2 on different surfaces as examples, I would like to demonstrate the usefulness of time-resolved APXPS for the elucidation of surface species and their evolution as well as for the observation of substrate processes such as oxygen transport. Such information allows to formulate ALD reaction mechanisms. In specific cases, we observe reaction pathways that deviate from the standard models of ALD surface chemistry, we find that surface hydroxylation is not always a prerequisite for oxide ALD, and for reducible supports we find that oxygen ion transport may play a major role in the initial ALD. Hence, APXPS provides us with entirely new information on ALD reaction mechanisms, which is important input for the future optimisation of ALD processes.

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ALD Fundamentals
Room Grand Ballroom E-G - Session AF2-WeM
High Aspects

Moderator: Prof. Riikka Puurunen, Aalto University, Finland

10:45am **AF2-WeM-12 Preparation and Characterization of Well-Defined Mixed-Oxide and Metal-Oxide Interfaces in Porous Catalysts using ALD***, **Francisco Zaera,*** Department of Chemistry

As the chemistry of solids is in most instances determined by the nature of their surfaces, control over the nature of surface sites during preparation is critical to the design of materials for specific applications. This is a difficult task, especially when complex multicomponent atomic ensembles are required. In this presentation we illustrate how atomic layer deposition (ALD) may be used to prepare such sites, with a particular focus on the design of unique mixed-oxide and metal-oxide interfaces for catalysis.

First, we will provide details on the deposition and characterization of alumina and titania films on SBA-15, a silica support with well-defined nm-sized one-dimensional pores, and for the growth of silica films on alumina supports. Specific issues related to ALD on porous solids will be highlighted, including possible incomplete deposition inside the pores and possible precursor condensation and pore clogging.

Characterization of the deposition process and the resulting oxide films will be presented, with emphasis on the use of pore size distributions, pore area and pore volumedata from N_2 adsorption-desorption isotherms to follow the rate and quality of the film growing process. The assessment of the initial nucleation steps using NMR will also be introduced, and a discussion on the crystallinity and optical properties of the resulting films will be provided. The quantitative determination of the evolution of the surface hydroxide sites that act as nucleation centers using infrared absorption spectroscopy (IR) will be illustrated.

The unique properties of the mixed-oxide surfaces produced via ALD will be discussed. These include the creation of new Lewis and Brønsted acid sites, which can be titrated by using IR, and the ability of the new surface sites to undergo facile and reversible reduction-oxidation interconversions, as seen by IR-based CO titrations as well as by EPR spectroscopy.

Finally, new catalysts were made by adding nanoparticles of metals such as gold or platinum into these ALD-made mixed-oxide solids, either before or after the ALD. The final products were tested for reactions such as CO oxidation and the selective hydrogenation of CO_2 and of unsaturated aldehydes. In all cases, optimum catalytic performance was observed at half a monolayer of the coverage of the new oxide, strongly suggesting that the active catalytic sites may be comprised of mixed oxide local structures involving Si–O–Ti or Si–O–Al bonds. It is thanks to the sub-monolayer control of the thickness of the deposited films that such optimum catalytic performances could be attained.

11:00am **AF2-WeM-13 A Toolbox for Characterization of Film Penetration Depth in High Aspect Ratio Structures***, **Anish Philip**, M. Utriainen, J. Kinnunen, P. Hyttinen,* Chipmetrics Ltd, Finland*; V. Korpelainen, B. Sauvet,* VTT Technical Research Centre of Finland*; W. Kessels, M. Poll, B. Macco,* Eindhoven University of Technology, The Netherlands

3D semiconductor devices have often dry etched vertical high aspect ratio holes, with 20 -200 nm critical dimensions. Conformality of the ALD/CVD thin film process in those high aspect ratio (HAR) structures is important for the functionality of the devices. HAR structures can be either lateral (LHAR) or vertical (VHAR). In this study, we focused on two less known factors of ALD growth in HAR structures, namely difference between vertical and lateral HAR geometries as well as the effect of the surface roughness. The PillarHall® lateral high aspect ratio (LHAR) test structure and measurement method is an effective way for fast and easy conformality characterization of the thin film processes[1]. PillarHall LHAR is a wide trench with nominal gap height 500 nm.The unique feature of PillarHall LHAR-method is an accurate and repeatable film penetration depth (PD) profile that allows to quantify step coverage for any aspect ratio as well as to characterize reaction kinetics in the sub-micrometre dimensions and molecular diffusion conditions. The compared HAR structures (Fig.1) were on commercial test chips VHAR1 (vertical holes) and PillarHall LHAR4 (lateral trenches) by Chipmetrics Ltd, as well as a modified version of LHAR chip (M-LHAR). The ALD process used in this study was TMA/H_2O Al_2O_3 at 300 °C in Beneq TFS-200. The Gordon model [2] is a useful approach to compare and predict the film PD performance in both HAR structure types. According to Gordon model, all structures had the same feature dimensions while their roughness varied. An inverse relationship between surface roughness and PD was revealed as the measured PD was highest for M-LHAR (Rq=0.17 nm) and lowest for VHAR1 (Rq=4.8 nm). The results indicate that surface roughness together with HAR geometry and gap height are the important factors that affects the model accuracy. In this study, NIR optical reflectometry was used to precisely measure the lateral trench gap height. We show also initial results from highly sensitive and PillarHall compatible measurement tools, such as contrast imaging SEM, UV-reflectometer (Fig.2) and imaging ellipsometer. They enable to measure PD of ultra-thin films with thickness < 10 nm. The presented toolkit concept is an efficient platform consisting of several well-specified test chips, measurement instruments, and modelling tools to execute highly accurate and repeatable film penetration depth analyses of ALD processes.

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11:15am **AF2-WeM-14 Understanding Process Parameters of ALD on Silica Aerogels and Their Effects on Mechanical Properties***, **Victor Vogt**, A. Gayle, Z. Berquist, A. Manon, A. Lenert, N. Dasgupta,* University of Michigan

Atomic layer deposition (ALD) is a powerful tool to modify ultra-high-aspect-ratio structures with unparalleled conformality. We have recently demonstrated the ability of ALD to modify silica aerogels with aspect ratios greater than 60,000:1 and improve their thermal stability from ~600°C to ~800°C, for applications in concentrated solar thermal energy generation.[1] To facilitate conformal ALD modifications on these extreme aspect ratios, a reaction-diffusion model was developed to precisely predict infiltration into the aerogel as a function of exposure time and number of doses, enabling tunable control of the infiltration depth.[2] To build upon this work, in this study, we examine the impact of key process parameters, including deposition temperature, precursor temperature, and purging procedures, and quantify the manufacturing tradeoffs between total ALD process time and precursor utilization. Additionally, we quantify the impacts of ALD modification on the optical, thermal, and mechanical properties of silica aerogels, which are critical for their usage in solar thermal applications.

In this study, we have built upon our previous reaction-diffusion model to explore the effects of deposition temperature, precursor temperature, and purging procedure on throughput and precursor utilization. A non-intuitive inverse relationship is observed between deposition temperature and infiltration depth, which is attributed to ideal-gas-law effects on precursor dosing, and this relationship is confirmed experimentally. Next, the impact of single cycle alumina-based modifications on mechanical properties is explored through 3-point bend and compression testing, including localized strain mapping via digital image correlation (DIC). The ALD modification is found to increase the elastic modulus of silica aerogels, and the results are compared with density scaling relationships for bare silica aerogels established in literature. Understanding the effect of ALD modification on aerogel mechanical properties is critical to implementation in engineering applications and provides a potential new pathway to tailoring the mechanical properties of aerogels and other high aspect-ratio structures.

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11:30am **AF2-WeM-15 Tuning Properties of ZnO Deposited via ALD for Applications in Sensing and Porous Material Development***, A. Coclite, **Lisanne Demelius**,* Graz University of Technology, Austria **INVITED**

The material properties and application related to zinc oxide, ZnO,have been heavily researched for decades and still produces new scientific output every year. ZnO is characterized by versatile and unique material properties that are an asset for applications ranging from cosmetics to optoelectronics. Emerging applications employ ZnO in transparent conductive oxides or piezoelectric nanogenerators. In particular, atomic layer deposition allows to deposit ZnO with a preferential orientation, which depends on the growth temperature and is directly liked to its piezoelectricity. In this talk, an example of application of piezoelectric ZnO deposited from ALD will be shown for sensing. A force, humidity and

temperature responsive electronic skin will be presented, obtained by combining piezoelectric ZnO and a thermoresponsive hydrogel into core-shell nanostructures using ALD and initiated chemical vapor deposition.

In addition, introducing porosity to ZnO thin films increases the performance drastically and opens up new fields of applications. Different methods were used to deposit porous ZnO i.e., ALD growth in non-saturated conditions or by using organic spacers which were subsequently eliminated by calcination. In-situ ellipsometric porosimetry showed that films with porosity up to 24% were obtained. Metal-organic frameworks of ZIF-8 were synthesized by subjecting porous ZnO thin films to a 2-methylimidazole vapor. The impact of the porosity of the ZnO films onto the resulting ZIF-8 layers will be shown. Our results provide new insight into the link between deposition parameters of PE-ALD deposited ZnO and properties of the resulting ZIF-8 thin films – namely crystallographic orientation, thickness, coverage and roughness – thus making it possible to tailor them towards specific applications.

Atomic Layer Etching
Room Grand Ballroom A-C - Session ALE1-WeM

Si and SiO_2 ALE

Moderators: Prof. Austin Minnich, Caltech, Prof. Gregory N. Parsons, North Carolina State University

8:00am **ALE1-WeM-1 Plasma-Enhanced Atomic Layer Etching for Metals and Dielectric Materials*, Heeyeop Chae,*** Sungkyunkwan University (SKKU), Republic of Korea **INVITED**

The critical dimensions of semiconductor devices are continuously shrinking with 3D device structure and are approaching to nanometer scale. The demand for dimension control in angstrom level is drastically increasing also in etching processes. Atomic layer etching (ALE) processes are being actively studied and developed for various semiconductor and dielectric materials as well as metals. In this talk, various plasma-enhanced ALE (PEALE) processes will be discussed for isotropic and anisotropic patterning of metals and dielectric materials such as molibdenum, ruthenium, cobalt, titanium nitride, tantalum nitride, halfnium oxide, zirconium oxides. [1-6] Typical ALE processes consist of surface modification step and removal step. For the surface modification, various fluorination, chlorination and oxidation schemes were applied including fluorocarbon deposition, halogenation, oxidation with radicals generated plasmas. For the removal or etching step, various schemes were applied including ion-bomardment, heating, ligand volatilization, ligand exchange, and halogenation. The surface characteristics and requirements of plasma-enhanced ALE will be also discussed.

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8:30am **ALE1-WeM-3 Controlling the Hole Profile of High Aspect Ratio Structures in Atomic Layer Etching of SiO2 by Utilizing Dc-Superposition in Capacitively Coupled Plasmas*, Kang-Yi Lin,*** *E. Hirsch, P. Wang,* TEL Technology Center, America, LLC, USA

As semiconductor manufacturing advances to nanometer scale processing nodes, the development of contact and via in middle-of-line (MOL) and back-end-of-line (BEOL) schemes continuously shrinks critical dimension (CD) with higher aspect ratio structures. The etching process faces the demand for better control of the profile, including taper angle and the etching selectivity of SiO_2 to the mask and etch stop layer. Conventional approaches, such as continuous-wave plasma, using a mixture of etchants and passivation precursors for selective removal undergo the bottleneck as the feature moves to the nanometer scale. Aspect ratio-dependent transportation impedes the processing window to meet the criteria on etching profile and selectivity. Atomic layer etching (ALE) is an emerging approach that separates the surface functionalization and etching byproduct activation steps to enable selective removal in a self-limited fashion and to mitigate aspect ratio-dependent etching. Our capacitively coupled plasma (CCP) etcher enables a feature that imposes a negative direct current (DC) bias on the top electrode, which attracts ions for sputtering reactions and produces Si deposition and ballistic secondary electrons to the bottom electrode. We studied the effect of DC-superposition (DCS) in CCP under an ALE sequence on the hole profile, including the coating thickness on the substrate, the thickness loss of the mask and etch stop layer, and the etching profile. Other surface characterization methods, including x-ray photoelectron spectroscopy (XPS), were used to understand the surface evolution of each step during the ALE sequence. Experimental results show that DCS can be used to control the etching selectivity and taper angle. The optimal condition delivers a vertical taper angle close to 90° on the etch stop layer with neglectable mask losses. Exploiting DCS in an ALE sequence under CCP offers a novel processing window to improve etching profiles in the nanometer scale feature.

8:45am **ALE1-WeM-4 Damage Analysis of Reactive Ion and Quasi-Atomic Layer Etched Silicon**, *A. Karimi,* AlixLabs AB, Sweden*; M. Alabrash,* Lund University, Sweden*; R. Jafari Jam,* AlixLabs AB, Sweden*; D. Lishan,* Plasma-Therm LLC*; H. Aslan, J. Garnæs,* Danish Fundamental Metrology, Denmark*; A. Uvarov,* Plasma-Therm Europe, France*; Y. Ilarionova,* ***Dmitry Suyatin****, J. Sundqvist,* AlixLabs AB, Sweden*; S. Khan,* Danish Fundamental Metrology, Denmark*; I. Maximov,* Lund University, Sweden

Atomic layer etching (ALE) is a cyclic technique based on self-limiting processes, such as reactive gas adsorption and material removal by low-energy ion bombardment. In a typical ALE process Ar^+ ions with energies of 20-60 eV are used to desorb the reaction products, e.g. $SiCl_x$ for the Si ALE. Compared to a corresponding continuous reactive ion etching (RIE), where the ion energies often exceed 100 eV, the ALE should yield less surface damage due to low ion energy and its cyclic nature. However, there are few publications only dealing with studies of the surface damage in ALE.

For Si etching experiments with Cl_2 and Ar as etch gases, we used a commercial Inductively Coupled Plasma RIE Takachi™ tool from Plasma-Therm LLC. The system was operating in a quasi-ALE (Q-ALE) regime with some RIE contribution during the removal step due to residual Cl_2. In order to avoid surface contamination by lithographic masks, a custom-made metal shadow masks were used to protect some Si areas from the Ar^+ ion bombardment. The Kelvin Probe Force Microscopy (KPFM) measurements were then performed both on the reference and the etched places to calculate the contact potential difference (CPD) values for the RIE and Q-ALE samples.

Here we present our results on application of KPFM to evaluate the surface damage of Si for both Cl_2/Ar-based RIE and Q-ALE processes. We used two methods for chlorinating the Si surface: a) molecular chlorination where plasma was only ignited during the Ar^+ etching step and b) plasma chlorination where plasma was ignited during the entire process and pulsed during etching step. The KPFM is used to measure the CPD between the etched Si surface and the tip and this potential difference reflects the surface damage. At the same time, a surface morphology was also characterized in an atomic force microscopy mode. Both the CPD and the surface roughness are used to evaluate the damage after cyclic ALE processes at different RF-bias power. The results were then compared with a sample that had undergone RIE in order to provide a comprehensive evaluation of the impact of the etching process on the surface morphology of the samples.

We present and discuss the CPD and surface roughness data as a function of bias voltages for both RIE and Q-ALE. The experimental results in this study show that the CPD of Si after the Q-ALE processes are in close proximity to the theoretically calculated value. However, if the samples are subjected to continuous RIE with the same parameters, the surface potential deviates significantly from the theoretical value. This may indicate that the Q-ALE process gives a significantly lower damage of Si compared to a standard RIE.

9:00am **ALE1-WeM-5 Atomic Layer Etching of SiO_2 via H_2/SF_6 Plasma and TMA*, David Catherall,*** *A. Minnich,* California Institute of Technology

The quality factor of ultrahigh Q silica microdisk resonators has reached values exceeding one billion but remains at around an order of magnitude below intrinsic upper limits due to surface-roughness scattering. Atomic layer etching (ALE) has potential to mitigate this scattering because of its ability to smooth surfaces to sub-nanometer length scales. Here, we report an ALE process for etching of SiO_2 using sequential exposures of TMA and $Ar/H_2/SF_6$ plasma. The $Ar/H_2/SF_6$ plasma has been reported to enable in-situ production of HF, enabling HF exposures in the ALE process without the

need for an external source of HF vapor. We observe etch rates up to 0.6 Å per cycle and examine the effect on surface roughness. This work advances a process of relevance to ultrahigh Q silica resonators which are fundamental elements of on-chip photonic devices such as frequency combs.

9:15am **ALE1-WeM-6 Learnings and Mitigations of Nonuniformity in Oxide Quasi Ale Applied to Contact Patterning*, Francois BOULARD*,** *A. RONCO, N. POSSEME,* CEA/LETI-University Grenoble Alpes, France

Ideal Atomic Layer Etching (ALE) with truly self-limited half cycle offers many advantages to conventional etching processes. The independent control of the modification and the removal steps offers higher etch selectivity, could smooth surfaces, or minimizes the dependence to aspect ratio and wafer location [1]. However, in oxide quasi ALE based on FluoroCarbon (FC) plasma, where a thin FC film is deposited, self-limitation is not obvious. In such circumstance, the return to a pristine surface between cycles is no longer guaranteed and the Etch Per Cycle (EPC) or surface roughness become very sensitive to process conditions [2]. Moreover, in a throughput perspective, the removal step should be shortened as much as possible, stressing even more the process window. In this paper, we present recent experimental results obtained on 300 mm blanket and contact patterned SiO_2 etch. A multi-frequency capacitively coupled plasma with C_4F_6/Ar chemistry is used. A particular attention is paid to the wafer uniformity of deposition and removal activation. We analyze the impacts of deposition and activation times on the EPC and roughness uniformities. We show how intentional nonuniform deposition and removal half cycles could help to optimize the quasi ALE process. Finally, we apply these understandings on contact etching for Si qubits and FDSOI advanced nodes technologies with stringent soft landing requirements.

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9:30am **ALE1-WeM-7 Adopting a Low Global Warming Potential Fluorocarbon Precursor (C_6F_6) to Atomic Layer Etching of Sio_2 with Fluorocarbon Plasmas*, Inho Seong*,** *Y. You, Y. Lee,* Chungnam National University, Republic of Korea*; G. Yeom,* Sungkyunkwan University, Republic of Korea*; S. You,* Chungnam National University, Republic of Korea

Reducing the greenhouse effect induced in plasma etching with the use of greenhouse gases such as CF_4 and C_4F_8 have been attracting enormous interests in the industry and academia. In SiO_2 atomic layer etching (ALE) with fluorocarbon plasma, we adopt an alternative precursor, C_6F_6, that has been known to have significantly low global warming potential, for gas mixtures with CF_4 and C_4F_8, which is one of the most widely used precursors while has a high GWP. The ALE results obtained with different gas chemistry are monitored by in situ ellipsometry and their ALE characteristics such as self-limiting behaviors are discussed in this paper. We expect this result to provide an opportunity for low global warming potential precursors to be adopted more widely in the etching process.

9:45am **ALE1-WeM-8 Thermal ALE Reactants for Semiconductor Processing*, Martin McBriarty,*** EMD Electronics

The devices that enable our digital future require clean, selective atomic layer processes to shape their complex 3-D nanoarchitectures. Isotropic ALE is a critical part of this toolkit, but each ALE process will be burdened with strict requirements for high selectivity and low levels of impurities and residues. Bringing such processes online requires ALE reactants that are not only effective, but also safe, sustainable, and readily integrated into the fab. Thermal ALE reactants from EMD Electronics are poised to meet these challenges. Etch performance and selectivity are efficiently tested using high-throughput process screening on 300mm ALE tools, followed by fab-grade physical and electrical characterization. For denser memory devices, we demonstrate ALE methods to shape high-*k* dielectrics which leave minimal residues without requiring the use of corrosive gases. For the interconnects and vias that tie together ever-shrinking transistors, we show ALE processes that selectively and precisely etch metals without compromising their electrical performance. The ALE processes discussed herein can be performed in the vapor phase, without requiring plasma generation, wet etch steps, or corrosive gas facilitization, enabling facile integration of isotropic ALE onto atomic layer processing tools.

Atomic Layer Etching
Room Grand Ballroom A-C - Session ALE2-WeM

Plasma and Energy-Enhanced ALE

Moderator: Prof. Dr. Heeyeop Chae, Sungkyunkwan University (SKKU)

10:45am **ALE2-WeM-12 Isotropic Plasma-Thermal Atomic Layer Etching of Aluminum Nitride Using SF_6 Plasma and $Al(CH_3)_3$*, Austin Minnich,*** Caltech **INVITED**

We report the isotropic plasma atomic layer etching (ALE) of aluminum nitride using sequential exposures of SF_6 plasma and trimethylaluminum ($Al(CH_3)_3$, TMA). ALE was observed at temperatures greater than 200 C, with a maximum etch rate of 1.9 Å/cycle observed at 300C as measured using ex-situ ellipsometry. After ALE, the etched surface was found to contain a lower concentration of oxygen compared to the original surface and exhibited a ∼35% decrease in surface roughness. These findings have relevance for applications of AlN in nonlinear photonics and wide bandgap semiconductor devices. [arXiv:2209.00150]

11:15am **ALE2-WeM-14 Gan Atomic Layer Etching Using SF_6 and Ar Plasmas Controlled by RFEA and Langmuir Probe Measurements*, Remi Dussart,*** Universite d'Orleans - CNRS, France*; L. Hamraoui, T. Zhang, A. Crespi,* Universite d'Orleans, France*; M. Boufnichel,* STMicroelectronics, France*; P. Lefaucheux,* CNRS, France*; T. Tillocher,* Universite d'Orleans, France

Chlorine based plasmas are usually preferred to etch GaN because of the formation of $GaCl_3$ molecules at the surface, which are quite volatile[1]. In fluorine-based plasmas, GaF_3 molecules are formed at the surface as well, but they are not volatile except at a very high temperature[1]. However, in atomic layer etching, SF_6 plasma can be used to control the etching at the atomic scale. Indeed, the Ga surface can be saturated of fluorine, producing a monolayer of GaF_x sites, which are supposed to not desorb during the modification step. Then, this modified layer can be sputtered selectively during the argon plasma removal step if the sputtering threshold of this layer is lower than that of GaN.

In this presentation, we would like to highlight the advantage of using probes such as ion Retarding Field Energy Analyzer (RFEA) and Langmuir probes to control the ALE process. With such plasma diagnostics, it is possible to evaluate the energy of the ions bombarding the surface and adjust theprocess parameters in order to avoid direct sputtering of GaN, and selectively remove the modified layer.

We used an Inductively Coupled Plasma (ICP) reactor excited at a frequency of 13.56 MHz with an RF generator to perform the experiments. The self-bias voltage was varied using an independent RF power supply operating at the same frequency. Experiments were performed at different source powers and different pressures of argon. This study led to an optimized etching process, which enables the control of the etching at the atomic scale, monolayer by monolayer. An energy scan was carried out and the synergy of the ALE process was evaluated. In certain ion flux conditions during the removal step with the Ar plasma, a self-limiting regime could be obtained.

In parallel, we used and adapted the global model developed by Pascal Chabert's team[2] at the "Laboratoire de Physique des Plasmas" in Palaiseau, France, to our reactor in order to simulate the plasma parameters for both Ar and SF_6 plasmas under different experimental conditions. Finally, some material characterization experiments (AFM, XPS, and ToF SIMS) were performed to analyze the GaN surface after the ALE process.

Acknowledgment

The authors appreciate the support provided by the European Union (IPCEI: Important Project of Commun European Interest) and Région Centre Val de Loire for the Nano2022 project. We also thank the CERTeM 2020 platform, which supplied the majority of the equipment.

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11:30am **ALE2-WeM-15 Speedy and Smooth Atomic Layer Etching for Silicon Carbide with DC Bias-Pulsing*, Julian Michaels,*** University of Illinois at Urbana-Champaign*; N. Delegan,* Argonne National Laboratory, USA*; Y. Tsaturyan,* University of Chicago*; R. Renzas,* Oxford Instruments*; D. Awschalom,* University of Chicago*; G. Eden,* University of Illinois at Urbana-Champaign*; J. Heremans,* Argonne National Laboratory

Atomic layer etching (ALE) is a cyclical process that shows promise for precisely fabricating nanostructures in a variety of materials. Silicon carbide

(SiC) is a wide bandgap semiconductor material known for its excellent electrical, thermal, and mechanical properties. These properties make SiC a common material for power electronics, optoelectronics, and quantum optics. Conventional dry etching techniques for SiC suffer from poor selectivity, roughness, and damage the crystalline structure. ALE offers a solution to these shortcomings by utilizing self-limiting chemical reactions to remove individual atomic layers of SiC, resulting in precise etching that leaves smooth surfaces.

We present a novel execution of ALE for SiC using a bias-pulsing scheme and demonstrate self-limiting single dimer (i.e. the Si-C doublet) removal with an Ar/Cl2 inductively coupled plasma reactive ion etching (ICP RIE) system by only pulsing the plasma DC bias. Gases are not purged between etch steps, which leads to etch cycles of merely 6 seconds, which are far shorter than those of conventional ALE methods. Our results show that this ALE process can achieve precise etching with sub-angstrom surface roughness. We believe that this technique will enable new SiC-based quantum devices, especially those that are sensitive to surface quality, and that bias-pulsed ALE can be applied to other material systems to provide a more rapid solution for ALE.

11:45am **ALE2-WeM-16 Thermal Atomic Layer Etching of MoS_2 Films***, J. Soares,* ***John Hues,*** Micron School of Material Science and Engineering, Boise State University*; A. Mane, D. Choudhury, S. Letourneau,* Applied Materials Division, Argonne National Laboratory*; S. Hues,* Micron School of Material Science and Engineering, Boise State University*; J. Elam,* Applied Materials Division, Argonne National Laboratory*; E. Graugnard,* Micron School of Material Science and Engineering, Boise State University

2D materials can offer promise for a wide range of application within semiconductor manufacturing. Of these materials, molybdenum disulfide (MoS_2) is of great interest due to its high mobility, measured on/off ratio, tunable band gap, and a film thickness ideal for scaling. In order to move this material closer to integration with semiconductor manufacturing, a great amount of processing control is required. Atomic layer processing techniques can accommodate this needed precision, where both the deposition and removal of MoS_2 has been studied. In this work we report a thermal atomic layer etching (ALE) process for MoS_2 using MoF_6 and H_2O as precursor reactants. Here, we will discuss atomic layer etching of both amorphous as-deposited and crystalline MoS_2 films. In situ quartz crystal microbalance measurements (QCM) indicate removal of as-deposited films when switching from a deposition chemistry (MoF_6 + H_2S) to the proposed etching chemistry (MoF_6 + H_2O). Saturation curves for the etching process were additionally identified with QCM by studying the mass gained per cycle versus the precursor dose duration. Films deposited on planar coupons were characterized with ellipsometry and X-ray reflectance to determine the etch per cycle. We propose the chemical reaction equations for the etch process as guided by residual gas analysis of byproduct formation, Gibbs free energy calculations, and QCM mass ratio analysis. After ALD and subsequent ALE processing, we produced few layer crystalline MoS_2 films once annealed. With the many application of both amorphous and crystalline MoS_2, this work helps to identify and expand current atomic layer processing chemistries.

ALD for Manufacturing
Room Regency Ballroom A-C - Session AM-WeM
Manufacturing

Moderators: Dr. Arrelaine Dameron, Forge Nano, Ganesh Sundaram, Veeco-CNT

8:00am **AM-WeM-1 Atomic Layer Technologies for III-V Nitride Epitaxy, High-K/Metal Gate, Ferroelectric Negative Capacitance, and Area-Selective Deposition***,* ***Miin-Jang Chen****, C. Chou, T. Chang, W. Lee,* National Taiwan University, Taiwan **INVITED**

We report the recent progress from conventional atomic layer deposition (ALD) toward a variety of atomic layer technologies, such as atomic layer annealing, crystallization, densification, epitaxy, etching, etc. The topics in this presentation include (1) atomic layer annealing (ALA) for atomic layer epitaxy (ALEp) of GaN and AlN at a low deposition temperature of only 300°C, (2) Atomic layer tailoring for the realization of sub-10 nm, wake-up free ferroelectric $Hf_{0.5}Zr_{0.5}O_2$ thin films with high remnant polarization and low thermal budget, (3) transient negative capacitance in ferroelectric capacitors, (4) atomic layer crystallization and densification induced by substrate biasing for the enhancement of ferroelectric and dielectric properties, (5) ALA for high-K/metal gate, including the improvements in dielectric constant, leakage current, reliability, and the modulation of work function, and (6) atomic layer nucleation engineering (ALNE) for inhibitor-free area-selective ALD with high selectivity. The results demonstrate the promising potential of atomic layer technologies for the precise engineering and fabrication of nanoscale materials and devices.

8:30am **AM-WeM-3 Optimizing Vessel Design for Pulsed Delivery of Solid Precursors***,* ***James Maslar****, V. Khromchenko, B. Kalanyan,* National Institute of Standards and Technology (NIST)

Solid precursors are widely employed in ALD processes and are often delivered to a deposition surface by entraining the precursor vapor in a carrier gas. Unfortunately, it can be difficult to reproducibly deliver solid precursors in this manner. This difficulty is often due to an inability to maintain carrier gas saturation in the precursor vessel head space, resulting in less than the maximum precursor amount being delivered. While this situation may not be an issue for an ideal ALD process (unless the total precursor dose is insufficient to saturate all surface reactive sites), this situation could negatively impact a non-ideal ALD process. The degree of carrier gas saturation depends on numerous factors including vessel design, precursor physicochemical properties, carrier gas flow rate, pressure, and idle time. (For many ALD processes, at least one precursor is idled – there is no flow from the precursor vessel - during a deposition cycle.) The goal of this work is to characterize the performance of different vessel designs for pulsed delivery of solid precursors and to identify relationships between vessel design aspects, precursor properties, and gas flow conditions that can be used to maximize the amount and reproducibility of precursor delivered. Computational fluid dynamics (CFD) were employed to simulate mass carryover for a range of vessel designs and conditions. For select cases, CFD mass carryover values were benchmarked to values measured using optical gas analyzers. The results of this investigation should improve the understanding of the relationships between vessel design, precursor properties, and gas flow conditions, thereby permitting a more informed selection of precursor vessel design for pulsed delivery of a particular precursor within a particular process parameter range.

8:45am **AM-WeM-4 Accurate Precursor Dose Delivery with Realtime Closed Loop Control***, J. Ye, J. Ding,* ***Guy Rosenzweig,*** MKS Instruments, Inc.

Atomic Layer Deposition (ALD) and Atomic Layer Etching (ALE) processes are the key technologies which are enabling the use of new materials and three-dimensional designs in advanced chip manufacturing. The ALD and ALE processes become a vital factor in the applications of *self-aligned patterning, 3D NAND and FinFet*. Consistent precursor delivery is required for generating a stable and homogenous deposition. Unstable deposition will cause defects and create wafer to wafer and batch to batch variations. A consistent precursor dose delivery also further improves process throughput and cuts the waste of precursors by reducing overdosing.

The technical challenge of achieving precursor delivery consistency comes from two aspects: 1) The capability of measuring the precursor concentration in the delivery line in real time; 2) The capability of quickly adapting the precursor pulse shape to control the delivered dose at the pulse level.

MKS Instruments is researching and testing a device that integrates a precursor concentration sensing module and a precursor pulsing module. The device is expected to tolerate up to 200°C to accommodate most of the precursor delivery processes. The precursor concentration sensing module measures the concentration out of the source in real time and feeds the readings to the pulsing module immediately downstream. The pulsing module adjusts the delivery rate instantaneously based on the concentration and the amount of precursor has been delivered, such that the precursor dose delivered in each pulse is constant.

9:00am **AM-WeM-5 Fast and Efficient Large Format ALD***, D. Lindblad,* ***Matthew Weimer****, A. Damerson, J. Ragonesi,* Forge Nano*; O. Snef,* Sundew Technologies

Manufacturing of large format objects, such as solar absorbers, optics, electrolizers, and sensors, can benefit from a multitude of ALD applications, from conformal protective coatings to device-enabling films. However, largeformat ALD has struggled to maintain a foothold in manufacturing for various reasons. Simply increasing the reactor volume and precursor delivery amount does not solve the problem, instead, it tends to exacerbate the limitations. Low precursor efficiency and slow cycle times in these large volume chambers can make the application of ALD financially nonviable in all but the most price insensitive applications. Additionally, thickness uniformity can suffer on such a large scale to compensate for increasing precursor costs. To improve the field of large format ALD, Forge Nano has

technology that can deposit uniform films, in thickness and composition, over a scalable area. Our standard wafer ALD reactor is designed for a 200mm diameter deposition area, yet we have demonstrated that, through the judicious placement of individual precursor dosing valve stacks (*Figure 1*), one can easily scale to a 525mm diameter, or approximately 7 times larger deposition area (*Figure 2*). Standard processes for Al_2O_3, TiO_2, and SiO_2 have been demonstrated at 125°C to have short cycle times and reasonable uniformity, less than 5% full range thickness, across the entire 525mm diameter area. A full comparison of qualified processes, between the 200 and 525mm diameter tools, will be discussed in detail, with specific examples shown in *Table 1*. This effective scaling has been accomplished with a unique chamber design and custom, proprietary, ALD fast-pneumatic valves (FPV). These valves can be constructed into sets of continuous precursor delivery stacks and are capable of actuating at sub-1ms speeds in environments up to 200°C. Coupled with a unique chamber design, these FPVs enable low precursor consumption and enable short purge times. This work demonstrates that increasing the number of delivery points, using our proprietary valves and chamber design, will allow for the scaling of large-format ALD at production capable speeds while maintaining efficient use of precursor.

9:15am **AM-WeM-6 Mechatronic Spatial Atomic Layer Deposition for Closed-Loop Process Control**, ***Daniel Penley***, *T. Cho, A. Brooks, L. Ranshoff, H. Park, E. Herman, O. Trejo, K. Barton, N. Dasgupta,* University of Michigan, Ann Arbor

Close-proximity atmospheric-pressure spatial atomic layer deposition (AP-SALD) holds promise to address the large-scale manufacturing needs of interfacial engineering at the nanoscale. A variety of system designs have been demonstrated and, notably, this technique has been industrialized for batch passivation of solar cells. Typically, close-proximity AP-SALD systems have fixed geometric parameters such as the gap size and relative alignment between the depositor head and substrate. While many systems have been designed to alter these parameters manually, there are few examples where digitally-controlled sensors and actuators are used to actively monitor and adjust geometric process parameters in real time. Therefore, there is limited scientific understanding of the importance of tolerances to these adjustable process parameters.

In this study, we describe a customized AP-SALD system that enables mechatronic control of key process parameters. A showerhead depositor design delivers precursors to the substrate surface while linear actuators and capacitance probes maintain gap size and relative alignment through multiple-axis tilt and closed-loop feedback. Two precision motorized stages control the substrate velocity and positioning, and independent control of gas flow rates and pressure is facilitated by a fluid control system. Digital control of process variables with active monitoring is facilitated with a software control package. We demonstrate and validate the system by performing AP-SALD of TiO2. We probe the dependence of film quality and uniformity on gap size variance, relative alignment tolerances, and two-axis printing, with results supported by finite-element analysis. In the future, this mechatronic design will enable experimental tuning of parameters which can inform multi-physics modeling to gain a deeper understanding of AP-SALD process tolerances, pushing this technology towards manufacturing at the large scale.

9:30am **AM-WeM-7 Spatial Atomic Layer Deposition: A New Revolution in Ultra-Fast Production of Conformal Optical Coatings**, *J. Rönn, S. Virtanen, P. Maydannik, K. Niiranen,* ***Sami Sneck,*** Beneq, Finland

Since its invention in 1974, atomic layer deposition (ALD) has shown tremendous performance in depositing thin film structures for various applications in physical, chemical, biological, and medical sciences. Due to the unique layer-by-layer growth mechanism of ALD, thin films with exceptional uniformity, conformality and quality can be deposited not only on planar substrates, but also on the most complicated surfaces. In optical systems, these properties, often absent in traditional physical or chemical vapor deposition techniques, are of utmost importance when it comes to depositing thin films on complex geometries, such as integrated waveguides, highly curved lenses, or micro lens arrays. However, this comes at a price; traditional ALD suffers from relatively low deposition rates (<30 nm/h), which has greatly limited ALD's application in many optical systems where thin films with thicknesses comparable to the wavelength of light are often required.

In this work, we present a new-generation ALD technology that revolutionizes the production of conformal optical coatings: the rotary spatial ALD. In rotary spatial ALD, the substrate is rotated across successive process zones to achieve ultra-fast and high-precision thin film deposition. We present our latest results obtained with our novel C2R plasma-enhanced rotary spatial ALD system, including the fabrication of SiO_2, Ta_2O_5 and Al_2O_3 with deposition rates reaching >1 µm/h. We also show that these materials exhibit low surface roughness (<1 Å RMS), low optical loss (<10 ppm @ 1064 nm) and excellent non-uniformity (<2% over 200 mm), ultimately paving the way for ALD to breakthrough in the optics industry once and for all.

9:45am **AM-WeM-8 Spatial ALD of Iridium Oxide Electro-Catalyst Layers for PEM Electrolysis**, *C. Frijters,* SparkNano, Netherlands; *J. Shen, M. Ameen,* TNO/Holst Center, Netherlands; *J. Greer,* Air Liquide Advanced Materials, Germany; *N. Blasco,* Air Liquide Advanced Materials, France; ***Paul Poodt,*** SparkNano, Netherlands

Proton Exchange Membrane Water Electrolysis (PEMWE) is a commonly used technique to produce green hydrogen from water. A massive up-scaling of PEMWE installations is required in the coming decade to keep up with the foreseen demand for green hydrogen. State-of-the-art PEM electrolyzers make use of iridium-based electro-catalyst layers with iridium loadings of 1-2 mg/cm^2. The high cost and limited availability of iridium will limit the scalability of PEMWE if the iridium loading cannot be reduced.

Atomic Layer Deposition can be used to apply thin and highly conformal IrO_2 films on porous substrates with atomic-scale control of the amount of material that is deposited. When applied to PEM electrolyzers, this can be used to significantly reduce the loading of IrO_2. Recently, IrO2 catalyst layers for PEM electrolyzers applied by Spatial ALD with iridium loadings well below 0.1 mg/cm^2 have been reported [1]

We will present plasma enhanced Spatial ALD of iridium oxide and metallic iridium films using a new iridium precursor developed by Air Liquide Advanced Materials. The electro-catalytic efficiency and stability has been characterized using RDE, showing that IrO2 films of just a few nanometer demonstrate an excellent catalytic activity and stability. IrO_2 films have been conformally deposited on high surface area titanium porous transport layers (PTL's) as well as Nafion membranes. First demonstrations on full PEM stack scale show that Spatial ALD can enable iridium loads 10-100x lower than the state of the art while demonstrating an excellent stability in accelerated stress tests.

We will also discuss how Spatial ALD of IrO2 films can be up-scaled to mass production, with emphasis on efficiency or precursor utilization and precursor recovery for recycling.

[1]: https://www.tno.nl/en/newsroom/2022/10/breakthrough-electrolyser-development/

Emerging Materials
Room Regency Ballroom A-C - Session EM-WeM
EUV Litho Materials

Moderator: Ms. Haripin Chandra, EMD Electronics, USA

10:45am **EM-WeM-12 Novel Organic-Inorganic Hybrid Thin Films Deposited by Molecular Atomic Layer Deposition (MALD) for EUV Resist Applications**, ***Jiyoung Kim,*** University of Texas at Dallas **INVITED**

Continued extreme downscaling of semiconductor devices and their high-volume manufacturing hinge on EUV lithography (λ=13.5 nm, EUVL), especially the soon-planned implementation of high numerical aperture (NA) EUVL. Photoresist (PR) materials are a crucial area that demands significant improvement for the high NA EUVL, particularly in achieving ultrathin thickness, uniform composition and high patterning performance (e.g., EUV sensitivity, pattern resolution, critical dimension uniformity), as well as increased etch resistance.

In this talk, we will introduce an innovative synthesis route for organic-inorganic hybrid photoresists, which leverages the molecular atomic layer deposition (MALD) of ultrathin films comprised of organic and inorganic components. Specifically, we will discuss the fabrication of a hybrid resist system, which is composed of trimethylaluminum (TMA) and hydroquinone (HQ), and its characteristics under exposure using a low energy electron beam to mimic expensive and rare EUV lithography. Most importantly, we will focus on the low-energy electron exposure characteristics, investigated using an *in-situ* infrared spectroscopy system. The TMA-HQ hybrid resists not only exhibited a comparable 100 kV EBL performance to that of HSQ (hydrogen silsesquioxane), a commercial negative-tone EBL resist but also sustained the negative tone under low-energy electron exposures down to ~100 eV and lower electron energy (evaluated in diluted AZ 300 MIF solution). Furthermore, the dose-dependent characteristics of the MALD

hybrid resists were also investigated at various low electron energies via EBL and electron flood gun system. The post-development remaining thickness of the exposure dose matrices was determined using atomic force microscopy (AFM), in which the required dose to maintain 50% of resist thickness (critical dose) was estimated to be approximately 8.4 mC/cm^2 at 100 eV. The obtained *in-situ* IR absorbance spectra suggested that chemical reactions involving aromatic rings of HQ as well as the reduction of C–O bonding are contributed to the formation of a crosslinking network within the TMA-HQ hybrid resist. We will also briefly go over the dry etching characteristics of the resist, identifying a potential process window for dry development.

This study is supported by the GRC-NMP program (task# 3035.001) through SRC.

11:15am **EM-WeM-14 Inorganic Cluster Synthesis and Characterization via Atomically Precise ALD in Polymers***, T. Kunene, **Alex Martinson**,* Argonne National Laboratory

Precision inorganic clusters, with atom-count between single-atom-sites and nanoparticles, offer an enticing complement of atom-efficiency, unique composition and structure that may defy bulk extended solids, and a total atom count that allows affordable first-principles computation of structure-function relationships. In previous work we demonstrated a novel route to few-atom inorganic cluster synthesis in a polymer matrix [ACS Nano 2020, 14, 11, 14846–14860] through sequential infiltration synthesis (SIS) of inorganic solids in analogy to atomic layer deposition (ALD) but that occurs within (vs upon) a soft material template. Careful control of synthesis conditions affords few-atom clusters of indium oxyhydroxide with relatively uniform structure. In more recent work, we probe the unique optical and vibrational properties of these small InOxHy clusters and begin to consider their potential for CO2 capture and conversion. We describe a refinement of the SIS process that favors the formation of new clusters in the first cycle, while favoring cluster growth only in subsequent cycles. This approach affords more uniform cluster growth with characteristic vibrational spectra as acquired with in situ infrared spectroscopy. Spectral analysis provides insight into cluster size and chemical functionality that evolves with additional SIS cycles (i.e. cluster growth). Optical absorption spectroscopy further reveals the unique and size-dependent properties of the few-atom clusters relative to bulk phases. Gentle thermal treatment of the polymer-embedded clusters provides the first insight into SIS-derived cluster stability, which exceeds 200 °C.

11:30am **EM-WeM-15 Molecular Layer Deposition of Al- and Hf-Based Hybrid Resists for Electron-Beam and EUV Lithography***, A. Ravi, J. Shi, J. Lewis, **Stacey Bent**,* Stanford University

The development of new resist materials is required to enable extreme ultraviolet (EUV) lithography for next-generation microelectronics. Inorganic resists are a promising class of materials because compared to traditional organic resists, they have higher etch resistance, are more impervious to pattern collapse, and are more absorbing of EUV radiation. However, there is limited understanding about how they behave under irradiation as well as what chemical and structural properties of the resist are most beneficial. In this work, we study the molecular layer deposition (MLD) of Hf- and Al-based hybrid thin film resists, known as “hafnicone” and “alucone.” These materials are grown at 100 ºC using the metal precursors tetrakis(dimethylamido)hafnium(IV) and trimethylaluminum together with ethylene glycol as the organic counterreactant. Both alucone and hafnicone are tested against electron beam exposure to inform their behavior under EUV, and results show that they behave as negative tone resists. Hafnicone exhibits a sensitivity of 400 $\mu C/cm^2$ and the ability to resolve 50 nm line widths. Alucone’s line patterns are more sharply defined than those of hafnicone, suggesting higher resolution. However, whereas alucone’s sensitivity is 4800 $\mu C/cm^2$ using 0.125 M HCl as the developer, hafnicone’s sensitivity is 400 $\mu C/cm^2$ using 3 M HCl. The MLD resists are additionally characterized via X-ray photoelectron and infrared spectroscopy to investigate the patterning mechanism, which is described in the context of classical nucleation theory. This study of hafnicone and alucone hybrid MLD offers new insight into structural features of an MLD film that can lead to desired EUV-responsive behavior. This insight may accelerate the development of vapor-deposited inorganic resists for use in electron-beam and EUV lithography.

11:45am **EM-WeM-16 High-resolution EUV Lithographic Patterning Characteristics of InO_x-PMMA Hybrid Photoresist Generated by Vapor-phase Infiltration***, A. Subramanian,* Stony Brook University*; N. Tiwale,* Brookhaven National Laboratory*; W. Lee,* Stony Brook University*; K. Kisslinger, M. Lu, A. Stein,* Brookhaven National Laboratory*; J. Kim,* University of Texas at Dallas*; **Chang-Yong Nam**,* Brookhaven National Laboratory/Stony Brook University

Continuing extreme downscaling of semiconductor devices is essential for high performance and energy efficiency of the current and future microelectronics. Adoption of extreme ultraviolet lithography (EUVL) is poised to drive the device miniaturization into the angstrom era in near future. However, there are several material-related challenges in EUVL, and one of them is the need for developing improved EUV photoresists that can feature simultaneously high sensitivity, resolution, and etch selectivity. One strategy being explored in the field is to synthesize inorganic-containing hybrid resists that utilize high EUV sensitivity and etch resistance of inorganic elements. However, currently available hybrid EUV photoresists are mostly chemically synthesized, requiring complex and slow development and processing steps for production or modification of resist properties, while suffering from a short shelf-life. Additionally, most of the reported systems are negative-tone, crosslinking resists, which are capable of patterning line gratings or pillars but require multiple exposures or complex processing for contact-hole patterning in memory devices. In this work, we demonstrate a new, positive-tone, organic-inorganic hybrid EUV resist that delivers the high-resolution EUVL and electron-beam lithography (EBL) patterning capability combined with high etch resistance and Si etch selectivity. The new resist, poly(methyl methacrylate) infiltrated with indium oxide (PMMA-InO_x), is generated via vapor-phase infiltration (VPI)–a gaseous material hybridization technique derived from atomic layer deposition (ALD). The weak binding nature of the gaseous indium precursor, trimethylindium (TMIn), to the carbonyl group in PMMA allows the synthesis of hybrids with inorganic content distributed uniformly across the thickness of the resist. The new hybrid resist achieves: (a) high EUVL and EBL sensitivities as low as 18 mJ/cm^2 and 300 $\mu C/cm^2$, respectively, (b) high-resolution positive-tone EUVL patterning capability (e.g., 40 nm half-pitch line-space and 50 nm diameter contact hole patterns), and (c) high Si etch selectivity (>30 – 40), when combined with optimized pre- and post-patterning resist process strategies comprising underlayer application and post-development descum procedures for addressing InO_x residues. The results not only hint at the potential of VPI-based ex-situ hybridization in developing novel hybrid EUV photoresists but also can pave the way for using infiltration-synthesized hybrid thin films as reliable positive-tone EUVL photoresists without chemical amplification.

ALD Applications
Room Grand Ballroom H-K - Session AA1-WeA
ULSI, Display, Optics, Metamaterials, and Bio Applications

Moderator: Charles Dezelah, ASM

1:30pm **AA1-WeA-1 Synthesis of Low-k SiCNO Thin Films by Plasma-enhanced Atomic-molecular Layer Deposition with Tetra-isocyanate-silane (TICS) and Phloroglucinol (Phl)***, G. Baek, J. Park, G. Park,* ***Haelin Yang,*** Hanyang University, Korea

Recently, as the nanoelectronics manufacturing process is ultra-miniaturized, high-level patterning technology is increasingly required. The "edge placement error(EPE)" accumulated during the repeated patterning process in back-end-of-line (BEOL) causes shorting or high resistance. To solve the EPE problem, a fully self-aligned via (FSAV) design is essential, and FSAV can be realized by increasing the spacing between the via and the metal line by using low-k materials[1]. Two ways to reduce the dielectric constant k are to reduce the number of dipoles in the film and to reduce its polarizability. The dielectric constant can be reduced by fabricating a film with almost perfect non-polar binding (ex, C–C) through the hybrid of SiO_2 and organic polymer. Therefore, it is essential to research a new molecular layer deposition (MLD) thin film fabrication process that can hybridize with Si-based atomic layer deposition (ALD). For nano scale thin film deposition, various Si precursor synthesis results have been reported for ALD SiO_2 and SiN_x thin film fabrication, and high-quality thin film fabrication is being studied through plasma enhanced atomic layer deposition (PEALD) application. Development of the MLD process using Si precursors is difficult to secure due to very low reactivity with organic precursors.

In order to induce Si-based PEALD and MLD hybrid processes, the surface adsorption reactivity of organic precursors should be increased. In this study, PEALD and MLD hybrid processes were developed using Tetra-isocyanate-silane (TICS) as a Si precursor and Phloroglucinol (Phl.) as an organic precursor for low-k material fabrication. The activation layer was fabricated with PEALD SiN_x using N_2 plasma to improve the hydroxyl reactivity. Subsequently, the SiCNO thin film was successfully fabricated through the Phl. MLD process with tri hydroxyl group. X-ray photoelectronic spectroscopy (XPS) has been used for analyzing SiCNO film composition. As the process temperature increased, the SiN_x surface oxidation was induced more strongly, and the nitrogen composition in the thin film decreased while the oxygen composition increased. Through I-V and C-V measurement, SiCNO deposited at 300 °C has a leakage current (at 1MV/cm) of 1.02 10^{-9} A/cm^2 and dielectric constant k of 3.02 compared to SiO_2 (k of 3.9).

[1] Yu, Xiaoyun, et al. "Area-selective molecular layer deposition of a silicon oxycarbide low-k dielectric." Chemistry of Materials 33.3 (2021): 902-909.

1:45pm **AA1-WeA-2 Performance and Thermal Stability Improvement of Vertical-Channel Thin-Film Transistor by Controlling Deposition Temperature of Gate Stack Prepared by Atomic Layer Deposition*****, Dong-Hee Lee,*** Kyung Hee university, Korea (Democratic People's Republic of)*; Y. Kwon, N. Seong, K. Choi,* NCD. Co., Korea (Democratic People's Republic of)*; S. Yoon,* Kyung Hee University, Korea (Democratic People's Republic of)

Vertical-channel structure is one of the promising candidates for scaling down the oxide semiconductor thin-film transistors (TFTs), in which the active channel and gate stack are formed along the vertical sidewall, as shown in Fig. 1a. Thus, the channel length of vertical-channel TFT (VTFT) can be shortened to nanometer regime by reducing the spacer thickness. An ALD technique is completely compatible with manufacturing the oxide VTFTs in terms of conformal deposition, and the device feasibilities of VTFTs using the ALD In-Ga-Zn-O (IGZO) channels have been well demonstrated. However, in lots of works, the impact of deposition temperature (T_D) for the gate stack on device performance have rarely been investigated. Considering that the IGZO channels can be sensitively influenced during the ALD process of gate stack, the T_D is one of the most critical process parameters determining device operation as well as thermal stability of the IGZO VTFTs. In this work, we focused on the relationship between the T_D and VTFT performance from the perspective of thermal stability at various post-annealing temperatures.

For the fabrication of IGZO VTFTs, a vertical sidewall was formed by patterning the PECVD SiO_2 spacer (150 nm) intervening between the ITO source and drain layers. Then, an IGZO (In:Ga:Zn=1:1:2, 5 nm) was deposited by ALD using triethyl indium (TEIn), In-Ga bimetallic, diethyl zinc (DEZn), and O_3 as source of In, Ga, Zn and O, respectively. The gate stack composed of Al_2O_3 protection layer (PL, 5 nm) and gate insulator (GI, 15 nm) was prepared by ALD at different T_D's of 200 (Dev. A), 250 (Dev. B), and 300 °C (Dev. C). Finally, gate electrode and contact pads were formed with Al-doped ZnO deposited by ALD. Figs. 1b and 1c show an optical image and a device layout of the VTFTs. To examine the thermal stability of the fabricated VTFTs, post-annealing was carried out in O_2 ambient with increasing the temperature up to 300 °C.

Fig. 2a shows the transfer curves of the fabricated VTFTs. The overall device performance was found to be enhanced with increasing the T_D and the Dev. C showed the highest current drivability (44 μA/μm). Even after post-annealing at 300 °C, all the VTFTs showed sound thermal stability (Fig. 2b) with excellent operational stability (Figs. 2c, 2d). It was noteworthy that the current drivability of Dev. C amounted above 55 μA/μm (Fig. 3a), which is remarkable improvement in the bench-mark plot shown in Fig. 3b. The T_D could be verified to have crucial impact on the current drivability of thermally-stable IGZO VTFTs. These achievements in device operation provide a path towards the highly-functional IGZO VTFTs.

2:00pm **AA1-WeA-3 Sequential Design of PEALD In-Ga-Zn-O Active Layer: Sub-cycle Engineering of Indium Oxide Layer for Highly Stable TFT*****, Taewon Hwang,*** *H. Yang, Y. Kim,* Hanyang University, Korea*; T. ONO, S. KAMIMURA, A. EIZAWA, T. TERAMOTO, C. DUSSARRAT,* Air Liquide Laboratories, Japan*; J. Park,* Hanyang University, Korea

Oxide semiconductors such as In-Ga-Zn-O (IGZO) are attracting considerable attention as active layers of next-generation displays such as AR/VR and automotive displays due to their excellent characteristics such as low leakage current, low deposition temperature, large area uniformity, and compliance mobility. For the application of 3D integration such as Fin-FET and memory/logic technology, atomic layer deposition (ALD) is a suitable method because it has the advantages of smooth surface, accurate thickness control in nanoscale, and conformal coating in complex structures due to its self-limiting characteristic. Furthermore, controlling the ALD sequence facilitates controlling the composition of the multi-component oxide semiconductor. In our previous study, we fabricated Indium-rich IGZO TFT with high mobility (≥70 cm^2/Vs) by controlling the indium sub-cycle of the ALD sequence[1]. However, it shows that excessive indium content can cause device degradation due to large carrier concentrations and crystallinity. This crystallinity-related device degradation needs to be solved for the application to future technology. We chose an advanced channel design to get the film with improved electrical properties by controlling the sub-cycle of the ALD sequence.
In this study, we suppressed the crystallinity of IGZO by inserting gallium and zinc layers into the indium layer through sequential design, and the electrical/reliability of the device was also evaluated. We confirmed that the indium crystallinity was suppressed as the interlayer of IGZO increased using the sequential design. As the indium crystallinity was suppressed, the roughness of the thin film was decreased by ~35 %, and the oxygen-related defect was also reduced. Furthermore, by adding an inter-layer to the Indium layer of IGZO, the S.S. reduced by ~45 % (from 0.42 V/decade to 0.23 V/decade), and the threshold voltage shift under PBS 3,600 s is decreased from 3.75 V to 0.83 V. The Sequential design method could be a breakthrough in improving the performance of the oxide semiconductor.

Reference

[1] Sheng, Jiazhen, et al. "Amorphous IGZO TFT with high mobility of∼ 70 cm2/(V s) via vertical dimension control using PEALD." ACS applied materials & interfaces 11.43 (2019): 40300-40309.

2:15pm **AA1-WeA-4 Bilayer Channel Combination Strategy via Atomic-Layer Deposition of In-Sn-O/In-Sn-Zn-O Structures for Highly-Functional Oxide Thin-Film Transistors*****, SHIN HO NOH,*** Kyunghee University, Republic of Korea*; Y. Kwon, N. Seong, K. Choi,* NCD Co. Ltd, Korea*; S. Yoon,* Kyunghee University, Republic of Korea

The introduction of a bi-layered channel structure is considered a highly effective approach to improve the device performance of oxide TFTs, which is composed of stacked 'prompt' and 'prime' channel layers with higher and lower carrier concentrations, respectively, owing to the impact of 2-dimensional electron gas (2DEG) formation at hetero-interfaces, leading to synergic roles in enhancing the carrier mobility and operation stability of the oxide TFTs. In this work, by means of ALD, a unique bilayer channel configuration exploiting In-Sn-O (ITO) prompt and In-Sn-Zn-O (ITZO) prime layers, where cationic compositions of each layer were carefully controlled and determined for realizing high-performance oxide TFTs showing both benefits of higher mobility and better stability.

Fig. 1 shows a schematic cross-section of the ITO/ITZO TFTs with overall process conditions of active channel compositions for single-layer and bilayer channel configurations. Bi-layered prime ITZO (7 nm) and prompt ITO (3 nm) thin films were successively deposited in ALD chamber at 150 °C. Cationic compositions of ITZO layers were adjusted by controlling the sub-cyclic ratios (TEIn:TDMASn:DEZn) to 2:1:2 and 2:1:4. Alternatively, the sub-cycles (TEIn:TDMASn) was fixed as 6:1 for the preparation of ITO layer.

Figs. 2a and 2b show the transfer characteristics of the fabricated ITZO and ITO/ITZO TFTs, respectively. Dev-C and Dev-D with bilayer channel configurations exhibited sound TFT operations, even though the turn-on positions were shifted in negative direction. While the field effect mobility (μ_{FE}) of the Dev-B was estimated to be only 23.0 cm^2/Vs, the μ_{FE} of the Dev-D was significantly improved above 30.8 cm^2/Vs. Figs. 3a-3d shows the variations in transfer curves with stress time evolution for the Dev-B and Dev-D, respectively. Noticeably, the Dev-D exhibited the shifts in threshold voltages of +0.05 and -0.07 V under positive- and negative-bias stress conditions, respectively, declaring stronger immunity against gate bias stress than the Dev-B. In other words, the implementation of hetero-junctions with 2DEG was verified to provide easier path of conduction electrons with simultaneously suppressing the charge-trapping events at front-channel interfaces. As results, the introduction of ALD-derived ITO prompt layer was found to enhance the device performance of conventional devices using ITZO single-layer channel.Consequently, the enhancement in device performance obtained from the ITO/ITZO bilayer channel TFTs clearly claim that the engineered bilayer channel configurations designed by the ALD process can extend the application fields of oxide TFTs.

2:30pm **AA1-WeA-5 Elaboration of Refractory Metamaterials by Atomic Layer Deposition for Tuning Thermal Emission at High Temperature***, **Syreina Sayegh,*** European Institute of Membranes, France*; A. NZIE,* CEMHTI, France*; M. Bechelany,* European Institute of Membranes, France*; O. ROZENBAUM,* CEMTHI, France*; Q. FLAMANT,* Saint Gobain, France

At high temperature, thermal radiation accounts for a large part of the heat transfer. Therefore, the ability to tune thermal emission is paramount to improve energy efficiency when heating and cooling. It is also one of the keys for converting efficiently heat into electricity in a thermophotovoltaic system.

Electromagnetic properties of natural materials are mainly determined by their chemical composition. The metamaterial approach provides additional degrees of freedom for tailoring these properties by playing on the internal structure. This accrued flexibility is of particular interest for the design of thermal emitters: it allows full spectral control and impedance matching with free space, thereby maximizing the emission for a chosen wavelength range.

Unfortunately, most existing metamaterials rely on metals with a low melting point such as gold or silver. So far, the attempts to realize refractory metamaterial emitters relied either on refractory metals (e.g. Ta, Mo, W) or on nitrides (e.g. TiN, AlN, ZrN). These materials do have high melting points but are prone to oxidation which limits their operating temperature in air.

In this presentation, we will show how using innovative fabrication approaches such as Atomic Layer Deposition (ALD) and making the proper choice for associating a conducting and a dielectric material allows elaborating refractory metamaterials with tunable emissivity in the near infrared (NIR) that can operate in air at temperatures exceeding 1000°C.

2:45pm **AA1-WeA-6 Optical Properties of Interconnected Plasmonic Nanostructures with sub-10 Nm Nanogaps by Area-Selective Atomic Layer Deposition***, **Brian Willis,** R. Raman, J. Grasso,* University of Connecticut

Nanostructures made of materials such as Cu, Ag, and Au have plasmonic resonances in the visible and near infrared spectral regions. These resonances enhance light - matter interactions by concentrating electric fields around nanostructures. Enhanced electric fields are useful for applications in spectroscopy, catalysis, and photodetection. Electric fields are especially strong in nanogaps between closely spaced particles, and there has been significant work to devise nanofabrication techniques to control interparticle distances with nanometer precision. The majority of work in plasmonics has investigated particles in solution or nanostructures deposited onto surfaces without electrical connections, but adding electrical contacts adds new functionality. In particular, adding electrical interconnects to plasmonic nanostructures provides opportunity for nanoscale light emitters and detectors, as well as energy harvesting. In this work, we investigate the design and fabrication of arrays of interconnected plasmonic nanostructures with sub-10 nm nanogaps. FDTD simulations model optical extinction properties of nanostructures fabricated on glass substrates, and ALD experiments create nanostructures with tunable nanogap spacing. We use glass substrates with nanostructure templates made by conventional nanofabrication methods, and subsequently coat those nanostructures with conformal layers of Cu by ALD to control interparticle distances. Cu ALD occurs selectively on Pd, and nanostructure templates are coated with Pd to promote growth. Selective area growth ensures that neighboring nanostructures remain electrically isolated. This configuration allows for electrical measurements during irradiation with light, see attached figure. Compared with Cu and Au, Pd is a poor plasmonic material, but Pd is necessary for promoting Cu growth. In this talk, we investigate several different approaches using both homodimers and heterodimers with different Au/Pd combinations. Optical extinction measurements reveal how plasmonic resonances evolve when Cu layers are added and nanogaps shrink. FDTD simulations provide insight to how complex changes of nanostructure size, thickness, and shape affect plasmonic properties. We also investigate how interconnect designs perturb plasmonic resonances compared to isolated nanorods. Our findings show that ALD can achieve sub-10 nm nanogaps for interconnected designs with plasmonic properties similar to isolated nanostructures, and that the process can scale to large arrays of devices. Results show that it should be possible to create electro-optic devices where intense electric fields from plasmonic resonances enable new functionality.

3:00pm **AA1-WeA-7 Electrochemically Active Antibacterial Electrodes for Neural Interfacing Applications***, **Shahram Amini,*** Pulse Technologies Inc.*; G. Feng, H. Khosla,* Villanova University

Miniaturization and electrochemical performance enhancement of electrodes and microelectrode arrays in emerging long-term implantable neural interfacing devices improves specificity, functionality, and performance of these devices. However, surgical site and post-implantation infections are amongst the most devastating complications after surgical procedures and implantations. Additionally, with the increased use of antimicrobial drugs, the threat of antimicrobial resistance is significant and is increasingly being recognized as a global problem. Therefore, the need for alternative strategies to eliminate post-implantation infections and reduce antibiotic consumption has led to development of medical devices with antibacterial properties. In this work, we report for the first time on the development of antibacterial platinum-iridium electrodes with ultra-high electrochemical performance using a two-step manufacturing process. Electrodes are first restructured using femtosecond-laser hierarchical surface restructuring technology yielding unprecedented performance values that significantly exceed those reported in the literature, e.g. charge storage capacity and specific capacitance were shown to have improved by two orders of magnitude and over 700-fold, respectively, compared to un-restructured electrodes. In the second step of the process, atomiclayer deposition was utilized to deposit conformal copper oxide thin films on the hierarchical surface structure of the electrodes to impart antibacterial properties to the electrodes. Electrochemical, morphological, compositional, and structural properties of the electrodes were studied using a suite of characterization techniques. Last, but not least, the antibacterial properties of the electrodes were also studied, particularly, the killing effect of the antibacterial electrodes on Escherichia coli and Staphylococcus aureus - two common types of bacteria responsible for implantation infections.

3:15pm **AA1-WeA-8 Ultrathin TiO_2 ALD Coatings Strongly Enhance Biological Response of Biomedical Materials***, **Jan Macak,*** University of Pardubice, Czechia

TiO_2 surfaces are in general recognized as excellent biocompatible materials owing to their low cytotoxicity, high stability, antibacterial properties, and wetting ability. Among various TiO_2 nanostructured surfaces that show very good cell interactions (various cell types) and osseointegration, anodized TiO_2 nanotube (TNT) layers have emerged as extremely suitable substrates. A pioneering work demonstrated that TNTs with diameter of 15 nm are the most suitable for the growth of various cells [1]. But numerous papers also showed that anodization is a very viable tool for nanostructuring of various biomedical alloys, including frequently used TiAlV.

Recently, we demonstrated that an ultrathin coating on TNT by suitable oxides (e.g. TiO_2) using Atomic Layer Deposition (ALD) can enhance cell growth and adhesion [2]. These properties make them excellent as final surfaces for medical and dental implants based on Ti alloys.

The presentation deals with the comparison of the influence of ultrathin ALD TiO_2 coatigs (achieved by few cycles of TiO_2 ALD process) on TNT layers, reference Ti foils and Ti biomedical alloys for the proliferation of fibroblast, osteoblast and neuroblasts cells. For that Ti sheets and anodized TNT layers

with a distinct inner diameter of 12 nm, 15 nm, and 100 nm were used as substrates, as they appear to be the most suitable for cell growth in general [2,3,4]. We investigated the shaping, adhesion, proliferation, and cell density on these substrates.

Moreover, the single-cell adhesion of the cells to the TNTs was studied by the bio-atomic force microscopy (bio-AMF) technique [3]. Last, but not least, black form of TiO^2 nanotubes was investigated for cell proliferation in comparison to classical TNTs [4],

References:

1. Park, J. et al. Small 2009, 6, pages:666 -671.

2. Motola, M. & Rousar, T.; &Macak, J.M. Thin TiO_2 Coatings by ALD Enhance the Cell Growth on TiO_2 Nanotubular and Flat Substrates. ACS Appl. Bio Mater. 2020, 3, 6447−6456.

3. Baishya, K. & Macak, J.M. Bio-AFM exploits enhanced Response of Human Gingival Fibroblast (hGFs) on TiO_2 Nanotubular Substrates with Thin TiO_2 Coatings. 2022, Applied Surface Science, submitted.

4. Sopha, H. & Rousar, T. & Macak, J.M., et al. Comparison of cellular effects between white and black anodic TiO_2 nanotubes, Surface and Coating Technology, 2023, submitted.

ALD Applications
Room Grand Ballroom H-K - Session AA2-WeA

Energy Solar

Moderators: Mike McSwiney, Applied Materials, Shaibal Sarkar, ITT Bombay

4:00pm **AA2-WeA-11 Atomic Layer Deposition of Highly Stable and Efficient Perovskite Solar Cells (~ 24%)***, H. Park, S. Shin, P. Nandi, D. Pal,* ***Hyunjung Shin,*** Sungkyunkwan University (SKKU), Republic of Korea **INVITED**

Power conversion efficiency (PCE) of Perovskite solar cells (PSCs) is over 25.7%. Their operational/environmental instability remains to be solved and restrict commercialization.[1] The state-of-the-art PSC is used pure a-$FAPbI_3$ and Spiro-OMeTAD in *n-i-p* structure of PSCs. A chemical-driven transition from photoactive α-$FAPbI_3$ to non-photoactive δ-$FAPbI_3$ is pointed as a significant challenge. Much lower stability of Spiro-OMeTAD is critical for the device instability. As an interlayer in between top metallic electrodes and Spiro-OMeTAD/a-$FAPbI_3$, inorganic HTLs prepared by a low-temperature ALD provide bi-functionality to stabilize the PSCs during operation. Transition metal oxide (TMO) can be a strong candidate. Most of TMO layers generally require a high processing temperature and the lack of *p*-type characteristics inhibits application to PSCs as hole-transporting interlayers. We adopt ALD to fabricate TMO layers at low temperatures (~ 50 °C) and intentionally induce oxygen deficient traps to form empty *d*-bands and further enhance hole transporting properties. We fabricated n-i-p normal structure PSCs of a-$FAPbI_3$ and Spiro-OMeTAD with ALD grown TMOs on top of Spiro-OMeTAD to enhance device stability. We also adopt ALD to form ultra-thin NiO and SnO_2 as charge transport layers (ETLs).[2,3] As a result, highly efficient PSCs of PCE of over 24% with TMOs are fabricated with pin-hole free hole transporting and protection bi-functional ALD layers.[2,3] The environmental stability of PSCs is over 90% initial PCE after 600 hrs, while without the interlayer started to be degraded under 80% of initial PCE just after around 200 hrs without any special encapsulation. Furthermore, this study shows the possibility that ALD TMOs can be also applicable to tandem device fabrication with p-i-n type PSCs and stable PSCs' commercialization.

[1] High Efficiency Perovskite Solar Cells, *Chem. Rev.* (2020) [2] Perovskite Solar Cells with Inorganic Electron and Hole Transporting Layers Exhibiting Long – Term (≈ 500 h) Stability at 85 °C under Continuous 1 Sun Illumination in Ambient Air, *Adv. Mater.* (2018) [3] Atomic Layer Deposition for Efficient and Stable Perovskite Solar Cells, *Chem. Comm.* (2019) [4] Cyclohexylammonium-Based 2D/3D Perovskite Heterojunction with Funnel-Like Energy Band Alignment for Efficient Solar Cells (23.91 %), *Adv. Energy Mater.*(2021) [5]Amorphous TiO_2 Coatings Stabilize Perovskite Solar Cells, *ACS Energy Lett*(2021)[6] Hole Transporting Vanadium-Containing Oxide (V_2O_{5-x}) Interlayers Enhance Stability of a-$FAPbI_3$-Based Perovskite Solar Cells (~ 23%), *ACS Appl. Mater. & Interfaces,* (2022)

4:30pm **AA2-WeA-13 ALD of Niobium Oxide (Nb_2O_5) and Niobium-doped Titanium Oxide (Nb:TiO_2) for Solar Cell Applications***, T. VINCENT,* IPVF, France*; D. COUTANCIER,* CNRS, France*; P. Dally, M. AL-KATRIB, F. DONSANTI,* IPVF, France*; A. YAICHE,* EDF, France*; K. MEDJOUBI, M. PROVOST,* IPVF, France*; J. ROUSSET,* EDF, France*; M. BOUTTEMY,* ILV, France*;* ***Nathanaelle SCHNEIDER,*** CNRS, France

Atomic Layer Deposition (ALD) is increasingly contributing to the energy field and more specifically to the engineering of solar cells. Its conformity enables deposition on nanostructured substrates and its low growth temperature allows the deposition on temperature-sensitive substrates such as perovskite. Niobium oxide, Nb_2O_5, is a wide bandgap semiconductor that has been grown by different methods and has recently been used in solar cells. Its optical and electrical properties depend strongly of the technique used for its growth, opening access to a wide range of application, such as electron transport layer (ETL)or passivation layer [1,2]. It is also used for the doping of titanium oxide (TiO_2), a well-known ETL, to reach a better stability of the complete solar cell.

In this study, the growth of niobium-doped titanium oxide (TiO_2:Nb) thin films by atomic layer deposition (ALD) is reported. Films were obtained at 200°C from titanium (IV) i-propoxide (TTIP), (t-butylimido)tris(diethylamido)niobium(V) (TBTDEN), and water by introducing Nb_2O_5 growth cycle in a TiO_2 matrix. Process parameters such as the order of precursor introduction and the cycle ratio were optimized. The growth mechanisms and the effective Nb incorporation were investigated by in situ quartz crystal microbalance (QCM) and X-ray photoelectron spectroscopy (XPS). The as-deposited films were analyzed for their surface morphology, elemental stoichiometry, optoelectronic properties, and crystallinity using a variety of characterization techniques. Such as-deposited films are amorphous and a fine control of the Nb amount with the supercycle parameters along with a continuous evolution of their optical properties from the ones of TiO_2 to Nb_2O_5 bare oxides are observed. To allow a successful implementation in solar devices, a comprehensive annealing study under several temperatures and atmospheres was conducted and revealed an evolution of the optical bandgap after crystallization in the anatase phase. Ultimately, the incorporation of these 15 nm-thick films in mesoscopic perovskite solar cells (PSCs) as ETL shows an improvement of the cell performances and of their stability with increasing Nb amount, reaching power conversion efficiency (PCE) up to 19.8%.

[1] Subbiah, et al (2019). *Energy Technology, 8*(4), 1900878. https://doi.org/10.1002/ente.201900878

[2] Macco et al, (2018). *Solar Energy Materials and Solar Cells, 184*, 98-104. https://doi.org/j.solmat.2018.04.037

4:45pm **AA2-WeA-14 Closing Remarks***,*

ALD Fundamentals
Room Grand Ballroom E-G - Session AF1-WeA

Computational ALD I

Moderators: Prof. Dr. Michael Nolan, University College Cork, Atsushi Sakurai, ADEKA CORPORATION

1:30pm **AF1-WeA-1 Effect of Inhibitor Adsorption on the Mechanisms for Selectivity Loss***,* ***Tania Sandoval,*** Technical University Federico Santa Maria, Chile **INVITED**

Area selective atomic layer deposition (AS-ALD) addresses some of the challenges that can occur in nanofabrication of complex multilayers structures, where different surfaces require patterning and alignment at the atomic scale. In this case, AS-ALD allows ALD to occur only on the surface that is desired through different strategies that include the use of inhibitor molecules. For the past few years, the use of small molecule inhibitors (SMIs) has gained attention as they show promise for implementation in high-volume manufacturing. However, selectivity values continue to be low, which could be attributed to the challenges in achieving suitable selective adsorption, and the need for understanding of the mechanisms behind selectivity loss.

In this presentation, theoretical studies on the fundamental understanding of the mechanism for selectivity loss will be discussed. Using a combination of both static and dynamic density functional theory (DFT) calculations, insights into t he displacement of acetylacetone by trimethylaluminum (TMA) and dimethylaluminum isopropoxide (DMAI) were studied. The

results revealed the dependence between the inhibitor adsorption configuration, temperature, and selectivity loss. Due to the high reactivity and small size, TMA shows a higher probability to displace adsorbed Hacac than DMAI. We found that the adsorption mechanism for the SMI influence the probability of displacement, as the energetics determines the driving forces of the process. Moreover, by calculating thermochemistry it is possible to determine the extent of how much the selectivity can be improve with temperature within the AS-ALD process.

Overall, these results are keen in helping with proper selection of inhibitor molecules for AS-ALD.

2:00pm **AF1-WeA-3 Electronic Structure of ALD Al_2O_3/TiO_2 Heterointerfaces: A First-principles Study**, ***Hyobin Eom**, C. Ahn, J. Park, B. Shong,* Hongik University, Republic of Korea

Two-dimensional electron gas (2DEG) is a group of free electrons that is localized at thin region at an interface. 2DEG often exhibits high anisotropic carrier mobility along the in-plane horizontal direction, and large charge concentration. Because of such advantages, 2DEG can be applied to semiconductor devices such as high-electron-mobility transistors (HEMTs). Recent studies show that quasi-2DEG can be manifested at Al_2O_3/TiO_2 heterointerfaces formed via atomic layer deposition (ALD) [1]. Such low-lying donor states originate from the oxygen vacancy on the TiO_2 surface chemically formed by trimethylaluminum (TMA) [2]. In this work, various continuous bulk heterojunction structures of Al_2O_3 and TiO_2 with buried oxygen vacancies are studied through density functional theory (DFT) calculations. Analyses of density of states (DOS) along with local charge distribution show that the donor states are localized at the two-dimensional interface between Al_2O_3/TiO_2 where the oxygen vacancies are located. The structural stability of the heterojunction interface structures is confirmed using ab-initio molecular dynamics (AIMD) simulations. Non-equilibrium Green's function (NEGF) simulations prove high anisotropicity in electron transport of these structures. Current work provides atomistic understanding on electronic properties of ALD-formed emergent interfacial structures.

References [1] Chem. Mater. 2020, 32(18), 7662; [2] Mater. Today Adv. 2021, 12, 100195.

2:15pm **AF1-WeA-4 Reaction Mechanism of Bifunctional Organic Reactants and Diethylzinc for Atomic and Molecular Layer Deposition**, ***Miso Kim**, H. Oh, B. Shong,* Hongik University, Republic of Korea

In molecular layer deposition (MLD) processes, bifunctional organic reactants often show different growth behaviors depending on the chain length of their molecular backbone. For example, MLD using 1,2-ethanediol (1,2-ED) and diethylzinc (DEZ) results in organic-inorganic hybrid thin film of "zincone" containing stoichiometric amount of carbon.[1] In contrast, in a process using 1,5-pentanediol (1,5-PD) and DEZ, atomic layer deposition (ALD) of ZnO thin film without carbon impurities is reported.[2] Also, MLD thin films of Mo-thiolates shows decreased C content when dithiol with longer chain is used.[3] However, the molecular mechanism for the governing factor for removal of the carbonaceous moieties from the MLD thin films is yet unclear. In this study, the chemistry of DEZ and bifunctional organic reactants (linear $HX-C_nH_{2n}-XH$, X=O or S, n=2-6) according to the length of the backbone of bifunctional reactants was investigated through density functional theory (DFT) calculations. Several intramolecular reaction pathways in which $Zn-C_nH_{2n}-XH$ on the surface is converted to Zn-OH were investigated. By comparing the reactivity according to the backbone length of the bifunctional reactant structures, it was confirmed that the activation energy for forming Zn-XH decreases as the number of carbon increases, possibly resulting in inorganic ALD thin films without C.

References

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2:30pm **AF1-WeA-5 Simulated Conformality of ALD Growth Inside Lateral HAR Channels: Comparison between a Diffusion-Reaction Model and a Ballistic Transport-Reaction Model**, *J. Järvilehto, J. Velasco, J. Yim, C. Gonsalves, **Riikka Puurunen**,* Aalto University, Finland

Atomic layer deposition (ALD) is known for its ability to produce films of controllable thickness, even in narrow, high-aspect-ratio (HAR) structures [1]. These films can be highly conformal, meaning that the structure is covered by a film of uniform thickness [1,2]. However, when the structure's aspect ratio is increased sufficiently, deposition becomes limited by the diffusion of the reactants into the deep end of the structure, potentially resulting in the formation of an adsorption front, followed by a region of lower coverage [3]. Theoretical models have been developed to predict film conformality in HAR structures, as reviewed in Ref. 2.

This work presents a comparison of a diffusion-reaction model (DRM) developed by Ylilammi et al. [4,5] (Model A) and a ballistic transport-reaction model (BTRM) by Yanguas-Gil and Elam [6,7] (Model B). For the comparison, saturation profiles were generated using both models with similar simulation parameters (Knudsen number Kn >>1).

Qualitatively, both models produced similar trends in terms of half-coverage penetration depth and slope at half-coverage penetration depth. The saturation profiles were similar in shape, except for the film growth observed at the channel end in Model B. Quantitative examination yielded consistently higher half-coverage penetration depths in Model B. Model A produced steeper slopes at half-coverage penetration depth. In Model B, the discretization resolution was found to affect the penetration depth.

While the models gave qualitatively similar results, quantitatively extracted parameters differed. This finding is consistent with a previous comparison of a DRM and BTRM in the context of low pressure chemical vapor deposition [8]. The quantitative differences are relevant, for example, when the models are fitted to experimental data for the extraction of kinetic parameters, such as the sticking coefficient.

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[7] A. Yanguas-Gil and J.W. Elam, (2013) https://github.com/aldsim/machball, accessed Feb 13 2023.
[8] M.K. Jain et al., J. Electrochem. Soc. 140 (1993) 242.

2:45pm **AF1-WeA-6 Simulated Conformality of ALD in Lateral High Aspect Ratio Channels: Impact of Knudsen Number on the Saturation Profile**, ***Christine Gonsalves**, J. A. Velasco, J. Järvilehto, J. Yim, V. Vuorinen, R. L. Puurunen,* Aalto University, Finland

Due to its unparalleled conformality, atomic layer deposition (ALD) is often the method of choice for coating nanostructures having complex geometries with atomic level precision [1]. However, conformality in high-aspect-ratio (HAR) surface features evolves with time and depends on process parameters and chemistry [2,3]. Different models have been developed to simulate ALD growth in HAR structures [2,3]: diffusion–reaction models, Monte Carlo models and ballistic transport–reaction models.

Studies of ALD growth in HAR (AR ≥ 100) features typically assume free molecular flow conditions (Knudsen number *Kn* >> 1), with the molecule's mean free path much larger than the feature size. However, depending on the limiting feature size and pressure, the free molecular flow assumption may not be fully valid in real ALD processes.

In this work, we mapped the evolution of conformality in lateral high-aspect-ratio (LHAR) channels in terms of the Knudsen number from free molecular flow governed by Knudsen diffusion (*Kn*>>1) through the transition regime (Kn~1) to continuum flow conditions governed by molecular diffusion (*Kn*<<1). The mapping was done by varying the LHAR channel height and reactant partial pressure; Knudsen number was varied by 13 orders of magnitude. Thiele modulus was kept above one, so that diffusion-limited conditions prevailed and the simplified model by Ylilammi et al. [4] re-implemented earlier [3], could be used for the simulations. Reactant exposure was kept constant.

When *Kn*>>1, regardless of the partial pressure of the reactant and the channel height, the same characteristic saturation profile was obtained. When *Kn*~1 and *Kn*<<1, the penetration depth decreased and the steepness of the adsorption front increased with decreasing Knudsen number.

The slope method by Arts et al. [5] was used to back-extract the sticking coefficient from simulated saturation profile, up to demonstrating how the slope method breaks when conditions deviate from free molecular flow. Using the slope method for conditions where the Knudsen diffusion

assumption is not valid, would lead to an incorrect (too high) interpretation of the sticking coefficient (even unphysical values above one).

References

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3:00pm **AF1-WeA-7 Atomistic Modeling of Thin-Film Deposition with Carrier Gases**, *S. Natarajan, P. Khomyakov, J. Wellendorff,* Synopsys Denmark*; **Baiyu Zhang**, A. Blom,* Synopsys, Inc.

Advances in thin film deposition techniques are at the core of atomically fine-tuned manufacturing of next-generation semi-conductor devices. Extreme fabrication limits require optimization of existing and development of new thin film deposition setups for maximum process capability and yield. In silico modeling approaches can be of particular importance when developing new deposition processes where experimental data are unavailable or expensive and time-consuming to obtain. We have previously shown how machine learning based atomic-scale modeling of ALD processes, e.g., ALD of HfO_2, [1] with Synopsys QuantumATK software [2,3] was used to simulate energetics, dynamics, and mechanisms of precursor molecule interaction with a substrate material, and provide important parameters, such as sticking probabilities and growth rates, for further physical modeling with topography tools, such as Sentaurus Topography.

In this talk, we will present an enhancement of this deposition simulation workflow by including the effect of carrier gases. The impact of carrier gases becomes critical at higher pressures, as carrier gas molecules collide with precursor molecules and alter growth rates. We will demonstrate the enhanced complete workflow in QuantumATK, including density functional theory-based thermochemistry, reaction kinetics and classical molecular dynamics, and show results for Si deposition using disilane precursor and hydrogen carrier gas at varying pressures.

In the first step, we identify the most probable reactive gas phase species and evaluate their equilibrium concentrations in gas mixtures, which are present in the reactor at the process conditions. This is achieved by comparing Gibbs free energy profiles of many possible gas phase decomposition reactions. Since the above results do not include kinetic information, they are usually valid only when the activation barriers of the considered reactions are fully breached by thermal energy. Thus, in the second step, we compute reaction kinetics which involves obtaining rates and branching ratios of the most probable reactions from step 1 to identify the flux ratios of the reactive species. These flux ratios inform us of the fractions of the dissociated species in the reactor along with the intact precursor molecules at the process conditions. In the final step, we perform molecular dynamics simulations with the flux ratio from kinetic studies to compute the sticking probabilities and growth rates.

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3:15pm **AF1-WeA-8 Chemistry of Plasma-Enhanced and Thermal Atomic Layer Deposition of Metal and Intermetallic Thin Films: The Role of Substrates and Reducing Agent**, ***Ji Liu**, M. Nolan,* Tyndall National Institute, University College Cork, Ireland

Atomic layer deposition (ALD) is widely used in microelectronics and catalysis to deposit metal thin films. The key advantages of ALD are the conformality and precise thickness control at the atomic scale. Cobalt (Co) is an interesting material in the semiconductor industry due to its attractive electrical and physical properties. The replacement of Cu with Co as contacts or interconnects in semiconductor devices serves as an illustrative example and is an ongoing process driven by large device manufacturers.

In this presentation, I will present our recent work on the plasma enhanced (PE) and thermal ALD growth of Co from first principles calculations. For PE-ALD of Co using $CoCp_2$ and N-plasma, we first addressed the surface reaction mechanism in the metal precursor pulse and plasma half-cycle on NH_x-terminated Co surfaces, which corresponds to the steady growth for the PE-ALD. The reactions at the initial stages on a series of Si surface terminations are investigated to gain detailed atomic insights on the effect of different substrates on the elimination of Cp ligands.

For thermal ALD of Co, our collaborators have shown that Co thin films deposited with ALD are metallic and Zn-free. We modelled the reaction mechanism of $CoCl_2$(TMEDA) and a reducing agent, $Zn(DMP)_2$. Our DFT calculations indicate that the reactions proceed via initial ligand exchange of DMP and Cl on Co(111) surface with $CoCl_2$ termination and Zn is removed via ZnCl(DMP) formation and desorption, resulting $Co(DMP)_2$ termination on the surface. The two DMP ligands are removed via C-C bond formation in a straightforward way.

Further, we presented our recent collaborative work of a new type of ALD process for intermetallic FeZn thin films, where diethyl zinc (DEZ) serves as a coreactant. The $FeCl_3$ + DEZ process yields in situ crystalline Fe_4Zn_9 thin films. DFT calculations indicate that the favorable pathway of eliminating the Cl group and the Et ligand is via butane and subsequent EtCl formation and desorption.

Our DFT studies show that substrate terminations and reducing agents have significant impact on ALD deposited metallic thin films.

ALD Fundamentals
Room Grand Ballroom E-G - Session AF2-WeA
Computational ALD II

Moderator: Dr. Tania Sandoval, Technical University Federico Santa Maria

4:00pm **AF2-WeA-11 Revealing Process-Structure Relationships for ALD Amorphous Oxide Semiconductors with XANES and First-Principles Modeling**, ***Orlando Trejo**,* Applied Materials*; T. Cho,* University of Michigan, Ann Arbor*; S. Sainio,* University of Oulu, Finland*; N. Dasgupta,* University of Michigan, Ann Arbor

Amorphous oxide semiconductors (AOS) lack the long-range order characteristic of crystalline materials but possess short-range order that gives rise to a vast parameter space to design and optimize their properties. To accelerate efforts to control their functional properties and optimize device performance, an increased fundamental understanding of the complex process−structure−property relationships of AOS is needed. Recent research efforts have provided an initial framework to understand how short-range order in AOS determine their properties. The structure and interconnection of the metal-oxygen (M-O) polyhedra in AOS depend on the material system (i.e., the composition and types of elements) and the synthesis conditions (e.g., solution, physical or chemical vapor deposition). Given its atomic-level synthesis control and technological relevance, ALD chemistry facilitates and encourages a systematic structural analysis of AOS that are material and process specific.

In our previous work, we optimized the performance of amorphous ALD zinc tin oxide (ZTO) thin-film transistors by turning the Zn-to-Sn ratio and annealing temperature.[1] However, prior work has not been able to fully uncover the mechanistic origins of the differences in performance among samples. To address this knowledge gap, here we leverage ALD's capability to finely tune the composition of ZTO films along with systematic annealing to reveal how cation composition and annealing temperature influence the geometric and electronic structure in an AOS.[2] The ZTO films are characterized with XRD, XPS, and synchrotron x-ray absorption near-edge spectroscopy (XANES) measurements of the O K-edge, Sn M-edge, and Zn L-edge. The XANES spectra are analyzed with ab initio and nonlinear statistical modeling. The resulting multimodal analysis of ALD ZTO reveals how process conditions give rise to gradual or abrupt changes in the coordination environment of the Zn−O and Sn−O polyhedra, which in turn translate into changes in the relative contribution of the Zn and Sn s orbitals to the density of states near the conduction band minimum. Thus, this multimodal X-ray analysis and modeling framework can be applied to understand the process-structure relationships needed to optimize AOS performance in devices.

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4:15pm **AF2-WeA-12 Machine-Learning Aided Understanding of ALD Processes**, *A. Arunachalam,* University of Texas at Dallas; ***S. Novia Berriel,*** *U. Kumar,* University of Central Florida; *S. Das,* University of Texas at Dallas; *S. Seal,* University of Central Florida; *K. Basu,* University of Texas at Dallas; *P. Banerjee,* University of Central Florida

ALD processes are controlled via an array of hardware-based, independent process parameters. Typically, 'recipes' are built that enable these parameters to be set to specific values during an ALD process. Example parameters include chuck and chamber temperatures, line and precursor temperatures, gas flow rates, etc. While each of these play an important role in the growth rate and final thickness of an ALD film, there is currently no measure of the magnitude of their impact on the film thickness and quality. Further, there is no way to predict film thickness purely based on process parameters without running numerous experiments to get an estimated growth rate. We propose the use of machine learning (ML) approaches to generate 'feature importance maps' that graphically depict the impact of these parameters in determining and predicting film thickness.

Our ML method begins with a set of 78 process parameters recorded from an ALD process from a Veeco® Fiji Gen2 ALD system for a CeO_2 film. The ALD process has been described in detail elsewhere[1]. A random forest ML algorithm then identifies the top-ten 'critical' independent process parameters that affect film thickness at a given deposition temperature. These include a list of heater zones around the reaction chamber, line pressure of the precursor delivery line, etc. A temperature dependent (from 185 °C – 320 °C) series is then generated. The model is able to predict with up to 99.99% accuracy the time variation of thickness during the growth, verified via in situ spectroscopic ellipsometry. Our talk will include detailed considerations in generating the ML model, as well as results for a range of process temperatures for CeO_2 ALD.

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4:30pm **AF2-WeA-13 Digital Twin and Experimental Platform for AI-Driven Optimization of ALD Processes**, ***Angel Yanguas-Gil,*** *N. Paulson, J. Elam,* Argonne National Laboratory

Atomic layer deposition is an ideal platform for exploring AI-driven optimization and discovery: first, ALD's step-by-step nature defines a natural design space where a growth is defined by sequences of cycles, each of which driven by their own timings; Second, ALD tools already come with the required control software and hardware to integrate with AI engines. Finally, its integration into cluster tools with automatic wafer handling systems in microelectronics opens up the possibility of fully automatic growth-characterization-decision cycles to develop novel materials.

In this work we describe an experimental setup for AI-driven process optimization as well as a digital twin for the development and validation of novel algorithms for self-driving labs. Building on prior research where we used simulated quartz crystal microbalance data, here we expand the range of techniques to incorporate optimization based on in-situ spectroscopic ellipsometry. In addition to algorithms to optimize the dose and purge times of single processes, we have also explored algorithms to find optimal sequences of ALD cycles for binary and ternary compounds based on target optical properties.

From an experimental perspective, we have demonstrated the optimization of ALD processes based on in-situ techniques. While the results are demonstrated in a specific cross-flow reactor, the methodology and algorithms developed can be easily adapted to other reactor configurations and characterization techniques.

This research has been supported through Argonne's Laboratory Directed Research and Development program.

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4:45pm **AF2-WeA-14 Closing Remarks in Grand Ballroom H-K**,

Emerging Materials
Room Regency Ballroom A-C - Session EM1-WeA

Molecular Layer Deposition

Moderator: Prof. Dr. Jiyoung Kim, University of Texas at Dallas

1:30pm **EM1-WeA-1 MLD/ALD of Hybrid Dielectrics for Flexible Electronic Devices**, *X. Wang,* School of Advanced Materials, Shenzhen Graduate School, Peking University, China; ***Min Zhang,*** School of Electronic and Computer Engineering, Shenzhen Graduate School, Peking University, China **INVITED**

Modern information technologies have tremendous demands on flexible electronic devices such as thin-film transistors (TFTs). As the flexible TFT technology continues to advance, the properties of the gate dielectric become a bottleneck for the flexible TFTs to achieve fast switching speed, low operation voltage, and downscaling. The gate dielectric layer should be sufficiently thin, insulating, and flexible, and therefore, hybrid organic-inorganic dielectrics are of great promise for this purpose. In this work, we develop an MLD/ALD technique to grow a hybrid material of polyimide and Al_2O_3 (HPA) and show that the afforded HPA films are well suited as the bendable gate dielectrics for flexible electronic applications. The MLD/ALD growth mechanism is carefully investigated, and it is found that the growth of polyimide is strongly affected by the Al_2O_3 surface and therefore exhibits a two-stage behavior. We further show that the HPA films can serve as a good gate dielectric to realize the intrinsic flexibility of transistors and circuits based on carbon-nanotubes (CNTs). With this hybrid dielectric, high-performance all-CNT TFTs and integrated circuits of inverters, ring oscillators, and logic gates are demonstrated. Particularly, the inverters exhibit a remarkably high gain of 342.5 and can be used as an analog amplifier for millivolt small signals. Ultralow voltage (50 mV) operation is also feasible, which highlights the great promise for low-power applications.

2:00pm **EM1-WeA-3 The Molecular Evolution of Zno Sequential Infiltration Synthesis**, *I. Weisbord, M. Barzilay,* Department of Chemical Engineering, Technion, Israel; *A. Kuzmin, A. Anspoks,* Institute of Solid State Physics, University of Latvia; *E. Welter,* Deutsches Elektronen-Synchrotron, Germany; ***Tamar Segal-Peretz,*** Department of Chemical Engineering, Technion, Israel

Sequential infiltration synthesis (SIS) has emerged in the past decade as a powerful technique for hybrid material fabrication through high-precision growth of inorganic materials within polymers using atomic layer deposition (ALD) chemistry.In SIS, ALD precursors diffuse into the polymer and interact with it, leading to inorganic materials growth within the polymer's free volume. If desired, the polymer can later be removed, yielding polymer-templated inorganic structures.Among the limited but growing list of inorganic materials demonstrated via SIS, ZnO stands out as a promising material in wide and diverse applications which can harness SIS abilities for low-cost, large-area, and high-quality nanostructure fabrication.

In this study, we have probed the development of ZnO, grown within various polymers *via* SIS. We combined high-resolution scanning transmission electron microscopy (STEM) and *in-situ* thermal TEM, together with synchrotron-based X-ray absorption near edge structures (XANES)and show, for the first time, the evolution of polycrystalline Wurtzite ZnO cluster and nanoparticles- from the onset of crystallinity after just single SIS cycle, through the cycle-by-cycle 3D growth of the particles. *In-situ* growth analysis using microgravimetry and FTIR enabled us to shed light on the growth mechanism and its deviation from classic ALD-like growth, as well as to understand the role of polymer chemistry on the growth nucleation and particle density within the polymer. Annealing the hybrid ZnO-polymer films in air removes the polymers and consolidates the as-grown clusters and nanoparticles into a network of polycrystalline ZnO particles. Our findings lay the foundations for ZnO SIS design rules and rational hybrid and inorganic nanostructures design.

2:15pm **EM1-WeA-4 Conformal ALD/MLD of Perfectly Stable Zn-Benzenedithiol Thin Films**, *T. Jussila,* Aalto University, Finland; *A. Philip, J. Kinnunen,* Chipmetrics Oy, Finland; *D. Zanders,* Ruhr-University Bochum, Germany; *M. Utriainen,* Chipmetrics Oy, Finland; *A. Devi,* Ruhr-University Bochum, Germany; ***Maarit Karppinen,*** Aalto University, Finland

The combined atomic/molecular layer deposition (ALD/MLD) technique is an ideal route for high-quality metal-organic thin films;[1] it enables well-

controlled integration of the inorganic and organic components through strong chemical bonding. Moreover, these hybrid thin films can be deposited even on high aspect ratio 3D substrates. Here we introduce a novel ALD/MLD process for amorphous, ambient air-stable Zn-BDT thin films grown from $Zn(DMP)_2$ (bis-3-(N,N-dimethylamino)propyl)[2,3] and BDT (benzene-1,4-dithiol) precursors. The film growth shows clear saturation with 3 s pulse length for both precursors and the growth-per-cycle (4.5 Å/cycle) remains nearly constant even with excessive 30 s pulsing times. Moreover, the process has a stable temperature window of at least 60 – 70 °C and the film growth is perfectly linear. Most excitingly, due to the nearly ideal ALD/MLD growth characteristics, the deposition process is well-suited for coating of high-aspect ratio surfaces; we demonstrate the excellent fitness of our Zn-BDT process for PillarHall LHAR4[4] structures using excessive 30 s pulse lengths for both precursors to obtain high penetration depth without any noticeable effect on the growth rate. Composition of the amorphous films is characterized with FTIR and Raman spectroscopy while the coverage and penetration of the conformal films are analysed with optical microscopy, SEM, and Line scan optical reflectometry. This work demonstrates the excellent feasibility of the state-of-the-art ALD/MLD for high-aspect ratio surfaces.

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2:30pm **EM1-WeA-5 Recent Developments in Oxidative Molecular Layer Deposition (oMLD)***, **Matthias Young**, Q. Wyatt, K. Brathwaite, M. Ardiansyah, N. Paranamana, K. Brorsen,* University of Missouri

The first demonstration of oxidative molecular layer deposition (oMLD) was reported in 2014, forming poly(3,4 ethylenedioxythiophene) (PEDOT) using sequential self-limiting exposures of ethylenedioxythiophene (EDOT) monomers and an $MoCl_5$ chemical oxidant. In the last few years, the number of chemistries that have been demonstrated using oMLD has expanded to include at least four additional monomers, with successful demonstrations using at least three different chemical oxidants. However, limited mechanistic understanding of oMLD is impairing progress in this field. Here, we report on recent work examining the mechanisms for oMLD growth. We examine oMLD growth using EDOT, pyrrole (Py), paraphenylenediamine (PDA), thiophene (Thi), and furan (Fu) monomers. We specifically identify the importance of a two-electron chemical oxidant in these reactions, which must have sufficient oxidation strength to oxidize both a surface and a gas-phase monomer to enable oMLD growth. The mechanistic insights from these studies provides a conceptual framework to enable rational molecular assembly of copolymer structures by oMLD.Using this concept, we generate copolymer structures with improved electrochemical properties over the corresponding isolated homopolymers. The insights from this study suggest a pathway to address previously intractable questions regarding the molecular origins of polymer properties, and allowing us to control and optimize polymer structure and properties for electrochemical applications including energy storage, water desalination, and sensors.

2:45pm **EM1-WeA-6 In Situ Analysis of Growth Mechanism During Molecular Layer Deposition of Polyurea***, **Wallis E. Scholl,*** Colorado School of Mines*; E. Hudson, L. Belau,* Lam Research Corporation*; S. Agarwal,* Colorado School of Mines

Although molecular layer deposition (MLD) has been studies for more than two decades, the mechanism of MLD film growth is not well understood. In idealized MLD, each bifunctional precursor reacts with the substrate surface through only one functional group, depositing a single monomer layer. Although previous research has shown a linear growth per cycle, the film thickness deposited per cycle is often much lower than the length of one repeat unit of the polymer chain[1]. This has previously been attributed to reactive site consumption by double reactions, in which both ends of a precursor react with the surface, reducing the number of reactive sites for the next cycle. Re-nucleation of chains through precursor adsorption may account for continuation of growth after terminations reduce the number of surface sites.[1,2]

In this study, we used *in situ* attenuated total reflection Fourier transform infrared spectroscopy and *in situ* four-wavelength ellipsometry to monitor film composition and thickness throughout molecular layer deposition of polyurea with 1,4 diisocyanatobutane (DICB)/diethylenetriamine (DETA). Figure 1 shows the infrared absorbance change throughout the first 5 cycles of MLD. We show that the stretching mode for N=C=O functional group in DICB, which is associated with the number of reactive sites following the DICB half cycle, gradually decreased with increasing number of MLD cycles. Despite this loss of reactive sites, film growth continued even at a high number of cycles, which suggests that new site creation drives continuation of growth. This progression is supported by film thickness measured by *in situ* ellipsometry (see Figure 2); initial growth rates gradually slow down as double reactions consume reactive sites, until a steady growth rate is reached in which site consumption via double reactions and site creation via precursor adsorption is balanced. Further, we found that MLD growth is highly dependent on substrate surface preparation, which dictates the initial number of surface sites available. When initial reactive sites are below a critical density, precursor absorption is unable to compensate and film growth remains low throughout deposition.

[1] Bergsman *et al.*, *Chem. Mater.*, 30, 1, 2018.

[2] Nye *et al.*, *Dalton Trans.,* 51, 2022.

3:00pm **EM1-WeA-7 A Chemist's Lego Blocks: Molecular Layer Deposition (MLD) for Nanoelectronic Applications***, **Michelle Paquette,*** University of Missouri-Kansas City **INVITED**

Molecular layer deposition (MLD), similarly to atomic layer deposition (ALD), consists of layer-by-layer deposition via sequential self-limiting reaction half cycles. In contrast to ALD, MLD uses as fundamental building blocks organic molecules rather than single atoms. So-called hybrid MLD processes make use of both atomic and molecular building blocks. Both ALD and MLD have risen dramatically in popularity over the last several decades due to their control over thin-film conformality as well as quality, thickness, and uniformity at the nanoscale. This talk will cover the different classes of MLD schemes and materials and their use and potential advantage in nanoelectronics, including front-end-of-the-line, back-end-of-the-line, memory, and patterning applications.

Late-breaking Abstracts
Room Grand Ballroom A-C - Session LB1-WeA

Late Breaking ALD

Moderator: Dr. Sumit Agarwal, Colorado School of Mines

1:45pm **LB1-WeA-2 Recent Advances for Spatial Atomic Layer Deposition Process: Microreactor Direct Atomic Layer Processing (µDALP™)***, **Maksym Plakhotnyuk**, A. Varga, I. Kundrata,* ATLANT 3D, Denmark*; J. Bachmann,* FreFriedrich-Alexander Universität, Germany

In parallel to additive manufacturing leading the revolution in traditional manufacturing, the same principles can revolutionize traditional thin film deposition techniques. Where lithography and vapor phase deposition techniques struggle, for example, with rapid iterations for prototyping or incompatibility with the used chemistry, additive manufacturing can shine. Indeed, several approaches are in development for 3D nanopriting[1,2,3].

Atomic Layer Deposition, and in more general Atomic Layer Processing, offers a unique opportunity for localized 3D processing/printing due to its two-step process. While simple in theory, due to well-developed examples of Spatial Atomic Layer Deposition (SALD), in practice miniturization of SALD requires substantial effort into the creation of suitable micro-nozzles. Uniquely, ATLANT 3D has developed proprietary Spatial ALD micronozzles, naming the process microreactor Direct Atomic Layer Processing - µDALP™.

In recent years, the team at ATLANT 3D has been able to significantly develop the technology to reduce the µDALP™ resolution, increase material capabilities, assessable morphologies, and new instruments. Giving one example of recent development in morphologies; films deposited with µDALP™ have conformal coverage of gratings,

microchannels and trenches up to a depth of 25 µm using a Platinum deposition process (**Figure 1**). Substrates with a surface roughness including Carbon nanograss (**Figure 2**), black silicon and anodized Aluminum Oxide membranes were also conformally coated with roughness up to an aspect ratio of 1:25 again with Platinum and TiO_2. Our results demonstrate how a given ALD material process (in this case, Pt and TiO_2) can be used with ATLANT 3D technology to deposit localized area conformal coatings of complex surfaces with an aspect ratio of 1:25. The µDALP™ technology enables rapid prototyping and manufacturing for an array of applications from sensors (temperature, pressure, gas sensing and capacitive) to optics, all with sensitivities that meet or exceed those of devices made using conventional vapor phase deposition techniques.[4] In addition, rapid localized processing facilitated by ATLANT 3D technology of such devices enables design innovation and optimization not possible with other thin film deposition techniques and lithography.

[1] Kundrata I. et al., *ALD/ALE 2022 [Int. Conf.]*,**2022**

[2] de la Huerta C. A. M. et al., *arXiv*, **2020**, 0523.

[3] Winkler, R. et al., *J. Appl. Phys.*, **2019**, *125*, 210901

[4] Kundrata I., et al., *Small Methods.*, **2022**, *6 (5)*, 2101546

2:00pm **LB1-WeA-3 Towards Improved Conversion of Wet Waste to Jet Fuel with Atomic Layer Deposition-Coated Hydrodeoxygenation Catalysts***,*
W. Wilson McNeary*, J. Miller, S. Tacey,* National Renewable Energy Laboratory*; J. Travis,* Forge Nano*; M. Griffin, K. Jungjohann, G. Teeter,* National Renewable Energy Laboratory*; T. Eralp Erden,* Johnson Matthey, UK*; C. Farberow,* National Renewable Energy Laboratory*; L. Tuxworth, M. Watson,* Johnson Matthey, UK*; A. Dameron,* Forge Nano*; D. Vardon,* Alder Fuels

The U.S. aviation sector has set a target for 50% reduction in CO_2 emissions by 2050 (vs. 2005 levels) which will require rapid, large-scale deployment of sustainable aviation fuel (SAF). State-of-the-art SAF production relies on hydrotreating esters and fatty acids (HEFA); however, this pathway is limited by insufficient supplies of esters and fatty acids to meet future jet fuel demand, relatively high feedstock cost, and, in some cases, direct competition with food crops. Wet waste (e.g., food waste, animal manure, wastewater sludge) represents an untapped domestic resource, as most of the wet waste generated annually in the U.S., which contains more than 1.3 petajoules (10^{15} J) of energy, is either landfilled or fed to anaerobic digestors to make biogas for heat and/or electricity. To broaden the pool of renewable carbon sources available for SAF production and avoid the drawbacks of the HEFA pathway, wet waste may instead be harnessed as a SAF feedstock.

The conversion of wet waste-derived volatile fatty acids (VFAs) into jet fuel-range hydrocarbons is a promising route for increasing SAF production; however, the cost and moderate alkane selectivity of Pt-based hydrodeoxygenation (HDO) catalysts present challenges for commercialization. To address this, we used atomic layer deposition to apply TiO_2 overcoats to Pt/Al_2O_3 catalysts and create new interface sites that exhibited 8 times higher site time yield of the desirable n-alkane product than uncoated catalyst. Through a combination of temperature programmed reduction, NH_3 temperature programmed desorption, X-ray photoelectron spectroscopy, diffuse reflectance infrared Fourier transform spectroscopy, and density functional theory calculations, we found that the increased selectivity of the ALD-coated catalyst was due to the creation of O vacancies at the Pt-TiO_2 interface under reducing conditions, resulting in new Ti^{3+} acid sites near the active metal. This ALD coating strategy was used to improve the alkane selectivity of the base 0.5 wt % Pt/Al_2O_3 catalyst beyond that of an uncoated catalyst with an order-of-magnitude more Pt, which illustrates the benefit of utilizing the nanoscale precision of ALD to tailor interface sites and increase the atom efficiency of precious-metal catalysts.

2:15pm **LB1-WeA-4 A Kinetic Model for Heterogeneous Nucleation in ALD and CVD***,*
Andreas Werbrouck*, S. Bent,* Stanford University

As atomic layer deposition (ALD) becomes an increasingly mature technique, sound models that describe all stages of the growth are needed. Here, we develop a kinetic model for heterogeneous ALD nucleation and growth: we describe how an ALD film forms on a starting surface that is different from the steady-state growth surface, and the subsequent growth of the material after the initial surface has been covered. Understanding nucleation is relevant for any ALD process, but especially important for metal-on-dielectric deposition, where island growth is often observed, and for area-selective deposition, where nucleation on the non-growth surface is to be avoided. Steady-state growth and precursor reaction kinetics are relatively well-understood and other models for heterogeneous nucleation have been published before. Our model, in the form of a system of differential equations, describes heterogenous nucleation kinetics in a continuous, macroscopic way as a function of time, from initial nucleus formation to coalescence and beyond. A key element of the model is the introduction of both homogeneous and heterogeneous sticking coefficients, and a description of the perimeter of the covered part of the surface. This perimeter is dependent on the ratio of the sticking coefficients. We modeled the perimeter evolution with a changing coverage for various homogeneous and heterogeneous sticking coefficients based off Monte Carlo simulations.
In the first part of the presentation, we will discuss results of our model describing heterogeneous nucleation for chemical vapor deposition. We show that the nucleation delay depends on the interplay between the homogeneous and heterogeneous sticking coefficient. In the second part, we will extend the model to a two-precursor ALD system. Due to the use of time as a parameter, the model allows us to discern between the surface change per ALD cycle and the surface change per unit time, and we report on the effect of exposure per cycle (for both precursors) on nucleation delay and growth. Thickness and coverage results can then be compared to experiment. In the final part, we will a) link the model to earlier work on catalytic surfaces b) compare the model to literature models for ALD nucleation (Avrami equation, population balance equation) and c) fit the model to literature data.
Our model allows one to describe the generation of new nuclei intuitively through the heterogeneous sticking coefficient, and to explain nucleation enhancement, delay, and breakthrough behavior, while avoiding assumptions on (hemi-)spherical particles. In future work, we will expand our model to incorporate surface diffusion and substrate geometry.

2:30pm **LB1-WeA-5 Intrinsic Area Selective Atomic Layer Deposition of MoS_2 Thin Films***,*
J. Soares, ***Wesley Jen****,* Boise State University*; J. Wensel,* Micron Technology*; S. Hues, E. Graugnard,* Boise State University

As the critical dimensions in today's semiconductor devices continue to shrink, new methods for device fabrication are paramount for continued reduction in scaling. These fabrication processes must be adaptable in order to evolve with future technology nodes and scales, while providing flexible material integration techniques within the high complexity of device structures. Area selective atomic layer deposition (ASALD) is a deposition technique that utilizes a bottom-up patterning approach for self-alignment of deposited materials. ASALD operates on the basis that functional groups either present or absent on a growth surface will promote or inhibit nucleation. This contrast can lead to selective deposition. In addition to compatible processing techniques, next generation materials also need to be studied. Layered two-dimensional (2D) molybdenum disulfide (MoS_2) is a semiconducting material that shows great promise due to its atomically thin structure and impressive electrical properties. In this work, we report the ASALD of MoS_2 on patterned template substrates of common dielectric materials versus thermal silicon oxide and nitride. Growth and non-growth surfaces were initially screened with X-ray photoelectron spectroscopy (XPS) characterization of blanket MoS_2 films after numerous ALD cycles. The selectivity parameter between surfaces was calculated using XPS, revealing a high selectivity of S = 0.94 after 20 ALD cycles for growth on ALD alumina versus thermal silicon oxide. These results identified contrasting surfaces that were then patterned to investigate area selectivity. MoS_2 ALD was performed at 200 °C on patterned surfaces that were then annealed at 650 °C for 30 minutes. Samples were characterized using Raman spectroscopy maps of crystalline MoS_2 modes and time-of-flight-secondary ion mass spectroscopy (ToF-SIMS) elemental mapping, which confirmed ASALD. These results hold promise for advancing the integration of 2D materials into device manufacturing.

2:45pm **LB1-WeA-6 Selective Deposition of HfO_2 on Aminosilane-treated TiN/SiO_2 Substrates***,*
Yujin Lee*,* Stanford University*; H. Kim,* Samsung Advanced Institute of Technology, Republic of Korea*; S. Bent,* Stanford University

For the continued downscaling of semiconductor devices,new approaches are requiredto meet the fabrication challenges. Area-selective atomic layer deposition(AS-ALD) is a bottom-up fabrication process that provides a great opportunity to overcome the problems associated with current top-down fabrication processes such as cost and complexity.Toward the implementation of an AS-ALD process at the sub-10 nm level, studies on AS-ALD using small molecule inhibitors (SMIs) having angstrom level

thickness have been reported. However, since SMIs contain carbon species, their use in an inhibitor layer could affect the device's characteristics such as dielectric constant and leakage current density. On the other hand, various techniques of readily-available surface treatments can be utilized to functionalize the surfaces so that they are deactivated for reducing nucleation without adding carbon species.

In this study, we develop a surface treatment process that uses an aminosilane molecule to block the adsorption of Hf precursors for HfO_2 ALD. We show that SiO_2 surfaces functionalized by the aminosilanes add only terminal $-SiH_3$ to the surface without attaching carbon species. In addition, because both standard ALD and AS-ALD processes are strongly dependent on the precursor, tuning the ALD precursor provides another variable by which selectivity may be achieved.We first investigate the effect of ALD precursor on the growth characteristics and film properties for three different Hf precursors with alkylamide, alkoxide, and halide ligands, respectively. Using these three different optimized HfO_2 ALD processes and adding surface functionalization steps, we perform AS-ALD on TiN/SiO_2 substrates. ALD blocking results show that the resulting hydride ($-SiH_3$)-functionalized SiO_2 surface can successfully inhibit the adsorption of the Hf precursor without the need for carbon species at the surface. Best results were found using the Hf alkoxide precursor, for which selectivities of greater than80% were achieved after 30 cycles of HfO_2 ALD. This work introduces a new surface treatment together with considerations for ALD precursor selection to enable an AS-ALD process.

3:00pm **LB1-WeA-7 Atomic Layer Deposited Zr-doped HfO_2 (HZO) and Indium Gallium Oxide (IGO) Thin Films for 3D Gate-All-Around FeFET**, ***Boncheol Ku**, J. Hur, J. Jeong, C. Choi,* Hanyang University, Korea

Recently, HfO_2-based ferroelectric (FE) field effect transistors (FeFETs) have gained attention for NAND flash memory applications due to their superior advantages compared to $SiO_2/Si_3N_4/SiO_2$ (ONO)-based FETs. These advantages include faster write/erase speeds, non-destructive readout, lower operation voltage, higher scalability, and CMOS compatibility. However, when FE thin films are applied to poly-Si, there can be issues such as grain-dependent threshold voltage (V_{th}) degradation and temperature-induced V_{th} instability due to the low-k interfacial layer formed at the interface between FE-HfO_2 and poly-Si. With this regard, materials system using suitable FE thin film and oxide semiconductor should be explored and corresponding device feasibility needs to be investigated. To address this, we have proposed using atomic layer deposited (ALD) FE thin film and oxide semiconductors (OS) as charge trapping layer and alternative channel, respectively, in 3D NAND architecture.

In this study, we successfully demonstrated ALD Zr-doped HfO_2 (HZO) FE thin film and an indium-gallium oxide (IGO) channel for a 3D vertical Gate-All-Around (GAA) NAND flash memory device using with gate length (L_g) and spacer length (L_s) of 50 nm. [Fig. 1] These FE and OS thin films are adopted as an alternative charge trapping layer and channel layer alternative ONO and poly-Si, respectively. The I_d-V_g characteristic of the 3D GAA FeFET device indicates high-quality interface between the HZO and IGO thin films, with subthreshold swing of 90 mV/dec and almost no hysteresis under bias sweeping. The device shows a maximum memory window (MW) of 2.5 V, allowing for potential multilevel cell (MLC) operation. The stable sub-loop switching of ferroelectricity for MLC memory operation is an important factor, and stable 2 bits/cell retention properties up to 10^4 sec at room temperature are achieved, extrapolated to 10 years retention time. [Fig. 2]. These results suggest that ALD FE thin film and OS materials can be a promising alternative to current ONO/poly-Si materials for advanced V-NAND flash memory applications.

3:15pm **LB1-WeA-8 Development of Robust Gate Insulators for MIS-HEMT Structures Based on ALD/PEALD Techniques**, ***Messaoud Bedjaoui**, S. Cadot, J. Amiran, R. Contie, A. Thiam, C. Bout,* CEA/LETI-University Grenoble Alpes, France; *P. Fernandes Paes Pinto Rocha,* CEA/LETI-University Grenoble Alpes, Grenoble INP-LTM, France

In the past few years, AlGaN/GaN based metal-insulator-semiconductor high-electron-mobility transistors (MIS-HEMTs) have attracted considerable interest, providing unprecedented power levels and efficiencies. The dielectric quality as well as the GaN-dielectric interface play a critical role in the performances of such devices. Atomic Layer Deposition (ALD) and Plasma Enhanced-ALD are the most suitable techniques to address the challenge of MIS gate dielectrics. As such, the Al_2O_3 layers grown by ALD are materials of choice due to high dielectric constant, high breakdown field and high conduction-band offset on GaN. However, the dielectric performances of Al_2O_3 rapidly degrade at high temperature (above 800°C) due to the crystallization. One promising strategy for high quality gate dielectrics consists in combining SiO_2 and Al_2O_3 deposits in order to prevent the dielectric crystallization.

In this work, we analyse the general performance of MIS gate dielectrics (with and without post deposition annealing or PDA) using physico-chemical (X-ray photoelectron spectroscopy, X-ray reflectometry, grazing incidence X-ray diffraction) and electrical analyses (Hg probe measurements, MOSCAPs). We primarily focused on the evaluation Al_2O_3/SiO_2-based films (thickness range 20-30nm) obtained by two thermal ALD modes (300°C) on silicon substrates: (i) alternating the deposition of separate SiO_2 and Al_2O_3 layers (nanolaminate); (ii) combination of ALD super cycles allowing the formation of $AlSiO_x$ layers.

For the ALD super cycles approach (50% SiO_2 content according to XPS analysis), XRR density and permittivity values of $AlSiO_x$ layers are around 2.8 and 5, respectively. We outline the close correlation between the Al/Si ALD process ratio and the $AlSiO_x$ composition. $AlSiO_x$ layers preserve their density and permittivity values after PDA treatment unlike Al_2O_3 layers (using H_2O or O_3 oxidant, see Fig. 1 and 2). This is attributable to the fact that $AlSiO_x$ stays amorphous up to 850°C, as revealed by GIXRD analyses (see Fig. 3). We report a drastic decrease of leakage current and an increase of breakdown field in comparison to Al_2O_3 layers before and after PDA treatment at 850°C (see Fig.4). This trend prevails for both ALD multilayer and ALD super-cycles approaches confirming the deep impact of SiO_2 fraction in the $AlSiO_x$ layers composition and subsequently on the general electrical performances. Furthermore, preliminary evaluation of interface passivation layers (such as *in*-situ plasma clean or PEALD-deposited AlN barrier) underlines the great potential of ALD/PEALD techniques in the fabrication of robust gate insulators for AlGaN/GaN-based HEMTs.

Late-breaking Abstracts
Room Grand Ballroom A-C - Session LB2-WeA

Late Breaking Computational Modeling

Moderator: Benjamin Greenberg, Naval Research Laboratory

4:00pm **LB2-WeA-11 Exploring the Blocking Mechanism of Small Molecule Inhibitors by Density Functional Theory**, ***Fabian Pieck**, R. Tonner-Zech,* Wilhelm-Ostwald-Institut Physikalische und Theoretische Chemie, Germany

Within area-selective atomic layer deposition selectivity is achieved by various approaches. A common strategy is to block growth on the non-growth surface by the deposition of small molecule inhibitors (SMI) prior to the ALD process. However, to obtain selectivity the properties of those SMIs, especially their reactivity, has to be tuned with respect to the surface and ALD process. Here, a sound knowledge of the actual blocking mechanism of the SMIs can guide their selection and tuning.

We use ab initio modelling by density functional theory to explore the blocking mechanism of SMIs by investigating their on-surface reactivity. Here, alkoxysilanes like trimethoxypropylsilane (TMPS) [1] and methanesulfonic acid (MSA) are studied as SMIs for the area-selective ALD of Al_2O_3 whereby SiO_2 and Cu(111) are targeted as non-growth surface, respectively. Reaction paths are calculated with the nudged elastic band method to identify the most likely reaction steps while the most stable structures are identified based on Gibbs free energies. The observed reaction paths show that both SMIs behave fundamentally different on the SiO_2 and Cu(111) surface resulting in different blocking mechanisms. Consequently, these SMIs can be used to target different non-growth surfaces within the area-selective ALD of Al_2O_3.

[1] J. Yarbrough, F. Pieck, D. Grigjanis, I.-K. Oh, P. Maue, R. Tonner-Zech, S. F. Bent, *Chem. Mater.* **2022**, *34*, 4646 – 4659.

4:15pm **LB2-WeA-12 Reaction Mechanism of Atomic Layer Deposition of Pt from First Principles**, ***Sylwia Klejna**,* AGH University of Krakow, Poland

Atomic layer deposition of Pt is one of the best studied deposition processes of noble metals. Yet, the reaction mechanism is still unknown. In this study, we use density functional theory (DFT) to investigate reaction steps involved in the ALD of Pt from $MeCpPtMe_3$ (MeCp – methylcyclopenthadienyl ligand, $CH_3C_5H_4$; Me – methyl group, CH_3) and O_2. In this process transient metal oxide may be generated and that can greatly facilitate noble metal ALD[1]. Adsorption, decomposition and dehydrogenation pathways during metal precursor pulse are computed. Surface bound species as well as possible volatile by-products are identified. The most abounded surface intermediates after the saturation with metal precursor are: MeCp-surf and Me-surf. The temperature influence on the stability of these species is investigated. Next, we model

the O_2 co-reactant pulse to evaluate whether the nuclei of the transient oxide surface can form. We discuss the possibility of production of transient surface bound OH groups predicted in the previous study[2] and other by-products, *e.g*. CH_4 identified in the experiment[3]. The factors that facilitate nucleation are examined. This will allow to propose appropriate conditions, reagents and chemical processes to control and improve efficiency of the atomic layer deposition of other noble metals.

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4:45pm **LB2-WeA-14 Closing Remarks in Grand Ballroom H-K***,*

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