ALD Fundamentals
Room Grand Ballroom H-K - Session AF1-MoA
ALD Growth Mechanisms I

Moderators: Simon Elliot, Schrödinger, Inc., Angel Yanguas-Gil, Argonne National Lab

1:30pm **AF1-MoA-1 Hybrid Computational Fluid Dynamics / Machine Learning Approaches to Reactor Scale Simulations and Optimization of ALD, ALEt, and LPCVD Processes***, **Angel Yanguas-Gil**, S Letourneau, A Lancaster, J Elam,* Argonne National Laboratory

As the range of potential applications of atomic layer deposition increases, it is becoming increasingly important to understand how processes scale up to large area substrates and complex substrate geometries. Compared to the number of processes available, there is still a scarcity of tools to explore the interaction between surface kinetics, gas phase transport, and thin film growth at a reactor scale. These tools can help us answer not only key questions regarding the economics or scalability of a given process in terms of throughput or precursor utilization, but they can help us develop a better understanding and intuition of processes and simulate the output of commonly used in-situ techniques such as quartz crystal microbalance or mass spectrometry.

In this work we describe an open source code developed at Argonne to simulate processes based on self-limited and non-self limited surface kinetics at a reactor scale. This code, which is freely available, is built on top of OpenFOAM, a free, open source Computational Fluid Dynamics software. In combination with open source mesh generators such as GMSH, our code provides a simple workflow to explore the role of surface kinetics and the scale up of ALD, ALEt, and LPCVD processes.

To validate our model, we have established a comparison between simulations and experimental results obtained at two different cross-flow ALD reactors. We have then used synthetic growth profiles as a starting point to explore the ability of machine learning approaches to extract relevant information from growth profiles and other experimental datasets. In particular, we have explored the use of artificial neural networks to extract relevant kinetic data from reactor profiles and extrapolate saturation profiles based on a reduced set of experiments.

1:45pm **AF1-MoA-2 Scalable Kinetic Monte-Carlo Model for Parasitic Reactions in Silicon Nitride Growth using 3DMAS Precursor***, **Gem Shoute**, T Muneshwar,* Synthergy Inc., Canada*; D Barlage, K Cadien,* University of Alberta, Canada

Atomic layer deposition (ALD) is a cyclical self-limiting reaction deposition technique that heavily depends on the characteristics of the chosen precursor. Currently, there are a limited number of ALD models that can give insight into key growth characteristics of a precursor such as ideal growth per cycle (GPC). Whether a self-limiting reaction can be achieved is determined by several factors related to the precursor itself, including its exposure and purge times and substrate temperature (T_{SUB}), all which affect the GPC of the desired material. For instance, the silicon nitride (Si_xN_y) precursor, tris[dimethylamino]silane (3DMAS), saturates at T_{SUB} up to ~150 °C but beyond this temperature window, it exhibits dependence on its exposure time resulting in a non-saturated growth. While saturation indicates ideal ALD behavior, the latter observation implies the presence of parasitic reactions that are concurrent with ALD reactions, resulting in non-ideal ALD growth. These non-idealities are especially prominent in aggressive topologies such as high aspect-ratio structures which are a staple of numerous applications today. In this study, we will model the expected GPC of 3DMAS using a scalable kinetic Monte-Carlo approach (sKMC). The expected GPC vs. T_{SUB} relationship is compared to the experimental results of 3DMAS Si_xN_y. The discrepancies between the expected and experimental GPCs are attributed to additional parasitic reactions and interpreted through the lens of the sKMC model. Further developing these models is an important step towards rapid characterization of precursors and would serve as a useful tool for selecting the appropriate precursor for a given application.

2:00pm **AF1-MoA-3 Diffusion and Aggregation in Island-Growth and Area-Selective Deposition***, **Fabio Grillo**,* ETH Zurich, Switzerland **INVITED**

Diffusion and aggregation phenomena play an essential role in many thin film processes [1]. Yet, their importance in atomic layer deposition (ALD) has been overlooked by most fundamental studies, which focus primarily on surface chemistry. This is not surprising because the latter governs the growth process when this proceeds in a layer-by-layer fashion, which is often the case. However, chemistry alone cannot account for the formation and growth of islands or nanoparticles during the so-called "nucleation delay". In this talk, I will present a theoretical framework that captures the kinetics of island-growth in ALD by accounting for diffusion and aggregation phenomena [2-4]. The framework is based on rate-equation and Kinetic-Monte-Carlo (KMC) models that build not only on the classic formulations of thin film nucleation kinetics but also on insights borrowed from research fields such as colloidal synthesis and catalyst sintering. These models describe the growth process as a balance between the cyclic generation of adatoms, arising from ALD surface reactions, and their aggregation due to non-equilibrium physical phenomena. The latter include: (1) adatom diffusion, (2) island formation by adatom aggregation, (3) island migration and coalescence (i.e., dynamic coalescence), (4) adatom attachment, and (5) inter-island exchange of atoms driven by the Gibbs–Thomson effect (i.e., Ostwald ripening). Throughout the talk I will demonstrate how these models can be used to relate the evolution of experimental observables such as the island-size distribution to well-defined growth mechanisms. For example, I will show how dynamic coalescence can govern nanoparticle growth during ALD of noble metals and how different surface diffusion rates can have a dramatic effect on the extent of the "nucleation delay". Finally, I will present KMC simulations showing how surface diffusion can induce topography-dependent growth in area-selective ALD.

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2:30pm **AF1-MoA-5 Surface Kinetics in ALD and ALE: Computing the Cooperative Effect by Automated Enumeration of Reaction Pathways with Spectator Adsorbates***, **Thomas Mustard**,* Schrödinger, Inc.*; S Elliot,* Schrödinger, Inc.*; T Hughes, A Bochevarov, L Jacobson, S Kwak,* Schrödinger, Inc.*; T Morisato,* Schrödinger K.K., Japan*; J Gavartin,* Schrödinger, Inc., UK*; S Pandiyan,* Schrödinger, Inc., India*; M Halls,* Schrödinger, Inc.

The deposition or etching of solid films by ALD or ALE proceeds via reactions between gas-phase molecules and surfaces. The kinetics of such reactions have been previously computed to be strongly influenced by the local environment on the surface around the reaction site, which is called the 'cooperative effect' [1]. The activation energy at a reactive site has been shown to be affected by, or even dictated by, the presence of nearby co-adsorbed fragments or molecules, which otherwise take no part in the reaction and so may be termed 'spectators'. In the case of ALD, this means that previously-inert ligand remnants on the surface can become reactive once sufficient numbers of other ligands adsorb in their neighborhood. This has been experimentally verified in the case of low-temperature ALD of Al_2O_3 from TMA+H_2O [2].

Including a proper description of the cooperative effect is a serious challenge for first principles simulations of surface reactivity. One way forward is to sample the chemical space by automating the systematic investigation of the factors contributing to the cooperative effect. Specifically, we show how spectator Lewis acids and bases at various coverages and distances affect the activation energy for adsorption and proton transfer on the functionalized surfaces that are typically present during ALD of Al_2O_3.

To study the surface reactivity, we have generated an $(Al_2O_3)_{16}$-based cluster model of the (1 0 0) bilayer structure of q-Al_2O_3. We computed the activation energy for adsorption of H_2O onto an open Al site at the center of the cluster and for its dissociation into H+OH. The cluster is terminated with OH groups on its sides, but has space on top for up to 32 spectator molecules to surround the reactive site at distances ranging 2-6 Å. As spectator molecules we have considered various sizes of alkyl, alkoxyl, hydroxyl and halide groups, so as to probe both electronic and steric effects. All possible arrangements of spectator adsorbates were generated automatically with enumeration tools in the Schrödinger *Materials Science Suite* [3]. The reaction pathway for dissociative adsorption of H_2O was then re-computed for each new spectator environment revealing how the activation energy changes with spectator identity and proximity.

We discuss the importance of the results for our understanding of thin film deposition and related fields such as heterogeneous catalysis. We also look

forward to the prospects for efficient and systematic computation of complex surfaces.

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2:45pm **AF1-MoA-6 An Immiscible Fluids Approach for Correctly Predicting Agglomerate Dynamics during Particle Atomic Layer Deposition (Particle ALD)***, **Julia Hartig**, A Weimer,* University of Colorado - Boulder

Particle agglomeration can significantly impact performance of fluidized bed reactors when running particle atomic layer deposition (Particle ALD). The fine powders frequently used in Particle ALD tend to agglomerate due to large interparticle forces, blocking surface sites and inhibiting surface coating uniformity. By modeling the agglomeration process during coating, steps can be taken to facilitate agglomerate breakup and mixing, thereby enhancing surface coating uniformity. However, current models of gas-solid flows which preserve the gas-solid interface, an important component for modeling ALD, have several limitations when incorporating agglomeration. Many of these approaches fail to address agglomerate size distributions or the dynamic formation and breakup process of fluidized agglomerates, shortcomings which remain a significant challenge to studying fluidized bed Particle ALD. In this work, we propose an alternative modeling approach which naturally accounts for the dynamic nature of fluidized agglomerates by treating the fluidizing gas and particles as two immiscible (non-interpenetrating) fluids. Agglomerates are modeled using dynamic “bubbles” whose interior consists of many primary particles from the solids phase. The position, shape and formation/breakup of these agglomerate “bubbles” are allowed to change with time as dictated by the corresponding transport equations. With this model, we can investigate the formation and breakup of agglomerates without prior knowledge of the agglomerate size characteristics. This study provides some preliminary agglomerate size distribution results from fluidized bed Particle ALD simulations and compares these results to experimental data from previous literature studies.

3:00pm **AF1-MoA-7 The Time-Resolved Interface between ALD and CVD***, **Henrik Pedersen**,* Linköping University, Sweden **INVITED**

ALD (atomic layer deposition) is possibly the most important evolution of CVD (chemical vapor deposition). To a first approximation, ALD can be described as CVD where the precursor flows are separated in time. In other words, ALD is a time-resolved form of CVD. Despite this, CVD typically has a negative connotation in the ALD community. The phrase “CVD-component” is used to point to a process deviating from the idealized ALD behavior, where continual growth occurs.

The time-resolved precursor supply in ALD enables the self-limiting surface chemistry, rendering the very high degree of surface control which is the hallmark of ALD. However, CVD does not need to be time-resolved to have a very high degree of surface control. There are several examples in the literature of continuous CVD filling deep trench structures.[1,2] A time-resolved precursor supply without a self-limiting surface chemistry is another important evolution of CVD as it can be used for growing semiconducting nanowires on a patterned surface without the need for a catalyst[3] and can afford deposition of ternary or quaternary materials in some materials systems[4].

CVD can also be made time-resolved by controlling the amount of energy available to the process over time. While this is difficult to do with a thermally activated CVD process, a process driven by the energy provided in a plasma discharge can easily be time-resolved in energy. This has allowed self-limiting processes with constant flow of precursors[5] and an enhanced ability to use ionic species for film deposition[6].

This talk will discuss the time-resolved interface between CVD and ALD but also how continuous CVD can outcompete time-resolved CVD for some films: a recent example is nearly conformal B-C films in a 2000:1 structure by continuous CVD at 700 °C and 5 kPa.[7] The talk will also seek to nuance the view of a “CVD-component” in ALD processes and discuss how the time component can be used as a process knob in ALD.

References:

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ALD Fundamentals
Room Grand Ballroom E-G - Session AF2-MoA
ALD Precursors I

Moderators: Daniel Alvarez, RASIRC, Charles H. Winter, Wayne State University

1:30pm **AF2-MoA-1 The Materials Supplier Challenge: Flawless Execution from Precursor Design to High Volume Manufacturing***, **Madhukar B. Rao**,* Versum Materials **INVITED**

Advancements in scaling and architecture in logic and memory devices are driving the development of new precursors which provide more precise control of film thickness, composition, morphology and electrical properties. The challenge for materials suppliers is to design new precursors that can meet the performance requirements, and scale-up the precursors to high volume, while meeting the cost of ownership targets. At Versum Materials, the process starts with defining technical requirements of the precursor through close collaboration with the customer and equipment vendor. We use our in-depth understanding of the structure-property relationships between precursor and final film to identify and synthesize promising new precursors on the laboratory scale and rapidly test new precursors using our in-house deposition capabilities to confirm the film performance. These results are validated with our collaboration partners and this defines the potential candidates for further scale-up.

Converting promising laboratory discoveries into viable commercial products is a complex and resource-intensive effort. The product development work must scale up and validate a low-cost synthetic route and purification methods, identify and quantify EH&S risks (e.g., toxicity, stability, reactivity), develop analytical methods to fingerprint incoming raw materials and ensure final product quality, design and validate suitable containers for delivery, ensure supplier quality and supply-chain readiness and prepare for container life-cycle management. This presentation highlights the key steps and technical challenges in the product development process and highlights the importance of close collaboration with customers, suppliers, and equipment manufacturers to make new products HVM ready.

2:00pm **AF2-MoA-3 Precursor and Co-Reactant Selection: A Figure of Merit***, **Seán Barry**, M Griffiths,* Carleton University, Canada

Developing novel precursors for atomic layer deposition (ALD) processes is a complicated task: the selected chemical compounds must be volatile and thermally stable, yet reactive with a surface, and perhaps even demonstrate selective reactivity among several different surfaces. Additionally, it is helpful if the precursors are liquid (for handling and to improve the kinetics of evaporation) and robust to a change in the chemical environment.

To initially study a compound for potential use as a precursor, one must understand both the volatility and thermal stability. We have recently established a Figure of Merit (FoM) for potential precursor compounds based on volatility and decomposition. Conceptually, this FoM alters the ratio in temperature between a judiciously chosen onset of decomposition and onset of thermolysis and modifies that with respect to the residual mass left behind in a standard thermogravimetric ramp experiment. In this way, the larger the value for the FoM, the better the precursor, with negative values representing compounds that decompose before acceptable volatility is achieved.

Selection of the onset of volatility and decomposition, as well as the construction of this Figure of Merit will be examined with respect to potential precursors for transition metals (Ni, Co, W, Mo, Au, Ag, Cu) as well as main group metals (Al, Ga, In, Sn, Pb) that are presently being developed in our group.

2:15pm **AF2-MoA-4 Designing Thermal Atomic Layer Deposition Processes for Gold Metal using New Organogold Precursors and Co-reageants**, ***Matthew Griffiths**, G Bačić, A Varga, S Barry,* Carleton University, Canada

Gold nanoparticles have been studied extensively by virtue of their plasmonic properties and their ability to act as photocatalysts for CO_2 reduction and hydrogenation. In 2016, our group showed that $(PMe_3)AuMe_3$ would deposit gold nanoparticles by atomic layer deposition (ALD) using oxygen plasma and water as co-reagents. Recently, Van Daele et al. showed that the same compound could deposit gold with hydrogen plasma as a co-reagent at temperatures as low as 50 °C. The development of a process that uses thermal co-reagents is ongoing in our laboratory in order to circumvent the use of harsh co-reagents.

Bimolecular reductive coupling is believed to catalyze the on-surface decomposition of $(PMe_3)AuMe$ on Au. Thus, increasing the steric bulk of the alkyl ligand should increase the activation energy of this process and produce a surface species that resists decomposition to metallic gold. We synthesized a series of $(PMe_3)AuR$ compounds (R = Me, CH_2SiMe_3, $CH(SiMe_3)_2$, and $C(SiMe_3)_3$) with a stepwise increase in steric bulk. We then developed a screening process to test their ability to form self-limiting surface monolayers with an *in situ* quartz crystal microbalance (QCM). At equal vapour pressures and equal deposition temperatures, the rate of CVD decreased with increasing steric bulk, but was never fully prevented.

N-heterocyclic carbenes (NHCs) are ubiquitous ligands in modern chemistry, and they also form robust self-assembled monolayers on gold. We envisioned a second strategy where an NHC ligand bound to Au(I) in the general formula (NHC)AuR could play the role of the self-limiting ligand in an ALD process. All that would be needed is a co-reagent which could remove the NHC from the metallic gold surface to complete the cycle. A series of alkylgold(I) NHCs were synthesized and tested with a focus on small alkyl groups and stable, sterically unhindered NHCs to facilitate efficient packing on the surface. Using our QCM methodology, we compared the various compounds for their ability to form self-limiting monolayers, and we analyzed the gas-phase products of the ALD reactions using *in situ* quadrupole mass-spectrometry (QMS).

Finally, exploration of a third strategy was initiated by our discovery that a thermally stable *N*-heterocyclic silylene (NHSi) reacted with our previously reported and stubbornly inert gold ALD precursor $(PMe_3)AuMe_3$. We identified a highly reactive silylgold(I) silylene species by solution-phase NMR spectroscopy and set out to develop an ALD process using these two compounds. The surface chemistry was studied using our combined QCM and QMS methodology, and the final film properties were evaluated *ex-situ* by 4-point probe, XPS, and XRD.

2:30pm **AF2-MoA-5 A New Carbene Based Silver Precursor Applied in APP-ALD Yielding Conductive and Transparent Ag Films: A Promising Precursor Class for Ag Metal ALD**, ***Nils Boysen**,* Ruhr University Bochum, Germany*; T Hasselmann, D Theirich, T Riedl,* University of Wuppertal, Germany*; A Devi,* Ruhr University Bochum, Germany

The realization of transparent electrodes for solar cells and light-emitting devices based on metals like silver still remains a challenge due to a preferred Volmer-Weber growth mode in the initial stages of thin film growth. This results in a typically observed metal island formation with a high sheet resistance (R_{sh}) at a low film thickness. Atomic layer deposition (ALD) can be the method of choice to effectively lower the percolation threshold and to afford electrically conductive but at the same time optically transparent silver thin films. While the influence of different reducing agents in thermally- and plasma-activated silver ALD processes was studied in the past, the employment of different silver precursors and their influence on the growth behavior and percolation threshold of silver thin films was not coherently studied before due to the limited number of volatile and thermally stable silver precursors. To overcome this issue and to set a starting point for further comprehensive studies, we herein report the synthesis and evaluation of a new fluorine-, oxygen- and phosphorous-free volatile N-heterocyclic carbene (NHC)-based silver precursor.[1] The successful synthesis of the new NHC-based silver amide compound 1,3-di-*tert*-butyl-imidazolin-2-ylidene silver(I) bis(trimethylsilyl)amide [(NHC)Ag(hmds)] was confirmed *via* ^{1}H- and ^{13}C-NMR spectroscopy, elemental analysis and EI-MS, while the thermal characteristics of the compound were determined *via* thermogravimetric and isothermal thermogravimetric analysis. Subsequently, the volatile silver precursor [(NHC)Ag(hmds)] was employed in spatial atmospheric plasma-enhanced ALD (APP-ALD) yielding high purity conductive silver thin films at temperatures as low as 100 °C and with a low resistivity of 10^{-5} Wcm utilizing an Ar/H_2 plasma. The growth characteristics were investigated, and the resulting thin films were analysed *via* SEM, XPS, optical transmittance (UV-Vis) and RBS. Compared to a nominally identical process employing the commercially available silver precursor $[Ag(fod)(PEt_3)]$, [(NHC)Ag(hmds)] was able to considerably enhance the growth rate and prohibit unwanted contaminants like fluorine, oxygen and phosphorous. This renders the new precursor as a promising alternative to the currently established $[Ag(fod)(PEt_3)]$. The current study marks the first example of a carbene stabilized Ag complex that was successfully employed for ALD applications of Ag metal layers. In addition, these promising results create a basis for the development of new metal ALD precursors as there is only a very limited number of ALD precursors known, especially for silver metal ALD.

2:45pm **AF2-MoA-6 Transition Metal β-ketoiminates: A Promising Precursor Class for Atomic Layer Deposition of Binary and Ternary Oxide Thin Films**, ***Dennis Zywitzki**, A Devi,* Ruhr University Bochum, Germany

Due to their abundancy in the earth's crust and promising characteristics in (photo-) electrocatalysis and energy storage devices, binary and ternary oxide films of first row transition metals such as Fe, Co, Ni, Zn have gained increasing attention in recent years. ALD is a promising technique for such applications, as it guarantees excellent interface quality to the underlying substrate and enables the conformal coating of large and nanostructured surfaces. Precursors for these metals however remain limited especially for water assisted processes. While ALD processes for ZnO are dominated by the pyrophoric alkyl compounds such as diethyl zinc, few other precursors were reported thus far. On the other hand, for Fe, Co and Ni, metal cyclopentadienyls and β-diketonates, which require strong oxidizing agents like ozone, have often been used. Water assisted process were realized by utilization of the amidinate ligand system for Fe, Co and Ni. In order to find a compromise between the stable but less reactive metal β-diketonates and the highly reactive metal β-ketiminates, metal β-ketoiminates have been found to be a promising precursor class, which can easily be tuned in terms of volatility and reactivity by employing different substitutions at the imino moiety.

A series of new β-ketoiminato precursors, suitable for ALD have been developed for transition metals. As representative examples, Fe, Co, Ni and Zn β-ketoiminates have been synthesized in good yields and were thoroughly characterized with regard to their purity, composition and molecular structure by NMR spectroscopy, elemental analysis, EI-MS and single crystal XRD. The spectroscopically pure and monomeric compounds were reactive toward water. Their volatility and decomposition behavior was evaluated by thermal analysis and were found suitable for ALD. The introduction of etheric sidechains led to lower melting points, ensuring a steady evaporation rate. Subsequently, water assisted ALD processes with Fe and Zn β-ketoiminate precursors were developed. The typical ALD characteristics were confirmed in terms of ALD window, saturation and thickness dependence. Lastly, the resulting films were analyzed for their structure, morphology, composition and the optical properties were investigated.

With the successful synthesis and characterization of transition metal β-ketominates, the library of potential precursors for first row transition metals was expanded. As representative examples, the successful development of water assisted ALD processes for iron and zinc oxide is demonstrated. The similarity in the physico-chemical properties of these precursors is an advantage to grow ternary metal oxides.

3:00pm **AF2-MoA-7 A New and Promising ALD Process for Molybdenum Oxide Thin Films: From Process Development to Hydrogen Gas Sensing Applications**, ***Jan-Lucas Wree**,* Ruhr University Bochum, Germany*; M Mattinen,* University of Helsinki, Finland*; E Ciftyürek, K Schierbaum,* Heinrich Heine University Düsseldorf, Germany*; M Ritala, M Leskelä,* University of Helsinki, Finland*; A Devi,* Ruhr University Bochum, Germany

The oxides of molybdenum are well known for their versatile properties and therefore serve as excellent materials for a wide range of applications like (photo)catalysis, optoelectronics, and gas sensors for a variety of gas species. Molybdenum oxide can occur in several oxidation states that exhibit very different properties. The different oxides can be distinguished by their crystalline structures as well as by their mechanical and electrical properties. While the different crystalline phases of MoO_3 (α, β, h) are semiconducting with wide band gaps between 2.7 eV and 3.5 eV, the less common suboxides such as Mo_4O_{11} exhibit higher electrical conductivity and the dioxide MoO_2 is even known as pure metallic conductor.[1] Recent studies have shown that α-MoO_3 is a promising material for gas sensing applications owing to its high activity towards gases such as ammonia, nitrogen dioxide and hydrogen at moderate temperatures.[2] Although various oxides of Mo have been tested for the sensing of hydrogen, which

is an important source for clean energy, the suboxides of Mo are not well explored for hydrogen sensing.

In this study, we have investigated the feasibility of using the bis(tertbutylimido)bis(N,N'-diisopropyl-acetamidinato) compound of molybdenum [$Mo(N^tBu)_2(dpamd)_2$] as a potential precursor for atomic layer deposition (ALD) of MoO_x films. In the first part of the study, the focus was to optimize a new ALD process using this precursor together with ozone as the oxygen source. The phase and composition of the layers could be tuned by varying the process parameters which resulted in amorphous (≤250 °C), crystalline suboxide (275 °C), a mixture of suboxide and α-MoO_3 (300 °C), or pure α-MoO_3 (≥325 °C) films. The evaluation of the layers using synchrotron-based surface enhanced photoemission spectroscopy revealed a high amount of oxygen vacancies on the surface of MoO_x suboxide films deposited at 275 °C, which is relevant for sensing applications. Owing to the composition control that could be achieved, the second part of this study focused on evaluating the electrical properties of the MoO_x layers. The temperature dependent resistivity of the MoO_x films suggested them to be suitable for gas sensing applications. In this context, a simple hydrogen gas sensor device was built using 50 nm suboxide MoO_x films which showed reversible and fast response to hydrogen gas at low temperatures.[3] The results derived from this study are very encouraging and form a solid foundation for in-depth studies on tuning the crystallinity of the suboxides for applications beyond gas sensing such as catalysis and energy storage.

3:15pm **AF2-MoA-8 Atomic Layer Deposition of Gallium Oxide Thin Films using Pentamethylcyclopentadienyl Gallium and Combinations of H_2O and O_2 Plasma**, ***Fumikazu Mizutani,*** *S Higashi,* Kojundo Chemical Laboratory Co., Ltd., Japan*; M Inoue, T Nabatame,* National Institute for Materials Science, Japan

Pentamethylcyclopentadienyl gallium (GaCp*) was synthesized as a new precursor for atomic layer deposition of Ga_2O_3 thin films. GaCp* has higher vapor pressure compared with ethylcyclopentadienyl indium (InEtCp), which we reported previously [1, 2]. GaCp* is a cyclopentadienyl compound having a pentahapto half-sandwich structure as well as the InEtCp. Therefore, Ga_2O_3 thin films could be deposited in a similar way. In this paper, we investigated the role of the combinations of oxidant gases, H_2O followed by O_2 plasma (WpO), H_2O followed by O_2 (WO), and solely O_2 plasma (pO), on deposition mechanism of Ga_2O_3 films by the ALD process with GaCp* precursor.

During WpO process at 200 °C, linear growth with no nucleation delay and with a growth rate (GPC) of approximately 0.06 nm/cycle was observed, when 0.1 s GaCp*, 3 s H_2O, and 50 s O_2 plasma pulse times were applied. For the WpO process, a self-limiting surface reaction occurred when an GaCp* pulse time of 0.1-0.3 s, a H_2O pulse time of 1-5 s and an O_2 plasma pulse time of 40-90 s were applied at 200 °C. At this time, with a short O_2 plasma pulse time of less than 40 s, the oxidation reaction insufficiently carried out and resulted in thinner Ga_2O_3 films.

To understand the role of the surface oxidation step in the ALD process on the GPC, GPCs at 200 °C for WpO process with shorter O_2 plasma pulse time of 14 s (0.1 s GaCp* and 3 s H_2O) and WO process (0.1 s GaCp*, 3 s H_2O, and 50 s O_2) were examined. The GPC for the WO and for the pO process were 0.04 nm/cycle and 0.003 nm/cycle, respectively. If the O_2 plasma pulse time is shortened for WpO process, the GPC becomes slightly smaller. On the other hand, GPC becomes negligibly small without plasma (WO).

Next, the role of the H_2O step on the GPC was investigated. The GPC at 200 °C for pO process (0.1 s GaCp* and 50 s O_2 plasma) was 0.05 nm/cycle, indicating that the oxidation is insufficient compared with WpO process.

The Ga_2O_3 films by plasma-enhanced ALD using a new GaCp* precursor was demonstrated. Based on these experimental data, note that the Ga_2O_3 surface oxidation step is found to be extremely important.

References

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ALD Fundamentals

Room Grand Ballroom E-G - Session AF3-MoA

Growth and Characterization I

Moderators: Somilkumar Rathi, Eugenus, Inc., Sumit Agarwal, Colorado School of Mines

4:00pm **AF3-MoA-11 Understanding Elemental Steps of ALD on Oxidation Catalysts**, ***Kristian Knemeyer,*** *M Piernavieja Hermida, R Naumann d'Alnoncourt,* Technische Universität Berlin, Germany*; A Trunschke, R Schlögl,* Fritz Haber Institute of the Max Planck Society, Germany*; M Driess,* Technische Universität Berlin, Germany*; F Rosowski,* BASF SE, Germany

Since the invention in the 1970s, Atomic layer deposition (ALD) has been extensively studied. Over the course of 40 years, its benefits for the microelectronic industry have been spread to numerous different fields such as medicine, batteries and catalysts[1]. Despite being applied and investigated for such a long time the deposition mechanism is barely understood. Typically, ALD is applied by performing hundreds of cycles to grow layers in the range from nanometers to micrometers and most of the times the first cycles show different growth behavior than the following ones. The first cycles might not be of interest for depositing films but they are crucial for us, as our aim in catalyst synthesis and modification is a film thickness in the nm range which is achieved with only few cycles.

We focused on understanding the first cycles of ALD on vanadium pentoxide as oxidation catalyst. Phosphorous oxide ALD on V_2O_5 was conducted with two different precursors (P^{5+} and P^{3+}) and then compared to the highly investigated mechanism of TMA/H_2O. ALD was performed in a magnetic suspension balance to track the mass gain in situ[2]. Surface species were analyzed not only by ^{31}P-NMR but also by in-situ DRIFTS measurements of the second half cycle. XPS was conducted to determine oxidation states of bulk and surface species after each half cycle. STEM-EDX shows highly distributed P on the surface and no additional phases were found. With the combination of these analytics we will show that the ALD mechanism depends heavily on the substrate and that ALD on oxidation catalysts is clearly different than on typical catalyst supports, such as SiO_2 or Al_2O_3.

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4:15pm **AF3-MoA-12 Advanced Lateral High Aspect Ratio Test Structures for Conformality Characterization by Optical Microscopy**, ***Oili Ylivaara,*** *P Hyttinen,* VTT Technical Research Centre of Finland Ltd, Finland*; K Arts,* Eindhoven University of Technology, Netherlands*; F Gao,* VTT Technical Research Centre of Finland Ltd, Finland*; E Kessels,* Eindhoven University of Technology, Netherlands*; R Puurunen,* Aalto University, Finland*; M Utriainen,* VTT Technical Research Centre of Finland Ltd, Finland

Atomic Layer Deposition (ALD) is a key technology in 3D microelectronics enabling conformal coatings into deep microscopic trenches and high aspect ratio cavities. However, conformality characterization in 3D trench walls is challenging and requires sample preparation. The MEMS-based all-silicon Lateral High Aspect Ratio (LHAR) test structure, developed at VTT, named PillarHall® [1-3], provides a fast and accurate substrate and characterization concept for the thin film conformality analysis [4,5]. The most important outcome from the PillarHall® characterization is the film saturation profile, which provides valuable data for reaction kinetics modelling and quantifying conformality. Since the LHAR enables utilization of planar metrology instruments, multiple approaches are compatible.

In this study, we focus on characterization methods suitable to extract the saturation profile and show the advantage of simple optical microscopy image analysis. Studied material was prototypical ALD Al_2O_3 (40-50 nm thick layers) made in two separate research facilities. The study consisted of SEM/EDX planar view, micro-spot reflectometry and ellipsometry and optical microscopy image analyses. These experiments were carried out by two research labs and supported by leading edge optical metrology tool vendors, Semilab Ltd, JA Woollam and Filmetrics.

We also introduce advanced LHAR 4th generation design, which enables characterization of the penetration depth profile with distinct advantages. Namely, new pillar design enables employment of optical line scanners up to 50 µm spot sizes. Furthermore, internal distance indicators support positioning the characterization tools more accurately. These features are illustrated in Supplementary Material Fig S1.

The results show that the gray-scale optical microscopy image analysis with the thickness determination in opening area gives similar results as the reflectometry or ellipsometry line scans, within the accuracy limits. Optical thickness/λ of the film is a limitation for the image analysis, but designing the experiments properly, the grayscale optical micrograph can be a powerful, widely compatible and easy method for conformality analysis.

Support from Semilab Ltd is gratefully acknowledged.

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4:30pm **AF3-MoA-13 Dopant Concentration Analysis of ALD Thin Films in 3D Structures by ToF-SIMS**, *A Kia, **Wenke Weinreich**,* Fraunhofer-Institut fur Photonische Mikrosysteme (IPMS), Germany; *M Utriainen,* VTT Technical Research Centre of Finland Ltd, Finland; *R Puurunen,* Aalto University, Finland; *N Haufe,* Fraunhofer-Institut fur Photonische Mikrosysteme (IPMS), Germany

Self-limiting nature of atomic layer deposition (ALD) proposes a unique deposition mechanism which can produce extremely good step coverage within high aspect ratio (HAR) structures. This layer-by-layer deposition method also provides fine control on different features of deposition techniques such as controlling the dopant distribution in the direction of growth.

The quantity of dopant per layer is controlled, by applying saturation coverage delivering adequate dose rate for each precursor/reactant mixture. There are different parameters that contribute to control the dopant concentration in both 2D and 3D structures. To understand the reasons and characterize the precursors' behavior in deep trench structures, we used dynamic SIMS. Time of flight secondary ion mass spectrometry (ToF-SIMS) is a well-known method due to high detection sensitivity for the measurement of concentration levels of the dopant materials. Nevertheless, due to the geometry of the vertical HAR structures, it is challenging to characterize samples by ToF-SIMS. The absence of a simple and immediately available 3D structure for analyzing thin films produced by ALD has led most studies being made on flat surfaces.

A potential approach to circumvent the challenges is a MEMS-based all-silicon lateral high aspect ratio (LHAR) test structure, PillarHall® developed at VTT[1-2]. After removal of the top membrane (Fig.a-c) the LHAR test chip enables utilization planar characterization tools to examine the properties of deposited thin film on the 3D trench wall. This study focuses on semiquantitative characterization of different doping concentrations of La-doped HfO_2 with using LHAR. The LHAR Test Chips (LHAR3-series, AR2:1-10000:1, 500nm gap height) were used on carrier wafers in a 12 in wafer ALD process (Jusung Eureka 3000).

The findings show that the main difficulties with respect to the geometry for elemental analysis in non-planar structures can be resolved with LHAR. In particular, with the power of ToF-SIMS in data imaging (Fig.d) and integrating of data point from interested area (Fig.e), we are able to quantify doping profile along with understanding the properties of the trench wall in depth penetration.

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4:45pm **AF3-MoA-14 Metallic Ruthenium Coating on SiO_2 Powder by Atomic Layer Deposition using H_2O Reactant.**, *H Lee, **Chi Thang Nguyen**,* Incheon National University, Republic of Korea

Ruthenium has been many times studied by atomic layer deposition (ALD) for various applications, such as metal-insulator-metal capacitors (MIMCAP), diffusion barriers, and electrodes for dynamic random access memory (DRAM), due to its good thermal and chemical stability, high conductivity (resistivity of Ru ~ 7.4 μΩ.cm) and high work function (4.7 eV). Most of the ALD Ru films reported were deposited by the oxidants such as O_2 and O_3, and the main mechanism of Ru deposition was combustion reactions by the oxidant. So, Ru oxide phases were unintentionally formed under overexposure condition of oxidant. In this study, we used H_2O as a reactant to deposit metallic Ru film by ALD. We proposed an abnormal reaction mechanism between H_2O and the new beta-diketonate Ru precursors (5-methyl- 2,4- hexanediketonato) Ru(II), Carish, $C_{16}H_{22}O_6Ru$) led to the formation of Ru metallic film without the appearance of oxide phase under overexposure condition of the reactant. The formation of metallic Ru film by H_2O was analyzed with experimental and theoretical approaches, including the X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM) and Density functional theory (DFT). Also, the cyclic voltammetry (CV) testing was performed on ALD Ru on SiO_2 powders.

5:00pm **AF3-MoA-15 Low Energy Ion Scattering Study of Pt@Al_2O_3 Nanoparticle Coarsening**, ***Philipp Brüner**,* IONTOF GmbH, Germany; *E Solano,* ALBA Synchrotron Light Source, Spain; *C Detavernier, J Dendooven,* Ghent University, Belgium

Coarsening of dispersed Pt nanoparticles has been shown to occur at elevated temperatures [1], leading to the formation of larger particles, and consequently a reduction of the total number of particles. This has important consequences in real-world applications of Pt nanostructures, such as heterogeneous catalysis, where a high number of small, highly dispersed particles are desirable to maintain high catalytic activity.

One attempt to prevent coarsening is to coat the Pt nanoparticles by a thin Al_2O_3 shell deposited by atomic layer deposition (ALD). Advanced surface analytical techniques are required to study the resulting complex structures. In this study, low energy ion scattering (LEIS) is used to support existing data obtained by grazing incidence small angle X-ray scattering applied to Pt nanoparticle model systems prepared by ALD [1]. In LEIS, the energy spectrum of noble gas ions scattered from the sample surface is recorded. The evaluation of elemental peaks in the resulting spectra allows the quantification of the elemental composition of the first atomic layer [2]. This extreme surface sensitivity of just a single atomic layer, combined with composition analysis, is unique to LEIS and makes it especially useful in the study of nanoscale systems. In addition, sub-surface scattering signal from deeper layers gives information about sample composition and layer thickness up to depths of 10 nm.

We show how the monolayer surface sensitivity of LEIS enables the precise determination of the areal density of the deposited nanoparticles and the particle surface coverage of sub-monolayer Al_2O_3 shells. Furthermore, cracking of the shells by annealing has been observed. By measuring layer thickness values, average particle sizes are determined, which give insight into coarsening processes. The thickness of Al_2O_3 shells can be determined precisely over a wide range of values, including ultra-thin sub-monolayer shells after just five cycles of Al_2O_3 deposition.

The results demonstrate that the effectiveness of the Al_2O_3 shell depends on the process conditions during the deposition of the Pt nanoparticles. $MeCpPtMe_3$ was used as a precursor, with either O_2 gas or N_2 plasma as reactants [3]. In the former case, even a sub-monolayer Al_2O_3 shell can completely prevent particle coarsening. In the latter case, the N_2 plasma based Pt process results in a denser collection of smaller Pt nanoparticles and stabilization with an Al_2O_3 overcoat is proven to be more difficult.

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5:15pm **AF3-MoA-16 Physical and Electrical Characterization of ALD Chalcogenide Materials for 3D Memory Applications**, ***Vijay K. Narasimhan**, V Adinolfi, L Cheng, M McBriarty,* Intermolecular, Inc.; *M Utriainen, F Gao,* VTT Technical Research Centre of Finland Ltd, Finland; *R Puurunen,* Aalto University, Finland; *K Littau,* Intermolecular, Inc.

In three-dimensional memory integration schemes, like those used for current NAND Flash memory technologies, the active layers of the memory devices are filled into vias with aspect ratios of 40:1 or greater. It is important for the deposited films to demonstrate consistent properties all the way through the depth of the via. Recently, novel ALD chalcogenide materials have emerged [1-3] that could be used as phase-change memory (PCM) and ovonic threshold switch (OTS) selectors. ALD chalcogenides are attractive because they could be compatible with 3D integration schemes; however, the properties of these films in high-aspect ratio structures have not been extensively investigated.

In this study, we use PillarHall® Lateral High Aspect Ratio (LHAR) test chips [4-6] to elucidate the properties of ALD chalcogenides on a trench wall using standard in-plane metrology techniques without fabricating full device stacks. The PillarHall all-silicon LHAR test chip includes multiple trenches in the aspect ratio range 2:1 - 10000:1 with constant 500 nm gap

height [6]. LHAR chips are used as substrates for ALD binary and ternary chalcogenide films using $HGeCl_3$, $[(CH_3)_3Si]_2Te$, $[(CH_3)_3Si]_2Se$, and $(C_2H_5O)_4Te$ as precursors. Using optical microscopy, scanning electron microscopy with energy-dispersive x-ray spectroscopy, and scanning-probe techniques, we describe the chemical, physical, mechanical, and electrical properties of these films. We show that the thickness and atomic composition of certain chalcogenide films changes dramatically inside of high-aspect ratio features (Fig. S1). Furthermore, we perform optical profilometry on silicon micro-membranes on the PillarHall test chips (Fig. S2) to rapidly estimate the ALD film stress on the microscopic level, which is not directly measurable in devices today despite its importance in 3D architectures. We use these results to comment on the ALD reaction kinetics and discuss implications for future research on ALD chalcogenide films.

Combining high-aspect ratio and stress measurements on a single test chip can accelerate R&D of ALD chalcogenides for applications in PCMs and OTSs as well as other microscopic 3D applications of ALD thin films.

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5:30pm **AF3-MoA-17 The Tailoring of the Single Metal Atom-Oxide Interface*, Bin Zhang, Y Qin,*** Institute of Coal Chemistry, Chinese Academy of Sciences, China

The metal-oxide interface plays important roles in the metal-based heterogeneous catalyst. By sample tailoring the types of interface, size and crystal structure of metal and oxides, etc, the catalytic performance of the catalyst changes dramatically. Thus, the preciously tailoring the metal-oxide interface in atomic scale is a key and most important strategy to design an effective metal-based catalyst. Atomic layer deposition (ALD) is a promising and controllable approach to precisely design and tailor the metal-oxide interface because of its atom-level thickness control, excellent uniformity and conformality and good repeatability in film or particle deposition. Recently, we have developed new strategies for the tailoring of the interface structure by building a serial of nanostructures, such as the core-shell structures, inverse oxide/metal structure, porous sandwich structure, multiple confined metal nanoparticles in oxide nanotubes, and tube-in-tube structure with multiple metal-oxide interfaces. In many case, the metal−oxide interface forms at the cost of metal surface sites through ALD overcoating or modification. In order to increse the ratio of metal-oxide interface and utilization of metal, the building of single metal atom-oxide interface with high loading of metal is a good but challenge strategy since the unstability of single atoms. We have realized this in many ways, such as developing new ALD deposition approachs, depositing oxide site in advance, and changing the deposition dynamic conditions etc. Pt/FeO_x, $Cu-TiO_2$, and $Pt-CeO_2$ single metal atom-oxide interface showed high catalytic performance in selecitive hydrogenation with high efficiency.

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ALD Fundamentals
Room Grand Ballroom H-K - Session AF4-MoA
Growth Mechanisms II

Moderators: Viljami Pore, ASM, Mikko Ritala, University of Helsinki

4:00pm **AF4-MoA-11 Monolithic Integration of Single Crystal Perovskites on Semiconductors with ALD*, John Ekerdt,*** University of Texas at Austin **INVITED**

The semiconductor industry faces new challenges in the sub-10 nm era as scaling will no longer dominate performance improvement. New materials provide opportunity to improve performance with minimal architectural overhaul. For example, high-mobility channels of Ge and III-V semiconductors can provide both lower power consumption and faster computing speeds. In certain applications significant advantages are gained by monolithic integration of the oxides directly on the substrates that will host other devices/components. Perovskite oxides offer a wide range of properties from high-k to multiferroic affording the device designer a suite of possibilities and are particularly important due to their common structure and lattice-matching with common semiconductors.

Here, we report the fabrication of monolithically integrated, single crystal, metal-ferroelectric-semiconductor structures. This talk demonstrates the possibilities through the monolithic integration of perovskite oxides on Si(001) for applications in silicon nanophotonic devices and low-power transistors. Barium titanate (BTO) films, and $BTO/La_xSr_{1-x}TiO_3$ ($x \leq 0.15$) perovskite heterostructures are grown on strontium titanate (STO)-buffered Si(001) using atomic layer deposition at 225 °C. Film strain and *c*-axis orientation are manipulated by growth and annealing conditions. Piezoresponse force microscopy (PFM), electrical and electro-optic measurements establish BTO film ferroelectric (FE) behavior at the µm-scale. The $La_xSr_{1-x}TiO_3$ ($x \leq 0.15$) perovskite heterostructures sandwiched between Si(001) and BTO permits examination of a quantum metal between Si and a FE film.

It is possible to grow crystalline perovskites directly on Ge(001) by ALD and we have used this to deposit STO, BTO, $SrHfO_3$, $Sr(HfTi)O_3$, $SrZrO_3$, and $SrSnO_3$ directly on Ge(001). We will also present the growth and properties of theses perovskite layers directly on Ge(001) and will discuss the how the interface chemistry and structure control the interfacial reactions that allow for crystalline film formation during ALD, and how they affect film properties.

4:30pm **AF4-MoA-13 Introducing the Concept of Pulsed Vapor Phase Copper-free Surface Click-chemistry using the ALD Technique*, Iva Saric,*** *R Peter, M Kolympadi Markovic, I Jelovica Badovinac,* University of Rijeka, Croatia*; C Rogero,* Materials Physics Center (CSIC-UPV/EHU), Spain*; M Ilyn,* Donostia International Physics Center (DIPC), Spain*; M Knez,* CIC nanoGUNE, Spain*; G Ambrozic,* University of Rijeka, Croatia

While ALD allows deposition of a broad variety of inorganic materials, MLD typically relies on very few basic organic reactivity concepts and therefore is not yet as versatile as it could or should be. Given the great promise of ALD/MLD, it is highly demanded to extend the choice of available chemistries, providing a greater choice of suitable organic precursors. The idea behind our work is to extend the range of possible surface chemical reactions by introducing click chemistry as an additional option into the organic chemical vapor phase deposition concept. Click chemistry, initially developed for drug delivery, has recently gained increasing attention in surface patterning with important applications in biotechnology and in development of nanomaterials. Here we report for the first time on a model gas phase copper-free azide-alkyne click reaction performed in an ALD instrumentation [1]. The newly developed process is based on an *in-situ* two-step pulsed vapor phase sequence consisting of initial exposure of ZnO to propiolic acid as the first precursor, followed by gas-phase click-chemistry coupling of benzyl azide as the second precursor. The organic phase compositions were analyzed by XPS and FTIR, while the preservation of ZnO surface morphology was investigated by SEM and STEM. When compared to known state-of-the-art *ex-situ* gas phase click reactions [2,3], the ALD/MLD processing conditions ensure reproducibility and improve the time and surface coverage efficiency. The resulting hybrid material exhibits no surface contaminations with physisorbed organic precursors and/or by-products deriving from organic precursor degradation. This study offers great potential toward the development and fabrication of complex functional organic layers on metal oxide surfaces by selective azide-alkyne cycloadditions performed in an ALD/MLD instrument and broadens the variation range of applicable chemistry in MLD. Variation of the functionalities of the organic precursors will allow MLD type of polymer

growth based on click chemistry and add degrees of freedom for the design of functional polymeric coatings.

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4:45pm **AF4-MoA-14 Surface Enhanced Raman Spectroscopy Studies of Aluminum ALD Precursors for Al_2O_3 Growth***, **Michael Foody**,* Illinois Institute of Technology

Trimethylaluminum (TMA) is perhaps the most widely employed and emblematic ALD precursor – mainly for its robust reactivity with hydroxyl surface species and well-behaved ALD growth. Although one would expect other alkyl aluminum compounds to have similar properties, we have found the highly pyrophoric compound triisobutylaluminum (TiBA) does not grow alumina under similar ALD-like conditions. Unlike many other thin-film deposition techniques, ALD is driven by the reactivity at the vapor-substrate interface, and the stark divergence between these chemically similar precursors offers insight into the fundamental principles of ALD.

In this work, we use surface enhanced Raman spectroscopy (SERS) to show the limited reactivity between surface alkyl groups and water. SERS shows when TiBA is exposed to a 3-mercaptopropionic acid surface, only small signals corresponding to Al-C and isobutyl bond modes appear. The small signal corresponding to isobutyl peaks remains even after treatment with water indicating no reactivity between the isobutyl alkyl surface and water. These measurements suggest a mechanism in which proton transfer acts as the limiting step.

This knowledge informed the design of new precursors to test the structural and electronic effects of Al precursors. As a comparison, two additional aluminum precursors were synthesized, and used to grow alumina thin films by ALD. The two new precursors have varying alkyl groups – analogous to TMA and TiBA – as a way to compare the proton transfer reactivity to a methyl group and an isobutyl group at the vapor-substrate interface. Measurements were made using QCM and SERS, and were found to be consistent with our findings of the reactivity profiles of TMA and TiBA. The methyl aluminum complex was found to be a robust precursor for alumina deposition with water, while the isobutyl analogue did not deposit any mass or show films by ellipsometry on silica. All depositions were done under 200C, and SERS measurements were made at 100C, thus demonstrating the relatively low-temperature deposition conditions of these compounds. The SERS measurements presented here are among the first reports using SERS to evaluate ALD systems. They provide powerful insights into deposition mechanism by measuring bond vibrational modes over a much larger range of frequencies than more common methods (FTIR). The measurements (along with QCM) provide a new understanding of the reactivity of alkyl aluminum precursors, which have broader implications for general precursor design.

5:00pm **AF4-MoA-15 Atomic Layer Deposition of Aluminum, Hafnium and Zirconium Oxyfluoride Films with Tunable Stoichiometry***, **Neha Mahuli**, J Wallas, S George,* University of Colorado - Boulder

The reactivity of metal oxide films with halogen chemistries can be reduced by incorporating fluorine into the metal oxide during film deposition. This study explored the atomic layer deposition (ALD) of various metal oxyfluorides such as aluminum oxyfluoride (AlO_xF_y), hafnium oxyfluoride (HfO_xF_y) and zirconium oxyfluoride (ZrO_xF_y). Techniques were developed to obtain tunable stoichiometry of the metal oxyfluoride films.

The metal oxyfluoride ALD films were deposited at 150°C. H_2O and HF-pyridine were used as the oxygen and fluorine sources. $Al(CH_3)_3$ was used as the Al source and Hf and Zr amidinates precursors were used as the Hf and Zr metal sources. The metal oxyfluorides were deposited using either (1) the halide-exchange method (see Supplemental Figure 1) or (2) the nano-laminate method (see Supplemental Figure 2). Both methods were evaluated using *in situ* quartz crystal microbalance (QCM) measurements and *ex situ* X-ray photoelectron spectroscopy (XPS) analysis.

The halide-exchange method is based on the facile exchange of oxygen by fluorine from HF. HF exposures after deposition of the metal oxide easily replaced oxygen with fluorine. In addition, the fluorine also diffused into the underlying metal oxide film. The oxygen/fluorine exchange and fluorine diffusion complicates the control of the stoichiometry of the metal oxyfluoride film.

Compositional control was achieved by the halide-exchange mechanism using either metal oxide layers with various thicknesses or different HF pressures. The stoichiometry could also be tuned using the nano-laminate methods with different numbers of metal oxide ALD and metal fluoride ALD cycles. These two methods gave rise to tunable stoichiometry from pristine metal oxide to adjustable oxyfluoride to pristine metal fluoride.

5:15pm **AF4-MoA-16 Fundamental Study on the SiO_2 Growth Mechanism of Electronegativity Difference of Metal-O in the High-*k* Underlayers by PE-ALD Method***, **Erika Maeda**,* Shibaura Institute of Technology, Japan*; T Nabatame,* National Institute for Materials Science, Japan*; M Hirose,* Shibaura Institute of Technology, Japan*; M Inoue, A Ohi, N Ikeda,* National Institute for Materials Science, Japan*; M Takahashi, K Ito,* Osaka University, Japan*; H Kiyono,* Shibaura Institute of Technology, Japan

To fabricate silicate films such as $HfSiO_x$ and $AlSiO_x$ as gate insulator of GaN power devices, the HfO_2/SiO_2 and Al_2O_3/SiO_2 laminates was initially deposited by atomic layer deposition (ALD) process [1]. Understanding the SiO_2 growth mechanism on HfO_2 and Al_2O_3 layers is an important in terms of the design of the $HfSiO_x$ and $AlSiO_x$ formation. In this study, we systematically investigate the growth rate of SiO_2 film on various high-*k* underlayers (Metal-O) by plasma-enhanced ALD (PEALD) using Tris(dimethylamino)silane (TDMAS) precursor and O_2 plasma gas, and we also discuss about role of the electronegativity difference in Metal-O on the SiO_2 growth mechanism.

At first, 30-nm-thick HfO_2, TiO_2, and Al_2O_3 layers and 5-nm-thick SiO_2 layer on Si substrates were prepared as Metal-O. The thicknesses of the SiO_2 films were varied on Metal-O by changing ALD cycles during PEALD at 300 °C. The thickness of the SiO_2 film was estimated using spectroscopic ellipsometry and Si_{2p} intensities of XPS.

All data of the SiO_2 thickness on HfO_2, TiO_2, Al_2O_3, and SiO_2 layers as a function of ALD cycle satisfied the linear relationship. The growth per cycle (GPC) value of the SiO_2 film was increased in the following order: SiO_2 (0.036 nm/cycle) < Al_2O_3 (0.090) < TiO_2 (0.11) < HfO_2 (0.13). Here, we pay attention to the electronegativity values of the Si, Al, Ti, Hf, and O atoms of Metal-O. Note that the GPC increased as the difference of electronegativity such as Si-O (1.76), Al-O (2.03), Ti-O (2.18), and Hf-O (2.27) in the Metal-O increased [2]. Based of these experimental data, we proposed one idea of the SiO_2 growth mechanism. In the TDAMS precursor supply step during PEALD, the adsorption of TDMAS precursor on the surface of Metal-O must be strongly influenced by the difference of electronegativity. This is because Si atom of the TDMAS precursor is easily attracted to oxygen atoms having a large electron density of Metal-O. Therefore, the adsorbed amount of the TDMAS precursor increases as the electron density of oxygen atoms becomes higher in the following order: Si-O < Al-O < Ti-O < Hf-O. This behavior was observed up to ALD 10 cycles. When the ALD cycle increases more than 10 times, the GPC became the same value (0.036 nm/cycle) as SiO_2 regardless of underlayer materials. This suggests that the adsorption amount of the TDMAS is similar to that of SiO_2 because the 1.2-nm-thick SiO_2 layer covered on the underlayer materials. To understand the SiO_2 growth mechanism, we should pay attention to the difference of electronegativity of Metal-O in underlayer.

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5:30pm **AF4-MoA-17 Low Temperature Aluminium Nitride Deposition: Comparing Hydrazine and Ammonia***, **Aswin L.N. Kondusamy**, S Hwang, A Lucero, Z Qin, X Meng,* The University of Texas at Dallas*; D Alvarez, J Spiegelman,* RASIRC*; J Kim,* The University of Texas at Dallas

Aluminium nitride is a wide bandgap material having high thermal conductivity [1]. Depositing thin films of high thermal conductivity such as Aluminium nitride as a capping layer or a passivation layer by a CMOS compatible method is a viable approach to tackle the heat management issue that arises with scaling down of devices. Compatibility demands lower deposition temperature (<300 °C) and improved conformality over high-aspect ratio structures. AlN_x ALD using low reactive NH_3 results in incomplete reaction below 300 °C [2], resulting in carbon and hydrogen impurities and Plasma enhanced ALD (PEALD) frequently exhibits poor conformality. Thermal ALD (t-ALD) with a more reactive nitrogen precursor such as hydrazine is expected to overcome these problems. Newly available ultra-high purity hydrazine sources have been successfully used to deposit metal nitrides at low temperature [3]. In this work we study the low temperature t-ALD growth characteristics of aluminium nitride using hydrazine and trimethylaluminium (TMA) and evaluate the properties of the films. t-ALD results with hydrazine will be compared to films grown by

t-ALD with NH_3 and PEALD with NH_3 plasma, all using the same ALD reactor in the same temperature range.

AlN_x films were deposited using a custom-made ALD reactor from 175-350 °C. Hydrazine is supplied from a BRUTE hydrazine source. Growth with hydrazine shows saturation behavior, with growth per cycle (GPC) saturating at hydrazine exposure as low as 0.1 s (~10^4 L). High GPC of 2.8-3.2 Å/cycle is observed at 300 °C with refractive index of 1.890 whereas t-ALD with NH_3 shows lower GPC (1.1 Å/cycle) for similar exposure, which is expected due to superior reactivity of hydrazine. AlN_x growth using hydrazine shows high temperature dependence in the range 175-300 °C. X-ray photoelectron spectroscopy is used to confirm film stoichiometry: films with low carbon (1%) impurities can be achieved. Films deposited below 250 °C get oxidized easily under air due to low film density. A novel densification method is proposed to obtain denser films at these temperatures to overcome this problem. The denser films are expected to have higher thermal conductivity. The detailed experimental results will be presented.

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[2] R. L. Puurunen, M. Lindblad, A. Root, A. O. I. Krause, Phys. Chem. Chem. Phys., 3 (2001) 1093-1102

[3] D. Alvarez, J. Spiegelman, R. Holmes, K. Andachi, M. Raynor, H. Shimizu, ECS Transactions, 77 (2017) 219-225

ALD Fundamentals
Room Evergreen Ballroom & Foyer - Session AF1-MoP
Precursor Synthesis and Process Development Poster Session

AF1-MoP-1 Atomic Layer Deposition of Molybdenum Films from Molybdenum Pentachloride Precursor*, **Changwon Lee**, S Lee, M Kim,* Versum Materials, Republic of Korea*; S Ivanov,* Versum Materials, Inc.

The lower resistivity WL (Word Line) material is very attractive to the 3DNAND device makers, because they could reduce the cell stack height while maintaining the device speed. Current POR material of 3DNAND WL is tungsten made by tungsten hexafluoride ALD. However, it is well-known that fluorine results in fatal defects in the device critical layer. Fluorine free tungsten precursors such as tungsten pentachloride has been evaluated recently worldwide not only for 3DNAND application but also other memory and logic devices application. Molybdenum is considered as an attractive WL material for next generation 3DNAND devices. Molybdenum has almost same level of low bulk resistivity comparing to tungsten, but it has smaller EMFP (Electron Mean Free Path), so the effective resistivity, a product of bulk resistivity and EMFP, is expected to be lower compare to tungsten for films less than 10nm. Molybdenum chlorides are considered as potential precursors for deposition of molybdenum films from fluorine free precursors.

Here, we report thermal ALD of molybdenum films on PVD titanium nitride substrates up to 500°C from heated solid high-purity molybdenum pentachloride precursor. Hydrogen was used as a reactant gas under cyclic CVD and ALD conditions. Thickness of molybdenum and titanium nitride films was measured with XRF. Sheet resistance of molybdenum films was measured using 4-point probe technique. The films have been also characterized with TEM and XPS for conformality at aspect ratio 15 trench pattern and impurity depth profile in the film.

We've found that the etching of titanium nitride could be controlled lower than 0.5nm during the molybdenum deposition by variation of molybdenum pentachloride delivery rate. Molybdenum GPC was 0.06 nm per cycle at 500°C wafer temperature. The dependence of step coverage on deposition conditions was investigated and will be discussed. The properties of molybdenum films deposited from molybdenum pentachloride will be compared to properties of tungsten films deposited from similar tungsten pentachloride precursor. Preliminary results suggest that resistivity of the molybdenum films is lower compare to resistivity of tungsten films at 10-15 nm of film thickness. Rapid thermal annealing at 700°C further reduced the sheet resistance of the films.

In this paper, we demonstrated thermal molybdenum ALD with fluorine free molybdenum precursor, which shows low etch of titanium nitride substrate and relatively low resistivity compared to tungsten; which is important for next 3DNAND's WL forming application. Details of the deposition study and properties of the molybdenum films will be presented.

AF1-MoP-2 Atomic Layer Deposition of Silver Metal Films: Synthesis and Characterization of Thermally Stable Silver Metal Precursors*, **Harshani J. Arachchilage**, C Winter,* Wayne State University

Silver metal has the lowest resistivity (1.59 μΩ cm) of all metals and has applications in plasmonic devices. Growth by thermal atomic layer deposition (ALD) has been hampered by the low thermal stabilities of virtually all silver precursors. The low precursor thermal stabilities is complicated by the positive electrochemical potential of the silver(I) ion (E° ($Ag^+ + e^- \leftrightarrow Ag$) = 0.7996 V). Herein, we will describe volatile and highly thermally stable silver pyrazolate precursors. The silver pyrazolates $[Ag(3,5-(CF_3)_2pz)]_3$ and $[Ag(3-{}^tBu-5-(CF_2CF_2CF_3)pz)]_3$ were synthesized and their volatility thermal stabilities were evaluated by sublimation studies, solid-state thermal decomposition experiments, and thermogravimetric analysis (TGA). $[Ag(3,5-(CF_3)_2pz)]_3$ was used with 1,1-dimethylhydrazine to deposit silver metal films on SiO_2 substrates at 180 °C with a growth rate of 0.82 Å/cycle. A plot of growth rate versus substrate temperature showed an ALD window of 170 to 220 °C. Saturative self-limited growth was demonstrated in both $[Ag(3,5-(CF_3)_2pz)]_3$ and 1,1-dimethylhydrazine at 180 °C. The as-deposited films were crystalline. We will also describe the synthesis and characterization of silver pyrazolate complexes containing N-heterocyclic carbene (NHC) ligands. Treatment of $[Ag(3,5-(CF_3)_2pz)]_3$ and $[Ag(3-{}^tBu-5-(CF_2CF_2CF_3)pz)]_3$ with three equivalent of the NHC ligands afforded complexes afforded new monomeric complexes of the formula $Ag(R_2pz)(NHC)$. X-ray crystal structures, sublimation data, and the thermal stability of these complexes will also be presented.

AF1-MoP-3 Atomic Layer Deposition of Lanthanum Oxide Using Heteroleptic La Precursors*, **Daehyeon Kim**, J Lee, W Noh,* Air Liquide Laboratories Korea, South Korea

Rare earth-based oxides are of interest for their potential application in future logic and memory technologies, and lanthanum oxide (La_2O_3) is a well known high-k material for metal gate transistors and a dopant for high-k materials. In past studies, heteroleptic precursors which have alkylcyclopentadienyl and amidinate ligands, $La(RCp)_2(R'\text{-amd})$, have been developed to aim to be liquid and to enhance volatility and thermal stability. In this work, three heteroleptic precursors, $La(MeCp)_2(iPr\text{-amd})$, $La(EtCp)_2(iPr\text{-amd})$, $La(iPrCp)_2(iPr\text{-amd})$, were synthesized, and their physical properties were compared. $La(EtCp)_2(iPr\text{-amd})$ and $La(iPrCp)_2(iPr\text{-amd})$ were liquid at RT, and very thermally stable. ALD evaluation of $La(EtCp)_2(iPr\text{-amd})$, which is more promising than $La(iPrCp)_2(iPr\text{-amd})$ in terms of the vapor pressure and the viscosity, was performed with O_3 and H_2O as a co-reactant. Both processes had two plateaus in the ALD windows which were at low and high temperature, respectively. The desired ALD window will be the plateau at higher temperature (>350 ℃), because of low C impurity. The plateau at lower temperature might be useful for another processes. Carbon impurity at the low temperature was drastically decreased below detection limit, after post annealing in N_2 atmosphere. In case of ozone process, the cubic phase was observed at 400 ℃ while all films with water process showed amorphous phase even at 400 ℃.

AF1-MoP-4 Synthesis and Thermal Characterization of New Molybdenum Precursors for Atomic Layer Deposition of Molybdenum Metal*, **Michael Land**,* Carleton University, Canada*; K Robertson,* Saint Mary's University, Canada*; S Barry,* Carleton University, Canada

To keep pace with "Moore's Law" (i.e., the number of transistors in an integrated circuit doubles every 18 months), the size regime of high-performance transistors has now shrunk to ≤ 10 nm. With this decrease of size, traditional metallization materials (e.g., Cu, Al) begin to fail. When microelectronic interconnects – the wiring of integrated circuits – become smaller than 10 nm, the resistivity of the material increases due to electromigration of the metal atoms within the interconnect. Promising metals to replace copper are molybdenum, osmium, iridium, ruthenium, rhodium, and tungsten, because they all have high melting temperature and relatively low bulk resistivities (~4-10 μΩ.cm), leading to lower electromigration.

A method of choice that can be used for the preparation of these small interconnects is atomic layer deposition (ALD). The goal of this project is to develop a chemical precursor compound for the ALD of molybdenum metal. To date, there has only been one reported ALD process for molybdenum metal, however that process utilized harsh co-reagents, and the resulting films had high resistivities. We have chosen the known *bis*(*tert*-butylimido)molybdenum(VI)dichloride as a synthetic starting material, and it has been derivatized with various neutral coordinating ligands, such as ethers, phosphines, amines, and carbenes The ligands were found to have varying effects on the thermal stability of the precursors (up to 300 ºC for the 2,2'-bipyridine adduct), which sometimes came at the cost of poor volatility. However, complexes incorporating less Lewis basic ligands, such as the 1,2-dimethoxyethane adduct, was found to have a large thermal range, with an onset of volatilization of 80 ºC and thermal decomposition at 180 ºC.

These compounds have been characterized in the condensed state, using traditional spectroscopic techniques, and their solid-state structures have been determined using single crystal X-ray diffraction. Their mechanisms of volatilization will also be proposed, based on results from thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), and the resulting sublimation products. Finally, the thermal stabilities of these compounds have been studied using DSC and thermolysis in flame-sealed NMR tubes, and non-volatile decomposition products were characterized using a scanning electron microscope (SEM) with energy-dispersive X-ray spectroscopy (EDS). From these results, mechanisms of thermal decomposition will also be proposed, including methods to prevent low temperature decomposition pathways and furnish viable vapour deposition precursors.

AF1-MoP-6 A Novel Hf Precursor with Linked Cyclopentadienyl-Amido Ligand for Thermal Atomic Layer Deposition of HfO_2 Thin Film*, **Jeong do Oh**, M Nim, J An, J Seok, J Park,* Hansol Chemical, Republic of Korea

HfO_2 thin film has been widely used as gate oxide layer in the complementary metal oxide semiconductor (CMOS) device as well as dynamic random access memory (DRAM) due to suitable band offset with Si, high thermodynamic stability on Si, and high permittivity [1].

In this study, we investigated a novel Hf precursor, CMENHa, which is coordinated by cyclopentadienyl-amido ligand. The physical characteristics of precursor and film properties of the ALD HfO_2 thin films were analyzed via TGA, viscometer, XPS, XRD and TEM. As compare to widely applied CpTDMAH precursor, CMENHa precursor showed higher thermal stability due to chelate effect of bidentate ligand, lower residue (0.6%) and lower viscosity. In addition, CMENHa was observed wide ALD window range up to 400℃ with low carbon impurity contents and good electrical properties such as high dielectric constant and low leakage current density. Base on excellent step coverage, purity and thermal stability, the CMENHa precursor has demonstrated potential as dielectric material for use in CMOS device and DRAM capacitor.

Reference [1] J. Robertson et al., *Rep. Prog. Phys.***69**, 327−396. (2006).

AF1-MoP-7 Atomic Layer Deposition of WS_2 using a New Metal-Organic Precursor and H_2S Molecules*, **Deok Hyun Kim**, D Nandi, S Kim,* Yeungnam University, Republic of Korea

Transition metal dichalcogenides (TDMCs) are exntesively researched in past few years due to their 2D layerd structure similar to graphne . This group of materials offer tunable opto-electronic properties depending on the number of layers and therefore have wide range of applications. Tungten disulfide (WS_2) is one of such TMDCs that has relatively less studied compared to MoS_2. WS_2 has an indirect bandgap of 1.3–1.4 eV in bulk, which have trigonal prismatic coordination around tungsten. The bandgap of WS_2 increases with decreasing thickness and, intriguingly, becomes direct at monolayer thickness with a magnitude of approximately 2.3 eV for the optical bandgap. Such tunability of WS_2 makes it suitable for many semiconductor applications such as field-effect transistors, photodetectors, and photocatalysis, while other promising applications include electrocatalysis and electrochemical energy storage. Atomic layer deposition (ALD) can be adopted very efficiently to control the thickness of WS_2 and hence its properties. Therefore, in this study is WS_2 thin films are grown on several types of substrates by ALD using a new metal-organic precursor [tris(hexyne) tungsten monocarbonyl, $W(CO)(CH_3CH_2C{\equiv}CCH_2CH_3)$ and H_2S at a relatively low temperature of 300°C.The typical self-limiting film growth (growth rate of ~0.13 nm/cycle) is clearly observed with both the precursor and reactant pulsing time. The as-grown films are amorphous with considerable S-deficiency but can be crystallized as WS_2 film with (002) preferential orientation by post-annealing in H_2S/Ar atmosphere at 800 °C. Moreover, the post-annealing helps to reduce the C and O content in the film signififcantly as confirmed by the X-ray photoelectron spectroscopy. Further characterizations of the as-deposited and annealed films are perfomed using several other spectroscopic measurements like Raman, Rutherford backscattering, and UV-vis spectroscopy. The current study thus establishes a new and efficient route to obtain WS_2 thin films which could find several potential applications in future.

Acknowledgements

This work was financially supported by the Ministry of Trade, Industry & Energy (MOTIE; #10080651) and Korea Semiconductor Research Consortium (KSRC) support program for the development of the future semiconductor device. The precursor used in this study was provided by UP Chemical Co. Ltd., Korea.

AF1-MoP-8 Recent Advances in the Development of Metal Organic Precursors for Atomic Layer Deposition*, **Anjana Devi**, L Mai, D Zywitzki, S Beer, N Boysen, D Zanders, J Wree, M Wilken, H Parala,* Ruhr University Bochum, Germany

Atomic layer deposition (ALD) has gained significant attention from the research community and industry due to the distinct advantages in terms of uniform and conformal coating with precisely tunable stoichiometry and thin film thickness. Since ALD is a chemical vapor phase technique, one of the important parameters governing the process is the precursor employed, which most often is in the form of a metal organic complex. The precursor must be volatile and at the same time it must possess a certain thermal stability to avoid decomposition. Furthermore, due to the surface driven reactions the precursor has to be reactive toward the reactive surface sites and in the second reaction step toward co-reactants to achieve a self-limiting behavior to obtain the desired material. However, the library of precursors for various material systems is not very large and for certain metals there are limited precursors commercially available.

This prompts researchers to develop new precursors or fine tune the characteristics of the already adopted precursors to improve upon the properties relevant for ALD. Over the years, our research group focused on developmental precursor chemistry spanning the periodic system and identified several ligand systems bound to the metal center that are well suited for ALD conditions. Herein, we present an overview of our research work including the synthetic strategies for various ligands, namely guanidinates, amidinates, b-ketoiminates, cyclopentadienyls, diazadienes, N-heterocyclic carbenes and alkylamines. Potential precursor solutions for group III, IV, V and VI transition metals as well as lanthanides are presented employing guanidinates and amidinates among which Y, Hf, Mo, W, Gd and Er were already successfully used in ALD processes. For the fourth period transition metals ranging from Fe to Zn, employing b-ketoimines and diazadienes resulted in promising precursors. Noble metals like Cu and Ag can be deposited using N-heterocyclic carbene complexes. Precursors for main group III metals such as Al, Ga and In, were fine tuned for both, low and high temperature ALD processes employing either alkylamines, amidinates or guanidinates. Furthermore, we identified and developed ligand systems which were combined with Sn, Pb for main group IV metals and Sb for main group V, resulting in potential ALD precursors.

In this presentation, precursor systems covering a range of metals will be presented alongside representative examples for the application in ALD processes. We will also demonstrate that this large library is not only suitable for inorganic oxides, or nitrides but also compatible with organic co-reactants in ALD/MLD processes.

AF1-MoP-9 Synthesis of Group VI Oxyhalide Adducts and Mo Metal Film Growth on TiN Surfaces*, **David Ermert**, R Wright Jr., T Baum,* Entegris, Inc.

Molybdenum and tungsten metal films are being widely considered for logic and memory (DRAM/NAND) devices, a result of their low-resistivity and high melting points (low electromigration). Challenges to more widespread adoption of group VI film growth using chemical vapor deposition (CVD) and atomic layer deposition (ALD) stem, in part, from the availability of suitable metal-containing precursors. When considering materials for CVD/ALD applications, halide-saturated MX_n species (e.g. $MoCl_5$, WF_6) offer suitable volatility and can deposit high-quality metal films, but may not be compatible with neighboring films within the device. For example, the resulting HCl or HF byproducts may be detrimental to diffusion barrier performance within the device.

Zero-valent metal carbonyls are logical choices for metal deposition as they display suitable vapor pressures and do not require chemical reduction during thermal decomposition on a surface. Barriers to adoption of these precursors include prohibitively high decomposition temperatures, the formation of metal carbides via incorporation of carbon in the films, and the release of toxic carbon monoxide by-products. In general, volatile organometallic precursors that can be deposited at low temperatures offer attractive alternatives for film deposition provided the deposited films are carbon-free.

Here, we describe a general approach to CVD/ALD precursor design and subsequent growth of molybdenum metal films, at moderate surface temperatures, using a molybdenum oxyhalide species and H_2 co-reactant. Group VI oxychloride adducts of the general formula $MO_2Cl_2L_n$ (where M = Mo, W with L = Lewis base adduct and n = 1, 2) are prepared and screened as potential ALD candidates. Precursor characterization and use in thermal deposition studies will be described. Deposited metal film resistivity approaching 50 μΩ-cm were observed at temperatures below 500 °C. Film composition studies, carried out by XRF spectroscopy, demonstrated a strong substrate temperature-dependence on film identity.

AF1-MoP-10 Gallium Precursor Development for ALD Film Applications*, **Atsushi Sakurai**, M Hatase, N Okada, A Yamashita,* ADEKA Corporation, Japan

Gallium-based films such as gallium oxide and gallium nitride have been attracting the world's attention of those who are looking at future power electric devices with high power, high breakdown voltage, and energy-saving benefit. Although ALD process could be useful for producing many kinds of metal oxide, nitride, carbide thin films with execellent quality and conformality, many studies have not yet been done regarding gallium precursor screening for ALD applications.

Trimethylgallium (TMG) is the well-known gallium precursor to make various kinds of Ga-based thin films such as gallium nitride and gallium arsenide. However, TMG with remote oxygen plasma ALD process still left over some carbon impurity in the gallium oxide film [1]. Furthermore, it has been pointed out that TMG has undesirable pyrophoric nature when exposed to air.

We are looking for various kinds of gallium precursors which have non-pyrophoric nature, good volatility, enough thermal stability, and high ALD reactivity to produce gallium-based thin film even with gentle ALD process conditions. Fig.1 indicates that our new precursor of GNP-7 has the highest

vapor pressure of several kinds of N-based gallium molecules. Thermal ALD process using GNP-7 and H_2O co-reactant produced the amorphous gallium oxide film with good ALD process window at low temperature domain (Fig.2). We are also demonstrating gallium nitride films using GNP-7 and NH_3, whose results will be shown in our presentation then.

[1] Xiao Chen et al., ALD 2018 technical program & abstract book, p128, AA3+AF+EM-WeM6

AF1-MoP-11 Design and Optimization of Heteroleptic Zirconium Precursors by Density Function Theory Calculation*, **Romel Hidayat**,* Sejong University, Republic of Korea*; J Cho, H Lim, B Yang, J Park, W Chae,* DNF Co. Ltd, Republic of Korea*; H Kim,* Sejong University, Republic of Korea*; S Lee,* DNF Co. Ltd, Republic of Korea*; W Lee,* Sejong University, Republic of Korea

The stack capacitor of DRAM is continuously developed by decreasing the horizontal dimension, increasing the aspect ratio, and adopting dielectric materials with higher dielectric constants (k). Zirconium oxide (ZrO_2) is a high-k material currently in use in dynamic random access memory (DRAM) devices. The deposition of high-k dielectric materials with excellent conformality and accurate thickness control is required, and the atomic layer deposition (ALD) technology is the best choice. The high-temperature ALD process is desirable for the high dielectric constant and low leakage current density of the deposited film, so the thermal stability of the precursor should be excellent. The reactivity of the precursor is an essential factor to obtain a better conformal film. Also, the precursors must have excellent reactivity for conformal deposition of the film on high-aspect-ratio patterns. A new heteroleptic zirconium precursor for ALD of ZrO_2 has been developed to meet these requirements, and the deposition process and thin film properties using this precursor were presented [1]. The result showed a wide ALD temperature window and excellent step coverage. In the present work, we present the design and optimization of the zirconium precursors by using density functional theory (DFT) calculations. We compared zirconium compounds with different numbers of triamine and dimethylamine ligands to determine the most stable structure. Then, we optimized the alkyl groups in triamine ligand in terms of thermal stability, reactivity, and viscosity. The optimized zirconium compound with a triamine ligand showed better reactivity and stability as compared with the cyclopentadienyl tris-dimethylamine zirconium [$CpZr(N(CH_3)_2)_3$], which is in a good agreement with deposition experiments. DFT calculation is a powerful tool for designing new precursors for ALD process to obtain the desired thermal stability, reactivity, and viscosity.

Figure 1. Lewis base indices and zirconium charge densities of triamine-type zirconium compounds with different combinations of alkyl groups.

[1] H.-D. Lim *et al.*, ALD 2018, AF2-TuA13.

AF1-MoP-12 Low Temperature Plasma-Enhanced Atomic Layer Deposition of ZnO from a New Non-Pyrophoric Zn Precursor*, **Lukas Mai**, F Mitschker, P Awakowicz, A Devi,* Ruhr University Bochum, Germany

With its high transparency to visible light and tunable conductivity, zinc oxide (ZnO) is a transparent conductive oxide (TCO) and promising candidate for microelectronic applications such as thin film transistors (TFTs), solar cells or chemical sensors. Furthermore, with a direct band gap of E_g= 3.37 eV it can not only be used for electrical but optical applications e.g. in UV-light emitting diodes (LEDs), too. Owing to its high density, ZnO layers can be employed as protective coating as well and could serve as conductive and protective gas barrier layer (GBL) at the same time on polymers in flexible electronics. For high quality GBLs, the thin films should be very uniform, dense and conformal over the whole surface. With atomic layer deposition (ALD), it is possible to fabricate such thin films at low temperatures with a precise thickness control. For the ALD of ZnO, diethylzinc ([$ZnEt_2$], DEZ) is the most commonly used precursor. Despite the inherent advantages of DEZ in terms of high volatility and reactivity toward a range of co-reactants at low temperatures, there are certain issues with DEZ such as its pyrophoric behavior and not well-defined ALD window. Thus, we attempted the synthesis of an alternative Zn precursor.

Here, we present the synthesis and detailed characterization of bis-3-(dimethylamino)propyl zinc, [$Zn(DMP)_2$] as an alternative precursor for ALD of ZnO. As already demonstrated for aluminum precursors,[1] the DMP ligand stabilizes the zinc center atom by a dative bond from the amine to the metal. This yields a favored 18 electron complex, causing a thermally stable, non-pyrophoric solid compound with a melting point at only 46 °C. The thermal properties are thoroughly characterized showing a high evaporation rate at only 55 °C. Using this precursor, a new plasma enhanced (PE)ALD process employing O_2 plasma was developed. The process is self-limiting at substrate temperatures between 60 °C and 140 °C on Si(100) with growth rates of 0.44 Å $cycle^{-1}$at 60 °C and 0.72 Å $cycle^{-1}$at 140 °C. The resulting ZnO thin films are conformal, uniform, smooth, dense and of high purity even at low deposition temperatures and were analyzed regarding their optical and electrical properties. For the investigation of the ZnO films as GBL, thin films of various thicknesses were deposited on PET substrates at 60 °C and the improvement of the gas barrier of the PET by a factor of 60 for a 10 nm thin film obtained by oxygen transmission rate (OTR) measurements. The thin film properties are of the same quality as for layers obtained from DEZ, rendering the new intramolecular stabilized precursor to be a promising and safe alternative for ALD of ZnO coatings.

AF1-MoP-13 Homoleptic and Heteroleptic Yttrium Precursor: Tuning of Volatility, Reactivity and Stability for ALD Applications*, **Sebastian Markus Josef Beer**, A Devi,* Ruhr University Bochum, Germany

Rare-earth (RE)-based materials in the form of thin films have gained significant attention due to their unique functional properties rendering them suitable for a broad variety of applications. Especially yttrium oxide (Y_2O_3) has been intensively studied for optics, protective coatings or high-k dielectrics. Furthermore, the ability to dope Y into other oxide material systems opens up new avenues for the development of high–performance materials as for instance yttrium doped zinc oxide (Y:ZnO), yttria stabilized zirconia (YSZ) or yttrium doped $SrSnO_3$.[1-3]

Atomic layer deposition (ALD) serves as a superior thin film processing technique enabling precise layer thickness control paired with conformal growth and uniformity fulfilling the main requirements for the fabrication of high-quality thin films. However, ALD processes strongly depend on the performance of the applied precursors. Therefore, the rational design and development of metalorganic compounds comprising optimal physico-chemical characteristics remains a key factor for ALD-based research. Over the years, various Y metalorganic precursors have been developed for ALD processes mainly focusing on homoleptic complexes such as β-diketonates [$Y(thd)_3$], silylamides [$Y(tmsa)_3$], amidinates [$Y(dpamd)_3$], guanidinates [$Y(dpdmg)_3$] or cyclopentadienyls [$Y(Cp)_3$]. Some of these compounds have high melting points, low volatility, reactivity or thermal stability which, in most cases, can be tuned through side-chain variations of the ligand moieties.

Another promising approach is to employ mixed ligand systems to form heteroleptic substituted compounds, ideally combining the characteristics of the respective homoleptic analogues. In earlier reports, RE precursor systems with combination of ligands were demonstrated by Leskelä *et al*[4] and Lansalot-Matras *et al*[5] where liquid precursors were successfully employed for RE oxide thin films. These approaches encouraged us to design and develop new metalorganic Y complexes with advantageous physico-chemical properties such as a high volatility, reactivity and stability thus ensuring applicability in ALD processes.

In our study, we focused on the guanidinate and amidinate ligand classes which provide pronounced reactivity toward co-reactants such as water through their Y-N bonds in combination with the cyclopentadienyl ligand, possessing good thermal stability due to the formation of robust leaving groups. Herein, we present a rational development and detailed characterization of new, spectroscopically pure heteroleptic and monomeric yttrium cyclopentadienyl guanidinate and yttrium cyclopentadienyl amidinate precursors for ALD processes of Y-based thin film materials.

AF1-MoP-14 Gallium ALD Precursor Development based on Mechanistic Study*, M Foody, Y Zhao,* ***Adam Hock***, Illinois Institute of Technology

Low temperature deposition of Ga_2O_3 remains a challenge, particularly in the absence of energetic oxygen sources (e.g. plasma or ozone). This is somewhat surprising given the close chemical relationship of aluminum to gallium. For example, trimethylaluminum is an incredibly well-behaved ALD precursor combined with a variety of oxygen sources, trimethylgallium requires the energetic reagent ozone as an ALD partner. We have synthesized a variety of gallium precursors that span the potential chemical space for gallium, e.g. 4, 5, and 6-coordinate complexes, alkyl, amide, and other ligands, etc. and conducted in depth mechanistic analyses of the potential ALD chemistry.

In this talk we discuss the effect of ligand coordination number, identity (N vs C, etc), and ALD partner reagent on nucleation and growth of gallium oxides. This includes QCM measurements under ALD conditions, solution model reactions, and synchrotron studies conducted at the Advanced Photon Source (APS) located at Argonne National Laboratory. The surface reaction of Ga precursors and half-reaction with oxygen sources were also observed by X-ray absorption spectroscopy (XAS). We have found that nucleation of GaOx growth can be achieved on a variety of substrates, however sustained growth of Ga_2O_3 requires forcing conditions for some

precursors. The results of these studies were applied to improved gallium oxide processes, including doping strategies. Film characterization will also be discussed as time allows.

AF1-MoP-15 Fluorine Doping of Aluminium Oxide Through In-situ Precursor Synthesis: Theory, Design and Application.*, Ben Peek,* University of Liverpool, UK

Fluorine doped metal oxides are technologically important as conducting thin films, for applications in photovoltaics, flat panel displays, mem resistive devices and power semiconductors. Conventional precursor sources for F-doping involve the use of harmful or toxic reagents such as hydrofluoric acid. Use of these precursors presents challenges in terms of handling and disposal.

Here we report a novel method to synthesise a fluorine precursor, $FAl(CH_3)_2$ in-situ, using mechanisms like those found in atomic layer etching. The method involves a pre-reaction between $Al(CH_3)_3$ and AlF_3 powder to generate the $FAl(CH_3)_2$ immediately before it is injected into the ALD reactor chamber. The intermediate fluorine product has been isolated and analysed using ^{19}F NMR. The effects of key process parameters, including the $Al(CH_3)_3$ dosing and AlF_3 powder bed temperature have been assessed and optimised. The design and fabrication of a system to generate the precursor is presented.

We demonstrate how the precursor has been exploited for the fluorine-doping of aluminium oxide grown by atomic layer deposition. The F-doped Al_2O_3 films have been characterised using low energy ion scattering as a probe of the surface and through-thickness distribution of fluorine in the doped films. This approach is used to elucidate the incorporation mechanisms and the composition of deposited materials.

This in-situ precursor generation technique, potentially opens new routes to doping of a wider range of ALD thin film materials. The full potential of the approach is discussed and other doped systems are considered.

ALD Fundamentals
Room Evergreen Ballroom & Foyer - Session AF2-MoP
Precursor Selection and Growth Optimization Poster Session

AF2-MoP-1 Atomic Layer Deposition of Cyclopentadienyl Based Hf Precursor With Various Oxidants*, **Jooho Lee**, D Kim, W Noh,* Air Liquide Laboratories Korea, South Korea

In electronic devices, a hafnium based oxide film has drawn a lot of attention, because it is a potential High-k material that can replace SiO_2 in a conventional transistor. Recently, hafnium based oxide films can be used for other applications, such as next generation DRAM capacitors and NAND flash memories. HfCl4 was one of the best precursor candidates for a HfO_2 film, however, there are some issues related to corrosive halide ligands, low vapor pressure, difficulty in delivering a solid precursor. In order to solve those issues, $Hf(RCp)(NMe_2)_3$ (R = H, Me), which are chlorine free precursors, were proposed. In this work, these precursors were evaluated for physical properties and ALD processes. Both precursors showed high thermal stability and clean evaporation in TG. $Hf(Cp)(NMe_2)_3$ and $Hf(MeCp)(NMe_2)_3$ have high vapor pressure (1 Torr at 90°C) and low viscosity (9 cP at 30°C). According to ALD evaluation, both precursors obtained high ALD windows up to 360 - 370°C with a growth rate of 0.9 - 1.0 Å/ cycle with ozone and a growth rate of around 0.5 Å/ cycle with water. X-ray photoelectron spectroscopy (XPS) showed that deposited thin films were pure, carbon and nitrogen impurities were below the detection limit. Step coverage of the film was excellent (~100%, AR= 1:40) at 360°C.

AF2-MoP-2 Atomic Layer Deposition of Magnesium Oxide Thin Films by using Bis(ethylcyclopentadienyl)Magnesium Precursor and H_2O, O_2 Plasma and O_3 Reactants*, **Moo-Sung Kim**, S Lee,* Versum Materials Korea, Republic of Korea*; S Ivanov,* Versum Materials, Inc.

Since MgO has high temperature stability, wide band gap, insulating, and diffusion barrier properties, it has been studied to use as a cathode coating layer in Li-ion battery, buffer layer for superconductors, high-k gate dielectric and ferroelectric non-volatile memory, a dopant for High K capacitors, etc.

In this work, deposition of magnesium oxide (MgO) thin films was conducted with liquid precursor Bis(ethylcyclopentadienyl) magnesium ($Mg(EtCp)_2$) and various reactants such as H_2O, O_2 plasma and O_3 by using atomic layer deposition (ALD) method. The MgO films were analyzed by ellipsometry, transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and X-ray reflectivity (XRR) to compare step coverage, chemical composition, crystallite orientation as well as film density of the films deposited with three different reactans.

ALD characteristic saturation behavior was observed for H_2O and O_2 plasma processes between 200 and 300°C with Mg saturation pulse time 1 sec and 1.5 sec, respectively. GPC of MgO at 250°C was 1 A/cy with H_2O and O_2 plasma processes. In the case of O_3 process, however, ALD characteristic saturation behavior was only observed above 250°C. MgO deposition rate was constant between 200°C and 300°C for O_2 plasma process only. MgO deposition rate was decreased with temperature in the case H_2O process, and was increased with the temperature in the case of O_3 process.

MgO films deposited with water thermal ALD and O_2 PEALD exhibited good stoichiometric composition about Mg:O = 1 : 1 with low carbon content and excellent step coverages at the deposition temperatures between 200 and 300°C. MgO film density with XRR was ~3.6g/cc at most deposition conditions. However, in O_3 process at 200°C, a large amount of carbon (~ 13%) was detected, which also led to poor step coverage (~ 68%). XRR density was less than 2.5g/cc, lower than other deposition conditions. In addition, it showed no MgO XRD peak suggesting deposition of amorphous film. On the contrary, O_3 process at 300°C showed sharp and strong MgO XRD peak with (200) dominant orientation, and film density was ~3.5g/cc, similar to H_2O and O_2 plasma processed MgO films.

In summary, we have demonstrated MgO ALD with $Mg(EtCp)_2$ and 3 types of reactants, H_2O, O_2 plasma, and O_3. Most conditions showed stoichiometric film composition, and good step coverage. Only O_2 plasma process showed constant ALD rate between 200 and 300°C. O_3 process below 250°C showed high carbon and oxygen content in the film, lower film density and poor step coverage. However, at 300°C, similar films were deposited with all three reactants.

AF2-MoP-3 Comparative Study between $CpTi(OMe)_3$ and $CpTi(NMe_2)_3$ for Atomic Layer Deposition of Titanium Oxide*, **Jaemin Kim**, S Kim, R Hidayat, Y Choi, H Kim, W Lee,* Sejong University, Republic of Korea

Titanium oxide (TiO_2) and titanium-based perovskites have been attracting attention as capacitor dielectric materials for the next-generation DRAM. Atomic layer deposition (ALD) is used as a deposition method because it can prepare conformal films over high-aspect-ratio capacitor structures. Titanium precursors capable of high-temperature ALD process were studied to produce high-quality TiO_2 films with excellent step coverage. The most common ALD precursors, tetrakis(dimethylamino)titanium and titanium tetraisopropoxide, showed low ALD temperatures due to their insufficient thermal stability. Heteroleptic titanium precursors having a cyclopentadienyl (Cp) ligand that binds strongly to titanium have been reported to increase the ALD process temperature [1]. There are two types of the titanium precursors with a Cp ligand: alkylamines having dimethylamino (NMe_2) ligands and alkoxides having methoxy (OMe) ligands. However, no direct comparison between two types of precursors and ALD processes using them has been reported. In the present study, an alkylamine-type heteroleptic precursor, tris(dimethylamino) cyclopentadienyl titanium [$CpTi(NMe_2)_3$], and an alkoxide-type heteroleptic precursor, trimethoxy cyclopentadienyl titanium [$CpTi(OMe)_3$], were comparatively studied. Ozone was used as an oxidizing agent for ALD TiO_2. The saturation doses of both precursors were measured at different temperatures to determine the ALD temperature window. The results showed that $CpTi(OMe)_3$ has better reactivity and thermal stability compared to $CpTi(NMe_2)_3$., which is explained by density functional theory calculations. Both precursors showed excellent step coverage and relatively wide bandgap at the temperature at which the thin film grows only by the ALD reaction. However, the poor step coverage and narrow bandgap were observed at temperatures at which the CVD reaction occurred due to the thermal decomposition of the precursor. Therefore, a titanium precursor capable of a high-temperature ALD process is essential, and the alkoxide-type titanium precursor is superior to the amine-type titanium precursor.

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AF2-MoP-4 Tin Nitride Atomic Layer Deposition using Hydrazine*, **Ann Greenaway**, A Tamboli, S Christensen,* National Renewable Energy Laboratory

There is substantial lag in the development of atomic layer deposition (ALD) processes for nitridescompared to the high-quality, conformal oxides for which ALD has become the standard. A major factor in this disparity is the ready availability of highly reactive oxygen sources (mainly H_2O, O_2, and H_2O_2). High-energy nitrogen precursors are similarly required for the

efficient incorporation of nitrogen in a film. Ammonia has often been used in conjunction with metal chlorides but requires relatively high temperatures for thermal ALD. Plasma-enhanced ALD can utilize molecular nitrogen as a precursor but can reduce film conformality on complex supports and damage the underlying substrate.

Hydrazine (N_2H_4) is an alternative precursor which has been rarely explored for the fabrication of nitrides in ALD, but which is experiencing a surge in popularity due to its high reactivity, which enables the deposition of nitrides as-yet undemonstrated by ALD.[1] The added reactivity and volatility of liquid hydrazine may enable new reaction mechanisms, lower deposition temperatures, and conformality for high aspect ratio applications.

Sn_3N_4 is a metastable semiconductor which shares a crystal structure with its analog, Si_3N_4; unlike Si_3N_4, Sn_3N_4 has only recently been grown by ALD,[2] being synthesized much more often through reactive sputtering.[3] As a binary, Sn_3N_4 has applications as a battery anode material, for photoelectrochemistry, and optoelectronic devices. We will report progress on the deposition of Sn_xN_y films from tetrakis(dimethylamido) tin (TDMASn) and N_2H_4. Growth per cycle of this material (determined by x-ray reflectivity) is 0.4 Å at 200 °C, similar to the sole report of Sn_3N_4 from PE-ALD,[5] despite films being substantially Sn-rich. Identification of ALD growth window and self-limiting deposition characteristics are underway; initial testing indicates a competing chemical vapor deposition process which can be eliminated with adequate tuning of pulse/purge characteristics. A comparison of film conductivity and optical absorption at different growth temperatures will be presented. General issues of N_2H_4 purity and routes to prevent or control oxynitride formation will be discussed.

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AF2-MoP-5 Growing Polycrystalline Indium Oxide Film by Atomic Layer Deposition, ***Chien-Wei Chen,*** ITRC, NARL, Republic of China

In light-emitting diode (LED) and thin film transistors (TFT) displays industry, In_2O_3 could be a high quality transparent conducting oxide (TCO) layer for enhancing the optical and electrical properties. Therefore, thickness control and uniformity of the film is important in the preparation of ultra-thin In_2O_3 film. In this study, the uniform polycrystalline In_2O_3 films were successfully grown on the 4" silicon(100) substrate at 300℃. Trimethylindium (TMI) and water were chosen as the metal and non-metal precursors, respectively. The In_2O_3 growing temperature is between 100℃ to 300℃ and the growth rate per cycle (GPC) increases and the surface roughness reduces with the temperature increasing. The GPC of In_2O_3 film grown at 300°C is 0.5Å and the refractive index n is found to be 1.98 at the wavelength of 632 nm which is close to the bulk. The linear growth rate of In_2O_3 and saturation behavior of TMI with different pulse time is shown in Fig.1 and Fig.2, respectively. Fig.3 (a) shows the TEM cross sectional image of In_2O_3 grown at 300°C. The lattice stacking shown in Fig.3 (b) presents the formation of poly crystalline In_2O_3 film.

AF2-MoP-6 Low Temperature Tin Oxide by Atomic Layer Deposition, ***Yu-Chiao Lin****, B Liu, Y Yu, C Kei, C Lin,* National Applied Research Laboratories, Republic of China

Tin oxide (SnO_2) has attracted lots of attention because of its excellent chemical, electrical, and optical properties. SnO_2 films were deposited on Si(100) substrates by home-build atomic layer deposition (ALD) using tetrakis dimethylamino tin (TDMASn) as metal precursor and H_2O as oxidant at low substrates temperature. Low temperature SnO_2 ALD process is especially important due to low thermal budget consideration for thermally sensitive materials such as organic light emitting diodes and photovoltaic cells. Thickness and refraction index of SnO_2 films were determined by ellipsometry. The surface morphology and cross-sectional image were observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), respectively. As shown in Fig. 1, the growth rate of SnO_2 thin film at 150 °C was saturated about at 1.65 Å/cycle when TDMASn pulse time is larger than 0.7 s. The growth rate of SnO_2 thin film increased to about 2.55 Å/cycle as the substrate temperature was decreased to 50 °C. Top-view SEM image in Fig. 2 shows uniform SnO_2 thin films were deposited on Si wafer. Cross-section HRTEM image in Fig. 3 shows that the dense and continuous SnO_2 thin films of 32.4 nm at very low substrate temperature (50 °C).

AF2-MoP-7 Dielectric ALD with Hydrogen Peroxide: Comparitive Study of Growth and Film Characteristics for Anhydrous H_2O_2, H_2O_2/H_2O Mixtures and H_2O, ***Daniel Alvarez,*** RASIRC*; K Andachi, G Tsuchibuchi, K Suzuki,* Taiyo Nippon Sanso Corporation*; J Spiegelman,* RASIRC

ALD of dielectrics requires new precursor chemistries. Development efforts have focused on new Organometallic, Organosilicon and Organoaluminum precursors. Our research focus has been on oxidants, and specifically hydrogen peroxide reactivity. Due to this reactivity, hydrogen peroxide use may allow lower deposition temperatures and achieve distinct properties in the resulting film when compared to other oxidants. Our research study uses:

1. Gas-phase hydrogen peroxide, delivered from an anhydrous, ampoule-based formulation by use of a membrane delivery system.
2. High concentration H_2O_2/H_2O delivery by *in situ* concentration methods and use of a membrane vaporizer as a gas generator.

Initial results for ALD growth of ZrO_2 from anhydrous H_2O_2 and $CpZr(N(CH_3)_3)$ exhibit high quality growth of film at 260° C. Minimal saturation delay and a linear growth curve were observed. XPS and XRR were used to characterize ZrO_2 composition, showing significant similarities to films grown using ozone. Subsequently, films grown using ALD and H_2O_2 were placed into MIMCAP structures, which had high k values measured at 35. This was a slight improvement over films grown with 20% ozone concentration which had high k values of 32.

Novel Gas Generator

Our approach involved development of a novel gas generator that delivers H_2O_2/H_2O mixtures. A carrier gas is connected to this generator, which delivers up to 5% H_2O_2/21% H_2O gas by volume from 30wt% H_2O_2 liquid solution (H_2O/H_2O_2=4.2). This gas mixture enables SiO_2 films to be grown at highly reduced temperature compared to water. Testing was done with tris(dimethylaminosilane) $(N(CH_3)_2)_3SiH$ and H_2O_2/H_2O. SiO_2 was deposited at temperatures at least 200° C lower with the hydrogen peroxide mixture than with water.

For Al_2O_3 ALD, initial results show that anhydrous H_2O_2 generates higher density films with better initial nucleation as measured by *in situ* XPS. The presentation will compare Al_2O_3 film characterization for anhydrous H_2O_2, H_2O_2/H_2O mixtures and water. Data will be reported on wet etch rates, refractive index and capacitance.

AF2-MoP-8 Atomic Layer Deposition of Carbon Doped Silicon Oxide and Effect of Thermal Treatment or Hydrogen Plasma Treatment on The Films, ***Meiliang Wang****, H Chandra, X Lei, A Mallikarjunan, K Cuthill, M Xiao, M Rao,* Versum Materials, Inc.

Atomic Layer Deposition (ALD) of silicon oxide is commonly used in the semiconductor industry for its excellent thickness control and conformality. For some applications, films deposited at low temperatures with low wet etch rate or low dielectric constant (k) are required. Carbon doping is a known method to reduce the wet etch rate as well as the k value of the silicon oxide film. In this paper, ALD SiO_xC_y films were studied. The impact of oxidant concentration and deposition temperature on the carbon content, WER, k value and other properties of the deposited film, with and without post deposition annealing and post deposition hydrogen plasma treatment is discussed.

In ALD conference 2017[1], the impact of the precursor design for the number of Si-CH_3, Si-N and Si-H bonds on the reactivity, carbon content, and dHF WER of the deposited films were reported. It was demonstrated that precursors with only one Si-CH_3 bond substitution, eg. di-iso-propylaminomethylsilane (DIPAMS), could deposit silicon oxide film with a relatively high GPC and carbon doping up to 10 at. %. In this report, a new organosilane precursor "Precursor V" is designed and it provides higher reactivity and higher carbon content and lower WER than DIPAMS, films with up to ~20 at. % C are obtained. With thermal annealing at 600 ℃, film k value reduced from ~6 to < 4, almost no etch after 10min in 0.5% dHF dip, while film carbon content showed no change, and film shrinkage was < 2%. FTIR spectra show decreased Si-OH peak, and increased Si-O-Si network peak, indicating that Si-OH to Si-OH crosslinked to form Si-O-Si linkage at 600 ℃. In contrast, by annealing at 800 ℃, the film carbon content is reduced significantly, from 17 at. % to 6 at. %, and the film density is increased from 1.5 g/cm^3 to 2.0 g/cm^3. A high shrinkage of ~25% was also observed from the 800 °C anneal, indicating a significant densification of the film with carbon removal. Direct hydrogen plasma treatment on the film was also studied. The film k value reduced from around 6 to < 4. The film develops a dense surface layer with higher WER, between 10-40 Å. However, WER of the bulk film remains unchanged compared to as-

deposited film. Corresponding to this observation, the film surface carbon is reduced, but the bulk film carbon content is kept constant. FTIR shows Si-OH decrease, Si-O-Si increase, and Si-H increase, indicating crosslinking of Si-OH bonds to form Si-O-Si network and generation of Si-H bonds during H_2 plasma treatment. The hydrogen plasma treatment forms a densified SiO_2 layer with removal of carbon near surface region and protecting the bulk film from carbon depletion.

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AF2-MoP-9 DFT Study on Atomic Layer Deposition of Al_2O_3 with Various Oxidants*, Seunggi Seo*, *T Nam,* Yonsei University, Republic of Korea*; H Lee,* Incheon National University, Republic of Korea*; B Shong,* Hongik University, Republic of Korea*; H Kim,* Yonsei University, Republic of Korea

Atomic layer deposition (ALD) is a vapor phase thin film deposition technique, which enables deposition of thin films with high material quality, good uniformity, high conformality, and sub-nanometer thickness controllability. Therefore, ALD has been regarded as one of the most suitable deposition technologies for semiconductor device fabrication. Since ALD is based on sequential self-limited reactions on surfaces, understanding the surface chemical reaction mechanism is crucial for development of ALD process.

ALD of Al_2O_3 has been widely investigated owing to its wide ALD temperature window, high vapor pressure of Al precursors such as trimethylaluminum (TMA), and wide applicability of Al_2O_3. It is known that the reaction between surface adsorbed precursors and reactants, and the resulting material properties of deposited Al_2O_3, are affected by the type of the oxidant. However, relatively small research effort has been focused on the chemical reaction mechanisms of each oxidants during ALD.

In this study, we investigate the reaction mechanism of various oxidants such as H_2O, H_2O_2 and O_3 during ALD of Al_2O_3 with TMA. Density functional theory (DFT) calculations at B97D3/6-311+G* level of theory were performed using Gaussian 09 suite of programs. Our results show that the methyl groups adsorbed on the surface can be oxidized into hydroxyls with all considered oxidants with ease. The number of oxidant molecules required for the reaction is one for H_2O, and two for O_3 or H_2O_2. According to the activation energy of the considered reactions, it is suggested that O_3 is the most reactive oxidant for Al_2O_3 ALD with TMA.

AF2-MoP-10 Effect of Heteroleptic Structure on Atomic Layer Deposited HfO_2 Using $Hf(N(CH_3)_2)_4$ and $CpHf(N(CH_3)_2)_3$ Precursors*, Sung Min Park*, *B Park, S Lee, H Yoon,* Yonsei University, Republic of Korea*; M Lee, S Kim,* Yeungnam University, Republic of Korea*; H Kim,* Yonsei University, Republic of Korea

With scaling down of complementary metal-oxide semiconductor (CMOS), atomic layer deposition of HfO_2 is a key technology for ultra-thin and high-*k*gate dielectrics. To obtain high-quality HfO_2 and good devices performances, various Hf precursors, such as Hf halides, alkylamides, and alkoxides, have been employed. However, these precursors have clear limitations such as low reactivity of halides and alkoxides and poor thermal stability of alkylamids. Recently, heteroleptic precursors have been investigated as alternatives to the existing homoleptic precursors. Among them, partial substitution with a cyclopentadiene (Cp)-based ligand has been reported to control volatility and thermal stability of the precursor. Despite of the promising usages, there is still lack of systematic studies on the film properties associated with growth characteristics of ALD HfO_2 using Cp-containing precursors.This could be due to the complexity of the Cp-containing precursors, which makes difficult to conduct theoretical studies to support the growth mechanism.

In this study, we investigated the effects of substituting Cp ligands for high-*k*properties of ALD HfO_2 by using $Hf(N(CH_3)_2)_4$ and $CpHf(N(CH_3)_2)_3$. The Cp ligand improved the thermal stability of precursor to withstand thermal decomposition up to 350 °C, but decreased the saturated GPC in the ALD window. The growth characteristics were discussed with the theoretical calculations utilizing geometrical information on the precursor and density functional theory. In addition, we analyzed the chemical composition such as C impurities and oxygen vacancies through XPS and the microstructure such as crystallinity, density, and interlayer through XRD, XRR and TEM. These results were comparatively studied in relation to the electrical properties of ALD HfO_2. This study can provide researchers with a broad insight to select proper precursor for the fabrication of high quality dielectric layer in future nanoscale devices.

AF2-MoP-11 Effect of Co-Reactant on the Atomic Layer Deposition of Copper Oxide*, Jason Avila*, *N Nepal, V Wheeler,* U.S. Naval Research Laboratory

Atomic layer deposition (ALD) of copper oxide presents a powerful opportunity to grow p-type semiconductor material for a wide variety of applications such as transparent conducting oxide, solar fuels catalysis, and power devices. There are, however, very few ALD processes to facilitate the growth of copper oxide. Cu(II) bis(dmiethylamino-2-propoxide) (Cudmap) has previously been used to grow copper metal using a reducing source such as tertiary butyl hydrazine.[1,2] Cudmap has also been demonstrated to grow Cu_2O using water as a co-reactant, self-reducing from Cu(II) to Cu(I) in the presence of water.[3] This study will examine the effect of ALD co-reactants, ozone and water, on the copper oxidation state of copper oxide films grown using Cudmap.

Copper oxide films were grown in a Veeco Savannah ALD reactor using Cudmap and ozone or water at 150 °C on Si and c-plane sapphire. This is the first experimental demonstration of CuO films using Cudmap and ozone. Using ozone, a growth rate of 0.18 Å/cycle was achieved at 150 °C, far higher than the measured growth rate of 0.04 Å/cycle when growing with water. Additionally, XPS was able to confirm only the Cu(II) oxidation state with a Cu/O ratio of 1 verifying CuO films. For comparison, films grown with water show the presence of only Cu(I) oxidation state and have a nearly stoichiometric with a Cu/O ratio of 2:1. AFM also indicated uniform film growth as low as 2 nm independent of co-reactant, with CuO films grown with ozone being rougher than Cu_xO films grown with water. Initial optical and electrical properties of the films will be examined for p-type semiconductor applications.

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AF2-MoP-12 A Systematic Study on Atomic Layer Deposition of ZrO_2 Thin Films*, X Wang, J Cai, Xiangbo Meng,* University of Arkansas

Zirconium oxide (ZrO_2) is an attractive material with many applications because of its excellent mechanical, thermal, optical, and electrical characteristics [1-3]. ZrO_2 can present three crystalline structures, i.e., monoclinic (below 1170 °C), tetragonal (1170-2370 °C), and cubic (above 2370 °C) [1]. To synthesize ZrO_2 nanomaterials, there have to date many methods developed. ALD is a unique thin-film technique, featuring its tremendous capabilities for depositing conformal and uniform thin films with the atomic preciseness [4, 5]. Using Tetrakis(dimethylamido)zirconium and water as precursors, previous studies [6, 7] have deposited ZrO_2 on carbon substrates in the range of 100 – 250 ^{o}C. However, these studies have not fully investigated the growth mechanism and film characteristics of the ALD ZrO_2. Applying *in situ* quartz crystal microbalance (QCM), in this study we optimized growth parameters and then further studied the growth characteristics in the range of 50 – 275 ^{o}C. We found that the growth rate of the ALD ZrO_2 decreases with increasing temperature in the range of 50 – 225 ^{o}C, but the growth of the ALD ZrO_2 at 250 and 275 ^{o}C terminated after the first several ten cycles. Furthermore, we applied synchrotron-based techniques to study crystallinity and film thickness of the ALD ZrO_2 deposited at different temperatures, including X-ray diffraction and X-ray reflectivity. In addition, we studied the films' composition using X-ray photoelectron spectroscopy, observed the films' morphology using scanning electron microscopy, and analyzed the films' structure using transmission electron microscopy. These studies provided us an integral understanding on the growth mechanism and films' characteristics of ALD ZrO_2.

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AF2-MoP-13 Hydrophobic SiO_x Thin Film Deposition using Low-Temperature Atomic Layer Deposition*, **Taewook Nam**, H Kim,* Yonsei University, Republic of Korea

A hydrophobic coating has been widely used in various applications from passivation coating on electronics to medical or even pharmaceutical devices. In many applications, organic material coatings such as fluorocarbon or hydrocarbon compounds have been used for hydrophobic coating due to their low material cost, simple coating process, and chemical stability. However, organic coatings have several disadvantages in practical applications, chiefly their inherently poor mechanical durability and thermal stability. Hydrophobicity was also found in a few inorganic metal oxides. However, hydrophobicity using inorganic metal oxide was not retained after high-temperature annealing or UV exposure because of the generation of the surface hydroxyl group. To overcome these problems, hydrophobic coating using rare-earth oxide (REO) was reported. Although its superior thermal and chemical stability, however, REO is expensive because of its scarcity and has some deleterious effects on the human body. In addition, the relatively high process temperature is an obstacle for coating on a thermally fragile substrate, such as fabric or polymer substrate. Therefore, it is highly required to fabricate a hydrophobic surface with low cost and safety material at low temperature.

Silicon oxide (SiOx) is a well-known material in semiconductor industries. Since it can be easily formed by using vapor deposition, exhibiting good chemical, mechanical, and electrical properties, it has been greatly investigated for various applications. SiOx is inherently hydrophilic material because of the presence of silanol (Si-OH) groups on the surface. Therefore, it is hard to make a hydrophobic surface of SiOx without surface treatment or functionalization.

In this study, hydrophobic ALD SiOx was obtained at the low growth temperature without any post-treatment. The water contact angle of ALD SiOx grown at 50 °C is 94 °. However, when the growth temperature is 100 and 150 °C, the water contact angles were decreased to 74 and 53 °, respectively. This hydrophobic characteristic of ALD SiOx was retained after the annealing at 300 °C. To analyze this phenomenon, various analysis including XPS and AFM had proceeded. To obtain superhydrophobicity, ALD SiOx was coated on the silicon nanowire (SiNW) at 50 °C. On SiOx-coated SiNW, superhydrophobicity is observed for water, blood, and 10 wt% ethanol solution. Owing to its low process temperature, hydrophobic SiOx can be also coated on the thermally fragile cloth, cotton or spandex, for instance, enhancing the waterproof characteristics. The detailed experimentation and origin of hydrophobicity of low-temperature ALD SiOx will be discussed.

AF2-MoP-14 Characteristics of High-temperature ALD SiO_2 Thin Films Using a Si Precursor with Excellent Thermal Stability*, **Jae-Seok An**, J Park, M Nim,* Hansol Chemical, Republic of Korea*; Y Kim, J Gu, S Kim,* Sejong University, Republic of Korea*; J Seok, J Park,* Hansol Chemical, Republic of Korea*; W Lee,* Sejong University, Republic of Korea

In recent years, technologies for stacking semiconductor devices in three dimensions have been introduced as a method for overcoming the limitations of the two-dimensional scaling of devices. Thus, there is an increasing interest in atomic layer deposition (ALD) which can deposit thin films with excellent conformality in high-aspect-ratio three-dimensional patterns. In particular, SiO_2 and SiN thin films used as tunneling oxide, trap layer, and blocking oxide in 3-dimensional vertical NAND devices must have excellent step coverage in channel hole as well as good physical and electrical characteristics. In the conventional ALD processes of silicon oxide, the physical and electrical properties of the deposited thin film are improved as the deposition temperature increases, however, at high temperatures above 500°C, the thermal decomposition the Si precursor occurs, resulting in poor step coverage and film properties [1]. In the present work, we developed an ALD process using a Si precursor with excellent thermal stability, which does not cause a step coverage degradation due to thermal decomposition up to 750°C. The thermal decomposition of the Si precursor was evaluated by examining the growth rate change with the feeding time of Si precursor at 600°C or higher temperatures. The step coverage, composition, density, and leakage current of silicon oxide films deposited at different temperatures were investigated and compared with thermal oxide. The effects of the oxidizing agent on the deposition kinetics and the film properties were also investigated and discussed.

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AF2-MoP-15 Developing Routes Toward Atomic Layer Deposition of Tungsten using Fluorine-Free W Precursor and Various Reactants with Density Functional Theory*, **Tae Hyun Kim**, D Nandi, M Lee,* Yeungnam University, Republic of Korea*; R Hidayat, S Kim, W Lee,* Sejong University, Republic of Korea*; S Kim,* Yeungnam University, Republic of Korea

The W-ALD process using WF_6 is applied to the fabrication of the nucleation layer for W-plug and W gate or bit line in the current semiconductor device manufacturing. However, the highly corrosive nature of the F contained in the precursor, damages the underlying oxide and metal film, and degrade the electrical characteristics and reliability of the device. Therefore, it is necessary to develop an ALD process with F-free W (FFW) precursor. In this study, $EtCpW(CO)_3H$ is selected as a FFW metal-organic precursor, while suitable reactants (reducing agents) among various ones, molecular H_2, H_2 plasma (which provides highly reactive H radical), trimethyl aluminum triethyl aluminum, TBH (tert-butyl hydrazine), diethylamineborane (DEAB), dimethylamineborane (DMAB) NH_3 etc. are adopted based on the density functional theory (DFT) calculation. Following the DFT predictions, successful ALD-W films are prepared using the reducing agents diethylamineborane (DEAB) and H_2 plasma at a deposition temperature of 325°C. The growth rate observed using DEAB reactant is ~1.3Å /cycle. On the other hand, H_2 plasma, as a reactant, offers relatively lower growth rate of ~ 0.4 Å/cycle. The crystalline and amorphous phase of the as-deposited W films are confirmed using X-ray diffraction (XRD) for H_2 plasma and DEAB, respectively, Furthermore, the XRD reveals a mix-phase of β-W and tungsten carbide (WC) for the films grown by H_2 plasma and the X-ray photoelectron spectroscopy analyses confirm considerable impurities (Boron, Carbon, Nitrogen, Oxygen) in the films grown by DEAB. However, a post-annealing could further improve the properties of these films.

AF2-MoP-16 ALD HfO_2 with Anhydrous H_2O_2 in a 300 mm Cross-flow Reactor – Comparison with H_2O and O_3 Oxidants*, **Steven Consiglio**, R Clark, C Wajda, G Leusink,* TEL Technology Center, America, LLC

HfO_2-based dielectrics deposited by ALD have been utilized in CMOS manufacturing since the 45 nm node [1]. In addition to applications of ALD HfO_2-based dielectrics in CMOS and DRAM, the recent discovery of ferroelectricity in HfO_2-based dielectrics [2] shows promise for applications in emerging non-volatile memory [3] and neuromorphic computing [4]. Thus, improving and modifying the growth of ALD HfO_2 is of significant industrial interest.

For ALD growth of HfO_2, H_2O and O_3 are the most commonly used oxidants. The drawbacks of H_2O include low oxidative reactivity and strong adsorption to surfaces in the deposition chamber which requires long purge times. Although the use of the strong oxidant O_3 in ALD typically uses reduced cycle times compared to H_2O, O_3 exposure can lead to unwanted oxidation of the underlying substrate which can significantly impact final device properties. In this regard, H_2O_2, which has an oxidation potential greater than H_2O but less than O_3, is an attractive candidate as an alternative oxidant for ALD growth of metal oxides.

In this study we evaluated a source for anhydrous H_2O_2 delivery which overcomes some of the drawbacks of H_2O_2/H_2O solutions, which have a low concentration of H_2O_2 in the vapor phase. The novel source and delivery system (RASIRC® BRUTE™ Peroxide) consists of > 99% H_2O_2 dissolved in non-volatile solvent passed through a tubular membrane which is selective to H_2O_2.[5-7]

By optimizing the hardware and delivery setup to minimize vapor phase H_2O_2 decomposition and depletion effects, we were able to demonstrate uniform ALD HfO_2 growth across a 300 mm wafer in a cross-flow deposition chamber. In order to compare the performance of H_2O_2 with the other commonly used oxidants, we compared ALD HfO_2 growth with well-established processes using H_2O and O_3 [8]. Dose dependence of H_2O_2 was investigated to determine reactant saturation. Using a saturated H_2O_2 pulse we obtained > 50% increase in growth-per-cycle compared to both H_2O and O_3 while also significantly improving within-wafer-uniformity. Further optimization of purge times and carrier Ar flow rate achieved a reduced cycle time for H_2O_2 process which was > 50% less than the cycle time required for H_2O process and approaching the optimized cycle time for the O_3 process.

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AF2-MoP-17 Atomic Layer Deposition of Copper (I) Chloride using Liquid 1-Chlorobutane Precursor, ***Richard Krumpolec**, D Cameron, D Bača, J Humlíček, O Caha,* Masaryk University, Czech Republic

Zinc blende-structure γ-copper (I) chloride is a wide, direct bandgap semiconductor with the potential for applications in UV optoelectronics. Atomic layer deposition has previously been applied to deposition of copper chloride CuCl thin films and nanocrystallites [1,2]. The ALD-like process was reported using solid precursors [Bis(trimethylsilyl)acetylene]-(hexafluoroacetylacetonato)copper(I) and Pyridine HCl [3]. In this paper, we worked with anhydrous 1-Chlorobutane as a Cl precursor for deposition of CuCl thin films. The advantage of this liquid precursor is high vapour pressure enabling short pulsing times. The CuCl films were deposited on crystalline silicon with different pretreatment protocols and also on flexible polyimide polymeric substrates. The structural, chemical, optical and photoluminescent properties of CuCl thin films were studied by SEM, XRD, AFM, XPS, optical reflectance and photoluminescence. Figure 1 shows the SEM images of a layer of CuCl crystallites on a silicon substrate cleaned by RCA protocol and deposited using liquid 1-Chlorobutane. The deposition using a liquid 1-chlorobutane precursor is compared to the process using previously reported solid Pyridine hydrochloride precursor.

Figure 1: SEM images of a layer of CuCl crystallites on a silicon substrate cleaned by RCA protocol.

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AF2-MoP-18 Number Effect of Si Atoms Contained in Precursor for SiN Atomic Layer Deposition, ***Seungbae Park**, H Ji, H Yang, S Yoon,* DUKSAN Techopia company, Republic of Korea*; I Park,* Hanyang University, Republic of Korea

Silicon nitride (SiN) films have been widely applied to the in solid-state devices as functional and process layers. The examples include charge trap layer in flash memory, gate dielectric layer in thin film transistors. gate spacer in FinFET transistor, etch stop layer in CMP, and capping layers in interconnection. The requirements of thin and smooth film, its uniform thickness and composition distribution, and high conformal coating on complicated structure have allowed ALD method to be widely introduced to make SiN films. In SiN-ALD process, the selection of Si precursor is significant because of the variability of film characteristics such as growth rate and material/dielectric/electrical properties. In this work, the number of Si atoms in precursor has focused on fabricating SiN-ALD films to investigate its linkage to growth and materials properties of SiN films.

Three precursors of SiCl4, Si2Cl6, and Si3Cl8 were used as Si source for ALD for the model materials with the 1, 2, and 3 Si atoms. The ALD-SiN were performed at plasma system with NH3 reactant. For the growth rate of SiN, Si2Cl6 has the highest value of 1.44 A/cycle at the deposition temperature of 400 C. The Si : N ratio of all SiN films was analyzed by using XPS measurement, was the same with 1 : 1.16 near the surface, and kept constant with depth. The contamination of Cl and C was under the limit of XPS resolution. With the increase of Si number in precursor, the oxygen content in SiN was apparently reduced. The increased Si number make the SiN film much dense, and hence their wet etch rate against diluted HF solution was reduced from 0.55 A/sec to 0.36 A/sec for SiCl4 to Si3Cl8. The SiN film properties compared with Si numbers in precursor presented in this work will be useful for the fast and robust film formation.

ALD Fundamentals
Room Evergreen Ballroom & Foyer - Session AF3-MoP
Growth Mechanisms and In Situ Studies Poster Session

AF3-MoP-1 Langasite Crystal Microbalance (LCM) for In-situ Process Monitoring of ALD up to 440 º C, ***Masafumi Kumano**,* Tohoku University, Japan*; K Inoue,* Piezo Studio, Japan*; K Hikichi,* Technofine co. Ltd, Japan*; M Shimizu, S Tanaka,* Tohoku University, Japan

A quartz crystal microbalance (QCM) is often used as an in-situ monitoring tool for ALD process. The piezoelectric constant of quartz crystal starts to decrease at 300 º C and disappears at 573 º C . In addition, it's temperature coefficient of frequency (TCF) around the turn over temperature increases above 300 ℃ . Therefore, QCM is generally limited in use under 300 º C . In a higher temperature range, $GaPO_4$ is only a material practically used for a microbalance[1]. However, the crystal growth of $GaPO_4$ is not industrially established like quartz, and the crystal size is limited.

Langasite $Ca_3TaGa_3Si_2O_{14}$ is a new candidate for a high temperature microbalance. It keeps piezoelectricity in a wide temperature range without any phase transition, and a large crystal can be potentially grown in an industrial scale. Around the turnover temperature range, a Langasite crystal microbalance (LCM) shows a much smaller TCF than the conventional QCM (Fig. 1).

The Langasite has a dielectric constant about 5 times as larger as that of quartz. This must be taken into account of to use an available QCM oscillator circuit. As shown in Fig. 2, the active area of the LCM, i.e. the center part where the electrodes on both sides overlap, is smaller than that of the QCM. Fig. 3 shows the resonance impedance characteristic of the LCM. The resonance frequency is 6 MHz, and the electromechanical coupling factor is 2.6%. A weak spurious mode remains in Fig. 3, but it can be swept out by polishing the crystal surface to a convex shape.

The LCM was applied for TMA/H_2O cycle up to 440º C. The inside of a LCM holder is purged by pulsed pressure synchronized to the ALD cycle to avoid internal deposition. Transient temperature fluctuation is repetitive and reproducible over the ALD sequence and can be separated from a mass change by averaging over sequence numbers. The measured LCM frequency change by a mass change of each cycle is 1.6 Hz at 395º C and 2.2 Hz at 280º C, which is smaller than that of the QCM (3.5 Hz/cycle at 285 º C). The sensitivity is improved using a larger active area of LCM in conjunction with a dedicated oscillator circuit.

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AF3-MoP-2 In-Situ Process Monitoring of Precursor Delivery Using Infra-Red Spectroscopic Method, ***Robert Wright**, T Baum,* Entegris, Inc.

ALD processing is an increasingly critical deposition method for conformally coating high-aspect ratio features in advanced logic and memory devices. Accurate, consistent and controllable delivery of precursor materials to the deposition system is a necessity. To achieve reliable, low-cost deposition processes, *a sensitive and non-destructive real-time method for monitoring the precursor concentration is increasingly important. A*n IR method offers chemical specific information for both the reactant and the reaction by-products. An IR based system was developed and used to measure the 'direct' flux from a solid source in real time. The real-time measurement of precursor concentrations in the gas-phase can be applied to process monitoring, process control and towards the detailed characterization of key variables in the precursor delivery. Further, this method can be used to characterize ampoule performance under different pressure, temperature and flow conditions for a specific chemical precursor.

AF3-MoP-3 Quantitative Analysis of High-k ALD Precursors for Trace Elemental Impurities by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS), ***Jinjin Wang**,* Air Liquide Electronics – Balazs NanoAnalysis

The scaling of logic technology node following Moore's law has reached <10 nm. Consequently, high-k dielectrics are prevalent in modern microelectronic devices. They are insulating thin films of metal oxides, metal nitrides or other types of metallic compounds with much higher dielectric constant k ranging from 8 to 32, in contrast to SiO_2 with 3.9. These thin films are deposited from high-k dielectric precursors, which are organometallic or inorganic compounds, via atomic layer deposition (ALD) technology. The ALD allows growth of thin films of high conformity and uniformity downscaled to single nm. In order for these thin films to function in micro devices, the films must be free of contamination, especially elemental impurities that causes defects of microelectronic devices. Therefore, for quality control of the ALD process, all high-k precursors used must be completely free of elemental impurities. As a

result, each batch of high-k precursors is now analyzed for elemental impurities before it can be used in the ALD process.

ICP-MS is the preferred technique for analysis of these high-k precursors for trace metals at ppb and sub ppb level. High-k dielectric precursors generally contain a metal atom bound to a ligand or other organic components, and often react violently with water and moisture in atmosphere. Both metal and organic components create various matrix effects and mass interferences, both of which affect the accuracy of the precursor analysis. One of the matrix effects is known as "space-charge-effects" due to high concentration of the metal atom present in the precursor sample. The "space-charge-effects" suppress the signal of many elements of interested and result in low spike recovery and analytical accuracy. Two types of mass interferences result from both metal matrix and organic components, caused by polyatomic molecular ions and isobaric ion species. The polyatomic molecular ions include and are not limited to metal oxide, metal argide and metal carbide, formed by high concentration metal ions reacting with organic components and other species in the plasma. Doubly charged ions are another form of mass interferences that affect the analysis.

ICP-MS methods have been developed to reduce and eliminate all these matrix effects and mass interferences. The methods are able to drive detection limits (DL) low. We will present these low DL that we have improved. Our method capability analysis (MCA) showed that our analyses have low DL, good repeatability and accuracy as demonstrated by spike recovery experiments. The MCA also showed that the matrix effects and the mass interferences have significantly been reduced or eliminated.

AF3-MoP-4 Numerical Studies of the Fluid Dynamics and Chemical Kinetics of Spatial Atomic Layer Deposition of Al_2O_3*, Dongqing Pan,* University of North Alabama

Low throughput is a major limitation for industrial level atomic layer deposition (ALD) applications. Spatial ALD is regarded as a promising solution to this issue. With numerical simulations, this paper studies an in-line spatial ALD reactor by investigating the effects of gap size, temperature, and pumping pressure on the flow and surface chemical deposition processes in Al_2O_3 ALD. The precursor intermixing is a critical issue in spatial ALD system design, and it is highly dependent on the flow and material distributions. By numerical studies, it's found that bigger gap, e.g., 2 mm, results in less precursor intermixing, but generates slightly lower saturated deposition rate. Wafer temperature is shown as a significant factor in both flow and surface deposition processes. Higher temperature accelerates the diffusive mass transport, which largely contributes to the precursor intermixing. On the other hand, higher temperature increases film deposition rate. Well-maintained pumping pressure is beneficial to decrease the precursor intermixing level, while its effect on the chemical process is shown very weak. It is revealed that the time scale of in-line spatial ALD cycle is in tens of milliseconds, i.e., 15 ms. Considering that the in-line spatial ALD is a continuous process without purging step, the ALD cycle time is greatly shortened, and the overall throughput is shown as high as 4 nm/s, compared to several nm/min in traditional ALD.

AF3-MoP-5 Mechanistic Understanding of Dicholosilane Thermal Decomposition during Atomic Layer Deposition of Silicon Nitride*, Gyeong Hwang,* *G Hartmann,* University of Texas at Austin*; P Ventzek,* Tokyo Electron America Inc.*; T Iwao, K Ishibashi,* Tokyo Electron Ltd.

Silicon nitride (SiN) thin films have been widely employed for various applications including microelectronics, but their deposition presents a challenge especially when highly conformal layers are necessary on nanoscale features with high aspect ratios. Plasma-enhanced atomic layer deposition (PEALD) has been demonstrated to be a promising technique for controlled growth of SiN thin films at relatively low temperatures (< 400 °C), in which thermal decomposition of Si-containing precursors on a N-rich surface is a critical step. In this talk, we will present our recent findings regarding potential underlying mechanisms leading to facile thermal decomposition of dicholosilane (DCS, SiH_2Cl_2) on the N-rich SiN surface, based on periodic density functional theory calculations. Our study highlights the importance of high hydrogen content on the N-rich surface, rendering primary and secondary amine groups. When the N-rich SiN surface is fully hydrogenated, the molecular adsorption of DCS is predicted to be exothermic by 0.6 eV. In this case, DCS decomposition appears to be initiated by nucleophilic attack by an amine lone-pair on the electrophilic Si, leading to the formation of a DCS-amine adduct intermediate followed by release of a Cl- anion and a proton. The predicted activation barrier for the DCS decomposition reaction is only 0.3 eV or less, depending on its adsorption configuration. We will also discuss the formation and role of HCl, the subsequent formation and nature of Si-N bonds, and the interaction between adsorbed DCS molecules. While clearly demonstrating advantageous features of DCS as a Si precursor, this work suggests that thermal decomposition of Si precursors, and in turn the ALD kinetics and resulting film quality, can be strongly influenced by surface functional groups, in addition to product accumulation and precursor coverage.

AF3-MoP-6 New Challenges of the Channeled Spectroscopic Ellipsometry for ALD Applications*, Gai Chin,* ULVAC Inc., Japan

The channeled spectroscopic ellipsometry is a snapshot method for the spectrally resolved polarization analysis. Two high-order retarders are utilized to generate a channeled spectrum carrying information about the wavelength-dependent multiple parameters of polarization of light. This method does not requires mechanical or active components for polarization-control, such as a rotating compensator and electro-optic modulator. It can measure the thickness and optical constants of thin films at an ultra-high speed. Its data acquisition time is as short as 10 ms per measurement.

This innovative technology created great opportunities for new applications of the spectroscopic ellipsometry in which the compactness, the simplicity and the rapid response are extremely important. It can be integrated into many kind of deposition tools and successfully measured thin films in-situ and ex-situ. Obviously, ALD is one of the promising applications for this novel spectroscopic ellipsometry.

This paper describes the principle, system configuration and new challenges on developing this compact high-speed spectroscopic ellipsometry to satisfy daily increasing in-situ monitoring requirements from the ALD industrial and R&D users.

Some of the successful ALD applications will be introduced, such as measurement data obtained on Al_2O_3, HfO_2, TiO_2, Ta_2O_5 and TiN thin films etc. By acquiring thickness and optical constants data from this spectroscopic ellipsometry, the layer by layer growth and material properties of the films can be studied in detail. The growth rate per cycle was determined directly, and an automatic process control can be realized by feedback and feed-forward approach on the ALD tools.

AF3-MoP-7 *In-situ Ellipsometric Analysis of the Plasma Influence on Atomic Layer Deposited AlN Thin Films, Necmi Biyikli,* *S Ilhom, D Shukla, A Mohammad, B Willis,* University of Connecticut

In this report we have carried out real-time process monitoring to understand the impact of RF-plasma power and plasma exposure time on aluminum nitride (AlN) growth and film properties via *in-situ*ellipsometry. AlN thin films were grown on Si(100) substrates with plasma-enhanced atomic layer deposition (PE-ALD) using trimethyl-aluminum (TMA) as metal precursor and $Ar/N_2/H_2$plasma as co-reactant. Saturation experiments have been employed in the range of 25-200 W plasma power and 30-120 s plasma exposure time within 100 - 250 °C substrate temperature. *In-situ*multiwavelength ellipsometry provided the necessary sensitivity to identify single chemical adsorption (chemisorption) and plasma-assisted ligand removal events, as well as changes in growth-per-cycle (GPC) with respect to plasma power. Our real-time dynamic *in-situ*monitoring study revealed mainly the following insights about the plasma power influence on AlN growth: GPC and TMA chemisorption amount exhibited plasma-power dependent saturation behavior at 30 seconds of plasma duration. The amount of chemisorption saturated at ~2.25 Å for higher RF-power levels, while for 25 and 50 W it went to below 1 Å, which was attributed to insufficient ligand removal. Besides *in-situ*characterization, ex-situ measurements to identify optical, structural, and chemical properties were also carried out on 500-cycle AlN films as a function of plasma power. AlN samples displayed single-phase hexagonal crystal structure with (002) preferred orientation for 150 and 200 W, while the dominant orientation shifted towards (100) at 100 W. On the other hand, 50 and 25 W resulted in films with amorphous character with no apparent crystal signature. Furthermore, it was found that when the plasma exposure time was increased from 30 to 120 s for 25 and 50 W, the amount of chemisorption exceeded the thickness gain values recorded for 150-200 W: ~2.4Å . However, such a recovery in chemisorption did not reveal crystalline material as the AlN films grown at sub-50 W both showed amorphous character.

AF3-MoP-8 Reaction Mechanisms of Thermal and Plasma-Modified ALD Growth Studied by *In-Situ* Mass Spectrometry*, Thomas J. Larrabee, L Ruppalt,* U.S. Naval Research Laboratory

Mechanisms of gas-surface chemical reactions, and reactions caused by plasma-surface interactions, have been studied to understand different aspects of the atomic layer deposition (ALD) of zinc oxide (ZnO) and niobium oxide (NbO_x) using a differentially-pumped, highly-sensitive *in-situ* quadrupole mass spectrometer to detect reactant and product gas species. Examination and comparison of the gaseous reaction products of these two ALD processes aid our understanding of how to use plasmas to modify ALD oxide growth, generally.

In some of these cases, the ALD process was modified by inserting argon/hydrogen plasma steps, which has been shown to alter the stoichiometry of ZnO and NbO_x (*i.e.* Nb_2O_5 to NbO_2), driving metal-enriched films and lower oxidation states. To date, it has been unclear what the mechanism of the plasma-surface reactions is in these processes or precisely how the thermal ALD growth has been altered by the insertion of argon/hydrogen plasma steps. By examining the reactant and product gas species detected by the *in-situ* quadrupole mass spectrometer, we are able to investigate the chemical reactions that occur during the ALD process, uncovering information not only about the impact of the plasma steps, but also the underlying mechanism of the thermal growth process, itself. Reagents used were diethylzinc for ZnO and (t-butylimido)tris(diethylamino)niobium(V) for NbO_x, repectively, and water as the oxidant. In plasma experiments, capacitively-coupled plasmas of H_2/Ar and Ar alone were used to alter surface chemistry.

Comparison was made between thermal reactions, and inserting plasma steps at different parts of an ALD sequence. Evidence for a mechanism involving metal-organic ligand desorption and possible further reaction with the plasma is to be presented for both the Zn and Nb precursors. No evidence demonstrating removal of oxygen atoms from the growing film, either by O_2 or H_2O gas evolution was found for ZnO. The chemistry of the NbO_x growth, both for thermal and plasma-modified reactions will also be presented. Results are relevant for the nearly ubiquitous alkyl-amino transition metal precursors.

Metal precursor saturation has been investigated, from which inference about physisorption vs. chemisorption may be gleaned. Relative abundances and the dynamics of reactant and product peaks are explored to clarify the problem of peaks appearing both as reactants and as products, which has previously obfuscated interpretation of mechanisms by examining QMS data alone.

AF3-MoP-10 In-situ Quartz Crystal Microbalance Study of Poly(3,4-ethylenedioxythiophene) (PEDOT) by Oxidative Molecular Layer Deposition (o-MLD)*, G Parsons, Jungsik Kim, A Volk,* North Carolina State University

Molecular Layer Deposition (MLD) has emerged as a promising vapor-phase deposition technique due to its self-limiting reactions and conformal film growth. This work investigates oxidative MLD (o-MLD) of poly(3,4-ethylenedioxythiophene) (PEDOT) by using a volatile liquid oxidant agent and 3,4-ethylenedioxythiophene monomer (EDOT). Traditionally, PEDOT growth has been synthesized through solution-based processes involving oxidation and deprotonation steps. Despite its simplicity, poor solubility of PEDOT requires a water-soluble polyanion, poly(styrenesulfonate) (PSS), often increasing the film resistivity. Alternative vapor-phase methods such as oxidative chemical vapor deposition (o-CVD) have been reported, but chemical additives/post treatments are necessary to obtain high conductivity. Previously, Atanasov et al.has reported an o-MLD process of PEDOT using molybdenum(V) chloride oxidant ($MoCl_5$) and EDOT [1]. However, the low vapor pressure of $MoCl_5$ limits deposition temperature and facile dosing. Moreover, few basic growth analyses such as in-situ quartz crystal microbalance (QCM) have been carried out to understand PEDOT growth by o-MLD.

In this work, in-depth PEDOT growth behavior during o-MLD has been studied. The relationship between the film growth and various deposition conditions such as precursor dose/purge time, working pressure, and chamber/precursor temperature was investigated. The mass change per cycle is linear with the number of cycles for two different oxidant dose times. However, much longer purge times are required for the longer oxidant dose to remove the byproducts. QCM, X-ray photoelectron spectroscopy (XPS), spectroscopic ellipsometry (SE), and scanning electron microscopy (SEM) show that PEDOT film has been uniformly deposited at 100 ℃, with a growth rate of ~1.5 Å/cycle. At higher chamber temperature, the growth rate decreases; above 150 ℃, PEDOT growth is hindered by decomposition of precursors and monomer limited adsorption, resulting in rapid decrease of film growth. These QCM studies will play a pivotal role for understanding nucleation and growth mechanism of PEDOT via o-MLD and developing area selective MLD processes.

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ALD Fundamentals
Room Evergreen Ballroom & Foyer - Session AF4-MoP
Plasma Enhanced ALD Poster Session

AF4-MoP-1 Low-temperature Atomic Layer Deposition of Yttrium Oxide using tris(butylcyclopentadienyl)yttrium and a Plasma-Excited Humidified Argon*, Kentaro Saito, K Yosida, K Kanomata, M Miura, B Ahmmad, K Shigeru, F Hirose,* Yamagata University, Japan

Yttria (Y_2O_3) is attracting much attention since it has a high dielectric constant and it is expected to be used as an oxide insulator in the field of large scale integration. Conventionally Y_2O_3 film has been deposited by chemical vapor deposition (CVD) and atomic layer deposition (ALD). These require heating at 200 °C or higher. This high temperature process is not suitable for the fabrication of flexible electronics. To decrease the process temperature, we developed a low-temperature ALD of Y_2O_3 using tris(butylcyclopentadienyl)yttrium ($(BuCp)_3Y$) as the Y precursor and a plasma-excited humidified argon as an oxidizer.

We used a double-side polished p-type Si (100) with a size of 20 × 20 mm^2 as a sample. Y_2O_3 ALD was performed by introducing a precursor from the heated container at 140 °C and the oxidizer alternately into a cumber at 80 °C. We designed the process condition of ALD as follows, $(BuCp)_3Y$ injection of 300 sec and plasma excited humidified argon of 600 sec. The evacuation times after the $(BuCp)_3Y$ and plasma excited humidified argon are 30 sec and 90 sec, respectively. We measured chemical status of Y_2O_3 films by X-ray photoelectron spectroscopy (XPS) to confirm the presence of Y_2O_3. We extracted a growth per cycle of ALD by spectroscopic ellipsometry. In fig. 1, we show a wide scan XPS spectrum obtained from the 80 °C grown Y_2O_3 film. Fig. 2 shows Y_2O_3 thicknesses as a function of ALD growth cycles. We estimated the growth per cycle of 0.084 nm/cycle.

In this work, we succeeded in 80 °C ALD of Y_2O_3. It must be possible to form Y_2O_3 films on most of flexible substrates by this process, because the process temperature was limited below 80 °C in this ALD process. In the conference, we show the related results and discuss the reaction mechanism.

AF4-MoP-2 Plasma Enhanced Atomic Layer Deposition of Silicon Nitride Thin Film by Organosilane Precursor and Process Engineering*, Se-Won Lee, C Lee, M Kim,* Versum Materials Korea, Republic of Korea*; S Yi, X Lei,* Versum Materials, Inc.

In this study, we demonstrated that a multi chloride ligand organosilane precursor with no oxygen content, designated as Precursor T to deposit SiN film at the identical deposition temperature for a possible low thermal budget and reliable device operating in industrial applications. Precursor T was used as a Si precursor, and NH3 and N2 were used as the reactants. Ar gas was used as a main and a carrier gas. Plasma enhanced ALD (PEALD) method was conducted to obtain SiN film at 300 oC wafer temperature. SiN PEALD deposition conditions with two different reactants are as follows; Precursor T/purge/NH3*/purge (process A,* denotes plasma use), Precursor T/purge/N2*/purge (process B), Precursor T/purge/NH3*/purge/N2*/purge (process C, applied additional N2 plasma after NH3 plasma) and Precursor T/purge/N2*/purge/NH3*/purge (process D, applied additional NH3 plasma after N2 plasma).

Deposited SiN film with process A and process C exhibited good stoichiometric film compositions at about Si : N ratio of 3 : 4 with low oxygen and carbon contents and excellent SC of more than 95 %. SiN film with process D also showed good stoichiometric characteristic but, SC was ~ 65 % which is not good property than the above two methods. SiN film with process B showed a higher level of impurities over 3 % carbon and chlorine and 20 % oxygen contents, and a poor SC less than 20 % was found. Consistent with the above results, the XRR results also differed significantly from the other three process in SiN film with process B. The film density from process A to D were 2.65, 2.44, 2.73, and 2.73 g/cm3, respectively, which show that the film density of process B are not perfect SiN film.

For the WER performance with 0.1% HF solution, SiN with process C shows the lowest WER of 10 A/min among the four conditions. (WERs of process

A, process B and process D SiN films were 88, 187 and 15 A/min, respectively.) It is demonstrated that WER is improved with combinatorial deposition with NH3*/N2* compared to the deposition with NH3* or N2* alone.

In summary, we have deposited SiN film by using a multi chloride ligand organosilane precursor and ALD process design. SiN film was deposited with NH3 and N2 reactant gases by PEALD. Excellent SC and WER results were obtained for SiN film deposited with Precursor T/NH3*/N2* PEALD process. These results would be able to be applied to spacers or passivation layer, etc. by depositing SiN films with process engineering and would be expected to reduce thermal budget or to obtain reliable device operation.

AF4-MoP-3 Understanding the Effect of Plasma Gas Chemistry and Reactor Pressure on the Crystallinity of AlN Films Grown via Plasma-Assisted Atomic Layer Deposition*, **Saidjafarzoda Ilhom**, D Shukla, A Mohammad, N Biyikli, B Willis,* University of Connecticut

In this study we investigate the correlation between the structural properties of AlN thin films and the plasma gas composition as well as the ALD reactor pressure. Towards this aim, AlN films were grown on Si(100) substrates via hollow-cathode plasma-assisted atomic layer deposition (HCPA-ALD) using trimethyl-aluminum (TMA) and $Ar/N_2/H_2$plasma as metal precursor and co-reactant, respectively. Growth saturation experiments have been carried out within 0-100 sccm range for each co-reactant gas, at 100W RF-plasma power and 200°C substrate temperature. *In-situ*ellipsometry was utilized to monitor the growth-per-cycle (GPC) characteristics and real-time surface reactions including chemisorption and plasma-assisted ligand removal and nitrogen incorporation events. GPC values showed a fairly constant behavior at lower pressures followed by a considerable decrease at ~1 Torr. Our real-time dynamic *in-situ*monitoring suggests that the decline in GPC at higher pressures, and thus higher co-reactant gas flow rates, is mainly due to incomplete removal of surface ligand groups. Each of the plasma gas content was decoupled by keeping two of the co-reactants at an optimal flow rate and changing one over the range of 5-100 sccm in order to observe the GPC behaviour. In general, decoupling of N_2 and H_2 showed that the GPC is reduced at lowest and highest flow rates with rather a higher and fairly constant value in between. On the other hand, for Ar the GPC increased under low flow rates followed by a decay at higher flow rates. Moreover, N_2 and H_2 plasma gas mixture were also decoupled in time domain to investigate the GPC behavior in such a regime. We have observed that GPC was reduced for shorter H_2 plasma exposure times of 5 and 10 seconds followed with higher and constant value for longer durations, which was correlated to the incomplete ligand removal at the shorter H_2 plasma exposure that was supported by the single-cycle real-time *in-situ*measurements data. Also, extended 500-cycle long runs of AlN growth were carried out as a function of different plasma gas content and pressure. All AlN samples displayed single-phase wurtzite polycrystalline character, which exhibited preferred (002) crystalline orientation with peak intensity values changing as a function of Ar flow rate.

AF4-MoP-4 Plasma Enhanced Atomic Layer Deposition of Aluminum and Aluminum Fluoride*, **Daniel Messina**, Z Haung, B Eller, F Koeck, P Scowen, R Nemanich,* Arizona State University

Plasma enhanced atomic layer deposition (PEALD) is an emerging energy enhanced ALD technique that utilizes plasma radicals to drive surface reactions rather than thermal energy, as in traditional ALD. PEALD allows for lower impurities, increased growth rates, improved stoichiometry, and lower deposition temperatures, which are essential for the development of high reflectivity VUV structures and multilayer Fabry-Perot bandpass filters. The goal of this project is to develop an oxygen and nitrogen free ALD process to grow both aluminum and AlF_3 in the same chamber to enable UV optical filters that can be operated at <120 nm. The system is designed to deposit aluminum on a hydrogen terminated Si substrate, by sequential exposures of trimethylaluminum (TMA), an Ar purge, and a hydrogen plasma. The deposition of metal fluorides has been limited by difficulty in handling, and storing, anhydrous HF. The use of Pyridine-HF as the fluoride source reduces the risk for deposition of UV fluoride layers including AlF_3 and MgF_2. The process designed for the growth of AlF_3 layers proceeds by exposing the fresh PEALD Al to HF followed by an Ar purge. The process is designed for growth of Al and AlF_3 at 100-300° C. The PEALD system is connected to an X-ray photoelectron spectroscopy (XPS) system for elemental analysis and a UV spectrometer for far UV optical properties. *Ex-situ* characterization was conducted using atomic force microscopy (AFM), Rutherford backscattering (RBS), UV-VIS ellipsometry, and X-ray topography (XRT).

Research supported by NASA through grant NNX16AC30G.

AF4-MoP-5 High-temperature Hollow Cathode Plasma Enhanced Atomic Layer Deposition of Silicon Nitride (SiN_x) Thin Films using Hexachlorodisilane (HCDS)*, **Su Min Hwang**, A Kondusamy, Q Zhiyang, H Kim, J Kim,* University of Texas at Dallas*; X Zhou, B Hwang,* Dow Chemicals

Recently, plasma enhanced atomic layer deposition (PEALD) is expected to overcome the limitation of conventional LPCVD and PECVD processes and could be used to deposit conformal thin films in convoluted high aspect ratio structures with thickness scalability.[1] A number of studies on PEALD SiN_x process have been reported and mostly capacitively coupled plasma (CCP), inductively coupled plasma (ICP) or microwave (MW) plasma source was employed.[2] The characteristics of the plasmas, such as low plasma density in CCP, high plasma damage in ICP and high oxygen contamination in MW, etc., can be problematic for film properties, especially wet etch resistance. On the other hand, hollow cathode plasma (HCP) can be applied for high-quality silicon nitride films due to its lower oxygen contamination, higher plasma density and lower plasma damage. Inspired by the unique characteristics of HCP, we proposed to explore the feasibility of high-quality PEALD-SiN_x films by improving the films properties with HCP. Additionally, the relationship between plasma source and PEALD-SiN_x films properties has rarely been studied.

In this work, we not only clarified the effect of plasma source on the oxygen contamination of PEALD SiN_x films, but also achieved high-quality SiN_x films using hollow cathode PEALD. PEALD system with ICP or HCP source was employed to study SiN_x films comprehensively. Hexachlorodisilane (HCDS, Si_2Cl_6) was used as the silicon precursor due to its higher reactivity than $SiCl_4$ and SiH_2Cl_2 while exhibiting a distinct self-limiting growth behavior. We explored the effect of process temperature (310−570 °C), precursor exposure, and plasma gas composition (NH_3/N_2 or NH_3/Ar) on the film properties. Within a range of process temperature window (310−480 °C), the combination of Si_2Cl_6 and NH_3 plasma showed the distinct self-limiting growth behavior at a low precursor exposure (5×10^2 L). In plasma source comparison, the SiN_x films deposited with ICP source showed higher oxygen contamination (> 7.0 at%) than the HCP-PEALD SiN_x films (> 3.5 at%). Particularly, the HCP-PEALD SiN_x film deposited at 480 °C had the wet etch resistance in HF acid (> 0.4 nm/min, 200:1 HF) and film density (2.9 g/cm^3) comparable to the LPCVD SiN_x films. These result could pave the way for achieving high-quality SiN_x films using the unique HCP source.

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AF4-MoP-6 Effects of Ion Bombardment in Plasma Enhanced Atomic Layer Deposition Processes*, **Hu Li**,* Tokyo Electron Technology Solutions Ltd., Japan*; T Ito,* Osaka University, Japan*; M Kagaya, T Moriya,* Tokyo Electron Technology Solutions Ltd., Japan*; K Karahashi, S Hamaguchi,* Osaka University, Japan*; M Matsukuma,* Tokyo Electron Technology Solutions Ltd., Japan

Plasma enhanced technology has been widely used in the fabrication of thin films. In an atomic layer process, for example in a plasma enhanced atomic layer deposition (PEALD) process, chemically reactive plasma is expected to achieve high growth per cycle (GPC) at relatively low process temperature. A typical PEALD process may also be used in multiple patterning. In such patterning processes, much more precise resolution of film patterning is highly required for the nanoscale pattering. However, the film surfaces suffer the bombardment of energetic ion species, which are generated in the plasma. In such processes, film properties are affected. Therefore, the goal of this study is to clarify the effects of ions or radicals in the plasma enhanced atomic layer processes and gain a further understanding of deposition mechanisms.

In this study, we have estimated the sputtering yields of a SiO_2 film deposited by a PEALD process, by an oxygen ion (O^+) beam as well as inert gas species with the use of a mass-selected ion beam system. We have also examined the effects of low-energy ion bombardment on a precursor-absorbed SiO_2 or Si surface. After precursor exposure, the surface was exposed to energetic argon ions (Ar^+). The surface chemical compositions after ion bombardment were analyzed by *in-situ* X-ray Photoelectron Spectroscopy (XPS). From the XPS observations, it has been found that impurities, such as nitrogen (N) and carbon © originating from the organic precursor molecules, remain in the surface region even after Ar^+ ion

bombardment. We have also examined the effects of oxygen, which will be discussed in the presentation.

**AF4-MoP-8 Microwave Generated Plasma Enhanced Atomic Layer Deposition of Oxides*, Ji Hye Kim*, *Y Tak, Y Lee,* ISAC Research Inc., Republic of Korea*; A Poruba, J Dolak,* SVCS Process Innovation s.r.o., Czech Republic*; H Park,* ISAC Research Inc., Republic of Korea

With the continued down scaling of devices and structure changed to 3-dimensional, new ALD processes are in great demand. Microwave surfatron plasma is considered new plasma source because it enables very low-temperature deposition and good film quality due to its low electron temperature and higher plasma density.

In this work, surfatron plasma source was incorporated to ALD reactor. We studied the characteristics of oxide films grown by microwave plasma enhanced ALD in the reactor. The films had high growth rate and low impurities, and they grew conformally on 6-inch Si wafer. The successful incorporation of surfatron plasma source to ALD reactor encourages the study of challenging ALD processes.

AF4-MoP-9 Epitaxial Growth of GaN by Plasma-Enhanced Atomic Layer Deposition*, Sanjie Liu*, *X Zheng,* University of Science and Technology Beijing, China

In this work, the epitaxial growth of single crystalline GaN films on sapphire substrate is realized by plasma-enhanced atomic layer deposition (PEALD) at a growth temperature of 350 ℃. The XRD patterns show that the GaN films are single-crystalline and display a single hexagonal (002) phase. The high-resolution transmission electron microscopy reveals a nanoscale single-crystal GaN heteroepitaxy and a sharp interface. The full width at half-maximum of the X-ray rocking curve of the GaN epilalyers is 709 arcsec. The hetero-epitaxial GaN thin films have broaden its application in photovoltaic area, such as improving the performance of the solar cells.

AF4-MoP-10 Improving Plasma Enhanced Atomic Layer Deposition of Silicon Nitride with A Halodisilane*, B Hwang, C Lee,* ***Xiaobing Zhou****, A Foss,* DuPont*; T Sunderland, A Millward,* Dow Chemicals*; S Hwang, J Kim, A Lucero, A Kondusamy,* University of Texas at Dallas

In our continuous evaluation of disilane compounds as silicon source precursors for plasma enhanced atomic layer deposition of silicon nitride films (PEALD SiN), a halodisilane is found to give a superior film-forming performance and film properties. The halodisilane having 99% purity was evaluated with ammonia plasma on a PEALD tool with a remote hollow cathode plasma source. SiN films were deposited at about 1 Å/cycle growth rate within the ALD window up to about 450 ^{o}C. This growth rate represents a 20% improvement over the growth rate of hexachlorodisilane (HCDS). The wet etch rate (WER) of the PEALD SiN films of the halodisilane is 50% lower than that of HCDS in 200:1 HF. The step coverage is comparable to that of HCDS in high aspect ratio trenches. The PEALD SiN film results of this precursor including saturation behavior, ALD window, composition, refractive index, uniformity, density, wet etch rate and step coverage are summarized and compared with those of HCDS and pentachlorodisilane (PCDS) in this presentation.

AF4-MoP-11 Characteristics of Silicon Nitride Film Deposited by Multi-electrode VHF (162 MHz)-PEALD*, **Ki Hyun Kim**, K Kim, Y Ji, J Byun,* Sungkyunkwan University, Republic of Korea*; A Ellingboe,* Dublin City University*; G Yeom,* Sungkyunkwan University, Republic of Korea

Silicon nitride (SiN_x) thin films are used as passivation layers, diffusion barrier materials, and structural materials for various micro-electro-mechanical systems (MEMS) due to their excellent chemical and mechanical properties. The conventional plasma enhanced chemical vapor deposition (PECVD) process couldn't meet recent stringent requirements such as high conformality on a high aspect ratio pattern, high chemical stability, and high film density at low temperatures. To overcome these limitations, recently, atomic layer deposition (ALD) has received widespread attention as an alternative process for PECVD. In this study, a very high frequency (VHF, 162 MHz) multi-tile push-pull plasma source was applied to plasma enhanced atomic layer deposition (PEALD) of silicon nitride. As the silicon precursor and nitrogen atomic source, Di-isopropylamino Silane (DIPAS) and nitrogen (N_2) plasma were used, respectively, and the characteristics of silicon nitride deposited by the 162MHz VHF PEALD were investigated. XPS data showed that the silicon nitride film deposited by 162MHz VHF PEALD has a high nitrogen percentage in the SiN_x film which is close to the stoichiometric silicon nitride possibly due to a high dissociation rate of nitrogen at 162MHz VHF. Furthermore, a uniform step coverage of silicon nitride over a high aspect ratio trench (> 25 : 1) was confirmed by cross-sectional scanning electron microscope (SEM).

AF4-MoP-12 Characteristics of Low Damage Cobalt Films Deposited by Very High Frequency Plasma Enhanced Atomic Layer Deposition*, **Changhoon Song**, W Yeom, Y Shin, G Kim, G Yeom,* Sungkyunkwan University, Republic of Korea

In this study, to improve the properties of thin films deposited by plasma enhanced atomic layer deposition (PEALD), two different very high frequency (VHF) plasmas (60MHz, 100MHz)were used for the deposition of cobalt film by PEALD and, the characteristics of plasmas and cobalt films deposited by different frequencies were investigated. For the characterization of VHF plasmas, ion density and electron temperature were measured using a Langmuir probe. It is found that the higher frequency showed a higher plasma density with a lower electron temperature at the same rf power. When the NH radicals, which are required to remove the ligands of the cobalt precursor during the plasma exposure step in the ALD cycle, w ere measured by OES, the intensity of NH peak at 100 MHz was higher than that at 60 MHz, indicating that more NH_3 plasma dissociation at the higher frequency. The composition and the RMS surface roughness of the deposited cobalt films were measured by XPS and AFM, respectively. AFM data showed the lower RMS surface roughness value at the higher frequency possibly indicating denser films due to more active surface reactions at the higher frequency. As a result, it is expected that the cobalt thin films deposited by the higher VHF PE-ALD will improve the characteristics of deposited thin films.

Keywords : Very high frequency (VHF) plasma, Atomic layer deposition (ALD), Cobalt, dissociation, radical

ALD Fundamentals
Room Evergreen Ballroom & Foyer - Session AF5-MoP
Characterization of ALD Films Poster Session

AF5-MoP-1 Film Thickness and Trace Metal Analysis of Compound Semiconductor Stacks through Direct Film Stripping (DFS) followed by ICP-MS/OES*, **Vijay (Jaya) Chowdhury**, J Huang,* ChemTrace*; P Sun,* UCT - ChemTrace*; E Appiah,* ChemTrace

Advances in the deposition of thin film and heterojunctions have revolutionized the photonics and LED markets. Promising gate dielectric deposition techniques such as atomic layer deposition (ALD) on compound semiconductors such as Sapphire and Gallium Nitride (GaN) have accelerated the scalability and high yield manufacturability. Deposition of high quality and scalable thin films through ALD involve some sequential use of gaseous precursors introduced to the substrate surface within a reaction chamber. In order to achieve ultra-high purity products, essentially free from trace metals and organic impurities, the film precursors need to be fully qualified and the deposited films require full characterization for process optimization to eliminate device critical contaminants in the mature process. Several techniques are available for the analysis of film thicknesses and impurity levels on the surface and bulk of the stacks keeping in view the precision and accuracy requirements. One of the technical challenges for in-film trace metal contamination analysis is the lack of selective film stripping sample preparation methods.

In this paper, we will discuss the direct film stripping (DFS) technique developed for top metal oxide film analysis on Sapphire/GaN substrates with minimal etching of the substrate. Using the optimized direct film stripping sample preparation method followed by ICP-MS/OES, trace metals in a single film layer can be analyzed with minimum etching of the substrate below. Efficient film removal selectivity and satisfactory method detection limits are achieved. We will also share a film depth study done on HfO_2/Al_2O_3 stack on silicon wafers using ICP-OES. The study results provided an excellent stoichiometric quantification of the Al and Hf elements and good correlation with a beam based technique, Rutherford Backscattering (RBS). A combination of the two techniques can be useful for the study of thin film analysis. The direct film stripping technique developed in this study can be expanded for trace metal analyses of other films stacks.

Keywords: *Direct film stripping (DFS), Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), trace metals, Gallium Nitride (GaN)*

AF5-MoP-2 Overview of Doctoral Theses on Atomic Layer Deposition Worldwide - Outcome of the Virtual Project on the History of ALD, *J Aarik,* University of Tartu, Estonia*; J Aav, E Ahvenniemi,* Aalto University, Finland*; A Akbashev,* Stanford University*; S Ali,* Aalto University, Finland*; M Bechelany,* Institut Européen des Membranes, France*; M Berdova,* Aalto University, Finland*; I Bodalyov,* St. Petersburg State Institute of Technology, Russian Federation*; S Boyadjiev,* Bulgarian Academy of Sciences, Bulgaria*; D Cameron,* Masaryk University, Czech Republic*; N Chekurov,* Oxford Instruments Analytical Oy, Finland*; R Cheng,* Huazhong University of Science and Technology, China*; M Chubarov,* The Pennsylvania State University*; V Cremers,* Ghent University, Belgium*; A Devi,* Ruhr University Bochum, Germany*; V Drozd,* St. Petersburg State Institute of Technology, Russian Federation*; L Elnikova,* Institute for Theoretical and Experimental Physics, Russian Federation*; G Gottardi,* Fondazione Bruno Kessler, Center for Materials and Microsystems, Italy*; **J. Ruud van Ommen**,* Delft University of Technology, Netherlands*; R Puurunen,* Aalto University, Finland

Atomic Layer Deposition (ALD) is a materials growth technique that has become globally important during the past decades. In 2018 the Finnish inventor of ALD, Tuomo Suntola, received the Millennium Technology Prize.

ALD has been discovered independently twice, under the names Molecular Layering (ML) in the 1960s in the USSR and Atomic Layer Epitaxy (ALE) in 1974 in Finland. The Virtual Project on the History of ALD (VPHA) is a volunteer-based Open Science effort set up in 2013 [2] to clarify the early days of ALD. Especially the ML path has remained poorly known and acknowledged until recently. The core activity of VPHA is to overview early ALD publications up to 1986. VPHA has already resulted in four scientific journal articles [2-5] and several presentations at international conferences.

This poster will overview doctoral theses worldwide related to ALD up to year 2018. The doctoral thesis list has been built by combining the lists of Ref. 4 and the exhibition material 40 Years of ALD in Finland - Photos, Stories (FinALD40) [6], and allowing volunteers to enter missing information (open list in http://vph-ald.com/VPHAopenfiles.html). At the time of writing the abstract, the doctoral thesis collection contains close to 500 entries. The list is likely not yet complete and more entries are welcome. More volunteers are also still welcome to join and contribute in the VPHA.

Acknowledgements: R.L.P. thanks Tuomo Suntola for his support during the VPHA. Aziz Abdulagatov and Annina Titoff are acknowledged for significant help during the initiation of VPHA. The authors are grateful for all volunteers, who in addition to the current authors have shared at least one comment in the ALD-history-evolving-file during VPHA (as of Feb. 11, 2019): S.D. Elliott, D.C. Smith. The author list is intentionally in alphabetical order.

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AF5-MoP-3 Nanoscale Chemical Characterization of Ultrathin Films via PiFM, ***Sung Park**, D Nowak, W Morrison,* Molecular Vista

Chemical analysis of ultrathin films with nanometer scale lateral spatial resolution remains a challenge for the nanotechnology community. In this poster, we introduce a new nanoscale and non-destructive chemical imaging technique called photo-induced force microscopy (PiFM) where the dipole-dipole force due to optical response of the sample is measured by an atomic force microscope (AFM) along with the standard AFM topography [1]. This dipole-dipole optical force interaction between the AFM tip and the sample is strongly enhanced at the apex of the metal-coated tip due to the antenna effect and leads to a routine spatial resolution that is better than 10 nm. Since both the optical excitation and detection are accomplished in near-field, the optical information can be acquired without the far-field background interference, making the technique easy-to-use compared to other near-field techniques. PiFM can be coupled with a tunable infrared (IR) light sources to probe the IR absorption of various organic and inorganic materials for identification of molecular materials and their relationship to local topography. PiFM is surface sensitive due to the short interaction range of the measured dipole-dipole force and can detect monolayer of materials with good sensitivity, making it an ideal tool for characterizing ultrathin films.

PiFM works equally well with both organic and inorganic materials and lends itself as an excellent analytical to characterize ALD, molecular layer deposition, and organic-inorganic hybrid materials.

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AF5-MoP-4 The Effect of Impurities on Film Properties in the $Y(MeCp)_3/O_3$ Process, *J Kalliomäki, T Lehto, M Kääriä, T Sarnet, **Jani Kivioja**,* Picosun Oy, Finland

Y_2O_3 thin films are utilized as insulating materials in electronic devices, hydrophobic layers and corrosion inhibiting coatings. Several different yttrium ALD precursors have been demonstrated in the literature, from β-diketonates to heteroleptic cyclopentadienyls. When the deposition temperature is below 300 °C, authors usually report deterioration of film properties, such as crystallinity and density, with increasing impurity levels. [1,2] Nevertheless, further studies on the impurities are often outside the scope of the research found in literature.

The cyclopentadienyl-based ligands are commonly used in rare earth metal precursors, and the reaction mechanisms for them are proposed in literature. [3] However, the effect of deposition temperature over the full available range is not as widely researched.

This work focuses on the effects the reaction mechanism of the $Y(MeCp)_3/O_3$ process has on the type of carbon-based impurity species that result in the deposition temperature range 150-425 °C. The change in coordination/bonding of the impurities, and associated effect on film properties, is considered.

The experiments were made with a PICOSUN™ R-200 Advanced hot-wall ALD system. Si wafers with native oxide layers were used as substrates.

According to the results, the deposition temperature range can be divided into three regions that produce films with notably different materials properties (Figures 1-2). Each region is categorized by its distinct type of carbon-based impurity content, and the effect on optical, structural and electrical film properties will be discussed.

Understanding the underlying mechanism of growth, and how it can change and shape the process and the properties of the resulting films, is one key factor to widen the effective deposition temperature range of known oxide processes. Knowing the impact of the reaction mechanisms on the film properties allows more accurate process controls for specific applications and ultimately will help to create more high-quality end products.

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AF5-MoP-6 Internal Photoemission Spectroscopy Measurement of Barrier Heights between ALD Ru and Al_2O_3, ***Melanie Jenkins**, M Hayes, K Holden, J Conley, Jr.,* Oregon State University

ALD metals are of growing interest for applications that require conformal, pinhole free conductive films, particularly for high aspect-ratio structures. Ru, due to relatively low bulk resistivity, high work-function, a conductive oxide (RuO_2), and ease of etching, is of interest as a gate electrode for MOS transistors, metal-insulator-metal (MIM) capacitors, RRAM, and tunnel diodes, and well as a conductive Cu diffusion barrier/liner for Cu interconnects. A recent ALD process for Ru using $Ru(DMBD)(CO)_3$ and O_2 shows near zero nucleation, low roughness, and low resistivity.[1] The electrode performance depends strongly on the effective work function ($\Phi_{M,eff}$) or barrier height (ϕ_{Bn}) of the metal in direct contact with an insulator. Although capacitance-voltage (C-V) measurements may be used to estimate $\Phi_{Ru,eff}$ using MOS devices with a series of insulator thicknesses, this procedure is not possible in MIM devices. Internal photoemission (IPE) spectroscopy is the only analytical technique capable of directly

determining metal-insulator ϕ_{Bn} in device structures.[2-5] To date, little IPE work has been reported on ALD metals. In this work, we use IPE to directly measure the ϕ_{Bn} between ALD dielectrics and ALD Ru.

10 nm ALD Al_2O_3 was deposited at 300 °C using TMA and H_2O in a Picosun Sunale R-200, immediately followed by 12 nm of ALD Ru at 260 °C using $Ru(DMBD)(CO)_3$ and O_2.[1,2] TaN and TiN were used for bottom metal electrodes in MIM devices. For direct comparison to C-V extracted $\Phi_{Ru\text{-}eff}$, MOS devices were also measured. Some devices were annealed at 500 °C for 60 min in H_2/N_2.

Representative (IPE yield)$^{1/2}$ vs. photon energy (2-5 eV) plots (Fig. 1) under negative and positive polarity allow extraction of voltage dependent spectral thresholds for the (a) Ru/Al_2O_3 interface and (b) TaN/Al_2O_3 interface, respectively. Schottky plots of spectral thresholds vs. field$^{1/2}$ reveal ϕ_{Bn} of 3.7 eV and 2.9 eV for as-deposited Ru and TaN, respectively (Fig. 2). Using an electron affinity of 1.4 eV for Al_2O_3, we estimate $\Phi_{M,eff}$ at 5.1 eV and 4.3 eV for Ru and TaN, respectively, both consistent with reports for sputtered films.[5]

ALD Ru and RuO_2 ϕ_{Bn} with Al_2O_3 and HfO_2 in MIM and MOS devices before and after annealing in H_2/N_2 will be reported and compared to $\Phi_{Ru\text{-}eff}$ extracted using C-V techniques as well as IPE results on amorphous metals[3,4] and reported values for sputtered Ru.

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AF5-MoP-7 Growth and Characterization: Low Temperature ALD*, Birol Kuyel, A Alphonse, K Hong, J Marshall,* Nano-Master, Inc.

Growth and film deposition characteristic in a downstream ICP PEALD reactor are studied using a unique new process called Continuous Flow Process* that cuts the cycle time in half. This process is implemented in a PEALD reactor where uniform variable density O_2 and N_2 or H_2 plasmas are produced but any contact of the plasma with the substrate is prevented. Precursors are not allowed to enter the plasma production region making it possible to obtain repeatable operation free of deposits or plasma instabilities. This Continuous Flow Process is used for depositing PEALD GaN, Al_2O_3, and AlN films on Si substrates. It is shown that with this process ultra-smooth and uniform films with thickness linearly proportional to the number of cycles are deposited. Then it is applied to low temperature deposition of Si_3N_4 and SiO_2 films on Si wafers. The film surface roughness, thickness, uniformity, index of refraction, composition, and stress are studied down to room temperature depositions. Results are compared to thermal deposition in the same reactor and others' reported findings.

*US Patent # 9,972,501 B1 May 15, 2018

AF5-MoP-8 Etch Rate Characterization of Oxide ALD Films*, Martin M. Winterkorn, H Kim, J Provine, F Prinz, T Kenny,* Stanford University

For designing any kind of nanofabrication process, knowing the etch rates of available thin films, as well as their compatibility with commonly used processing chemicals is crucially important. Previous work by Williams et al. [1][2] tabulating rates for large numbers of film-etchant combinations has gained great popularity in the nanofabrication community, but does not include any ALD films. While there have been examinations [3] for select ALD processes and etchants since, the etch rates of ALD films have not yet been studied in comprehensive fashion.

We report on the characterization of the etch rates of 9 oxide ALD films in 20 different wet and vapor etchants, which include many commonly used silicon etchants, oxide etchants and metal etchants, as well as solvents, cleaning solutions and photoresist strippers. Each of the 180 etch rates is based on data from a minimum of 4 separate etches, with a total of over 1500 thickness measurements performed by ellipsometry. To allow efficient coverage of such a large scope, a high-throughput sample fabrication and measurement workflow was developed and successfully employed. Extension of the work to nitride ALD films is currently underway.

All oxide films were deposited at 200°C in Veeco / Cambridge Nanotech Fiji F202 ALD reactors, employing both thermal and plasma-enhanced ALD (PEALD), when available. To achieve representative results, standard deposition recipes were used, which are not optimized for low etch rates or any other specific metric, but have been developed for general purpose use. Chemicals were freshly poured for all wet etching. Film compositions as deposited were characterized using X-ray photoelectron spectroscopy (XPS).

References

[1] K. Williams, and R. Muller, Etch Rates for Micromachining Processing, *JMEMS* 5 (**1996**) 256.

[2] K. Williams, K. Gupta, and M. Wasilik, Etch Rates for Micromachining Processing - Part II, JMEMS 12 (**2003**), 761.

[3] J Provine, P. Schindler, Y. Kim, S. Walch, H.J. Kim, K.H. Kim, and F. Prinz, Correlation of film density and wet etch rate in hydrofluoric acid of plasma enhanced atomic layer deposited silicon nitride, *AIP Advances* 6 (**2016**).

AF5-MoP-9 Structure and Properties of Amorphous Thin Films Vary with Nanometric Thickness*, Yael Etinger-Geller,* Technion-Israel Institute of Technology, Israel

Amorphous materials, in contrast to crystalline ones, lack long-range order. Its order decays rapidly with the distance and while the local environment for a particular type of atom is quite similar, it is not identical; these fine changes in the atomistic structure of the materials lead to new and very interesting phenomena which are unique for amorphous materials. Although many aspects of science and technology rely on amorphous materials, much less research is conducted about their structure than on their crystalline counterparts.

In nature there are many organisms that use crystallization via an amorphous phase in order to achieve controlled mineralization. One of the main advantages of this method is that it enables the organism to exert control over the resulting polymorph, which is not necessarily the thermodynamically-stable one, by first controlling the short-range order in the amorphous phase.

In this research we draw inspiration from nature and study the ability to control various structural aspects of amorphous materials via nanometer size effects. We chose atomic layer deposition (ALD) as our material deposition method, since it is a technique that can provide extremely precise, sub-nanometric, thickness control and can deposit conformal and pinhole-free amorphous films of various materials.

Amorphous thin films of aluminum oxide deposited by atomic layer deposition method were found to vary structurally as a function of size; thinner films, as predicted previously, exhibited more 4-coordinated Al sites. These atomistic alterations were expected to change the amorphous thin film's average density, and indeed it was found to vary with the alumina layer thickness. This effect is explained in terms of the deposition process, where each newly deposited layer is a new surface layer that 'remembers' its structure, resulting in thin films of substantially lower density. This further encouraged us to study the effect of size on different density-dependent properties and it was indeed found that the refractive index and dielectric constant of these layers also change with the thin films' thickness. We believe that the ability to tune one property or another solely by size, according to a specific requirement, can open new possibilities for materials selections and applications, in science and technology.

AF5-MoP-10 Structural Aspects of Nanometer Size Amorphous Materials*, Yael Etinger-Geller, A Katsman, B Pokroy,* Technion - Israel Institute of Technology, Israel

Crystallization in the course of biomineralization, often occurs via an amorphous precursor phase, allowing additional control over the mineralization process. One of the main advantages of this method is that it enables organisms to exert control over the resulting polymorph, which is not necessarily the thermodynamically-stable one, by manipulating the short-range order of the amorphous phase.

Although many aspects of science and technology rely on amorphous materials, considerably less research focuses on the structure of amorphous materials as compared to their crystalline counterparts. In this research, we draw inspiration from nature and study the ability to control the short-range ordering in amorphous materials via nanometer size effects. We chose atomic layer deposition (ALD) to deposit thin amorphous oxides since this a technique that can provide extremely precise, sub-nanometric, thickness control and can deposit conformal and pinhole-free amorphous films of various materials.

Amorphous thin films of Al_2O_3, deposited by ALD, were characterized by EELS, AR-XPS, SS-NMR and GI-XANES at SOLEIL synchrotron and found to vary structurally as a function of size. Moreover, it was shown that these films exhibit surface layer of a different short-range ordering, in comparison to its "bulk". We explain this effect from a thermodynamic

point-of-view and relate it to surface reconstruction that occurs, in order to reduce the energy of the system. The structural variations were expected to cause a change within the density of the thin film and indeed, it was experimentally found the amorphous thin film's average density changes with size, as well as other density-related properties. Similar finding were obtained for other systems as well, meaning that this effect is not restricted to the Al_2O_3 case but may exist in different amorphous materials. We believe that the ability to tune one property or another solely by size, can open new possibilities for materials selections and applications, in science and technology.

1. Y. Etinger-Geller et al., *Chem Mater*, 2017, 29

2. Y. Etinger-Geller et al., *J Appl Phys*, 2019, 125

ALD Fundamentals
Room Grand Ballroom A-C - Session AF1-TuM
In-Situ Characterization of ALD Processes

Moderators: Christophe Vallée, LTM/CNRS-UJF, France, Erwin Kessels, Eindhoven University of Technology, the Netherlands

8:00am **AF1-TuM-1 Surface Chemistry during ALD of Nickel Sulfide*, Xinwei Wang,*** Peking University, China

ALD of metal sulfides has recently aroused great interest, and many new sulfide ALD processes have emerged during the past several years. Surface chemistry plays a key role in ALD, but it remains yet to be investigated for many recently developed sulfide ALD processes. In this representation, I will report our study on the surface chemistry of the ALD of nickel sulfide (NiS) from a Ni amidinate precursor ($Ni(amd)_2$) and H_2S, using the in situ characterization techniques of X-ray photoelectron spectroscopy (XPS), low-energy ion scattering (LEIS), quartz crystal microbalance (QCM), and quadrupole mass spectrometry (QMS). The surface chemistry is found to deviate from the conventional ligand-exchange ALD scheme, and a formation of a nonvolatile acid-base complex from acidic surface sulfhydryl and basic amidine is suggested during the H_2S half-cycle [1]. We further investigate the initial ALD growth of NiS on a SiO_x surface, and the initial growth mechanism is found to be rather different from that in the later steady film growth. In the initial ALD cycles, the XPS results show a drastic cyclic variation of the signals for the Ni−O bonds, with prominently observable Ni−O signals after each $Ni(amd)_2$ dose but almost negligible after the subsequent H_2S dose. These results suggest that the Ni−O bonds are first formed on the surface in the $Ni(amd)_2$ half-cycles and then mostly converted to NiS in the following H_2S half-cycles. To describe this initial ALD growth process, a reaction-agglomeration mechanistic scheme is proposed [2].

References

[1] R. Zhao, Z. Guo, X. Wang, *J. Phys. Chem. C* (2018) 122, 21514.

[2] R. Zhao, X. Wang, *Chem. Mater.* (2019) 31, 445.

8:15am **AF1-TuM-2 In situ and In vacuo Studies on Plasma Enhanced Atomic Layer Deposited Cobalt Films*, Johanna Reif,*** *M Knaut, S Killge, N Hampel, M Albert, J Bartha,* Technische Universität Dresden, Germany

Outstanding properties like high thermal and electrical conductivity as well as an unique magnetic behavior make cobalt thin films suitable for demanding applications in modern microelectronic devices. With physical vapor deposition (PVD) and chemical vapor deposition (CVD) techniques, it is already possible to deposit such films with high quality. However, cobalt metal film growth by atomic layer deposition (ALD) is required to satisfy conformality and thickness requirements in nanoscale devices.

In this report we will present experiments and results on the deposition of cobalt films with various plasma enhanced ALD (PEALD) processes using different standard cobalt precursors (e.g., cyclopentadienylcobalt dicarbonyl ($CpCo(CO)_2$), cobaltocene ($CoCp_2$) and tricarbonylnitrosylcobalt ($Co(CO)_3NO$)) combined with hydrogen, nitrogen, ammonia and argon based plasma gases. All our experiments were performed in a cross-flow ALD reactor, which is equipped with a capacitively coupled hallow-cathode plasma source, specially designed for the deposition of conductive films. In situ and in real-time highly sensitive quartz crystal microbalances (QCM) measurements allowed a rapid and low-cost process development. The utilized ALD reactor was clustered to an ultra-high vacuum analytic system for direct surface analysis like X-ray photoelectron spectroscopy (XPS) and scanning probe microscopy (SPM). The combination with a non-destructive analytic system enabled a sample transfer without vacuum break and thereby a direct qualification and quantification of the chemical surface composition under quasi in situ conditions. The high sensitivity of these measurements allowed investigations of interface reactions for a single PEALD pulse as well as initial film growth mechanism on different substrate materials. Furthermore we studied the impact of various cobalt precursors combined with different plasma gas compositions on the resulting film properties. The influence of process parameters (e.g., pulse times, plasma power, pressure and substrate temperature) on the film composition and film properties was also investigated. Cobalt films grown using the precursor $CpCo(CO)_2$ and H_2/N_2 plasma as coreactant showed a stable film composition of 75 at.% cobalt, 4 at.% carbon and 21 at.% nitrogen. Using scanning electron microscopy and four point probe measurements a moderate electrical resistivity of about 80 µΩcm is calculated for a 14 nm thick film.

Beyond those results in our publication we will discuss the suitability of the precursors for the deposition of high-quality cobalt films as well as the occurrence of sputtering and temperature effects due to high plasma powers.

8:30am **AF1-TuM-3 Investigation of PEALD Grown HfO_2 Thin Films via Near Ambient Pressure XPS: Precursor Tuning, Process Design and a New In-situ Examination Approach for Studying Film Surfaces Exposed to Reactive Gases*, David Zanders,*** Ruhr University Bochum, Germany*; E Ciftyurek,* Heinrich Heine University Düsseldorf, Germany*; C Bock, A Devi,* Ruhr University Bochum, Germany*; K Schierbaum,* Heinrich Heine University Düsseldorf, Germany

Hafnium (IV) oxide (HfO_2) is a high-k dielectric whose thin films have become a fundamental part of electronics since their commercial usage in CMOSFETs in 2008.[1] Furthermore, interest in orthorhombic HfO_2 is arising owing to the discovery of its ferroelectric nature in 2011,[2] which may lead to electronics beyond present limits.[3] Atomic layer deposition (ALD) and plasma enhanced (PE)ALD are favorable for such applications due to the low processing temperatures, precise control of thickness as well as dense and conformal coverage over complex device geometries. Furthermore, it must be ensured that films exhibit the desired stoichiometries with only low surface defect densities as the presence of surface defects, allows interactions with reactive gases and moisture that can initiate surface degradation of the dielectric, having a negative effect on its electrical properties.[4]

We report on the development of a promising PEALD process employing a precursor originating from the novel mono-guanidinato tris-alkylamido class. Four variants were subjected to thermal and chemical analysis proving their tunable volatility and thermal stability (Fig. 1). Typical ALD growth characteristics in terms of saturation, ALD window and linearity were confirmed and the growth behaviour upon variation of plasma pulse lengths was studied (Fig. 2). The obtained HfO_2 layers exhibited high quality evidenced by XRR, AFM, RBS/NRA and XPS investigations. Selected films were exposed to reactive gases such as H_2, O_2 and H_2O vapor at different temperatures and *in-situ* characterized by near ambient pressure (NAP)-XPS. Surface compositional changes and responses were monitored in a new methodical approach that has not been reported so far for thin films to the best of our knowledge. Finally, metal-insulator-semiconductor (MIS) capacitors were fabricated using HfO_2 as dielectric layer to assess its performance in device structures. This is a first report on a highly promising PEALD process for HfO_2 in a broad temperature range (60 – 240) °C developed from a new Hf precursor exhibiting optimal properties for ALD. Employing NAP-XPS is shown to be a promising development as investigations of surfaces during exposure to defined reactive gas atmospheres leads to new in-sights into stability or triggered changes of composition and states indicating either presence, absence or formation of surface defects which strongly influence the functional properties of the layers.

[1] Ahvenniemi, E.;*et al.*; *JVST A:***2017**, *35*, 10801.

[2] Park, M. H.; et al.;*MRC***2018**, *8*, 795–808.

[3] Hoffmann, M.; et al.;*Nature***2019**, *565*, 464–467.

[4] Wen, L.; Doctoral dissertation. Hdl.handle.net/1969.1/3225.

8:45am **AF1-TuM-4 Surface Science Studies of GaN Substrates Subjected to Plasma-Assisted Atomic Layer Processes*, Samantha G. Rosenberg,*** ASEE*; D Pennachio,* University of California, Santa Barbara*; E Young, Y Chang, H Inbar,* University of California Santa Barbara*; J Woodward,* U.S. Naval Research Laboratory*; Z Robinson,* SUNY College at Brockport*; J Grzeskowiak,* University at Albany-SUNY*; C Ventrice, Jr.,* SUNY Polytechnic Institute*; C Palmstrøm,* University of California Santa Barbara*; C Eddy, Jr.,* U.S. Naval Research Laboratory

III-N semiconductors are well suited for applications in several important technological areas, including high current, normally-off power switches.[1,2] Such devices require heterostructures not readily achievable by conventional growth methods. Therefore, we have developed a technique adapted from ALD, called plasma-assisted atomic layer epitaxy (ALEp).[2] Using surface science techniques, we strive to develop not only a fundamental understanding of the ALEp growth process but also complimentary atomic level processes (ALPs) that will result in the best preparation method for a pristine GaN starting surface for ALEp.

Here we employ *in-situ* and *in-vacuo* surface studies of GaN substrate preparation to advance fundamental understanding of the ALEp process.

Having optimized our GaN surface preparation process (gallium flash off ALP),[3] we conduct *in-vacuo* X-ray photoelectron spectroscopy (XPS), reflection high-energy electron diffraction (RHEED), and scanning tunneling microscopy (STM) studies conducted at the Palmstrøm Lab at UCSB to further refine both our process and our understanding. Preliminary XPS results show that a GFO ALP conducted at 250°C for 12 cycles reduces the oxygen content by 5% but shows no reduction in the carbon content, while a GFO ALP conducted at 400°C for 30 cycles reduces the carbon content by 60% but shows no reduction in the oxygen content. In addition, we conducted comparable temperature program desorption (TPD) and low energy electron diffraction (LEED) experiments at SUNY Polytechnic Institute to correlate structural and chemical changes that occur on the GaN surface during our GFO ALP. TPD shows that NH_3 is released from GaN surfaces not subjected to GFO ALP as it is heated past 150°C, while GFO ALP GaN surfaces show no NH_3 release upon subsequent TPD experiments. Both GaN surfaces show an unreconstructed 1x1diffraction pattern in LEED.

1. N. Nepal, et al., Appl. Phys. Lett. 103, 082110 (2013)

2. C. R. Eddy, Jr, et al., J. Vac. Sci. Technol. A 31(5), 058501 (2013)

3. S. Rosenberg, et. al., J. Vac. Sci. Technol. A 37, 020908 (2019)

9:00am **AF1-TuM-5 Infrared and Optical Emission Spectroscopy on Atmospheric-Pressure Plasma-Enhanced Spatial ALD of Al_2O_3,** ***Maria Antonietta Mione****, R Engeln, E Kessels,* Eindhoven University of Technology, Netherlands*; F Roozeboom,* Eindhoven University of Technology and TNO, Netherlands

In the past decade, atmospheric pressure spatial atomic layer deposition (AP-SALD) has gained momentum as a fast deposition technology for functional thin layers. The unparalleled merits of conventional ALD, such as superior control of layer thickness, conformality and homogeneity, joined with the high throughput offered by the spatially separated half-reactions and the cost-effectiveness of vacuum technology free systems, make AP-SALD well-suited for industrial large-area applications. Additionally, the use of atmospheric pressure plasmas as co-reactants enables to rapidly deposit high-quality, dense films at relatively low temperatures. [1]

Despite its industrial relevance, the chemistry at the base of the atmospheric pressure plasma-enhanced spatial ALD processes largely remains unaddressed. Effective ALD metrology techniques are of great importance to gain detailed insight into the nature of the process as well as to improve its perfomance thus opening the way to its wide industrial implementation. However, due to the dynamic nature of the spatial concept, monitoring AP-SALD processes can be rather challenging, especially in the case of close-proximity systems where the substrate is at ~100 micrometer distances from the gas injection head.

In this work, we employed optical emission spectroscopy (OES) and infrared spectroscopy on effluent plasma gasses as diagnostic tools to study the underlying chemistry of the AP-SALD process of Al_2O_3 films prepared using $Al(CH_3)_3$ and Ar-O_2 plasma. We identified the main reaction products and studied their trend as a function of the exposure time to the precursor to verify the ALD layer-by-layer growth characteristic. Findings show that the spatial separation of the ALD half-reactions and the use of an atmospheric pressure plasma as the reactant give rise to a complex underlying chemistry. Infrared absorbance spectra show CO, CO_2, H_2O and CH_4 as the main ALD reaction byproducts originating from 1) combustion-like reactions of the methylated surface with oxygen plasma radicals and ozone, and 2) a concurrent latent thermal component due to surrounding substrate. In addition, CH_2O and CH_3OH are identified as ALD reaction byproducts either formed at the surface or in the plasma by electron-induced dissociation. Furthermore, the investigated trends in CO_2, CO and CH_4 formed as a function of the exposure time confirmed self-limiting ALD behavior. Finally, OES results corroborated that, as soon as the plasma-enhanced SALD process takes place, emission from OH and CH arises while excited oxygen species are consumed.

[1] Mione *et al.*, ECS J. Solid State Sci. Technol. **6**, N243 (2017), and references therein.

9:15am **AF1-TuM-6 Fingerprinting of ALD Reaction Products with Time-Resolved In situ Mass Spectrometry***,* ***Andreas Werbrouck****, F Mattelaer, J Dendooven, C Detavernier,* Ghent University, Belgium

The importance of in-situ process monitoring during atomic layer deposition has been highlighted extensively by, among others, the review of Knapas and Ritala [1]. However, the examination of ALD processes via quadrupole mass spectrometry (QMS) is especially hard (compared to other fields where it is employed) since there is only a limited amount of reaction products, which are present in the chamber for only a fleeting moment. This shows the need for time-resolved measurements. However, most commonly available equipment is limited to a real-time resolution of only a few ion/radical masses. In QMS measurements, incoming molecules are cracked and ionized into a composite 'fingerprint' spectrum of several mass-to-charge (m/z) ratios. Thus, it is very likely that information is lost if only a few individual masses are tracked, in particular because the decision on which mass-over-charge ratios have to be measured usually depends on preliminary assumptions, knowledge of the precursor ligands and gut feeling. This limits the practical use of QMS to the detection of simple reaction products and may introduce a bias towards certain reaction chemistries. A novel data acquisition method is described which allows for time-resolved measurements of full m/z-spectra. This allows for 'fingerprinting' molecules present at a certain time instead of using a priori assumptions to decide which m/z ratios have to be monitored.

ALD processes have the exploitable advantage that they are of cyclic nature. Hence after the first cycles where initial growth effects could be of importance, the chemistry of each cycle should be identical and can be repeated as often as necessary to obtain data with good signal-to-noise ratio. In this work, we combine data from several ALD cycles to construct a time-resolved m/z spectrum of one cycle, over the full relevant range of the process, measured with a standard quadrupole mass spectrometer (Hiden HPR-30). As such, complete time-resolved mass spectrum analyses of ALD reaction chemistries is enabled.

A proof of concept is delivered with the standard TMA-H_2O chemistry, before we move on to the reaction mechanism of a more complex process. Lithium hexamethyl disilyl azide (LiHMDS) and trimethyl phosphate (TMP) can be combined to grow a crystalline lithium phosphate. As is shown in the accompanying figure, time-resolved measurements offer a unique and unbiased insight in the growth mechanism of this process.

[1] Kjell Knapas & Mikko Ritala (2013) In Situ Studies on Reaction Mechanisms in Atomic Layer Deposition,

Critical Reviews in Solid State and Materials Sciences, 38:3, 167-202, DOI: 10.1080/10408436.2012.693460

9:30am **AF1-TuM-7 Studying Pt and Pd Nanoparticle ALD through X-ray based In situ Characterization***,* ***Jolien Dendooven****, J Feng,* Ghent University, Belgium*; E Solano,* ALBA Synchrotron Light Source, Spain*; R Ramachandran, M Minjauw, M Van Daele,* Ghent University, Belgium*; D Hermida-Merino,* ESRF European Synchrotron, France*; A Coati,* Synchrotron SOLEIL, France*; C Detavernier,* Ghent University, Belgium **INVITED**

The performance of supported nanoparticles (NPs) in heterogeneous catalysis is closely related to their size, shape and interparticle distance. Tailoring the structural properties of noble metal NPs is attractive to elucidate performance-structure relationships and tune the catalytic activity, selectivity and stability. In this regard, there is an increasing interest in ALD to conformally deposit noble metal NPs with atomic-scale control over the metal loading (atoms per cm^2) and NP size. Here, we aim to demonstrate that in situ X-ray fluorescence (XRF) and grazing incidence small angle X-ray scattering (GISAXS) can offer unique insights in the ALD growth and thermal stability of metal NPs, offering approaches towards superior size and coverage control, and improved stability.

In a first study, the $Me_3(MeCp)Pt$ precursor is combined with either O_2 gas or N_2 plasma to grow Pt NPs on planar SiO_2 surfaces, and in situ XRF and GISAXS measurements provide the evolution of Pt loading, NP dimensions and spacing. It is found that O_2 induces atom and cluster surface diffusion and promotes the ripening of the Pt NPs, while diffusion phenomena seem to be suppressed during N_2 plasma-based ALD. This insight inspired a tuning strategy that combines both processes and offers independent control over NP size and coverage [Nat. Comm. 8, 1074 (2017)]. Next, in situ GISAXS is used to investigate the coarsening behavior of the Pt NPs [Nanoscale 9, 13159 (2017)] and probe the influence of stabilizing Al_2O_3 overcoats. The overcoat thickness required to stabilize the NPs is investigated for different Pt NP coverages and sizes, revealing that one single ALD cycle is sufficient to stabilize widely spaced NPs, while it is challenging to avoid NP coarsening for closely packed Pt NPs.

A second case study concerns plasma-enhanced ALD of Pd NPs on planar Al_2O_3 surfaces with the $Pd(hfac)_2$ precursor at 150°C, comparing a purely reducing chemistry (H_2 plasma as reactant) with three-step processes that include an oxidizing agent (sequential dosing of H_2 plasma and O_2 plasma or vice versa). The choice of reactant and reactant sequence has a clear impact on the initial nucleation density. The highest areal density is obtained for the three-step process that uses H_2 plasma followed by O_2 plasma, explained by the cleaning role of O radicals towards poisoning hfac ligands on the Al_2O_3 surface. Finally, the use of TMA to clear the surface

from site-blocking species [APL 95, 143106 (2009)] is systematically investigated on planar SiO_2 using in situ GISAXS, providing a way to control the Pd NP coverage.

ALD Fundamentals
Room Grand Ballroom H-K - Session AF2-TuM
ALD Precursors II

Moderators: Jin-Seong Park, Hanyang University, Seán Barry, Carleton University

8:00am **AF2-TuM-1 Characterizing Water Delivery for ALD Processes***,* ***James Maslar****, B Sperling, W Kimes,* National Institute of Standards and Technology*; W Kimmerle, K Kimmerle,* NSI*; E Woelk,* CeeVeeTech

Water is utilized as the oxygen source for many metal oxide ALD processes. Water is commonly delivered in an inert carrier gas from a bubbler (an ampoule with a dip tube) or a vapor draw ampoule (an ampoule with no dip tube: the gas in and gas out ports open directly into the ampoule headspace). While it is relatively simple to implement a delivery system based on such ampoules, it can be difficult to reproducibly deliver water from such ampoules. This is at least in part due to evaporative cooling, i.e., cooling reduces the water vapor pressure and hence the amount of material entrained in the carrier gas. For an ideal ALD process, irreproducible water delivery may not lead to undesirable changes in the deposited film properties (unless the dose is insufficient to saturate the reactive surface sites). However, if the ALD process involves a chemical vapor deposition component, irreproducible water delivery can result in undesired film properties. The goal of this work is to obtain a better understanding of the factors influencing water delivery from bubblers and vapor draw ampoules. To achieve this goal, both the amount of water delivered from an ampoule and the temperature distribution of the water in the ampoule were measured under a range of process conditions, in bubblers and vapor draw ampoules. The amount of water delivered and the water temperature vertical distribution in the ampoule were measured using a tunable diode laser spectroscopy system and a five-element temperature sensor array, respectively. These data were used determine the degree to which the amount of water delivered was correlated to evaporative cooling in the ampoule. For bubblers, this determination was relatively straight-forward as bubbling tended to homogenize the water temperature. For vapor draw ampoules, however, this determination was complicated by a temperature gradient that existed during flow. The focus of this investigation was on commercial 1.5 L ampoules (with a maximum fill of 1.2 L), although different ampoule designs were examined. The results from this work could facilitate development of ALD process recipes, delivery control methods, and improved ampoule designs.

8:15am **AF2-TuM-2 A Nickel Chloride Adduct Complex as a Precursor for Low-Resistivity Nickel Nitride Thin Films with Tert-butylhydrazine as a Coreactant***, K Väyrynen, T Hatanpää, M Mattinen, M Heikkilä, K Mizohata, J Räisänen,* University of Helsinki, Finland*; J Link, R Stern,* National Institute of Chemical Physics and Biophysics, Estonia*; M Leskelä,* ***Mikko Ritala****,* University of Helsinki, Finland

From the very beginning of ALD, metal chlorides have been extensively used precursors because of their high thermal stability and reactivity as well as low cost. However, not all metal chlorides are volatile enough to be used in ALD. Cobalt and nickel chlorides for example have a polymeric structure and therefore low volatility. To circumvent this limitation, we have recently explored a strategy of adducting these chlorides with chelating ligands. With properly selected diamines the adduct complexes are monomeric and thermally stable enough to be volatilized and used in ALD. These compounds have been earlier been used for deposition of CoO [1] and intermetallics Co_3Sn_2 and Ni_3Sn_2 as a novel class of ALD materials [2].

Herein, we have studied ALD of nickel nitride and nickel thin films using $NiCl_2$(TMPDA) (TMPDA = *N,N,N',N',*-tetramethyl-1,3-propanediamine) as the metal precursor and tert-butylhydrazine (TBH) as a nitrogen containing reducing agent. The films were grown at low temperatures of 190–250 °C. This is one of the few low-temperature ALD processes that can be used to grow Ni_3N and Ni metal on both insulating and conductive substrates. X-ray diffraction showed reflections compatible with either hexagonal Ni or Ni_3N. ToF-ERDA analyses showed that the films were close to stoichiometric Ni_3N. Upon annealing the films at 150 °C in 10% forming gas their nitrogen content lowered down to 1.2 at.%, and the nonmagnetic nitride films were converted to ferromagnetic Ni metal.

[1] K. Väyrynen, K. Mizohata, J. Räisänen, D. Peeters, A. Devi, M. Ritala, M. Leskelä, *Chem. Mater.***2017**, *29*, 6502.

[2] K. Väyrynen, T. Hatanpää, M. Mattinen, K. Mizohata, K. Meinander, J. Räisänen, J. Link, R. Stern, M. Ritala, M. Leskelä, *Adv. Mater. Interfaces***2018**, *12*, 1801291.

8:30am **AF2-TuM-3 Simple, Rationally Designed Aluminum Precursors for the Deposition of Low-impurity AlN Films***,* ***Sydney Buttera****, S Barry,* Carleton University, Canada*; H Pedersen,* Linköping University, Sweden

Main group chemistry has been integral in the field of ALD since its inception, particularly concerning the extensive work on the most fundamental ALD process: the deposition of aluminum oxide from trimethylaluminum (TMA) and water. It is surprising that strategically functionalized analogues to this fundamental precursor have not been more extensively studied in order to optimize subsequent deposition processes. A simple, rationally designed precursor can regulate surface chemistry and limit decomposition pathways, permitting straightforward reactivity. Our focus is to enable the deposition of low-impurity aluminum nitride by ALD.

This presentation will describe the study of a set of simple molecules that are novel as ALD precursors, based on a substituted TMA framework (Figure 1a-c). Tris(dimethylamido)aluminum(III) is a direct analogue of TMA with methyl groups replaced by dimethylamido ligands. It demonstrates excellent ALD precursor behaviour with a 1 Torr temperature of 67 °C and no decomposition visible by TGA, likely attributed to the stabilization of the Al centre by the coordinative donation from the bridging NMe_2. This precursor deposited aluminum oxide and aluminum oxy-nitride films with carbon impurities lower than those reported using TMA.[1] From this, it was deduced that metal-nitrogen bonds in precursor design were beneficial to stabilizing the metal centre, and importantly, in lowering carbon contamination in deposited films by eliminating direct Al-C bonds.

Using the same TMA framework, $AlH_x(NMe_2)_{3-x}$ (x = 1, 2) compounds were prepared due to the potential for the reducing ability of the hydride ligand and a maintained absence of metal-carbon bonds. These compounds were also found to be volatile and thermally stable, and thus suitable as potential AlN precursors.

This led to the study of further nitrogen-containing ligands: the family $Al(^{Me}NacNac)_x(NMe_2)_{3-x}$ (x = 1, 3) similarly showed excellent volatility and thermal stability. Interestingly, an Al species with one monoanionic and one doubly anionic ^{Me}NacNac ligand was discovered (Figure 1d) and presented this novel reduced ligand for potential use in ALD precursors. This compound was synthesized via reduction of the ^{Me}NacNac ligand, and its thermal characterization and reactivity, as well as that of contrarily unsuitable ALD candidates using these ligands, will also be discussed in this presentation.

[1] Buttera, S. C.; Mandia, D. J.; Barry, S. T. Tris(dimethylamido)aluminum(III): An Overlooked Atomic Layer Deposition Precursor. *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.***2017**, *35* (35), 1–128.

8:45am **AF2-TuM-4 Atomic Layer Deposition of Lead(II) Sulfide at Temperatures Below 100 °C***,* ***Georgi Popov,*** University of Helsinki, Finland*; G Bačić,* Carleton University, Canada*; M Mattinen, M Vehkamäki, K Mizohata, M Kemell,* University of Helsinki, Finland*; S Barry,* Carleton University, Canada*; J Räisänen, M Leskelä, M Ritala,* University of Helsinki, Finland

Lead(II) sulfide (PbS) is one of the oldest known semiconductors. It has a narrow band-gap of 0.4 eV that can be widened by quantum confinement effects. Owing to these properties, PbS is a recognized material in IR detection and quantum dot (QD) based devices such as light emitting diodes (LEDs) and photovoltaics. Photovoltaics are also central to our study. The aim is to develop an ALD PbS process that can be applied in halide perovskite solar cells.

ALD processes for PbS exist at least since 1990[1], however we discovered that known ALD PbS processes are incompatible with halide perovskites such as $CH_3NH_3PbI_3$ due to their extremely low thermal budget[2]. To our knowledge the lowest temperature at which PbS can be deposited with existing ALD processes is 130 °C.[3] $CH_3NH_3PbI_3$ film degrades completely at that temperature in our ALD reactors. Thus, we set out for a new PbS process that would work at even lower temperatures. From our previous studies on ALD of PbI_2 we already knew one lead precursor suitable for low temperature ALD: lead(II) bis[bis(trimethylsilyl)amide] or $Pb(btsa)_2$.[4] Recently Bačić et al. reported another suitable candidate: lead(II) *rac-N*^{2},*N*^{3}-di-*tert*-butylbutane-2,3-diamide or Pb(dbda).[5] With these lead precursors

and H_2S as a co-reactant we developed two new processes capable of depositing PbS even below 100 °C.

$Pb(btsa)_2$-H_2S process produces uniform, high-quality, crystalline PbS films in the 65 – 155 °C range. TOF-ERDA composition analysis revealed exceptionally high purity for such low deposition temperatures. The process exhibits two regions with temperature independent growth per cycle values (GPC) of 0.50 Å and 0.15 Å at 65 – 80 °C and 115 – 155 °C, respectively. The GPC saturates rapidly with respect to both precursor pulses and is independent of the purge duration and number of deposition cycles. $CH_3NH_3PbI_3$ films survive the PbS deposition at the lowest deposition temperatures and studies of perovskite stability after PbS deposition are ongoing.

With Pb(dbda) film deposition occurs in an even wider temperature range of 45 – 155 °C. However, XRD measurements show that at 95 °C and above, the films contain crystalline impurities. Nevertheless, high-quality polycrystalline PbS films can be deposited at temperatures as low as 45 – 75 °C. We are currently conducting studies on the influence of process parameters on the PbS film properties.

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9:00am **AF2-TuM-5 Development and Characterization of a Novel Atomic Layer Deposition Process for Transparent p-Type Semiconducting Nickel Oxide using $Ni(^{tBu2}DAD)_2$ and Ozone***, **Konner Holden,*** Oregon State University*; C Dezelah,* EMD Performance Materials*; J Conley, Jr.,* Oregon State University

Nickel oxide (NiO), a wide band gap p-type oxide semiconductor, is of interest for applications in solar energy conversion,[1] electrocatalysis,[2] and as a tunnel barrier for metal/insulator/metal (MIM) diodes for infrared energy harvesting.[3] ALD is an ideal technique for the highly conformal, uniform thin films needed for these applications. We develop a new process for ALD of NiO using $Ni(^{tBu2}DAD)_2$ and O_3-.

ALD growth of metallic Ni was demonstrated recently using $Ni(^{tBu2}DAD)_2$ and *tert*-butylamine.[4] ALD of metallic Co and cobalt oxide have been reported using $Co(^{tBu2}DAD)_2$ with formic acid and O_3, respectively.[5,6] Taking a similar approach, we deposit NiO in a Picosun Sunale R-150 using N_2-purge-separated cycles of $Ni(^{tBu2}DAD)_2$ held at 150°C and an O_3/O_2 mixture of ~10%. NiO films were characterized using grazing-incidence x-ray diffraction (GIXRD), x-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), variable angle spectroscopic ellipsometry (VASE), and p-NiO/n-Si heterojunction diodes.

A plot of GPC vs. temperature for depositions using a 5/30/4/30 s $Ni(^{tBu2}DAD)_2/N_2/O_3/N_2$ pulse sequence shows a clear ALD "window" of constant GPC = 0.12 nm/cycle from 185-200 °C (Fig. 1) in which $Ni(^{tBu2}DAD)_2$ and O_3 pulses saturate after ~5 s and ~4 s, respectively (Fig. 2). Below the temperature window, condensation of $Ni(^{tBu2}DAD)_2$ occurs resulting in uncontrolled growth with 1.2% C and 0.7 % N impurities (XPS) at 150 °C. Above the window, from 200-230 °C, desorption of $Ni(^{tBu2}DAD)_2$ occurs, followed by decomposition of $Ni(^{tBu2}DAD)_2$ above 230 °C on the chamber walls upstream of the wafer, both contributing to decreased GPC. Inside the temperature window, for saturating films deposited at 200 °C, GIXRD shows randomly-oriented polycrystalline cubic NiO (Fig. 3), consistent with XPS elemental analysis showing a Ni:O ratio near unity, without any detectable C or N impurities. VASE reveals that refractive index (~2.4) and band-gap (~3.8 eV) are close to bulk values while AFM RMS roughness was 0.6 nm for an 18 nm thick film (Fig. 4). p-NiO/n-Si diodes show highly asymmetric ($I_+/I_{-,MAX} \approx 10^4$) behavior. All results point towards an as-deposited transparent p-type semiconducting NiO. Further growth studies, characterization, and electrical measurements will be discussed at the meeting.

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3. N. Alimardani et al. Appl. Phys. Lett. 105, 082902 (2014).
4. M. M. Kerrigan et al., ACS Appl. Mat. & Interfaces. 10, 14200 (2018).
5. J. P. Klesko, M. M. Kerrigan, and C. H. Winter, Chem. Mater. 28, 700 (2016).
6. J. Kim et al., Chem. Mater. 29, 5796 (2017).

9:15am **AF2-TuM-6 Blocking Thermolysis in Diamido Plumbylenes***, **Goran Bacic,*** Carleton University, Canada*; D Zanders,* Ruhr University Bochum, Germany*; I Frankel,* Carleton University, Canada*; J Masuda,* Saint Mary's University, Canada*; T Zeng,* Carleton University, Canada*; B Mallick, A Devi,* Ruhr University Bochum, Germany*; S Barry,* Carleton University, Canada

Lead-containing nanomaterials like PbS quantum dots and $CH_3NH_3PbI_3$ perovskite films have received a frenzy of attention because of their unique optoelectronic properties. Atomic layer deposition (ALD) is an especially attractive method for their fabrication as it can deposit uniform, conformal films over large areas at low temperatures with subnanometer thickness control. However, current lead-containing ALD processes have rarely been adopted due to their poor thermal budget, the low volatility of known precursors, and the small library of thermally robust lead complexes. Our interest in the deposition of lead-containing materials prompted us to study amido ligands because of their low cost, flexibility, and proven effectiveness of other group 14 diamido complexes as precursors for ALD.

In a pilot study,[1] we identified the thermally stable (dec. >100 °C) and highly volatile (subl. 40 °C/0.01 Torr) 5-membered *N*-heterocyclic plumbylene *rac*-N^2,N^3-di-*tert*-butylbutane-2,3-diamido lead(II) (**1**), however it failed to cleanly react with our sulfur-source *tert*-butylthiol below its decomposition temperature. To explore safe (i.e., less reactive) co-reagents for ALD, we needed to push the thermal stability even higher through a mechanistic understanding of the decomposition pathways of diamido plumbylenes. With few reports on the mechanisms of their thermolysis, we decided to undertake a combined synthetic and theoretical approach to this problem. The two most promising examples in the literature, **1** and $Pb[N(SiMe_3)_2]$, suggested both cyclic and acyclic scaffolds were viable.

We postulated two dominant thermolysis pathways for plumbylenes: formation of metallacycles by π-overlap of *N*-substituents and the $6p^0$ orbital of lead (**A**); and concerted pericyclic cycloreversion reactions (**B**). We found experimentally that known acyclic complexes were dominated by **A,** and 5-membered cyclic derivatives were found to be dominated by pathway **B** so we designed bespoke ligands to block thermolysis through two strategies: coordinatively saturating lead with a Lewis base to hinder **A**, and rigid ligands to block **B**. *Ab initio* calculations were performed on a model set of plumbylenes to help reveal the way forward to indefinitely robust and volatile plumbylenes for deposition, and provide a better understanding of the unique ligand-metal cooperation required for lead.

[1] Bačić, G., Zanders, D., Mallick, Devi, A., Barry, S.T.Designing Stability into Thermally Reactive Plumbylenes. *Inorg. Chem.***2018**, *57* (14), pp 8218-8226.

9:30am **AF2-TuM-7 ALD of Sc_2O_3 with $Sc(cp)_3$ and a Novel Heteroleptic Precursors***, T Ivanova, **Perttu Sippola,*** ASM, Finland*; G Verni, Q Xie,* ASM, Belgium*; M Givens,* ASM, Finland

The deposition and the properties of rare earth oxide thin films have been extensively studied for applications as protective coatings, optics and microelectronics. Sc_2O_3 thin films have recently attracted a strong interest for application as gate dielectrics for metal-oxide-semiconductor field-effect transistors (MOSFET) because they have a dielectric constant of 14, a band gap of 6.3 eV and excellent thermal stability. Despite its advantages, very few studies have investigated Sc_2O_3 on Si. We therefore investigated growth characteristics of Sc_2O_3 films deposited by atomic layer deposition (ALD) from $Sc(cp)_3$ and a novel liquid heteroleptic cyclopentadienyl containing Sc precursor, which are thermally stable (>300 ˚C), volatile, with a good reactivity to H_2O. The depositions were done in a hot-wall cross-flow-type ASM Pulsar® 3000 reactor connected to a Polygon 8300 platform.

The film growth properties, such as growth per cycle, impurity concentrations, and thickness uniformity on 300 mm Si (100) wafers were studied. A growth rate per cycle of 0.46 Å/ cycles and 0.52 Å/cycle was obtained at 225 ˚C with novel Sc based precursor and $Sc(cp)_3$, respectively. The Sc_2O_3 film non-uniformity was about 1 % and 5 % with novel Sc heteroleptic precursor and $Sc(cp)_3$, respectively. Sc_2O_3 films based on the novel Sc precursor were stoichiometric, with a low C impurity content of <1%, while films based on $Sc(cp)_3$ precursor exhibited ~4.5 % of residual carbon impurity level under similar processing conditions.

Electrical measurements were done on planar TiN gated MOS capacitor (MOSCAP) with high k thickness ~8 nm. $Sc(cp)_3$ based Sc_2O_3 exhibited a leakage current density of 1.5 x 10^{-4} A/cm² and an effective work function (eWF) of 4.05 eV for an equivalent oxide thickness (EOT) of 3.43 nm at 1.0 V, which is significantly lower than TiN eWF (~4.8 eV) indicating considerable positive fixed charges incorporated in deposited Sc_2O_3 film.

While novel heteroleptic Sc based Sc_2O_3 films exhibited much lower leakage current density of 1.0 x 10^{-8} A/cm^2 and close to TiN eWF of 4.77 eV for an EOT of 3.15 nm at 1.0 V. It was shown that good quality and low defects Sc_2O_3 films can be obtained by using the novel heteroleptic Sc precursor.

9:45am **AF2-TuM-8 A Novel Self-limited Atomic Layer Deposition of WS_2 based on the Chemisorption and Reduction of bis(t-butylimido)bis(dimethylamino) Complexes***, **Nicola Pinna,*** Humboldt-Universtät zu Berlin, Germany

A novel self-terminating chemical approach for the deposition of WS_2 by atomic layer deposition based on chemisorption of bis(t-butylimido)bis(dimethylamino)tungsten(VI) followed by sulfurization by H_2S is reported. A broad spectrum of reaction parameters including temperatures of the reaction chamber and the precursor and durations of every ALD step are investigated and optimized to reach a high growth per cycle of 1.7 Å and a high quality of the deposited thin films. The self-terminating behaviour of this reaction is determined by the variation of the dose of the precursors. The physical, chemical and morphological properties are characterized by a combination of analytical techniques. XRD, XPS and Raman prove that highly pure and well-defined WS_2 layers can be synthesized by ALD. TEM and AFM images show that WS_2 grows as platelets with a thickness of 6^{-10} nm and diameter of 30 nm, which do not vary dramatically with the number of ALD cycles. A low deposition temperature process followed by a post annealing under H_2S is also investigated in order to produce a conformal WS_2 film. Finally, a reaction mechanism could be proposed by studying the chemisorption of bis(t-butylimido)bis(dimethylamino)tungsten(VI) onto silica, and the thermal and chemical reactivity of chemisorbed species by ^{1}H NMR, GC-MS and FT-IR.

ALD Fundamentals
Room Grand Ballroom A-C - Session AF3-TuM
Growth and Characterization II

Moderators: Jolien Dendooven, Ghent University, Belgium, Henrik Pedersen, Linköping University, Sweden

10:45am **AF3-TuM-12 Enabling Nucleation Phenomena Studies of ALD Deposited Films by In-situ High-Resolution TEM***, **Stephanie Burgmann**, A Dadlani, A Bin Afif,* Norwegian University of Science and Technology, Norway*; J Provine,* Aligned Carbon*; A van Helvoort, J Torgesen,* Norwegian University of Science and Technology, Norway

Understanding the nucleation stage and growth characteristics of atomic layer deposition (ALD) is indispensable for the fabrication of quantum dots or very thin films of just a few nanometers thickness. The tools for analyzing such small features and films are limited and often include post deposition characterization failing to capture the initial nucleation step. Enabling ALD processes in a closed gas-cell system inside a transmission electron microscope (TEM) allows manufacturing and characterization during film evolution at working conditions, a significant component in optimizing the nucleation phase.

In-situ characterization of deposition processes could be performed in an environmental TEM (ETEM) or a separated closed gas-cell holder system in a TEM preserving all analytical signals and TEM imaging capabilities as well as possible. A gas-cell reactor promises benefits in terms of versatility, controllability, and a defined deposition area. A successful implementation of ALD in a closed gas-cell system necessitates a gas-cell rector, a microscale heating system, a heated gas injection system, and an evacuation system to be placed into the limited space of a TEM holder.

An *in-situ* gas-cell holder system allowing deposition of different materials in a TEM has to be tailored to the delicate temperature sensitive ALD processes. To avoid contamination due to outgassing of sealing components, a gas-cell is designed based on a single wafer process, using the “Sandbox” process as basis. A layered structure employing ALD Al_2O_3 as etch stop layer and window material gives the opportunity to create a buried channeling system. Precursor gases will be injected from the back side of the chip using the two outer openings as inlet and exhaust. The central opening is the area where the electron beam is transmitted through the chip for imaging purposes. Al_2O_3 layers are used as functional windows with only a few atomic layers in thickness to achieve best possible high-resolution imaging and serve as a substrate for deposition. The design of the gas cell on a single wafer enhances the possibility to use characteristic x-ray signals for compositional analysis due to higher signal yield and simplifies the preparation for TEM studies involving environmental conditions.

The *in-situ* gas-cell reactor system is currently prototyped and will be tested thoroughly before its application inside the TEM. Ultimately, we envision that it enables controlled deposition inside any TEM, opening up new opportunities in nucleation studies for various researchers working on functional thin films around the world, opportunities not necessarily limited to ALD only.

11:00am **AF3-TuM-13 *In-situ* ellipsometric analysis of plasma assisted ALD grown- stoichiometric and crystalline AlN films***, **Adnan Mohammad**, D Shukla, S Ilhom, B Willis,* University of Connecticut*; B Johs,* Film Sense LLC*; A Okyay,* Stanford University*; N Biyikli,* University of Connecticut

The self-limiting aluminum nitride (AlN) plasma-assisted ALD (PA-ALD) growth process is monitored in dynamic real-time mode by in-situ multi-wavelength ellipsometry. AlN thin films are deposited on Si(100) substrates by PA-ALD reactor featuring a capacitively-coupled hollow-cathode plasma source and using trimethyl-aluminum (TMA) and Ar/N2/H2 plasma as metal precursor and coreactant, respectively. The temperature range for the saturation experiments is 100 – 250 °C, while each growth parameter variation is carried out for 10-cycle sub-runs. The sensitivity of the multi-wavelength ellipsometry has provided sufficient resolution to capture not only the subtle changes in the growth-per-cycle (GPC) parameter, but as well the single chemical surface reactions including precursor adsorption and plasma-assisted ligand removal and nitrogen incorporation. GPC values showed a slight increase with temperature slope within 100 – 200 °C, followed by a stronger surge at 250 °C, signaling the onset of thermal decomposition of TMA. The real-time dynamic in-situ monitoring depicted mainly the following perceptions into the HCPA-ALD process of AlN: (i) The GPC and TMA chemisorption amount showed plasma-power dependent saturation behavior which was also correlated with the substrate temperature; (ii) The cycle dependent refractive index profile shows a faster increase

within the first ~100 cycles followed by a slower increase as the AlN film gets thicker; (iii) The crystallinity is improved particularly when substrate temperature exceeded 200 °C. In terms of additional materials characterization, optical, structural, and chemical properties are studied via ex-situ measurements on 500-cycle grown AlN films as a function of substrate temperature. The single-phase wurtzite polycrystalline character was confirmed for all AlN samples with no detectable carbon and relatively low (< 5%) oxygen content within the bulk of the films. Moreover, the highly stoichiometric (~1:1) elemental composition was also noticed as well for all AlN samples, regardless of the substrate temperature. A detailed comparative analysis with previously published reports on PA-ALD grown AlN will be presented.

11:15am **AF3-TuM-14 Film Properties of ALD SiNx Deposited by Trisilylamine and N_2 Plasma***, **Markus Bosund**, E Salmi, K Niiranen,* Beneq Oy, Finland

Silicon nitride is a widely used material in semiconductor applications, such as gate dielectrics, III/V surface passivation and etch stop layer.

PEALD SiNx films have been previously grown using aminosilanes like BTBAS with N_2 plasma [1]. These processes generally have a relatively low growth rate of 0.15 - 0.21 Å/cycle and high film quality can only be reached at above 300 °C deposition temperatures. Trisilylamine (TSA) has been previously combined with N_2/H_2 plasma at 300–400 °C [2], NH_3 plasma at 50–400 °C [3] and N_2 plasma at 250 – 350 °C [4] to grow PEALD SiNx films. However, in these works the low temperature range has remained either inaccessible or uncharted.

In this work we explored the PEALD TSA-N2 plasma process with a wide deposition temperature range from 50 to 350 °C. Focus was given to the electrical and optical properties of the films. A Beneq TFS 200 capacitively coupled hot wall plasma ALD reactor was used at direct plasma mode. It was found that reactor temperature, and plasma power and time had the highest impact on the film properties. Film deposition was observed at temperatures as low as 50 °C. Metal insulator semiconductor (MIS) structures were used to determine the breakdown field and leakage current at different temperatures. Films were dipped in 1 % HF solution for etch rate determination.

[1] KNOOPS, Harm CM, et al. Atomic layer deposition of silicon nitride from Bis (tert-butylamino) silane and N2 plasma. ACS applied materials & interfaces, 2015, 7.35: 19857-19862.

[2] TRIYOSO, Dina H., et al. Evaluation of low temperature silicon nitride spacer for high-k metal gate integration. ECS Journal of Solid State Science and Technology, 2013, 2.11: N222-N227.

[3] JANG, Woochool, et al. Temperature dependence of silicon nitride deposited by remote plasma atomic layer deposition. physica status solidi (a), 2014, 211.9: 2166-2171.

[4] WEEKS, Stephen, et al. Plasma enhanced atomic layer deposition of silicon nitride using neopentasilane. Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films, 2016, 34.1: 01A140.

11:30am **AF3-TuM-15 Comparison of Properties of Conductive Nitride Films Prepared by PEALD using Quartz and Sapphire Plasma Sources***, I Krylov, X Xu, K Weinfeld,* ***Valentina Korchnoy****, D Ritter, M Eizenberg,* Technion - Israel Institute of Technology, Israel

We report on the properties of various conductive nitrides (TiN, ZrN, TaN) prepared by PEALD using either quartz or sapphire inductively coupled plasma (ICP) sources. Quartz and sapphire are two commonly used ICP source materials. The films were deposited at 300°C in Ultratech/Cambridge Fiji G2 PEALD system using metal-organic precursors and plasma half-cycles, separated by a purge period. Different reactive gases (N2, NH3, and H2) and various pressures during the plasma half-cycle were examined. All deposited films were ~ 30nm thick. TiN deposition rates are higher for the processes with the sapphire ICP source compared to those with the quartz source (Fig.1). The difference in deposition rates increases if the hydrogen based reactive gases are used for deposition. The low deposition rates of H2 plasma-grown TiN obtained using the quartz source may indicate a significant chemical etch of the quartz source by H radicals. Quartz tube etching is manifested by oxygen contamination in the deposited films, especially at processes with high H_2 flow (Fig.2). All deposited TiN films were found crystalline with a strong preferential orientation (XRD data is shown in Fig.3). The ICP source material has a significant role on film morphology if a H_2 plasma is used for deposition. Films deposited using the quartz source consist of small (a few nm size) grains. Deposition using the sapphire ICP source results in films with large (~20nm size) columnar grains (Fig.4). The most technologically important parameter of conductive nitrides is film resistivity. At thicknesses significantly higher than the electron mean free path film resistivity is increased due to scattering at grain boundaries and point defects. Therefore, the main parameters determining film resistivity of the deposited 30nm thick TiN films are the grain size and the oxygen contamination. For all examined nitrides, the lowest film resistivity and the highest film density was obtained for the H2 plasma-grown films deposited using the sapphire based ICP source (Fig.5,6). Sapphire source enabled higher deposition rates, better crystallization, lower film resistivity, and lower oxygen contamination. This indicates a superior chemical resistivity of sapphire to etching by hydrogen radicals compared to that of quartz. The advantage of the sapphire based ICP source is pronounced when a H_2 plasma and/or at high reactive gas flow are used for nitride deposition. The influence of ICP source material choice on the nitride film quality may be minimized if nitrogen based reactive gases and low flow conditions are used for nitride deposition. Optimal deposition conditions for both ICP source materials are determined.

11:45am **AF3-TuM-16 Role of Hydrogen Radicals in the Surface Reactions of Trimethyl-Indium (TMI) with Ar/N_2 Plasma in Hollow-Cathode Plasma-Assisted ALD***,* ***Saidjafarzoda Ilhom****, A Mohammad, D Shukla, N Biyikli, B Willis,* University of Connecticut

In this work we investigate the surface reactions of trimethyl-indium (TMI) with varying nitrogen plasma compositions. Extended 600-cycle long runs were carried out to grow thin films on Si(100) substrates via hollow-cathode plasma-assisted atomic layer deposition (HCPA-ALD). TMI and variants of $Ar/N_2/H_2$ plasma (N_2-only, Ar/N_2, and $Ar/N_2/H_2$) were utilized as metal precursor and nitrogen co-reactant, respectively. Growth experiments have been performed within 50 - 200 W plasma power range and 120 - 240 °C substrate temperature. Dynamic *in-situ*ellipsometry was employed to monitor the growth-per-cycle (GPC) characteristics and real-time growth behavior. In addition to *in-situ*analysis, *ex-situ*characterizations were done to identify structural, chemical, and optical properties of the grown InO_xN_yfilms. It was found that samples displayed polycrystalline single-phase hexagonal InN only when Ar/N_2-plasma was utilized. However, introducing H_2gas to the nitrogen plasma led to the growth of crystalline indium oxide (In_2O_3) films. In general, all In_2O_3samples displayed polycrystalline character, which exhibited preferred (222) crystalline orientation with peak intensity values changing as a function of RF-plasma power and substrate temperature. Interestingly, in the film grown at 160 °C the dominant crystal orientation shifted towards (321) with additional appearance of two metallic indium crystalline peaks. The role of H_2in possible reaction mechanisms resulting in the replacement of nitrogen with oxygen will be discussed based on the correlation of XRD and XPS results. The analysis of *in-situ*and *ex-situ*ellipsometry data will provide additional insight into the optical properties of the films as well as how the single chemisorption, ligand removal, and nitrogen/oxygen incorporation events possibly occur along the ALD cycles.

ALD Fundamentals
Room Grand Ballroom A-C - Session AF-TuA
Plasma ALD: Growth and Characterization

Moderators: HyeongTag Jeon, Hanyang University, Korea, Jiyoung Kim, University of Texas at Dallas

1:30pm **AF-TuA-1 Low Temperature High Quality Silicon Dioxide by Neutral Beam Enhanced Atomic Layer Deposition**, ***Hua-Hsuan Chen**, D Ohori, T Ozaki,* Tohoku University, Japan*; M Utsuno, T Kubota, T Nozawa,* ASM Japan K.K., Japan*; S Samukawa,* Tohoku University, Japan

Atomic layer deposition (ALD) has shown to have high control of conformality on thin films in recent decades. Instead of conventional deposition technique, such as physical vapor deposition and plasma-enhanced chemical vapor deposition, it is usually used to deposit thin layers on complex structures due to its thickness control ability. Plasma-enhanced ALD (PEALD) and thermal ALD are the examples. However, there are some serious problems. For instance, plasma irradiation and charge accumulation existed in PEALD [1] can cause defects in thin films; high temperature is also needed in thermal ALD. In previous studies, neutral beam technology has shown advantages on depositing high quality films, such as low-k SiOCH film [2] and nitrogen doping diamond-like carbon film [3]. Here, we demonstrated the atomic layer growth of SiO_2 film on Si using novel neutral beam-enhanced deposition (NBEALD) technique, which was deposited at room temperature, and serves as an important material in various applications.

Neutral beam enhanced atomic layer deposition system consists of a large-radius ALD process chamber and an inductively coupled plasma source. We used Aminosilane as the precursor and O_2 as the neutral beam source to deposit films on the Si substrate. The stage temperature was controlled at 30°C. After the ALD cycle which was composed of: precursor feed, precursor purge, O_2 injection, neutral beam irradiation and O_2 purge, the SiO_2 film was grown on silicon wafers. We used spectroscopic ellipsometry to measure film thickness; the atomic force microscope was used to investigate the surface morphology; the X-ray photoelectron spectroscopy (XPS), X-ray reflectivity (XRR) and secondary ion mass spectrometry (SIMS) were used to analyze the chemical composition of the films for investigating the SiO_2 film quality.

The ALD cycle shows the thickness is linearly dependent on the number of cycles with growth per cycle comparable to that of PEALD [4]. The uniformity of the film was obtained by measuring thickness on different places of 8 inch wafer, and the result shows the film has good uniformity. For the XPS, XRR and SIMS results, high quality and high density SiO_2 film composition was confirmed. Furthermore, the excellent surface morphology could be seen on SiO_2 films as no difference for thickness discrepancy. Therefore, we succeeded to make high quality SiO_2 films using NBEALD technique under room temperature.

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[2] Y. Kikuchi et al, *J. of Phys. D: Appl. Phys.* Vol. 46 (2013)

[3] S. Yasuhara et al, *J. of Phys. D: Appl. Phys.* Vol. 43 (2010)

[4] S. J. Won et al, *IEEE Elec. Dev. Lett*. Vol. 31, No. 8 (2010)

1:45pm **AF-TuA-2 Radical Surface Recombination Probabilities during Plasma ALD of SiO_2, TiO_2 and Al_2O_3 Determined from Film Conformality**, ***Karsten Arts**,* Eindhoven University of Technology, Netherlands*; M Utriainen,* VTT Technical Research Centre of Finland, Finland*; R Puurunen,* Aalto University, Finland*; E Kessels,* Eindhoven University of Technology, Netherlands*; H Knoops,* Oxford Instruments Plasma Technology, UK

This work addresses the growth of conformal films on high aspect ratio (AR) structures by plasma ALD, which can be challenging due to loss of the reactive radicals through surface recombination. Using plasma ALD of SiO_2, TiO_2 and Al_2O_3 as case studies, we show that the AR up to which film growth is achieved gives quantitative insight into the recombination probability *r* of plasma radicals on given material surfaces. Such quantitative information on *r* is often not available in the literature and difficult to obtain by conventional methods, while it is essential for predicting and understanding the conformality achieved by plasma ALD. Applications of plasma ALD such as the conformal growth of SiO_2 spacers for self-aligned patterning can thus benefit from this work.

In this study we use microscopic lateral-high-aspect-ratio structures[1] supplied by VTT (PillarHall® LHAR4) to assess the conformality of plasma ALD processes. As these chips have extremely high AR trenches (AR<10000) deposition is typically limited up to a certain penetration depth. For the first time, we demonstrate that this penetration depth can be used to quantify *r* during plasma ALD.

By carrying out plasma ALD of SiO_2 using $SiH_2(N(C_2H_5)_2)_2$ and different O_2/Ar plasma exposure times, we have observed that the penetration depth increases logarithmically with the plasma time used in the ALD cycle. This relation is well described by a simple analytical model which can be used to calculate *r*. For plasma ALD of SiO_2 this gives $r=(6\pm3)\cdot10^{-5}$, which compares well to reported literature values.[2] Using a long plasma exposure, deposition of SiO_2 is achieved up to an AR as high as 900. Similarly, growth of TiO_2 using $Ti(N(CH_3)_2)_4$ reaches AR>250. In contrast, plasma ALD of Al_2O_3 using $Al(CH_3)_3$ shows a surprisingly low penetration (AR~80) compared to the thermal ALD process, even with long plasma exposure, which indicates the impact of a relatively high surface recombination probability. Estimations of the corresponding values of *r* and additional insights will be provided in this contribution. These results demonstrate that our method is a powerful and straightforward way to gain knowledge on surface recombination during plasma ALD and its strong effect on film conformality.

1. Arts, Vandalon, Gao, Utriainen, Puurunen, Kessels and Knoops, 18th Int. Conf. At. Layer Depos. ALD 2018 – Proc., (2018)

2. Kim and Boudart, Langmuir 7, 2999 (1991)

2:00pm **AF-TuA-3 A Robust Method for In-situ Gas Monitoring of ALD Processes using Optical Emission Spectroscopy of a Pulsed Remote Plasma**, ***Joe Brindley**, B Daniel, V Bellido-Gonzalez,* Gencoa Limited, UK*; R Potter, B Peek,* University of Liverpool, UK

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

Conventional quadrupole residual gas analyzers 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 $1E^{-4}$ 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 and TiO_2 ALD processes are discussed; this includes detection of contaminants, optimizing purge cycle length and monitoring the reaction dynamics in terms of precursor gas consumption and reaction by-products.

2:15pm **AF-TuA-4 Near Room Temperature Plasma Enhanced Atomic Layer Deposition of Gold Metal**, ***Michiel Van Daele**,* Ghent University, Belgium*; M Griffiths,* Carleton University, Canada*; A Raza,* Ghent University - IMEC, Belgium*; M Minjauw,* Ghent University, Belgium*; S Barry,* Carleton University, Canada*; R Baets,* Ghent University - IMEC, Belgium*; C Detavernier, J Dendooven,* Ghent University, Belgium

Currently only two Au ALD processes exist, using two different precursors. The first Au ALD process, reported by Griffiths et al. [1], is a three step process using Me_3AuPMe_3 as the precursor in combination with an oxygen plasma and water vapour as the reactants. The deposition of metallic gold was reported at a deposition temperature of 120°C, with only some carbon and oxygen impurities present in the film (6.65% C and 1.83% O). A growth per cycle of 0.05 nm per cycle was achieved. The Au ALD process, reported

by Mäkelä et al. [2], uses $Me_2Au(S_2CNEt_2)$ as the precursor and ozone as the reactant. Deposition between 120-180°C was reported with self-limiting growth at 180°C and a growth rate of 0.09 nm per cycle. The deposited films had low resistivity values (4-16μΩ cm) and were chemically pure with few impurities, O (2.9%), H (0.9%), C (0.2%), and N (0.2%).

A new plasma enhanced ALD process has been developed using Me_3AuPMe_3 and H_2 plasma as the precursor and reactant, respectively. Both precursor and reactant exhibit saturating behaviour, with a growth per cycle of 0.03 nm per cycle. A temperature window between 50°C and 120°C is achieved, with decomposition of the precursor above 120°C. The as-deposited gold films are polycrystalline and pure, with no phosphorous present in the film and very few carbon impurities (0.3%). Measured resistivity values (5.85μΩ cm) were close to the expected bulk value of gold (2.44 μΩ cm).

The surface chemistry and growth mechanism were investigated using in-situ RAIRS measurements, optical emission spectroscopy, and mass-spectrometry, pointing to an abbreviated growth cycle, instead of a complete one [3]. The initial growth starts off with the nucleation of gold particles on the surface. The formed gold nanoparticles grow and coalesce during the ALD process, as characterized using SEM measurements. The spacing of the gold particles makes this process interesting for surface enhanced Raman spectroscopy (SERS). Free space Raman measurements were performed on some of the samples and these showed excellent surface enhancement of the Raman signal. As far as we know this is the first report of an ALD gold film that shows SERS properties. In contrast to other SERS substrate fabrication methods, often involving lithography, this ALD process provides a direct way to fabricate SERS substrates without the need for a lot of process steps.

[1] M. B. E. Griffiths, P. J. Pallister, D. J. Mandia, and S. T. Barry, Chem. Mater. 28(1) (2016) 44-46

[2] M. Mäkelä, T. Hatanpää, K. Mizohata, J. Räisänen, M. Ritala, and M. Leskelä, Chem. Mater. 29(14) (2017) 6130-6136

[3] S. Elliott, G. Dev, and Y. Maimaiti, J. Chem. Phys. 146(5) (2017) 052822

2:30pm **AF-TuA-5 Low-Temperature Deposition of Gallium Oxide and Aluminum Oxide with Arrays of Microcavity Plasma Enhanced Atomic Layer Deposition**, ***Jinhong Kim***, *A Mironov, S Park, J Eden,* University of Illinois at Urbana-Champaign

A new atomic layer deposition (ALD) technology has been developed with an array of microcavity plasma devices which enable to grow the atomic layers at low temperature and enhance the growth rate with less defects and contamination. Confining low temperature plasmas to an array of microcavities yields uniform, glow discharges operating at pressures of 1 atmosphere and beyond. Not only are electron densities above 10^{16} cm^{-3} now routine, but the plasma electron temperature (T_e) and the ratio of the local electric field strength to the gas number density (E/N) are also increased significantly relative to conventional (macroscopic) plasmas. All of these characteristics are ideal for plasma chemical processing to generate oxidants efficiently compared to conventional RF or others existing source technology. A compact ALD system of which volume reduced by at least a factor of five was realized thanks to the miniztурized microplasma source operating in lower frequency ac waveform. The uniform and conformal gallium oxide (Ga_2O_3) and aluminum oxide (Al_2O_3) thin films were deposited at low temperatures (< 50 °C) on silicon, quartz, and even polyethylene terephthalate (PET). Due to the complete reaction between precursors, the stoichiometric value of films presents ~ 1.5 in crystalline state, indicating the presence of negligible levels of impurities. MOSCAP was fabricated to analyze the electrical characteristic of 30 nm thickness of Al_2O_3 film. This MOSCAP exhibits higher breakdown electric field of 6.1 MV than conventional Al_2O_3 thin film . Hysteresis width from the sweep bias voltage was measured to less than 1 mV which is close to ideal MOSCAP electrical characteristics. In addition, Ga_2O_3 films deposited on PET were used to fabricate for transparent and flexible solar-blind photodetector with metal-semiconductor-metal junction structure. The crystallinity of films was analyzed using Transmission electron microscope (TEM) and X-ray diffraction (XRD). Post annealing (> 800 C) with argon environment was essential to produce polycrystalline β-Ga_2O_3. Bandgap was calculated by optical characteristics of the films from UV spectrophotometer. The photoresponse properties of photodetectors were investigated by the current-voltage characteristics and time-dependent photoresponse curves. Various thin film grown by microplasma enhanced ALD demonstrates improved optical and electrical properties. The scientific inspiration of this new deposition technology as well as the prospect for commercial application will be discussed in this presentation.

2:45pm **AF-TuA-6 The Effects of Varying Plasma Conditions on Plasma Assisted Atomic Layer Epitaxy**, ***David Boris***, *V Wheeler, N Nepal, S Rosenberg, J Avila, J Woodward, V Anderson, S Walton, C Eddy, Jr.,* U.S. Naval Research Laboratory

Plasma assisted atomic layer deposition (PA-ALD) is a low temperature, conformal, layer-by-layer deposition technique that is based on a pair of self-terminating and self-limiting gas-surface half-reactions, in which at least one half-reaction involves species from a plasma. This approach generally offers the benefit of substantially reduced growth temperatures and greater flexibility in tailoring the gas phase chemistry to produce varying film characteristics. The flexibility and lower growth temperatures that plasmas provide come at the cost of a complex array of process variables that often require great care on the part of the user.

In response to this challenge, this work focuses on the use of plasma diagnostics to inform the choice of process conditions for PA-ALD systems. In this work we employ VUV-NIR spectroscopy, charged particle collectors near the substrate, and spatially resolved Langmuir probe measurements to characterize the inductively coupled plasma source used in a Fiji 200 (Ultratech/CNT) PA-ALD tool. In particular, we assess the total ion flux reaching the substrate surface, spatial variation of plasma properties, and the relative fractions of atomic and molecular species generated in the plasma under a variety of pressures and gas input flow fractions in context of PA-ALD of AlN, InN, TiO_2 and Ga_2O_3 films. Changes in plasma parameters are then linked with changes in film characteristics.

3:00pm **AF-TuA-7 Plasma-Enhanced Atomic Layer Epitaxy of Ultra-wide Bandgap Ga_2O_3 and $(Al_xGa_{1-x})_2O_3$ Films**, ***Virginia Wheeler***, *N Nepal, D Boris, S Walton, S Qadri, J Avila, D Meyer, B Downey, V Gokhale,* U.S. Naval Research Laboratory; *L Nyakiti,* Texas A&M University; *M Tadjer,* U.S. Naval Research Laboratory; *M Goorsky,* University of California Los Angeles; *C Eddy Jr.,* U.S. Naval Research Laboratory **INVITED**

Ga_2O_3 has emerged as a promising material for next generation power electronics. While β-Ga_2O_3 (monoclinic) is the most stable and studied of five Ga_2O_3 polymorphs, the slightly less energetically favorable α- and ε-Ga_2O_3 phases have unique characteristics that can be exploited. α -Ga_2O_3 (rhombohedral, corundum) has the largest bandgap of 5.3 eV and can be alloyed with α-Al_2O_3 and α-In_2O_3 for bandgap engineering. ε-Ga_2O_3 phase (hexagonal, wurtzite) is polar, with a predicted polarization strength that is 10 and 3 times larger than that of GaN and AlN, respectively. Like the III-N system, polarization induced charges can lead to higher charge densities and mobilities in two-dimensional electron channels formed at heterojunctions, which would improve the viability of Ga_2O_3 electronic devices. Plasma-enhanced atomic layer deposition (PEALD) is a popular, conformal, energy-enhanced synthesis method for thin films due to its many advantages, including: deposition at reduced growth temperatures, access to metastable phases and improved crystallinity, and increased growth rates. In this work, we use PEALD to produce high-quality heteroepitaxial Ga_2O_3 and $(Al_xGa_{1-x})_2O_3$ (AlGO) films, and investigate phase selectivity as a function of substrate, growth temperature (T_g), plasma gas phase chemistry and gas pressure.

All Ga_2O_3 films were deposited in a Veeco Fiji G2 reactor equipped with a load lock and turbo pump using trimethygallium and O_2 plasma. Initial studies on c-plane sapphire substrates at 350°C and 8 mTorr, show the phase could be altered from β to α by a varying the O_2 flow during plasma pulse from 5-40 sccm. Optical emission spectroscopy indicate that the O^*/O_2 ratio is crucial for phase selectivity while the high ion flux to the surface can contribute to the crystallinity at low T_g. To grow ε-Ga_2O_3 on c-plane sapphire required going to much higher temperature (500°C), pressure (100's mTorr), and O_2 flow (100sccm) . Under no conditions was pure ε-Ga_2O_3 on sapphire achieved. Using optimum growth conditions for the three phases on sapphire, films were deposited on GaN and diamond to determine the effect of substrate structure. While films on diamond resulted in mixed β/ε phases, pure ε-phase films were attained on GaN and the strain varied with pressure and T_g. To investigate favorable heterojunctions for 2DEG formation, AlGO films were developed. While the full stoichiometric range could be reached using a PEALD digital alloying method, crystallinity was lost above ≈30 %Al, independent of phase. Initial electrical results on breakdown voltage and heterojunctions will be shown in order to establish the feasibility of these films in device applications.

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