Monday Morning, June 28, 2021

Live Session
Room Live - Session LI-MoM

Plenary & Awards Live Session

Moderators: Prof. Sean Barry, Carleton University, Canada, Prof. Dr. Stacey Bent, Stanford University, Dr. Jane P. Chang, University of California, Los Angeles, Dr. Scott Clendenning, Intel Corporation, Dr. Thorsten Lill, Lam Research Corporation, Prof. Mikko Ritala, University of Helsinki

10:00am **LI-MoM-1 Opening Remarks & Welcome**, ***Scott Clendenning,*** Intel; *S. Barry,* Carleton University, Canada; *J. Chang,* University of California, Los Angeles; *T. Lill,* Lam Research Corp.

Welcome to the ALD/ALE 2021 Virtual Meeting! We hope you will enjoy the event1

10:10am **LI-MoM-3 Plenary Lecture: Materials & Innovation - Essential Elements that Underpin the Next Industrial Revolution**, ***Todd Younkin,*** SRC **INVITED**

All of us can see the next industrial revolution on the horizon. There are generational opportunities in hyperscaled computing, artificial intelligence (AI), autonomous driving, 5G/6G communications, integrated photonics, and even quantum computing and quantum sensing. Yet, as computing systems create new markets and move into these domains, the underlying hardware performance required to truly unleash these markets at scale is faced with constraints driven by fundamental physical limits. The opportunities of tomorrow are simply unachievable through anticipated hardware technologies and our old two dimensional (2D-) scaling playbook. A paradigm shift is underway to create new value propositions with semiconductor technologies and fabrication as the key drivers.

In response to this emerging crisis, SRC convened scientists from industry, academia, and government to outline a ten year R&D plan, the 2030 Decadal Plan for Semiconductors, as a scientific call to action.[1,2] Therein, we have outlined the global drivers and constraints for future information and communication technology (ICT) systems, providing goal-driven yet creative solutions to seek measured progress and real world impact. The document outlines five “seismic shifts” that are shaping the future of chip technologies for smart sensing, memory and storage, communication, security, and energy efficient computing.

At the heart of these advances lies chipmaking which requires materials innovation, new precursors, new chip fabrication equipment, an understanding of material interfaces, the continued development of process knowledge, and skilled workers that embody these essential elements. The tribal knowledge and research activity in these areas must evolve beyond 2D-scaling to contribute to heterogeneous and 3D-monolithic integration that is informed by a rapidly-changing state of the art in packaging and assembly, design, and novel ICT architectures.

In this talk, I will share my perspective on the evolving global R&D landscape for semiconductors, illustrate the five “seismic shift” drivers behind future ICT chip advances, and give specific examples of ALD- and ALE-based research that map to today’s and tomorrow’s efforts. I hope to leave the audience with a clearer picture of the needs and opportunities we see for the years ahead. The “Roaring 20s” will not be boring if you are interested in materials-driven semiconductor advances and are a disciplined imaginator!

[1] 2030 Decadal Plan for Semiconductors, https://www.src.org/about/decadal-plan/

[2] Newly-Announced $3.4 Billion Plan Aims to Stimulate US Semiconductor R&D, https://www.allaboutcircuits.com/news/newly-announced-3point4-billion-plan-aims-stimulate-us-semiconductor-rd/

10:40am **LI-MoM-9 Introduction to ALD and ALE Student Finalists**, ***Seán Barry,*** Carleton University, Canada; *J. Chang,* University of California, Los Angeles

We now introduce you to our 2021 ALD/ALE Student Award Finalists.

10:45am **LI-MoM-10 ALD Student Award Finalist Talk: Enhanced Surface Adsorption in Electric Field/Potential Assisted Atomic Layer Deposition (EA-ALD) of Ultrathin Ru Film**, ***Yoon Jeong Kim***, *J. Han, J. Heo, T. Park,* Hanyang University, Korea

Ru metal has high work function of 4.7 eV, a low bulk resistivity (∼7 μΩ·cm). It has good thermal and chemical stability on metal state. Furthermore, Ru forms a conductive oxide phase, RuO_2, with work function of ~5 eV and resistivity as low as ~ 30 μΩ·cm, which prevents the formation of insulating interfacial layers in contact with oxides. As the size of semiconductor devices decreases, electronic applications require a nanometer-range of conformal thin film deposition in complex 3D structures. Among various thin film deposition technologies, atomic layer deposition (ALD) is considered to be promising in the development of nanometer device manufacturing technology due to its excellent step coverage and thickness control. [1]

However, continuous Ru film of under certain thickness (~6 nm) is difficult to form since they exhibit significant nucleation delay on various surfaces. The nucleation delay leads to increased process time and consumes a lot of precursor. For short nucleation delay time, high nucleation density is required.The high nucleation density forms continuous thin film with a smoother surface than obtained with low nucleation density. Therefore, the early nucleation density is important for metal film formation.

Using electric field/potential assisted atomic layer deposition (EA-ALD) can reduce the grain size and the critical thickness of the continuous film. When voltage is applied during precursor injection, it changes the surface potential of the substrate to promote chemical reactions. The electric field attracts the metal precursor molecules onto the substrate to improve the early nucleation density.As a result, the saturation of Ru layer density was increased on the substrate and a higher density thin film was deposited. It is possible to deposit continuous Ru ultrathin films with superior physical and electrical properties.

References [1] Chem. Mater. 2017, 29, 4654−4666

11:00am **LI-MoM-13 ALE Student Award Finalist Talk: Cryo-ALE of Silicon Based Materials**, ***Jack Nos***, *G. Antoun, T. Tillocher, P. Lefaucheux,* GREMI CNRS/Université d'Orléans, France; *J. Faguet,* Tokyo Electron America Inc.,; *K. Maekawa,* TEL Technology Center America; *R. Dussart,* GREMI CNRS/Université d'Orléans, France

Cryogenic Atomic Layer Etching (Cryo-ALE) has been presented in the previous ALE workshops (2019 & 2020) as a different approach to achieve ALE of SiO_2. In this process, C_4F_8 is injected in gas phase during the “modification” step, in order to physisorb on a cooled SiO_2 surface. The temperature window of this process was between -120°C and -90°C [1,2]. The etching is then achieved using an Ar plasma with a low energy ion bombardment. Nevertheless, the results were only reported on SiO_2 as no significant selectivity was observed over Si or Si_3N_4. Indeed, when using a fluorocarbon feed gas, the principle way to achieve a high selectivity of SiO_2 etch over Si or Si_3N_4 consists in creating a CF_X passivation layer on the surface of these materials. In cryo-ALE, as $C_4F_8$is injected in gas phase, $C_4F_8$is not dissociated and physisorption is not selective. Therefore, to try to etch other materials with higher selectivity, another gas chemistry has to be tested.

In 1996, Royer *et al.* studied the chemisorption of fluorine and sulfur on Si during a simultaneous exposure to SF_6 gas and Ne^+ ion beam. In this study, they showed by XPS measurements that the fluorine amount at the Si surface increases as the temperature decreases, for a process window between 20°C and –130°C [3]. In addition, it is well known that SF_6 plasma can be used to etch Si. For both reasons, SF_6 was chosen as a new feed gas instead of C_4F_8 to perform cryo-ALE of Si.

This work was carried out using a cryogenic ICP reactor. In-situ diagnostics are coupled to the reactor such as QMS and a Spectroscopic Ellipsometer. QMS measurements enabled to characterize the SF_6 physisorption and its surface residence time. SE measurements helped monitoring the thickness evolution over time during a process. Tests were performed on SiO_2, Si_3N_4 and p-Si coupons glued on SiO_2 6” carrier wafers.

First, SF_6 physisorption is studied and will be presented in order to optimize the process parameters, such as the temperature and the purge step time. Then, tests carried out on SiO_2 will be compared to the results obtained with C_4F_8. Finally, tests performed on Si will be reported showing the possibility to etch it over SiO_2.

These tests have hence enabled to prove that cryo-ALE can be achieved on different materials and that selectivity can be adjusted by changing the feed gas chemistry.

The authors would like to thank S. Tahara for all the helpful discussions.

This work was supported by CERTeM 2020 platform, which provides most of the equipment.

1. Antoun *et al.*, *Appl. Phys. Lett.***115**, 153109, 2019

2. Antoun *et al.*, *Sci. Rep.* 10, 2021

3. Royer *et al.,J. Vac. Sci. Technol. A***14**, 234–239, 1996

11:20am **LI-MoM-17 ALD Student Award Finalist Talk: What Controls the Conformality of Plasma ALD in High-Aspect-Ratio Applications?***, **Karsten Arts**, S. Deijkers, T. Faraz,* Eindhoven University of Technology, Netherlands*; R. Puurunen,* Aalto University, Finland*; E. Kessels, H. Knoops,* Eindhoven University of Technology, Netherlands

This work discusses the role and impact of the plasma on film conformality during plasma ALD, using the material systems SiO_2 and TiO_2 as industry-relevant case studies. Specifically, detailed insight into the impact of radical recombination and ion bombardment is provided. This is essential for predicting and further advancing the film conformality, especially for future applications with extremely high-aspect-ratio (AR) features.

First of all, the loss of reactive plasma radicals through surface recombination is often considered a major factor limiting film conformality during plasma ALD. To pinpoint what level of film conformality can still be achieved, we have developed a method to determine the surface recombination probability *r* of the radicals.[1] This method is based on the film penetration into high-AR trench structures. For plasma ALD of SiO_2 and TiO_2 very low values of r~10^{-4} are determined, where *r* is observed to further decrease with temperature and pressure down to ~10^{-5}. Accordingly, film growth up to an AR as high as 200:1 or even 800:1 is achieved within reasonable cycle times, depending on temperature and pressure.[2] These results demonstrate that extremely challenging applications such as the coating of porous materials are feasible under specific process conditions.

Secondly, we demonstrate that ion bombardment can also have an important impact on film conformality during plasma ALD, even under mild plasma conditions with low-energy (<20 eV) ions. Specifically, it is observed that (low-energy) ions contribute to the film quality of SiO_2,[3] can induce crystallization during plasma ALD of TiO_2,[4] and can alter the growth per cycle by a factor of up to ~2 (for both SiO_2 and TiO_2). This can significantly affect the film conformality obtained on 3D nanostructures. Furthermore, we reveal that the magnitude of the influence of ions can be controlled by the ion energy dose, where a minimal effect is obtained when supplying a dose of <1 eV nm^{-2} $cycle^{-1}$, or a strong effect when supplying a dose of >100 eV nm^{-2} $cycle^{-1}$.[3,4]

In conclusion, we provide key insights that can further advance plasma ALD, particularly to meet the conformality requirements in demanding future applications.

1. K. Arts *et al*., J. Phys. Chem. C 123, 27030 (2019).
2. K. Arts *et al*., Oxygen recombination probability data for plasma-assisted atomic layer deposition of SiO_2 and TiO_2 (to be published)
3. K. Arts *et al*., Appl. Phys. Lett. 117, 031602 (2020).
4. K. Arts *et al*., Impact of ions on film conformality and crystallinity during plasma-assisted atomic layer deposition of TiO_2 (to be published).

11:35am **LI-MoM-20 ALE Student Award Finalist Talk: Modelling Atomic Layer Etching of Thin Film Metal Oxides***, **Rita Mullins**,* Tyndall National Institute, University College Cork, Ireland*; S. Kondati Natarajan,* Synopsys , Denmark*; M. Nolan,* Tyndall National Institute, University College Cork, Ireland

HfO_2 and ZrO_2 are two high-k materials that are crucial in semiconductor devices. Atomic level control of material processing is required for fabrication of thin films of these materials at nanoscale device sizes. Atomic layer deposition (ALD) and thermal atomic layer etching (ALE) allow fabrication of ultra-thin films for semiconductor device processing. ALD is a well-known metal oxide thin film deposition technique that enables a high level of control over film thickness. Thermal ALE, which is growing in importance, uses self-limiting halogenation (e.g. HF exposure) producing a non-volatile modified layer. Subsequent ligand exchange reactions remove up to a monolayer of the metal oxide. This modern approach for controlled etching is the reverse of ALD.

Given that it is difficult to investigate ALE reactions directly using experimental techniques, first-principles-based atomic-level simulations using density functional theory (DFT) can give deep insights into the precursor chemistry and the reactions that drive the etch of different materials. This contribution presents first-principles density functional theory modelling to examine the etch chemistry of thin films of HfO_2 and ZrO_2. HF exposures on the surfaces of HfO_2 and ZrO_2 are studied. HF coverages ranging from 1.0 ± 0.3 to 17.0 ± 0.3 HF/nm^2 are investigated and a mixture of molecularly and dissociatively adsorbed HF molecules is present at higher coverages. Theoretical etch rates of -0.61 ± 0.02 Å /cycle for HfO_2 and -0.57 ± 0.02 Å /cycle ZrO_2 were calculated using maximum coverages of 7.0 ± 0.3 and 6.5 ± 0.3 M-F bonds/nm^2 respectively (M = Hf, Zr). These calculations involve perfect, crystalline oxide substrates. To widen the scope of this work, we also compare the ALE chemistry using HF on amorphous HfO_2 and the chemistry using HCl as the first pulse reagent.

11:50am **LI-MoM-23 ALD Student Award Finalist Talk: Surface Passivation Using Aminosilanes for Area-Selective Atomic Layer Deposition***, **Kaat Van Dongen**,* KU Leuven, Belgium*; R. Nye,* North Carolina State University*; D. De Simone, A. Delabie,* IMEC, Belgium

EUV lithography (EUVL) is one of the main drivers in the innovation of nano-electronic devices, as it can print structures of 14nm with a single exposure, and further downscaling is being studied. However, EUVL requires ultra-thin resist films to prevent pattern collapse, complicating the pattern transfer to the underlying layer. A possible solution is the combination of EUVL with area-selective deposition (ASD) of hard masks. ASD aims to deposit material only on the desired growth areas while no deposition occurs on the non-growth areas. ALD allows to deposit conformal films with atomic scale control, but most ALD processes have limited inherent selectivity. Surface passivation can improve the selectivity of ALD. Aminosilanes, such as dimethylamino trimethylsilane (DMATMS) and hexamethyldisilazane (HMDS), can work as passivating agents for SiO2 surfaces as trimethylsilyl (TMS) surface groups are introduced. To get a high selectivity, we need to optimize the TMS surface coverage and understand the impact on the passivation towards ALD.

We have therefore studied reactions of a hydroxylated SiO2 surface with DMATMS and HMDS and the effectiveness of the passivation towards TiO2 ALD (TiCl4/H2O). Both reactions are self-limiting, but the obtained TMS surface coverage is different. The reaction with DMATMS at 250°C saturates after 300 s and results in a TMS coverage of 2.1 TMS/nm2, close to theoretical limit of 2.41 TMS/nm2 (1), and a WCA of 101±1°. Lower temperature slightly reduces the WCA value (98±1° and 97±1° for 180°C and 135°C, respectively). This has only a minor effect on the selectivity for 3.41 nm TiO2 on the hydroxylated SiO2 (0.95, 0.92 and 0.90 for 250°C, 180°C and 135°C, respectively (RBS)). Contrarily, the HMDS reaction at 135°C and 180°C saturates after 600 s but the TMS coverage is at most 1.5 TMS/nm2 (XPS) and the WCA value is lower (80±6°). This leaves 0.9±0.7 OH/nm2 available for reaction with TiO2. The TiO2 selectivity is low, 0.13 for 3.41 nm TiO2 on the non-passivated SiO2. Possible explanations for the different surface coverage at saturation are the difference in chemistry, the HMDS could be too large to reach the remaining OH groups, or a difference in process conditions (e.g., partial pressure), since the reactions are carried out in different deposition tools. Sequential HMDS (180°C, 300s) and DMATMS (250°C, 300s) reactions result in a similar WCA but the selectivity towards TiO2 ALD drops faster compared to a single DMATMS reaction.

(1)Soethoudt, J. et al., J. Mater. Chem. C, 2019, 7, 11911

12:05pm **LI-MoM-26 ALD Student Award Finalist Talk: Electron-Enhanced Atomic Layer Deposition of Ruthenium Thin Films Using (DMBD)Ru(CO)₃***, **Michael Collings**, S. George,* University of Colorado, Boulder

Electron-enhanced atomic layer deposition (EE-ALD) has been demonstrated as an effective method to rapidly nucleate and grow thin films at low temperatures [1,2]. During EE-ALD, electrons are used as a “reactant” in an ALD process. The role of the electrons is to remove surface ligands via electron stimulated desorption. In this work, EE-ALD was used to grow Ru thin films using dimethylbutadiene (DMBD) ruthenium tricarbonyl, or $(DMBD)Ru(CO)_3$, at low temperatures.

The sequential surface reactions for Ru EE-ALD are shown in Figure 1. During this reaction sequence, a hollow cathode plasma electron source (HC-PES) provided a high flux of electrons. The HC-PES is chemically robust and can operate at reactor pressures as large as 1 mTorr. Our HC-PES can emit electron currents ≥ 100 mA over surface areas of 50 cm^2. The electron energy employed for the Ru EE-ALD was 125 eV. Ru growth during EE-ALD was measured with in-situ spectroscopic ellipsometry. The Ru films were grown on silicon substrates with a native oxide.

Ru film growth was demonstrated at both 100°C and 160°C. Film thickness measured by ellipsometry showed that the Ru films nucleate and grow from the very first EE-ALD cycle. Linear film growth was observed over 600 cycles with growth rates of 0.17 Å/cycle and 0.23 Å/cycle at 100°C and

160°C, respectively. Spectroscopic ellipsometry measurements for 600 cycles of Ru EE-ALD at 160°C are shown in Figure 2. Self-limiting growth behavior was observed with respect to both $(DMBD)Ru(CO)_3$ and electron exposures. XPS was used to determine the purity of the Ru films. Oxygen was observed to be as low as 0.3 at%. Carbon was also low but could not be quantified because of the overlap of the C and Ru XPS peaks.

[1] Z.C. Sobell, A.S. Cavanagh and S.M. George, "Growth of Cobalt Films at Room Temperature Using Sequential Exposures of Cobalt Tricarbonyl Nitrosyl and Low Energy Electrons", *J. Vac. Sci. Technol. A***37**, 060906 (2019).

[2] J.K. Sprenger, H. Sun, A.S. Cavanagh, A. Roshko, P.T. Blanchard and S.M. George, "Electron-Enhanced Atomic Layer Deposition (EE-ALD) of Boron Nitride Thin Films at Room Temperature and 100°C", *J. Phys. Chem. C***122**, 9455-9464 (2018).

12:20pm **LI-MoM-29 Plenary Lecture: Mechanisms of Thermal Atomic Layer Etching***, **Steven George,*** University of Colorado Boulder **INVITED**

Atomic layer deposition (ALD) and atomic layer etching (ALE) are defined by two sequential, self-limiting surface reactions. ALE is based on surface modification by the first reactant. The second reactant then leads to volatile release of the modified surface. There are two types of ALE:plasma and thermal. Plasma ALE methods employ energetic ion or neutral species to release the modified material anisotropically using sputtering. Thermal ALE processes utilize gas species to release the modified material isotropically using thermal reactions [1]. Thermal ALE can be viewed as the "reverse of ALD".

One important mechanism for thermal ALE is surface modification by fluorination and volatile release by ligand-exchange reactions. Fluorination is thermochemically favorable because metal fluorides are more stable than metal oxides. The metal fluorides can then be volatilized when a ligand from an incoming metal precursor exchanges with F from the metal fluoride. This fluorination and ligand-exchange mechanism is applicable to the thermal ALE of many metal oxides such as Al_2O_3. Conversion reactions are able to extend the range of materials that can be etched using thermal ALE. Conversion reactions occur when an incoming metal precursor reacts with the surface of an initial material and converts the surface layer into another material. This new material may have etching pathways that were not accessible to the initial material.

Another thermal ALE mechanism is based on oxidation and ligand-addition reactions. This mechanism is particularly important for etching elemental metals. Oxidation first changes the oxidation state of the elemental metal. Subsequently, ligands can add to the oxidized metal center and form stable and volatile metal compounds. An example of oxidation and ligand-addition is thermal Ni ALE using SO_2Cl_2 and $P(CH_3)_3$. Chlorination by SO_2Cl_2 changes the oxidation state and then $P(CH_3)_3$ adds to the oxidized Ni center and forms volatile $NiCl_2(P(CH_3)_3)_2$.

Different mechanisms for thermal ALE can lead to selectivity in etching between various materials. Etching results if the sequential, self-limiting surface reactions produce stable and volatile compounds. Selectivity between materials occurs if the etching products for one material are not stable or volatile. A good example is the selectivity between Al_2O_3 and ZrO_2 using HF and $Al(CH_3)_3$ as the reactants. ZrO_2 is not etched and can be used to define a monolayer etch stop for the HF and $Al(CH_3)_3$ reactants.

[1] S.M. George, "Mechanisms of Thermal Atomic Layer Etching", *Acc. Chem. Res.* **53**, 1151 (2020).

12:55pm **LI-MoM-36 Introduction to 2021 ALD Innovator Awardee Stacey Bent, Stanford University, USA: Up, Down and All Around: Controlling Atomic Placement in ALD***, **Seán Barry,*** Carleton University, Canada

With the increased importance of functional nanoscale materials for applications such as electronics, catalysts, and batteries, the interest in atomic layer deposition (ALD) as a method for fabricating structures with atomic-level control is intensifying. Based on sequential, self-limiting gas-surface reactions, ALD provides excellent capabilities for depositing thin solid films, nanoparticles, and other nanoscale materials while offering exceptional conformality, thickness control at the angstrom level, and tunable film composition. Yet despite the powerful film growth capabilities already attained with ALD, there is a compelling need to push the technique even further and control atomic placement not just in the direction of film growth, but also laterally. In this talk, I will describe research into the fundamental processes that drive ALD and ways to manipulate the chemistry to achieve area selective deposition, a bottom-up growth strategy in which deposition is directed only to desired regions of a patterned substrate. Mechanistically, the reaction chemistry of both the ALD precursor and the co-reactant at the growth surface play important roles in the ALD process and can influence both nucleation and growth. Importantly, by modifying the substrate properties, e.g., by the application of molecular monolayers or other surface treatments, the native reactivity of the surface with the ALD precursors can be altered to allow for area selective ALD. I will describe how area selectivity can be achieved across a range of different substrate and film materials, and also highlight challenges and potential solutions to reaching even high selectivities than currently possible.

1:00pm **LI-MoM-37 ALD Student Award Finalist Talk: Tuning Properties of Vapor Deposited ZIF-8 Thin Films With Preferred Orientation***, **Marianne Kräuter,*** Graz University of Technology, Austria

Recent years saw a rise of solvent-free methods for synthesis of metal organic frameworks with the aim of accessing new application fields and facile processing. Since vapor deposition excels at these key points we employed a two-step chemical vapor deposition process, that allows for the delivery of high-quality, homogeneous thin films of zeolitic imidazole framework 8 (ZIF-8) from ZnO[1].

First, an ultrathin ZnO seed layer is deposited via plasma-enhanced atomic layer deposition (PE-ALD). Acting on the substrate temperature, ranging from room temperature to 200°C, the preferred crystal orientation can be switched from (100) to (002). ZIF-8 thin films are subsequently grown by subjecting the ZnO-layer to a 2-methyl imidazole vapor. To our knowledge, this is the first time that PE-ALD has been employed for the growth of ZIF-8.

To gain better control over the still novel deposition technique, the impact of crystal orientation and thickness of the ZnO precursor onto the resulting ZIF-8 thin films was investigated. The results show that ZIF-8 was successfully synthesized. Furthermore, X-ray diffraction studies reveal a powder-like structure together with a strong (100) orientation of ZIF-8 crystals. ZIF-8 coverage on the substrate increases for thicker ZnO layers with ZIF-8 particles exhibiting average thicknesses as high as (93 ± 9) nm for ZIF-8 from 3 nm ZnO and (192 ± 11) nm for ZIF-8 from 10 nm ZnO. The thickness increase during conversion rises to about 1600% as a function of ZnO thickness. ZnO orientation weakly influences the thickness increase during conversion and, via differing densities, also the crystallinity of the resulting ZIF-8. Our results provide vital knowledge about the link between deposition parameters of ZnO and properties of the resulting ZIF-8 thin films, namely coverage, thickness, roughness and orientation, thus making it possible to tailor them towards specific applications.

(1) Stassen, I.; Styles, M.; Grenci, G.; Van Gorp, H.; Vanderlinden, W.; De Feyter, S.; Falcaro, P.; De Vos, D.; Vereecken, P.; Ameloot, R. Chemical Vapour Deposition of Zeolitic Imidazolate Framework Thin Films. *Nat. Mater.***2016**, *15* (3), 304–310. https://doi.org/10.1038/nmat4509.

1:15pm **LI-MoM-40 ALE Student Award Finalist Talk: Reaction Pathways Leading to Anisotropic Pattering of Cu***, **Xia (Gary) Sang**, M. Martirez, T. Smith, E. Carter, J. Chang,* University of California at Los Angeles

Plasma-thermal atomic layer etching (ALE) is a promising technique for enabling nanometer-level metal patterning. Utilizing the anisotropic nature of low energy ions, a modified layer is defined directionally in the plasma exposure step. The subsequently introduced isotropic etchant molecules only react with the modified region, leaving a final feature with ideal directionality and selectivity. This technique has been proven effective on patterning etch-resistant metals such as Ni.

In this work, the directional Cu etch is demonstrated with the plasma-thermal ALE process using low energy oxygen ions from an oxygen plasma to achieve directional modification and formic acid vapor to realize selective removal of the modified layer. This cyclic process yielded an etch rate of 2.4 nm/cycle at 80°C. The etch selectivity by gas-phase formic acid of copper oxide over metallic copper is high based on preliminary results and being quantified in this work. A 1.5 micrometer line structure with 55 nm Cu under a 135 nm thick SiCN hard mask was successfully patterned with high selectivity against the hard mask and relatively vertical sidewalls. The reaction products, postulated as copper formate (Cu(COOH)2), were measured by analyzing the condensates from the chemical vapor after the cyclic etching process with inductively coupled plasma mass spectroscopy (ICP-MS) and nuclear magnetic resonance (NMR). The surface chemical states after the etching process were quantified by XPS, showing the formation of Cu(I) and Cu(II) oxides upon oxygen plasma exposure and its subsequent removal after formic acid exposure, with the percentage of Cu(OH)2 increased after the vapor was introduced to the surface. To

corroborate these findings, density Functional Theory (DFT) calculations were carried with experimental conditions. It was found that a water-free dimeric tetra(μ-formato)dicopper(II) “paddlewheel” complex (Cu2(HCOO)4) is the most favorable etching product, with its formation reaching equilibrium conditions from Cu(II). The most likely precursor for the dimer is the diformatodi(formic acid)copper(II) monomer, which favorably dimerizes under the same water-lean condition at which the dimer persists. Finally, DFT simulation is compared to the NMR measurements.

1:30pm **LI-MoM-43 ALE Student Award Finalist Talk: Thermal Atomic Layer Etching of Cobalt Using SO_2Cl_2 and $P(CH_3)_3$**, ***Jessica Murdzek**, S. George,* University of Colorado Boulder

Thermal metal ALE is challenging because the oxidation state of the volatile metal etch products are usually different than the zero oxidation state of the elemental metal.In this work, cobalt ALE was developed by first oxidizing the cobalt via chlorination using SO_2Cl_2. Then the Co was etched by the binding of trimethyl phosphine (PMe_3) ligands that can volatilize the cobalt chloride.Thermal Co ALE was achieved at 150 °C by properly balancing the SO_2Cl_2 exposures that chlorinate cobalt and the PMe_3 exposures that remove the cobalt chloride (Figure 1).

The logic of this approach is based on the Covalent Bond Classification (CBC) method.The CBC method indicates that most organo-metallic complexes obey the 18 or 16 electron rule. We have shown previously that this method works for the thermal ALE of nickel. In the CBC method, a chloride ligand donates one electron to the metal center and is referred to as an X ligand. PMe_3 is a two-electron donor and is designated an L ligand. The nickel ALE process was accomplished using these sequential steps: chlorination to $NiCl_2$ and ligand addition to form NiX_2L_2, or $NiCl_2P(Me_3)_2$, resulting in an etch process. For cobalt, the most likely compounds to be created using chloride and trimethyl phosphine ligands are CoX_2L_4, CoX_2L_2, or CoX_3L_3. These compounds have cobalt in the +2 or +3 oxidation states.

Co ALE process was demonstrated with SO_2Cl_2 and PMe_3 exposures at 150 °C using in situ quartz crystal microbalance (QCM) measurements. The QCM experiments indicated that cobalt very readily chlorinates when exposed to SO_2Cl_2. A typical mass gain with one exposure of SO_2Cl_2 on cobalt can be up to 1400 ng/cm^2.In contrast, an identical exposure of SO_2Cl_2 on nickel results in a mass gain of only 100-150 ng/cm^2. The PMe_3 step was also different on cobalt when compared with nickel. For nickel ALE, one exposure of PMe_3 removes all available $NiCl_2$. An identical exposure of PMe_3 on $CoCl_2$ only removes ~20% of the available $CoCl_2$.Consequently, multiple PMe_3 exposures are required to remove the $CoCl_2$.

Co ALE requires a careful balance between the SO_2Cl_2 and PMe_3 exposures.Too much cobalt chlorination with SO_2Cl_2 will lead to difficulties removing all the cobalt chloride with PMe_3.Cobalt chloride that is not removed during one ALE cycle will build up and a cobalt chloride top layer will grow with successive ALE cycles.Optimizing Co ALE was based on determining the number of PMe_3 exposures required to remove the top cobalt chloride layer.Using the optimum exposures of SO_2Cl_2 and PMe_3 results in high etch rates for cobalt ALE of 3-5 Å/cycle at 150 °C (Figure 2).

1:45pm **LI-MoM-46 ALD Student Award Finalist Talk: Insight into Film Growth Mechanisms in Polyurea Molecular Layer Deposition (MLD) Using New and Combined Precursors**, ***Siyao Wang**, R. Nye, G. Parsons,* North Carolina State University

Analogous to atomic layer deposition (ALD), organic molecular layer deposition (MLD), enabling controlled deposition of materials at the molecular level, has emerged in recent years as a vapor phase method for depositing ultrathin polymeric films to be used in microelectronics, catalysts, and battery electrodes etc. However, lack of fundamental understanding in film growth behavior and underlying mechanisms is still impeding further development and application of MLD. In this study, our goal is to gain understanding on deposition mechanisms to achieve better control over film properties by employing new and innovative combinations of MLD precursors, with the aid of in situ characterization capability and the establishment of a kinetic model.

Specifically, we choose four polyurea precursors including p-phenylene diisocyanate (PDIC), 1,6-hexamethylenediisocyanate (HDIC), ethylenediamine (ED) and 1,6-hexanediamine (HD), in which HDIC is utilized for the first time to deposit MLD films, and proves to be a feasible alternative with improved thermal stability compared to PDIC. The polyurea films are deposited on hydroxylated SiO2 substrates at 45 °C-60 °C and measured every cycle using in situ ellipsometry (every ten cycles for PDIC/HD). As shown in Figure 1, accelerated initial growth within the first ~20 cycles is observed for all films, followed by a steady growth regime. Significantly higher growth at the initial stage is attributed to the higher density of reactive sites on the starting SiO2 surface. As growth proceeds and polymer chains become more entwined, the active site density decreases due to site-terminating double reactions (DRs) and site blocking, which leads to a decrease in growth rate. The steady growth rates for each polymer increase with precursor rigidity, with 0.32, 0.13, 0.020, and 0.020 nm/cycle for PDIC/ED, PDIC/HD, HDIC/ED, and HDIC/HD, respectively, consistent with more prevalent DRs for more flexible polymers.

To further explore the growth initiation and transition mechanism, we deposit hybrid polyurea films by alternating precursors. As shown in Figure 2, when deposited on HDIC/ED substrate, PDIC/ED films exhibit an accelerated thickness increase followed by a subsequent decrease to steady growth rate, due to competition between reactive site regeneration and consumption. Additionally, to describe and predict growth behavior, a model with a simple decay parameter is established (Figure 1). Meanwhile, more advanced modeling based on reactive site termination and generation rates is being constructed to gain fundamental knowledge on growth mechanisms, facilitating future depositions of unique precursors and combinations.

2:00pm **LI-MoM-49 Closing Remarks & Thank Yous**, *J. Chang,* University of California, Los Angeles*; **Thorsten Lill**,* Lam Research Corp.*; S. Barry,* Carleton University, Canada*; S. Clendenning,* Intel

Thank you for attending today's Plenary and Award Session. We will see you tomorrow!

Live Session
Room Live - Session LI-ALD-TuM1
Precursors (AF): ALD Processes Live Session

Moderators: Prof. Jin-Seong Park, Hanyang University, Dr. Tania Sandoval, Technical University Federico Santa Maria, Dr. Matthias Young, University of Missouri-Columbia

9:30am **LI-ALD-TuM1-1 Welcome, Thank Yous & Session Instructions***, **Jin-Seong Park**,* Hanyang University, Korea (Republic of)

Thank you for attending and we hope you will enjoy the session!

9:35am **LI-ALD-TuM1-2 Atomic Layer Deposition of Amorphous/Nanocrystalline Phase-Composite Nanolayers***, **Myung-Mo Sung**,* Hanyang University, Republic of Korea **INVITED**

Interparticle electronic coupling is essential for quantum dot solids to fulfill its expected wide-tunable electrical and optoelectrical properties but has been limited by disorder. Here, we approach alternatively to disorder-immune coupling by synthesizing quantum dot solids based on amorphous/nanocrystalline phase-composite monolayers. The ZnO amorphous matrix, which infills voids of the less regularly ordered ZnO nanocrystal array, mediates electronic coupling between neighboring quantum-confined nanocrystals by means of resonant wavefunction overlap generating a quantized conducting state without forming tunneling barriers. Thin-film transistors based on the phase-composite semiconductors show delocalized band-like transport with superior field-effect mobility value compared to amorphous or polycrystalline ZnO semiconductors. Calculation of charge transport properties is executed using non-equilibrium Green's function method under various degrees of disorder. For two distinct types of phase-composite quantum dot solids, embedding periodic and disordered nanocrystals, the reproduced conductivities are unexpectedly comparable because the amorphous-mediated interparticle coupling is tolerant against disorder-induced degradation. Furthermore, this facile and stable coupling demonstrates wafer-scale uniform deposition and bias-illumination stability of our phase-composite quantum dot solids.

9:55am **LI-ALD-TuM1-6 Density Functional Study on ALD Precursors for Hexagonal Boron Nitride Deposition***, **Naoya Uene**, T. Mabuchi,* Tohoku University, Japan*; J. Yong,* Japan Advanced Chemicals Ltd., China*; M. Zaitsu, S. Yasuhara,* Japan Advanced Chemicals Ltd., Japan*; T. Tokumasu,* Tohoku University, Japan

Hexagonal BN (*h*-BN) has been considered as a promising dielectric film for 2D material-based electronics because of its atomically smooth and charge-free interface with an in-plane lattice constant similar to that of graphene. The atomic layer deposition (ALD) technique is a way to deposit conformal and ultrathin dielectrics directly on insulators or semiconductors at relatively low temperatures than a catalytic CVD process.

The purpose of this study is to provide a path to a new precursor design through theoretical investigations on several precursor's stabilities used in BN-ALD. At present, there are only a few types of BN-ALD precursors that satisfy favorable characteristics and no studies that systematically verify their stability as far as we know. The systematic and theoretical investigation of the BN-ALD precursor is also helpful for engineeringly critical nitride deposition processes such as TiN, AlN, and GaN.Herein, the BN-ALD using BCl_3 and $B(NMe_2)_3$ precursors on OH terminated SiO_2 substrates was studied. They have been attractive precursors for depositing ultra-thin dielectrics and are relatively easy to simulate.

All DFT calculations were performed within spin-polarized generalized gradient approximation (GGA) parameterized by Perdew–Burke–Ernzerhof (PBE) exchange–correlation as implemented in Materials Studio 2018 software $Dmol^3$ packages. The average bond length of B–Cl is found to be 1.734 Å, which is in good agreement with 1.794 Å in the previous study at the MP2 level. Also, in $B(NMe_2)_3$, the average bond length of B–N is 1.433 Å, and C–N is 1.431 Å. These calculations also show that the both structures are very symmetrical. From a bond energy calculation, 114.7–114.8 kcal/mol is obtained for the B–Cl bond in BCl_3. In $B(NMe_2)_3$, 105.6–105.7 kcal/mol for B–N bond and 88.3–88.4 kcal/mol C–N bond are obtained. These results indicate that both precursors are sufficiently stable at room temperature. The $B(NMe_2)_3$ thermally decomposes at lower temperatures than BCl_3, and organic precursors may be more suitable for low-temperature processes. Further studies are planned on the effect of ligand type on bond energy in BN precursors. Besides, we will investigate the kinetic stability by obtaining an activation barrier for providing the way to a new precursor design.

10:10am **LI-ALD-TuM1-9 A Novel co-Precursor Approach for Atomic Layer Deposition of Various Semiconductor Thin Films***, **Kok Chew Tan**,* Soulbrain, Korea (Republic of)*; J. Jung, C. Yeon,* Soulbrain , Korea (Republic of)*; J. Kim, J. Kim,* Soulbrain, Korea (Republic of)*; S. Kim, T. Eom,* Soulbrain , Korea (Republic of)*; S. Lee,* Soulbrain , Korea (Republic of)*; Y. Park,* Soulbrain , Korea (Republic of)

Film quality and conformality are some of the critical concerns in deposition technology, especially in ever increasing complex geometry such as high aspect ratio feature and three dimensional (3D) device. In this work, we present an innovative approach that involves an additional step of co-precursor pulse in conventional atomic layer deposition (ALD) process to overcome challenges of depositing high quality and conformal thin films. One of the key ideas of this co-precursor pulse is to induce ligand exchange with the main precursor, which leads to desirable effects on the film quality in terms of impurity contents, density, surface roughness and crystallinity. In addition, film growth rate could be controlled by altering the pulsing sequence of co-precursor in ALD process cycle. This strategy enables considerable improvement in film conformality, particularly in high aspect ratio feature.

Our experimental evidences demonstrate wide applicability of this innovative approach in various areas, for example: in ALD of nitride film, high-*k* oxide film and MoN_x film. By pulsing co-precursor in ALD process, **Fig. 1** shows a noticeable 50% improvement in TiN film resistivity due partly to large decrease in Cl impurity of more than 50% as determined by SIMS depth profiles **[1]**. For ALD of high-*k* oxide (HfO_2) film at 320°C, in addition to the improvements in film density and significant 58% decrease in carbon impurity, co-precursor pulse in ALD is also capable of enhancing high-*k* dielectric film electrical performances, with 20% reduction in leakage currents and 8% increase in capacitance, as demonstrated in **Fig. 2a**. In terms of the effects of co-precursor pulse on ALD of MoN_x, **Fig. 3** reveals improvement in film resistivity at deposition temperatures of 380, 400 and 420°C, with the largest observable improvement of 46% at 420°C. All experimental results exhibit improved step coverage which are made possible by this innovative approach, for example as illustrated in **Fig. 2b**.

All these findings give clear evidences of the promising capability of co-precursor pulse in ALD for achieving superior film quality, high film conformality and excellent electrical performances. This innovative approach of co-precursor pulse in ALD process could open up various opportunities in applications such as low resistive metal gate interconnects for future technology node, high aspect ratio 3D metal-insulator-metal (MIM) capacitor, DRAM trench capacitor, and other 3D device architectures such as 3D gate-all-around (GAA) and 3D NAND.

Reference:

1. C. Yeon, J. Jung, H. Byun, K.C. Tan, T. Song, S. Kim, J.H. Kim, S.J. Lee and Y. Park, AIP Advances 11, 015218 (2021).

10:25am **LI-ALD-TuM1-12 Tuneable YAlOx Protective Coatings Against Plasma Damage to Meet the Requirements in Future Semiconductor Fabrication Processes***, J. Kalliomaki, M. Kaaria, K. Dorai, **Tiina McKee**,* Picosun Oy, Finland

Atomic Layer Deposition (ALD) enabled corrosion protection solutions against plasma etch are becoming more sought after in the semiconductor industry. Current wafer fabrication process flows include several steps where plasma etching is necessary. An inevitable consequence of using such strong etching chemicals is that the tool itself will be etched. This tool damage can be managed by applying a corrosion-resistant coating to the etch tool to minimize plasma damage [1]. ALD is especially useful for coating tool components having 3D or high aspect ratio features. Nevertheless, even there are challenges. A common industrial solution is several-hundred-nm-thick Y_2O_3 film, which by ALD tends to be a very hygroscopic film product as-deposited. If the ALD deposition uses H_2O as a co-reactant, the deposited material will retain some of that H_2O and releases it during the subsequent Y-precursor pulse causing CVD-like growth [2]. This phenomenon becomes more pronounced as the film thickness increases, making it difficult to accurately control the process. Another option would be to completely purge the H_2O and stay within the ALD regime, but that makes the processing times unfeasibly long for an industrial solution.

Our approach is to combine the highly-etch-resistant Y_2O_3 ALD process with more robust ALD processes, such as Al_2O_3 or ZrO_2. It has been shown that to gain most of the benefits from Y_2O_3 its molar concentration can be less

than half in a composite oxide [3]. Here we demonstrate that a high performance ALD corrosion barrier deposition with the speed and convenience of Al_2O_3 process and durability of Y_2O_3 can be achieved by carefully controlling the film composition, and that the process is transferrable to an industrial scale deposition chamber.

This study shows how fluorine-based plasma etch rate results from films deposited in a batch ALD tool (Picosun P-300B) at 300 °C correlates with the composition of the oxide film and suggests reasonable compromises between extremely low plasma etch rates and throughput and conformality of the ALD process. The variance in composition was made by altering the ratio between Al_2O_3 and Y_2O_3 cycles in the recipe. The etching was made with CF_4/O_2 plasma to determine the etch rate. The results suggest that by making a compromise to increase the etch rate by factor of 1.5, we can gain an order of magnitude benefit in throughput, film uniformity and conformality. This can be translated to a significant reduction of manufacturing costs by increasing the maintenance interval of etch tools.

1 Shih, ISBN: 978-953-51-0467-4

2 Abdulagatov et al., doi:10.1134/S1063739719010025

3 Kim et al., doi:10.1111/j.1551-2916.2011.04589.x

10:50am **LI-ALD-TuM1-17 ALD of Boron Nitride by Polymer Derived Ceramics chemistry***, W. Hao, T. Saboo, C. Journet, **Catherine Marichy**,* Univ Lyon, France **INVITED**

Scientific interest for hexagonal boron nitride (h-BN) material, especially as thin film and nano-/hetero-structures, is growing due to its potential use in various domains such as microelectronic, energy and environment. Atomic Layer Deposition (ALD) is a technique of choice for fabrication of such thin films and complex nanostructured material. Some ALD processes of BN have been reported; mostly based on ammonia and/or halide precursors. In all cases, the crystalline quality of the as-deposited layers remains insufficient and post-annealing treatments are currently performed. Despite these limitations, ALD already demonstrates suited to fabricate BN layers that can successfully be integrated into electronic devices. Based on polymer derived ceramics chemistry, we developed a two-step ALD process of BN that permits access to various BN thin films and complex nano-/hetero-structures. It consists of the growth layer by layer of a preceramic BN films, onto various substrates, at low temperature, and then to its densification into pure BN by annealing process.

Herein, the potential of the ALD process based on PDCs route for BN thin films will be discussed. Indeed, BN thin films were successfully deposited in a controlled manner on various inorganic and organic substrates/templates. In particular, functional quality crystalline BN nano/heterostructures have been fabricated using substrates or templates with different dimensionalities. Their applications as protective coatings as well as filters and absorbers to purify polluted water from organic/oil have been investigated. The involved mechanism will be also introduced.

11:10am **LI-ALD-TuM1-21 Process Parameter and Substrate Dependence of Sticking Coefficients in Atomic Layer Deposition Processes***, **Martin Knaut**,* TU Dresden, Germany*; L. Jäckel,* Fraunhofer ENAS, Germany*; M. Albert, T. Mikolajick,* TU Dresden, Germany

Surface reaction probabilities in atomic layer deposition (ALD) processes are often described by simplified sticking coefficients. For ALD processes carried out with sufficiently high reactant doses to enable saturated and self-limiting surface reactions these sticking coefficients are only of minor interest. As a measure of how many surface interactions are necessary for a successful chemisorption they mainly quantify the efficiency of a process. Consequently, knowledge about sticking coefficients can help to make processes more efficient or to select the most cost-effective chemistry. These aspects are becoming increasingly important for the coating of porous materials and three-dimensional structures. Such demanding substrates are much more sensitive to surface reaction probabilities and insufficient reactant doses may result in thickness profiles which strongly depend on the sticking coefficients. This sensitivity was used to investigate the sticking coefficients of alumina and tantalum nitride ALD processes by analyzing thickness profiles grown in a narrow gap between two silicon wafers. The narrow gap impedes the transport of reactants which can generate an unsaturated coating with a transition from a fully coated wafer edge to an uncoated wafer center. Based on the thickness profiles measured by scanning spectroscopic ellipsometry predictions about the sticking coefficients can be made with regard to process parameters, precursor chemistry and substrate properties.

In this paper the experimental results regarding the sticking coefficients during the initial and the homogeneous film growth of alumina or tantalum nitride on wafers with different reactive surface groups are presented and discussed. The experiments confirmed the dependence of the sticking coefficients from process parameters like co-reactants, doses and temperatures as well as different film growth mechanisms for the heterogeneous growth on a substrate material and the homogeneous layer-by-layer growth. The differing sticking coefficients were investigated by analyzing the characteristic thickness profiles during the initial film growth and after the transition to the homogeneous film growth. Pre-coated test wafer were used to verify these effects and to separate process parameter and substrate impacts.

The applied approach is presented as a simple and versatile tool to study novel precursors and processes and to investigate substrate effects on the ALD film growth. Further, the attainable findings can help to improve processes and to adapt them to specific substrates and demanding surface topographies.

11:25am **LI-ALD-TuM1-24 Volatile Cerium and Ytterbium Precursors for Atomic Layer Deposition: Synthesis, DFT and Application***, **Parmish Kaur**,* Ruhr University Bochum, Germany*; A. Muriqi,* Tyndall National Institute, University College Cork, Ireland*; R. Ghiyasi,* Aalto University, Finland*; M. Nolan,* Tyndall National Institute, University College Cork, Ireland*; M. Karppinen,* Aalto University, Finland*; A. Devi,* Ruhr University Bochum, Germany

Cerium-containing thin films find a broad range of applications in diverse areas such as catalysis, sensors, solid oxide fuel cells, water splitting, possible high-*k* gate dielectric material to name a few. Ytterbium-containing films have attracted increasing attention for the advancement of semiconductor devices such as Ytterbium-doped optical fibers that are useful for high power laser applications. Atomic layer deposition (ALD) is an appealing technique to grow high-quality thin films with precise thickness control and large area homogeneity. However, there are a limited number of suitable ALD precursors for Ce and Yb and thus new metalorganic precursors are much sought after.

Herein, we report a systematic study on the rational development of homoleptic tris-guanidinate $[Ln(guan)_3]$ and tris-amidinate $[Ln(amd)_3]$ where the lanthanide Ln = Ce and Yb.[2] The C on the N-C-N backbone is functionalised with Me, NMe_2, NEt_2; (Me=methyl, Et=ethyl) and N is functionalised with symmetrical iso-propyl (^{i}Pr) and asymmetrical tertiary-butyl (^{t}Bu) and Et groups (Figure 1) to study their influence on the physicochemical properties. The compounds are analyzed for their structure, spectroscopic purity, and composition. The solid-state structures obtained for guanidinates of Ce and Yb reveal the monomeric nature of the compounds and the reactive M-N bonds present could be favourable for ALD. Thermogravimetric (TG) studies show that the complexes are volatile, and the symmetrical complexes are thermally more stable than asymmetrical ones. Density functional theory (DFT) modelling is performed to study the reactivity of the complexes with water and molecular oxygen. It is found that in the presence of water, tris-guanidinates are more reactive than tris-amidinates and the Ce complexes are even reactive with molecular oxygen. As a representative precursor for ALD, $[Ce(dpdmg)_3]$ is used for the deposition of CeO_2 using water as the co-reactant. The process yielded polycrystalline CeO_2 films on Si(100) substrates at 160 °C deposition temperature and thin-film analysis is done using XRR, GIXRD, XPS, UV-Vis spectroscopy. While the GIXRD analysis revealed no other peaks except those for the CeO_2 phase, the XPS analysis indicated beside the Ce^{4+} features, an evidence of co-existence of some Ce^{3+} features in the films. (Figure 2). This study further confirms that the nitrogen coordinated lanthanide complexes are very appealing for ALD applications.

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

2. P. Kaur, L. Mai, A. Muriqi, D. Zanders, R. Ghiyasi, M. Safdar, N. Boysen, M. Winter, M. Nolan, M. Karppinen, A. Devi, *Chem. Eur. J.***2021**, *27*, 1–15. DOI: 10.1002/chem.202005268

11:40am **LI-ALD-TuM1-27 Predicting Precursor Volatility With Machine Learning***, **Simon D. Elliott**, A. Chandrasinghe, A. Chandrasekaran, Y. An, M. Halls,* Schrödinger

The success of deposition and etch processes depends crucially on the properties of the metalorganic precursor chemicals and much innovation in this field centers around developing new precursors. The space of possible ligands is vast, much too large to be explored systematically in the lab. The area is therefore ripe for computational screening and design, as long as the relevant properties can be computed quickly and accurately.

Volatility is a key property for vapor-based deposition or etch processes, but one that is difficult to compute from first principles. Here we utilize a machine learning (ML) approach to train surrogate models for pressure-temperature relationships. The first step involves the curation of volatility data from experimental vapor pressure curves for over 1,000 purely organic molecules. A variety of ML algorithms (Random Forest, Neural Networks *etc.*) are studied in conjunction with different chemoinformatic descriptors and fingerprints. The trained ML model is capable of predicting the evaporation temperatures for 1 Torr and 10 Torr partial pressure of the organic compounds with a mean error of 25°C. We show how the model may be applied to metalorganic complexes, accounting mostly for the intermolecular interaction between ligand shells. The ML model not only allows the identification of salient molecular descriptors but also provides insights to extend the approach to more accurately include the effect of the metal center. We discuss the prospects for informatics-based design and optimization of specialty chemicals.

11:55am **LI-ALD-TuM1-30 Surface Chemistry of Deposition and Etch from First Principles Simulations*, Michael Nolan,*** Tyndall Institute, Ireland **INVITED**

First principles simulations are a powerful tool to enable the investigation of surface chemistries and since atomic level processing is driven by self-limiting surface chemistries simulations can provide deep insights into Atomic Layer Deposition, Molecular Layer Deposition and Atomic Layer Etch. Key information is obtained from modelling the elementary steps of a process, including precursor adsorption, ligand elimination and substrate chemistry. In this contribution, we will discuss our work on first principles modelling of ALD, MLD and ALE processes.

For ALD, we present DFT studies of Co and Ru PEALD (using H2/Nitrogen), for future interconnects in which Co and Ru replace Cu or be incorporated into TaN to give thinner barrier/liner stacks [1-4]. The post-plasma metal surface is modelled as an NH/NH2-terminated surface [1] with predicted composition under ALD conditions. We explore Ru(Cp)2 and Co(Cp)2 precursors and their chemistry on nitrided surfaces- ligand elimination, the role of multiple precursors and coverage. Initial results on the chemistry of plasma species is presented to explore how ligands are eliminated.

For MLD, we present an overview of our DFT work on the chemistry of metalcone growth [5,6], highlighting insights into the impact of the organic precursor on MLD growth; in particular differences between bifunctional ethylene glycol and glycerol . The chemistry at different oxides will also be discussed.

We discuss our studies of ALE of W [7] and Co [8]. For W we present a detailed analysis of the chemistry in a process using partial metal oxidation and WClx half-reactions. For Cp, we discuss the development of a process chemistry that uses mild oxidation agents and CO to promote etching.

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12:30pm **LI-ALD-TuM1-37 Atomic Layer Deposition of Functional Dielectrics and Metals for the Emerging Non-Volatile Memories*, Anna Chernikova,*** *M. Kozodaev, R. Khakimov, Y. Lebedinskii, A. Markeev,* Moscow Institute of Physics and Technology, Russian Federation **INVITED**

Since the first discovery of ferroelectricity in nanometer-scale hafnium oxide (HfO_2) it is considered very attractive for the emerging non-volatile ferroelectric random access memory (FeRAM). A notable feature of ferroelectric HfO_2 is complete compatibility with the semiconductor fabrication process. Besides the technologically suitable intrinsic properties of HfO_2, atomic layer deposition (ALD) may be successfully applied for its growth. Moreover, TiN, which usually serves as top and bottom electrodes for HfO_2-based FeRAM stacks, is also routinely grown by ALD. However, TiN is chemically reactive and readily oxidizes during ferroelectric film crystallization leading to the formation of the oxygen-poor interface with HfO_2-based films. Eventually, it causes instability of ferroelectric response, revealing itself in some undesired features of ferroelectric capacitors as wake-up, imprint, etc. The natural demand for electrode materials replacement faces some challenges. The ferroelectric response of HfO2-based stacks depends on many factors, including the electrodes' crystallinity, morphology, chemical properties of the interfaces, etc. Moreover, the cross-correlation between the effect of the electrodes and intrinsic properties of the given HfO_2-based film, determined by the dopant element and concentration, thickness, etc, is expected.

Thus, the search for better electrodes and HfO2-based ferroelectric film combination is still outgoing. Considering the ferroelectric material ALD provides the great possibility to improve the ferroelectric response due to the high level of doping control. Regarding the electrodes noble metals and their oxides, which can be also grown by ALD, are especially promising because they can resist oxidation during FeRAM stack manufacture.

In this work, the possibility to utilize Ru/RuO_2 electrodes and complex doped HfO_2-ZrO_2 oxides, both grown by ALD to improve the ferroelectric properties of capacitors is discussed. Special attention is paid to the ability to control the interface properties between electrodes and ferroelectric films by the ALD conditions and to the effect of the electrodes on the crystalline structure of the different HfO_2-based films grown by ALD.

12:50pm **LI-ALD-TuM1-41 Crystallinity Control via Atomic Level Scaffolding*, Elham Rafie Borujeny,*** *K. Cadien,* University of Alberta, Canada

Conventional methods for the growth of epitaxial thin films rely on the crystallographic relationship between the growing film and the underlying substrate. For the case of homoepitaxy (i.e., where the film and the substrate consist of the same material), achieving high quality crystalline films is relatively easy and can be facilitated by providing adequate energy for the deposition process using, for example, higher deposition temperatures, plasma-assisted processes, and laser-assisted processes. On the other hand, for the case of heteroepitaxy (i.e., where the film and the substrate consist of different materials), achieving the desired crystallinity of the thin film is much more challenging specially in cases where a suitable substrate that can induce a certain crystal structure in the growing film is either not accessible or not technologically useful.

In this work, we provide a strategy to precisely control the crystallinity of the ALD films by creating atomic scale scaffolds that can steer the atoms into forming the desired film crystal structure during the deposition process and minimize the role of the substrate in achieving film crystallinity. We explain the criteria for choosing the scaffold and elaborate on the unique role of ALD in exploiting the potentials of the atomic level scaffolding strategy in growing crystalline phases of technologically important thin films. We show that creating the atomic scale scaffold can be easily incorporated into the conventional ALD cycles by adding additional dose and purge steps therefore making it possible to seamlessly integrate this scaffolding process into conventional ALD processes.

This work is especially important in heteroepitaxy where minimizing the role of the substrate as a result of this scaffolding strategy provides a means by which metastable and stable phases of materials in thin film form could be grown on foreign substrates that were not conventionally possible.

1:05pm **LI-ALD-TuM1-44 Plasma-Enhanced Atomic Layer Deposition of Copper Oxide Semiconductors With Tunable Phase, Oxidation State, and Morphology for P-Type Thin Film Transistors*, Julia D. Lenef,*** *J. Jo, O. Trejo,* University of Michigan, Ann Arbor*; D. Mandia ,* Argonne National Laboratory, USA*; R. Peterson, N. Dasgupta ,* University of Michigan, Ann Arbor

Although advances in p-type metal oxide semiconductors are more infrequently reported than their n-type counterparts, Cu_2O—a p-type metal oxide—has been shown to be a viable candidate due to its moderate optical bandgap (2.0-2.6 eV)[1] and high measured Hall mobility (> 100 cm^2/V-s).[2] Previous works indicate that grain size, crystallinity, oxidation state, and phaseof the CuO_x films directly impact the resulting electronic properties for devices such as solar cells and thin film transistors. However, little work has been done to (1) obtain precise control over phase, oxidation and morphology and (2) explore the coupled effects between the materials synthesis, film structure and composition on the p-type semiconducting properties.

To address this knowledge gap, plasma-enhanced atomic layer deposition (PE-ALD) of CuO_x was performed with select ratios of hydrogen and oxygen plasma and a non-fluorinated copper amidinate precursor.[3] The phase of CuO_x was successfully controlled to synthesize Cu, Cu_2O, or CuO, verified by grazing-incidence x-ray diffraction. Furthermore, post-deposition annealing of the as-deposited films provides an additional process knob to tune the phase, oxidation state and morphology. Vacuum annealing resulted in up to a ~8 times increase in the grain size, and reduction in the copper oxidation state quantified by atomic force microscopy and synchrotron x-ray absorption spectroscopy, respectively. Next, to correlate the process-structure relationships observed with the p-type semiconductor properties, bottom-gate TFTs were constructed, and a maximum mobility (~0.01 cm^2/V-s) and on/off current ratio of (~10^5) for PE-ALD films was achieved for films with the largest Cu(I) content and grain size.

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1:20pm **LI-ALD-TuM1-47 Tuning Coercive Field and Polarization in Inherently Ferroelectric HZO Film Deposited Using HfD-04 and ZrD-04*, Raisul Islam*,** *M. McBriarty, M. Laudato, R. Clarke, S. Hoang, C. Chen, G. Panaman, K. Littau,* EMD Electronics, USA

Data transfer throughput in off-chip memory devices are bottlenecked by the "memory wall", where the data movement throughput does not scale with the technology node, and which cannot be solved by the current on-chip solutions like SRAM because of its large area requirement. Ferroelectric memory devices utilizing the switching of the polarization of electric dipoles in certain materials can offer ultra-low energy switching, scalability and they are on-chip BEOL compatible making them attractive for neuromorphic computing application. Alloys of HfO_2 and ZrO_2, $Hf_{0.5}Zr_{0.5}O_2$ (HZO), are shown to have excellent ferroelectricity and are CMOS compatible, making them one of the most widely studied FE materials for memory applications.

In this paper, inherently ferroelectric HZO was demonstrated, deposited by atomic layer deposition using the alternating pulsing of HfD-04 and ZrD-04 precursors with ozone as the reactant. We observed that the ALD window (300 °C-400 °C) is wide and higher in deposition temperature compared to some other Hf and Zr precursors. This wide temperature window allows the FE orthorhombic phase to be stabilized as deposited, resulting in inherent ferroelectricity. We further investigated the effect of the stack design, ALD process parameters, and post processing such as annealing on the ferroelectric properties of the HZO films in the capacitor. We report $2P_r$ values of nearly 30 µC/cm^2 under optimized conditions. Most significantly, we also observe that the coercive field can be reduced making the films more reliable under memory switching cycles. Coercive field tuning to values as low as ~1 MV/cm is demonstrated.

In summary, we have demonstrated inherently FE capacitors of HZO deposited by ALD of HfD-04 and ZrD-04 precursors where the FE properties can be tuned using the design of the capacitor stack, process conditions, and post process operations. Our work demonstrates how choice of Hf and Zr ligands and the widening of the ALD temperature window can enable a method of depositing FE films for on-chip memory application.

1:35pm **LI-ALD-TuM1-50 Ferroelectric Devices: From Applications to Microstructures*, Asif Khan,*** Georgia Institute of Technology **INVITED**

The microelectronics industry is poised to enter the fourth wave of massive expansion, to support the explosion of Big Data and data-centric computing applications and the upcoming fourth industrial revolution. Ferroelectricity, standing on the remarkable streak of discoveries and innovations over the last 100 years, will be central to this new paradigm. In this talk, we will highlight the prospects and challenges of newly discovered fluorite-structure ferroelectrics (such as HfO_2 and its alloyed variants and ZrO_2) for advanced microelectronic applications [2]. The first part of the talk will focus on the application drivers of ferroelectric technologies such as embedded memories and ferroelectric neural networks [2,3]. The second part will describe the microscopic phenomena that underlies the macroscopic ferroic responses in fluorite-structure oxides as unveiled by a combination of multi-scale electron microscopy and first principles density functional theory-based calculations [4].

This research is supported by the National Science Foundation, the Defense Advanced Research Program Agency (DARPA), the Semiconductor Research Corporation (SRC) - Global Research Collaboration (GRC) program, the Applications and Systems-Driven Center for Energy-Efficient Integrated Nano Technologies (ASCENT), one of six centers in the Joint University Microelectronics Program (JUMP), a SRC program sponsored by the DARPA, and an Intel Rising Star award.

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1:55pm **LI-ALD-TuM1-54 Closing Remarks & Thank Yous*, Tania Sandoval,*** Technical University Federico Santa Maria, Chile

We hope you enjoyed the session! We will see you tomorrow!

Live Session
Room Live - Session LI-ALD-TuM2

ALD Applications (AA) Live Session

Moderators: Prof. Annelies Delabie, IMEC, Prof. Jolien Dendooven, Ghent University, Belgium, Prof. Xiangbo Meng, University of Arkansas

9:30am **LI-ALD-TuM2-1 Welcome, Thank Yous & Instructions***, **Jolien Dendooven,*** Ghent University, Belgium

Thank you for attending and we hope you will enjoy the session!

9:35am **LI-ALD-TuM2-2 ALD Growth of Low Work Function Metal Gate for FinFET Technology***, **Jinjuan Xiang**, C. Zhao,* Institute of Microelectronics, Chinese Academy of Sciences, China*; Y. Ding,* Chemical and Material Engineering, Jiangnan University, China*; C. Xu,* Nata Opto-electronic Material Co., Ltd., China*; L. Du,* Chemical and Material Engineering, Jiangnan University, China*; J. Li, X. Wang,* Institute of Microelectronics, Chinese Academy of Sciences, China **INVITED**

As the feature size of CMOS device shrinks to 22 nm technology node, Fin field-effect-transistor (FinFET) structure with higher aspect ratio is introduced, resulting in difficulty for conformal deposition of gate stack on the 3D channel surface. Atomic layer deposition (ALD) is considered as the best way to conquer the above challenge. Plasma enhanced ALD of low work function metal has been studied for the N-type metal. The plasma during the ALD deposition might bring damage to the underlying dielectric, which might lead degradation to the device performance. Our works developed a thermal ALD method of growing low work function metal TiAlC and TaAlC without plasma. The lowest effective work function can be 4.24 eV. In this paper, thermal ALD of Al-containing alloys TiAlC and TaAlC are systematically investigated, including the deposition conditions, the material properties of the resultant metal and the effective work functions. It is demonstrated that the thermal ALD TiAlC or TaAlC films are promising gate metal candidates for FinFET device of 14nm technology node and beyond.

9:55am **LI-ALD-TuM2-6 Atomic Layer Deposition of GeTe/Sb_2Te_3 Superlattice for Large-Capacity and Low-Power Phase Change Memory***, **Chanyoung Yoo**, E. Park, W. Kim, J. Jeon, W. Choi, B. Park, G. Han,* Seoul National University, Korea (Republic of)*; Y. Lee,* Jeonbuk National University, Korea (Republic of)*; C. Hwang,* Seoul National University, Korea (Republic of)

Despite the extensive research and available commercial memory products based on the phase-change-material (PCM), the advantages of Ge-Sb-Te alloy PCM for high-density and low-power memories have not been fully accomplished. This is primarily due to the current PCM architecture that relies on cross-point (X-point) arrays. The X-point cannot keep up with the ultra-high density demands of low cost per bit due to the increased fabrication cost by the lithography steps and masks required for each stacking layer. It can be best solved with the state-of-the-art vertical architecture, which is a proven technology with more than 150 layer stacks in V-NAND technology. To fabricate highly integrated vertical crossbar array (V-CBA) memory, the Ge-Sb-Te phase change layer should be deposited conformally on the etched sidewalls in this vertical architecture, and thus, Atomic Layer Deposition (ALD) technique is essential. Meanwhile, the high power consumption of the Ge-Sb-Te PCM during the writing operation is also a remaining challenge. Simpson et al.[1] suggested a GeTe/Sb_2Te_3 superlattice material as a substitute to solve such an issue. They argued that resistance change could be achieved with a lower current by flipping the Ge atom between octahedral sites and lower-coordination sites at the superlattice layers' interface.

This work demonstrates the development GeTe/Sb_2Te_3 superlattice film utilizing ALD to achieve high-performance V-CBA memory devices. The GeTe/Sb_2Te_3 superlattice thin film was successfully deposited as in Figures 1 and 2, where the out-of-plane directions of the two-component layers precisely matched the c-axis, while the in-plane directions were random. The superlattice films showed seven times (Figure 3) lower RESET than the conventional $Ge_2Sb_2Te_5$ alloy films, with the mushroom memory cell configuration. The reduction of RESET current with the alignment of the GeTe/Sb_2Te_3 superlattice films was also feasible in the vertical structure, showing the potential of the current process for the V-CBA memory of the GeTe/Sb_2Te_3 superlattice.

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10:10am **LI-ALD-TuM2-9 Atomic Layer Deposited p-type SnO Thin Films with c-axis Preferred Orientation and the Associated Device Applications***, **Hye-mi Kim**, S. Choi, H. Jeong, J. Park,* Hanyang University, Korea

Tin monoxide (SnO) films were fabricated by atomic layer deposition method using a N,N'-tert-butyl-1,1-dimethylethylenediamine stannylene (II) and deionized (DI) water as a precursor and reactant, respectively. In this study, we investigated film properties of SnO by annealing temperature with the focus on the relation of the crystal structure and phase transition with electrical characteristics. As annealing temperature was increased, phase transition occurred from SnO to SnO_2. Based on the experimental results such as the band gap, crystal structure, film composition, band structure, we conclude that 300℃ is optimized temperature in film properties which shows preferential growth in (001) plane. The highest hall mobility is observed (5.01 cm^2/Vs) at the 300℃ annealed temperature which may results from the reported low effective hole mass (m_h^*) along the [001] direction. Also, 400℃ is critical temperature for considering that the phase transition starts at the temperature from SnO to SnO_2. SnO channel based staggered bottom gate structure TFTs were fabricated and nitrogen annealing was followed. SnO TFTs showed p-type switching performance, when the device is exposed to the annealing condition of 300℃, in terms of threshold voltage (5.1±0.5 V and 1.7±0.4 V), field-effect mobility (6.0±0.0 cm^2/Vs and 4.9±0.2 cm^2/Vs), sub-threshold swing (4.6±0.2 V/decade and 4.4±0.2 V/decade) with high on-current/off-current ratio (2.7 x 10^2 and 2.5 x 10^2), at drain voltage is -0.1 V and -10.1 V, respectively. Also, threshold voltage shift was obtained during positive bias stress (+2.5 V) and negative bias stress (-7.7 V) at drain voltage is -10.1 V and gate bias stress is ±10 V. Additionally, observed conducting or degraded transfer curves in other annealing conditions indicates that understanding the film properties by annealing sequence leads to achieve improved p-type TFT fabrications.

10:25am **LI-ALD-TuM2-12 Atomic Layer Deposition of Highly Conductive Co_9S_8 Thin Films Using Diamine Adducts of Cobalt(II) Halides and H_2S***, **Miika Mattinen**,* Eindhoven University of Technology, Netherlands*; T. Hatanpää, K. Mizohata, J. Räisänen, M. Leskelä, M. Ritala,* University of Helsinki, Finland

ALD of metal sulfides has enjoyed a renaissance in the past decade, with some tens of new processes and 17 new binary sulfides reported since 2010.[1] Many of the processes deposit semiconducting sulfides such as MoS_2, SnS_2, and ZnS. However, for a multitude of applications, high electrical conductivity and/or metallic behavior are preferred. Cobalt pentlandite, Co_9S_8, is a highly conductive sulfide material that has shown promise as an electrode in a variety of energy applications ranging from water splitting to rechargeable batteries, supercapacitors, and solar cell electrodes. So far, only one ALD process using an expensive cobalt amidinate precursor has been reported in the literature, which results in films with a rather high resistivity of 3–5 mΩcm.[2]

We have developed a new Co_9S_8 ALD process using a recently reported[3] $CoCl_2$(TMEDA) (TMEDA = *N,N,N`,N`*-tetramethylethylenediamine) precursor with H_2S at 180–275 °C. The highest growth rate (~0.6 Å/cycle) and best film properties including the lowest amount of impurities (~3% total) and resistivity (ρ ≈ 70 μΩcm) are achieved at 275 °C. We have also evaluated a variety of similar cobalt precursors with different halide and diamine adduct ligands that exhibit adequate thermal properties as ALD precursors and afford Co_9S_8 growth with H_2S. All of these precursors can be easily synthesized using inexpensive starting materials.

The $CoCl_2$(TMEDA) + H_2S process enables growth of conductive films as thin as approximately 3 nm on silicon with native oxide. The process is also inherently selective, such that at least a 5 nm thick film can be grown on native silicon oxide with negligible growth on Si-H. Besides SiO_2, films can be grown on a range of substrates. We have also deposited the first epitaxial Co_9S_8 films in the literature using a hexagonal (0001)GaN substrate. The deposited Co_9S_8 films exhibit excellent thermal stability under a N_2 atmosphere up to at least 750 °C. The ability to deposit thin, continuous, highly conductive, and thermally stable Co_9S_8 films suggests that our process may be interesting for metal barrier and seed layer as well for various energy applications.

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10:50am **LI-ALD-TuM2-17 ALD-Oxide Materials and Surface Modification for Next-Generation PV Devices*, Nathanaelle Schneider,*** Institut Photovoltaïque d'Ile de France **INVITED**

Zinc oxide is an extensively studied n-type semiconductor for various applications such as light emitting devices, detection of chemicals or solar cells, which often needs to be doped, modified or protected.

Doped-ZnO films can replace conventional transparent conductive oxides (TCO), especially in high aspect ratio structures. Silicon nanowire (Si NW) solar cells are interesting PV technology but challenging to contact.[1] Use of ALD-Ti:ZnO (TZO) as the top electrode for Si NW solar cells has proven the applicability of ALD-TZO as TCO and the unique capabilities of ALD, showing superior optoelectrical properties, conformally covering the Si NWs, and yielding a PV diode behavior with external quantum efficiency response surpassing ITO.[2]

In other cases, it can be beneficial to modify the properties of the ZnO surface by the grafting of organic molecules.[3] ALD-ZnO surfaces were modified by phosphonic acid derivatives with different spacer and functionalizing groups (2-AEPA, 4-ABzPA and 4-FBzPA), characterized, used to passivate the reactive ZnO/perovskite interface and solar cell devices were prepared.[4]

Finally, ZnO-based films often need to be protected to prevent their degradation. Al:ZnO (AZO) window layer is reported as the primary component responsible for the degradation of CIGS solar cells. The feasibility to prevent AZO degradation and encapsulate module-level (10×10 cm^2) CIGS solar devices by a 10 nm ALD-Al_2O_3 barrier layer was demonstrated.[5] However, solar panels in field operation are also exposed to various chemical air pollutants such as in $(NH_4)_2SO_4$ in rural, and NaCl in marine environments. Their effects were studied by placing AZO w/ and w/o encapsulation in specific climatic test conditions. This demonstrated the necessity to consider atmospheric chemistry when evaluating barrier protection capacities of encapsulants and assessing the durability of PV materials and devices.[6]

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11:10am **LI-ALD-TuM2-21 Particle Atomic Layer Deposition as an Effective Way to Enhance the Li-S Battery Energy Density*, Mato Knez,*** *S. Garcia,* CIC nanoGUNE, Spain

Lithium-sulfur (Li-S) batteries are the most promising candidates for succeeding lithium ion batteries. However, there exist some challenges which should be faced to increase its commercial possibilities. Those include detrimental mechanisms during operation (*e.g.* shuttle effect, low capacity retention, anode corrosion, *etc.*) and sulfur cathode processing limitations (*e.g.* poor mechanical stability of S cathodes, defects, low S loading, *etc.*).

From the industrial perspective, sulfur cathode manufacturing should be improved as uniform and highly sulfur-loaded cathodes are required in order to ensure energy densities above 400 $Wh \cdot kg^{-1}$, to become commercially competitive. The sulfur cathode manufacturing limitations are related to solvent evaporation upon drying, which commonly results in a significant cathode volume reduction. It provokes the formation of cracks and pores in the cathode, which negatively affect the electrochemical performance of the cell. This issue has been addressed by several strategies, including *(i)* varying the binder nature and content, *(ii)* gluing microporous nanoparticles into secondary particles of few microns, and *(iii)* introducing conductive polymers. Even immobilizers and physically confining structures have been developed, but in most of the cases, those materials tend to significantly increase the weight and volume of the cathode, thereby reducing the energy density of the Li-S battery.

Atomic layer deposition (ALD) with alumina (Al_2O_3) has been applied to sulfur cathode surfaces to improve the electrochemical behavior of Li-S technology as it minimizes discharge product dissolution and hence, it reduces detrimental mechanisms during operation. However, the improvement of sulfur cathode processing remains unsolved. Even high-cost approaches have been proposed in the state-of-the-art which unfortunately are not viable for realistic applications. In this work, for first time atomic layer deposition (ALD) in a fluidized bed reactor (FBR) is carried out to coat sulfur-carbon (S/C) composite particles with Al_2O_3 prior to electrode manufacturing. The present approach provides a precise control of S/C composite agglomeration, which improves sulfur cathode processing while maintaining the well-known satisfactory operational mechanisms related to Al_2O_3 coating. We report on the FBR-ALD technique as a promising strategy for fabricating high specific energy density Li-S batteries with an increased sulfur loading, being double of that obtained for a standard sulfur cathode (3.6 vs. 1.8 mg_{sulfur} cm^{-2}).

11:25am **LI-ALD-TuM2-24 Advanced ALD Technologies Platform to Enable Future Applications and Scaling & Review of Emerging Applications for Sensors, Mems, Energy Harvesters, Transparent Electronics and Coated Powder for Composites*, Noureddine Adjeroud,*** Luxembourg Institute of Science and Technology (LIST), Luxembourg

The Luxembourg Institute of Science and Technology (LIST) proposes a large atomic layer deposition (ALD) platform with complementary tools for the development of new coating processes and the improvement of existing ALD processes. The platform allows processing of various types of inorganic or organic substrates, flat or 3D objects, flexible substrates and powders by FBR (Fluidized Bed Reactor) with up-scaling capabilities. The ALD platform is completed by other thin film deposition facilities, by cleanroom microfabrication capabilities to realize functional chips, and by a characterization platform (SEM-EDS, ellipsometry, contact angle, XRD, XPS, SIMS, AFM, UV-Vis-NIR spectrophotometry, Raman, photoluminescence, I(V), Resistivity) for quality control of the deposited thin films. This abstract is aiming to present ALD activities of our Technologies Platform covering the requests and specifications from fundamental research partners on breakthrough materials to the development and small production processing for industrial partners. A selection of ALD developments will be presented in the framework of LIST research and development projects addressing Lithium ion battery application (Co2O3), MEMS (MicroElectroMechanical Systems) and sensors (Figure 1), Energy Harvesters (Figure 2), Transparent Conducting Oxides such as ZnMgO, ZnSnO, ZnAlO, for transparent electronics (Figure 3), Example of Ag nano wires covered with conformal ALD ZnO film (Figure 4) and fillers' coating for composites (5). We are finishing a project that is looking at novel Aluminium nitride (AlN) film to be used in innovative energy harvesting applications, by the means of thermal ALD and Plasma-Enhanced ALD (PEALD). We developed a library of different thin films and multilayers processes including oxides (SnO, ZnO, TiO2, Al2O3, SiO2, MgO), nitride (AlN, TiN), metals (Ag, Co, Ni) (Figure 5) aiming both fundamental Research and applicative systems. Example of powder coating by FBR will be given (Figure 6).

11:40am **LI-ALD-TuM2-27 Molecular Layer Deposition of Li-Ion Conducting "Lithicone" Solid Electrolytes***, E. Kazyak, M. Shin, W. LePage, T. Cho,* ***Neil Dasgupta,*** University of Michigan, Ann Arbor

Atomic layer deposition (ALD) and its organic equivalent molecular layer deposition (MLD) have gained widespread attention as ultrathin functional materials in batteries, and have also been applied for interfacial coatings to stabilize electrode-electrolyte interfaces in battery systems. In particular, there is great interest in developing ALD/MLD films that are ionically-conductive and electronically insulating, which enables their use as solid electrolytes for either thin-film solid-state batteries or "artificial SEI" layers. MLD provides an important potential benefit over ALD films, due to improved mechanical compliance. MLD films are especially beneficial for interfacial coating of high-volume expansion electrodes and solid-state batteries. However, despite these promising characteristics, there have been only a few Li-containing MLD films reported to date, and no previous reports of ionic conductivity in MLD films.

In this work, we demonstrate the fabrication of Li-containing thin films ("lithicone") prepared via MLD, process using lithium *tert*-butoxide and ethylene glycol as precursors [1]. We demonstrate that the lithicone film grows in a self-limiting manner, using both spectroscopic ellipsometry and *in situ* quartz crystal microbalance (QCM) measurements. The evolution of the film morphology was revealed using glovebox-integrated atomic force microscopy (AFM) analysis, which eliminates artifacts from air exposure.

Glovebox-integrated X-ray photoelectron spectroscopy (XPS) measurements show that the bonding environment of lithicone films has C-O-Li moieties, which is distinct from that of lithium carbonate or alucone MLD films. To demonstrate the feasibility of using lithicone as a solid electrolyte or ionically conducting interlayer materials, the ionic conductivity of lithicone was measured systematically. The annealed lithicone film shows ionic conductivity of $3.6–5 \times 10^{-8}$S cm^{-1} with activation energy of ~0.6 eV. The measured electronic conductivity of the films was 5-6 orders of magnitude lower than the ionic conductivity, resulting in a transference number greater than 99.999%, and demonstrating that the lithicone films act as a solid electrolyte. This is the first quantified measurement of Li-ion conductivity in MLD thin film to-date, and will serve as a springboard to develop advanced organic/inorganic hybrid thin films for use in future battery applications.

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11:55am **LI-ALD-TuM2-30 Atomic-Level Precision at Large Scale: Opportunities and Challenges of ALD***, **Fatemeh Hashemi**,* TNO Science and Industry, the Netherlands **INVITED**

Atomic layer deposition (ALD) is a well-established method for the deposition of a variety of materials at a large scale and in industrial processing. While there are ever-growing efforts in the ALD community on the development of deposition materials with new properties and employing new chemistries, the well-developed processes have been scaled-up through innovative equipment designs, advanced precursor chemistries, and deposition methods.

In this talk, I will highlight some of the applications of ALD at large-scale including semiconductor electronics, powder coating, and photovoltaics (PV) manufacturing. I will focus on some basic concepts regarding the different design configurations and equipment that allow performing these processes and how the fundamental lab-scale studies in these areas have helped with accelerating the large-scale thin film deposition. To better understand the opportunities and challenges of ALD in these areas, I will discuss three specific studies including concepts related to area-selective ALD (AS-ALD) of metal oxides, nanoparticle deposition, and metal oxide barrier coating for solar cells.

First, I will highlight the advantages that the AS-ALD process brings to the large-scale fabrication of semiconductor electronics, recent efforts in the lab-scale focusing on metal-oxide deposition via ALD and the limitations that the field is facing. I will then briefly highlight the powder coating technology and what ALD can bring to the game, the state of the art, and the limitations. Lastly, I will show some examples of metal-oxides ALD as barrier or passivating layers in PV, specifically thin-film silicon solar cells, and how a combination of smart ALD process design with other state-of-the-art large-scale thin-film deposition techniques such as pulsed laser deposition (PLD) can result in high surface passivation and improved efficiency for silicon solar cells at large-scale. One example that I will focus on is the case of alumina ALD development for thin film PV which gave a boost to the PERC technology (Passivated Emitter Rear Cell) and opened up the industrial potential of ALD in PV.

12:30pm **LI-ALD-TuM2-37 ALD in Photovoltaics: From Extremely Thin to Ultrathin Layers, Physical Insight, and Chemical Methods Development***, P. Büttner, D. Döhler, Y. Cao, V. Koch, F. Scheler,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany*; C. Pointer,* Lehigh University*; S. Korenko, M. Barr, I. Mínguez-Bacho,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany*; E. Young,* lehigh University*; **Julien Bachmann**,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany **INVITED**

Atomic layer deposition (ALD) is ideally suited to the generation of 'extremely thin absorber' (ETA) solar cells, in which three distinct semiconductors are combined as electron transport layer (SnO_2, TiO_2, ZnO), light absorption layer (Sb_2S_3, Sb_2Se_3), and hole transport layer (V_2O_5 or spin-coated organics).

We have used ALD to explore and optimize individual geometric parameters of planar and nanostructured ETA cells. In the planar case, the compromise between light absorption and charge collection in Sb_2S_3 yields 60 nm as the optimal light absorber thickness. An underlying ZnS layer serves to improve adhesion between Sb_2S_3 and the oxide, and behaves as a tunnel barrier. Here, the ideal thickness that best balances an efficient direct electron transfer with a blocked recombination lies at 1.0 nm.

This materials system can also be implemented in parallel arrays of coaxial, cylindrical p-i-n heterojunctions. In that situation, the cylinder length that maximizes the overall solar energy conversion efficiency is 750 nm. Dewetting of heavy chalcogenides becomes an issue in such geometries that feature strongly curved surfaces. It can be prevented by a sacrificial ZnO layer that is removed after annealing. In that procedure, we find that an undesired barrier to charge transfer is formed due to redox chemistry at the interface. However, the formation of this barrier can be prevented by carefully oxidizing the surface of Sb_2S_3preliminary step. This trick even allows for the conformal coating of nanospheres, and the generation of solar cells based on nanosphere monolayers that feature interesting photonic effects.

Similarly structured coaxial p-i-n heterojunctions cannot be generated with hybrid perovskites as the light absorber, given that the ionic nature of perovskites renders them inaccessible from gaseous precursors. For this purpose, we have developed ALD from precursors in solution, or sALD. This new method yields high-quality semiconductors, even crystalline ones, at or near room temperature.

Taken together, these results demonstrate the power and versatility of ALD to control and engineer each layer of a photovoltaic stack, but also each interface between them, down to the level of individual atoms.

12:50pm **LI-ALD-TuM2-41 Demonstration of Pt-Wire Temperature Sensors Fabricated by Atomic-Layer 3D Printer Using $MeCpPtMe_3$ and O_3***, **Gabriel Vanko**, B. Hudec,* Slovak Academy of Sciences, Slovakia*; M. Precner,* Institute of Electrical Engineering, Slovak Academy of Sciences, Bratislava, Slovakia*; I. Kundrata, M. Plakhotnyuk,* ATLANT 3D Nanosystems, Denmark*; J. Bachmann,* Friedrich-Alexander Universität Erlangen-Nürnberg, Germany*; K. Fröhlich,* Slovak Academy of Sciences, Slovakia

This case study demonstrates Pt-wire temperature sensors fabricated by a rapid prototyping atomic-layer 3D printer utilizing a combination of ALD, microfluidics and high precision 3D printing [1], first time introduced at AVS ALD 2020 [2].

The printer nozzle moves relative to the substrate in a highly controlled manner (in this case ~2 mm/s) following a pre-programmed pattern. The nozzle is a miniature spatial ALD system where the precursor ($MeCpPtMe_3$ in this case) flows out of the center of the nozzle, surrounded by a concentric rings of vacuum and a reactant gas (O_3). The result is an area-selective ALD of pre-programmed patterns, where each nozzle pass over the substrate equals to one ALD cycle.

In this demonstration, >2 mm long Pt-wires of different thicknesses were printed using 100-500 ALD cycles at 200, 225 and 250 °C, where the width of the wires (~400 µm) was defined by the used nozzle geometry.

Morphology studies of the Pt surface by scanning electron microscopy revealed the island-like growth mechanism, typical for this thermal ALD Pt process [4], as well as certain effects on the wire edges, discussed in detail in [3].

The sensor was annealed for 30 min at 600 °C in N_2 atmosphere as a first step to ensure thermal stability. The wires' ends were capped by Au contact pads 2 mm apart (using e-beam PVD through a shadow mask) and measured electrically for their temperature sensor characteristics in the 25-400 °C range, as well as in cryogenic temperatures down to 3 K.

Interestingly, higher temperature sensitivity S was found for samples made by 200 ALD cycles, with a morphology of a network of interconnected Pt grains.

The comparison of temperature coefficient of resistivity α (normalized sensitivity) clearly shown that the printed ALD Pt demonstrate better temperature sensing characteristics than the conventional 30 nm e-beam PVD Pt thin film, and is comparable also to the Pt100 standard.

We will also discuss sensors printed on corrugated surfaces, i.e. black Si and Si gratings.

Online suppl. figures show the fabrication flow, SEM micrographs and electrical properties. The authors acknowledge the support of the H2020-EU ATOPLOT project (grant ID: 950785).

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1:05pm **LI-ALD-TuM2-44 Optimization of 1D Core-Shell Heterostructures for Gas Sensing***, M. Raza, **Nicola Pinna**,* Humboldt University Berlin, Germany

Hierarchical core-shell heterostructures composed of p- and n-type metal oxide shells deposited onto carbon nanotubes (CNTs) were synthesized using atomic layer deposition. Precisely controlled films of alternating metal oxides were uniformly deposited onto the inner and outer walls of the CNTs. The morphological, microstructural and electrical characteristics of the as prepared core-shell heterostructures were thoroughly investigated. The electrical resistance measurements highlighted the large influence of the metal oxides thickness and charge carriers types on increasing of many order of magnitude the baseline resistance of the core-shell heterostructures with various thicknesses of the metal oxide shell layers, suggesting that the conductivity of the sensors is dominated by Schottky barrier junctions across the n-p interfaces.

The behavior of our sensors was investigated for low concentrations of volatile organic compounds and pollutants. The gas sensing response of the heterostructures showed a strong dependence on the thickness of the metal oxide shell layers and the type of heterostructures formed. On the basis of the morphological, microstructural and electrical characterization and sensing results, the sensing mechanism which accounts for the marked variation in the resistance during the interaction of the target gas molecules will be discussed.

1:20pm **LI-ALD-TuM2-47 Bridging the Synthesis Gap in Vapor-Phase Deposition using Ionic Liquid as Solvent***, **Jingwei Shi**, S. Bent,* Stanford University

Molecular layer deposition (MLD) is a vapor-phase organic thin film deposition method useful for applications such as photolithography, lithium batteries, and microelectronics. However, while MLD offers excellent control over thickness and conformality, there is a more limited range of possible film chemistries compared to wet deposition techniques. We introduce a modified MLD technique, termed ionic liquid assisted MLD (IL-MLD) to overcome these limitations. The surface reactions of an IL-MLD process are performed inside an ultrathin layer of a suitable ionic liquid (IL) to replicate solvent effects inside a vacuum system, widening the number of possible chemical reactions used. The IL-MLD of polyetherketoneketone, an industrially and research-relevant, high performance thermoplastic, is demonstrated with this technique. By this proof-of-concept, we show that IL-MLD can enable the synthesis of ultra-thin polymeric films via solvent-mediated reactions which may be adapted to other vapor deposition techniques as well.

1:35pm **LI-ALD-TuM2-50 A Model of ALD Particle Coating in Fluidized Bed Reactors: Comparison With Experiments and Other Particle Coating Techniques***, **Angel Yanguas-Gil**, Z. Lu, P. Darapaneni, D. Kang, A. Mane, J. Kropf, C. Marshall, J. Elam,* Argonne National Laboratory

The ability to efficiently coat large batches of particles by atomic layer deposition is crucial for applications such as energy storage and catalysis. In recent years, fluidized bed reactors have shown strong promise as a pathway towards scale up of ALD in particles. In this work, we present a model of ALD in fluidized bed reactors. Using some fundamental approximations, we reduce the model to a set of analytic expressions that provide the time evolution of surface coverage inside the reactor as well as of precursor and byproduct species in the downstream area, using fundamental process and reactor parameters as inputs. A comparison between the model and experimental results on the ALD of Al_2O_3 using TMA and water in a commercial fluidized bed tool shows that the model is able to capture the main behaviors experimentally observed using in-situ mass spectrometry.

We then use this model to explore and compare the scale up of particle coating using fluidized bed reactors, rotating drum reactors both under constant flow and static dose conditions, and spatial ALD approaches using particle agitation, all methods that have been explored in the literature. The results obtained provide upper boundaries for dose times (throughput) and precursor utilization based on fundamental aspects of the precursor-surface interaction, such as the growth per cycle or the initial reaction or sticking probability, the maximum mass rates achievable for ALD precursors, and the volume and surface area of the particles. The resulting models can be used to explore the integration of ALD particle coating into more complex process flows.

1:50pm **LI-ALD-TuM2-53 Closing Remarks & Thank Yous***, X. Meng,* University of Arkansas

We hope you enjoyed the session! We will see you tomorrow!

Live Session

Room Live - Session LI-ALE-TuM3

Atomic Layer Etching Live Session I

Moderators: Prof. Gottlieb Oehrlein, University of Maryland, Dr. Dmitry Suyatin, Lund University

9:30am **LI-ALE-TuM3-1 Welcome, Thank Yous, & Instructions**, ***Dmitry Suyatin,*** Lund University, Sweden*; G. Oehrlein,* University of Maryland

Welcome to the session! We hope you will enjoy the it!

9:35am **LI-ALE-TuM3-2 Atomic Scale Profile Control in Fine Pitch Patterning and High Aspect Ratio Contact Hole Etching**, ***Tetsuya Nishizuka,*** *S. Kumakura, T. Katsunuma, Y. Kihara, M. Honda,* Tokyo Electron Miyagi, Ltd., Japan **INVITED**

In recent semiconductor device manufacturing processes, high aspect ratio contact hole etch has been the most challenging one. As the aspect ratio (AR) increases along with smaller critical dimension (CD) and vertically stacked 3D device structure, satisfying both vertical profile and selectivity to mask layer is getting harder. Especially "bow" profile which is caused by side etch generated under the mask is the top issue to address. Conventional approach to mitigate those problem is optimizing etching conditions such as gas chemistry or radio frequency (RF) power in accordance with the depth. Namely that controls radical species of etch/deposition balance and ion energy. However, since the deposition in this case is a kind of PECVD, its low step coverage characteristic causes clogging at the opening of mask and lack of thickness for sidewall protection in high AR structure. An alternate approach is separating etching and deposition steps, and cycling them. In this way, ALD can be applied as the deposition step. ALD's conformal coverage and atomic level controllability enable sufficient sidewall protection, and avoid clogging. Recently some results show a potential of excellent profile controllability which was impossible by conventional approach [1, 2]. Whereas in terms of bow improvement, even ALD is not always ideal because sidewall protection is necessary at only shallow area of contact hole while the bottom area and mask opening need to keep CD as wide as possible. This time we developed more ideal coverage ALD technique by utilizing under-saturation region and optimizing gas condition in the activation step. By combining this novel sidewall protection technique and etching reaction, more flexible etching process for high AR structure is realized.

1. F. Roozeboom et.al., ECS J. Solid State Sci. Technol. 4 N5067 (2015)

2. M. Honda et.al., Proc. of SPIE Vol. 11329 (2020)

9:55am **LI-ALE-TuM3-6 Nanoscale Cryogenic Process for Highly Selective Etch of Si_3N_4 Over Si**, ***Gaelle Antoun,*** *T. Tillocher, P. Lefaucheux,* GREMI CNRS/Université d'Orléans, France*; A. Girard,* IMN CNRS/Université de Nantes, France*; C. Cardinaud,* IMN CNRS/Université d'Orléans, France*; J. Faguet,* Tokyo Electron America Inc.,*; K. Maekawa, D. Zhang, H. Kim, M. Wang,* TEL Technology Center, America, LLC*; R. Dussart,* GREMI CNRS/Université d'Orléans, France

In 1988, Tachi *et al.* developed a cryogenic process using SF_6 plasma in order to etch Si anisotropically [1]. Since, many other studies were conducted in order to understand the mechanisms involved in cryo-etching. It was shown that oxygen is needed to build a passivation layer on the trench sidewalls [2]. This passivation layer can only be formed at low temperature and is desorbed once brought back to room temperature. Cryogenic processes present several advantages such as the limitation of material damage and reactor wall contamination [3].

In a previous work, we proposed an SiO_2 cryo-ALE process based on the physisorption of C_4F_8 during the modification step. However, this process was only demonstrated for temperatures between -120°C and -90°C [4] and selectivity to Si and Si_3N_4 was limited.

In this work, a different approach is proposed at low temperature (between -100°C and -50°C) to perform highly selective nanoscale etching. It this process, the modification step consists in depositing in plasma phase a layer stable only at low temperature. The etching step is an Ar plasma with low ion bombardment energy.

A cryogenic ICP reactor has been used to carry out this work. An in-situ Spectroscopic Ellipsometer is coupled to this reactor in order to monitor the surface thickness evolution over time. Quasi in-situ XPS measurements have also been performed. The equipment is composed of an ICP reactor coupled to the XPS chamber. A coupon is fixed on a transfer rod that can be cooled with liquid nitrogen and biased. Therefore, once processed, the sample can be transferred to the analysis chamber while remaining at low temperature.

Tests were performed on Si_3N_4 and p-Si coupons glued on a SiO_2 6" carrier wafers.

First, the influence of the modification step on the two materials was investigated at different temperatures. The same study was repeated to perform XPS measurements and characterize the modified surface. At room temperature, the established process is in a deposition regime for both materials. However, at low temperature, it becomes possible to switch to an etching regime. It has been evidenced that the threshold temperature for switching from deposition to etching is different for each material. Therefore, it is possible to etch Si_3N_4 selectively to Si at nanoscale by tuning wisely the substrate temperature.

The authors thank S. Tahara for all the helpful discussions.

This work was supported by CERTeM 2020 platform, which provides most of the equipment.

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2. Blauw et al.,J. Vac. Sci. Technol. B **18**,3453,2000
3. Dussart et al.,J. Phys. D: Appl. Phys. **47**,123001,2014
4. Antoun et al.,Sci Rep **11**,357,2021

10:10am **LI-ALE-TuM3-9 Using Selective Surface Functionalization of SiN_x to Increase SiO_2 to SiN_x ALE Selectivity**, *R. Gasvoda,* ***Xue Wang,*** Colorado School of Mines, USA*; P. Kumar, Z. Zhang, E. Hudson,* Lam Research Corporation*; S. Agarwal,* Colorado School of Mines, USA

Atomic layer etching (ALE) and its derivatives can provide high etch fidelity, atomic–scale precision, directionality, and high selectivity that is required for manufacturing of sub–7–nm node semiconductor devices. Specifically, ultra–high etch selectivity for SiO_2 vs. SiN_x is required in the manufacturing sequence, especially in the self–aligned contact etch approach. Plasma–assisted ALE of SiO_2 typically consists of two sequential half–cycles: fluorocarbon (CF_x) deposition from a fluorocarbon plasma followed by an Ar plasma activation step. Generally, ALE process parameters can be tuned to maximize overall SiO_2 vs SiN_x etch selectivity (similar to continuous etching). Recently, we have identified a novel approach to enhance the etch selectivity by selectively pre–functionalizing the SiN_x surface to protect against the etch process.

In this study, we used *in situ* attenuated total reflection Fourier transform infrared (ATR–FTIR) spectroscopy in combination with *in situ* 4–wavelength ellipsometry to monitor surface reactions, film composition as well as etch per cycle during ALE. Further, the ion energy distribution (IED) in the Ar plasma activation half–cycle is characterized with a retarding field energy analyzer. We have previously demonstrated that aldehydes can be used to selectively functionalize SiN_x from the gas phase without plasma, with minimal effect on SiO_2. In particular, benzaldehyde selectively functionalizes only the SiN_x surface with sp^2–hybridized–carbon (see Fig. 1a and 1b). We show that the overall SiO_2:SiN_x etch selectivity for a target SiO_2 etch of ~15 nm can be increased from ~2.1 to 4.5 simply by pre–functionalizing the SiN_x surface with benzaldehyde prior to beginning ALE (see Fig. 2a). Additionally, the infrared spectrum of the benzaldehyde functionalized SiN_x surface post etch shows more graphitic hydrofluorocarbon film accumulation than the infrared spectrum of the bare SiN_x surface, indicating that the added sp^2–hybridized–carbon from benzaldehyde remains on the surface leading to a reduction in the overall etch (see Fig 2b). We will also discuss various re–functionalization sequences in order to further maximize the overall SiO_2:SiN_x etch selectivity. Further, we discuss the effect of maximum ion energy and IEDs in the activation step on overall etch selectivity with specific focus on non–ideal Ar plasma activation steps where the maximum ion energy is above the sputtering threshold of both SiO_2 and SiN_x.

10:25am **LI-ALE-TuM3-12 Etch-stop Mechanisms in Plasma-assisted Atomic Layer Etching of Silicon Nitride: A Molecular Dynamics Study**, ***Jomar Tercero,*** University of the Philippines*; A. Hirata,* Sony Semiconductor Solutions Corporation, Japan*; M. Isobe,* Osaka University, Japan*; M. Fukasawa,* Sony Semiconductor Solutions Corporation, Japan*; M. Vasquez, Jr.,* University of the Philippines*; S. Hamaguchi,* Osaka University, Japan

Plasma etching is one of the most technically demanding processes used in the fabrication of advanced semiconductor devices. Recently atomic-scale control of etching processes has become a topic of wide interest, following the urgent needs in developing manufacturing technologies for nano-meter-scale devices in the modern semiconductor industry [1-3]. To

achieve atomic-scale control of etching processes, a better understanding of surface reaction mechanisms of the existing etching processes is the first key step. In earlier experiments, the etch stop in atomic layer etching (ALE) processes of silicon nitride (Si_3N_4) was observed after several ALE cycles [4]. The goal of this study is to find the reason for this etch stop. In a typical ALE process, a cycle of the surface modification step and the removal step of the modified layer is repeated. In the ALE process mentioned above, a hydrofluorocarbon (HFC) layer is deposited on a Si_3N_4 surface in the surface modification step, and then the surface is exposed to low-energy Ar^+ ion bombardment in the removal step. In this study, molecular dynamics (MD) simulations were used to emulate the ALE processes. The simulations have shown that, during the removal step, the Si_3N_4 etching is enhanced by chemical reactions with HFC atoms but a large amount of carbon typically remains on the surface after the removal step. The carbon remnants increase the sticking probability of HFC radicals in the subsequent surface modification step and induce thicker HFC deposition, which leads to the etch stop eventually after a few cycles. The validity of the simulations was tested by comparing the simulation results with available experimental observations.

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10:50am **LI-ALE-TuM3-17 Landscape of Spontaneous Etch via Ligand-Exchange in Thermal Atomic Layer Etching**, ***Ann Lii-Rosales**, A. Cavanagh, S. George,* University of Colorado Boulder **INVITED**

Thermal atomic layer etching (ALE) utilizes sequential, self-limiting surface reactions to remove materials on the atomic level. Thermal ALE consists of two steps: (A) surface modification and (B) removal via volatilization. For metal oxide thermal ALE, surface modification usually involves fluorination using HF.[1] This fluorination creates a surface layer of metal fluoride. A strategy for volatilization can use ligand-exchange reactions. The exchange of F for Cl is an effective pathway, because metal chlorides are generally more volatile than the corresponding fluorides.[1] The resulting metal chloride can be thermally desorbed from the surface, leading to metal removal.

Both A and B steps are necessary for thermal ALE. However, material removal is achieved only by ligand-exchange. This renders the B step crucial for determining a metal's propensity for etching. Hence, a pre-fluorinated surface can be used as a model surface, which assumes the form of the fluorinated metal surface. One can use ligand-exchange reactions with the model fluorinated surface as an indicator for spontaneous etch.

A new reactor was constructed to probe the ligand-exchange reaction. The reactor uses *in situ* quadrupole mass spectrometry (QMS) to detect gas-phase products generated during ligand-exchange. Metal fluoride powders were used as model surfaces. Precursors for ligand-exchange were flowed through the powder over a wide temperature range, while gas-phase products were monitored by QMS in real time. This new reactor is unique in that the etch products are entrained in a molecular beam that has line-of-sight to the QMS ionizer. This configuration enables direct and accurate analysis.

The landscape for ligand-exchange reactions turned out to be unexpectedly rich. By surveying a variety of systems, the landscape can be categorized as the follow: (1) Ligand-exchange and volatile etch products occur at similar temperature; (2) Ligand-exchange happens at low temperature, but etch products do not desorb until high temperature; and (3) ligand-exchange happens, but there are no etch products. Representative systems are AlF_3 + $Al(CH_3)_3$ and SnF_4 + $TiCl_4$ for category (1), HfF_4 + $SiCl_4$ and InF_3 + $SiCl_4$ for category (2), and AlF_3 + $SiCl_4$ for category (3). The categories can be visualized from the intensity traces of precursor vs. etch product as a function of temperature. The new QMS reactor revealed the complexity of ligand-exchange and showed that the spontaneous etch systems can serve as predictors for thermal ALE of new materials.

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11:10am **LI-ALE-TuM3-21 Mechanisms of Self-Limiting Processes in Thermal Atomic Layer Etching of Nickel by β-diketones**, ***Abdulrahman Basher**, I. Hamada, T. Ito, K. Karahashi , S. Hamaguchi,* Osaka University, Japan

Thermal atomic layer etching (ALE) is one of the key manufacturing technologies for nano-scale electronic devices [1] as it can be used for precise and damageless etching of metals. The mechanisms of thermal ALE of Ni with hfacH were examined in detail in previous studies [2-4]. It starts with the deprotonation of hfacH molecules after oxidizing the Ni surface. By increasing the surface temperature in the range of 300 ~ 400 °C, volatile nickel complex $Ni(hfac)_2$ and water H_2O molecules are formed on the surface and remove the NiO layer. In this process, once a new metallic Ni surface appears, no further etching occurs, which ensures the self-liming nature of the thermal ALE process [3-5]. It has been known experimentally [5,6] that, when hfacH molecules are supplied to a metallic Ni surface, they decompose and form neither $Ni(hfac)_2$ nor H_2O molecules, and as a result no etching of Ni takes place. The origin of the self-limiting process in the thermal ALE of Ni with hfacH exposure was discussed in an earlier study[4]. The aim of this work is to clarify the mechanisms of decomposition of other β-diketones on a metallic Ni surface and the effect of surface roughness on the decomposition concerning thermal ALE. In this study, van der Waals inclusive [7] periodic DFT is employed to investigate the adsorption and reaction processes of β-diketones such as hfacH, tfacH, and acacH on flat and rough metallic Ni surfaces, using a STATE code [8]. It has been found that the physisorption energies of those β-diketones are almost the same while the chemisorption energy is higher for a β-diketone with a higher polarity and the van der Waals forces play a decisive role in determining the adsorption energy. The dissociation processes of β-diketones have been studied with a climbing image nudged elastic band method, which has shown the cleavage of a C-F bond of a β-diketone is more likely to take place than the deprotonation. The surface roughness can also help to form C-Ni bonds, which were also observed in experiments. In this way, our simulations have demonstrated the self-limiting nature of thermal ALE for Ni with β-diketone gases in general, which is consistent with earlier experimental observations [5,6].

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11:25am **LI-ALE-TuM3-24 Oxidation Influences Etch Quality in the Low-Temperature Thermal ALE of Copper**, ***Martin McBriarty**, J. McWilliams, M. Moinpour, R. Kanjolia, K. Littau,* EMD Electronics

Low-temperature thermal atomic layer etching (ALE) of copper is an appealing approach to controlled isotropic removal of Cu for emerging middle- and back-end-of-line (MOL and BEOL) steps in semiconductor device manufacturing. Cu ALE can proceed by controlled oxidation of the Cu surface followed by the volatilization of copper oxide. The isotropic removal of Cu with minimal surface roughening is critical for process integration, and a low-temperature process is necessary to avoid migration of highly mobile Cu to adjacent parts of the device or structure of interest. We investigated the plasma-free low-temperature oxidation of physical vapor deposited (PVD) Cu thin films by various oxidizing agents, as well as the subsequent volatilization of surface copper oxide by the beta-diketone hexafluoroacetylacetone (Hhfac). Depending on the oxidant and process conditions, we measure the removal of <0.5 Å to >5.0 Å of Cu per ALE cycle. We determine the influence of oxidation chemistry and kinetics on the etch behavior, surface chemistry, and film morphology, guiding the development of rapid, atomically precise, and selective low-temperature ALE processes for Cu.

11:40am **LI-ALE-TuM3-27 Thermal Atomic Layer Etching of Al_2O_3 and AlN Using HF or XeF_2 for Fluorination and BCl_3 for Ligand-Exchange**, ***Austin Cano**, S. George,* University of Colorado at Boulder

Thermal atomic layer etching (ALE) of Al_2O_3 and AlN can be performed using HF or XeF_2 as the fluorination reactant and BCl_3 as the ligand-exchange reactant. To investigate the etching mechanism, in-situ FTIR spectroscopy was used to identify the surface species and in-situ

spectroscopic ellipsometry was employed to measure the etch rates. Quadrupole mass spectrometry was also employed to identify the volatile etch products. The Al_2O_3 studies were performed using Al_2O_3 ALD films grown using trimethylaluminum (TMA) and water as the reactants. The AlN investigations were conducted using crystalline AlN to explore the etch rates. The FTIR experiments employed AlN films grown by ALD using tris(dimethylamido)aluminum and ammonia as the reactants.

When BCl_3 is used as a reactant, the ALE mechanism could occur by BCl_3 conversion of Al_2O_3 to B_2O_3 or AlN to BN. Alternatively, BCl_3 could undergo ligand-exchange with the fluorinated AlF_3 surface. For thermal Al_2O_3 ALE, FTIR studies revealed strong evidence for a conversion reaction during the initial BCl_3 exposure on Al_2O_3. The original Al-O vibrational modes were converted to B-O vibrational modes by the initial BCl_3 exposures as shown in Figure 1. However, after the first ALE cycle using sequential HF and BCl_3 exposures, there was no more evidence of conversion and the Al_2O_3 etching proceeded through a fluorination and ligand-exchange mechanism. Quadrupole mass spectrometry measurements observed that BCl_3 exposures to AlF_3 yielded BCl_2F and $AlCl_3$ reaction products. In situ ellipsometry measurements determined that the Al_2O_3 ALE etch rate using HF and BCl_3 as the reactants varied with temperature from 0.01 Å/cycle at 270°C to 0.19 Å/cycle at 330°C.

In-situ FTIR and spectroscopic ellipsometry were also used to explore thermal AlN ALE. FTIR studies revealed that the initial BCl_3 exposures created a thin BN layer on the surface. Subsequent HF and BCl_3 exposures were consistent with AlN fluorination by HF and subsequent F/Cl exchange to form volatile $AlCl_3$ product during BCl_3 exposures. The Al-N vibrational stretch decreased progressively versus number of HF/BCl_3 cycles as displayed in Figure 2. HF was not able to fluorinate single crystalline AlN substrates. Consequently, XeF_2 was required as a stronger fluorination source. When combining viscous flow XeF_2 exposures with static BCl_3 exposures, ellipsometry measurements showed that AlN etching occurred at temperatures above 220°C. An etch rate of 0.81 Å/cycle was obtained at 255°C. In contrast, growth of a top layer that may be composed of AlF_xCl_y was observed at lower temperatures. This top layer could be removed by long static BCl_3 exposures.

11:55am **LI-ALE-TuM3-30 Closing Remarks & Thank Yous***, Gottlieb* ***Oehrlein,*** University of Maryland*; D. Suyatin,* Lund University, Sweden

Thank you for attending today's session. We will see you tomorrow!

Live Session

Room Live - Session LI-ALD-WeM1

Selective Deposition (AS) Live Session

Moderators: Prof. Adam Hock, Illinois Institute of Technology, Prof. Henrik Pedersen, Linköping University, Sweden, Prof. Matti Putkonen, University of Helsinki

9:30am **LI-ALD-WeM1-1 Welcome, Thank Yous & Instructions***, **Matti Putkonen**,* University of Helsinki, Finland

Thank you for attending today's session. We hope you will enjoy the session!

9:35am **LI-ALD-WeM1-2 Another Opportunity in Area Selective Atomic Layer Deposition using Precursor Inhibitors***, **Han-Bo-Ram Lee**,* Incheon National University, Republic of Korea **INVITED**

Area-selective atomic layer deposition (AS-ALD) is envisioned to play a key role in next-generation nanofabrication for Si devices. Basics concept of AS-ALD is that an original surface is changed to activated or deactivated surfaces toward following ALD reactions, resulting in selective growth in one substrate. Although self-assembled monolayers (SAMs) have been successfully introduced for the change of surface properties and showed promising results in the early study of AS-ALD, they still have several disadvantages for high volume manufacturing (HVM), such as the low thermal stability and pattern interference from their inherent size. Several years ago, our research group has suggested that many ALD precursors could be used for an inhibitor of AS-ALD by utilizing their adsorption selectivity on surfaces and reaction selectivity with counter reactant. Because the inhibitor, itself, is a precursor, it has high compatibility in HVM and multifunctionality between the roles of inhibitor and precursor. In this presentation, various types of precursor inhibitors studied in our group will be summarized and another opportunity of our AS-ALD will be discussed. A combined process of AS-ALD and atomic layer etching (ALE) was studied by designing process sequence and combination of inhibitor and counter reactants. In addition, another concept of selective deposition by using a homogeneous precursor inhibitor was proposed for thickness control of ALD thin films inside 3D structures. The chemical and physical interactions of inhibitors with precursors were successfully explained through theoretical calculations by density functional theory (DFT)and Monte Carlo simulation. The results could provide insights for the next generation patterning process using ALD.

9:55am **LI-ALD-WeM1-6 Direct Deposition of High-resolution 3D Nanostructures by Atomic-Layer Additive Manufacturing (ALAM)***, **Sarah Tymek**,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany*; I. Kundrata,* ATLANT, Germany*; M. Barr,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany*; P. Wiesner,* ATLANT, Germany*; M. Plakhotnyuk,* ATLANT, Denmark*; J. Bachmann,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany

Confining spatial ALD (atomic layer deposition) laterally to a spot with a size in the micron range allows one to perform ALD cycles by repeated passes of the deposition head above the substrate. The pattern defined by the motions of the deposition head may be arbitrarily complex. This concept allows for the definition of deposits in three dimensions in the manner of classical additive manufacturing (3D printing). However, the vertical resolution of the shapes generated is defined by the surface chemical principles of ALD, and therefore is on the order of single atoms. The lateral resolution depends on the printing head and the gas flows and is currently on the order of hundreds of µm.

We have demonstrated the self-limiting behavior of this atomic-layer additive manufacturing (ALAM) procedure for several materials. Under atmospheric conditions, the deposition of TiO_2 occurs with the same growth per pass as in conventional ALD. The cross-section of a deposit exhibits a horizontal surface and sharp edges. The self-limiting behavior of the surface chemistry is maintained. As an example of a noble metal, Pt grows in a highly crystalline and even oriented form. Air-sensitive precursors such as the metal alkyls can be handled safely in aerobic conditions, and the growth of Al_2O_3 and ZnO occurs with familiar characteristics.

Thus, ALAM is a novel method allowing for the direct generation of multimaterial structures without the need for preliminary or subsequent patterning. The combination of several materials in not only lateral juxtaposition but also vertical arrangement further enables one to use sacrificial deposits and generate complex three-dimensional structures.

10:10am **LI-ALD-WeM1-9 The Relation between Reactive Surface Sites and Precursor Choice for Area-Selective Atomic Layer Deposition***, **Marc Merkx**, A. Angelidis, J. Li,* Eindhoven University of Technology, Netherlands*; D. Hausmann,* Lam Research Corp.*; E. Kessels,* Eindhoven University of Technology, Netherlands*; T. Sandoval,* Universidad Técnica Federico Santa Mariá, Chile*; A. Mackus,* Eindhoven University of Technology, Netherlands

Small and volatile molecules are of interest as alternative inhibitor for area-selective ALD to better meet the requirements for industrial processing.[1,2] However, due to their size and lack of surface ordering, it is much more challenging to achieve the high surface packing density that is required to block precursor adsorption through steric hinderance (i.e. physical shielding). In this work, we explore the central question whether area-selective ALD with high selectivity requires; (i) physical shielding through steric effects, (ii) chemical passivation by eliminating the reactive surface sites required for precursor adsorption, or (iii) a combination of both physical shielding and chemical passivation. At the same time, we investigate why some precursors are more difficult to block than others.

Precursor blocking was studied using *in-situ* infrared (IR) spectroscopy for trimethylaluminum (TMA), dimethylaluminum isopropoxide (DMAI), tris(dimethylamino)aluminum (TDMAA), and bis(diethylamino)silane (BDEAS) precursors using acetylacetone (Hacac) as inhibitor. It was found that TMA can adsorb on both isolated and H-bonded (i.e. vicinal) OH groups, whereas DMAI, TDMAA, BDEAS and the Hacac inhibitor only adsorb on isolated OH groups. Correspondingly, it was found that blocking TMA adsorption is much more challenging as compared to the other precursors. In addition, the IR spectra show a consumption of vicinal OH groups when dosing TMA on a Hacac-functionalized Al_2O_3 surface, which indicates that TMA can adsorb on the vicinal OH groups in between the Hacac inhibitor molecules. Taken together, it can be concluded that precursor blocking is more effective if the inhibitor and precursor adsorb on the same surface sites during area-selective ALD. To achieve this required overlap it is vital to carefully consider the choice of the precursor.

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10:25am **LI-ALD-WeM1-12 Diffusion-Mediated Ruthenium Area-Selective Atomic Layer Deposition in Nanopatterns***, **Jan-Willem J Clerix**, E. Marques, J. Soethoudt,* KU Leuven / imec, Belgium*; F. Grillo,* ETH Zurich, Switzerland*; G. Pourtois,* imec, Belgium*; J. Van Ommen,* TU Delft, Netherlands*; A. Delabie,* KU Leuven / imec, Belgium

Area-selective deposition (ASD) opens up new avenues in the fabrication of next-generation nanoelectronic devices, as this bottom-up approach can complement conventional top-down lithographic patterning. However, a major challenge is defectivity due to the undesired growth of nanoparticles on the non-growth area. In this work, we model Ruthenium ASD by (ethylbenzyl)(1-ethyl-1,4-cyclohexadienyl)Ru/O_2 Atomic Layer Deposition (ALD) with Kinetic Monte Carlo (KMC) methods to investigate the ASD mechanism on line-space nanopatterns with different dimensions. ASD is governed by adsorption as well as diffusion, and diffusion of Ru adatoms and nanoparticles from the non-growth to growth surface becomes more important when pattern dimensions decrease. A key feature of the Ru ALD process is the size-dependent mobility and reactivity of Ru nanoparticles. Nanoparticles that are too small to catalyze O_2 dissociation do not grow via precursor adsorption, but they diffuse and aggregate with each other or at the interface with the growth area. This results in nearly full depletion of Ru on the non-growth pattern for widths of 50 nm and smaller for a large number of cycles, as all Ru adspecies are captured at the growth interface before growth by adsorption is catalysed and before they become immobile. In addition, we observe a depletion zone near the interface with the growth area for patterns with larger dimensions. Overall, this mechanism results in smaller and fewer Ru nanoparticles on the non-growth surface, which is highly beneficial for etch-based defect mitigation (Figure 1). These predictions are supported by the experimental observation of reduced defectivity on the non-growth area near the interface with the growth area in nanoscale line-space patterns (Figure 2). We provide a promising outlook for defect mitigation for Ru ASD by passivation/deposition/etch cycles and for Ru ASD in nanopatterns with even smaller dimensions.

10:50am **LI-ALD-WeM1-17 Area-Selective CVD of Metallic Films on Oxide Substrates With Acidic or Basic Hydroxyl Groups***, **Laurent Souqui,*** University of Illinois at Urbana-Champaign*; Z. Zhang,* Applied Materials*; S. Liu,* University of California - Riverside*; E. Mohimi,* LAM Research*; G. Girolami, J. Abelson,* University of Illinois at Urbana-Champaign **INVITED**

Area-selective deposition of thin films affords the maskless propagation of existing substrate patterns in bottom-up fabrication of microelectronic or nanoscale devices. This can be achieved in low temperature chemical vapor deposition by identifying precursors, sometimes in combination with added inhibitors, that exhibit greatly varying nucleation delays – very short on the desired growth surface, and very long on the intended non-growth surface.Then, a growth interval can be found such that the desired film thickness is deposited on the growth surface, while few to no nuclei form on the non-growth surface.

Focusing on the deposition of metals on oxides by CVD, we investigated how selectivity for Mo, Ru, Fe and Co can be achieved between oxides of different acidity, and also between metals and oxides. We found that $Fe(CO)_5$, $Mo(CO)_6$ and $Ru_3(CO)_{12}$ afford the deposition of metal or metal carbide films on acidic oxides, but that growth is inhibited on basic oxides. On the contrary, $Co_2(CO)_8$ nucleation is faster on basic oxides than on acidic oxides. The opposite reactivity of the two carbonyl precursors towards oxide surfaces is attributed to differences in the kinetic stability of reaction intermediates on the surfaces. Additionally, the selectivity of $Co_2(CO)_8$ can be further enhanced by exposing the surface to NH_3. Finally, selectivity against metal surfaces can be achieved by first oxidizing the metal surface, then performing CVD, and finally reducing the oxide to restore the original metal surface.

11:10am **LI-ALD-WeM1-21 Inhibiting Plasma Enhanced Atomic Layer Deposition of SiO_2 on Cu using Thiol Multilayers in an ABC Cycle***, **Rohit Narayanan Kavassery Ramesh,** W. Xu, R. Gasvoda,* Colorado School of Mines, USA*; X. Lei, B. Zope, H. Chandra, R. Ridgeway, X. Jiang, G. Liu, R. Kanjolia, A. Derecskei, R. Pearlstein,* EMD Electronics, USA*; S. Agarwal,* Colorado School of Mines, USA

Atomic layer deposition (ALD) offers the potential for area-selective deposition of patterned structures to enable a bottom-up fabrication of semiconductor devices. Area-selective ALD can be achieved by selectively attaching a blocking molecule to a specific surface. SiO_2 ALD is unique in the sense that O_3 or an O_2 plasma is preferable for high throughput and cleaner process: Halogenated silane such as $SiCl_4$ and H_2O/pyridine process yield pyridinium salt as byproduct. The need for O_3 or O radicals for growth makes the use of organic blocking layers to inhibit growth challenging as hydrocarbons get rapidly combusted in the presence of O radicals. In this study, we explore area-selective, O_2-plasma-assisted ALD of SiO_2 on SiO_2 while inhibiting growth on Cu with fluorinated thiols that are resistant to combustion.

The surface species during the selective ALD on the growth (SiO_2) and nongrowth (Cu) surfaces was monitored using *in situ* reflection-absorbance infrared spectroscopy (RAIRS). SiO_2 ALD was done at 100 °C using di-sec-butyl-aminosilane (DSBAS) as the Si precursor and a remote O_2 plasma. The nongrowth surface, CMP Cu with the native oxide (CuO_x),was functionalized with 1H,1H,2H,2H-perfluorodecanethiol (Step A)at 100 °C. The *in situ* infrared spectrum of the Cu surface after functionalization showed a sharp increase in absorbance in the CF_2 stretching region (~1250 cm^{-1}) indicating thiol attachment to CuO_x. The functionalized Cu surface was then exposed to DSBAS (Step B) and O_2 plasma (Step C). The corresponding infrared spectra showed no surface $O\text{-}SiH_3$ species after the DSBAS cycle but indicated removal of 10-15% of the thiol after the O_2 plasma cycle. To maintain the inhibitor coverage on the surface, it was redosed in the subsequent cycle. This A-B-C type ALD process (A: PFDT, B: DSBAS, C: O_2 plasma)(see Fig. 1(a) and (b)) was repeated for 35 cycles, which yielded ~6 nm of growth on the SiO_2 surface. No evidence of SiO_2 deposition on the Cu surface was observed after 35 A-B-C cycles with RAIRS and x-ray photoelectron spectroscopy (XPS), as shown in Fig. 1 (c) and (d), respectively. Characterization of surface morphology with atomic force microscopy (AFM) revealed no evidence of damage or roughening of the Cu surface. After ALD, the inhibitor on the Cu surface was decomposed by high temperature annealing followed by cleaning of the residue with a proprietary formulation. The XPS data after cleaning indicated that Cu surface was reduced with no detectable SiO_2, as shown in Fig. 1 (e) and (f). Thus, PFDT was not only able to protect the Cu surface in an O_2 plasma process, but also inhibited the growth of SiO_2 on the Cu surface.

11:25am **LI-ALD-WeM1-24 Sequential Area Selective Deposition of Poly(3,4-ethylenedioxythiophene) (PEDOT) and Tungsten on SiO_2/Si-H Substrates***, **Hwan Oh,** J. Kim, S. Song, G. Parsons,* North Carolina State University

In nanopatterning, area-selective deposition (ASD) is gaining attention as a promising vapor-phase “bottom-up” process to overcome challenges such as edge-placement errors (EPEs) and high costs associated with the conventional “top-down” approaches.[1] However, to date, most ASD processes have addressed only individual dielectric or metal depositions. Accordingly, co-compatible integration of multiple ASD steps is desired for future advanced device fabrication. We have recently demonstrated a sequential ASD of titanium dioxide (TiO_2) and tungsten (W) films on SiO_2/Si-H line patterned substrates based on the understanding of two individual ASDs, i.e., TiO_2 ASD[2] (on SiO_2 vs. Si-H) and W ASD[3] (on Si-H vs. SiO_{-2}).

In this work, we have extended the established concept to polymeric dielectric and metal pairs, i.e., a sequential ASD of poly(3,4-ethylenedioxythiophene) (PEDOT) and W on SiO_2/Si-H substrates (Scheme 1). In the PEDOT step, inherent PEDOT ASD on SiO_2 vs. Si-H was performed using 3,4-ethylenedioxythiophene (EDOT) as a monomer and antimony pentachloride ($SbCl_5$) as a volatile liquid oxidant *via* oxidative chemical vapor deposition (o-CVD). This process led to a thickness of ~ 13 nm PEDOT films with 10 s of o-CVD while maintaining selectivity above 0.9 (Figure 1). In the W step, W ASD on Si-H (after o-CVD) vs. PEDOT deposited on SiO_2 was conducted using sequential exposure of silane (SiH_4) and tungsten hexafluoride (WF_6) *via* atomic layer deposition (ALD). Herein, PEDOT films on SiO_2 serve as a blocking layer against W deposition, and selective deposition of W films on Si-H (after o-CVD) was confirmed by X-ray photoelectron spectroscopy (XPS) (Figure 2).

More systematic studies, for example, the origin of selectivity and film properties such as roughness and conductivity, will be investigated in the future. This concept will be demonstrated on the nm-scaled pattern substrates. Overall, we anticipate our results to offer insight into developing a more advanced process pathway to integrating multiple ASDs of polymeric low-k dielectrics and metal.

11:40am **LI-ALD-WeM1-27 Atomic Precision Advanced Manufacturing and Lessons for Area-Selective Deposition***, **Scott Schmucker,** E. Frederick, Q. Campbell, J. Ivie, E. Anderson,* Sandia National Laboratories, USA*; K. Dwyer,* University of Maryland, College Park*; A. Baczewski, G. Wang,* Sandia National Laboratories, USA*; R. Butera,* Laboratory for Physical Sciences*; S. Misra,* Sandia National Laboratories, USA

Area-selective chemisorption templated by lithographic desorption of monatomic functional groups on semiconductor surfaces has enabled a technology termed Atomic Precision Advanced Manufacturing (APAM). Among other things, APAM can be used for ultra-doping Si with n-type and p-type dopants from gaseous precursors and it is a technology extensible to other surface reactions relevant to atomic layer deposition (ALD).These gas-phase precursors are commonly hydrogenated or halogenated molecules (e.g. PH_3, AsH_3, B_2H_6, $AlCl_3$) delivered to Si(100) in ultrahigh vacuum.Within this environment, it is possible by surface characterization (e.g. scanning tunneling microscopy (STM)) and DFT modeling to understand the chemical interactions between the precursor and reactive surface sites.Additionally, electron-stimulated desorption (ESD) via STM can selectively desorb atoms from the resist at scales ranging from Angstroms to microns; thereby, dopants are precisely placed by selective chemisorption in depassivated areas in countable quantities or in two-dimensional ultra-doped films.

A distinctive advantage of APAM surface templating is the high selectivity it can realize.In the case of PH_3 on Si(100) 2×1, a hydrogen resist can provide selectivity >1000:1.One enabling factor is a link between process development and surface science.As one example, the most common defect on the Si(100) 2×1:H surface is an isolated dangling bond where a single H atom is missing. Dissociative chemisorption of PH_3 can be impeded on this defect and appropriate thermal treatment can remove reaction biproducts from the surface before dopants are incorporated into the Si lattice, preserving selectivity.

Although historically focused on dopants in semiconductors, the surface reactions of APAM are largely equivalent to ALD half-cycles.By surface functionalization and ESD, surface reactivity can be controlled for area-selective ALD. Here, we discuss efforts to generalize APAM technology to common ALD co-reactants, extend APAM beyond group-IV substrates, and assess ALD selectivity on APAM resists.

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11:55am **LI-ALD-WeM1-30 The Role of Precursor-Inhibitor Interactions in Area-Selective Atomic Layer Deposition***, **Tania Sandoval**,* Universidad Técnica Federico Santa María, Chile **INVITED**

Area-selective deposition by surface deactivation has been an extensive area of research. Strategies for deactivation include the use of polymers, self-assembled monolayers, and most recently, small molecules. These inhibitor molecules act to block deposition on the non-growth area; however, the mechanisms by which selectivity is achieved and more importantly, how it is lost are still poorly understood. ASD processes are often plagued by low selectivity. Some important requirements for a good inhibitor molecule include strong adsorption and high coverage on the non-growth area, and weak (or none) interactions with the growth area, and with the incoming precursor. In the case of small inhibitor molecules, precursor-inhibitor interactions have been found to depend on the adsorption mechanism and adsorbate configurations of the inhibitor molecule, where adsorption configurations that lead to unreacted functional groups are more prone to be displaced and contribute to selectivity loss.[1]

In this presentation, theoretical studies on the fundamental understanding of the interactions between precursor and small inhibitor molecules, and the mechanism of selectivity loss will be discussed. The precursors trimethylaluminum (TMA), dimethylaluminum isopropoxide (DMAI), tris(dimethylamino)aluminum (TDMAA), and bis(diethylamino)silane (BDEAS) and inhibitor molecules acetylacetone, acetic acid, and tetramethylheptanedione were studied. The results showed that the formation of hydrogen bonds between unreacted functional groups of the inhibitor and incoming precursor lead to stronger interactions than the cases where all functional groups of the inhibitor reacted with the non-growth surface. Moreover, the results for TMA showed a higher probability to displace the inhibitor molecule than the other precursors tested, due to the more favorable interactions with the different adsorbed inhibitor configurations. Overall, this study provides fundamental insight into the importance of considering both the precursor and inhibitor molecule in achieving maximum selectivities.

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12:30pm **LI-ALD-WeM1-37 Spatially Controlled Atomic Layer Deposition within Polymer Templates for Multi-Material Nanorods and Nanowires Fabrication***, **Rotem Azoulay**, T. Segal Peretz,* Technion, Israel

Today's nanofabrication techniques require multistep and costly processes in order to fabricate complex, multi-materials nanostructures. Performing atomic layer deposition (ALD) within polymeric templates can offer a simple solution for nanostructure fabrication. In this process, named sequential infiltration synthesis (SIS), high partial pressures and long exposures times lead to inorganic materials growth within polymers. Sequential polymer removal results in polymer-templated inorganic nanostructure. While SIS shows great potential in fabricating large variety of structures, it is currently limited to a single material growth process.

In this research, we demonstrated, for the first time, multi-material SIS process with control over the spatial location of each material and fabricate heterostructure nanorods and nanowires. We studied SIS within self-assembled block copolymer (BCP) films and electrospun polymer fibers and developed multi-material SIS, where two metal oxides are grown together in a single process, with precise control over their location within the polymer template. We used cylinder forming poly (styrene-block-methyl methacrylate) (PS-b-PMMA) films and electrospun PMMA as the polymeric template and DEZ (diethyl zinc), TMA (trimethyl aluminum) and $TiCl_4$ (titanium tetrachloride) as the organometallic precursors. We achieved control over the growth location of each metal oxide by tuning the organometallic precursors diffusion time, forming heterostructures after polymer removal. A short exposure of the first precursor resulted in a limited growth only at the outer part of the polymer, while a long exposure of the second precursor enabled it to reach the full depth of the polymer besides the section which was already occupied by the first precursor. An exposure to water completed the cycle. We demonstrated this process on BCP films to achieve AlOx-ZnO nanorods arrays (Figure 1) and on polymer fibers to achieve AlOx-ZnO fibers. We performed structural characterization using scanning and transmission electron microscopy (SEM and TEM, respectively) to characterize the nanowires and nanorods as well as three-dimensional characterization scanning TEM (STEM) tomography and energy-dispersive X-ray spectroscopy (EDS) STEM tomography in order to probe the structure and the chemical composition in 3D (Figure 2). This research opens new pathways for multi-materials nano scale structure fabrication through ALD-based growth within polymers.

12:45pm **LI-ALD-WeM1-40 Maskless Patterned Spatial ALD for Thin-Film Encapsulation***, C. Frijters,* SALDtech B.V., Netherlands*; Y. Creyghton,* Holst Centre / TNO, Netherlands*; **Paul Poodt**,* SALDtech B.V., Netherlands

Atmospheric pressure Spatial ALD is able to deliver high deposition rates while maintaining the advantages of conventional ALD, such as low defect density, high conformality and thickness uniformity. First industrial applications of Spatial ALD include passivation of c-Si solar cells and roll-to-roll manufacturing of flexible barrier foils. An emerging application for Spatial ALD is flat panel (OLED) displays. Examples include semiconductor and dielectric layers for use in thin-film transistors, and thin-film encapsulation for flexible OLED displays. As today's displays are fabricated using glass panels in the order of several square meters, a remaining challenge is the development of large-area Spatial ALD deposition technology that is able to combine high throughput with uniform performance across very large areas.

Encapsulation of OLED devices requires thin, dense films with very low pinhole densities and water vapor transmission rates. In most cases, the materials used are dielectric (e.g.SiN and Al2O3) and deposition of these materials on electrical interconnects placed next to the OLED device is undesirable. In case PECVD or PVD is used to deposit encapsulation layers, shadow masks can be used to prevent deposition on the interconnects. However, shadow masks will not work in combination of ALD as there will be substantial deposition under the mask as ALD is a high step coverage method.

We are developing a mask-less, plasma enhanced Spatial ALD method to do direct patterned deposition, only on the devices and prevent deposition in between. It uses a similar approach to patterned deposition as used in slot-die coating, by combining intermittent coating with stripe coating to deposit rectangular patterns of tunable dimensions. Essential is the use of an atmospheric pressure plasma source that can be switched on and off efficiently to pattern the deposition. The main challenge is to achieve sharp transitions between film and no film, where the target is to reach a transition width of approximately 200 µm, similar to the transition width achieved in e.g. PECVD in combination with shadow masks.

We will explain how we do mask-less patterned deposition and how the transition width can be minimized through a combination of optimizing both the ALD process as well as the spatial ALD injector design. Finally we will show results of mask-less patterned deposition by Spatial ALD on substrate sizes as large as 30 cm x 40 cm and explain how we will scale up to substrate sizes of 1.5 m^2 and beyond.

1:00pm **LI-ALD-WeM1-43 Y_2O_3 Atomic Layer Deposition Process Scale-Up to Very Large Batch Size***, **Lassi Leppilahti**, P. Päivike, M. Saarniheimo, S. Sneck,* Beneq, Finland

Yttrium oxide (Y_2O_3) thin film coatings have shown great potential as fluoride plasma resistant protective coatings on semiconductor process equipment parts. Many of these parts are large with complex designs often containing high-aspect-ratio gas channels making them challenging to coat. Conformal, dense and pinhole free ALD coatings overcome these challenges and enable more stable processes, greater yields, and longer service times between maintenance. Here we report the results from a study on the very large batch scalability of ALD yttrium oxide. 30 mock-up showerhead parts were coated in a Beneq P800 reactor at 250 °C using tris(methylcyclopentadienyl)yttrium ($(MeCp)_3Y$) and water (H_2O) as the precursors. The reaction chamber was loaded with the mock-up showerhead parts slotted in 15 stacked frames. The total surface area of the reaction chamber inner surfaces, frames and substrates was 22.1 m^2 without considering the surface roughness. The film quality was evaluated on silicon pieces cut from blank wafers spread throughout the reaction chamber. Preliminary ellipsometry results showed ±8 % 1σ within-batch non-uniformity. The growth-per-cycle ranged between 2.13 Å/c and 2.54 Å/c. The high growth per cycle is believed to be caused by the strong water adsorption on the yttrium oxide surface resulting in a CVD-like component in the deposition process. A handful of characterisation techniques were used to determine the film composition. ToF–ERDA showed the film was close to stoichiometric Y_2O_3. LA–ICP–MS analysis revealed the film contained little impurities. XRD confirmed the microstructure was cubic yttria. This contribution describes the process scale-up in more detail, discusses the related challenges and summarises the latest results.

1:15pm **LI-ALD-WeM1-46 Low Temperature Thermal Atomic Layer Deposition of Elemental Tellurium Using and a Novel Tellurium Precursor and Nitrogen-Based Coreactants***, A. Upadhyay,* Wayne State University*; K. Woods,* Applied Materials*; M. Saly, T. Knisley,* Applied Materials Inc.*;* ***Charles Winter,*** Wayne State University

Phase change memory (PCM) is made possible by the large difference in resistivity between the amorphous and crystalline forms of certain materials. Heating either form by light pulses or electrically leads to cycling between the amorphous and crystalline states. The most widely studied PCM is $Ge_2Sb_2Te_5$ (GST), because of its non-volatility, scalability, fast conversion between amorphous and crystalline states, and extremely long service life. There is considerable interest in the atomic layer deposition (ALD) growth of GST, because of the thickness control and conformal coverage and also because some properties of GST are improved in thinner films (rate of amorphous to crystalline state interconversion). Previous ALD growth chemistry has relied largely upon silyl elimination reactions between halides or alkoxides and Sb and Te trialkylsilyl compounds. While these ALD routes have provided desired thin films, they target specific stoichiometric compositions such as GeTe, GeSb, Sb_2Te, Sb_2Te_3, and others. There is recent interest in controlling the element compositions in GST beyond the $Ge_2Sb_2Te_5$ composition, to adjust properties such as crystallization temperatures and resistivities. Moreover, many of the currently available Ge, Sb, and Te ALD precursors have low thermal stabilities, which limit their upper deposition limits often to temperatures below 100 °C. This issue is most acute with Te precursors, since the electrochemical potential of Te ion is most positive among the three element ions (E° $Te^{4+} \leftrightarrow Te$ = 0.568 V; E° $Ge^{2+} \leftrightarrow Ge$ = 0.24 V; E° $Sb_2O_3 + 6 H^+ + 6 e^- \leftrightarrow 2 Sb + 3 H_2O$ = 0.152 V). Herein, we will describe the ALD of elemental tellurium (Te) films using novel tellurium precursors and nitrogen sources such as hydrazine. These precursors presumably form Te_3N_4, which is unstable and loses N_2 to afford elemental Te. Properties of these tellurium precursors will be described. A liquid Te precursor with a decomposition temperature of 257 °C was identified from this screening. ALD studies revealed growth temperatures between 75 and 200 °C, although highly crystalline, rough films were obtained at >110 °C. The growth rate was 0.10 Å/cycle at substrate temperatures of 75 to 100 °C. X-ray diffraction showed elemental Te in the hexagonal phase. The composition of the film was evaluated using X-ray photoelectron spectroscopy and showed high purity Te.

1:30pm **LI-ALD-WeM1-49 When Complex Becomes Complicated – Strategies for Succeeding with Arduous Ternary Oxide Processes***, **Henrik Soensteby,*** University of Oslo, Norway **INVITED**

Atomic layer deposition (ALD) has been an invaluable technique in the miniturization of electronic components over the last 15 years. As continued downscaling is pushing silicon technology to its inherent physical limits, the community is looking for new materials, technologies and architectures to inherit the Si-hegemony. With ALD being a mature deposition technique in electronics industry, it is in a unique position to take part in new paradigms within microelectronics. A requirement is that ALD can provide processes for new functional and technologically relevant materials under conditions that are attainable to the microelectronics industry.

Complex oxides come in a wide variety of flavours. High-k dielectricity, ferroelectricity, memristivity and metallicity are believed to be important properties in future electronics and can all be found in different complex oxides, *e.g.* $SrTiO_3$, $BaTiO_3$, $SmNiO_3$ and $LaNiO_3$, respectively. Unfortunately, deposition of high quality films of complex oxides, with a few exceptions, have been limited to physical techniques such as pulsed laser deposition and molecular beam epitaxy.

With recent progress in ALD of complex oxides, however, the ALD toolbox of functional materials is growing fast. Concurrently, this has lead to increased understanding in the growth- and control mechanisms of ternary+ oxides. This includes effects of precursors, temperature, sub-cycle arrangements, co-reactants, substrates *etc.*

In this talk, I will discuss how and why a range of variables affect complex oxide ALD. I will convey some strategies that have allowed us to develop a broad range of complex oxide processes, and try to generalize in a set of tips and tricks for complex process development. Complex does not have to be complicated, but thoughtful process development is a requirement to succeed!

1:50pm **LI-ALD-WeM1-53 Announcement of ALD and ALE Student Awardees, Closing Remarks & Thank Yous***, **Scott Clendenning,*** Intel

Thank you for attending the ALD/ALE 2021 Virtual Meeting! We will see you at ALD/ALE 2022, June 26-29, 2022, Ghent, Belgium.

Live Session
Room Live - Session LI-ALD-WeM2
AM/AF (in-situ metro) Live Session

Moderators: Dr. Alex Martinson, Argonne National Laboratory, Dr. Nathanaelle Schneider, CNRS-IPVF, Dr. Virginia Wheeler, U.S. Naval Research Laboratory

9:30am **LI-ALD-WeM2-1 Welcome, Thank Yous & Instructions***, **Nathanelle Schneider,*** CNRS-IPVF, France

Thank you for attending today's session! We hope you will enjoy the session!

9:35am **LI-ALD-WeM2-2 Surface Modification of TiO_2 Nanoparticles by Ultrathin SiO_2 Films, Cu_2O and Pt Nanoclusters for Enhanced Photocatalytic Activity Using Atomic Layer Deposition in a Fluidized Bed Reactor: A Comparative Study***, **Hao Van Bui,*** Phenikaa University, Viet Nam*; D. Benz, J. van Ommen,* Delft University of Technology, Netherlands **INVITED**

Titanium dioxide (TiO_2) is the most popularly used photocatalyst in many practical applications, such as air purification, water treatment, and hydrogen production due to its excellent photocatalytic properties, high structural and chemical stabilities, low environmental impact, and abundance in nature. However, the rapid recombination of photogenerated electrons and holes is a major limiting factor to achieve high photocatalytic efficiencies. To address this issue, the surface of TiO_2 is usually engineered by coupling with a thin film or nanoclusters of other materials. This is to promote the charge transfer at the interface between the TiO_2 and the deposited materials, which consequently reduces the charge recombination in the TiO_2.

Due to their high catalytic activities, noble metals are most popularly used. In addition to promoting electron transfer, noble metals can also act as co-catalysts, providing further catalytic enhancement. Nevertheless, long exposures to UV-irradiation may cause local photocatalytic oxidation of the metal at the metal/TiO_2 interfaces, which creates new electron-hole recombination centers and consequently decreases the photocatalytic efficiency. In addition, despite their excellent activity, the use of noble metals is not desirable due to their high cost and scarcity, especially for large-scale production. Therefore, the surface modification of TiO_2 by oxides such as CuO, Cu_2O, Fe_2O_3, and SiO_2 has recently been more attractive.

Our presentation will focus on the use of ALD in a fluidized bed reactor operating at atmospheric pressure (APALD-FBR) for the surface modification of TiO_2 nanoparticles. Three different ALD processes are demonstrated: ALD of ultrathin SiO_2 films using $TiCl_4$ and H_2O, ALD of Cu_2O using Cu(I)(hfac)(TMVS) and H_2O, and ALD of Pt using $MeCpPtMe_3$ and O_2. We will show that APALD-FBR not only provides the ability to control the deposition of SiO_2, Cu_2O, and Pt at the sub-nanometer scale but also enables the deposition at temperatures significantly lower than the conventional ALD processes. We will further demonstrate that the photocatalytic activity of TiO_2 depends strongly on the loading of the deposited material (SiO_2, Cu_2O, or Pt) and by controlling the loading, the photocatalytic activity of TiO_2 can be significantly enhanced. A comparison of the photocatalytic activities of TiO_2/SiO_2, TiO_2/Cu_2O, and TiO_2/Pt photocatalysts toward the degradation of various organic dyes will be presented and discussed.

9:55am **LI-ALD-WeM2-6 In-Situ High Temperature XRD of Atomic Layer Deposited Gallia-Ceria Mixed Oxides***, **Fatemeh Gashoul Daresibi,*** University of Tehran, Iran*; M. Heikkilä, M. Ritala,* University of Helsinki, Finland*; A. Khodadadi, Y. Mortazavi,* University of Tehran, Iran

Ceria is well-known for its oxygen storage-release capacity [1]. Catalytic behavior of ceria can be tuned by mixing it with different oxides including those of V [2], Ga [3] and Zr [4]. Although the control on the stoichiometry and close contact of oxides is highly challenging [5], recent studies on atomic layer deposition [6] showed its capability in synthesizing conformal and uniform film with atomically precise control of composition.

Herein, we synthesized $Ga_xCe_yO_z$ with super-cyclic ALD using $Ce(thd)_4$, $Ga(acac)_3$ and O_3. Studies on the growth rate showed surface enhanced and linear growth at low and high number of cycles respectively. The in-situ HT-XRD of pure ceria showed changes of crystal structure at high temperatures starting from 650°C under H_2 and a constant lattice structure under air. The XRD pattern of $Ga_xCe_yO_z$ in oxidizing atmosphere under air did not show any specific peak from RT up to 600°C due to incorporation of Ga in cerium oxide and then characteristic peaks of crystalline ceria appeared at higher temperatures as a sign of segregation and phase separation [7]. In reducing atmosphere, under H_2, the evolution of a weak crystalline structure was monitored which peered to be related to the ceria when the partially reduced gallium oxide started to evaporate and leave the mixed oxide film [8]. The results showed that this surface segregation only happens at temperatures high enough to locally reduce and sublime the gallium species. Ex-situ Raman spectra and atomic force microscopy of the samples calcined at various temperatures also confirmed the crystallization/roughening of the films at high calcination temperatures. Therefore, the ALD-$GaCeO_x$ thin film keeps its amorphous mixed structure stable up to around 600°C suitable for many catalytic reactions.

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10:10am **LI-ALD-WeM2-9 Using Ambient Pressure X-Ray Photoelectron Spectroscopy to Study ALD in real-time***, **Esko Kokkonen,*** Max IV Laboratory, Sweden*; M. Kaipio, H. Nieminen,* University of Helsinki, Finland*; F. Rehman,* Lund University, Sweden*; V. Miikkulainen,* Aalto University, Finland*; M. Putkonen, M. Ritala, S. Huotari,* University of Helsinki, Finland*; J. Schnadt,* Lund University, Sweden*; S. Urpelainen,* University of Oulu, Finland

Ambient pressure X-ray photoelectron spectroscopy (APXPS) is a powerful tool to study surfaces in elevated pressure and temperature conditions. We have recently developed an ambient pressure cell (AP cell) dedicated to ALD research. The cell allows studying the surface of a substrate where ALD reactions take place. Importantly, since the cell makes it possible to conduct XPS measurements at millibar pressure regimes, it is possible to measure the chemical state of the surface in real-time as the ALD precursors react with the surface. The cell is intended for chemical characterization of intermediate products that are short-lived and might not be present on the surface once saturation of the surface has been achieved and therefore are not visible in post-process XPS identification. Experiments such as these have gained noticeable traction within a few years. [1,2]

The system is installed on the SPECIES beamline [3] at the MAX IV Laboratory in Lund, Sweden. SPECIES is a soft X-ray beamline with one beam branch dedicated to APXPS. The beamline offers a wide photon energy range of 30-1500 eV, which enables to study most core-levels using XPS, but also makes it possible to focus on valence band investigations using UPS and lower photon energies and high photon flux. The endstation consists of different equipment for sample characterization and preparation, with the main instrument being an electron analyser capable of high energy and time resolution.

The ALD cell has been designed with realistic gas flow dynamics in mind. The cell can be operated with a maximum pressure of 20 mbar, with the intention of creating a laminar-like flow across the substrate surface that is being investigated using XPS. The outlet (pump) line of the cell is connected to a quadrupole mass spectrometer (QMS) via a leak valve. The QMS allows to simultaneously follow masses of important ligands and synchronize this data acquisition with the XPS data.

Here, we will give a brief overview of the system including its design and operating parameters. Some results from example cases are given which demonstrate the capability of the ALD cell for studying substrates during ALD reactions.

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10:25am **LI-ALD-WeM2-12 Observing the Crystallization of Ultrathin Alumina and Polymorphic Transformations of Gallium Oxide Using *in Situ* Reflection High Energy Electron Diffraction*, Alexandra Howzen,*** *N. Strandwitz,* Lehigh University

The maximum amount of thermal energy available during atomic layer deposition (ALD) is generally determined by the decomposition temperature of the precursors which also sets the maximum temperature for the "ALD window". This maximum temperature limits the structural perfection and extent of crystallization in resulting films for many ALD precursor chemistries. Intermittent annealing during the film growth in between ALD chemical exposures has been explored previously and is shown to increase the density and quality of ALD films[1]. However, the ability to directly monitor structural changes of ALD films is expected to provide new insight regarding film crystallization temperature, surface roughening, and dependence on gas ambient.

In this work, we integrate reflection high energy electron diffraction (RHEED) into a home-built ALD system to monitor structural and morphological transformations during ALD growth and thermally-induced structural transformations. RHEED is a surface sensitive diffraction technique that utilizes high energy (> 10 keV) electrons at a glancing angle, and is most commonly utilized in molecular beam epitaxy and pulsed laser deposition systems. We will use *in situ* RHEED to observe the thermal crystallization of an ultrathin, amorphous alumina film deposited on sapphire. Similarly, we will show the thermally induced structural evolution of an ultrathin (1-20 ALD cycles) Ga_2O_3 film deposited on sapphire with TMGa/O_2 precursors. Ga_2O_3 films display multiple polymorphs (α, β, γ, δ, ε) which can be controlled depending on substrate crystal structure and crystallization temperature. Therefore, this work shows the structural transformations available to ultrathin Ga_2O_3 films deposited by ALD as a function of temperature up to the film's complete desorption. The integration of RHEED with ALD offers a slow-motion picture of the structural transformations that occur during traditional epitaxial growth techniques by decoupling the deposition and crystallization steps with simultaneous monitoring of the surface structure.

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10:50am **LI-ALD-WeM2-17 Novel Functional Metal-Organic Materials by ALD/MLD*, Maarit Karppinen,*** Aalto University, Finland **INVITED**

Atomic layer deposition (ALD) technology is one of the cornerstones of modern microelectronics, where it is exploited in the fabrication of high-quality conformal inorganic thin films. Its counterpart for organic thin films – molecular layer deposition (MLD) – has also been known for long but little exploited. Currently, the hybrid of these techniques – ALD/MLD – is strongly emerging as a state-of-the-art route for designer's metal-organic thin films. In ALD/MLD, a metal-bearing precursor is combined with an organic precursor to deposit metal-organic thin films in which the organic molecules naturally link the metal atoms. Interestingly, some of these processes yield in-situ crystalline films. Another intriguing aspect is that many of the metal-organic materials realized through ALD/MLD are fundamentally new and difficult if not impossible to be obtained through conventional synthesis. In this presentation my intension is to [1-7]: (*i*) briefly introduce the breath of the ALD/MLD processes developed, (*ii*) address the constraints/possibilities for growing in-situ crystalline metal-organic thin films, and (*iii*) highlight some exciting ALD/MLD materials and their application potential e.g. in microbatteries, solar cells and flexible magnets.

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11:10am **LI-ALD-WeM2-21 Ultrathin Hybrid Siloxane-Alumina Dielectric Films by Ring Opening Molecular Layer Deposition of Cyclic Tetrasiloxane*, Kristina Ashurbekova,*** Dagestan State University , Russian Federation*; K. Ashurbekova,* CIC nanoGUNE BRTA, Spain*; I. Saric,* University of Rijeka , Croatia*; M. Gobbi, E. Modin, A. Chuvilin,* CIC nanoGUNE BRTA, Spain*; M. Petravic,* University of Rijeka, Croatia*; I. Abdulagatov,* Dagestan State University, Russian Federation*; M. Knez,* CIC nanoGUNE BRTA, Spain

Siloxane-based materials have gained interest for various important applications such as insulating layers in microelectronics, thin film encapsulation layers, biocompatible coatings, and barriers. The ring-opening polymerization (ROP) of cyclic siloxanes is a way to synthesize such materials using solution-based techniques and is a rare example of an entropically driven polymerization. The vibrational and rotational freedom achievable in the linear siloxane units is much greater than in the cyclic structures. In this work, we introduce cyclic siloxanes as a new class of silicon precursors for ROP- Molecular layer deposition (MLD), uncommon because of the lack of reactive groups, but reactive because of the ring structure of the cyclosiloxane.

MLD is a powerful vapor phase approach for growing thin polymer films with molecular level thickness control. In the present work, hybrid organic-inorganic siloxane-alumina films were grown by applying a ring-opening MLD using sequential surface reactions between 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane (V_4D_4) and trimethylaluminum (TMA). *In-situ* QCM analysis showed a linear mass increase with the number of MLD cycles within a processing temperature window between 120 and 200 °C and revealed a self-limiting surface chemistry between TMA and V_4D_4. A growth per cycle of 1.4 and 1.6 Å and a density of 1.9 and 2.2 g/cm^3 were determined by X-ray reflectivity (XRR) for the V_4D_4/TMA film deposited at 150 and 200 °C, respectively. X-ray photoelectron spectroscopy (XPS), attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), and in-situ QCM were employed to analyze the structural changes, composition of the film and to suggest a realistic V_4D_4/TMA reaction mechanism. High-resolution transmission electron microscopy (HRTEM) showed that the MLD process enables the formation of highly conformal coating of zirconia nanoparticles. The grown siloxane-alumina film, even as thin as 12 nm, showed an extremely low leakage current density (lower than 5.1×10^{-8} A cm^{-2} at ± 2.5 MV cm^{-1}), a dielectric constant (k) of 4.7, and a good thermal stability after one-hour annealing in air at 1100 °C. The pinhole-free nature and conformal growth inherent to the MLD technique allow the formation of high-quality siloxane-alumina thin films withexcellent insulating properties and thermal stability that are promising as ultrathin insulating coatings in field-effect transistors, flash memories, and capacitors in modern electronic systems. [1]

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11:25am **LI-ALD-WeM2-24 Optically Controlled Large-Coercivity Room-Temperature Thin-Film Magnets Through ALD/MLD*, Anish Philip,*** *M. Karppinen,* Aalto University, Finland

Optically controlled magnetic materials could enable magnetic ultra-fast recording at high density. Such dream materials designed from multiple functionalities could open new horizons for many other application fields as well requiring photo-controlled nanoswitchers.[1] Though there are several families of photomagnetic materials known, including the prussian blue analogues,magnetic nanoparticles modified with photochromic molecules and inorganic materials intercalated with photoresponsive molecules, the real challenges of discovering photo-magnets performing at room-temperature and fabricated in thin films using an industrially feasible technology have never been addressed.

Here we address the challenge by taking the advantage of the atomic/molecular layer deposition (ALD/MLD) technique.[2–4]We deposited ε-Fe_2O_3:azobenzoate superlattice structures with sub-nm scale accuracy from $FeCl_3$, H_2O and azobenzene-4,4′-dicarboxylic acid precursors. The ε-Fe_2O_3 phase was chosen due to its unique room-temperature multiferroic properties including an exceptionally high coercive field.Azobenzene is a

well-known photochromic molecule and has been used for integrating into several functional materials as it undergoes reversible isomerization (trans-cis) around the N=N bond upon light irradiation of suitable wavelengths.By combining the RT hard ferrimagnet ε-Fe_2O_3 and the photoresponsive azobenzene,we demonstrate the reversible photo-switching functionality on the coercivity and magnetization values with alternating irradiations of the films with UV and visible light. Interestingly, the azobenzene layers not only add the switching functionality but also enhance the overall magnetic performance of the ε-Fe_2O_3 matrix. For example, the room-temperature coercivity was found to be 2.6 kOe for ε-Fe_2O_3-azobenzoate superlattice structures, while it was 2.0 kOe for a ε-Fe_2O_3 film of the same overall thickness.

A vibrating sample magnetometer (VSM) was used for studying the magnetic properties of the films. The structure, chemical composition and photoresponsive nature of the films were investigated using XRR, GIXRD, SEM, FTIR and UV-Vis studies.

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11:40am **LI-ALD-WeM2-27 Deposition of Thermally Stable Polybenzimidazole (PBI) Thin Films by Molecular Layer Deposition Technique***, **Saba Ghafourisaleh**, M. Leskelä, M. Putkonen, M. Ritala,* University of Helsinki, Finland

We report the deposition of polybenzimidazoles (PBI) thin films with Molecular Layer Deposition (MLD) for the first time. Imidazole derivatives are known to be thermally stable and withstand harsh acidic, basic, and oxidizing environments. MLD process for PBI-like polymers would open up numerous application fields where conformal organic thin films can be used as protective layers for more sensitive materials, like thermally resistant textile fibers, thermal insulation parts of semiconductor devices, high-temperature matrix resins, adhesives, and foams. Previously inorganic ALD materials, like Al_2O_3, have been used for protecting polymers.[1,2]

Isophthalic acid (IPA), 3, 3'-diaminobenzidine (DAB) were used as monomers and TMA was used as a promoting precursor in this process. The monomers were pulsed and purged sequentially and the condensation reactions of the adsorbed monomers on the surface resulted in PBI thin film growth with growth are of 6.0 Å/cycle. PBI films were characterized in detail by FTIR, SEM, TGA/DTA, and AFM.

Sublimation temperatures for the IPA and DAB were 160-165 ^oC and 210-220 ^oC, respectively. The reaction temperature was within a range of 225-300 ^oC. The films were uniform and transparent on a silicon substrate. The thickness non-uniformity along the 5x5 cm^2 substrate was less than 2 %. The films were smooth with a low degree of roughness (500 nm x 500 nm, Rq=0,48 nm for 1µm thick film). Thermogravimetry (TGA) analysis in nitrogen (N_2) and air showed that PBI films were thermally stable.

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11:55am **LI-ALD-WeM2-30 Future of Membrane Separations through Atomic Layer Processing***, **David Bergsman**,* University of Washington **INVITED**

Recent years have seen a surge of interest into improving the scalability of atomic layer processing (ALP) tools, such as work in spatial atomic layer deposition (ALD), molecular layer deposition (MLD), and vapor-phase infiltration (VPI). This improved scalability, along with a continued decrease in the cost of these processes, has allowed these tools to be considered outside the semiconductor industry, such as in solar cells and battery electrodes. These are technologies for which precise control over thickness, structure, and composition is critical to achieve optimum device performance. One technology area that has yet to see commercialization of these tools is in membrane separations. Similar to solar cells and batteries, membranes also rely upon precise materials properties to operate effectively, requiring narrow pore size distributions, non-fouling surface chemistries, and robust rheological properties. As a result, membranes are an excellent candidate for the implementation of atomic layer processing tools in their synthesis.

This presentation will highlight the potential use of atomic layer processing tools for membrane separations, reviewing recent advancements in this area. Generally, these tools can either be used to enhance an already existing material, such as by coating a porous structure or infiltrating a bulk material, or they can be used to create the selective layer itself, through the deposition of a thin selective layer. First, the use of ALD, MLD, and VPI to enhance membrane performance will be highlighted, including work to decorate membrane surfaces, control pore sizes, and infiltrate polymers to impart conductivity or chemical resilience. Then, cases where ALD and MLD have been used to create the active separating layer will be discussed, such as in ALD-based inorganic ion conductors, MLD-based desalination membranes, and hybrid ALD/MLD-based porous layers. Finally, promising future directions and the improvements that will ultimately be necessary for these tools to be used in commercial membrane synthesis will be explored.

12:30pm **LI-ALD-WeM2-37 Molecular Layer Deposition of All-Organic Polyamide Nylon 6,2***, **Marcel Junige**, S. George,* University of Colorado at Boulder

We developed an MLD process for the all-organic polyamide nylon 6,2 using separate, sequential exposures of ethylene diamine and adipoyl chloride. Our hot-wall, viscous-flow vacuum reactor featured a small gas volume, laminar gas flow conditions, and isothermal heating. We utilized *in situ* spectroscopic ellipsometry (iSE) to study MLD nucleation and growth; as well as x-ray reflectometry (XRR), atomic force microscopy (AFM), x-ray photoelectron spectroscopy, Raman spectroscopy, and grazing-incidence small- & wide-angle x-ray scattering to characterize MLD film properties.

In the steady-state growth regime, iSE verified the MLD characteristics: Multiple exposures of neither monomer alone could produce a significant thickness gain; both the half-reactions were self-terminating. The MLD exhibited a linear growth per cycle (GPC) of 3.7 Å at 115ºC. The GPC decreased by approximately 1/3 with every 10ºC increase in temperature.

The refractive index of a ~100 nm nylon 6,2 MLD film was extracted from an iSE multi-time-slice analysis and exhibited uniaxial anisotropy. This anisotropy indicated an orderly alignment of individual polymer chains. Amine hydrogen from one polyamide chain can bridge bond with carbonyl oxygen from another. These intermolecular forces can hold nylon chains together very tightly. XRR measured a mass density of 1.38 $^g/_{cm^3}$, matching the calculated crystal density value. AFM imaged the surface of a ~17 nm nylon 6,2 MLD film: The rms roughness of 4.4 Å was characterized from the topography image; the Young's modulus, averaging 3.6±0.5 GPa, was extracted from force-distance curves in pinpoint mode at every pixel. This verified uniform nanomechanical film properties without pinholes.

We also tested the stability of nylon 6,2 MLD films in various atmospheres at temperatures from 115 to 350ºC. Nylon 6,2 MLD films started to lose thickness in argon around 150ºC. Neither acetone vapor nor molecular oxygen etched nylon 6,2 at 135°C. In contrast, hydrogen peroxide vapor and ozone spontaneously etched nylon 6,2.

In related work, we have demonstrated area selectivity of nylon 6,2 MLD on industrial test features with nucleation and growth on amorphous carbon lines versus inhibition on passivated silica trenches.[1] We utilized secondary electron microscopy to image the test features before and after area-selective MLD. This demonstrated the potential to repair the amorphous carbon hard mask that eroded by reactive ion etching during pattern transfer. The all-organic polymer nylon 6,2 was preferable because no residue was left after ashing of the MLD films.

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12:45pm **LI-ALD-WeM2-40 Vapor Phase Conversion of Pt Nanoparticles Into Pt-Sn Bimetallic Nanoparticles***, **Nithin Poonkottil**, R. Ramachandran,* Ghent University, Belgium*; E. Solano,* ALBA Synchrotron, Spain*; N. Veeraraghavan Srinath, J. Feng, A. Werbrouck, M. Van Daele, M. M. Minjauw, M. Filez, H. Poelman,* Ghent University, Belgium*; A. Coati,* Synchrotron SOLEIL, France*; C. Detavernier, J. Dendooven,* Ghent University, Belgium

Bimetallic nanoparticles (BMNPs) offer interesting size and composition-dependent properties. Pt-Sn BMNPs are important in the field of catalysis, highlighted by their widespread industrial use for propylene production. They are widely accepted as a model system in fundamental studies of structure-performance relationships. ALD has proven successful in preparing catalytic systems with fine control over NP sizes and compositions, but the creation of non-noble metal-containing alloys often requires a high temperature reduction step. We report the vapour phase conversion of Pt NPs into Pt-Sn BMNPs based on the selective decomposition of tetrakis(dimethylamido)tin (TDMASn), a common Sn ALD precursor, on Pt, which induces a solid-state reaction of metallic Sn with Pt to form BMNPs at low temperature.

The decomposition of ALD precursors is often mainly considered a temperature dependent property. However, TDMASn provides an example where the precursor decomposition is also a substrate dependent property. We found that TDMASn selectively decomposes on Pt in a temperature range of 150-300°C, whereas no decomposition was observed on other substrates like SiO_2, Al_2O_3 and TiN (Fig.1a). The decomposition of TDMASn on Pt thin films led to the formation of different Pt-Sn alloys (Fig.1b). The exposure of ALD-grown Pt NPs (Fig.2a) to TDMASn pulses resulted in their conversion to Pt-Sn BMNPs, but the conversion process induced extensive particle ripening, leading to large and non-uniform particle sizes, undesired for catalytic applications (Fig.2c). Interestingly, the conversion process could be improved by using an alternating pulsing sequence of TDMASn and H_2 exposures. The introduction of H_2 substantially aids in retaining the small NP sizes of the original Pt NPs (Fig.2b). In situ mass spectrometry data during this process showed the removal of organic ligands during the H_2 pulse. The Sn uptake was monitored by in situ X-ray fluorescence (XRF), revealing saturation of the Sn incorporation in the Pt NPs as a function of the number of TDMASn-H_2 conversion cycles (Fig.3a). Moreover, the amount of inserted Sn can be controlled via the deposition temperature. PtSn versus Pt_3Sn is accomplished by varying the deposition temperature during this process from 150-250°C (Fig.3b). Finally, we confirmed the compatibility of this method with high surface area supports by the successful conversion of a mesoporous Pt/SiO_2 catalyst.

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This work is funded by the European Union's Horizon 2020 research and innovation program under the Marie Skłodowska-Curie grant agreement No.765378.

1:00pm **LI-ALD-WeM2-43 Atomic Layer Deposition of Zirconium Sulfide***, **Xiangbo Meng**,* University of Arkansas

Zirconium disulfide (ZrS_2) is one of two-dimensional (2D) transition metal dichalcogenides (TMDs), which is promising in many applications, such as lubrication, optoelectronic, catalysis, and energy storage. However, few studies have been devoted to developing ZrS_2. As a unique technique, atomic layer deposition (ALD) has been reported for a variety of sulfide processes in the past decades and recently emerged as a new tool for nanofabrication of 2D TMDs.[1, 2] Using tetrakis(dimethylamido)zirconium(TDMA-Zr) and 4% H_2S as precursors, recently we have developed a novel ALD process to grow ZrS_x. Similar precursors have been used in our previous studies.[3-5] We first investigated the ALD ZrS_x process using an *in situ* quartz crystal microbalance (QCM) and our QCM measurements confirmed repeatable saturation growth of ZrS_x at different temperatures. Our study further revealed that this ALD process enables large-scale growth of nanoscale ZrS_x films uniformly in the temperature range of 75 – 300 ℃ on various substrates. Furthermore, we characterized the ALD ZrS_x films using a suite of tools, including scanning electron microscopy, transmission electron microscopy, synchrotron-based X-ray diffraction, and X-ray photoelectron spectroscopy to clarify their morphology, crystallinity, and composition. We found that the growth of ZrS_x per cycle decreases from 1.17 Å/cycle at 75 ℃ to 0.28 Å/cycle at 300 ℃. In addition, our work revealed that the crystallinity and composition of ZrS_x compounds vary with deposition temperature. This study may pave an avenue to grow large-scale 2D ZrS_2 films, which potentially provide new solutions to some emerging applications.

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1:15pm **LI-ALD-WeM2-46 Vapor Phase Infiltration of Titanium Tetrachloride Into Polyaniline (PANI): Process Kinetics, Electronic Properties and Optical Response***, **Mark Losego**, S. Gregory, Y. Li, K. Malinowski,* Georgia Tech

This talk with discuss our use of vapor phase infiltration (VPI) to alter the optoelectronic properties of conducting polymer poly(aniline) (PAni). VPI is similar to atomic layer deposition (ALD), but instead of cycling viscous flows of co-reactants, VPI doses a single reactant vapor in a static atmosphere followed by a pump-purge cycle. ALD typically provides conformal surface coatings while VPI enables extensive sub-surface diffusion and reactions within organic substrates. In particular to our study, PAni was VPI treated with a single cycle of $TiCl_4$--H_2O, and the resulting hybrid films showed unique optoelectronic properties that have not been previously reported. As VPI hold time increased, PAni films turned from blue to nearly transparent to green. This color transition is because of the formation of polaronic charge carriers concomitant with the formation of TiO_x; the polaronic carriers absorb the red-NIR-MIR spectra (700- 5000 nm) while TiO_{-x} absorb the blue-UV region (450 - 350 nm). This combination of optical absorbances in PAni has not been observed before. Furthermore, these polaronic carriers enabled electrical conductivities as high at 0.2 S/cm. By varying the $TiCl_4$ exposure time and measuring *ex-situ-* optical signatures, an effective diffusion coefficient of *ca.* $1 \cdot 10^{-15}$ cm^2/s was measured. Lastly, XPS measurements elucidated a reaction mechanism for the formation of TiO_{-x} and PAni polarons. Both oxidative doping and acid doping due to the HCl byproduct is observed. By better understanding this reaction mechanism and kinetics, ALD and VPI can be optimized for future organic semiconductor doping processes.

1:30pm **LI-ALD-WeM2-49 Atomic/Molecular Layer Deposition for Batteries Materials***, **Chunmei Ban**,* University of Colorado Boulder **INVITED**

The atomic layer deposition (ALD) technique has proven itself to be the best method to deposit continuous, conformal and pinhole-free films. Ultrathin metal oxides coating via ALD has been applied on battery materials in mitigating the parasitic side reactions between the electrolyte and the electrode surface, which results in the greatly improved performance of lithium-ion electrodes. Based on the similar deposition mechanism, we have developed molecular layer deposition (MLD) to integrate organic groups into the metal oxides matrix, in order to simultaneously address both mechanical strength and surface stability. It is found that the inherent non-passivating behavior of electrode materials in the organic lithium-ion battery electrolyte results in large irreversible capacity loss and gradual electrolyte consumption during operation. Such interaction between electrolyte and electrode becomes more pronounced for intermetallic alloy and lithium-metal anode materials and high-voltage cathode materials. This presentation will discuss the mitigation strategies which are based on atomic/molecular deposition techniques and their impact on electrochemical behavior of battery materials. With the capability to modify the surface and interface through the control of composition, thickness and mechanical properties, MLD would chemically or physically change the surface chemistry and structure of battery materials, while accommodating dramatic volumetric change associated with high-capacity intermetallic anodes. Combining with the results from advanced characterization techniques, this talk will emphasize the unique chemical interaction between the electrolyte and the surface of intermetallic electrodes, and exploit surface modification strategies to dictate the interface chemistry and manipulating the chemi-physical properties of the electrode-electrolyte interphase for efficient electrochemical reactions.

1:50pm **LI-ALD-WeM2-53 Announcement of ALD and ALE Student Awardees, Closing Remarks & Thank Yous***, **Seán Barry**,* Carleton University, Canada

Thank you for attending the ALD/ALE 2021 Virtual Meeting! We will see you at ALD/ALE 2022, June 26-29, 2022, Ghent, Belgium.

Live Session
Room Live - Session LI-ALE-WeM3
Atomic Layer Etching Live Session II

Moderators: Prof. Satoshi Hamaguchi, Osaka University, Japan, Dr. Angelique Raley, TEL Technology Center, America, LLC, USA

9:30am **LI-ALE-WeM3-1 Welcome, Thank Yous, & Instructions**, ***Satoshi Hamaguchi,*** Osaka University, Japan; *A. Raley,* TEL Technology Center, America, LLC

Thank you for attending and we hope you will enjoy the session!

9:35am **LI-ALE-WeM3-2 Precise Atomic Layer Control of 2D MoS_2 by ALE Technique for Device Applications**, ***Geun Young Yeom,*** Sungkyunkwan University, Republic of Korea; *K. Kim, J. Kang,* Sungkyunkwan University, Korea, Korea (Democratic People's Republic of); *K. Kim,* Sungkyunkwan University, Korea, Massachusetts Institute of Technology **INVITED**

One of the two dimensional chalcogenide materials, MoS_2, is widely investigated as potential next generation devices for photodetector, solar cell, biomedical devices, etc. especially due to the change of bandgap energy and the change from indirect bandgap to direct bandgap with the change of MoS_2 layer thickness. Some of the important factors in the fabrication of various MoS_2 devices are the precise control of the layer thickness and the n/p doping on the MoS_2 layer surface. In this study, using atomic layer etching (ALE) method, MoS_2 layer thickness was precisely controlled and the characteristics of the MoS_2 heterojunction devices fabricated by the ALE methods were investigated. Also, using the precise ion bombardment energy used for the anisotropic ALE, the surface sulfur on MoS_2 was preferentially removed and/or replaced with nitrogen, and their material properties and device characteristics were also investigated. This presentation will show some potential applications of ALE techniques for next generation devices using 2D materials including graphene, MoS_2, $MoSe_2$, etc.

9:55am **LI-ALE-WeM3-6 Structural and Compositional Evolution of SiN Surfaces Under Low Energy Ar^+ Bombardment**, ***Erik Cheng,*** *G. Hwang,* University of Texas at Austin; *P. Ventzek, Z. Chen,* Tokyo Electron America

In ALE of many materials, a low energy ion bombardment step is critical for achieving etch. The nature of the nonequilibrium chemistry happening under such conditions, however, has not yet been thoroughly examined. In this talk, we present our recent work utilizing density functional tight binding (DFTBMD) simulations to elucidate the underlying mechanisms governing the substrate-precursor-ion interactions in the ALE of silicon nitride (SiN) and the resulting film structure and composition. We have found that in the absence of adsorbed precursors, surfaces of all conditions (N-rich, Si-rich, amorphous, crystalline) tend to converge towards an amorphous Si-rich surface with many coordination defects. The Si:N ratio at the surface, which starts around 75%, linearly increases to 82% after 20 bombardments on a 15Å × 15Å surface, while the surface defect density grows from 0% to around 30%, with a predicted saturation around 50% based on a power law fit. The formation of this quasi-equilibrium structure can largely be attributed to the sputtering of H and N-containing moieties being strongly favored over the sputtering of Si-containing moieties. In the presence of an adsorbed monolayer, sputtering can be suppressed, but largely shows the same trends. Interestingly, in the presence of a fluorocarbon monolayer, relatively few N-C and Si-F bonds are formed, suggesting that reaction pathways for this process may not be in line with previously thought. Furthermore, the highly damaged surfaces due to ion bombardment have been seen to be far less reactive than previously expected. In this talk, we will also discuss the underlying reasons for these peculiar behaviors.

10:10am **LI-ALE-WeM3-9 Demonstration of Atomic-Layer-Etching of SiO_2 in a small-plasma-volume incorporating 162MHz CCP source and 27MHz substrate bias using CHF_3 and Ar/O_2**, ***Cleo Harvey,*** *B. Ellingboe,* Dublin City University, Ireland

Atomic-scale-processing control of SiO_2 is one of the main requirements to achieve nanoscale device fabrication. Here, we demonstrate a self-limiting Atomic-Layer-Etching process of SiO_2 in a large-area dual-frequency CCP using cyclic CHF_3 and Ar/O_2. The plasma reactor is a modification of an industrial low-volume CCP for 300mm wafer processing. The original upper grounded electrode is replaced with a multi-tile array excited differentially at 162MHz. Ion-energy is controlled via 27MHz power coupled to the electro-static-chuck and wafer. The ALE process involves alternating gases and VHF excitation for cyclic fluorocarbon deposition and etch-back. The unique plasma chemistry and low-energy sheath of high-VHF limits ion-driven surface mixing; this in turn promotes an etch plateau resulting in a broader process window with a fully-self-limiting removal half-cycle. In this study, we present the effect of VHF and LF power coupling on plasma parameters in the dual-excited reactor; namely electron density from hairpin probe, relative radical species density from OES, and ion energy effects inferred from sputter rates. The results provide insight into the operational window and favourable conditions to realise ALE behaviour in our experimental system. Thickness changes are measured by an in-vacuo Phase-Modulated-Spectroscopic-Ellipsometer (PMSE) and further validated in an ex-situ commercial ellipsometer. The atomic composition and chemical bonding structure of the deposited layers and the surface following etch-back are analysed by x-ray photoelectron spectroscopy (XPS). Following fluorocarbon deposition, etch-back thickness changes plateaus after 30 seconds, demonstrating fully-self-limiting removal process, and producing an etch-per-cycle of 0.4-0.5nm/cycle. Optical emission tracking of the CO etch by-product signal exhibits a decay and plateau time consistent with the active-etch-period. Surface composition of the SiO_2 surface after several cycles of ALE by XPS does not show evidence of a carbon-rich (such as C-C bond) residue.

10:25am **LI-ALE-WeM3-12 Vacuum Ultraviolet Enhanced Atomic Layer Etching of Metal Films**, ***Xin Yang,*** *H. Nallan,* University of Texas at Austin; *B. Coffey,* Lam Research; *J. Ekerdt,* University of Texas at Austin

Electroless Cu deposition is widely applied in nanofabrication processes as it can be incorporated into roll-to-roll processing and operated at low temperatures for flexible electronics. Cu patterns can be created using a base or noble metal catalyst (Pd, Ru, etc.) since the electroless deposition only happens where the catalyst is present. These patterns are used in flexible display technologies, such as transparent conductive electrodes. Since Cu nucleates on all catalyst present, fine control over catalyst growth regions is critical. Area selective atomic layer deposition (AS-ALD) is explored to create catalyst patterns. However, a shortcoming that AS-ALD suffers is finite selectivity, which leads to metal nucleation in undesired regions. We present an atomic layer etching (ALE) process to remove undesired metal clusters/islands after AS-ALD growth without significantly affecting the metal film thickness.

Low-temperature, plasma-free ALE of Pd, and Ru is demonstrated. Etching of Pd and Ru is achieved at 50 – 200 °C, with approximate material removal rates of 2.8 and 0.9 Å/cycle, respectively, which is characterized *in situ* using X-ray photoelectron spectroscopy and *ex situ* using X-ray reflectivity. The metal film/islands are co-exposed to vacuum ultraviolet (VUV) light ($115 < \lambda < 400$ nm) and O_2 gas at 1 Torr for 2 – 5 min in the oxidation half-cycle. The amount of metal oxide formed in the near surface region can be controlled by the co-exposure time and substrate temperature. In the etch half-cycles, formic acid vapor is used to remove the metal oxides that formed without etching zero-valent metal. Atomic O is the main species responsible for oxidation from VUV/O_2 co-exposure. Density Functional Theory modeling of atomic O interaction with the metals and diffusion into the metals is discussed. The flux of atomic O is important in the oxidation process to overcome the energy barrier to subsurface O diffusion, which limits the depth of oxidation. ALE of continuous and discontinuous Pd films is presented to illustrate how VUV - ALE can be used to remove undesired metal growth due to differing oxidation behavior between those two films. Specifically, we observe a minimum of 3 min is required to partially oxidize a 20 nm uniformly thick film, while a 2 nm film is fully oxidized after 3 min at same substrate temperature. This variation is likely due to the different exposed surface areas. This could be exploited to remove materials in undesired regions after or during area-selective metal ALD under mild thermal conditions.

Keywords: atomic layer etching, atomic oxygen, vacuum ultraviolet photons, metals

10:50am **LI-ALE-WeM3-17 Plasma ALE for Anisotropic and Isotropic Etching**, ***Erwin Kessels,*** *A. Mackus,* Eindhoven University of Technology, Netherlands **INVITED**

Plasmas provide the unique ability to etch materials through chemical and physical processes that can be tuned by the choice of plasma gases and the level of ion bombardment. For anisotropic etching, most ALE processes rely on a chemically inert Ar plasma in which the energetic ions remove the modified surface layer in a directional manner. Plasmas can also be used for isotropic ALE when the plasma is used to create chemically reactive neutral species (plasma radicals) under conditions in which ion bombardment is negligible. Under such circumstances, the ALE process can benefit from the high and diverse reactivity that can be obtained by plasmas enabling a wider range of etch chemistries than thermal ALE

processes. Moreover, when using plasma-based processes, it is also possible to switch easily between anisotropic and isotropic etching which might be of interest for advanced feature control and other innovative etch processes that can become of interest.

In this presentation, two recent innovations will be discussed, one related to anisotropic ALE and one for isotropic ALE. For anisotropic ALE, very precise ion energy control through the so-called tailored-waveform biasing method will be presented. Although this method was first reported two decades ago, recently dedicated power supplies have become commercially available which is now being used in ALE processes [1]. The key advantage of this method that it leads to very narrow energy distributions for ion energies that can be precisely tuned between 20 and 200 eV such that chemical and physical sputtering thresholds can be probed and such that it is easier to work exactly in the ALE ion windows.For isotropic ALE, results will be presented as achieved by using a F-based plasma for the etching of oxides instead of HF. More in particular, isotropic ALE of Al_2O_3 will be demonstrated using a processes based on SF_6 plasma exposure and $Al(CH_3)_3$ dosing [2]. It will be demonstrated that this process yields higher etch rates and lower processing temperatures than thermal ALE.

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11:10am **LI-ALE-WeM3-21 Atomic Layer Etching of Gallium Nitride (Gan) Using SF_6/Ar Plasmas***, **Lamiae Hamraoui**, T. Tillocher, P. Lefaucheux, R. Dussart,* GREMI CNRS/Université d'Orléans, France*; M. Boufnichel,* STMicroelectronics, France

Due to its excellent electrical properties, Gallium nitride (GaN) is a promising semiconductor for the next generation of high-power devices as for example, the normally-off high electron mobility transistors (HEMTs). Plasma etching of GaN is involved in the fabrication of such components but damages the material and degrades its electric properties. Hence, there is a high interest in the atomic layer etching (ALE) processes, which are expected to provide high precision and damage-free etching.

So far, most of the research activity carried out on GaN ALE, has been performed using chlorine based chemistry for the modification step. The idea is to form $GaCl_3$, which is a quite volatile etch by-product [1], [2]. Fluorinated chemistries for ALE of GaN have also been studied to a lesser extent. For example, some authors have used a CF_4/O_2/Ar plasma mixture for the modification step in order to etch GaN [3]. Another team has reported on XeF_2 reactants in the modification step of a thermal ALE process to create the modified layer at the surface [4].

In this work, an SF_6 plasma is proposed for the modification step of GaN ALE. This process consists of cyclic SF_6 plasma chemisorption step and Ar plasma removal step. SF_6 plasma enables to form a layer of GaF_3. This etch by-product is non-volatile and has a boiling point as high as 1000 °C at atmospheric pressure [5]. The GaF_3 modified layer can be removed during the etching step under the effect of Ar^+ ion bombardment. Since the Ar^+ ion energy is adjusted so that unmodified GaN under-layers are not sputtered, self-limiting etching (SLE) can be achieved whereas the modified layer is depleted.

Tests were performed in an inductively coupled plasma (ICP) reactor. The influence of several parameters such as gas flow rates, modification and removal step times and bias voltage has been investigated. The etch depth and the surface roughness were measured using AFM.

GaN etched depth per cycle (EPC) increases slowly with the SF_6 exposure duration. After 100 cycles, we measured an average EPC as low as 0.1 nm/cycle, which shows that less than a monolayer is etched per cycle in these particular conditions.

This work is supported by the European Union (IPCEI) and Région Centre through the Nano2022 project. The CERTeM 2020 platform has provided most of the equipment.

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11:25am **LI-ALE-WeM3-24 Selective Atomic Layer Etching between GaN and SiN by Using HBr Neutral Beam***, **Takahiro Sawada**, D. Ohori,* Tohoku University, Japan*; K. Sugawara,* Sumitomo Electric Industries, Ltd., Japan*; M. Okada, K. Nakata, K. Inoue,* Sumitomo Electric Industries, Ltd, Japan*; D. Sato,* Showa Denko K.K., Japan*; S. Samukawa,* Tohoku University, Japan

AlGaN/GaN high electron mobility transistors (HEMTs) are promising for both high-power and high-frequency applications because their two-dimensional electron gas (2DEG) has high saturation velocity, high mobility, and high carrier concentration with a high breakdown field. However, in GaN HEMT structures for 5G communications, it has been pointed out that damage during the etching process in the recess gate process is causing the degradation in device performance and reliability. In the recess gate etching process, the SiN insulating film on the cap layer should be etched, but it is necessary to etch only the SiN layer and eliminate the etching of underlaying GaN layer. Namely, an atomic layer etching with defect-free and reasonable SiN/GaN etching selectivity is required. In this study, we investigated higher selective etching between SiN and GaN using HBr neutral beam (NB) and found that it exhibited a more selective reaction compared to Cl_2 NB.

The etching rate of GaN mainly depended on the desorption rate of the etching product ($GaCl_x$ or $GaBr_x$) assisted by the bombardment of NB. As a result, in the case of the HBr neutral beam, the GaN etching rate was drastically decreased at the atomic layer level because the vapor pressure of the etching product, $GaBr_x$, was much lower than that of $GaCl_x$. On the other hand, the dominant etching progression of SiN was mainly caused by neutral beam bombardment energy, and the desorption of the etching products ($SiCl_x$ or $SiBr_x$) was almost the same in both cases because the vapor pressures of the etching product, $SiCl_x$ and $SiBr_x$. Especially, in the case of the HBr neutral beam, the neutral beam energy dependence of the surface reaction layer of SiN was larger than that of Cl_2 NB. As a result, the etching selectivity between SiN and GaN in HBr NB improved to 2.1 at 10 W of bias power, whereas that with Cl_2 NB was saturated at 0.41 at more than 10 W of bias power. We found that the surface atomic layer etching reaction could precisely control the desorption rate of the etching product by optimizing the neutral beam bombardment energy and gas chemistry. The HBr neutral beam process can achieve atomic layer level selective reactions on the SiN/GaN structure.

11:40am **LI-ALE-WeM3-27 Study of Surface Damage Formation in Atomic Layer Etching of Si via Molecular Dynamics Simulation***, **Erin Joy Capdos Tinacba**, M. Isobe, S. Hamaguchi,* Osaka University, Japan

Etching of materials in atomic scale can provide a precise and highly controllable means to form nano-scale structures on a material surface. The atomic scale precision is especially desirable in etching of stacked materials such as those in self-aligned contacts. Such an etching process can be achieved by atomic layer etching (ALE), which has been widely studied to counter the challenges in manufacturing of ever-shrinking electronic devices in the semiconductor industry. A typical plasma enhanced ALE process is divided into two steps [1]. The first is the adsorption step, where a thin layer of the material's top surface is modified by the deposition of highly reactive species. In the case of silicon (Si), a chlorine (Cl) plasma is typically used to supply Cl radicals to the surface, as Cl is known to diffuse less deeply into the bulk material. The second is the desorption step, where the modified Si layer is etched by non-reactive energetic ions (e.g., Ar^+ ions) supplied by another plasma. Ideally, it is expected that no or very low damage is formed on the processed material surface by low-energy ion bombardment during the desorption step. However, there have been few published studies on the surface characterization of Si after ALE etching. In this study, molecular dynamics simulation was employed to examine the ALE of Si with Cl radicals in the adsorption step and Ar^+ ions in the desorption step. Effects of low and high Cl radical and Ar^+ ion doses as well as Ar^+ ion energy (20 to 60 eV) on the etch per cycle (EPC) and surface damage were studied. The simulated EPC, 1.55 Å/nm, with low Cl radical dose (~0.14×10^{16} radicals/cm^2) and 20 eV Ar^+ ion energy is consistent with available experimental data [2].

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12:00pm **LI-ALE-WeM3-31 Patterning High Density STT-MRAM with a Novel Atomic Layer Etch Process**, ***Samantha Tan**, W. Yang, T. Mukherjee, Z. El Otell, Y. Fan, R. Lin, S. Yun, K. Kanarik, T. Lill, Y. Pan, R. Gottscho,* Lam Research Corporation **INVITED**

Spin-Torque transfer magneto resistive random-access memory (SST-MRAM) has the benefits of a comparable integration density of DRAM and performance of SRAM, with its intrinsic characteristic of non-volatility, high endurance, and long retention time. STT-MRAM can directly be coupled with processors while simultaneously used as non-volatile storage, thus plays a variety of on-chip memory role in advanced VLSI technology.[1] However, SST-MRAM stacks are challenging to pattern since the stacks mainly consist of non-volatile ferromagnetic materials such as Co, Fe, Pt. Conventional reactive ion etch usually induces chemical damage to magnetic tunnel junction (MTJ) layers, which limits electrical performance.

Thermal ALE concept has recently been demonstrated to expand the pathway to chemically etch magnetic metals.[2] The process typically consists of two steps, oxidation or halogenation followed by ligand or organic vapor exposure to form volatile byproduct. J. Chang demonstrated a surface modification assisted organic chemical vapor etch for directional and isotropic etch of magnetic and noble metals, also developed a comprehensive framework for selecting viable chemistries.[3] R. Opila demonstrated Co thermal ALE with a sequential exposure to Cl_2 and hexafluoro acetylacetone and its molecular mechanism.[4]

Here, we developed a plasma assisted chemical etch approach for Co that forms volatile etch by-product. Based on the chemical etch mechanism, we developed a novel atomic layer etch process for STT-MRAM patterning. Combining the novel etch chemistry, ALE takes the advantages of process control that minimizes MTJ damage with minimum I/D loading. This breakthrough on the etch process enables tight pitch MRAM patterning not only for embedded MRAM, but also for standalone memory.

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12:20pm **LI-ALE-WeM3-35 Exploring Thermal Ale for Spin-Torque Majority Gate Applications**, ***Jean-Francois de Marneffe**,* imec v.z.w., Belgium*; P. Nguyen,* Air Liquide*; S. Couet, L. Souriau,* imec v.z.w., Belgium*; N. Stafford, P. Venkateswara,* Air Liquide*; S. De Gendt,* imec v.z.w. / KULeuven, Dpt of Chemistry, Belgium*; Y. Canvel,* imec v.z.w, Belgium

The spin-torque majority gate (STMG) [1] device is a competitive option for beyond-CMOS logic computing, enabling high density at low power consumption. In such a system, the information is stored in magnetic domain walls, i.e. interfaces separating regions with different magnetization direction. Based on quantum 'exchange' interactions between electrons, the domain walls propagate, interact, and the majority magnetization direction dominates. The majority gate device itself consists of a cross-shaped free layer that is common to 4 magnetic tunnel junctions (3 inputs, 1 output, all consisting of a so-called reference magnetic layer). The magnetization direction of the 3 'input' free layers is switched using spin transfer torque, by flowing a current through each of the magnetic tunnel junctions. The output state is measured by tunneling magnetoresistance. Amongst multiple manufacturing challenges, the etching of the magnetic tunnel junction is the most difficult, as it requires to etch pillars containing non-volatile metals and land selectively on the MgO tunnel barrier, which is 1nm thick. To reduce damage to the MgO, the development of soft-landing options is essential. In the current paper, the thermal atomic layer etching of CoFeB is studied, by means of a cycling process combining first surface chlorination, followed by reaction with hexafluoroacetylacetone (hfacH) [2]. This soft-landing process demonstrates efficient removal of Co, Fe and B, and good selectivity to the underlying MgO dielectric. The impact of the process on the perpendicular magnetic anisotropy is also studied.

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12:35pm **LI-ALE-WeM3-38 Topographic Selective Deposition (TSD) by Combining Plasma Enhanced Atomic Layer Deposition and Atomic Layer Etching Processes**, ***Moustapha Jaffal**, G. Lefevre, T. Yeghoyan, T. Chevolleau,* LTM, France*; R. Gassilloud, N. Posseme,* CEA-LETI, France*; M. Bonvalot,* LTM, France*; C. Vallee,* University Grenoble-Alpes, France

Topographic selective deposition (TSD) processes are attracting a strong interest in the advanced manufacturing of increasingly complex semiconductor devices [1]. For spacer definition, TSD can be obtained from a conformal deposition process on pitches and three-dimensional (3D) nanostructures using Plasma Enhanced Atomic Layer Deposition (PEALD), followed by a subsequent anisotropic etching process step of top and bottom deposits, in order to keep only vertical coatings on 3D feature sidewalls [2].This TSD route thus eliminates numerous and costly wafer-handling steps during the fabrication process and also avoids detrimental Edge Placement Errors (EPE) due to inherent limitation of photolithography[3;4].

In this work, we investigate a strategy for depositing spacers using an original super-cycle process route, composed of a Ta_2O_5 standard PEALD deposition whereby cycling is intercalated by Atomic Layer Etching (ALE) process steps. The ALE process consists first of a CF_4/H_2 plasma chemical treatment and second of an *in situ* anisotropic low energy Ar^+sputtering step of chemically modified Ta_2O_5 horizontal surfaces. This Two-step ALE process mitigates 3D substrate damages induced by energetic ion bombardment such as amorphization and horizontal surface roughness.

The optimization of both PEALD and ALE process steps has first been carried out on planar native Si substrates. It has then been transferred to 3D structures and led to a TSD on vertical sidewalls, as shown in Figure 1. This talk will outline the optimization strategies that we have developed for TSD and discuss the advantages and shortcomings of such a process. Special attention will be dedicated to cross contamination issues raised by the fluorine-rich ALE step.

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12:50pm **LI-ALE-WeM3-41 Surface Smoothing by Atomic Layer Deposition and Etching**, *S. Gerritsen, **Nicholas Chittock**, V. Vandalon, W. Kessels, A. Mackus,* Eindhoven University of Technology, Netherlands

In striving to produce smaller nanoelectronic devices ever thinner films are needed, which increasingly requires control of film roughness and line edge/width roughness. ALD and ALE processing have separately been observed to reduce the roughness of surfaces.[1,2] In this work, the mechanisms of surface smoothing by ALD and ALE are investigated, and the application of ALD + ALE for surface smoothing is discussed. The increased use of ALD and ALE provides the opportunity to better control the surface roughness while maintaining ultrathin film thicknesses.

Previous studies reporting on ALD/ALE smoothing effects ascribe the smoothing to conformal deposition/etching. In our work finite difference simulations were performed that model ALD/ALE as a uniform front from which the deposition/etching propagates isotropically at every point (similar to Huygens–Fresnel principle in optics). These simulations illustrate enhanced deposition in valleys due to geometrical constrains and the rounding of sharp peaks, together leading to a reduction in small scale roughness.

The smoothing effect described by the uniform front propagation model was validated by AFMmeasurements of Al_2O_3 films prepared by ALD from TMA/O_2 plasma and isotropic ALE from TMA/SF_6 plasma.[3]For ALD excellent agreement was seen, but comparatively faster smoothing was observed for ALE, which reveals that a second mechanism contributes to the smoothing. The enhanced smoothing for ALE is explained by considering that the fluorination of the film depends on the local curvature, corresponding to a higher concentration of fluorine at peaks and a lower concentration in valleys.

An extended model that includes both uniform front propagation and curvature-dependent fluorination showed good agreement between simulation and experimental results. This extended model enabled the evaluation of different strategies for using ALD + ALE to smoothen surfaces. The benefits of combining ALD + ALE to smoothen surfaces will be discussed, showing that significant smoothing can be obtained for relatively thin films.

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1:05pm **LI-ALE-WeM3-44 In Situ Analysis on Atomic Layer Etching of Al_2O_3**, ***Johanna Reif***, *M. Knaut, S. Killge, M. Albert, J. Bartha, T. Mikolajick,* Technische Universität Dresden, Germany

Controlled thin film etching is essential for future semiconductor devices, especially with complex high aspect ratio structures. Atomic layer etching (ALE) is a technique that can remove materials precisely with atomic layer control based on sequential, self-limiting surface reactions. ALE is considered to be one of the most promising techniques for achieving the low process variability at atomic-scale. In this work, the thermal ALE (tALE) process to etch Al_2O_3 using TMA as the metal precursor for ligand exchange and HF as the fluorination reactant was examined. For an in situ and real-time access to the etch process, the process chamber was equipped with a spectroscopic ellipsometer. Spectroscopic ellipsometry (SE) has widely served as a powerful non-invasive method to monitor time-continuous as well as time-discrete atomic scale processes in situ and even in real-time. While the ALE process modifies chemical compositions of the surface through a material removal, SE can observe these changes in the electronic structure of the surface in situ and in real-time. The SE measurements enabled the study of etch characteristics in dependence of process parameters like pulse time, process pressure, and substrate temperature. Additional, the utilized 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 provided unadulterated information about the chemical composition and roughness during the process. The high sensitivity of these measurements allowed investigations of interface reactions even for a single ALE pulse as well as analysis of the initial etch mechanism. Our studies observed linear thickness decrease versus the number of ALE cycles during the tALE process. The etch per cycle (EPC) increased from 0.92 Å/cyc at 50 Pa to 1.31 Å /cyc at 200 Pa. The fluoride thickness was observed to increase with process pressure, resulting in more etching during the ligand-exchange reaction with TMA. We investigated the transition between AlF_3 ALD at lower process temperatures and Al_2O_3 ALE at higher temperatures. The EPC varied from -0.4 Å/cyc at 200 °C to +1.38 Å/cyc at 350 °C. Additional analysis demonstrated the self-limiting behavior of the surface reactions. Furthermore, we examined the initial-stage etch of Al_2O_3 using in vacuo XPS measurements. In our presentation, we will show in detail that the combination of in situ and in vacuo studies leads to a better understanding of the ALE process and the reaction mechanism in the sub monolayer regime during tALE.

1:20pm **LI-ALE-WeM3-47 Announcement of ALE and ALD Student Awardees, Closing Remarks & Thank Yous**, *A. Raley,* TEL Technology Center, America, LLC; *S. Hamaguchi,* Osaka University, Japan; ***Thorsten Lill***, Lam Research Corp.

Thank you for attending the ALD/ALE 2021 Virtual Meeting! We will see you at ALD/ALE 2022, June 26-29, 2022, Ghent, Belgium.

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