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

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

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

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

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

References:

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

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

Detailed reaction mechanism studies help to understand ALD processes and advance the technology through the increased knowledge. As the film growth is dictated by reactions between the precursors on the substrate surface, many ALD processes can be designed around analogous reaction chemistry. One such group of processes is deposition of noble metals by using organometallic precursors together with O_2 as a counter reactant. The reaction pathway for the processes is mainly known, but not all mechanistic details have been confirmed directly in ALD conditions. For example the nature of the dissociated surface oxygen, adsorption of the organometallic precursor, completeness of the reactions and the nucleation of the metallic film require detailed investigation. This work aims to enlighten the mechanisms overall by studying metallic Ru and Pt processes with a set of *in situ* and *in vacuo* techniques.

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

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

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

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

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

2:15pm **ALD+ALE-MoA2-4 Student Award Finalist Talk: Conformality of Atmospheric-Pressure Plasma-Enhanced Spatial Atomic Layer Deposition of SiO--$_2$ and TiO_2***, **Mike van de Poll**,* Eindhoven University of Technology, Netherlands*; H. Jain,* TNO-Holst Centre & Eindhoven University of Technology, The Netherlands*; B. Macco, P. Poodt, E. Kessels,* Eindhoven University of Technology, Netherlands

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

atmospheric-pressure plasma-enhanced spatial ALD (PE-s-ALD) complementing our earlier work on temporal PE-ALD at low pressures [1].

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

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

2:30pm **ALD+ALE-MoA2-5 Student Award Finalist Talk: "Inverted ASD" with High Selectivity: Polymer on SiO_2 vs. Si-H and Polymer on Si-OH vs. SiO_2**,
***Nicholas Carroll**, H. Margavio, G. Parsons,* North Carolina State University

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

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

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

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

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

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

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

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

1. Zhang, Y. et al. Semicond Sci Technol 36, (2021).
2. Chittock, N. J. et al. Appl Phys Lett 117, 162107 (2020).
3. Johnson, N. R., et al. Appl Phys Lett 114, 243103 (2019).

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

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

reactivity, so that the etching of In or Ga by Zn would be the most preferrable, possibly resulting in decrease of In and Ga and increased Zn content in the deposited films. Our results show good correspondence with experimentally observed dependency of the compositions of IGZO on the sequence of the supercycle ALD.

References [1] J. Alloys Compd. 2022, 903, 163876; [2] ACS Appl. Mater. Interfaces 2021, 13 (33), 40134.

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

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

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

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

Acknowledgement

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

In this talk, I will discuss how the chemistry of some selected ALD and tALE processes depends on the nature of the surface. For metal deposition, we show that (001) and (100) surfaces of Co and Ru display rather different chemistry in both the stability of the surface post-H2/NH3 plasma step and the interaction with M(Cp)2 precursors. The role of surface structure is important in promoting particular chemistries. For Ru deposition on TaN,

we show how different TaN terminations with H/NH/NH2 promote different reactivity with Ru(Cp)2 and RuO4 precursors. The impact of amorphous *vs.* crystalline surfaces is exemplified through a comparison of the thermodynamics of fluorination in tALE of high-k dielectrics, where a higher etch rate is observed for the amorphous oxides. The role of hydroxyl groups that are generally present on these oxide surfaces will be discussed. Finally we present a brief analysis of the impact of different Si and SiO2 surface termination on the chemistry of plasma ALD of Co.

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

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

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

In this work, we report ALE of HfO_2 using WF_6 and BCl_3 at 275°C where ALE is performed sequentially within integrated ALD+ALE super-cycles, and the etch reaction is monitored *in-situ* using quartz crystal microbalance (QCM) using various super-cycle recipes. ALD is performed using TDMAHf and H_2O. This process was tested on various surfaces including cobalt with a native oxide (Co) and aluminum oxide (Al_2O_3). Within the ultrathin film regime, extremely close to the substrate, we find that the amount of HfO_2 removed per ALE cycle changes as etching proceeds, and the extent of change depends on the substrate on which HfO_2 is deposited.

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

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

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

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

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

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

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