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.

Author Index

Bold page numbers indicate presenter

— A —
Allen, D.: ALD+ALE-TuM-8, 2
Arellano, N.: ALD+ALE-TuM-4, 1
— B —
Borgharkar, N.: ALD+ALE-TuM-8, 2
— C —
Cavanagh, A.: ALD+ALE-TuM-3, **1**
— D —
Du, J.: ALD+ALE-TuM-8, 2
— G —
George, S.: ALD+ALE-TuM-3, 1
— H —
Huang, M.: ALD+ALE-TuM-8, 2
— K —
Keller, L.: ALD+ALE-TuM-4, 1; ALD+ALE-TuM-7, **2**
Kim, H.: ALD+ALE-TuM-8, **2**
— M —
Margavio, H.: ALD+ALE-TuM-4, **1**
— N —
Nolan, M.: ALD+ALE-TuM-5, **1**
— P —
Parsons, G.: ALD+ALE-TuM-1, **1**; ALD+ALE-TuM-4, 1; ALD+ALE-TuM-7, 2
Pierce, E.: ALD+ALE-TuM-8, 2
— W —
Wang, J.: ALD+ALE-TuM-8, 2
Wojtecki, R.: ALD+ALE-TuM-4, 1
Woo, K.: ALD+ALE-TuM-8, 2