## Atomic Scale Processing Mini-Symposium
## Room 316 - Session AP2+EL+PS+TF-FrM

## Enabling Atomic Scale Processing (ALD/ALE) by leveraging new Precursors and Surface Reactions

**Moderators: Prof. Austin Minnich**, California Institute of Technology, **Dr. Angel Yanguas-Gil**, Argonne National Laboratory

10:30am **AP2+EL+PS+TF-FrM-10 Plasma-Enhanced ALD of $SiO_2$ with an Alternative Precursor: From Mechanistic Insight to Area-Selective Deposition**, ***James Jensen***, *Jay Swarup, James Engstrom,* Cornell University

Silicon dioxide ($SiO_2$) is and has been an extremely important thin film material in microelectronics and related fields.The great majority of approaches to atomic layer deposition (ALD) of $SiO_2$ involve the use of plasma since, for example, the Si-H bond is resistant to reaction with molecules such as $H_2O$ and $O_2$.We have examined the use of an alternative Si precursor, which we refer to as di-isopropylamido trisilylamine [DiPA(TSA)], employing an $O_2$ plasma as the co-reactant. The precursor contains only Si-N and Si-H bonds.We have investigated the process using *in situ* real time quartz crystal microbalance (QCM) techniques in a custom-built hot-wall reactor, which provides detailed insight into the half-reactions, and the presence of nucleation delay.We find that ALD with DiPA(TSA) occurs over a large temperature window, spanning a range of $T$ = 120 – 285°C.The thickness deposited per cycle decreases with increasing temperature, from 4.7 Å-cycle$^{-1}$ at $T$ = 120°C to 2.9 Å-cycle$^{-1}$ at $T$ = 285°C.These rather large rates of growth from ALD reflect the silicon content in the precursor (three atoms per molecule).From QCM a nearly complete loss of the di-isopropylamido ligand is implicated in the precursor half reaction.The deposited thin films have been characterized using *ex situ* X-ray photoelectron spectroscopy (XPS), X-ray reflectivity (XRR), spectroscopic ellipsometry (SE) and atomic force microscopy (AFM).From XPS we find that the thin films are near stoichiometric (O:Si ~ 1.9) over the entire range of temperatures, while the expected impurities (e.g., C, N) are < 1%.From XRR we find that the thin film density increases from 2.24 g-cm$^{-3}$ at $T$ = 120 °C, to 2.38 g-cm$^{-3}$ at $T$ = 285 °C, which can be compared to the values for amorphous silica (2.20), and quartz (2.65).From AFM we find that the thin films are continuous and smooth exhibiting an average roughness of 0.54 nm at $T$ = 120 °C (19 nm thick film), and 0.30 nm at $T$ = 285 °C (13 nm thick film).Finally, we have conducted a preliminary set of studies concerning blocking PE-ALD growth of $SiO_2$ on $Al_2O_3$ using acetylacetone (Hacac) and we find the deposition can be blocked for at least 10 cycles, over the temperature range $T$ = 120-285 °C.

10:45am **AP2+EL+PS+TF-FrM-11 Temperature-Dependent Growth Behavior of Aluminum Oxide Using Dimethylaluminum Isopropoxide and Water**, ***Azeez O. Musa***, University of Missouri-Columbia*; Hemant Kumar, Campbell Sweet,* University of Missouri, Columbia*; Justin R. Walensky,* University of Missouri-Columbia*; Matthias J. Young,* University of Missouri, Columbia

Area-selective atomic layer deposition (AS-ALD) requires precursors with controlled surface reactivity to enable selective film growth on targeted regions while minimizing unwanted nucleation on non-growth surfaces. Dimethylaluminum isopropoxide (DMAI) has emerged as a promising alternative to trimethylaluminum (TMA) for AS-ALD applications due to its reduced reactivity and non-pyrophoric nature. However, experimental mechanistic studies of DMAI/$H_2O$ ALD and the influence of deposition temperature on growth behavior remain limited. In this work, the temperature-dependent growth characteristics of $Al_2O_3$ ALD using DMAI and $H_2O$ were investigated using in situ quartz crystal microbalance (QCM) measurements together with ex situ X-ray photoelectron spectroscopy (XPS), Fourier-transform infrared spectroscopy (FTIR), and spectroscopic ellipsometry. DMAI was synthesized from aluminum isopropoxide and trimethylaluminum in 79% yield and >95% purity, with product formation confirmed by $^1$H NMR spectroscopy. Real-time QCM measurements were used to examine precursor adsorption, ligand removal behavior, saturation conditions, and mass gain per cycle (MGPC) between 100 and 200 °C. $Al_2O_3$ growth at 100 °C exhibited a lower MGPC (~19 ng cm$^{-2}$ cycle$^{-1}$) and less stable saturation behavior compared to films deposited between 150 and 200 °C, where the average MGPC remained approximately constant at ~29 ng cm$^{-2}$ cycle$^{-1}$. Single-cycle QCM analysis further revealed distinct differences in surface reaction behavior between low- and intermediate-temperature growth regimes. These findings provide experimental insight into DMAI/$H_2O$ ALD surface chemistry and establish growth conditions relevant to the development of DMAI-based AS-ALD processes.

11:00am **AP2+EL+PS+TF-FrM-12 Void-free Thermal ALD BaTiO3 Thin Films Prepared by Removing Water Dose after Ba Precursor**, ***Jiayi Chen***, Georgia Institute of Technology, China*; Mark Losego,* Georgia Institute of Technology, USA*; Asif Khan,* Georgia Institute of Technology

This talk will discuss our efforts to develop a robust atomic layer deposition process (ALD) to create ferroelectric $BaTiO_3$ (BTO) thin films using Bis-(1,2,4 triisopropylcyclopentadienyl)-Barium and Titanium Isopropoxide precursors.Ferroelectric materials are potential candidates for future low voltage RAM and NAND memory because of their reversible two polarization states under low external electric field. While the CMOS compatible gate dielectric materials $HfO_2$ and $Hf_{0.5}Zr_{0.5}O_2$ are ferroelectric, they have high coercive fields that make it difficult to lower switching voltages below 1 V. Therefore, perovskite ferroelectric materials, like $BaTiO_3$ are desirable to use for these applications because their coercive voltages can be an order of magnitude lower, approaching 0.1 V.However, these ferroelectric films must be deposited by ALD to match the conformality and small thickness requirements desired for RAM and NAND memory. While reports exist for ALD processes of these materials, most if not all those reports use ALD recipe of "A metal precursor – oxidant – B metal precursor – oxidant". This talk will present our finding that high quality BTO films can still be deposited with recipe in the form of "$H_2O$ – Ba – Ti" or "$H_2O$ – Ba – Ba – Ti". A hypothetical ALD chemistry mechanism is proposed. These reactions can happen at 280 °C, but not 220 °C. Inverting the precursor sequence, such that $H_2O$ – Ti – Ba, does not work. XRD confirms the formation of BTO crystal lattices through these novel recipes. One benefit of these recipes is getting void-free BTO films after annealing, whereas our previous studies show that conventional ALD recipes produce BTO films with voids because of the evaporation of $H_2O$ during annealing. 40 nm BTO film deposited with this dehydration recipe shows high dielectric constant of 72 with low dielectric loss at the magnitude of $10^{-3}$.

11:15am **AP2+EL+PS+TF-FrM-13 Optimizing Molybdenum Pentachloride Delivery for Vapor Deposition Processes**, ***James Maslar***, *Vladimir Khromchenko, Berc Kalanyan,* NIST-Gaithersburg

Molybdenum metal has favorable properties for ultrathin layers compared to metals such as copper and tungsten and, therefore, has attracted much recent interest as a potential material for interconnects and gate metallization. A common method for forming ultrathin metal layers in high volume manufacturing is vapor deposition. For vapor deposition of molybdenum metal layers, molybdenum pentachloride is a common precursor. However, molybdenum pentachloride is a solid and can be difficult to reproducibly deliver from the precursor canister to the deposition surface in a tool, depending on delivery conditions and canister design. Also of concern is the presence of molybdenum oxychloride impurity species in the canister, and whether the oxychlorides are being generated during delivery or are present in the supplied material. The primary goal of this study was to characterize the process space for pulsed delivery of molybdenum pentachloride with respect to overall mass carryover, pulse-to-pulse stability, and impurity evolution. The approach used in this study was to quantify the amount of molybdenum pentachloride and molybdenum oxychlorides in an argon carrier gas as a function of carrier gas flow rate, system pressure, canister temperature, and canister design. Quantification was based on direct absorption measurements in the ultraviolet-visible and infrared spectral regions. The results of this study should facilitate the identification of process conditions that optimize molybdenum pentachloride for different applications.

11:30am **AP2+EL+PS+TF-FrM-14 Atomic Layer Modulation of Ru-Ir Alloy Thin Films for Low-Resistivity Interconnect Applications**, ***Yoonseo Choi***, *Wonjoong Kim, Byungchan Lee, Minhyeok Lee, Han-Bo-Ram Lee,* Incheon National University, Republic of Korea

As semiconductor devices continue to scale down, Ru and Ir have attracted attention as promising candidates to replace Cu interconnects because their short mean free path and low bulk resistivity lead to a low figure-of-merit (FOM). However, ALD-grown single Ru and Ir thin films suffer from increased resistivity at thicknesses comparable to their mean free path due to enhanced electron scattering, particularly surface scattering, and film discontinuity. In this study, a Ru-Ir system was designed and fabricated by atomic layer modulation (ALM) to mitigate the thickness-dependent resistivity. ALM sequentially exposes different precursors to the surface with purge steps between each precursor exposure, followed by co-counter reactant exposure, enabling multicomponent thin films growth within a single atomic-layer cycle. In particular, the ratio of each element is

controlled by the surface reactivity, adsorption behavior, and steric hindrance effects of the precursors, making ALM advantageous for forming compositionally uniform Ru-Ir alloy thin films even at reduced thicknesses. In this work, Ru-Ir alloy thin films were deposited at 250 ℃ by sequentially pulsing tricarbonyl(trimethylenemethane)ruthenium ($Ru(TMM)(CO)_3$) and tricarbonyl (1,2,3-η)-1,2,3-tri(tert-butyl)-cyclopropenyl iridium ($C_{18}H_{27}IrO_3$) as Ru and Ir precursors, respectively, with $O_2$ as the counter reactant. To design the process and understand the composition-control mechanism, density functional theory (DFT) and Monte Carlo (MC) simulations were used to analyze precursor surface reactions and their effects on film composition. In addition, a deep-learning-based framework (IDEAL) was used to explore candidate compositions and crystal structures for Ru-Ir alloy films. X-ray diffraction (XRD) and transmission electron microscopy (TEM) analyses confirmed that ALM-grown Ru-Ir films formed a solid solution without distinct phase separation. The electrical properties varied depending on the alloy composition; while single Ru and Ir films showed resistivity above 40 μΩ·cm at 7 nm, Ir-rich Ru-Ir films exhibited a relatively low resistivity of 37.6 μΩ·cm at 5 nm. The high crystallinity of the Ir-rich Ru-Ir films was also consistent with the IDEAL framework prediction. These results demonstrate that ALM-based Ru-Ir alloy thin films can overcome the thickness-scaling limitations of single-component Ru and Ir thin films and have potential as next-generation interconnect materials for replacing Cu.

11:45am **AP2+EL+PS+TF-FrM-15 Pulsed Thermal Etching of Amorphous $TiO_2$ Thin Films Using $MoCl_5$,** ***Hyuenwoo Yang,*** National Institute for Science and Technology (NIST)*; James Maslar, Berc Kalanyan,* NIST-Gaithersburg

Gas-phase pulsed etching has emerged as a promising approach for advanced thin-film processing, enabling controlled and potentially low-damage material removal with advantages in process integration over conventional continuous etching methods. Despite growing interest in pulsed etching, including atomic layer etching (ALE), the thermal etching chemistry of metal halides—particularly $MoCl_5$—remains largely unexplored for oxide materials. In this work, we investigate the pulsed thermal etching of amorphous $TiO_2$ thin films by $MoCl_5$ in a warm-walled viscous-flow reactor. Thickness changes were monitored in real time by in-situ spectroscopic ellipsometry during repeated $MoCl_5$/Ar cycles, while delivered precursor dose and impurity content were monitored upstream using a non-dispersive UV–vis gas analyzer.

Amorphous $TiO_2$ films on Si/native $SiO_2$ exhibited clear thickness loss under repeated $MoCl_5$ exposure, with etching behavior that depended strongly on substrate temperature, $MoCl_5$ source temperature, and Ar purge duration. Increasing the $MoCl_5$ source temperature increased the measured UV–vis absorbance signal and produced a corresponding increase in $TiO_2$ etch rate, indicating that precursor delivery is a key parameter controlling the etching behavior. A substrate-temperature-dependent process window was also observed: etching was strongly suppressed at 150 ℃ and 350 ℃, while the highest etch rate was observed near 250 ℃. Temperature-switching experiments further showed that the low-temperature suppression was reversible upon heating to 250 ℃, whereas exposure at 350 ℃ led to an etch-inactive state that did not recover after returning to 250 ℃.

To our knowledge, this is the first report of $TiO_2$ etching using pulsed $MoCl_5$ chemistry. This work establishes an initial process window for $MoCl_5$-based thermal oxide etching and identifies precursor dose, substrate temperature, delivery history, and purge duration as important variables governing pulsed $TiO_2$ etching.

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