ALD Fundamentals: Growth and Characterization
Room HB Plant Ballroom - Session AF1-WeM

Plasma Enhanced and Low Temperature ALD

Moderators: Jolien Dendooven, Ghent University, Belgium, **Mikko Ritala**, University of Helsinki

8:00am **AF1-WeM-1 Understanding Temporal Behavior of Adsorption and Desorption in ALD via Multiple Injections of Precursor***, **Yu-Sen Jiang,*** Stanford University*; Miso Kim,* Standford University*; Yukio Cho,* Stanford University*; Stacey Bent,* Standford University

Atomic layer deposition (ALD) is renowned for its self-limiting characteristics, enabling precise atomic-level control and high conformality. During an ALD half-cycle, precursors may adsorb onto the substrate as physisorbed species before reacting with surface ligands to chemisorb. However, even under nominally saturated conditions, full surface coverage may not be achieved due to phenomena such as steric hindrance or retention of excess physisorbed precursors. To address this limitation, multiple precursor injections within a single half-cycle are employed to increase the amount of chemisorbed precursor. The observation that ALD growth differs when performed with discrete injections compared to a single injection suggests that adsorbed precursors undergo dynamic behavior on the timescale of a pulse. The temporal effects of precursor adsorption, rearrangement and desorption have received less attention in ALD, for which a single precursor pulse is typically assumed to be fully saturating.

In this work, ALD of HfO_2 with multiple-pulse sequencing was used to elucidate fundamental ALD mechanisms. A single long pulse of Hf precursor (tetrakis(dimethylamido)hafnium, TDMAH) was divided into several shorter sub-pulses to enable a direct comparison between single and multiple pulses during ALD with water as the counteractant at 200°C. The HfO_2 films grown by multiple pulse injection show a 26 % higher growth per cycle, as well as increased grain size, film density, and crystallinity. The improvement is attributed to a denser surface arrangement enabled by staggered precursor exposure. *In situ* infrared spectroscopy reveals differences in the types of hydroxyl groups consumed by precursors between single and multiple pulse modes. Hydroxyl species that were difficult to react in a single pulse (e. g. hydrogen-bonded OH) became more accessible through the multiple feeding of precursors.

To isolate the contribution from each pulse, the Zr precursor (tetrakis(dimethylamido)zirconium, TDMAZ) was introduced into the TDMAH pulse sequence as a “chemical tag” in HfO_2 ALD for defining the specific pulse. This approach enables direct observation of the fractional growth contribution from individual pulses under different pulse-time and pulse-sequence combinations. The results of X-ray photoelectron spectroscopy and *in situ* ellipsometry measurements between 150°C to 220°C indicate that during short pulses, only ~50% of the total growth occurs during the first pulse, resulting in a more sparsely populated surface that allows additional precursors to react in later pulses. Our results reveal that precursor residence time scales with precursor population, implying a coverage-dependent desorption mechanism. Low precursor loading, especially in the unsaturated regime, facilitates desorption and surface rearrangement, thereby enhancing the benefits from multiple-pulse strategy. Further mechanistic analysis of the single versus multiple pulse ALD schemes will be discussed.

8:15am **AF1-WeM-2 Improved Atomic Layer Deposition of Ultra-Thin HfO_2 Dielectrics on Transition Metal Dichalcogenide Surfaces via Low Impact Plasma Pretreatments***, **Rebecca Dawley,*** University of Michigan*; Sudarat Lee, Wouter Mortelmans, Scott Clendenning,* Intel Corporation*; Ageeth Bol,* University of Michigan

2D transition metal dichalcogenides (TMDs) have shown to be promising candidates as alternative channel materials within scaled transistors in next generation electronics. As transistor dimensions continue to shrink and advanced device architectures evolve, there exists a need for the deposition of high quality, ultra-thin dielectrics onto semiconducting channels, typically via atomic layer deposition (ALD). However, deposition on pristine TMD basal planes is challenging due to the lack of dangling bonds and defect sites typically acting as ALD nucleation sites, thus resulting in nonuniform dielectric coverage.

In this work, we explore the effect of mild (low power, high pressure) H_2S plasma pretreatments to improve HfO_2 ALD on mono and few layer TMDs. First, we evaluate the effect of various plasma exposure duration times on monolayer WSe_2 at 250 °C. Minimal impact to WSe_2 following plasma exposure was confirmed via Raman, X-ray photoelectron, and photoluminescence spectroscopy. These plasma exposures were then applied to WSe_2 prior to ~ 3nm HfO_2 atomic layer deposition resulting in a significant improvement in dielectric nucleation and coverage on WSe_2 basal planes as compared to untreated control samples. To better understand the interplay between the plasma-pretreatment of the WSe_2 surface and the HfO_2 ALD process, we investigated the influence of the precursor (both Hf and O) dose times, number of precursor pulses, purge time, and stop flow pumping schemes on the microstructure of the HfO_2 deposited on pre-treated WSe_2. AFM, backscattered electron imaging, and Auger spectroscopy were utilized to determine an optimal combination of plasma exposure and HfO_2 ALD process parameters to yield uniform dielectrics across TMD basal planes.

After process optimization, we evaluated the minimum possible HfO_2 thickness allowed via our plasma pretreatment strategy while still maintaining fully coalesced films using AFM and cross-section TEM. Electrical measurements will demonstrate the capabilities of our technique in depositing high quality, ultra-thin dielectrics onto TMDs with minimal impact on TMD structural properties. This work will further enable the advancement of TMD based top gate and gate all around transistors with ultrathin dielectrics and addresses the concern of maintaining the integrity of underlying TMD channels during pre-treatments prior to ALD.

8:30am **AF1-WeM-3 Comparing HfO_2 Thin Films Grown by Low-temperature Thermal and Plasma ALD for Neuromorphic Functionality***, Alessandro Cataldo,* CNR-IMM, Italy*; Alan Durnez, Himadri N. Mohanty,* CNRS-C2N, France*; Seyed Ariana Mirshokraee, Sabina Spiga,* CNR-IMM, Italy*; Liza Herrera-Diez,* CNRS-C2N, France*; **Alessio Lamperti,*** CNR-IMM, Italy

The need for integration of materials in the fabrication of devices sensible to thermal budgets, such as in flexible, organic and bio-inspired electronics, requires the development and study of low thermal ALD processes. On this scope several attempts have been performed to tackle this issue from different sides, involving the development of innovative precursors and engineering of growth processes, including the extension of ALD regime down to 80 °C in thermal ALD or employing plasma ALD to deliver the energy required for the chemical reactivity.

In this context, HfO_2 has been, and still is, the subject of many efforts, driven by the need of both innovative scientific challenges and functionalities and the existing markets. Recently, its integration in neuromorphic and magnetoionic devices, shifted the attention from qualifying the material properties in terms of compact, dense, defect-free, crystalline films, to consider the type and degree of defects, the selective incorporation of additional elements, typically C, N and OH, in amorphous films. Thus, the need to redefine low temperature ALD processes targeting HfO_2 with such specifications.

Within this framework, here, we compare three processes where thermal or plasma ALD is considered, employing two different equipment. In details, we consider TEMAHf and TDMAH as Hf precursors, H_2O as oxidant in the thermal ALD processes or Oxygen from O_2 in 300 W plasma ALD process, with temperature in the 80 – 100 °C range. We target four HfO_2 thickness, 3, 5, 10 and 20 nm, grown on SiO_2/Si substrate, to have the minimal set for accurately verify the ALD window regime and compare any change in the growth per cycle.

Grown HfO_2 layers are characterized from XRR, XPS and ToF-SIMS to evaluate any change in the electron density, elemental chemistry and stoichiometry. We observe, depending on the growth process, a stoichiometry below the nominal O:Hf=2:1 ratio in all cases, the lowest value in HfO_2 films grown using plasma ALD, with a slight evolution of the stoichiometry with the film thickness. Further, we observe from XPS a significant amount of OH groups depending on the ALD process, in-line with the electron density value from XRR. We explain such changes in terms of purging time and engineering of the oxidant sub-cycle within each ALD cycle, and considering the interplay between oxidation and hydroxilation phenomena.

Further, we integrate HfO_2 films in simple MIM capacitors to extract their dielectric constant (k) and voltage breakdown (V_{BD}). k value results around 17 in HfO_2 films from thermal ALD lowering to k = 12 in HfO_2 from plasma ALD, while V_{BD} varies in the range 3.0-5.5 MV/cm. We tentatively explain such changes in terms of defectivity and ionic species inside the grown HfO_2 films.

Finally, we briefly report on how the so-grown HfO_2 films enable, or not, magnetoionic functionality, depending on the ALD process employed.

Financial support from EIC METASPIN project, grant n. 101098651.

8:45am **AF1-WeM-4 Germanium Oxide with Tunable Composition Using Low-Temperature PEALD*, Florian Preischel,*** Leibniz Institute for Solid State and Materials Research, Germany*; Karl Rönnby, Michael Nolan,* Tyndall National Institute, University College Cork, Ireland*; Harish Parala, Anjana Devi,* Leibniz Institute for Solid State and Materials Research, Germany

Germanium dioxide (GeO_2) is of particular interest in advanced microelectronics and is regarded as an ultrawide bandgap (UWBG) material for next-generation CMOS applications. With exceptional carrier mobility, it shows promise for high-frequency and high-power electronics,[1,2] while its optical properties make it appealing for, e.g., anti-reflection coatings.[3] Furthermore, two-dimensional (2D) GeO_2 has an inherently porous structure with molecular-sized holes and is thus of interest as a material for selective gas-separation membranes.[4,5]

To transition these applications from research to industrial applications, it is necessary to develop scalable processes that enable the deposition of high-quality, defect-free GeO_2 films. Owing to its self-limiting nature, ALD emerges as the most promising solution, offering precise control over thickness and morphology. Yet, ALD strongly relies on the underlying chemistry, and especially the development of low-temperature processes is currently restricted by the lack of suitable Ge precursors.

To address this challenge, we introduce tetrakis-(3-dimethylamino)propyl germanium(IV) [Ge(DMP)$_4$], designed to be highly thermally stable, volatile (see TGA in **Figure 1c**), and reactive, to facilitate low-temperature ALD processing of GeO_2. Using this new liquid, non-pyrophoric, and monomeric precursor (as confirmed by single-crystal XRD and DFT structure analysis in **Figure 1a,b**), we developed a PEALD process for GeO_2 using O_2 plasma as the co-reactant. The process operates across a broad temperature range from 40 °C to 240 °C (**Figure 2a**) with a linear GPC of 0.24 Å at 150 °C. By utilizing different plasma pulse durations (t_{plasma}), the composition of the films can be adjusted: with t_{plasma} = 500 ms, the thin films consist of GeO_2, GeO, and Ge, with a higher degree of sub-stoichiometric GeO_x species at higher deposition temperatures, whereas stochiometric GeO_2 is obtained with t_{plasma} = 50 ms (**Figure 2b, c**). Initial characterization revealed that the composition directly influences the optical behavior of GeO_x thin films, as seen in the UV/Vis spectra of GeO_x thin films deposited using different plasma durations and deposition temperatures (**Figure 3a**). Further, transmission electron spectroscopy revealed closed and uniform thin films with an amorphous structure (**Figure 3b**). Thereby, the rapid nucleation behavior of the process allowed the deposition of a thin film using only eight PEALD cycles. This enabled down-scaling to a film thickness of ≤1 nm (**Figure 3c**), approaching the theoretical thickness required for the bilayer structure and providing a strong foundation to explore the scalable growth and utilization of bilayer GeO_2.

By identifying [Ge(DMP)$_4$] as a new and promising Ge precursor, PEALD processing of GeO_2 and GeO_x becomes feasible at near-room-temperature conditions, advancing the use of GeO_2 and GeO_x thin films for new applications based on their unique properties.

9:00am **AF1-WeM-5 Low Temperature Thermal Atomic Layer Deposition of Bismuth Oxide Thin Films Using a Novel Precursor*, Taylor Currie,*** *Patrick Price, Ronald Goeke, Joseph Klesko,* Sandia National Laboratories

Binary, ternary, and multinary bismuth-containing oxide thin films have been synthesized by chemical vapor deposition and atomic layer deposition (ALD), and utilized in optical, ferroelectric, sensing, and catalytic applications. Binary bismuth oxide (Bi_2O_3) exists in several crystalline phases; however, deposition of a targeted single phase, as well as stoichiometric Bi_2O_3, by ALD remains challenging.

A recent study deposited Bi-rich α-Bi_2O_3 on Si(100) substrates by ALD using triphenylbismuth ($BiPh_3$) and ozone (O_3) as precursor and co-reactant, respectively, within an ALD window of 250-300 °C. Alternative substrates or annealing at temperatures between 700 - 800 °C was required to access additional phases (i.e., β and γ) and stoichiometric composition.

Herein, we report a thermal ALD process for Bi_2O_3 using methyldiphenylbismuth ($MePh_2Bi$) and O_3 as novel precursor and co-reactant, respectively. Saturation was achieved with a $MePh_2Bi$ precursor delivery temperature as low as 90 °C, and a growth per cycle of ~ 0.6 Å/cycle within the range of 100 - 170 °C. $MePh_2Bi$, a liquid, methyl-substituted, and thermally stable precursor exhibits higher volatility than its solid $BiPh_3$ analogue, enabling deposition on temperature-sensitive substrates. Characterization by x-ray photoelectron spectroscopy, atomic force microscopy, and grazing incidence x-ray diffraction of the as-deposited films is presented.

9:15am **AF1-WeM-6 Effect of Initial Surface Silanol Density and Aminosilane Structure on O2 Plasma-Assisted ALD of SiO_2*, Andrew Kaye,*** Colorado School of Mines*; Bhushan Zopé,* Intermolecular, Inc.*; Xinjian Lei, Agnes Derecskei, Ronald Pearlstein, Haripin Haripin Chandra,* EMD Electronics*; Sumit Agarwal,* Colorado School of Mines

SiO_2 is a commonly used dielectric material in semiconductor manufacturing, and aminosilanes are typically used as the Si precursor during radical-assisted atomic layer deposition (ALD) of SiO_2. This work explores the role of the initial surface Si−OH density, the substrate temperature, and the structure of the aminosilane precursor on the growth per cycle (GPC) for ALD on plasma-deposited SiO_2 substrates. Specifically, we studied O_2-plasma-assisted ALD of SiO_2 using two aminosilanes, di-*sec*-butylaminosilane (DSBAS) and dimethylamino trimethylsilane (DMATMS). The surface reactions during ALD were monitored using *in situ* attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy, and the GPC was monitored using *in situ* four-wavelength ellipsometry. On an SiO_2 surface with a high initial Si−OH group density, *in situ* ATR-FTIR spectroscopy shows that ~30% more Si−OH groups are consumed by DMATMS than DSBAS because DSBAS contains a bulkier amino leaving group than DMATMS. *In situ* ellipsometry shows that at an ALD temperature of 100 °C, the GPC using DSBAS and DMATMS are ~1.8 and ~1.2 Å, respectively. The higher GPC for DSBAS shows that the initial aminosilane coverage does not influence the GPC. We speculate that during the O_2 plasma step, O radicals can easily insert into Si−H bonds in adsorbed DSBAS. However, for adsorbed DMATMS, surface $Si-(CH_3)_3$ groups must be combusted, and then converted to Si−OH groups from species generated in the O_2 plasma.

On an SiO_2 surface with a low initial Si−OH group density, approximately the same number of Si−OH groups react with DMATMS and DSBAS. Therefore, we conclude that once the initial surface Si−OH density is sufficiently low, steric effects do not play a role in initial aminosilane adsorption on SiO_2. For both DMATMS and DSBAS, at a constant ALD temperature, the initial SiO_2 surface Si−OH group density has no effect on the GPC of SiO_2 ALD. *In situ* ellipsometry shows that on an SiO_2 surface with a low initial Si−OH group density, no nucleation delay is observed compared to a film with a high initial Si−OH group density. This implies that more Si−OH groups are produced during the first few O_2-plasma half-cycles compared to the initial density of adsorbed aminosilanes on the surface, allowing steady-state ALD to be reached within 5 ALD cycles. As ALD temperature for DSBAS increases, the GPC decreases. This is due to the thermal instability of reactive surface groups such as Si−OH and Si−H, and the areal density of these sites decreases with increasing temperature.

9:30am **AF1-WeM-7 Limits of Plasma Oxidation in Cr_2O_3 Ald: Over-Oxidation, Etching, and Defect Control*, Soumik Das,*** imec USA*; Huiyun Yang,* University of Michigan, Ann Arbor*; Sean McMitchell,* IMEC Belgium*; Becky (R. L.) Peterson,* University of Michigan, Ann Arbor

Plasma-enhanced atomic layer deposition (PE-ALD) introduces highly reactive oxidation pathways that can fundamentally alter growth mechanisms in multivalent oxides. In p-type Cr_2O_3, plasma exposure does not act as a single monotonic oxidant but instead drives two competing processes: stabilization of Cr^{3+} through efficient ligand removal, and over-oxidation to volatile Cr^{6+} species that induce net etching. In this work, we investigate oxygen plasma-based ALD of Cr_2O_3 using $Cr(acac)_3$, with ozone ALD used only to establish a phase-stable reference growth window. At 250 °C, aggressive plasma dosage conditions suppress net growth, consistent with an etch-dominated regime associated with $Cr^{3+} \rightarrow Cr^{6+}$ conversion and CrO_3 volatilization. Reducing plasma delivery partially restores growth but yields rough, non-uniform films, indicating a transition toward an oxidation-limited regime rather than a conventional ALD window. Atomic force microscopy reveals pronounced surface roughening and poor film uniformity. These results identify stabilization of the Cr^{3+} oxidation state as the central challenge for PE-ALD of Cr_2O_3 and define critical process limits for plasma oxidation in p-type oxide ALD targeting low-temperature electronics.

9:45am **AF1-WeM-8 Composition-Tunable Molybdenum Carbonitride Thin Films Prepared by Plasma-Enhanced Atomic Layer Deposition (PEALD) for Diffusion Barriers in Cu and Ru Interconnects*, Younjae Shin,*** *Chaehyun Park, Minjeong Kweon, Sang Bok Kim, Soo-Hyun Kim,* Ulsan National Institute of Science and Technology (UNIST), Republic of Korea

Mo-based materials (MoC_x, MoN_x, MoC_xN_y) exhibit high thermal and chemical stability as well as extremely low electrical resistivity. [1] Owing to these superior properties, Mo-based thin films are considered as promising diffusion barrier materials for advanced Cu and Ru interconnects. [2] In

MoC_xN_y, C and/or N occupy interstitial sites within the crystal structure, enabling tunable properties. To enable their integration into advanced semiconductor interconnects, MoC_xN_y thin films were deposited by PEALD using a N-free Mo precursor with an H_2+N_2 mixture plasma reactant. By adjusting the H_2:N_2 ratio, the composition of C and N in the MoC_xN_y thin films was systematically controlled. Notably, N incorporation played a decisive role in increasing the growth rate from an extremely low value of 0.3 Å/cycle under pure H_2 plasma to ~1.5 Å/cycle with the introduction of a small amount of N_2, indicating that N_2 promotes surface reactions during MoC_xN_y growth. Under an H_2-rich plasma condition (H_2:N_2 = 8:1), typical ALD behavior was observed, including self-limiting growth with respect to both precursor and reactant pulse times. A stable ALD window was also identified at 225-250 ℃, within which a saturated growth rate of ~1.5 Å/cycle and linear thickness evolution with the number of cycles were achieved. Moreover, both the growth rate (1.5-1.9 Å/cycle) and electrical resistivity (590-1490 μΩ·cm) were effectively tuned by varying the H_2:N_2 ratio from 8:1 to 1:8. Structural and compositional analyses using XRD and XPS confirmed the formation of conductive MoC_xN_y thin films with controlled C and N incorporation. Electrical characterization also revealed a strong correlation between film composition and resistivity. Finally, the PEALD-MoC_xN_y thin films were applied as diffusion barrier for Cu and Ru interconnects as well as gate electrode and the results will be presented at the conference.

References

[1] Kang, W. et al. *Journal of Vacuum Science & Technology a Vacuum Surfaces and Films* (2023): *41* (6).

[2] Tripathi, C. C et al. *Applied Surface Science* (2008): *255* (6), 3518–3522.

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