Area Selective ALD
Room Tampa Bay Salons 5-9 - Session AS-TuP
Area Selective ALD Poster Session

AS-TuP-1 Modifying Polymer Inhibitors for Enhanced Selectivity in Area-Selective ALD of Al_2O_3 on Silicon, ***Amnon Rothman***, *Renana Didi,* Ben Gurion University Be'er Sheva, Israel

Area-selective atomic layer deposition (AS-ALD) via area-deactivation using polymer inhibitors has emerged as a promising approach for achieving directional thin film growth without photolithography. While polystyrene (PS) has demonstrated effectiveness as a blocking agent, optimizing its chemical properties remains an underexplored avenue to enhance selectivity, particularly for ultra-thin film applications. This work investigates the impact of polymer structure modification on AS-ALD selectivity, specifically examining the use of fluorine-terminated polystyrene (PS-F) as an inhibitor for selective Al_2O_3 deposition on silicon substrates with native oxide.

The hypothesis underlying this study is that fluorine functionalization of polystyrene will provide superior blocking characteristics compared to unmodified polystyrene, enabling enhanced selectivity at reduced polymer film thicknesses. Both pristine polystyrene and fluoro-polystyrene were deposited onto silicon substrates via spin-coating, yielding distinct thickness profiles that were characterized through spectroscopic ellipsometry.

Subsequent to polymer deposition, selective Al_2O_3 ALD was performed using trimethylaluminum (TMA) and water as precursors. The selectivity was evaluated using complementary *ex-situ* characterization techniques: ellipsometry for film thickness measurement on both inhibitor-covered and unprotected regions, and X-ray photoelectron spectroscopy (XPS) for depth profiling and chemical composition analysis to confirm selective deposition and polymer decomposition behavior.

Preliminary aspects of this investigation also explore selective growth on patterned architectures, including potential applications on metallic (copper) surfaces, to assess the generalizability of the polymer-inhibitor approach across diverse substrate compositions. This work aims to establish structure-function relationships between polymer inhibitor design and AS-ALD selectivity, providing guidelines for rational optimization of blocking agents in selective film synthesis.

AS-TuP-2 Probing the Effects of Reaction Byproducts on Atomic Layer Deposition Selectivity, *Jessica Jones, Cong Liu,* ***Alex Martinson,*** Argonne National Laboratory

Reaction byproducts produced during ALD result in unintentional and variable exposure to small molecules, which may alter the site-specific mechanistic pathways for ALD nucleation. We observe that the wide variability in the nucleation density of ALD Al_2O_3 (with dimethylaluminum isopropoxide and water) on oxidized TiO_2(110) single crystals is reduced by intentional pretreatment with one of the reaction byproducts - isopropyl alcohol (IPA). The first cycle of ALD growth is observed to be an early and strong indicator of the ALD nucleation density, substantiating previously reported nucleation models that rely upon this largely untested assumption. Rapid and nondestructive small molecule pretreatments, including IPA and water, are also observed to be a probe of surface defects, including TiO_2(110) oxygen vacancies, that are correlated with site-selective ALD nucleation. The nonidealities associated with reaction byproduct production during ALD inspire novel surface pretreatment methods that improve reproducibility and may serve to more efficiently probe defects/minority sites surfaces. A detailed mechanistic understanding and control of site-selective ALD processes require consideration of reactivity for both chemical precursors and reaction byproducts.

AS-TuP-3 Inhibitor Selection for Area-Selective SiO Deposition: Limited Growth on SiO Surfaces and Unrestricted Growth on SiN Surfaces through Theoretical and Experimental Studies, ***Tomoya Nagahashi,*** *Kimihiko Nakatani, Takayuki Waseda, Shoma Miyata, Keitaro Hamada, Nozomu Takano, Hajime Karasawa, Ryota Horiike, Yoshitomo Hashimoto, Yoshiro Hirose,* KOKUSAI ELECTRIC CORPORATION, Japan

Silicon oxide (SiO) is a crucial insulator material for semiconductor devices, and area-selective deposition of SiO thin film on silicon nitride (SiN) surfaces, while avoiding deposition on SiO surfaces, is essential for further device scaling in logic, DRAM, and NAND applications. Area-selective deposition can be realized using inhibitors that adsorb on surfaces where deposition is undesired. Hydroxyl groups (–OH) on SiO surfaces serve as chemisorption sites for these inhibitors. In this study, we selected potential inhibitors from various molecules, including aminosilanes and halogenated silanes, through first-principles calculations to achieve higher selectivity, followed by experimental evaluation of the selected inhibitors.

Our theoretical approach focused on three key factors: chemisorption reactivity, by-product effects, and inhibitor size. For chemisorption reactivity, lower activation energy (Ea) and negative Gibbs free energy of formation (ΔG) for inhibitor adsorption onto –OH sites contribute to increased reactivity, leading to higher inhibitor coverage. The inhibitor chemisorption generates by-products, and their physisorption competes with inhibitor chemisorption, reducing inhibitor coverage; thus, preventing by-product physisorption is critical. Regarding inhibitor size, smaller molecules enable higher surface density on SiO surfaces, potentially enhancing inhibitor performance.

ΔG calculations indicated that by-product physisorption does not occur for any candidate inhibitors. We identified three highly reactive aminosilanes with the structure $(R_A)_3Si–N(R_B)_2$, where R_A is identical and R_B varies, influencing size. To assess the influence of molecular size on selectivity, we chose the largest and smallest inhibitors from these aminosilanes, AS_L and AS_S, for experimental evaluation. Chemisorption of AS_L and AS_S on SiO and SiN surfaces was analyzed using static secondary-ion mass spectrometry (static-SIMS). The static-SIMS analysis detected signals corresponding to the chemisorbed inhibitor structure $–Si(R_A)_3$ after gas exposure, with AS_S exhibiting greater coverage on SiO surfaces compared to AS_L. Both inhibitors exhibited preferential adsorption on SiO over SiN, improving selective deposition. Furthermore, SiO film deposition via atomic layer deposition (ALD) using AS_L as an inhibitor demonstrated significantly reduced growth on SiO surface compared to SiN surface, achieving far greater selectivity than without inhibitors. We anticipate even higher selectivity by employing AS_S and optimizing process conditions. Our combined theoretical and experimental findings pave the way for advanced area-selective deposition and continued device scaling.

AS-TuP-4 Inverse-Gradient Atomic Layer Deposition in High-Aspect-Ratio Structures Using Physical Interaction of a Removable Small Molecule Inhibitor, ***Jiwoo Oh,*** *Woohyuk Kim, Woo-Hee Kim,* Hanyang University, Republic of Korea

We report a topographically selective atomic layer deposition (ALD) strategy based on depth-dependent growth suppression that enables inverse-gradient growth of HfO_2 thin films in high-aspect-ratio (HAR) structures, in which the step coverage progressively increases from the top toward the bottom of the feature. This growth behavior is realized through an ABC-type supercycle ALD scheme incorporating a vapor-dosed surface protector (SP) that preferentially adsorbs on the more accessible top surfaces and upper sidewalls, thereby selectively suppressing film growth in these regions while enabling relatively enhanced deposition in the lower portions of HAR structures. X-ray photoelectron spectroscopy (XPS) analysis confirms the absence of residual carbon- or nitrogen-related impurities, indicating that the SP does not perturb the intrinsic film chemistry. The resulting HfO_2 films exhibit film density and electrical performance comparable to those of reference ALD films, including dielectric constant, leakage current density, and breakdown strength. Cross-sectional transmission electron microscopy (TEM) analysis further reveals a monotonic increase in film thickness along the trench depth, directly demonstrating effective inverse-gradient growth behavior. Overall, this strategy provides a practical route for conformality control in HAR structures under high-temperature ALD conditions, offering a viable process approach for advanced three-dimensional memory device fabrication.

AS-TuP-5 Perfluoroalkylpolyether Thin Layer–Induced Inhibition of Al_2O_3 Atomic Layer Deposition with a Trimethylaluminum Precursor, *Hiroaki Iwamoto,* ***Yuki Shibutani,*** AGC Inc., Japan

Area-selective atomic layer deposition (AS-ALD) is a promising approach for next-generation semiconductor device fabrication because it can reduce or eliminate conventional steps such as photolithography and etching when forming complex patterns.[1] To realize this, many studies have focused on enhancing selectivity through surface pretreatments or by modifying ALD processes, for example by introducing deposition/etch cycles.[2] One effective strategy is the use of inhibitor molecules that passivate non-growth regions toward ALD precursors and reactants. However, the size and chemical reactivity of the ALD precursors strongly affect the inhibitory performance of these molecules. As a result, highly selective AS-ALD has often relied on bulky, less reactive precursors, which typically exhibit low growth per cycle (GPC).[3] Although surface treatments by fluorinated molecules are known to reduce surface energy and suppress physisorption of various species, perfluoroalkyl-functionalized surfaces have shown only limited inhibition capability in Al_2O_3 ALD when trimethylaluminum (TMA)—a very small and highly reactive precursor—is used.[4]

In this study, we investigate a perfluoroalkylpolyether (PFPE)-substituted trialkoxysilane (inhibitor **1**) as an inhibitor that enables efficient suppression of Al_2O_3 growth in TMA-based ALD. PFPE possesses a highly flexible fluorinated backbone; unlike perfluoroalkanes, the ether oxygens reduce steric congestion and facilitate molecular mobility. The inhibitor monolayer was formed by coating the compound onto UV/O_3-treated Si substrates, followed by thermal treatment. Al_2O_3 ALD was then performed using TMA and H_2O at a substrate temperature of 200 °C, with a GPC of 0.7 Å. Inhibition performance was quantified by X-ray photoelectron spectroscopy (XPS), using the Al/(Al+Si) atomic ratio after ALD as an indicator of Al_2O_3 film growth. Inhibitor **1** (Mw = >5000 g/mol) maintained strong inhibition for at least 50 ALD cycles. For comparison, a short perfluoroalkyl-substituted trialkoxysilane (inhibitor **2**) was examined under the same conditions; its monolayer lost inhibitory effectiveness after approximately 20 ALD cycles. Water contact angle (WCA) measurements showed that inhibitor **1** produced more hydrophobic surfaces than inhibitor **2** (inhibitor **1**: 112.3°, inhibitor **2**: 107.2°). These results indicate that both molecular flexibility and high surface hydrophobicity are key molecular design parameters for inhibitors in AS-ALD processes employing highly reactive precursors such as TMA. Detailed surface characterization data and implications for future inhibitor design in AS-ALD will be discussed.

AS-TuP-6 Area-Selective Growth of HfO_2 Thin Film through a Cyclic Plasma-Enhanced Atomic Layer Process, ***Jun Seo Hwang***, *So Won Kim, Sung Hyun Lim, Hee Chul Lee Lee,* Tech University of Korea

Area-Selective Deposition (ASD) enables the formation of highly precise and uniform patterns through a bottom-up approach and has attracted significant attention as a technology capable of mitigating Edge Placement Error (EPE) issues in 3D device fabrication [1]. Recently, inhibitor-free ASD has been reported using thermal ALD after hydrogen or halogen treatments on amorphous carbon (a-C) surfaces [2]; however, these methods have limitations for in-situ integration with subsequent plasma-enhanced atomic layer etching (PE-ALE) processes. Therefore, in this study, inherent ASD was implemented by applying a PE-ALD/ALE supercycle without additional surface treatment, leveraging the intrinsic non-growth characteristics of a-C.

In this work, Si, SiO_2, and Si_3N_4 were used as growth surfaces (GS), while a-C was used as the non-growth surface (NGS), and the representative high-k material HfO_2 was selectively deposited on the GS regions. X-ray reflectivity (XRR) analysis showed that distinct thickness fringes appeared on the GS regions after 20 cycles, whereas fringe formation on the NGS regions was observed after 50 cycles, indicating cycle-dependent selectivity characteristics. Furthermore, cross-sectional SEM analysis revealed that up to 50 ALD cycles on the NGS region, approximately 7.2 nm of a-C etching, and about 2 nm of HfO_2 deposition occurred simultaneously. This behavior is interpreted as suppression of TEMA-Hf precursor adsorption during the initial ALD adsorption step, while the a-C surface was etched by O_2 radicals generated during the reactant supply step. After performing PE-ALE following 50 ALD cycles, the selectivity between GS and NGS was effectively close to infinity, confirming that surface-selective growth can be induced solely through the PE-ALD/ALE supercycle.

This study suggests that selective deposition can be achieved in the gate oxide deposition step following trench formation in cell transistor structure processes such as RCAT and BCAT, without additional masks or etch-back processes, thereby simplifying the process.

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AS-TuP-7 Inhibition of Hafnia and Alumina Using Silanes, ***Chad Brick,*** 11 Steel Road East

Area–selective deposition (ASD) has grown into an important paradigm in semiconductor process integration in the last decade. By directing film growth to predefined regions, ASD can reduce overall process complexity, decrease reliance on lithographic patterning, and improve dimensional accuracy by preventing overlay–related defects. This approach is particularly advantageous for filling or coating intricate 3D topographies—such as vias and both vertical and horizontal trench structures—where conventional lithography often encounters significant limitations.

While relatively robust information is available on the interaction of silanes with silica surfaces, comparable data with respect to other metal oxides such as hafnia or alumina is sparse. In this study, we demonstrate that relative to a reference SiO_2 deposition process, different silane compounds and inhibition strategies are required for optimal inhibition of silica, hafnia and alumina respectively.

AS-TuP-8 Impact of Aluminum Precursor on Selective Dielectric on Metal Deposition, ***Jiyeon Kim***, *Dennis Hausmann, Alex Fox,* LAM Research*; Florian Preischel, Harish Parala, Anjana Devi,* Leibniz Institute, IFW Dresden, Germany

Selective deposition of a dielectric film, such as aluminum oxide (Al_2O_3) or hafnium oxide (HfO_2), on metal or metal-oxide surfaces (also known as DoM), without growth on silicon dielectric surfaces, has numerous applications in semiconductor manufacturing. These include the selective deposition of hard masks to enhance dry etch performance. Typical growth surfaces include W, Mo, and Co, with or without their native oxides, whereas inhibited surfaces are usually doped (C, N)-silicon oxides.Typically, this is achieved using small-molecule inhibitors (SMI), such as dimethylaminotrimethylsilane (DMATMS), which selectively chemisorb onto silicon oxide surfaces but not onto metal/metal oxide surfaces. A DMATMS-modified SiO_2 surface exhibits a significant (~2 nm) nucleation delay from AlO_x deposition using dimethylaluminum isoproxide (DMAI)/H_2O, relative to an uninhibited surface. In this work, alternate aluminum precursors and their impact on selectivity are evaluated. Methods for assessing the selectivity failure modes are also examined in this context.

To evaluate the early stages of selectivity performance, we use vapor-phase decomposition mass spectrometry (VPD-MS). This method allows evaluation of film thicknesses as low as <0.0001 nm, enabling the determination and quantification of events during the initial nucleation period. The selectivity and nucleation behavior of several aluminum precursors and inhibitors are evaluated using VPD-MS, alongside ellipsometry and water contact angle (WCA), compared with a baseline process using DMAI/H_2O. Our findings show that selectivity failure is primarily due to the inability of the inhibitor to passivate all potentially reactive sites on the wafer surface, as opposed to the breakdown of the inhibitor or inhibition layer itself.

Figure 1. Comparison of Al_2O_3 ALD growth on the inhibited vs. the non-inhibited surface by the Al atom concentration (left) and the Al_2O_3 film thickness (right).

AS-TuP-9 Tuning Surface Reactivity by Uniform Chemical Modification with Organic Ligands for Area-Selective Processes, ***Andrew Teplyakov,*** University of Delaware

In modern microelectronics, area-selective processes have become the key to produce atomically-precise features. However, in these applications, chemical reactivity and passivation of a surface have to be considered in the context of a specific substrate and a specific deposition chemistry. In addition, surface modification may serve to either promote or suppress the deposition, and for some technological schemes, the ability to switch from non-growth to growth substrate may be needed. That is why small molecule organic modifiers present a challenging but extremely versatile platform to tune surface reactivity even on complex materials. This talk will use model ALD processes with TiO_2 (TDMAT/water and $TiCl_4$/water) or Al_2O_3 (TMA/water) to test the reactivity of modified semiconductor surfaces, targeting organic monolayers with switchable reactivity on silicon substrates and also addressing the uniformity of chemical modification of traditionally unreactive surfaces, like those of 2D van der Waals nanomaterials. These processes will be analyzed by spectroscopic and microscopic methods, and selected results will be evaluated using computational DFT approaches. Although the focus will be on AS-ALD applications, some of the conclusions will also be important to designing atomically precise etching schemes, especially for 2D structures.

AS-TuP-10 Computational and Experimental Approaches to Hydrofluoric Acid-treated SiO_2 and SiNx Surfaces for Area-Selective Atomic Layer Deposition*, **Namkyu Yoo**, Sanghun Lee, Tae Hyun Kim, Chanju Lee, Jisang Yoo,* Yonsei University, Korea*; Seung-min Chung,* Hoseo University, Republic of Korea*; Hyungjun Kim,* Yonsei University, Korea

Selective deposition of SiO_2 and SiN_x is a promising approach for advanced 3D NAND fabrication, which consists of oxide–nitride stack architectures for enabling discontinuous charge trap layers. Generally, area-selective atomic layer deposition (AS-ALD) relies on differences in surface functional groups; however, the presence of native oxide on SiN_x obscures these groups and degrades selectivity. Consequently, HF etching is commonly employed prior to deposition, yet its impact on surface chemistry remains controversial and often overlooked.

Therefore, this study investigates how HF treatment alters the surface chemistry of SiO_2 or SiN_x and its subsequent influence on AS-ALD. DFT calculations reveal distinct rate-limiting steps for HF etching of SiO_2 and SiN_x, resulting in Si–OH termination on SiO_2 surfaces and Si–F/Si–NH termination on SiN_x. Furthermore, simulations show that precursor adsorption on fluorine-terminated SiN_x is thermodynamically unfavorable, with an energy barrier exceeding 292.5 kJ/mol. Experimental results show that increasing the HF concentration from 1 % to 10 % raises the fluorine content on SiN_x surfaces from 1 % to 3.3 %, significantly enhancing SiO_2 deposition selectivity. The thickness difference of ALD SiO_2 on oxide and nitride substrates etched by 10 % HF solution was greater than 2 nm.

This work clarifies the kinetics of HF etching and the inhibitory effect of surface Si–F species on precursor adsorption using DFT calculation. Additionally, experimental results confirm that fluorine is present exclusively on SiN_x surfaces after HF treatment and plays a critical role in suppressing nucleation during ALD. These findings elucidate HF induced surface chemistry modifications in oxide and nitride materials and provide insights for achieving reliable area-selective ALD in nanoelectronic device fabrication.

Acknowledgement

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AS-TuP-11 Influence of Plasma Power and Supercycle Conditions on Selectivity in DIPAS-Based SiO_2 AS-ALD*, **Tae Hwan Lim,*** SK hynix Inc. Korea*; Rui Loureiro, José Fernandes,* International Iberian Nanotechnology Laboratory, Portugal*; Yu Sung Jin, Dong Kyun Lee, Deok Sin Kil, Jung Il Hwang, Sung Gon Jin,* SK hynix Inc., Korea*; Jennifer Teixeira, Pedro Salomé,* International Iberian Nanotechnology Laboratory, Portugal

As 3D NAND technology continues to scale toward higher layer counts and reduced feature dimensions, shrinkage of the oxide/nitride pitch in oxide–nitride–oxide (ONO) stacks has increased susceptibility to parasitic capacitive coupling between neighboring charge trap nitride (CTN) regions. This effect can be further exacerbated by enhanced capacitive coupling between the CTN layer and adjacent metal electrodes, leading to unintended cell-to-cell interference and electrical performance degradation. These challenges highlight the need for precise spatial control in dielectric and CTN deposition processes. Area-selective atomic layer deposition (AS-ALD), which enables material growth exclusively on target surfaces while suppressing nucleation on non-target regions, has therefore emerged as a key enabling technique for next-generation 3D NAND integration. Through this selective deposition approach, physical separation of adjacent CTN regions can be achieved, thereby mitigating cell-to-cell interference and preserving cell characteristics in highly stacked 3D NAND architectures. Accordingly, in this study, SiO_2 AS-ALD was employed to selectively deposit SiO_2 on SiO_2 surfaces while effectively suppressing SiO_2 growth on SiN_x. Specifically, a low-temperature DIPAS/O_3-based SiO_2 ALD process was developed by leveraging the inherent selectivity of DIPAS toward SiO_2 over SiN_x. Under source-saturated conditions, a reference process was established at 100 °C, yielding a SiO_2 thickness contrast of 1.71 nm between SiO_2 and SiN_x after 50 cycles. Cycle-dependent growth analysis revealed pronounced incubation behavior on SiN_x, extending up to ~20 cycles. To further regulate selective growth, remote plasma pretreatments using N_2, N_2/H_2, and NH_3 were applied prior to DIPAS exposure to modify surface terminations and suppress nucleation. At 100 W, the application of N_2, N_2/H_2, and NH_3 plasmas eliminated the SiO_2 thickness contrast between SiO_2 and SiN_x, indicating plasma-induced surface state equalization. In contrast, at 50 W, a 1:10 supercycle reduced the thickness contrast by 0.27 nm under N_2 plasma, while enhancing it by 0.49 nm under N_2/H_2 plasma. Moreover, a 1:50 supercycle at 50 W maintained the contrast under N_2/H_2 plasma but improved it by 0.43 nm and 0.31 nm under N_2 and NH_3 plasmas, respectively. These trends imply that plasma pretreatments modify surface reactivity, thereby affecting the relative DIPAS nucleation kinetics and incubation behavior between SiO_2 and SiN_x. In summary, these results demonstrate that appropriate tuning of plasma power and supercycle conditions enables the preservation or enhancement of selectivity, defining a viable process window in DIPAS-based AS-ALD.

AS-TuP-12 Alcohol-Mediated Modulation of Surface Chemical States for Inherent Area-Selective Atomic Layer Deposition*, **Kun Cao**, Weizhen Wang, Boxuan Li, Rong Chen,* Huazhong University of Science and Technology, China

Inherent area-selective atomic layer deposition (AS-ALD) fundamentally relies on a distinct disparity in surface chemical states between growth and non-growth area. For SiO2/Cu patterned architectures, the oxidation of the Cu surface serves as a primary driver for the loss of selectivity as the ALD process proceeds. In this presentation, an alcohol-mediated ASD process is introduced, utilizing alcohols with varying carbon chain lengths to precisely modulate surface chemical states to enhance selectivity. A competitive-synergistic mechanism involving surface reductive capability and steric hindrance is identified as the governing factor for process selectivity. Results demonstrate that while the reducing ability of alcohols on oxidized Cu surfaces diminishes with increasing carbon chain length, their steric hindrance increases. EtOH is identified as the optimal pretreatment agent, yielding an exceptional selectivity exceeding 99.9%. Moreover, the alcohol-mediated ALD process is successfully extended to other oxide systems with precursors bearing analogous ligands, demonstrating the generality of the proposed strategy. This work provides a versatile methodology for manipulating surface redox and physisorption effects to achieve high-selectivity AS-ALD.

AS-TuP-13 Site-Specific and Temperature Dependent Hydration of Faceted Alpha Hematite*, **Asare Dua**,* Illinois Institute of Technology*; Luke Nunzio,* Purdue University, USA*; Ashley Bielinski,* Argonne National Laboratory, USA*; Yue Li,* Argonne National Lab*; Cong Liu, Alex Martinson,* Argonne National Laboratory, USA*; Adam Hock,* Illinois Institute of Technology

Alpha hematite (–Fe_2O_3) is an abundant metal oxide whose surfaces and interfaces control key processes in catalysis, sensing, and photoelectrochemistry. While the more stable –Fe_2O_3 (001) surface is well studied, less stable facets such as (012) and (104) which are more relevant in the aforementioned applications due to higher surface activity remain least studied. Surface sites of –Fe_2O_3 (012) and (104), as well as their distinct stability were identified through temperature-dependent hydration by combining in situ infrared reflection absorption spectroscopy (IRAS) with density functional theory (DFT) vibrational analysis.

For α-Fe_2O_3 (012), we found sites that promoted the dissociative and molecular adsorption of D_2O. Dissociatively adsorbed D_2O were either terminal or bridging. In both cases the hydroxyls were either isolated or interacting with nearby species. Protons of bridging hydroxyls (μ_{3a}–OD (isolated); μ_{3b}–OD (interacting with nearby hydroxyls)) are bound to triply coordinated surface oxygens while terminal hydroxyls (μ_{1a}–OD (interacting with nearby hydroxyls)) were bound to octahedral surface Fe atoms (Fe_{oct}^{3+}). Similar to dissociatively adsorbed D_2O, molecularly adsorbed D_2O was either isolated (D_2O_a) or interacting with nearby hydroxyls (D_2O_b).

α-Fe_2O_3 (104) on the other hand exhibited an isolated doubly coordinated bridging hydroxyl (μ_{2a}–OD) and an interacting bridging species (μ_{2b}–OD) rather than triply coordinated bridging hydroxyls. This preference is backed by our DFT calculations which shows triply coordinated bridging hydroxyls were highly unstable on α-Fe_2O_3 (104). Results from IRAS showed two isolated terminal hydroxyls, μ_{1a}–OD and μ_{1b}–OD, were present on the surface of α-Fe_2O_3 (104). This indicates two types of undercoordinated surface atoms existed with the first being undercoordinated tetrahedral Fe atoms (Fe_{tet}^{3+}) since they’re the surface atoms of α-Fe_2O_3 (104), while the second is from the second layer of Fe atoms which have octahedral geometry. The undercoordination of Fe_{oct}^{3+}atoms however suggests oxygen vacancies (V_o) were present and some of these might migrate from surface to the second lattice of α-Fe_2O_3 (104). Our temperature dependent studies support this hypothesis since the population of μ_{1a}–OD, μ_{1b}–OD, and μ_{2a}–OD increased with increasing temperature when under vacuum (0.8 torr).

The distinct local environments of the sites on α-Fe_2O_3 (012) andα-Fe_2O_3 (104) and changes in properties with respect to temperature revealed through this work provide a fundamental to tool that may be used to engineer the surface of alpha hematite through site- or facet-selective atomic layer deposition.

AS-TuP-14 Inherently Selective Atomic Layer Deposition of Niobium Oxide Thin Films Using a Novel Precursor*, **Hyun-Kyu Ryu**, Sung-Woo Ahn, Myeong-Ho Kim, In-Jae Lee, Chae-Young Song, Jin-Sik Kim, Won Yong Koh,* R&D Center UPChem, Republic of Korea

Nb_2O_5 is a promising dielectric material with its relatively high dielectric constant (k≈ 29-60) and wide band gap (~3.6 eV), and its area-selective deposition (ASD) process becomes essential to enable the bottom-up patterning and simplified process integration on nanoscale and 3D DRAM manufacturing.

In this work, we demonstrate a robust ALD process for Nb_2O_5 thin films using a novel Nb precursor, "*UP-Nb*", designed and synthesized by UP Chemical. When evaluated at 300 °C with O_3 as the oxidant, *UP-Nb* exhibited clear self-limiting growth behavior, with a growth-per-cycle (GPC) of approximately ~0.3 Å/cycle as a function of precursor exposure time. X-ray photoelectron spectroscopy analysis of the Nb 3d core-level spectra confirmed a near-stoichiometric Nb_2O_5 composition, indicating chemically stable oxide formation. Furthermore, transmission electron microscopy analysis of high-aspect-ratio (20:1) patterned structures revealed highly conformal film growth, with step coverage exceeding 90%, demonstrating the suitability of the three-dimensional device architecture.

Beyond conventional ALD performance, *UP-Nb* enables inherently selective ALD behavior without the use of molecular inhibitors. Selective Nb_2O_5 growth was observed on TiN surfaces without an incubation delay, while nucleation on SiN substrates was effectively suppressed for up to ~20 ALD cycles. In contrast, a commercially available Nb precursor exhibited incubation-free growth on both TiN and SiN substrates under the same process conditions, indicating the absence of inherent selectivity. This clear distinction confirms that the selectivity originates from the intrinsic precursor–surface reactivity of *UP-Nb* rather than from process conditions. The demonstrated inhibitor-free inherent selectivity, combined with stable ALD characteristics and high conformality, highlights *UP-Nb* as a highly promising precursor for Nb_2O_5 AS-ALD process in next-generation nanoscale and 3D DRAM devices.

AS-TuP-15 Influence of Precursor Molecular Size on Aluminum Oxide Area-Selective Deposition*, **Sharmistha Bhattacharjee**,* Lehigh University*; Michelle Paquette,* University of Missouri-Kansas City*; Nicholas C. Strandwitz,* Lehigh University*; Sean King,* Intel Corporation

Area-selective atomic layer deposition (AS-ALD) is a bottom-up strategy for advancing nanoscale fabrication of electronic and functional devices. The effectiveness of AS-ALD is strongly governed by precursor–surface interactions. The factors such as molecular size, steric hindrance, and chemical reactivity determine whether the precursor will diffuse through a blocking self-assembled monolayer (SAM), react with the blocking layer, or react with a defect. Highly reactive aluminum precursors such as trimethylaluminum (TMA) are challenging to employ in AS-ALD due to their small size and high reactivity, which often results in precursor penetration into non-growth regions and subsequent loss of selectivity. Rational optimization of precursor ligand size, structure, and reactivity is therefore essential to suppress precursor infiltration on non-growth surfaces.

Here, we examine a series of alternative Al precursors including TMA, aluminum tri-sec-butoxide, and tri-i-butylaluminum for the growth of Al_2O_3 with H_2O co-reactant.We examined the ability to block the growth of alumina with these precursors using dodecanethiol SAMs on copper over a temperature window of 100 to 160 ºC. Film growth and density are evaluated using spectroscopic ellipsometry and X-ray reflectivity measurements. The blocking ability is examined by quantifying Al at% from X-ray photoelectron spectroscopy. Significantly increased blocking was found with the non-TMA precursors. 100% selectivity was sustained for aluminum tri-sec-butoxide, whereas tri-i-butylaluminum maintains selectivity above 90% after 100 ALD cycles of Al_2O_3. This study proves that combining a less reactive and sterically hindered precursor with a well-ordered SAM provides an effective strategy for maximizing blocking performance in AS-ALD.

Area Selective ALD

Room Tampa Bay Salons 3-4 - Session AS1-WeM

ASD Process I

Moderators: Sumit Agarwal, Colorado School of Mines, **Stacey Bent**, Stanford University

8:00am **AS1-WeM-1 ALD Outstanding Presentation Award Finalist: Triazolylidene Small Molecule Inhibitor for Area-Selective Atomic Layer Deposition of High *k*-Dielectric Materials***, Giang Hoang Pham,* Western University, Canada*; Jordan Bentely,* Wesleyan University, Canada*; Dana Nanan, Cathleen Crudden,* Queen's University, Canada*;* ***Paul Ragogna,*** Western University, Canada

High selectivity in area selective atomic layer deposition (AS-ALD) requires the effective performance of an inhibitor that must exhibit selectively binding mode on non-growth areas as well as strong thermal, and chemical stability to prevent degradation or decomposition during the semiconductor manufacturing process. N-heterocyclic carbenes (NHCs) have emerged as promising next-generation alternatives to conventional small-molecule inhibitors (SMIs) due to their strong σ-donor character and preferential binding to metal surfaces over a dielectric region. We have prepared and developed *triazolylidene* NHC (Tz) derivatives as a novel class of NHC inhibitor for selective high-k dielectric growth on SiO_2 over metallic bands reaching a selectivity factor of 93% after 50 dielectric deposition cycles. The selective adsorption behavior and dielectric blocking efficiency were systematically evaluated using time-of-flight secondary ion mass spectrometry (ToF-SIMS), and X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM). The practical applicability of the Tz inhibitor is further demonstrated through bottom-up fabrication of a working field-effect transistor, in which the NHC selectively protects metal electrodes during the deposition of metal oxide dielectric and semiconductor layers. This work paves an innovative pathway for exploring novel class of SMIs toward advanced AS-ALD applications.

Selected references: (1) D.A.R. Nanan, J.T. Lomax, J. Bentley, L. Misener, A.J. Veinot, W-T Shiu, L. Liu, P.J. Ragogna**,** C.M. Crudden *J. Am. Chem. Soc.***2025**, *147*, 5624–5631; **(2)**J.T. Lomax, E. Goodwin, M.D. Aloisio, A.J. Veinot, I. Singh, W-T Shiu, M. Bakiro, J. Bentley, J.F. DeJesus, P.G. Gordon, L. Liu, S.T. Barry, C.M. Crudden, P.J. Ragogna *Chem. Mater.***2024**, *36*, 5500–5507; **(3)** P.J. Ragogna, C.M. Crudden, D.A.R. Nanan, J.T. Lomax, A.J. Veinot, J. Bentley, “Method of Selective Deposition of Triazolylidenes on Metallic Surfaces”, International Patent Application No. PCT/CA2025/051508, filed: Nov. 12, 2025

8:30am **AS1-WeM-3 Maintaining Healthy Boundaries – Machine Learning Design of SMIs***,* ***Sean Barry,*** *Marshall Atherton,* Carleton University, Canada*; Dennis Hausmann, Jiyeon Kim,* Lam Research Corp.

Machine learning–guided molecular design is important for accelerating materials discovery, and we have applied it to area-selective atomic layer deposition (AS-ALD). In this work, we integrate machine learning with systematic experimental characterization to guide the development of amino-substituted silane small-molecule inhibitors (SMIs) to optimize volatility, thermal stability, and surface selectivity. By prioritizing data-driven structure–property relationships, this study helps establish a predictive framework for identifying viable SMIs while limiting experimental trial-and-error.

A diverse library of aminosilanes was synthesized using an environmentally benign nucleophilic substitution route involving disubstituted amines and chlorosilanes, with triethylamine as a sacrificial base. This approach avoids pyrophoric reagents and metal-containing intermediates, supporting sustainable scale-up. Thermal properties were evaluated using thermogravimetric analysis, vapour pressure measurements, and differential scanning calorimetry. Surface adsorption and selectivity were quantified using in situ quartz crystal microbalance measurements.

The experimentally derived thermophysical dataset was used to train ML models to map molecular structure and composition to key properties governing AS-ALD performance, including volatility and thermal stability. A chemistry-informed molecular property prediction platform (DeepAutoQSAR, Schrödinger) helped identify optimal model architectures. The resulting ML models were used to predict properties of previously untested silane precursors, enabling targeted selection of candidates for experimental validation. Comparison of predicted and measured properties demonstrates the effectiveness of this ML-guided workflow for accelerating inhibitor design.

8:45am **AS1-WeM-4 Role of Precursor and Aklanethiol Chain Length on Area Selective Deposition of Aluminum and Hafnium-Containing Films***,* ***Nicholas Strandwitz,*** Lehigh University

Area selective atomic layer deposition (AS-ALD) enables the selective placement of material based on differences in surface chemistry and is thus a promising strategy for device manufacturing by avoiding addition patterning steps and alignment issues.Key developments that are being sought include achieving high selectivity (near 100%) at high film thicknesses on growth surfaces, and expanding the palette of materials (such as new low-k materials) that can be grow in AS-ALD.In this talk I will explore two aspects of our work that work toward these developments: Examination of the role of alkanethiol chain length and examination of the role of alternative metal and co-reactant precursors on selectivity.

The stability and impermeability of monolayer-based blocking layers is critical to preventing film growth in certain regions.Few reports explicitly studied the effect of alkane chain length and temperature on selectivity, so we sought to do so with a series of alkanethiols of various alkane chain length on copper surfaces.We found that longer chain lengths achieved higher selectivity and all chain lengths to be unstable to the highest temperature investigated (180 °C).To isolate the precise breakdown mechanisms, we separately subjected the alkanethiol monolayers on copper to various individual ALD steps including elevated temperature, metal precursor exposure, or water exposure.We found that trimethylaluminum at elevated temperature induced alkanethiol desorption, whereas amido-based Hf precursors did not, thus demonstrating a chemical effect on monolayer stability.

To further investigate the role of film precursor, we studied an array of metal and non-metal precursors including alkyl aluminums, amido aluminum, aluminum alkoxide, and ethylene glycol.Importantly, we found that precursor size, rather than reactivity, was the prime determining factor in realizing high sensitivity.We found that molecular layer deposited films (using ethylene glycol) did not show significantly higher selectivity than traditional ALD growths with the same metal precursor.With certain combinations of large metal precursors and water, we were able to achieve high selectivity (>90%)at alumina film thicknesses greater than 15 nm on the growth surface.Thus, this work builds on existing reports from other groups that the precursor chemistry has a massive role in determining selectivity.

9:00am **AS1-WeM-5 Surface Blocking Effect of NH_3 in Selective Co-ALD with CCTBA Precursor***,* ***Naoki Tamaoki,*** *Jun Yamaguchi, Noboru Sato, Atsuhiro Tsukune, Yukihiro Shimogaki,* The University of Tokyo, Japan

As semiconductor devices continue to scale down, current densities in interconnects increase, leading to serious reliability degradation of Cu interconnects due to electromigration. The introduction of a metallic Co cap layer is expected to enhance adhesion between interconnects and dielectric layers, thereby extending the lifetime of Cu wiring. In Co atomic layer deposition (ALD) using CCTBA (Cobalt Carbonyl Tertiary-Butyl Acetylene) as a precursor, an incubation period exists in which film nucleation on SiO_2 dielectric surfaces is delayed compared with Cu surfaces, enabling selective growth [1]. In this study, the inhibitor effect of NH_3 was evaluated as a method to further enhance selectivity, motivated by previous reports on selective CVD using $Co_2(CO)_8$, where simultaneous NH_3 supply suppresses growth initiation and improves selectivity [2].

Deposition experiments were performed on Si substrates with a 300 nm thermally grown oxide layer at 120 °C using alternating CCTBA and H_2 pulses for 500 cycles, with in-situ monitoring by spectroscopic ellipsometry. Under standard conditions, no incubation period was observed and a growth-per-cycle (GPC) of 0.016 nm/cycle was obtained. When NH_3 was co-supplied during the CCTBA pulse, an incubation period of approximately 75 cycles appeared and the GPC decreased to 0.0099 nm/cycle, demonstrating that NH_3 functions effectively as an inhibitor.

Furthermore, surface reaction calculations using a machine-learning potential (PFP: Preferred Potential by Matlantis Corp.) suggest that NH_3 selectively adsorbs on OH groups on oxide surfaces, which serve as potential adsorption sites for CCTBA molecules, thereby blocking these reactive sites. These results indicate that NH_3 can act as a small-molecule inhibitor in Co-ALD using CCTBA, providing a promising approach for enhancing selective growth in Co capping processes for advanced interconnect applications.

The authors gratefully acknowledge Daikin Industries, Ltd. For their support and valuable discussions.

References

[1] J. Yamaguchi et al., AVS 24th International Conference on Atomic Layer Deposition, AA1-TuM-7 (2024).

[2] Z. V. Zhang et al., J. Vac. Sci. Technol. A 38, 033401 (2020).

9:15am **AS1-WeM-6 Fluorination Passivation for Area-Selective Deposition: Selective Passivation of SiO_2 vs SiN_x for Highly Selective TiO_2 Deposition using Water-Free $TiCl_4$/Ti(^{i}PrO)$_4$.**, ***Jeremy Thelven,*** *Gregory Parsons,* North Carolina State University

There is an acute need for new memory and computing device structures that are more energy efficient.[1] To minimize energy loss, new complex 3D architectures are needed with precisely aligned features. To address inherent alignment limitations in lithographic patterning, area selective deposition (ASD) is an attractive process because, in principle, the alignment between the starting pattern and the deposited feature is determined by differences in reactivity for the molecules on the desired growth and non-growth surfaces. Therefore, when the growth and non-growth surfaces have similar active surfaces sites, such as SiO_2 and SiN_x, identifying reactants that preferentially deposit on one surface versus another is particularly challenging. Recently, we found that when a patterned SiO_2/SiN_x surface was exposed to a fluorinating agent (such as MoF_6), the SiO_2 surface became preferentially passivated for deposition of TiO_2 ALD using $TiCl_4$/H_2O, allowing selectivity >93% for ~9.6 nm of TiO_2.[2] We hypothesized that as ALD proceeds, a primary reason for the observed loss of SiO_2 passivation was unwanted oxidation during the water exposure step.

To address this, we reconsidered a previously studied “waterless” TiO_2 ALD process using $TiCl_4$ and titanium isopropoxide (TTiP) at 210°C.[3] Using $TiCl_4$/TTiP ALD on blanket SiO_2 and SiN_x substrates, we found (Figure 1a and b) that after pre-treating the SiO_2 and SiN_x with only a brief dip in dilute $HF_{(aq)}$, the $TiCl_4$/TTiP process showed delayed deposition on both surfaces. However, the extent of delay was much more substantial on the SiO_2 vs SiN_x, allowing several nm of ASD. Subsequently, we tested the same SiO_2/SiN_x surfaces after dilute $HF_{(aq)}$ followed by exposure to MoF_6 for 1 second at 210°C. As shown in Figure 1c and d, initial results indicate substantially improved selectivity for the fluorine-passivated water-free TiO_2 ALD, enabling ~ 25 nm of TiO_2 on SiN_x vs. SiO_2 with exceptionally high selectivity. The lines in the figures correspond to fits obtained from an analytical nucleation model.[4] Confirmation of these findings will require testing the process on nanoscale patterned substrates. Overall, these results demonstrate how the combination of pretreatment and precursor selection can help achieve chemical contrast for ASD, even on starting surfaces with similar chemical structure and composition.

1.Datta, S.; Chakraborty, W.; Radosavljevic, M. Toward. Science 2022, 378 (6621), 733–740.

2.Thelven, J. M.; Parsons, G. N. et al., Adv Materials Technologies 2025, 10 (23), e00284.

3.Atanasov, S. E.; Kalanyan, B.; Parsons, G. N. JVSTA 2016, 34 (1), 01A148.

4.Parsons, G. N. JVSTA 2019, 37 (2), 020911.

9:30am **AS1-WeM-7 Chemical Selectivity in Atomic Layer Selectivity (ALD) via Gas-Phase Silylation using N-(trimethylsilyl)dimethylamine (TMSDMA)**, *Mohammed Sadam Alam,* ***Francisco Zaera,*** University of California at Riverside

The effectiveness of the silylation of both silicon oxide and copper surfaces using N-(trimethylsilyl)dimethylamine (TMSDMA) as a passivation agent in atomic layer depositions (ALDs) was evaluated and contrasted by using x-ray photoelectron spectroscopy (XPS). It was determined that on SiO_2 such silylation does indeed block the nucleation centers where the ALD precursors are activated and therefore inhibit film growth, but only temporarily; after a few ALD cycles, deposition becomes evident. By testing this chemistry on two types of SiO_2 surfaces, prepared by plasma-enhanced chemical vapor deposition (PE-CVD) and by chemical (RCA) treatment of Si(100) wafers, it was concluded that the nature of the initial substrate does not play a crucial role in the silylation or ALD blocking processes. The material being deposited, on the other hand, does make a difference: TiO_2 film growth can be blocked for almost 10 ALD cycles, whereas HfO_2 starts building up on the surface after less than 5 ALD cycles. Moreover, the steady-state deposition rate for TiO_2 was determined to be lower than for HfO_2. One of the key findings of this work is that the silylation can be carried out using either gas- or liquid-phase treatments. It was found that the extent of silylation and the inhibition of the subsequent ALD were comparable in both cases, but the gas-phase method was determined to be cleaner and to deposit less carbon contaminants.

On copper, by contrast, virtually no effect on the ALD of either TiO_2 or HfO_2 was observed upon silylation with TMSDMA. A slow but detectable initial rate of oxide deposition was observed either before or after treatment, similar in both cases: approximately 0.15 Å/cycle in the case of TiO_2, about 0.25 Å/cycle for HfO_2. On SiO_2, by contrast, these rates were measured to be ~0.6 and 1.2 Å/cycle, respectively, on the clean substrate, but only ~0.08 and 0.4 Å/cycle after silylation. Consequently, it is concluded that gas-phase silylation using TMSDMA can be used to selectively allow for the ALD of oxides on silica in the presence of copper, that is, for area-selective ALD (AS-ALD), albeit with limited contrast. It should be added that in some cases an induction period was observed before the start of the film growth. We speculate that this, and the non-zero deposition rates seen on Cu and silylated SiO_2, may be due to the possible existence of defects on the substrates acting as nucleation centers.

9:45am **AS1-WeM-8 Mechanistic Criteria for Area Selective Deposition of Multicomponent Al_xSi_yO Oxide Dielectrics**, *Eryan Gu, Zilian Qi, Kun Cao,* ***Rong Chen,*** Huazhong University of Science and Technology, China

As integrated circuit technology continues to evolve towards three-dimensional architectures, device density and interconnect layers are constantly increasing. Area selective deposition (ASD) offers significant advantages as a bottom-up approach for such patterning. In this talk, an ASD process and selectivity criterion for multicomponent oxide of AlxSiyO is presented. Combined experimental and mechanistic analysis, the interactions between Al and Si precursors and their interactions with inhibitor modified surfaces were revealed. A selectivity criterion driven by penetration depth of precursors into inhibitors and the reaction barrier of multiple precursors was established, enabling selective deposition through precursor selection and composition regulation. The growth of AlxSiyO films is controlled by the synergistic effect of catalytic activation, precursor ratio and temperature, and has tunable dielectric properties, which is expected to improve the RC delay problem. Inhibition of ligand elimination at low temperatures leads to moderate carbon incorporation, thereby enabling the film dielectric constant to reach 4.3. Highly selective growth of 10 nm AlxSiyO films was achieved on Cu/SiO2 patterned, demonstrating a viable strategy for integrating AlxSiyO into next-generation interconnect technologies.

Area Selective ALD
Room Tampa Bay Salons 3-4 - Session AS2-WeM
ASD Process II

Moderators: Anjana Devi, Leibniz Institute, IFW Dresden, **Nicholas Strandwitz**, Lehigh University

10:45am **AS2-WeM-12 Perfect Selectivity vs Practical Sustainability in ASD**, ***Nupur Bihari,*** Lam Research Corporation **INVITED**

Area selective deposition (ASD) continues to emerge as a pivotal technique for enabling next–generation semiconductor manufacturing, particularly as device geometries shrink and integration demands intensify. However, the long–standing goal of achieving perfectly selective growth often drives processes toward excessive complexity, high precursor consumption, and limited long–term sustainability. In this work, we explore the practical balance between achieving robust selectivity and maintaining overall process efficiency, emphasizing the potential benefits of reducing chemical usage without compromising integration–relevant performance. By adopting a more pragmatic viewpoint, we demonstrate that high–quality selectivity does not necessarily require aggressive surface treatments, extreme exposure times, or high precursor flows. Instead, a carefully tuned, eco–friendly process regime can deliver excellent material discrimination while significantly lowering chemical burden and overall environmental impact.

To evaluate performance under these more sustainable conditions, we employ top–down scanning electron microscopy (TDSEM) as a straightforward yet powerful metrology approach. TDSEM enables rapid assessment of nucleation behavior, feature–scale uniformity, and pattern fidelity, providing a clear window into the relationship between precursor flow, growth onset, and ultimate selectivity. Our results show that excellent selectivity can still be reliably achieved even when precursor usage is dramatically reduced, illustrating the feasibility of simplifying ASD processes for manufacturing–scale deployment. Electrical resistance–capacitance (RC) measurements and integrated wafer–level data further confirm that processes exhibiting modest deviations from perfect selectivity can nonetheless support high–performance interconnect scaling and patterning fidelity. These findings challenge the traditional assumption that optimal integration requires flawless selectivity and instead suggest that controlled, minimal nucleation on non–growth surfaces may be tolerable - especially when weighed against the benefits of lower cost, reduced chemical waste, and substantially improved throughput.

Taken together, this work highlights the value of shifting from a perfection–driven mindset to a more holistic framework that prioritizes precursor efficiency, environmental responsibility, and integration robustness. By demonstrating that sustainable, lower–chemistry ASD regimes can still meet stringent device requirements, we outline a more realistic and scalable pathway for adopting ASD in high–volume semiconductor manufacturing. This approach not only reduces overall process strain but also strengthens the connection between small–scale laboratory studies and real–world wafer–level performance, ultimately enabling faster development cycles and broader implementation of ASD–driven patterning strategies.

11:15am **AS2-WeM-14 Photoassisted Chemical Vapor Deposition as a Strategy for Area Selective Deposition of Ru:Implications for Developing an ALD Process***, Christopher Brewer,* University of Texas at Dallas*; Rashmi Singh,* University of Florida*; James Pugh, Anjali Sharma,* University of Florida*; Amy Walker,* University of Texas at Dallas*; **Lisa McElwee-White,*** University of Florida

Photoassisted chemical vapor deposition (PACVD) is a potentially attractive technique for metallization of thermally sensitive substrates. Prior PACVD results from (η^3-allyl)Ru(CO)$_3$Br, CpRu(CO)$_2$Me, and (COT)Ru(CO)$_3$ have demonstrated that allyl and Cp ligands remain incorporated in deposits, while the COT ligand was not detected. Subsequently, a library of (η^4-diene)Ru(CO)$_3$ and (η^2-alkene)Ru(CO)$_4$ precursors that undergo photochemical ligand loss at room temperature has been prepared and their solution photochemistry studied. Using -CH$_3$, -OH, and -COOH terminated self-assembled monolayers (SAMs) as model substrates, we have investigated the use of these precursors in area selective deposition. We demonstrate that the (η^4-diene)Ru(CO)$_3$ precursors show a strong deposition preference onto -COOH functionalized SAMs, while (η^2-alkene)Ru(CO)$_4$ precursors show a deposition preference onto the -COOH and -OH functionalized SAMs. The -CH$_3$ functionalized SAMs are a non-growth surface for all the precursors screened. The deposition results will be discussed in context of precursor design for ASD and development of related ALD processes.

11:30am **AS2-WeM-15 Highly Selective Ru Growth on Metallic Substrates against Dielectric Surface via Inherent Area-selective Atomic Layer Deposition Using a Novel Ru Precursor***, **Hideaki Nakatsubo**, Masato Iseki,* TANAKA PRECIOUS METAL TECHNOLOGIES Co., Ltd., Japan*; Shintaro Chiba,* EEJA Ltd., Japan*; Iaan Cho, Hyungjun Kim,* Yonsei University, Republic of Korea*; Bonggeun Shong,* Hanyang University, Republic of Korea*; Debananda Mohapatra, Jeongha Kim, Soo-Hyun Kim,* UNIST, Republic of Korea

Area-selective deposition via atomic layer deposition (AS-ALD) offers a bottom-up approach to fabricate complex and functional nanostructures, being robust for the scaled architectures even with any 3D structures compared to the conventional top-down approach using multi-patterning processes. Inherent-type AS-ALD is the most simplified process, exploiting intrinsic adsorption properties of the precursors depending on the substrates. Compared to inhibitor-assisted area-selective processes, the inherent AS-ALD also highlights practical advantages such as reducing fabrication steps or eliminating concerns of residual inhibitors, which is attractive for the application of interconnect metallization.

Although the inherent AS-ALD has typically suffered from a lower selectivity compared to that of inhibitor-assisted one, a higher inherent selectivity against Si-based dielectrics such as SiO$_2$, low-k or SiN is essential for the intended purposes (e.g., void-free/seamless bottom-up metallization). Therefore, we demonstrated high selectivity against SiO$_2$ via Ru thermal AS-ALD using a novel Ru precursor, [Ru(TMM)(*p*-cymene)], and O$_2$ as a reactant without any inhibitor or other area-selective activation methods. This precursor has two different ligands, trimethylenemethane (TMM) and isopropylmethylbenzene (*p*-cymene), and exhibits high thermal stability (> 400 °C). A previous report on this precursor revealed that a surprisingly long incubation period of >1000 cycles was observed on SiO$_2$ while only ~8 cycles were required on TiN at 300 °C [1], overcoming the challenges of high selectivity which previous Ru AS-ALDs have suffered from. Computational simulations in the same report also discovered that dissociative adsorption proceeds on metallic substrates such as Ru, but is energetically unfavorable on SiO$_2$, providing the theoretical support for the high inherent selectivity against SiO$_2$.

In this study, we expand our understanding of the inherent AS-ALD Ru on technologically important metallic substrates including Ru, TiN, Mo, W against dielectric substrates such as SiO$_2$, low-k, SiN, Al$_2$O$_3$. The results demonstrate that the high selectivity against dielectrics was confirmed both on blanket wafers and patterned substrates. We also discuss how process conditions affect the selectivity and the experimental factors required to emerge the selectivity with mechanistic insights.

[1] H. Nakatsubo *et.al.*, *Adv. Sci.*, **2025**, e19209.

11:45am **AS2-WeM-16 Mechanistic Insights into Area-Selective Etching of Ruthenium***, **Iaan Cho**,* Yonsei University, Republic of Korea*; Soo-Hyun Kim,* Ulsan National Institute of Science and Technology, Republic of Korea*; Hyungjun Kim,* Yonsei University, Republic of Korea*; Bonggeun Shong,* Hanyang University, Republic of Korea

As interconnect linewidths continue to scale down, ruthenium (Ru) is being considered as an alternative to copper (Cu) owing to its favorable resistivity and reliability at reduced dimensions. For practical integration, area-selective deposition (ASD) is suggested as an alternative fabrication method to confine Ru growth to conductive growth regions while suppressing deposition on dielectric non-growth areas (NGAs) [1]. However, since nucleation of Ru on the NGAs such as SiO$_2$ can limit the applicability of the process, addition of oxidative etch-back steps within ASD are suggested to enhance the overall deposition selectivity [2]. In this study, the mechanistic origin of the selectivity in oxidative etching of Ru was investigated using machine-learning interatomic potential (MLIP) based energetic analyses and molecular dynamics (MD) simulations. Several different environments of Ru nuclei on metallic and dielectric substrates, such as Ru adatoms, sub-nanometer clusters, and extended heterointerfaces are considered. The results indicate that Ru species on dielectric surfaces are readily oxidized and desorb as volatile RuO$_4$ upon exposure to oxidant such as O$_3$, whereas Ru on metallic surfaces are less susceptible to oxidative loss under comparable conditions. This substrate-dependent reactivity upon oxidation and desorption is consistent with experimentally reported selectivity enhancements in the supercycle ASD processes. These results clarify the selective oxidative etching of Ru and provide a mechanistic basis for optimizing Ru ASD for advanced interconnect integration. Acknowledgments. This work was supported by the Technology Innovation Program [Public-Private Joint Investment Semiconductor R&D Program (K-CHIPS) To Foster High-Quality Human Resources] [RS-2023-00236667, High Performance Ru-Tin Interconnects Via High Temperature Atomic Layer Deposition (ALD) and Development on New Interconnect Materials Based on ALD] funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea) (No. 1415187401).References. [1] Chem. Mater. 2024, 36, 18, 8663; [2] Chem. Mater. 2019, 31, 11, 3878

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