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

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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

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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.

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