Area Selective Deposition
Room Atrium Room - Session ASD-TuP
Area Selective Deposition Poster Session

ASD-TuP-1 Triazolylidene Small Molecule Inhibitor for Area-Selective Atomic Layer Deposition of High *κ*-Dielectric Materials, ***Giang Hoang Pham**, Marco Antonio Quintanilla-Riviere, Jordan Bentley,* University of Western Ontario, Canada*; Dana Nanan, Catheleen Crudden,* Queen's University, Canada*; Paul Ragogna,* University of Western Ontario, Canada

High selectivity in area selective atomic layer deposition (AS-ALD) requires the effective performance of an inhibitor that must exhibitselectively binding mode on non-growth areas as well as strong thermal, and chemical stability to prevent degradation or decomposition during the semiconductor manufacturing process [1]. 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 silicon oxide [2-5]. In this study, we synthesize and develop a *triazolylidene* molecule as a novel class of NHC inhibitor for selective growth ofhigh-*κ* dielectricon SiO_2 over Au bands. The selective adsorptionbehavior and dielectric blocking efficiency are systematically evaluated using time-of-flight secondary ion mass spectrometry, and X-ray photoelectron spectroscopy. The practical applicability of this NHC inhibitor is further demonstrated through bottom-up fabrication of a 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.

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ASD-TuP-3 Surface Dependent Ethanol Inhibition for Area Selective Deposition on SiO2 and TiN via DFT Calculations, ***Jiwan Hong**, Seoeun Yoon, Soomin Yoo, Woojin Jeon,* Department of Materials Science and Engineering, Kyung Hee University, Republic of Korea

Although ethanol is not the strongest inhibitor reported for area selective ALD, it is well suited as a model molecule for studying surface dependent inhibition behavior. Its simple molecular structure allows systematic investigation of inhibitor induced nucleation delay without introducing additional steric or chemical complexity.

In this study, density functional theory (DFT) calculations were used to analyze the adsorption behavior of ethanol on SiO_2 and TiN surfaces. The simulations indicate a preference for EtOH adsorption on hydroxyl terminated SiO_2 surfaces, where hydrogen bonding interactions stabilize physisorbed EtOH and effectively passivate reactive –OH sites. This passivation is expected to hinder chemisorption of the molybdenum precursor, thereby suppressing nucleation on SiO_2. In contrast, the DFT results show that EtOH interacts weakly with TiN surfaces due to the absence of hydroxyl termination and the metallic nature of the substrate, leading to unstable adsorption and easily desorption.

Consequently, surface sites on TiN remain accessible for Mo precursor adsorption, allowing normal chemisorption and film growth to proceed. With these results, EtOH was employed experimentally as a small-molecule inhibitor, resulting in selective inhibition on SiO_2 while preserving deposition on TiN.

ASD-TuP-5 Deriving Realistic Blocking Layer Models for Computational Approaches to Area-Selective Deposition, ***Fabian Pieck**, Ralf Tonner-Zech,* Leipzig University, Germany

Area-selective atomic layer deposition (AS-ALD) has emerged as a key strategy for nanoscale patterning in advanced material design complementing conventional lithography processes. However, achieving high selectivity and process reliability requires precise control of the surface chemistry. As this property is challenging to probe experimentally with atomic-level resolution, computational approaches are used to reveal the fundamental mechanisms governing selectivity. Such insights enable predictive tuning of inhibitor and precursor chemistry as well as substrate functionalization, guiding the rational design of selective deposition processes.

For inhibitor based AS-ALD several studies investigating the interactions of the inhibitor with the non-growth surface are available. [1] However, comprehensive investigations of interactions between precursor molecules and the blocking layer are still sparsely available as a realistic model for the blocking layer must be derived at first. With the present work we want to highlight the currently available approaches to derive realistic blocking layer models.These approaches span a wide range of size scales and balance accuracy against computational cost. Density functional theory (DFT) is frequently employed to identify the most stable blocking layer configurations with high accuracy. However, its use is typically restricted to a small number of structural variations and relatively small surface cells, which limits direct comparison to experimental coverages and defect structures. Random sequential adsorption (RSA) simulations provide an extremely fast way to generate inhibitor layers models on large surface models containing hundreds to thousands of adsorbates. As RSA simulations naturally sample many distinct packing motifs on extended surfaces, they are often closest to experiment. Still, RSA simulations rely on the quality and physical realism of the initial input parameters. More recently, machine-learning potentials (MLP) have enabled molecular dynamics and metadynamics simulations that are orders of magnitude faster than DFT while approaching DFT accuracy when trained on suitable reference data. These approaches enable us to explore the dynamical evolution and restructuring of blocking layers on large systems and timescales, albeit at higher cost than static RSA simulations. We firmly believe that the interplay of all three methods will enable efficient as well as accurate modelling of interactions between precursors and blocking layers in future investigations.

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ASD-TuP-7 Integrating Catalytic PMMA Etching with PMMA–Inhibited ASD of HfO_2, ***Enzo Novoselic**, Christophe Vallée, Natalya Tokranova,* SUNY College of Nanoscale Science and Engineering

Area-selective deposition (ASD) of thin films is critical for advanced semiconductor manufacturing, yet conventional methods often suffer from "mushrooming" defects due to poor selectivity at feature edges and lateral expansion of the isotropic growth. This work presents an alternative approach to ASD on cobalt (Co) substrates while avoiding mushrooming, leveraging catalytic dissociation for both polymer etching and selective deposition. The use of selective catalytic dissociation has been demonstrated for the etching and deposition steps. As an example, Zhang et al. [1] demonstrated selective etching on Pt/Ru/Cu/Ti, while Joseph et al. [2] demonstrated selective deposition on Pt. In this work, a polymethyl methacrylate (PMMA) material is non-selectively deposited on all exposed surfaces (Co and silicon). Through catalytic O_2 dissociation, PMMA atop Co is selectively etched in an atomic layer deposition (ALD) tool, while PMMA on silicon remains intact. Subsequently, the ALD step is performed in the same chamber at the same surface temperature, and under catalytic conditions, enabling selective growth on Co while suppressing nucleation on PMMA. Finally, PMMA is stripped, yielding structures exclusively on Co with sub-nanometer precision and vertical sidewalls. We expect to show results demonstrating that the catalytic processes achieve near-complete selectivity and eliminate lateral overgrowth, addressing the mushrooming effect common in ASD. The use of catalytic dissociation for both etching and deposition steps simplifies integration into existing fabrication workflows. This approach offers a scalable pathway for advanced node patterning, particularly in back-end-of-line (BEOL) metallization and gate oxide applications where material selectivity and feature definition are paramount. [1] Zhang, C.; Leskelä, M.; Ritala, M. Self-Aligned Thin-Film Patterning by Area-Selective Etching of Polymers. Coatings 2021, 11, 1124. https://doi.org/10.3390/coatings11091124 [2] Joseph A. Singh, Nick F. W. Thissen, Woo-Hee Kim, Hannah Johnson, Wilhelmus M. M. Kessels, Ageeth A. Bol, Stacey F. Bent, and Adriaan J. M. Mackus. Chemistry of Materials 2018 30 (3), 663-670. https://doi.org/10.1021/acs.chemmater.7b03818

ASD-TuP-9 Area-selective ALD of NbO_x on TiN/SiO_2 via catalytic O_2 dissociation on TiN for bottom electrode selective DRAM capacitor integration, ***Yujin Lim**,* Kyung Hee University, Republic of Korea*; Myeong Ho Kim, Jin-Sik Kim,* UP Chemical Co., Ltd., Republic of Korea*; Woojin Jeon,* Kyung Hee University, Republic of Korea

Inserting NbO_x ($1<x<2.5$) as an interlayer between the bottom electrode TiN and ZrO_2 in ZrO_2-based DRAM capacitors can promote ZrO_2 crystallization

behavior and enhance tetragonal phase stability to significantly improve electrical properties. However, due to the partially metallic property of NbO_x, non-selective deposition on SiO_2 insulating regions in high-density DRAM structures can cause electrode shorts or parasitic capacitance, leading to cell operation failure. Therefore, area-selective atomic layer deposition (AS-ALD) of NbO_x on the bottom electrode TiN is essential, requiring the development of AS-ALD process. In this study, AS-ALD of NbO_x was investigated on TiN/SiO_2 substrates using O_2 as a reactant. A single 20 s O_2 pretreatment was applied prior to ALD cycles, which comprised precursor feeding, precursor purge, O_2 feeding, and O_2 purge steps. NbO_x deposited using Nb precursor (Nb-1, UP Chemical Co., Ltd.) and O_2 reactant exhibited self-limiting growth behavior and excellent conformality. During the ALD sequence, O* active species only generated on the TiN surface due to catalytic effect of TiN on O_2 dissociation, inducing NbO_x deposition occurs exclusively to the TiN electrode. Therefore, NbO_x nucleation and growth occur exclusively on TiN up to ~150 ALD cycles with negligible deposition on SiO_2, demonstrating a selectivity of 0.96 with a thickness of 1 nm on TiN. This AS-ALD provides a robust platform that can enable direct integration into existing TiN/NbO_x/ZrO_2/TiN stack structures. This study demonstrates a scalable route to locally form NbO_x based interlayer only on TiN electrodes, minimizing area overhead and parasitic growth while improving dielectric performance for next-generation DRAM capacitors.

ASD-TuP-11 Catalytic Area-Selective Deposition of TiO_2 Dielectric Thin Films, ***Seungwoo Lee***, *Soomin Yoo, Gaeul Kim, Woojin Jeon,* Kyung Hee University, Republic of Korea

Rutile TiO_2 has been studied for next-generation nanodevice applications, including dynamic random-access memory capacitor dielectrics, due to its high dielectric constant (>100) and compatibility with atomic layer deposition (ALD) processes. Rutile TiO_2 can be obtained using O_3 as a reactant on conductive oxide electrodes with similar crystal structures, such as RuO_2 and MoO_2, at typical ALD process temperatures. Particularly, TiO_2 grown on MoO_2 has been reported to exhibit a high dielectric constant of ~150. [1] Therefore, the technology to selectively deposit rutile TiO_2 on specific areas, such as MoO_2, offers the possibility to improve the manufacturing efficiency of continuously downscaled nanodevices and enhance device performance. Generally employed inhibitor-blocking approaches for realizing area-selective deposition (ASD) are not industry-friendly and still present several challenges, including residual inhibitor molecules and limited packing density. On the other hand, Inherent ASD, achieved via the inherent selectivity of naturally occurring growth and non-growth surfaces, simplifies the process by eliminating additional processes such as inhibitor deposition and removal.

In this work, we demonstrate the ASD of TiO_2 dielectric thin films on MoO_2 using O_2 as a reactant. O_2 molecules are dissociated by a catalytic reaction on the MoO_2 surface, providing local active sites and enabling the adsorption of the Ti precursor and the growth of TiO_2. [2], [3] Additionally, oxygen transport can occur when two oxides with different oxygen chemical potentials form a heterogeneous interface, thereby facilitating crystallization or accelerating TiO_2 growth. [4], [5] Therefore, using O_2, a milder oxidant than O_3, can form oxygen-deficient TiO_2, which facilitates internal oxygen transfer from MoO_2 to TiO_2 during the deposition process, and consequently induces facile growth of TiO_2. We deposited TiO_2 thin films on SiO_2 and MoO_2 using O_2, and obtained a selectivity of 0.95 on MoO_2 at 320 ℃. The suppressed growth on SiO_2 indicates that the reaction between the Ti precursor and the O_2 reactant was suppressed. When TiO_2 was deposited using O_2 as the reactant, the oxidation state of MoO_2 was found to be reduced compared with deposition using O_3 as the reactant, as evidenced by X-ray photoelectron spectroscopy surface analysis. These results suggest that using O_2 as a reactant facilitated oxygen transport from MoO_2 to TiO_2.

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ASD-TuP-13 Area-Selective ALD of MoO_2 using Ethanol for DRAM Capacitor Electrodes, *Woojin Jeon,* ***Seoeun Yoon***, *Soomin Yoo, Jiwan Hong,* Kyung Hee University, Republic of Korea

Dynamic random access memory (DRAM) continues to scale toward higher density and performance.[1] To sustain sufficient capacitance, DRAM capacitors increasingly adopt high-aspect-ratio structures while both metal and insulator layers are thinned.[2] This trend significantly raises the difficulty of conventional lithography-based patterning, motivating alternative patterning approaches such as area-selective deposition (ASD) and atomic layer etching.

Molybdenum dioxide (MoO_2) has emerged as a promising electrode material. MoO_2 has a high work function of ~5.8 eV, which is higher than that of the currently used TiN (~4.5 eV), offering potential for improved leakage current suppression. Moreover, as a conductive oxide, it can provide a more stable interface with metal oxide dielectrics. It is also compatible with rutile-phase TiO_2, a higher-k dielectric candidate than the currently used ZrO_2. In particular, rutile TiO_2 exhibits low lattice mismatch withMoO_2 on TiN, suggesting that rutile-phase formation—despite rutile being the high-temperature stable phase— promoted during the ALD process without an additional annealing step.As storage-node spacing continues to shrink, unintended deposition on surrounding SiO_2 can create parasitic conductive pathways and electrical shorts. Therefore, selective growth of the MoO_2 electrodeon TiN-defined regions is essential.

In this study, we investigate EtOH-inhibited area-selective atomic layer deposition process of MoO_2. Ethanol (EtOH) can serve as an inhibitor for ASD by suppressing precursor adsorption.The experiments were performed on TiN and SiO_2 substrates using O3 as the reactant. The deposited film initially formed as MoO_x and was converted to MoO_2 via post-deposition annealing in an N_2/O_2 (5%) ambient, as confirmed by X-ray diffraction (XRD). With EtOH inhibition, clear selectivity between TiN and SiO_2 was achieved: MoO_2 grew preferentially on TiN while remaining suppressed on SiO_2, maintaining selectivity of XX up to XX-nanometers. We also investigated Mo precursor chemisorption behavior difference in TiN and SiO_2 using DFT calculation. On SiO_2, the -OH group of EtOH reacts with surface -OH groups to form strong bonds, which hinder subsequent precursor adsorption. In contrast, on metallic surfaces EtOH forms relatively unstable bonds and can readily desorb.

These results suggest a pathway to self-aligned MoO_2 electrode formation and subsequent implementation of high-k rutile TiO_2 in metal–insulator–metal DRAM capacitors.

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ASD-TuP-15 Silane Interactions with Non-Silicon Surfaces, ***Chad Brick***, 11 Steel Road East

Over the last fifteen years, area-selective deposition (ASD) has emerged as a transformative approach for semiconductor manufacturing, enabling reductions in process steps, minimizing lithography requirements, and improving pattern fidelity by eliminating overlay errors. ASD also facilitates precise material deposition in complex three-dimensional structures, including vertical and horizontal trenches and vias, where conventional lithographic techniques often fail.

In this study, we focus on silicon-based inhibitors as a means of surface passivation prior to selective deposition. Although the use of alkoxysilane and chlorosilane self-assembled monolayers (SAMs) and aminosilane small-molecule inhibitors (SMIs) on silicon dioxide is well established, significant uncertainties persist regarding their behavior on the heterogeneous surfaces encountered in advanced device integration. Our discussion addresses inhibitor interactions with non-silicon oxides (Al, Ti, Hf, Ta, W), metals (Cu, Ru), and semiconductors (Si, SiGe), as well as the thermal stability and robustness of these passivation layers under processing conditions.

ASD-TuP-17 Influence of Selective Nucleation on Crystallinity of Aln on Various Substrate Surface by ALD, ***Partha Mukhopadhyay***, Tokyo Electron America, USA*; Ivan Fletcher,* Tokyo Electron America*; Zuriel Caribe, Jim Fulford,* Tokyo Electron America, USA

Recent trend in GaN power devices is amorphous or nanocrystalline ALD ALN for passivation, gate dielectric & etch stop layer due to smoothness, conformality & low leakage. While crystalline ALD AlN is used for stress engineering & piezoelectric applications, a donor layer for enhanced 2DEG channel, Fig.1. Here, we have demonstrated highly uniform (3-sigma thickness variation of <0.5Å) AlN by 200 mm batch ALD of 100+ wafers. The crystalline quality of ALD AlN is highly selective to both substrate surface (Si, quartz, or GaN) & deposition temperature (T_D), evolving from amorphous films at low-T_D to enhanced crystallinity-particularly on GaN templates-at higher-T_D, Fig.2 TEM images. We observed that substrate surface critically controls AlN nucleation & the subsequent deposition dynamics in ALD process. Figure 3 shows that ALD AlN thickness increases linearly with the number of cycles, with a negative intercept indicating delayed nucleation on foreign substrates. Initial nucleation is slow due to the limited availability of reactive sites, requiring multiple incubation cycles

for stable nuclei formation. Once the substrate surface is sufficiently covered, growth accelerates, producing a slope exceeding unity, & an exponential increase in deposition rate. This behavior is characteristic of thermal ALD using TMA, where irreversible chemisorption & surface saturation governs early-stage growth. This delay develops cycle rates to be non-linear. However, high lattice compatibility of AlN with epitaxial AlGaN/GaN surface promotes faster nucleation, thereby, higher cycle rate than AlN/Si. Moreover, this wurtzite nature of the immediate substrate surface of AlGaN enhances crystallinity, evident in the Fig 4 XRD. Besides the reactive site limitation, nucleation delay may also arise from low precursor reactivity, thereby exploring the temperature range revealed faster dep-rate at higher T_D with better crystallinity, due to sufficient thermal energy. Understanding nucleation mechanisms enables precise control of film microstructure for advanced applications. As we observed, Al-O penetration is higher in amorphous AlN, while better crystallinity limits O-diffusion during ALD topping of Al_2O_3 on AlN to suppress its oxidation. The refractive index in this work is ~2.07@75nm on Si, while bulk AlN is 2.1 & thick epi-layer is 2.095. At 350°C AlN on AlGaN/GaN has *n* of 2.096@80nm, indicating a nice cohesive high-quality AlN by TEL ALPHA 8SE™i. In this work, selective nucleation results in amorphous AlN on Si & poly-to single-crystalline film on GaN under varying T_D, with abrupt heterointerfaces, low-C & negligible O-impurities, essential for high-power device integration.

ASD-TuP-19 Effect of NH_3 Addition on Bottom-Up Filling in Mo Ald Using $Mo(Co)_6$, ***Yukihiro Shimogaki****, Souga Nagai, Jun Yamaguchi, Noboru Sato, Naoki Tamaoki, Atsuhiro Tsukune,* The University of Tokyo, Japan

As ULSI scaling advances, interconnect resistance in logic and 3D-NAND devices continues to increase, and Mo is attracting attention as a potential alternative to Cu and W. For practical integration, Mo must be filled into high-aspect-ratio features under process temperature constraints (≤400 °C for logic and ≤600 °C for 3D-NAND). Atomic layer deposition (ALD) is well known for its excellent conformality; however, to avoid seam formation and to promote larger grain growth, bottom-up deposition is preferred. With the goal of realizing bottom-up filling by suppressing growth near the trench opening, we investigate the effect of NH_3 addition in Mo ALD using $Mo(CO)_6$ as the precursor.

Molecular dynamics (MD) simulations employing a machine-learning potential (PFP; Preferred Potential by Matlantis) suggest a strong dependence of $Mo(CO)_6$ adsorption on the surface termination of Mo_2N: $Mo(CO)_6$ undergoes dissociative adsorption when surface N atoms are not exposed, whereas adsorption is inhibited when N atoms are exposed at the surface. Motivated by this insight, we compared the growth per cycle (GPC) between (i) cyclic $Mo(CO)_6$ dosing and purging without NH_3 and (ii) a conventional ALD sequence with alternating $Mo(CO)_6$ and NH_3 exposures. The NH_3-assisted process exhibited a GPC that was approximately one order of magnitude lower than that obtained without NH_3. This reduction is consistent with the simulation trend that N-rich surfaces hinder $Mo(CO)_6$ adsorption, indicating that NH_3 can act as an inhibitor through surface nitridation.

Furthermore, in $Mo(CO)_6$-based deposition, a clear ALD half-cycle saturation behavior is not observed, implying that reactions during the precursor exposure step proceed in a CVD-like manner. NH_3 exposure is therefore expected to modify (nitridize) the surface and suppress subsequent precursor uptake. These findings suggest a route to bottom-up filling by controlling NH_3 delivery such that the degree of nitridation decays from the trench top toward the bottom, thereby preferentially suppressing growth near the opening. Experimentally, we have confirmed bottom-up growth in an ALD process using $Mo(CO)_6$ and NH_3, and we plan to further validate the underlying kinetics and establish the appropriate process window.

ASD-TuP-21 Selective Area Epitaxy of van der Waals Materials*, **Ryan Trice,** Stephanie Law,* Penn State University

Two-dimensional (2D) van der Waals (vdW) materials are interesting for a variety of applications ranging from optoelectronics and photocatalysis to energy storage and topological devices. However, vdW materials synthesized using common techniques like chemical or physical vapor deposition often have a high density of growth-related defects: ranging from grain boundaries and twin defects to pyramidal growth and spiral defects. While pyramidal growth can be minimized through higher growth temperatures, grain boundaries, twin defects, and spiral defects are much harder to overcome.For many applications, especially in electronics and optics, these defects lead to non-radiative recombination, electron scattering, and other undesirable effects. Furthermore, the fabrication of 2D materials into quantum dots (QDs) through bottom-up wet chemistry faces problems with precise location placement and polydispersity in the QDs diameters. This makes the QDs difficult to characterize and is not ideal for most quantum computing and optical setups. Top-down nanofabrication approaches fix this issue but often causes significant damage to the surfaces or edges of the materials. To address these issues, we used selective area epitaxy (SAE) to grow Bi_2Se_3 thin films. SAE is a technique in which thin films nucleate and grow in defined areas on a wafer. This is done through use of a patterned mask where growth conditions are selected such that the film will only nucleate inside the exposed pattern.

In this poster, we will describe SAE growth of Bi_2Se_3 on Al_2O_3(001) and Si (111) substrates using a SiO_2 mask. The mask was deposited onto a 10x10mm substrate by atomic layer deposition. Etching of the SiO_2 mask was done with standard photolithography techniques and a direct write laser beam lithography system, and the SiO_2 was removed from selected areas using a wet chemical etch, resulting in micron-scale holes of various shapes and sizes. The processed substrates were then loaded into a molecular beam epitaxy chamber for growth of the Bi_2Se_3 film. First, we will look at the effects of different substrate temperatures on the selective growth of the Bi_2Se_3 thin films. Second, we will present the geometric influence of variously shaped patterns on the crystal quality of the selectively grown films. Third, we present the effect and viability of nano-scale patterns for selective growth of vdW materials. Further studies will focus on using different materials for the substrate and mask.

ASD-TuP-23 Impact of Silica Surface Chemistry on Nucleation of Ruthenium Area-Selective Atomic Layer Deposition*, **Shixian Ha,*** Stony Brook University/Brookhaven National Laboratory, China*; Hwan Oh, Won Il Lee,* Brookhaven National Laboratory, Korea (Democratic People's Republic of)*; Md Istiaque Chowdhury,* Veeco Instruments Inc., Bangladesh*; Xiao Tong, Mingzhao Liu, Chang-Yong Nam,* Brookhaven National Laboratory

As semiconductortechnologyadvances toward sub-5 nm nodes, ruthenium (Ru)area-selective atomic layer deposition (AS-ALD) is of growing interestas a back-end-of-line (BEOL) interconnect metal due to its favorable scaling behavior over copper (Cu). In BEOL, silica is the dominant dielectric and intended non-growth surface, yet its formation-dependent surface chemistry and its impact on Ru nucleation remain insufficiently explored. Here, we investigate Ru ALD on native oxide SiO_x (N-SiO_x) and thermally grown SiO_2 (T-SiO_2) as model dielectric surfaces using bis(ethylcyclopentadienyl)ruthenium(II) [$Ru(EtCp)_2$] with an O_2 co-reactant at 200–300 °C. Cross-sectional scanning electron microscopy (SEM) with surface coverage analysis reveals that both surfaces exhibit intrinsically delayed nucleation, with different extentscorrelated to their surface hydroxyl (–OH) densities. The lower –OH density of T-SiO_2 results in sparse, island-like nucleation, whereas the higher –OH density of N-SiO_x promotes more uniform nucleation. Introducing a hydrogen-assisted ABC-type ($Ru/O_2/H_2$) sequence markedly shortens the nucleation delay, indicating that the H_2 step promotes nucleation on hydroxyl-deficient T-SiO_2, likely via insitu rehydroxylation. Furthermore, grazing-incidence X-ray diffraction (GI-XRD), atomic force microscopy (AFM), and four-point probe measurements show that these surface-dependent nucleation behaviors lead to distinct early-stage film evolution and associated Ru film properties, including phase, morphology, and resistivity. Overall, this work provides mechanistic insight into surface-chemistry-driven Ru nucleation and establishes design principles for controlling selective growth on dielectric surfaces, advancing ASD strategies for next-generation BEOL integration.

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ASD-TuP-25 Inhibition of Atomic Layer Deposition of Al_2O_3 with Trimethyl Aluminum Precursor by Perfluoroalkylpolyether Thin Layer*, **Hiroaki Iwamoto,*** Yuki Shibutani,* AGC Inc., Japan

Area-selective atomic layer deposition (AS-ALD) is a promising technique for advanced semiconductor manufacturing, capable of replacing conventional processes like photolithography and etching to fabricate complex patterns.[1] Significant efforts have focused on developing highly selective ALD processes through surface pretreatment or process modifications, such as deposition/etching cycles.[2] The use of inhibitors to deactivate non-growth areas against ALD precursors and reactants has

proven effective for area-selective deposition. However, the molecular size and chemical reactivity of the ALD precursors strongly affect inhibition performance. Achieving highly selective ALD processes often requires large, less reactive precursors, which exhibit lower growth rates.[3,4] While fluorine-containing surface modification materials can reduce surface energy and suppress molecule deposition, perfluoroalkyl-coated surfaces show limited inhibition performance in Al_2O_3 ALD with trimethylaluminum (TMA), a small and highly reactive precursor.[5]

In this study, a perfluoroalkylpolyether (PFPE)-substituted alkoxysilane inhibitor (inhibitor 1) was developed, exhibiting high inhibition performance for Al_2O_3 ALD using TMA as the precursor. PFPE features a flexible fluorinated structure that differs from perfluoroalkanes due to its ether moieties, which reduce steric hindrance and increase molecular rotation. The inhibitor was evaluated as follows: a monolayer was prepared by spin-coating the compound onto UV/O_3-treated silicon substrates, followed by post-annealing to remove residual solvent. After washing with fluorinated solvent, the ALD process was performed with TMA as the precursor, H_2O as the reactant, at a stage temperature of 200 °C, and a growth-per-cycle (GPC) value of 0.7 Å. The inhibition performance was measured using XPS analysis of the Al2O3 film thickness, specifically evaluating the Al/Si ratio. Inhibitor 1 maintained its performance through 50 ALD cycles. For comparison, a short perfluoroalkyl-substituted trialkoxysilane (inhibitor 2) underwent the same procedure, but its inhibition performance deteriorated after 20 cycles. Water contact angle (WCA) measurements revealed that inhibitor 1-coated surfaces were more hydrophobic (112.3°) than those coated with inhibitor **2** (107.2°). These results suggest that flexible molecular structures and high hydrophobicity are critical for achieving high inhibition performance in ALD processes using highly reactive precursors like TMA. Detailed surface profiles and insights into inhibitor development for AS-ALD processes will be presented.

ASD-TuP-27 Area Selective Atomic Layer Deposition of Ruthenium with Pinacolborane as a Small Molecule Inhibitor*, **Sundas Ismaeel,*** University of Helsinki, Finland*; Heta Elisa Nieminen,* ASM Microchemistry Ltd., Finland*; Mykhailo Chundak, Mikko Ritala,* University of Helsinki, Finland

With the downscaling of microelectronic devices, it is important to find efficient small molecule inhibitors (SMI) and processes to achieve selective growth between different materials on substrate surfaces. Ru is one of the promising alternatives to conventional interconnect metals, like Cu because of its better electrical performance concerning reliability and resistivity upon downscaling.[1, 2, 3, 4] Area Selective Atomic Layer Deposition (AS-ALD) of Ru would be useful in making interconnects bottom-up inside 3D features without formation of voids. AS-ALD can also overcome challenges of conventional patterning with lithography like cost and misalignment between subsequent layers of interconnect metallizations.[5] This study investigates pinacolborane as a SMI for the area selective ALD of Ru on native SiO_2, Pt, TiN, Co, Cu, HfO_2, and ZrO_2 surfaces. These surfaces were subjected to 8 exposures of a 10 s pulse of pinacolborane and 30 s of N_2 purging, followed by Ru film deposition using bis(cyclopentadienyl)ruthenium ($RuCp_2$) and O_2 at 340°C. The results from energy dispersive X-ray spectroscopy indicate that the Ru film growth is inhibited on native SiO_2, TiN, Co, Cu, HfO_2, and ZrO_2 surfaces, making them non-growth surfaces while the film grows normally on Pt, making it growth surface. It was also observed that Ru film grows on Ru surface in the presence of pinacolborane. X-ray photoelectron spectroscopy revealed the presence of boron on HfO_2 surface but not on Pt surface, after being exposed to pinacolborane. The optimization of temperature and effective pinacolborane dose is essential for achieving maximum selectivity.

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ASD-TuP-29 Topology-Directed Silicide Formation: An Explanation for the Growth of C49-Tisi₂ on the Si(100) Surface*, **Lukas Hückmann,*** *Jonathon Cottom, Jörg Meyer,* Leiden University, Netherlands*; Emilia Olsson,* University of Amsterdam, Netherlands

The optimization of metal-semiconductor (MS) junctions is a fundamental prerequisite for advancing electronic device performance. Titanium disilicide ($TiSi_2$) is a widely used material due to its low electrical resistivity, good chemical stability, and low Schottky barrier height at the MS interface [1]. In practice, the existence of multiple polymorphs makes it challenging to grow phase-pure films. Among these, the C54-$TiSi_2$ phase exhibits the desired beneficial properties; yet it is the metastable, high-resistivity C49-$TiSi_2$ modification that preferentially nucleates on Si substrates. The origin of C49-selective nucleation, however, remains debated [2]. We present a first-principles atomistic model of Ti adsorption on the *c*(4x2)Si(100) surface that highlights the key role of surface symmetry and reconstruction for the initial stages of the interfacial TiSi2 formation process [3]. Based on DFT calculations ranging from the dilute limit to a coverage of two monolayers, we identify the energetically most stable configuration as a Ti-Ti dimer pair consisting of a surface adatom and a first-subsurface interstitial. This specific pairing coincides with the local reversal of the Si(100) surface reconstruction, which creates a characteristic low-symmetry adsorption pattern that is unique to the C49-$TiSi_2$ phase and thereby serves as a nucleation template for C49.This model aligns with experimental observations like the Stranski-Krastanov growth mode, the preferential formation of C49-$TiSi_2$ despite being less favorable than the competing C54 phase, and why disrupting the surface structure via amorphization removes the nucleation template and restores thermodynamically driven growth of the latter. This atomistic perspective on phase-selective growth suggests that such surface pre-treatment could obviate the need for the C49-C54 transformation, thereby minimizing the thermal budget in the fabrication of next-generation nanoelectronic devices.

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ASD-TuP-31 Area Selective Deposition of Metal on Dielectric using Aldehyde Inhibitor and Novel Ruthenium Precursor*, **Chi Thang Nguyen,*** Argonne National Laboratory, USA and Leibniz-Institute for Solid State and Materials Research Dresden, Germany*; Bratin Sengupta,* Argonne National Laboratory, USA*; Harish Parala, Anjana Devi,* Leibniz Institute for Solid State and Materials Research Dresden, Germany*; Jeffrey W. Elam,* Argonne National Laboratory, USA

Area-selective atomic layer deposition (AS-ALD) is a promising bottom-up approach for enabling self-aligned patterning in semiconductor manufacturing, reducing process complexity, costs, and edge placement errors. In particular, AS-ALD of metals on dielectric surfaces (MoD) is gaining increasing attention for advanced interconnect applications, such as middle-of-line and back-end-of-line. The AS-ALD MoD process enables metal deposition on a target dielectric surface while blocking growth on other metal or dielectric surfaces. However, achieving selectivity between chemically similar dielectric surfaces – MoD/D (metal-on-dielectric with a non-growth dielectric area) remains highly challenging due to their comparable surface terminations, surface energies, and reactivity toward metal precursors.

In this study, we explore the selective deposition of Ru on SiO_2 versus Al_2O_3 surfaces using an aldehyde-based inhibitor, butyraldehyde (BTA), and a new Ru precursor, $C_4H_6Ru(CO)_3$. The results reveal selective Ru growth on SiO_2, but not on the BTA-inhibited Al_2O_3 surface. Interestingly, the aldehyde-based inhibitor was previously reported to adsorb on nitride surfaces but not on hydroxyl-terminated oxide surfaces. The adsorption behavior of the inhibitor on various surfaces was investigated using water contact angle (WCA) and Fourier transform infrared spectroscopy (FTIR). Selectivity was assessed through ellipsometry, X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM). This work introduces a new approach for AS-ALD of MoD/D and self-aligned Ru patterning for next-generation semiconductor fabrication.

ASD-TuP-33 Quantifying Fidelity and Resolution in Direct-Write Chemical Vapor Deposition*, **Eeshan Ketkar**,* University of Chicago*; Koichi Tanaka,* Argonne National Laboratory, USA*; Supratik Guha,* University of Chicago

Area-selective chemical vapor deposition (CVD) requires precise control over precursor transport, surface diffusion, and reaction kinetics in order to achieve reproducible, spatially confined growth. Here we investigate these governing processes in a direct-write CVD geometry, where precursor molecules are locally delivered through micro- and nanoscale printheads onto a laser-heated substrate, enabling controlled, site-specific deposition without masks.In this work we establish a quantitative framework that links nozzle geometry and operating conditions to measurable deposition outcomes using a modified Knudsen cosine emission model incorporating precursor diffusion and surface desorption. The framework enables systematic evaluation of three central performance metrics for area-selective CVD: fidelity, throughput, and resolution. Fidelity is defined through reproducibility of local deposition profiles, including height, feature width, precursor flux through micro- and nanochannels, and surface diffusion length. Throughput reflects the rate at which simple geometries can be patterned, while resolution describes the minimum achievable feature size. The model is applied to localized aluminum depositions on titanium-nitride-coated silicon substrates under varying temperature, pressure, and deposition time conditions using both pulled glass micropipettes (10 µm internal diameter) and microfabricated silicon printheads (600 nm apertures). The extracted diffusion length exhibits systematic and physically consistent trends with nozzle height, deposition time, and temperature, and correlates directly with feature broadening (FWHM), demonstrating internal consistency across geometry, height, and time scans. These results identify diffusion length as a unifying parameter governing feature confinement and provide mechanistic insight into the transport–reaction interplay that controls area-selective CVD. By establishing direct connections between transport physics, surface processes, and feature formation, this work advances a physics-based understanding of area-selective CVD and provides design rules for achieving high-fidelity, spatially selective growth across micro- and nanoscale length scales.

ASD-TuP-35 Selective Infiltration Into Polymeric Materials for Advanced Nanofabrication*, **Jordi Antoja-Lleonart**, Teresa Elenes-Cervantes, Olga Muntada, Sara Durán, Ricard Noy, Francesc Perez-Murano, Marta Fernández-Regúlez,* Institute of Microelectronics of Barcelona (IMB-CNM, CSIC), Spain

The advent of vapor phase infiltration (VPI) and related techniques has introduced a powerful method for the incorporation of inorganic materials with nanoscale precision, offering capabilities that are difficult to achieve with conventional lithography or deposition approaches. In particular, these techniques are highly relevant for the processing of semiconductor-based quantum devices, whose performance critically depends on their exceptional pattern quality.

Therefore, we combine advanced lithographic processes with VPI to selectively incorporate binary oxides into established polymeric materials, thereby enhancing pattern definition. This selective infiltration method results in hybrid organic-inorganic structures with improved line edge roughness (LER) and lower dry etch rates than conventional photoresists. By using plasma ashing after the VPI step, we may remove the organic fraction from these hybrid structures and convert them to fully inorganic oxide features that act as robust hard masks for high-fidelity pattern transfer.

In this work, we investigate VPI of Al_2O_3 in two technologically relevant thin-film platforms: (i) **PS–b–PMMA block copolymers (BCP)** used for bottom–up pattern formation and (ii) **pre–patterned resists** generated by electron beam lithography, representative of top–down lithographic processes. In BCP systems, nanoscale ordering is achieved through self-assembly and further alignment using directed self-assembly (DSA) processes on lithographically defined patterns (Fig. S1). VPI of aluminum oxide takes place selectively in the PMMA nanodomains of the films (Fig. S2), which allows us to generate hybrid or oxide structures of great interest to high-resolution, low-LER patterning.

Across both systems, we perform a systematic study of the infiltration kinetics, comparing precursor uptake, saturation behavior, and infiltration depth between homopolymers and nanostructured BCP domains with different morphologies. These measurements provide insight into how polymer chemistry, domain confinement, and pattern geometry control VPI growth.

ASD-TuP-37 Area Selective Deposition of Aluminum Oxide on Native Oxide Surfaces for Dielectric on Dielectric (DoD) and Dielectric on Metal (DoM) Applications*, **Drew Hood**, Rong Zhao,* Entegris

The area selective deposition (ASD) of aluminum oxide on multiply substrates is investigated with highly selective processes observed for both dielectric on dielectric (DoD) and dielectric on metal (DoM). Selectivity is achieved without the use of inhibitors on native oxide surfaces via precursor reactivity and oxidant choice. Using the same precursor selectivity for DoD or DoM can be achieved based on the choice of oxidant. Here we showcase how a small process change can lead to the complete inversion of selectivity. Mechanisms based on surface termination are explored to describe the underlining fundamentals behind the reversibility of selectivity.

ASD-TuP-39 Engineered MoO_3 Thickness Control for Area-Selective Chemical Vapor Deposition of Two-Dimensional MoS_2*, **Chu-Te Chen**,* Department of Materials Design and Innovation, The State University of New York at Buffalo*; Anthony Cabanillas, Huamin Li,* Department of Electrical Engineering, The State University of New York at Buffalo*; Fei Yao,* Department of Materials Design and Innovation, The State University of New York at Buffalo

The integration of two-dimensional (2D) semiconductors into Si-CMOS technology offers a promising pathway for next-generation nanoelectronics. However, achieving precise spatial control of 2D material synthesis, which is critical for scalability and device integration, remains a fundamental challenge. Area-selective chemical vapor deposition (CVD) addresses this need by enabling location-on-demand synthesis; however, systematic engineering of synthesis processes to achieve reproducible device-grade structures remains largely unexplored. This work advances area-selective CVD through rational two-stage optimization of precursor engineering and CVD parameters, establishing a viable approach for scalable, spatially controlled synthesis of 2D heterostructures.

We engineer MoO_3 precursor thickness through electron-beam evaporation followed by wet chemical etching. Quantitative AFM analysis reveals power-law dissolution kinetics, enabling deterministic control of the optimal precursor window with excellent reproducibility. This engineered area-selective seed layer undergoes sulfurization in a two-zone CVD furnace. Through systematic parameter optimization, we identify two critical control mechanisms: (1) Sulfur precursor saturation, where increasing carrier-gas flow at optimized temperature enhances MoS_2 coverage to a saturation regime and further flow increases yield negligible change. (2) Molybdenum temperature dominance, where optimizing the Mo precursor temperature produces a five-fold enhancement in MoS_2 lateral width, extending domain dimensions above 10 µm.

We demonstrate location-selective synthesis through multiple patterned architectures: arrays of MoS_2, transmission line model (TLM) structures, and complex designs including text and Hilbert curve motifs. Optimized synthesis yields reproducible MoS_2/α-MoO_3 heterostructures with precise spatial control and excellent pattern fidelity. Raman spectroscopy confirms MoS_2 formation and reveals that amorphous MoO_3 crystallizes to α-MoO_3 during CVD, creating a functional interfacial dielectric layer.

This work establishes a rational framework for engineering area-selective CVD of transition metal dichalcogenides through systematic precursor thickness engineering and parameter optimization, enabling scalable, spatially controlled synthesis of 2D heterostructures for advanced nanoelectronics.

ASD-TuP-41 Area Selective Deposition of Si Base Film by PECVD*, **Shivan Antar**,* University at Albany-SUNY

While Atomic Layer Deposition is the most popular process for Area Selective Deposition (ASD), in this work a plasma-enhanced chemical vapor deposition (PECVD) process is employed to selectively deposit a silicon-based film on metal oxide resist (MOR), silicon, and silicon dioxide surfaces while suppressing deposition on an organic planarization layer (OPL) carbon surface. With this (PECVD) process, selective growth is observed during the initial 20 seconds of the process, after which selectivity degrades and silicon deposition on the carbon surface begins as shown in (**Figure 1**). Furthermore, it has been found that the selectively deposited thickness is enhanced at reduced process pressures for deposition times below 30 seconds. This time dependent (ASD) by (PECVD) process has already been observed in previous publication [**1-2**] and the mechanisms behind this selectivity improvement for short time of process will be discussed based on an understanding of plasma/surface interactions based on in-situ and ex-situ characterization of the plasma and the materials.

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ASD-TuP-43 Enhanced Via Rc Reduction Using Advanced Self–Assembled Monolayers in Scaled BEOL Cu Barrier–Seed Integration, ***Zheng Ju***, AMAT

As BEOL technology scales into the sub–2–nm regime, via resistance (Rc) reduction in copper barrier–seed (CuBS) integration becomes increasingly challenging. Selective self–assembled monolayers (SAMs) have emerged as an effective approach to suppress unwanted bottom barrier and liner growth, enabling significant via Rc improvement. However, continued via dimension scaling requires further enhancement in SAM selectivity while maintaining robust removal behavior and dielectric compatibility.

This work presents an advanced SAM–enabled integration scheme designed to support further via Rc reduction in scaled BEOL interconnects. The developed SAM demonstrates improved metal selectivity relative to a production–like baseline, enabling more effective suppression of bottom barrier and liner deposition. Integration compatibility is evaluated across multiple metal substrates relevant to advanced BEOL applications.

Structural and surface analyses confirm reduced interfacial growth and effective SAM removal with minimal residual contamination. Electrical testing shows via resistance performance comparable to prior high–selectivity solutions and approximately 50% - 55% improvement relative to a non–SAM reference, with improved resistance distribution under optimized conditions. Overall, this approach provides a scalable and manufacturable pathway for continued via Rc reduction in advanced BEOL Cu interconnects.

ASD-TuP-45 Selective Liner for Via Rc Reduction in Advanced BEOL Cu Barrier Seed Integration, ***Yang Zhou***, AMAT

With the continued shrinkage of critical dimension (CD) and increase of aspect ratio (AR) of interconnect, the Cu gapfill and reduction of via resistance are becoming more and more challenging for Back-End of Line (BEOL) process. Advanced RuCo binary liner improves Cu gap fill performance in advanced node structures. Selective barrier with self-assembled monolayer (SAM), which is integrated in Cu Barrier Seed process, blocks the barrier growth at via bottom and reduces via Rc. In this paper, we propose a selective liner approach to further reduce the via Rc.

This work presents the selective Ru liner process which can further decrease the via Rc compared with selective barrier process. With the help of SAM, the selective Ru liner process selectively deposits Ru on via sidewall but not on via bottom. Ru on the sidewall improves Cu gapfill and no Ru on via bottom decreases via Rc. The Cu gapfill performance and via resistance reduction are achieved at the same time by selective Ru liner process.

Surface and elemental analyses with multiple blanket metal substrates and dual damascene structures confirm suppressed Ru growth on SAM. Electrical testing shows via resistance performance improvement of ~20% over benchmark selective barrier process. Integration compatibility is evaluated and certain integration challenges are identified to meet future technology scaling requirements. Overall, this selective liner approach provides a possible pathway of extending Cu Barrier Seed Integration scaling to sub 2nm node.

ASD-TuP-47 Influence of Substrate Interactions on the Growth of MoO_3 on Gr/Ru(0001) and HOPG, ***Buddhika Alupothe Gedara***, *Maria Sushko, Zdenek Dohnalek, Zbynek Novotny,* Pacific Northwest National Laboratory

Two-dimensional transition-metal oxides (TMOs) are promising for electronic applications due to their stability and favorable electrical and optical properties. Among them, MoO_3 stands out for its high dielectric constant, wide band gap (~2.9 eV), and catalytic activity, enabling diverse electronic and energy-related applications. In this work, we study the role of surface topography and charge transfer on the growth mechanism of MoO_3 on well-defined graphene (Gr) surfaces: atomically flat highly oriented pyrolytic graphite (HOPG; free-standing Gr) and metal-supported Gr on Ru(0001), exhibiting a moiré superstructure where C atoms from Gr arrange in a FCC (face-centered cubic), HCP (hexagonal close-packed), and atop pattern with respect to the Ru(0001) substrate. The molybdenum trioxide was deposited by sublimation of MoO_3 powder on the substrates held at room temperature,and the oxide growth was observed using scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS). The MoO_3 islands on Gr/Ru(0001) nucleate at both FCC and HCP regions and are smaller than those observed on HOPG. On both substrates, the size of the MoO_3 islands and their order increase with increasing annealing temperature. A distinct height difference of MoO_3 is observed on these two substrates. The height of MoO_3 islands on Gr/Ru(0001) corresponds to single layer of MoO_3, whereas the height of the MoO_3 island on HOPG corresponds to double layer. XPS data show that Mo in the islands on HOPG is predominantly in (6+) oxidation state while on Gr/Ru(0001) at least half is reduced to (5+). Quantitative XPS analysis shows the same MoO_3 stoichiometry on both substrates, indicating a substantial charge transfer between MoO_3 islands and Gr/Ru(0001). Our results demonstrate that substrate-induced interfacial interactions and charge transfer play a decisive role in controlling the nucleation, growth mode, thickness, and electronic structure of MoO_3 on graphene-based supports, providing a pathway to tailor 2D TMO heterostructures for electronic and catalytic applications.

Figure 1. Height differences of MoO_3 on Gr/Ru(0001) (a) and HOPG (b) following annealing at 500 K. (c) Height profiles along the blue line in image (a) and the green line in image (b).

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