

Sunday Afternoon, March 29, 2026

Tutorial

Room ETEC Atrium - Session TUT1

Tutorial Session I

Moderators: **Kandabara Tapily**, TEL TTCA, Albany, **Christophe Vallée**, University of Albany

1:00pm **TUT1-1 Direct Self-Assembly (DSA):From Materials to Integration**, **Patricia Pimenta Barros**, CEA-LETI, France **INVITED**

The Directed Self-Assembly (DSA) of block-copolymers (BCPs) has been intensively investigated as a cost-effective and complementary solution to conventional i193nm or EUV lithography for CMOS applications [1-3]. This technology has also showed an interest in beyond CMOS applications such as Single Electron Transistor devices [4], in the fabrication of nano-structures for optoelectronic [5] and photovoltaic devices [6], or in various other technology [7], due to its ability to precisely control nanopatterns over large macroscopic length scale.

This tutorial aims to give an overview of the selective processes required in DSA patterning technique. Indeed, the DSA patterning relies on the precise control of the surface modifications in order to orientate and localize the nanopatterns on the wafer surface. For that purpose, chemoepitaxy and graphoepitaxy approaches, which are the two main ways to perform DSA, will be explained and compared. Based on LETI's PS-b-PMMA BCP background, surface modifications solutions such as UV exposure, embedded neutral layers, sequential grafting will be then detailed [8-9]. After the self-assembly process, the nanopatterns created by the BCP is usually transferred into the underlayers. For that purpose, one block (ex: PMMA) has to be selectively removed over the other one (ex: PS) to create the final nanostructures. Different strategies for a selective etching of PMMA over PS will be exposed depending on the BCP morphology and applications (lines, contact or pillars). For example, cyclic PMMA dry etching steps [10], selective ALD [11] or Sequential Infiltration Synthesis (SIS) [12] methods will be discussed. The basics of the DSA patterning will be addressed through a few DSA application examples.

1. Tiron, R. et al, Proc. SPIE 8680, (2013)
2. Jeong, S-J. et al, Materials today 16 (12), (2013)
3. Lee, K. et al. MRS Commun. 15, 1269–1288 (2025)
4. Gharbi, A. et al, Proc. SPIE 10586, (2018)
5. Feougier, R. et al, Proc. SPIE PC12497, (2023)
6. Garozz C. et al, Phys. Status Solidi A 210, No. 8, (2013)
7. Segalman R. A., Materials Science and Engineering, Vol. 48, Issue 6, (2005)
8. Paquet, A. et al, Proc. SPIE 10958, (2019)
9. Pimenta-Barros, P. et al, Proc. SPIE 10584, (2018)
10. Sarrazin, A. et al, J. Vac Sci. Technol B36, 041803 (2018)
11. Gay, G. et al., Nanotechnology, 21, 435301 (2010)
12. Frascaroli, J. et al., ACS applied materials & interfaces 8 (49), (2016)

2:00pm **TUT1-5 Selectivity in Plasma Processes**, **Eric Liu**, TEL TTCA **INVITED**

3:30pm **TUT1-11 Selective Epitaxy Growth of Group IV Materials for CMOS Devices**, **Joël Kanyandkwwe**, **Justine Lespiaux**, **Jean-Michel Hartmann**, CEA/LETI-University Grenoble Alpes, France **INVITED**

In advanced logic devices, specific regions of transistors must be highly crystalline, with precise dopant concentration, particularly for junctions and contacts formation. The most effective method to fabricate these high-quality, highly doped regions is epitaxial growth in industrial RP-CVD (Reduced Pressure Chemical Vapor Deposition) reactors.

A critical requirement of this process is localization: epitaxial growth must be precisely confined to areas where crystalline seed layers are exposed, while dielectric regions have to remain free of deposits. Selective Epitaxy Growth (SEG) is a critical technological enabler in advanced Field Effect Transistors.

To achieve high quality selective epitaxy, several approaches have been explored. Historically, straightforward selective epitaxial growth was used to thicken, at relatively high temperatures (e.g. in the 600°C – 750°C range), sources and drains regions with heavily in-situ doped materials such as Si:P or SiGe:B. This was typically done using co-flow processes during which mainstream deposition and etchant gases (such as SiH₂Cl₂, GeH₄, B₂H₆, PH₃ and HCl) were simultaneously fed into the growth chamber. Co-flow processes were up to now well-suited for CMOS mass production as illustrated in *Figures 1-3*.

Several challenges must nowadays be overcome for advanced technological nodes. First, top transistors have to be fabricated with a drastically reduced thermal budget (e.g. lower than 500°C, ideally close to 400°C) above already existing transistors in monolithic 3D [1] and Complementary FET architectures (CFET) [2]). Second, the demand for aggressive device performance requires ultra-low electrical resistance materials (for sources/drains and contacts). This comes with stringent requirements in terms of morphology, the presence of new materials and aggressive doping levels, all being challenging in terms of growth selectivity control.

However, low-temperature SEG processes present major technical challenges, fueling intense research and innovation in the CVD epitaxy community [3][4][5].

In this presentation, we will describe some specific features and challenges of advanced SEG processes. We will notably present the innovative solutions implemented to have low temperature SEG, such as the use of new gaseous or liquid precursors, cyclic processes with the alternance of non-selective growth steps and selective etch steps for different process and so on.

[1] D. Bosch *et al.*, 2025, *IEDM*.

[2] S. Liao *et al.*, 2023, *IEDM*, pp. 1-4.

[3] E. Rosseel *et al.*, 2024, *Meet. Abstr. MA2024-02 2298*.

[4] R. Khazaka *et al.*, 2022, *Meet. Abstr. MA2022-02 1187*.

[5] J. Kanyandekwe *et al.*, 2022, *ECS Trans.* 109, 121.

4:30pm **TUT1-15 Selective Thermal Atomic Layer Etching or Spontaneous Etching**, **Marcel Junige**, **Steven M. George**, University of Colorado Boulder **INVITED**

Microelectronic devices have advanced from historic planar to complex 3D architectures. Corresponding nanomanufacturing needs selective atomic layer deposition (ALD) and etching (ALE). Vertical pattern transfer relies on unidirectional, anisotropic plasma ALE. Conversely, lateral pattern release without line of sight requires the omnidirectional, isotropic material removal that is provided by thermal ALE or spontaneous etching.

This tutorial will overview selectivity studies, describe materials that have been etched selectively by thermal chemistries, and provide explanations of this selectivity. Strategies to achieve selective thermal dry etching are based on different combinations of thin film materials and reactants, thermodynamic favorability of reactions, stability or volatility of reaction products, as well as reactant pressures and process temperature.

Selectivity has been observed during thermal ALE. Al₂O₃ thermal ALE is a model system defined by sequential fluorination using hydrogen fluoride (HF) and ligand exchange using Al(CH₃)₃. This Al₂O₃ etch mechanism exhibited high selectivity versus ZrO₂ non-etch because ZrF₄ did not ligand exchange with Al(CH₃)₃. Consequently, ZrF₄ provided an excellent etch stop after Al₂O₃ thermal ALE using HF and Al(CH₃)₃.

In contrast, ZrO₂ or HfO₂ thermal ALE using sequential HF and SiCl₄ exposures was selective versus Al₂O₃ non-etch. After fluorination, ZrF₄ or HfF₄ can ligand exchange with SiCl₄, whereas the reaction of AlF₃ with SiCl₄ is thermodynamically unfavorable at 250°C.

Selective TiN thermal ALE has been demonstrated via sequential oxidation using O₃, followed by halogenation to a volatile halide using HF. TiF₄ readily sublimed at 250°C. In contrast, AlF₃, ZrF₄, and HfF₄ are thermally stable even above 300°C. This resulted in Al₂O₃, ZrO₂, and HfO₂ non-etch using O₃ and HF.

Selectivity has also been observed during spontaneous etching. Selective Si spontaneous etching has been demonstrated using consecutive HF exposures that released volatile SiF₄ and H₂ products above 150°C. In contrast, HfF₄ is a thermally stable solid, resulting in HfO₂ non-etch using HF at 275°C.

Selective SiN_x versus SiO₂ spontaneous etching has also been discovered and depends on the presence of polar co-adsorbates during consecutive HF exposures. Anhydrous HF alone formed F⁻ surface species that selectively etched SiN_x. In contrast, co-dosing NH₃ with HF formed HF₂⁻ surface species that selectively etched SiO₂.

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Area Selective Deposition

Room ETEC Atrium - Session ASD1-MoM

ASD and Inhibitors I

Moderators: Annelies Delabie, imec and KU Leuven (University of Leuven), Rachel Nye de Castro, Lam Research

8:15am **ASD1-MoM-1 Welcome and Sponsor Thank You,**

8:30am **ASD1-MoM-2 From Concept to Reality: The Evolution and Impact of Area Selective ALD, Stacey Bent, Stanford University** INVITED

The continued downscaling of electronic device dimensions requires the development of new, precise patterning methods that are compatible with high-volume manufacturing. Area selective atomic layer deposition (AS-ALD) continues to gain attention as an important method to achieve nanoscale features at the sub-10 nm length scale. It is known that tuning the surface chemistry of the substrate can be used to either inhibit or enhance ALD nucleation, leading to selective deposition. Since proof of concept of AS-ALD was introduced more than 20 years ago, a key strategy has been the use of inhibitors that can alter the native surface reactivity to block nucleation. Initial studies used long-chain self-assembled monolayers as inhibitors, evolving more recently to also include small molecule inhibitors and other surface functionalization chemistries. This inhibition approach enables good selectivity in AS-ALD of thin films on a variety of substrate materials, including dielectrics and metals, and is in use today. As the field advances, additional process parameters will need to be tuned if we are to meet future AS-ALD application requirements, which are now dictating a wide breadth of materials systems (including dielectric/dielectric, metal/dielectric, carbon/dielectric, multicolor patterns, etc.) as well as a high degree of selectivity. I will start with a historical perspective and then introduce some of the approaches currently under development, including tuning the ALD precursor in concert with the inhibitor, and development of AS-ALD for new applications. Ultimately, developing molecular design rules for both inhibitors and ALD precursors will be critical for applying AS-ALD more widely to future challenges in nanoscale fabrication.

9:15am **ASD1-MoM-5 NHC 2.0: Surface-Dependant NHC Activation, Sean Barry, Carleton University, Canada; Zeng Rong Wong, Emmett DesRoche, Francesco Tumino, Queen's University, Canada; Shengzhao Wang, University of Minnesota; Eden Goodwin, Carleton University, Canada; Alastair McLean, Queen's University, Canada; Matthew Neurock, University of Minnesota; Cathleen Crudden, Queen's University, Canada**

N-heterocyclic (NHCs) are highly selective small molecule inhibitors (NHCs) for metal surfaces, while leaving dielectric surfaces free for deposition. Generally, NHCs are persistent, but they are not easily isolated due to a pathway that allows them to dimerise into ene-tetraamines. To prevent this, NHCs are delivered by the controlled thermal disassembly of the imidazolium bicarbonate salt, to produce one equivalent each of NHC, CO₂, and water. This can be a problem in sensitive workflows where an equivalent of water can interfere with surface chemistry.

We have recently synthesised an adduct of an N-heterocyclic carbene (NHC) and H₂, a novel molecular precursor to deliver NHCs in the gas phase. This NHC precursor undergoes volatilisation at 120°C without loss of H₂, unlike the imidazolium bicarbonate that generates free NHC before reaching the surface. Scanning tunnelling microscopy was used to discover the difference of surface chemistry on gold and copper metal surfaces: On Au (111) surfaces, surface-enabled dehydrogenation occurs selectively only at edge and kinked sites of the surface reconstruction. On a more reactive Cu (111) surface, ordered carbene monolayers form at room temperature on the crystal terrace, with a second deposition at 50°C resulting in extensive coverage of (111) faces. Density functional theory (DFT) calculations were used to interrogate the mechanism of the C-H activation: this occurs by sequential surface C-H activations.

9:30am **ASD1-MoM-6 Area Selective Ruthenium Deposition with Dual Inhibitors, Kai-Hung Yu, Tarek Dinar, TEL Technology Center America; Ryota Yonezawa, Yuji Otsuki, Takumi Nishinobo, TEL Technology Center America, Japan; Joshua Mayersky, Gyana Pattanaik, TEL Technology Center America; Hirokazu Aizawa, Hidenao Suzuki, TEL Technology Center America, Japan; Cory Wajda, TEL Technology Center America**

Area-selective deposition (ASD) has been pursued for decades in semiconductor manufacturing to cut reliance on costly masks and mitigate misalignment from wafer distortion. Self-aligned and self-limited ASD

schemes are integrated to protect electrical performance and preserve yield under aggressive scaling. In back-end-of-line (BEOL) processes, Cu interconnect scaling is becoming increasingly constrained at advanced nodes. Combining ASD techniques helps maintain Cu performance and reliability; selective barriers lower via resistance, and selective metal caps extend electromigration (EM) lifetime.

Building on the dual-inhibitor method reported at ASD 2024, we apply sequential surface treatments that widen the window for selective Ru deposition on Cu while suppressing nucleation on interlayer dielectrics (ILD). The approach employs two small-molecule inhibitors (SMIs) to passivate both Cu and low- k surfaces after chemical mechanical planarization (CMP). Under Ru deposition conditions, the passivation is lifted on Cu but retained on the ILD, enabling selectivity without additional masking. Inline tests (ILT) show reduced leakage current and an enhanced ability to extend queue times without degradation. This addresses queue-time control at fine pitches where the Cu/low- k spacing approaches critical dimensions. The ILT results illustrate delayed leakage degradation with either one SMI or both of two SMIs, and the SEM images and TEM cross sectional images confirms Ru selectivity on Cu with negligible ILD nucleation, indicating a path toward Cu interconnects with Ru wrap-around caps and improved electrical yield.

9:45am **ASD1-MoM-7 Blocking the Atomic Layer Deposition of Al₂O₃: Combined Effects of Precursor, Co-reactant, Blocking Molecule, and Reactor Temperature, Jay Swarup, James Jensen, Burke Combs, James Engstrom, Cornell University**

As semiconductor device dimensions shrink toward the atomic scale, area-selective deposition has become a critical technique for overcoming the alignment and scaling limitations of conventional top-down lithography. This bottom-up approach enables precise material placement by preventing growth on non-growth surfaces, typically through the use of blocking molecules that passivate reactive sites. The success of this process depends on the combined effects of the specific chemistry of the ALD precursor and co-reactant, the choice and method of application of the blocking molecule, and reactor temperature. We report a systematic examination of the combined effects of these variables for blocking deposition of Al₂O₃ on SiO₂. We compare the conventional trimethylaluminum (TMA) to BDMADA-Al, a non-pyrophoric alternative precursor containing only Al-N bonds and no Al-C bonds [1]. For co-reactants, we compare H₂O versus *t*-BuOH. For blocking molecules, we evaluated a solution-phase self-assembled monolayer octadecyl trichlorosilane (ODTS) and a smaller, vapor-phase blocking molecule dimethylamino trimethylsilane (DMATMS). Growth was monitored at two different temperatures *in situ* and in real-time via quartz-crystal microbalance (QCM), with deposited films characterized *ex situ* using X-ray photoelectron spectroscopy (XPS) and other techniques. While we have shown that pristine ALD runs (without inhibitors) between BDMADA-Al and TMA produce comparable film density, stoichiometry (C incorporation), and growth rates, significant differences emerged during blocking studies. Specifically, the bulkier BDMADA-Al was more effectively inhibited than the smaller TMA across all tested conditions. Similarly, for single-dose applications, the larger, solution-phase ODTS provided more robust blocking than the vapor-phase DMATMS, suggesting that larger precursor and blocking molecules improve blocking performance through steric hindrance. We also find that higher temperatures improved blocking efficacy under similar process chemistries. Additionally, the dosing sequence in the ALD cycle is a critical factor; repetitive pulsing of DMATMS in an "ABC" cycle provided superior inhibition compared to a single pre-exposure, ultimately outperforming ODTS in some tested conditions.

[1]J. V. Swarup, H.-R. Chuang, J. T. Jensen, J. Gao, A. L. You and J. R. Engstrom, *J. Vac. Sci. Technol. A* **43**, 022404 (2025).

Area Selective Deposition

Room ETEC Atrium - Session ASD2-MoM

ASD and Inhibitors II

Moderators: Sang Hoon Ahn, Samsung Electronics, Seán Barry, Carleton University

10:30am **ASD2-MoM-10 Enabling Area-Selective Atomic Layer Deposition through Locally Activated and Deactivated Approaches, Woo Hee Kim, Hanyang University ERICA, Republic of Korea** INVITED

Area-selective atomic layer deposition (AS-ALD) is a promising bottom-up process for advanced semiconductor integration as conventional

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lithography-based patterning increasingly faces limitations in alignment accuracy, process complexity, and cost. In three-dimensional architectures such as 3D NAND and DRAM, precise control of material placement is essential for atomic-scale thickness control and conformal film growth. AS-ALD enables self-aligned integration by locally modulating surface reactivity. This presentation overviews AS-ALD strategies based on locally activated and locally deactivated approaches, highlighting representative process concepts demonstrated in our recent studies. Locally activated AS-ALD relies on intrinsic surface reactivity without inhibitors. One strategy achieves selectivity through precursor-selective adsorption, where molecular design and surface chemistry drive preferential adsorption and nucleation on target substrates. A complementary strategy employs catalytic local activation, in which specific surface functional groups locally enhance reaction kinetics, enabling selective film growth under identical reactant exposure. Locally deactivated AS-ALD suppresses growth on non-growth areas. We demonstrate vapor-phase passivation using self-assembled monolayers (SAMs) and small-molecule inhibitors (SMIs), showing that long-chain SAMs can be introduced via optimized vapor dosing to achieve robust selectivity without solution-based processing. In addition, we introduce surface protectors (SPs) based on weak physical interactions. These transiently block precursor access through physisorption and are removed during subsequent reactant exposure, leaving no permanent surface modification. SP-based deactivation enables topographically selective growth control in three-dimensional structures by preferentially suppressing deposition on upper surfaces and sidewalls, improving conformality in high-aspect-ratio features. Furthermore, SP-assisted AS-ALD enables spatially confined engineering of metal/high-k dielectric interfaces relevant to DRAM capacitors, allowing selective interface stabilization while suppressing interfacial oxidation and lateral electrical coupling. This talk presents a unified framework for locally activated and deactivated AS-ALD and discusses their integration potential for next-generation three-dimensional memory devices.

11:00am **ASD2-MoM-12 Control of Selectivity in SiN ALD Using Hydrazine**, **Hayato Murata**, Kumamoto University, Japan; **Yoshifumi Wada**, **Hideharu Shimizu**, TAIYO NIPPON SANSO Corp., Japan; **Takeshi Momose**, Kumamoto University, Japan

This study developed a method to achieve both reduced incubation cycles and enhanced selectivity in area-selective atomic layer deposition (AS-ALD) of silicon nitride (SiN). It was demonstrated using dichlorosilane (SiH₂Cl₂, DCS) as the Si precursor and hydrazine (N₂H₄) as the nitriding agent, an alternative to the conventional ammonia (NH₃), on HF-treated Si (Si) and thermally grown SiO₂ (SiO₂). Incubation cycles on both underlayers were reduced by using the more reactive N₂H₄ instead of the conventional nitriding agent NH₃. Selectivity in SiN AS-ALD was further improved by introducing an N₂H₄ pretreatment before ALD. Thus, N₂H₄ is a highly promising nitriding agent for AS-ALD of SiN, enabling shorter incubation cycles and greater selectivity.

AS-ALD is gaining attention as a cost-effective bottom-up process over conventional top-down patterning [1]. However, even though AS-ALD would work successfully, incubation cycles result in lower throughput, which remains a critical issue in AS-ALD. In this study, the effect of using the more reactive N₂H₄ instead of NH₃ in SiN AS-ALD was examined. First, the dependence of the SiN film thickness on the ALD cycles was investigated for both NH₃ and N₂H₄ at 600°C. The results showed that using the more reactive N₂H₄ rather than NH₃ reduced the incubation cycles on both underlayers, thereby improving throughput. Subsequently, the selectivity window was determined as the difference in incubation cycles between Si and SiO₂. Additionally, the SiN film thickness grown on the growth area (Si) was evaluated when growth began on the nongrowth area (SiO₂). In these measurements, the SiN film thickness on the growth area was found to be 1.3 nm with N₂H₄, while 1.5 nm with NH₃. This indicates a trade-off: using N₂H₄ reduced incubation cycles and improved throughput; however, it resulted in a thinner SiN film on the growth area when growth began on the nongrowth area. To address this issue, an N₂H₄ pretreatment was introduced. This pretreatment increased the film thickness on the growth area (2.1 nm) compared to the untreated case (1.3 nm), while maintaining reduced incubation cycles and improved selectivity. In summary, this hybrid approach of using N₂H₄ for both pretreatment and as a nitriding agent offers a means to balance throughput, film thickness on the growth area when growth begins on the nongrowth area, and selectivity in SiN AS-ALD.

Reference [1] B. Karasulu, F. Roozeboom, and A. Mameli, *Adv. Mater.*, **35**, 2301204 (2023).

11:15am **ASD2-MoM-13 Selective Surface Reactivation of Small-Molecule Inhibitors to Enable Area-Selective Deposition**, **Joris Verdin**, IMEC / KU Leuven, Belgium; **Akhilsh Kumar Mandal**, IMEC, Belgium; **Ainhoa Romo Negreira**, Tokyo Electron, Belgium; **Marleen van der Veen**, IMEC, Belgium; **Takahiro Hakamata**, **Tadahiro Ishizaka**, Tokyo Electron, Belgium; **Robert Clark**, Tokyo Electron; **Annelies Delabie**, IMEC / KU Leuven, Belgium

Area-selective deposition (ASD) emerges as an important technique for nanoelectronic device fabrication. The use of small-molecule inhibitors (SMIs) for selectively blocking material deposition on the non-growth area (NGA) has gained attention as a potential strategy to achieve ASD. Numerous studies use (N,N-dimethylamino)trimethyl silane (DMA-TMS) as SMI to block growth on SiO₂, and the reaction between this SMI and the SiO₂ surface is well understood. In contrast, there is no consensus about the interaction of DMA-TMS with surfaces such as TiN, metal oxides and metals. Some papers report that a DMA-TMS treatment on TiN does not affect subsequent deposition, enabling ASD with TiN as a growth area (GA).^[1] Other papers report that a DMA-TMS treatment on TiN blocks subsequent deposition, enabling ASD with TiN as a NGA.^[2] These diverging observations highlight the need for investigations of the process conditions and their impact on surface reactivity. In this work, we demonstrate how air exposure influences the surface composition of a range of DMA-TMS-treated surfaces, as well as its impact on Ru ASD by chemical vapor deposition (CVD). We demonstrate that DMA-TMS reacts with TiN, leading to Ru growth inhibition if the surface is not exposed to air between the DMA-TMS treatment and Ru CVD. Air exposure between the DMA-TMS treatment and Ru CVD reactivates the TiN surface (Figure 1a). We propose that 1) DMA-TMS reacts with surface groups on TiN, leading to a trimethylsilyl-based passivation layer, and 2) air exposure results in the formation of volatile Si-species, consistent with surface reactivation. This hypothesis is supported by time-of-flight secondary-ion mass spectrometry (TOFSIMS, Figure 1b), which indicates the decrease of Si-content at the Ru/TiN interface when air exposure is performed between the DMA-TMS treatment and the Ru deposition. To understand the wider impact on the ASD material space with DMA-TMS as SMI, we investigate the impact of air exposure for a range of other materials, and we find different extents of surface reactivation by air exposure. These insights can enable the design of ASD processes for new GA and NGA material combinations, depending on the surface treatment and reactivation conditions.

[1] Van Dongen, K., et al. *J. Vac. Sci. Technol. A* **2023**, *41* (3), 032404.

[2] Lee, J.-M., et al. *Mater. Lett.* **2023**, *333*, 133574.

11:30am **ASD2-MoM-14 Dual-Purpose Catalyst and Inhibitor for Low-Temperature AS-ALD of SiO₂ Thin Films**, **Jeong-Min Lee**, **Stacey Bent**, Stanford University

Driven by the demand for atomic-scale precision patterning in advanced semiconductor processing, area-selective atomic layer deposition (AS-ALD) has emerged as a paradigm-shifting technique in nanofabrication, leveraging its bottom-up nature to enable spatially selective and precise film growth. In this work, we report a methodology for achieving accelerated deposition of SiO₂ thin films on SiO₂ surfaces while suppressing growth on metal or metal oxide surfaces using a single additive molecule that acts as both catalyst and inhibitor. Conventional AS-ALD processes for SiO₂ films often rely on strong oxidizing agents to compensate for the low reactivity of Si precursors at low temperatures, which compromises inhibitor stability and degrades deposition selectivity. To overcome this limitation, we introduce a catalytic SiO₂ ALD process employing a Lewis-base catalyst that not only promotes SiO₂ growth with mild H₂O reactants at temperatures as low as 100 °C, but also acts as an inhibitor on metal surfaces, thereby enabling metal-dielectric selectivity. We will show results of SiO₂ ALD on a variety of metal, metal oxide, and semiconductor surfaces (including Cu, Ru, W, Al₂O₃, TiO₂, and SiO₂) using amine additives. The results demonstrate proof of concept for the dual-purpose approach, achieving some selectivity for AS-ALD on SiO₂ substrates compared to the metal and metal oxides. We believe that this work provides a new strategy to broaden the applicability of SiO₂ AS-ALD by enabling dual-function catalytic control of both growth and blocking without requiring a separate inhibitor, simplifying process integration.

11:45am **ASD2-MoM-15 Octadecylphosphonic Acid Self-Assembled Monolayers for Selective Hardmask Deposition on a Carbon/Metal Oxide System**, **Anna Kolln**, **Maggy Harake**, Stanford University; **Stacey Bent**, Stanford University

Advances in semiconductor device manufacturing have pushed the scaling limits of top-down fabrication methods such as photolithography, revealing a need for novel fabrication techniques. One such technique is area-

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selective atomic layer deposition (AS-ALD), which provides a route to create nano-scale features from the bottom up. While a significant portion of AS-ALD research has focused on depositing dielectric or metal materials onto dielectric/metal patterns, there is demand for a broader range of substrate combinations. For example, carbon-based materials such as amorphous carbon (aC) hardmasks and photoresists are used in advanced patterning. Establishing selective depositions on carbon-based substrates expands the potential applications of AS-ALD, such as adding an etch-resistant layer to carbon.

In this work, we developed an AS-ALD process for an aC/MO_x (M = Al, Ti) system, with aC as the growth surface (GS) and MO_x as the nongrowth surface (NGS). AS-ALD can be achieved by employing self-assembled monolayers (SAMs), which selectively bind and form an inhibition layer on the NGS. Octadecylphosphonic acid (ODPA) was selected because it has previously been shown to form SAMs selectively on metal oxide surfaces over nonmetal surfaces. We observed that ODPA formed SAMs on MO_x surfaces while only depositing in small amounts on aC, as confirmed by water contact angle measurements and X-ray photoelectron spectroscopy (XPS).

For the etch stop deposition on the aC GS, we chose ZnO deposited with diethylzinc (DEZ) and water as precursors. ZnO is expected to have enhanced etch resistance compared to carbon-based films. In the aC/Al₂O₃ system, a selectivity of ≥ 0.95 was demonstrated for 3.1 nm (25 cycles) of ZnO film growth on the aC GS at 120°C, as characterized by XPS. In contrast, under the same conditions, the aC/TiO₂ system exhibited a lower selectivity of 0.88. Selectivities for both aC/MO_x systems were higher at 200°C than at 120°C, with the aC/Al₂O₃ system maintaining a selectivity of ≥ 0.95 for 20.9 nm (150 cycles) of ZnO film growth. The difference in selectivity between the two temperature conditions is attributed to decreased physisorption of DEZ to the SAM surface at elevated temperatures. The infiltration and conformality of the ZnO films on the aC surface were assessed using XPS depth profiling and atomic force microscopy, respectively. Finally, C/MO_x patterns were used to demonstrate selectivity of the ODPA SAM inhibitor for ZnO ALD.

12:00pm ASD2-MoM-16 Role of Precursor and Alkanethiol 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 grown 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 narrow in on the precise breakdown mechanisms, we 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.

Area Selective Deposition

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ASD for SC Applications

Moderators: Dennis Hausmann, Lam Research Corp, Erwin Kessels, Eindhoven University of Technology

1:30pm **ASD1-MoA-1 Atomic-Level Healing and Sculpting: The New Frontier of Area-Selective Deposition in Memory Fabrication, Francoise Fabreguette, Tim Quick, Erik Byers, Gurtej Sandhu, Micron Technology**
INVITED

Area-selective deposition (ASD) has rapidly evolved from a niche technique to a cornerstone of advanced memory fabrication, driven by the relentless pursuit of aggressive scaling and precision engineering. Traditionally, ASD has focused on depositing large volumes of selective films to enable pattern fidelity and integration. Today, the paradigm is shifting: rather than building bulk layers, we are entering an era of atomic-level healing and sculpting—where ASD is leveraged to correct nanoscale imperfections, tune interfaces, and selectively modify surfaces with unprecedented control. This approach not only enhances device reliability and yield but also unlocks new design freedoms for next-generation memory architectures. By embracing this ultimate healing methodology, the memory industry is redefining what “selectivity” means—transforming ASD from a deposition tool into a precision sculpting instrument for the atomic landscape of semiconductor devices. The case study of ASD TiN on TiN and not on oxide will be reviewed in this talk. Using standalone Oxide and TiN surfaces, the inhibition toolset efficiency will be thoroughly discussed, while the selectivity loss with respect to the deposited TiN thickness will be benchmarked for our suite of inhibitors. The potential application of healing metal electrode seams or cracks with this ASD process will also be presented. Finally, other examples of sculpting 3D-NAND memory devices with ASD for improved process margin will be showcased.

2:00pm **ASD1-MoA-3 Establishing High-Temperature Area-Selective Deposition Process of SiN through Controlled Surface Fluorination, Haonan Liu, Ken Okoshi, Hiroki Murakami, Yamato Tonegawa, Tokyo Electron Technology Solutions Limited, Japan**

Presently, research on area-selective atomic layer deposition (AS-ALD) is attracting strong interest. AS-ALD simplifies deposition on patterned substrates and high-aspect-ratio structures, holding promise for semiconductor manufacturing. In our previous work, we introduced an ASD-Loop technique employing HF as an inhibitor to achieve selective SiN deposition.¹ However, several issues remained, including potential silicon substrate damage and the need for ex-situ precleaning that increases process complexity. Here, we developed a novel Hybrid-ASD process, achieving high selectivity for Si or SiN over SiO₂ while protecting the silicon substrate and enabling insitu precleaning via precise surface fluorination control.

Experiments were conducted with a batch furnace capable of treating over one hundred 300 mm wafers simultaneously. 300 mm silicon wafers, some with blanket SiN and SiO₂ films, and various nanostructures, were tested. The Hybrid-ASD process flow is shown in Fig. 1. Chemical oxide removal (COR) was applied insitu with simultaneous HF and NH₃ supply at 65 °C. HF gas passivation was then employed at 630 °C for 10 minutes to selectively inhibit the SiO₂ surface. ALD SiN was deposited using dichlorosilane (SiH₂Cl₂) and NH₃ at 630 °C.

Our results show COR effectively removes native oxide without substrate damage, while selectively fluorinating and inhibiting SiO₂. As shown in Fig. 2, after 70 ALD cycles post-COR, 50 Å SiN was deposited on amorphous silicon and SiN surfaces, with no deposition on SiO₂. Based on this, we developed Hybrid-ASD to achieve ASD SiN with insitu native oxide removal and silicon protection. The first ASD step combined COR and ALD to form a protection layer, followed by an ASD-Loop that repeats HF flow and thermal ALD to extend deposition. After 16 ASD-Loops, 160 Å selective SiN was deposited on amorphous Si and SiN (Fig. 3), with EELS mapping confirming no substrate damage. The process achieved excellent within-wafer non-uniformity of just 1.5%. In summary, we developed a robust, high-temperature AS-ALD solution compatible with 300 mm wafers and complex nanostructures, featuring high selectivity, insitu oxide removal, and substrate protection. This Hybrid-ASD process offers a promising pathway for integrating AS-ALD into advanced nanofabrication and holds strong potential for next-generation semiconductor devices, including DRAM and 3D NAND.

References

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2:15pm **ASD1-MoA-4 Selective Deposition of HfO₂ Films, Rachel Nye de Castro, Francisco Freire-Fernandez, Elham Mohimi, Lam Research**

Area-selective deposition (ASD) of hafnium oxide (HfO₂) thin films is of interest for high-k or high etch resistant layers in logic applications. Development of selective HfO₂ films has been less well-reported in literature compared to other metal oxide and dielectric films (AlO_x, ZnO, TiO₂, SiO, SiN, etc).^{1,2} In this work, we evaluate HfO₂ selective deposition with inhibition on SiO and similar surfaces using inhibitor molecules. First, we characterize thermal HfO₂ ALD processes from several Hf precursors. We evaluate deposition rate, saturation, deposition temperature, and film properties. Then, we evaluate the blocking capability of different inhibitor molecules for the HfO₂ film on various metal and dielectric substrates.

HfO₂ thermal ALD demonstrates linear growth (Fig. 1a) and saturating behavior for each precursor studied. The temperature window of these ALD processes are compatible with the thermal budget for end applications and the thermal stability of inhibitor molecules (e.g. < ~500 °C). Film properties such as composition (XPS), density (XRR), and etch resistance (in dilute HF) are reported. Selective blocking of HfO₂ is demonstrated on native SiO₂ blanket coupons using ellipsometry and water contact angle measurements. This inhibition is extended to other dielectric surfaces (e.g. Si, SiN, SiCO, SiCON) while other metals and metal oxides (e.g. HfO₂, AlO_x, W, Mo) act as growth surfaces. Comparison between two Hf precursors demonstrates clear differences in blocking capability based on the Hf precursor and the inhibitor selected (Fig. 1b), for example showing differences in WCA degradation on an inhibited surface.

This HfO₂ ALD process and our inhibitor molecules are compatible with 300mm tool processing under HVM conditions to enable selective HfO₂ deposition on metals or metal oxides while inhibiting SiO and similar surfaces. Future work is needed to evaluate additional HfO₂ precursors to maximize selectivity, film quality, and deposition rate.

References

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2:30pm **ASD1-MoA-5 GeTe Thickness Profile Alteration by Proximity Effects During Area-Selective Atomic Layer Deposition in Nanotrenches, Annelies Delabie, imec and KU Leuven (University of Leuven), Belgium; Jyoti Sinha, KU Leuven and imec, Belgium; Marleen van der Veen, Laura Nyns, Johan Swerts, imec, Belgium; Nicholas M. Carroll, Gregory Parsons, North Carolina State University**

Area-selective deposition (ASD) has great potential to facilitate nano-electronic device fabrication, for example by improving the alignment of patterns or by bottom-up fill of nanometer scale holes and trenches. These applications require ASD with growth control near the atomic level on pre-patterned substrates with feature dimensions near the nanoscale. In such structures, the growth and non-growth areas are in close proximity. This implies that events on the growth area may affect the non-growth area and vice versa. Understanding the mechanisms behind proximity effects during ASD on nanopatterns is important to ensure the atomic scale precision of deposition.

In this work, we investigate proximity effects during chalcogenide ASD by atomic layer deposition (ALD) with the well-known dechlorosilylation chemistry, more specifically GeTe ALD from GeCl₂.C₄H₈O₂ and Te(Si(CH₃)₃)₂. When combined with an aminosilane small molecule inhibitor reaction, this chemistry becomes highly selective: the ASD thicknesses can reach 20 nm with minimal selectivity loss [1,2]. Interestingly, the GeTe thickness profile is altered when GeTe ASD by ALD is performed on TiN in nanotrenches between trimethylsilyl-passivated SiO₂ lines with a line spacing of 55 nm (Figure 1). The GeTe deposition shows an inverted U-shaped thickness profile, with GeTe growth inhibited near the adjacent trimethylsilyl-passivated SiO₂ sidewalls. This behavior is different than the planar thickness profile typically expected for ALD, but still well-controlled over multiple nanotrenches (Figure 1 b, c). This suggests that precursor and/or material rearrangements occur near the passivated sidewalls, in addition to the well-known self-limiting surface reactions of ALD. To get insight into this proximity effect, the ASD process in a nanotrench is mimicked using a previously developed stochastic lattice growth model. The modelled thickness profile agrees well with experiment when assuming repulsive

electrostatic interactions between the Te precursor ligands on the growth region and the trimethylsilyl-groups on the adjacent vertical trimethylsilyl-passivated SiO₂ sidewall. We conclude that fundamental understanding of mechanisms behind proximity effects is key to ensure atomic scale precision during ASD on nanopatterns. In addition, proximity effects may open opportunities for thickness profile tuning beyond planar deposition.

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2:45pm **ASD1-MoA-6 Area-Selective Atomic Layer Deposition Using Small Molecule Inhibitors in High Aspect Ratios Structures**, *Olaf Bolkenbaas, Mike van de Poll, Pengmei Yu, Marc Merckx, Wilhelmus Kessels*, Eindhoven University of Technology, The Netherlands; *Tania Sandoval*, Universidad Técnica Federico Santa María, Chile; *Adriaan Mackus*, Eindhoven University of Technology, The Netherlands

Semiconductor device architectures are moving towards more complex 3-dimensional structures, for example the complementary FET. To produce these highly-scaled devices in future generations, area-selective deposition (ASD) could be vital. However, ASD is most commonly studied on planar substrates. In this work, the effects the aspect ratio of a 3D structure can have on an area-selective deposition process and the translation of insights from studies on planar substrates to the 3rd dimension are investigated. To achieve this, area-selective atomic layer deposition (ALD) using small molecule inhibitors (SMIs) is performed on lateral trenches. In addition, a diffusion reaction model is combined with an Avrami model to predict the thickness evolution of an area-selective ALD process as a function of the aspect ratio. As expected, the model shows that to achieve a specific selectivity value regardless of aspect ratio, the SMI exposure should be high enough for the SMI coverage to penetrate into the entire trench. Experiments using acetic acid (Hac) as an SMI to block SiO₂ ALD on planar Al₂O₃ substrates show that the selectivity is very strongly influenced by a small decrease in the SMI coverage from saturation. Therefore, also on planar samples, a large SMI exposure is needed to maximize the selectivity of the process. When using the same SMI exposure on the lateral trench structures, a high selectivity is obtained up to aspect ratios of 400. However, due to displacement of Hac by the precursor, the selectivity is lower at the trench opening, where the precursor exposure is the highest. Therefore, the precursor exposure should be optimized for selectivity and conformality, while the SMI exposure is already sufficient to obtain selectivity at high aspect ratios. To conclude, translating area-selective ALD processes using SMIs on planar substrates to structures with a high aspect ratio does not simply require increasing the dose times of the reactants, as this results in reduced selectivity at different points inside the structure.

3:00pm **ASD1-MoA-7 Area-Selective Molecular Layer Deposition of Polyamide on EUV Resists versus Si-Based Underlayers for 300 nm Wafer Processing**, *Van Long Nguyen, Christophe Vallee*, University at Albany-SUNY; *Ornella Sathoud, Jonathan Abreu, Rinus Lee, Danny Newman, Cory Wajda, Kandabara Tapily, Gert Leusink*, TEL Technology Center, America, LLC, USA

In semiconductor manufacturing, critical dimensions of ~10 nm are already in production using EUV lithography. Continued scaling to smaller dimensions typically requires thinner EUV photoresists to mitigate pattern collapse. In addition, next-generation high-NA EUV lithography, currently in early implementation, also demands even thinner resists due to its significantly reduced depth of focus (DOF). As a result, EUV resists with thicknesses of <40 nm are increasingly employed, which can lead to an insufficient resist thickness budget for etch pattern transfer. Recently, area-selective deposition (ASD) has emerged as a promising post-lithography strategy to enhance the functionality of EUV resist patterns. In this work, we demonstrate ASD of molecular layer deposition (MLD) of Nylon 2,6 on EUV chemically amplified resist (CAR) (growth surface) versus Si-based underlayer (UL) (non-growth surface) (**Figure 1**). The selectivity is achieved by exploiting intrinsic differences in surface functional groups between the CAR and the Si-based UL, in combination with a passivation or inhibitor dosing. The inhibition treatment effectively passivates reactive hydroxyl groups on the UL that suppress the MLD nucleation, while exhibiting limited reactivity toward the relatively hydroxyl-deficient CAR surface. Corrosive hydrogen chloride, as a byproduct of the MLD process, damages the passivating layer quickly; therefore, re-passivation of the UL after a

certain number of MLD cycles is shown to be an effective approach for extending the selectivity window. In addition, with the inhibition treatment, Nylon 2,6 growth is also suppressed on CAR pattern sidewalls. Our hypothesis is that CAR sidewall chemistry is modified post exposure, rendering it more reactive toward the inhibition treatment and thereby passivating the sidewalls. Angle-resolved X-ray photoelectron spectroscopy (AR-XPS) is used to elucidate the surface chemistry of CAR and UL surfaces. Atomic force microscopy (AFM) reveals preferential Nylon 2,6 growth on CAR patterns with negligible deposition on the passivated Si-based UL. Cross-sectional transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDX) further confirm selective Nylon 2,6 film growth.

Area Selective Deposition Room ETEC Atrium - Session ASD2-MoA

ASD Metrology, Surface Characterization and Modeling

Moderators: Adrie Mackus, Eindhoven University of Technology, **Ralf Tonner-Zech**, Wilhelm-Ostwald-Institute für Physikalische und Theoretische Chemie

3:45pm **ASD2-MoA-10 Development of Area-Selective ALD Processes Using In Situ Optical Diagnostics**, *Sumit Agarwal*, Colorado School of Mines, USA

INVITED

Area-selective atomic layer deposition (AS-ALD) can be achieved through either inherent growth selectivity or by blocking reactive sites on the nongrowth surface with inhibitor molecules. However, inherent growth selectivity is generally not observed on chemically similar surfaces since their surface functional groups may have similar reactivity with ALD precursors. Therefore, development of AS-ALD processes for chemically similar growth and nongrowth surfaces is challenging. In this presentation, we will demonstrate that *in situ* optical diagnostics such as attenuated total reflection Fourier transform infrared spectroscopy and spectroscopic ellipsometry can be used to study the reaction of inhibitor molecules with different growth and nongrowth surfaces, and to understand how and when nucleation of ALD occurs on the nongrowth surface.

SiO₂ and SiN_x are the most extensively used dielectric materials in semiconductor manufacturing. Previously, we showed that area-selective ALD of Al₂O₃ can be achieved on SiN_x by passivating the SiO₂ surface with aminosilanes. We will show that the aminosilanes react with both the SiO₂ and SiN_x surfaces, but the coverage of aminosilanes on the SiN_x surface is incomplete, which does not prevent ALD of Al₂O₃ from dimethylaluminum isopropoxide (DMAI) and H₂O, but simply introduces a nucleation delay of 5-10 cycles. However, selective growth of Al₂O₃ on SiN_x was limited to 2-3 nm at which point DMAI started to react with the SiO₂ surface to nucleate film growth. Based on these initial studies, our hypothesis was that there are residual -SiOH groups that remain on the SiO₂ surface that react with DMAI to initiate growth of Al₂O₃. To extend the nucleation delay on SiO₂, we created a set of plasma-deposited SiO₂ surfaces with a controlled density of surface -SiOH groups by first preheating from the deposition temperature of 150 °C up to 500 °C, and then by cooling the substrate to a lower temperature prior to ALD of Al₂O₃. We used aminosilanes with different size head groups and leaving groups to optimize the surface passivation of SiO₂. Finally, we will show how this optimization influences the nucleation delay for ALD of SiO₂.

Acknowledgements: We would like to thank EMD Electronics for funding this work.

4:15pm **ASD2-MoA-12 Characterization of Thin and Selective Film Depositions on v-Groove ASD Test Structures**, *Thomas Werner*, Chipmetrics Oy, Germany; *Jussi Kinnunen, Feng Gao*, Chipmetrics Oy, Finland; *Rachel Nye de Castro*, Lam Research; *Karsten Lamann*, Tascon GmbH, Germany; *Lysann Kassner, Mathias Franz*, Fraunhofer ENAS, Germany

With the growing interest in introducing ASD processes at advanced technology nodes, many developers are faced with the question of the availability of suitable test structures. The challenge lies both in the very small feature sizes of modern semiconductor structures, typically below 100 nm, and in the combination of different materials serving as substrates for the ASD process under development. Chipmetrics has developed a patented approach in which various layers are deposited into a V-shaped silicon trench etched directly into silicon. After the trench is filled, the layers are planarized by CMP, resulting in a highly planar surface with alternating lines of different materials with widths below 100 nm. Owing to the wet-

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chemical patterning of the trenches, the lines exhibit very low line edge roughness, which has a positive impact on the evaluation of the results. Ultimately, this results in an array of planar lines of different materials, enabling an efficient evaluation of ASD results. The approach allows the combination of different dielectrics or combinations of metals and dielectrics. Another important aspect in the evaluation of ASD experiments is the use of suitable measurement techniques. For this purpose, various surface analysis methods (SEM-EDX, TOF-SIMS, TEM) for characterizing the described ASD structures were investigated and evaluated. Initial results from ASD experiments are presented, along with an outlook on the next development goals.

4:30pm ASD2-MoA-13 Co-optimized Process and Metrology Accelerates Molybdenum Contact Development, *Zhebo Chen*, Applied Materials

Z. Chen, M. Shifrin, M. Gage, S. Deshpande, Y. Huang, J. Tang, B. Brown, W. Lei, S. Patel, Y. Hwang, S. Zhang, R. Wang, Y. Lei, J. Lu, A. Jansen, K. Rachakonda, X. Tang, A. Gen, E. Itzkovitz

Applied Materials Inc., 3050 Bowers Ave., Santa Clara, California, USA

As device scaling continues and connections to the transistors become even thinner, traditional tungsten (W) contacts face challenges in their ability to efficiently conduct electrons. Molybdenum (Mo or "Moly"), with its lower electrical resistivity at smaller dimensions, emerges as a promising alternative for next-generation contact applications in both logic and memory devices. Since contacts form the smallest connections between interconnects and transistors, maintaining low resistance is critical to ensure maximum device performance and efficient power consumption.

The industry's gold standard has been Applied's Selective W, which lowers contact resistance by 40% compared to conventional W. Applied's Selective Mo metallization technology can achieve an additional 15% lower resistance compared to Selective W in the tiniest features, supporting continued device scaling for gate-all-around transistors. In this presentation, we discuss Applied's latest innovations for low resistance contacts, and how we co-optimize deposition, planarization, and inspection to enable a complete ecosystem of solutions to advance device scaling.

By combining Applied's advanced eBeam process and metrology tools with the Maydan Technology Center's rapid development environment, a novel Moly contact metrology system was created that leverages the Applied PROVision™ eBeam system. Close collaboration between the process and metrology teams enabled Applied to accelerate learning cycles, generating massive amounts of localized, on-device data in less than an hour with massive eBeam metrology.

4:45pm ASD2-MoA-14 Hydrogenolysis of Aniline on Transition Metal Surfaces: Effects of Temperature and Electronic Structure, *Matías Picuntureo*, Universidad Técnica Federico Santa María, Chile; *Marc J. M. Merx*, Eindhoven University of Technology, Netherlands; *Christopher Jezewski*, *Scott B. Clendinning*, Intel Corporation; *Adriaan J.M. Mackus*, Eindhoven University of Technology, Netherlands; *Tania E. Sandoval*, Universidad Técnica Federico Santa María, Chile

Area-selective atomic layer deposition (AS-ALD) enabled by small-molecule inhibitors (SMIs) relies on the formation of stable passivation layers that suppress ALD nucleation on selected surfaces. Recent temperature-dependent selectivity measurements for aniline-based inhibitors indicate that, at elevated temperatures, aniline undergoes hydrogenolysis on metal surfaces, leading to the accumulation of benzene-like fragments that constitute the dominant inhibitory species in the passivation layer. However, the atomistic mechanisms controlling their formation, stability, and surface selectivity across technologically relevant metals remain incompletely understood.

In this study, we use a combination of theoretical and experimental characterization to explore the hydrogen-assisted transformation of aniline molecules into carbonaceous species that enhance inhibition on transition-metal surfaces (Co, Ru, Mo, and W). These surfaces are selected for their relevance to advanced interconnect architectures. Temperature-dependent selectivity measurements reveal a clear metal-specific crossover in inhibition efficiency: Co and Ru exhibit higher selectivity at low temperatures, while W and Mo become highly selective at elevated temperatures ($S > 0.96$ for 6 nm films at 200 cycles). Kinetic and free energy analyses of density functional theory rationalize these trends by showing that hydrogen-assisted C-N bond cleavage in aniline becomes increasingly favorable in W and Mo with temperature, leading to the formation of stable benzene-like fragments, whereas in Co the reaction is already exergonic at low temperatures and in Ru it remains intermediate. The calculated decrease in the C-N cleavage barrier after hydrogenation, particularly

pronounced in W, and the corresponding stabilization of the hydrogenolysis products correlates with the experimentally observed change from optimum Co/Ru selectivity at low temperature to W/Mo at higher temperature, supporting a mechanism in which aromatic fragments derived from hydrogenolysis constitute the active passivation layer. Overall, these results provide fundamental understanding into the mechanism of hydrogen-assisted surface reactions (hydrogenolysis) of aromatic SMIs and its effect on temperature-dependent selectivity. Moreover, our results indicate that selectivity values change drastically across all metals studied and suggest that catalytic reactions may offer a pathway for metal differentiation that can be further explored for AS-ALD on multicolored surfaces.

5:00pm ASD2-MoA-15 Organic Functionalization of H-terminated Si Surfaces to Inhibit Atomic Layer Deposition of Al_2O_3 , *Andrew Kaye*, Colorado School of Mines; *Bhushan Zopé*, Intermolecular, Inc.; *Xinjian Lei*, *Ronald Pearlstein*, *Haripin Chandra*, EMD Electronics; *Sumit Agarwal*, Colorado School of Mines

After exposure to the ambient, Si surfaces form a native oxide layer, which changes the surface termination. Typically, native oxides are removed from these surfaces by etching in dilute HF, but it is desirable to remove these native oxides *in vacuo*. Using *in situ* attenuated total reflection Fourier-transform infrared spectroscopy, we first show that SiO_2 films that were plasma-deposited at 150 °C can be etched using atomic layer etching (ALE) based on half-cycles of HF vapor followed by a H_2O plasma. During ALE, we observed a net decrease in the Si-O-Si phonon mode. However, using a similar chemistry for ALE of an RCA oxides on Si(100) surfaces did not result in complete etching. Therefore, the H content and density of the SiO_2 film is important for ALE of SiO_2 . Next, we show that a H_2 plasma can remove an RCA oxide from Si(100) to form a H-terminated Si surface with some O atoms remaining, as stretching modes for surface $-SiH_x$ species that are back-bonded to O atoms and isolated Si-OH remain on the surface. These isolated Si-OH groups likely appear in the infrared spectra as the density of hydrogen-bonded Si-OH decreases upon reaction with the H_2 plasma, resulting in the net formation of the isolated modes (see Figure 1). In a separate set of experiments on a plasma-deposited hydrogenated Si surface, we observed the reaction of surface $-SiH_x$ species with 3,5,5-trimethylhexanal (TMH) at 150 °C resulting in surface alkoxides, which was apparent from the increase in absorbance for the Si-O-C stretching mode (see Figure 2). No reaction byproducts are produced in this reaction (see Figure 3). The alkoxide was shown to be thermally stable up to ~200 °C (see Figure 2). Using *in situ* ellipsometry we show that there is an inherent nucleation delay of Al_2O_3 ALD on H-terminated Si compared to SiO_2 surfaces for up to ~10 ALD cycles. However, pre-functionalization of the H-terminated surface with TMH did not increase the nucleation delay for ALD of Al_2O_3 using dimethylaluminum isopropoxide (DMAI) and H_2O . Our infrared spectra show that DMAI likely breaks Si-Si bonds allowing ALD to occur. We will show strategies for increasing the degree of surface passivation to further increase the nucleation delay for ALD of Al_2O_3 by increasing the surface coverage and passivating the strained Si-Si bonds with atomic hydrogen prior to exposure to an aldehyde. The H_2 plasma step for removal of surface SiO_x on Si will likely also passivate the strained Si-Si bonds.

5:15pm ASD2-MoA-16 Adsorption Behavior of ALD Precursors on Si, SiO_2 and SiN: Simulation and Experimental Investigation, *Genki Hayashi*, *Zeyuan Ni*, *Yumiko Kawano*, *Shinichi Ike*, *Shuji Azuma*, *Tetsuya Goto*, Tokyo Electron Technology Solutions Limited, Japan

Area-Selective Deposition (ASD) is an important process in semiconductor manufacturing [1]. It utilizes the differences in the surface chemical reaction between a precursor and different substrates. Surface reaction simulations are useful tools for searching for appropriate ASD precursors. In this study, we investigated the validity of adsorption energy calculation by comparing the calculation with the process outcomes.

We calculated the adsorption energies of Trimethylaluminum (TMA) and Triethylindium (TEIn) on H-terminated Si, OH-terminated SiO_2 , and NH- and F-terminated SiN substrates using the Machine Learning Potential [2] (Fig1). In the calculations, we considered several adsorption structures including both physisorption and chemisorption, and we picked up the lowest adsorption energy in Fig1. It is noted that fluorine appeared on the SiN surface after the DHF dip as shown in Fig2(XPS results), which agrees with the previous report [3]. For both TMA and TEIn, the calculated adsorption energy was lower in order of the $SiO_2(-OH)$, SiN(-NH), Si(-H), and SiN(-F) cases. These results indicate that TMA and TEIn are most likely to adsorb on

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SiO₂. The surface affinity of TMA and TEIn on SiN substrates might depend on the surface density of -NH and -F terminations.

To compare the calculation results with experiments, we introduced TMA and TEIn onto Si, SiO₂, and SiN substrates in a vacuum chamber. We dipped the samples into 0.5% DHF for 60 seconds before the molecule introduction in order to remove the native oxide. We set the condition of the molecule introduction so that the molecule did not decompose in the chamber and adsorption equilibrium was achieved. Fig3(a) shows the XPS spectra (Al 2p) of these substrates after TMA exposure and Fig3(b) shows the XPS spectra (In 3d) of these substrates after TEIn exposure. The largest amounts of both Aluminum and Indium were observed on the SiO₂ substrate, which agrees with the expectations from the simulation results. For SiN substrate, the amounts of Aluminum and Indium were lower than on SiO₂ and larger than on Si. Since -F and -NH termination might coexist, the surface affinity of TMA and TEIn is considered to be averaged. We need to quantify the surface densities of -NH and -F termination in order to investigate the adsorption of TMA and TEIn in more detail. Based on these results, the adsorption energy calculation can be a useful tool to estimate the adsorption selectivity in developing ASD.

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Area Selective Deposition

Room ETEC Atrium - Session ASD1-TuM

ASD: Plasma, Selective Etching and Sustainability

Moderators: Han-Bo-Ram Lee, Incheon National University, Marko Tuominen, ASM

8:30am **ASD1-TuM-1 Versatile Strategies for ASD Optimization Using Super-Cycles, Marceline Bonvalot, Martial Santorelli, LTM - MINATEC - CEA/LETI, France; Christophe Vallée, SUNY College of Nanoscale Science and Engineering**

INVITED

As the semiconductor industry advances toward extreme miniaturization and 3D integration, transistor architectures are progressively evolving toward gate-all-around devices based on stacked nanosheet channels. In parallel, emerging complementary field effect transistor (CFET) technologies further extend this concept by vertically stacking n- and p-type channels on top of each other within the same device footprint. The fabrication of such highly integrated architectures puts stringent demands on thin film deposition processes, making the development of innovative atomic layer deposition (ALD) approaches increasingly critical, owing to intrinsic advantages, such as high conformality, excellent uniformity over large surface areas and precise control of film composition at relatively low temperatures. ALD also provides numerous opportunities for the selective and precise placement of materials (semiconductors, dielectrics and metals) with nanoscale thickness control on horizontal and/or vertical surfaces, thereby enabling simplified integrated fabrication flows. This presentation will discuss various process routes based on ABC super-cycle strategies to achieve selective growth in semiconducting device fabrication. Tailoring precursor sequencing and surface chemistry through controlled adsorption, ligand exchange, and surface termination will be addressed, in the light of precise control of nucleation and selectivity required in complex 3D features in the context of extreme miniaturization.

9:00am **ASD1-TuM-3 Self-Aligned Patterning by Area-Selective Etching of Polymers and Area-Selective Atomic Layer Deposition: Decreasing Polymer Flow and Activating Noncatalytic Surface, Valtteri Lasonen, Piyumi Liyana Pathirana, Mykhailo Chundak, Marko Vehkamäki, University of Helsinki, Finland; Matthias Carnoy, Benjamin Borie, ATLANT 3D, Denmark; Silvia Armini, IMEC, Belgium; Mikko Ritala, University of Helsinki, Finland**

Area-selective etching (ASE) of polymers is a novel self-aligned patterning technique.¹⁻³ Polymer patterning is achieved by catalytic decomposition of the polymer film only on top of catalytically active surfaces, whereas the polymer film stays intact on top of the noncatalytic surfaces. After the self-aligned patterning, area-selective deposition can be done using the patterned polymer as an inhibition layer.

Previously, we have demonstrated the feasibility of the ASE process with three polymers: MLD-polyimide¹, poly(methyl methacrylate) (PMMA)², and poly(lactic acid) (PLA)³ – using Pt as the catalytic surface and native SiO₂ as the noncatalytic surface. Additionally, we showed that by choosing the right polymer, ASE can be achieved both in oxidative and non-oxidative atmospheres, and over a wide temperature range. Furthermore, we showed that the catalytic effect can be achieved with a very small amount of catalytic material, even less than a monolayer.² We demonstrated this with two catalytic materials, Pt and CeO₂. This means that metal surfaces can be converted to catalytic by depositing a small amount of Pt and dielectric surfaces by a small amount of CeO₂.

Here, we show that most metal oxide and nitride surfaces are noncatalytic, or their usage as a catalytic surface is unclear. We demonstrate this by testing two polymers, PMMA and PLA, in three different atmospheres, O₂, H₂, and inert. However, we convert a noncatalytic dielectric surface, HfO₂, to catalytic by depositing 30 cycles of ALD-CeO₂ (< 1 nm). After this, we deposit a line pattern of another noncatalytic material, TiO₂, via direct atomic layer processing (DALP⁴). We then spin-coat ~40 nm PMMA film on top and pattern the PMMA film by ASE in air. Finally, we deposit 50 cycles of ALD-ZrO₂ (~5 nm) area-selectively, using the ASE-patterned PMMA film as an inhibition layer. Furthermore, we show that only a thin layer of the noncatalytic TiO₂ (~3.5 nm) is enough to deactivate the catalytic effect of CeO₂. Additionally, we show that by increasing the molecular weight of the polymer, we can significantly decrease the polymer flow during the ASE process.

References

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3. Lasonen et al. *Chem. Mater.* **2024**, *36*, 11645

9:15am **ASD1-TuM-4 Leveraging Topographic Etch Selectivity: Atomic Layer Etch Pitch Splitting (Aps™), Robin Athle, Reza Jafari Jam, Yoana Ilarinova, Fabian Veid, Alfred Andersson, Svetlana Ivanova, Kishwar Sultana, Asif Muhammad, Mostafa Torbati, Intu Sharma, Hesamedin Safavi, AlixLabs A.B., Sweden; Fred Roozeboom, University of Twente, Netherlands; Dmitry Suyatin, Jonas Sundqvist, Amin Karimi, AlixLabs A.B., Sweden**

As the semiconductor industry pushes beyond sub-20-nm feature sizes, the limitations of traditional multiple patterning techniques, such as Self-Aligned Double/Quadruple Patterning (SADP/SAQP) and Litho-Etch-Litho-Etch (LELE), become increasingly apparent. These methods rely on complex, multi-step cycles of deposition, lithography, and etching, which escalate costs, increase variability, and significantly increase environmental impact. Atomic Layer Etch Pitch Splitting (APS™) technology enables multiple patterning by utilizing the topographic selectivity of Atomic Layer Etching (ALE) [1-4]. This topographic selectivity transforms nanostructure sidewalls into etch masks, eliminating the need for spacer layer deposition. As a result, APS™ provides a more affordable and sustainable alternative to achieve pitch multiplication with high precision. In this work, we demonstrate the versatility of APS™ across two critical integration paths: high-density scaling by a repeated application of the APS™ process and the APS™ process integration with different lithographic techniques. The process integrates seamlessly into existing industrial workflows, enabling the selective removal of material from the center of pre-patterned features. We show that initial features with critical dimensions (CDs) below 100 nm can be split without additional lithography steps or sacrificial spacer layers, achieving results comparable to state-of-the-art patterning techniques such as immersion ArF lithography (ArFi), Extreme Ultraviolet lithography (EUVL), and Nanoimprint lithography (NIL). At the same time, the reduced process complexity of APS™ directly translates into lower capital expenditures (CAPEX) and operating costs (OPEX), higher throughput, and reduced CO₂-equivalent emissions. These advantages position APS™ as a sustainable and scalable solution for next-generation logic and memory devices, offering a pathway to advanced resolution that bypasses the complexity and high costs of traditional multi-patterning. References: 1. Khan Md S. A., et al. US10930515 B2, Feb. 23, 2021, priority date March 14, 2017. 2. Khan Md S. A., et al. US11424130 B2, Aug. 23, 2022. 3. Khan Md S. A., et al., US20250259851 A1, Aug. 14, 2025. 4. Sundqvist J., et al. *Advanced Etch Technology and Process Integration for Nanopatterning XIV*. Vol. 13429, p. 134, SPIE, Apr. 22, 2025.

9:30am **ASD1-TuM-5 Phase and Surface Facet Dependent Etching of High-k Oxides for Selective Atomic Layer Etching, Michael Nolan, Rita Mullins, Tyndall Institute, Ireland**

Thermal Atomic Layer Etching (ALE) is investigated for its potential to deliver atomic level control over the etch of many materials and shows potential for use in future CMOS nodes with requirements for sub-nm levels of control on complex structures. It is performed using sequential surface modification and volatile release reactions. For metal oxides, HF fluorinates the initial surface to form a MF₄ layer (M = metal) which undergoes ligand-exchange with precursors such as TiCl₄ or SiCl₄, which volatilizes the MF₄ layer. The question of the role of the phase and surface facets in a deposited high-k metal oxide film has received little attention but can be addressed with first principles atomistic simulations. In this contribution we use density functional theory simulations to explore the effect of the phase and surfaces of HfO₂ and ZrO₂ on the HF modification half-cycle of ALE. The models used in this study representing polycrystalline materials are the (111) and (001) surface facets of monoclinic, orthorhombic and tetragonal HfO₂ and ZrO₂. Our thermodynamic analysis shows that for polycrystalline HfO₂ and ZrO₂, the HF pulse reacts in a self-limiting manner, and is preferred up to processing temperatures that are sensitive to the phase and surface. Models of HF coverage are used to compute calculated theoretical etch rates for the different oxide phases and surface facets and these show a strong dependence on both the crystal phase and the surface so that if different phases and facets are present an uneven etch profile will be seen. The stability, geometry and surface atomic coordination environments drive this dependence.

9:45am **ASD1-TuM-6 Enabling Bottom-up Gap Fill and Selective Metal Deposition via NH₃ Plasma-based AS-ALD, Yoenu Choi, Jeong Hyun Park, Yoona Choi, Woogjin Jeon, Kyung Hee University, Republic of Korea**

Atomic layer deposition (ALD) has attracted significant attention for next-generation semiconductor manufacturing due to its precise thickness control and excellent step coverage. In addition, active research has been conducted on realizing sub-10-nm devices with extremely high aspect ratios

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through area selectivity using small-molecule inhibitors, as well as on the fabrication of vertical structures by controlling chemisorption behavior depending on the substrate.

In this presentation, we introduce the results of area-selective atomic layer deposition (AS-ALD) enabled by plasma treatments. First, we demonstrate an approach to improve gap-fill characteristics by exploiting the inherently poor step coverage of plasma processes. During SiO₂ ALD, NH₃ plasma (NH₃⁺) treatment reduces the growth per cycle (GPC) due to inhibited chemisorption of the DIPAS precursor. By incorporating an NH₃⁺ treatment step into the SiO₂ ALD sequence for patterned structures, SiO₂ deposition is suppressed at the opening region, resulting in bottom-up gap-fill growth behavior.

We also present Co AS-ALD results on TiN and SiO₂ using NH₃⁺ treatment. The NH₃⁺ treatment simultaneously induces a decrease in GPC on SiO₂ and an increase in GPC on TiN. This behavior is attributed to suppressed chemisorption of the CpCo(CO)₂ Co precursor on SiO₂ due to surface NH_x termination, while on TiN, precursor chemisorption is enhanced by the removal of surface TiO_xN_y species.

These results indicate that NH₃⁺ treatment is a promising approach for enabling AS-ALD across a wide range of materials and device structures.

10:00am ASD1-TuM-7 Perfect Selectivity vs Practical Sustainability in ASD, Nupur Bihari, Lam Research Corporation

Area selective deposition (ASD) is increasingly viewed as a critical enabler for advanced semiconductor manufacturing, yet the pursuit of perfect selectivity often introduces excessive process complexity, high precursor consumption and limited sustainability. In this work, we investigate the balance between selectivity and practical process efficiency, with an emphasis on reducing precursor usage while maintaining integration-relevant performance. An eco-friendly process regime is demonstrated to provide robust selectivity without relying on aggressive chemistries or extended exposure conditions. Top-down scanning electron microscopy (TDSEM) is employed as a simple and effective metrology approach to evaluate selectivity, nucleation behavior and pattern fidelity under reduced precursor flow. The results show that excellent selectivity can be achieved with significantly lower precursor usage. Electrical resistance-capacitance (RC) characteristics and integration data indicate that ASD processes with minor selectivity loss still offer compelling advantages for patterning and interconnect scaling. These findings highlight that perfect selectivity is not a prerequisite for successful ASD implementation. Instead, a pragmatic approach that prioritizes precursor efficiency, environmental impact and integration robustness provides a more realistic and sustainable pathway for the adoption of ASD in high volume semiconductor manufacturing.

Area Selective Deposition

Room ETEC Atrium - Session ASD2-TuM

ASD of 2D and Al₂O₃

Moderators: Robert Clark, TEL, Gregory Parsons, North Carolina State University

10:45am ASD2-TuM-10 Selective Heterogeneous Integration of TMDs via Single-Source Spin-on Chemistry, Zakaria Al Balushi, University of California at Berkeley

INVITED

Two-dimensional (2D) semiconductors offer a compelling pathway beyond the scaling and energy-efficiency limits of silicon nanoelectronics, yet their manufacturable and heterogeneous integration remains a central challenge. Here we report a wafer-scale, conformal growth strategy for continuous mono- to few-layer transition-metal dichalcogenides (TMDs) based on spin-coating single-source dithioacid-derived organosulfur precursors. This chemistry provides an intrinsically high chalcogen-to-metal ratio that enables direct growth and integration without external chalcogen delivery. Upon mild annealing, the precursor undergoes conversion through metastable sulfur-rich intermediates, enabling uniform nucleation, thickness control, and continuous layer formation on both planar substrates and high-aspect-ratio topographies. In situ spectroscopy, molecular dynamics simulations, and density functional theory collectively elucidate the reaction pathway linking precursor chemistry to crystallization kinetics, grain size evolution, and defect formation. The resulting TMD films exhibit optical quality comparable to exfoliated monolayers, as evidenced by strong photoluminescence and well-resolved Raman modes, and enable selective-area growth as well as sub-5 nm high-k dielectric integration without seed layers. Devices fabricated from these films demonstrate robust field-effect transistor performance and vertically integrated

memristors exhibiting nanosecond-scale spike-timing-dependent plasticity. By decoupling TMD growth from gas-phase chalcogen chemistry, this intrinsically high-chalcogen single-source approach provides a general and scalable route to the direct heterogeneous integration of layered metal sulfides, establishing a practical foundation for manufacturable 2D electronic and neuromorphic systems.

11:15am ASD2-TuM-12 Self-Aligned Lateral MoS₂-TiS₂ Heterostructures via Area-Selective ALD of TiS₂ on CVD MoS₂, Lucas G. Cooper, University of Michigan; Pawan Kumar, Pierre Morin, Benjamin Groven, IMEC, Belgium; Ian E. Campbell, IMEC; Ageeth A. Bol, University of Michigan

High contact resistance is one of the main factors holding back the performance of TMD based FETs. One proposed solution to lowering contact resistance is through TMD edge contacts. Edge contacts are theorized to outperform top contacts due to more efficient charge carrier injection, aided by the conductivity anisotropy in TMDs. ALD is an ideal method to deposit these contacts, as it is based on self-limiting surface reactions and has the potential for area selective deposition. Area selectivity would allow for preferential deposition on the edge of the TMD channel rather than the basal plane to form self-aligned lateral heterostructures, allowing for precise contact placement and removing the need for excess lithography steps.

A thermal ALD process for TiS₂ was developed using tetrakis(dimethylamido) titanium(IV) and Ar/H₂S as the reactants. This process is shown to be inherently area selective, as we realize the formation of lateral heterostructures of CVD synthesized MoS₂ and ALD synthesized TiS₂. Beginning with an unclosed monolayer of MoS₂, we are able to selectively deposit on the exposed areas of substrate while avoiding depositions on the basal plane. This selectivity is shown through spectroscopic ellipsometry, AFM, Auger spectroscopy, and SEM.

We also demonstrate the ability to tune the resistivity, stoichiometry, and crystallinity of TiS₂ through altering deposition parameters. At a deposition temperature of 100°C, the material has a stoichiometry of Ti_{0.96}S₂ and a resistivity of . When increasing the deposition temperature to 150°C the film becomes more metal rich with a Ti:S ratio of Ti_{1.07}S₂. The more Ti-rich film has a resistivity of , lower than that of bulk TiS₂. We also show that the stoichiometry of the films has a direct impact on the crystallinity. By undersaturating the Ti precursor the excess metal can be modulated, resulting in more crystalline material. The impact of oxidation on the resistivity of TiS₂ is also explored. It was found that films with excess Ti maintain a low resistivity after exposure to ambient conditions, while films with little to no excess Ti have large increases in resistivity, showing an alternate mode of conductance based on stoichiometry.

In this research we demonstrate the ability to form lateral heterostructures through an inherently selective ALD process for TiS₂. We are also able to tune the properties of TiS₂ by modifying deposition temperature, and precursor dose time. This provides a clear path for the formation of TMD based FETs with TiS₂ contacts, and the ability to optimize these contacts through altering deposition parameters.

11:30am ASD2-TuM-13 Laser-Activated Area-Selective Atomic and Molecular Layer Deposition on 2D Materials, Aleksei Emelianov, New York University; Kamila Mentel, University of Jyväskylä, Finland; Amr Ghazy, Joonas Pekkanen, Aalto University, Finland; Yu-Han Wang, Andreas Johansson, University of Jyväskylä, Finland; Maarit Karppinen, Aalto University, Finland; Mika Pettersson, University of Jyväskylä, Finland

Developing controlled, defect-free, and spatially selective deposition of molecular and hybrid thin films on two-dimensional (2D) materials remains a key challenge due to their surface inertness and lack of reactive sites for atomic and molecular layer deposition precursors [1]. Here, we demonstrate area-selective atomic/molecular layer deposition (AS-ALD/MLD) of europium-organic (Eu-BDC) thin films on graphene and other 2D materials using direct femtosecond laser two-photon oxidation (TPO). Ultrafast laser irradiation locally introduces oxygen-containing functional groups on nanomaterials [2,3], enabling selective precursor chemisorption and nucleation in predefined regions. The laser dose defines the density of nucleation sites and allows precise control over Eu-BDC film thickness, uniformity, and selectivity with sub- μ m spatial resolution. By optimizing deposition parameters and the graphene transfer process, we achieve over 90% selectivity and high film homogeneity for Eu-organic films up to 11 nm [4]. The choice of transfer polymer strongly affects selectivity. Working with freshly grown 2D materials reduces surface contamination and allows for clean interfaces with deposited thin films.

The resulting graphene/Eu-BDC heterostructures exhibit strong photoluminescence upon 532 nm excitation, including emission features

not observed on Si/SiO₂ substrates. Photoluminescence quenching and shortened lifetimes indicate efficient energy and charge transfer at the graphene/Eu-organic interface, while electrical measurements reveal a controllable and reversible n-type doping of graphene induced by the Eu-organic layer. Annealing during growth restores graphene close to its initial electronic state.

The same TPO-assisted activation strategy is also demonstrated on other 2D materials, including MoS₂ and WS₂, where laser-induced oxides and defects act as active nucleation sites. This work establishes a scalable, maskless approach for AS-ALD/MLD on chemically inert 2D surfaces and enables patterned integration of metal-organic thin films with tunable optical and electronic properties.

References:

- [1] K. Kim et al., Nat. Commun. 2014, 5, 4781, DOI: 10.1038/ncomms5781
- [2] J. Aumanen et al., Nanoscale 2015, 7, 2851-2855, DOI: 10.1039/c4nr05207b
- [3] A. Emelianov et al., Adv. Mater. 2024, 36, 2402907, DOI: 10.1002/adma.202402907
- [4] A. Emelianov et al. ChemRxiv 2025 (under review), DOI: 10.26434/chemrxiv-2024-81qv0-v2

11:45am **ASD2-TuM-14 Acetic Acid-Modulated Al₂O₃ Atomic Layer Deposition on Monolayer MoS₂ for Controlled Nucleation**, *Hwan Oh*, Brookhaven National Laboratory, Republic of Korea; *Qin Wu*, Brookhaven National Laboratory, China; *Suji Park*, Brookhaven National Laboratory, Republic of Korea; *Kim Kisslinger*, Brookhaven National Laboratory; *Chang-Yong Nam*, Brookhaven National Laboratory, Republic of Korea

Ultrathin dielectric integration on 2D semiconductors is essential for continued device scaling in beyond-Si nanoelectronics. However, the chemical inertness of van der Waals basal planes remains a fundamental obstacle to uniform atomic layer deposition (ALD) nucleation and growth. Here, we present an acetic acid (HAc)-modulated ALD strategy implemented through an ABC-type sequence (HAc/TMA/H₂O) to regulate Al₂O₃ nucleation on monolayer (1L) MoS₂. In situ quartz crystal microbalance (QCM) measurements reveal robust HAc adsorption on Al₂O₃ and suppressed subsequent Al₂O₃ growth on passivated surfaces. Applied to 1L MoS₂, this inhibitory pathway mitigates 3D island coarsening and redirects precursor adsorption toward uncovered basal planes, enabling nearly continuous ultrathin (~1.5 nm) Al₂O₃ films with improved uniformity, as confirmed by atomic force microscopy (AFM) and cross-sectional scanning transmission electron microscopy (STEM) coupled with energy-dispersive X-ray spectroscopy (EDS). Density functional theory calculations further provide atomistic insight, showing the energetic preference of HAc for Al₂O₃ over 1L MoS₂ and attenuated TMA adsorption on HAc-passivated sites. Overall, this small molecule inhibitor-modulated pathway establishes a generalizable route to controlled ALD nucleation for reliable dielectric integration across diverse ALD chemistries and 2D materials, offering opportunities for next-generation nanoelectronics device fabrication.

12:00pm **ASD2-TuM-15 Aluminum Precursor Impact on Selectivity for Dielectric on Metal Selective Deposition**, *Florian Preischel*, Leibniz Institute for Solid State and Materials Research, Germany; *Jiyeon Kim*, *Dennis Hausmann*, *Alexander Fox*, LAM Research; *Harish Parala*, *Anjana Devi*, Leibniz Institute for Solid State and Materials Research, Germany

Selective deposition of a dielectric film, such as aluminum oxide (Al₂O₃) or hafnium oxide (HfO₂), 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. The DMATMS-modified SiO₂ surface exhibits a significant (~2 nm) nucleation delay relative to the uninhibited surface from AlO_x deposition from DMAI/H₂O. The goal of this work is to evaluate alternate aluminum precursors and determine their impact on selectivity. Methods for assessing the selectivity failure modes are also examined in the context of screening alternative precursors.

Evaluation of selectivity performance is primarily conducted using microscopy techniques such as TEM and SEM, spectroscopic methods such as FTIR and ellipsometry, and physical techniques such as water contact

angle (WCA) measurement. These methods typically do not provide information about the surface state of the inhibited surface prior to continuous film formation. We use vapor-phase decomposition mass spectrometry (VPD-MS), which can determine effective film thicknesses of <0.0001 nm. Compared with conventional methods, which require >0.1 nm of continuous film for detection, VPD-MS enables the determination and quantification of events during the initial nucleation period. The selectivity and nucleation behavior of several aluminum precursors are evaluated using ellipsometry, WCA, and VPD-MS, in comparison to the baseline process with DMAI/H₂O. In addition, the failure mode mechanisms revealed by this metrology are presented.

12:15pm **ASD2-TuM-16 Area-Selective Atomic Layer Deposition of Al₂O₃ Film Using Bulky Al Precursor AlMe₂(iPr-AMD)**, *Akihiro Nishida*, *Atsushi Yamashita*, *Takuya Takahashi*, *Masaki Enzu*, *Ryota Fukushima*, *Tomoharu Yoshino*, ADEKA CORPORATION, Japan

Trimethylaluminum (TMA) loses its selectivity within a short time, which is problematic because it exhibits excessively high reactivity toward H₂O and surface sites, an extremely small molecular size, and low thermal stability even if a passivation layer is used. To achieve high selectivity, precise control of the reaction between the precursor and the substrate surface and minimization of unwanted reactivity are essential. Therefore, to achieve excellent area-selective atomic layer deposition (AS-ALD), we thoroughly investigated novel precursors and found that AlMe₂(iPr-AMD) is an outstanding candidate that exhibits good thermal properties and high volatility. We carried out AS-ALD of an Al₂O₃ film on Cu and native oxide Si substrates using AlMe₂(iPr-AMD) with H₂O as a coreactant. For the dielectric-on-dielectric selective growth process, 1-dodecanethiol (DDT) was used as a self-assembled monolayer (SAM) passivant on the Cu surface. The Al₂O₃ film growth was inhibited on the Cu surface as a result of passivation by the SAM during deposition of a >100 Å-thick Al₂O₃ film onto the native oxide layer of a Si surface at 150 °C using AlMe₂(iPr-AMD). This result substantially exceeded that achieved with Dimethylaluminum isopropoxide (DMAI) under identical conditions. For the dielectric-on-metal selective growth process, n-octadecyltrichlorosilane (ODTS) was used as a SAM passivant on the dielectric surface. In contrast to the DDT SAM, the ODTS SAM showed restrained Al₂O₃ film growth on the Si surface and achieved Al₂O₃ film growth only on the Cu surface. These results indicate that the AlMe₂(iPr-AMD) precursor adsorption is strongly inhibited by SAM passivation as a result of its bulky structure, reduced Lewis acidity, and lower level of reactivity compared to TMA. In addition, results from AS-ALD processes employing not only DDT and ODTS but also additional passivation molecules will also be discussed.

Area Selective Deposition

Room ETEC Atrium - Session ASD1-TuA

ASD and Inhibitors III

Moderators: Anjana Devi, Leibniz Institute for Solid State and Materials Research, Paul Ragogna, Western University

1:30pm ASD1-TuA-1 Area-Selective ALD with Polymer Masks: Deposition Mechanisms and Trade-offs, Katherine Young, Andy Hsiao, Harley Hayden, Georgia Tech Research Institute; Amy Brummer, Chris Yang, Georgia Institute of Technology

INVITED

As devices have continued to scale down in size, fabrication of smaller features using novel deposition methods has become a necessity. Strict requirements of location and alignment are often necessary but difficult to achieve, which has led to studies of area selective deposition. Area selective deposition, such as area-selective atomic layer deposition (AS-ALD), can be achieved by manipulating deposition parameters to produce deposition preferences for different materials. A material is deposited selectively at certain locations based on the interaction of the precursors with different surface chemistries, so etching is not usually necessary. In fact, these techniques are often the only option for patterning different materials if the geometry of the substrate cannot be patterned lithographically. In contrast, single material substrates can achieve preferential deposition by first patterning an organic mask, which inhibits deposition, and then removing the mask to leave a patterned region. This technique is especially useful for patterning substrates that may be sensitive to etching. However, the selectivity between two different materials under certain deposition parameters limits the use of some materials and ALD precursors. Thus, a deeper understanding on the mechanism of AS-ALD is necessary to understand limitations on feature sizes.

This study describes the mechanisms for AS-ALD of common oxide materials and the effects of these deposition mechanisms on feature sizes. ALD of TiO_2 and HfO_2 were studied to understand the selectivity of the deposition on Si vs PMMA and how that selectivity affected feature size dimensions and film thickness. ALD of TiO_2 is highly selective for Si in comparison to PMMA; however, the effects of the PMMA side walls inhibit deposition so that the dimensions of the TiO_2 feature is smaller than the PMMA pattern. This side wall inhibition significantly affects possible feature sizes using TiO_2 and PMMA patterns. In contrast, HfO_2 is less selective than TiO_2 and demonstrates a mechanism combining selective deposition and lift-off. This lower selectivity limits possible HfO_2 thicknesses before there is blanket coverage, but it also exhibits less side wall inhibition. Significantly smaller feature sizes were obtained with HfO_2 compared to TiO_2 in these ALD conditions. These results suggest that the deposition mechanism itself, whether it is a truly area selective deposition or combined with liftoff, will always affect possible feature sizes.

2:00pm ASD1-TuA-3 Photoresists as Inhibitor for Area-Selective ALD of Oxide Thin Films, Ludovic Hahn, Chloé Guerin, Raphaël Feougier, Nicolas Gauthier, Marc Veillerot, Vincent Jousseau, CEA-LETI, France

Area-selective deposition (ASD) is a promising approach for selectively localizing a material on a specified growth surface. Organic molecules, such as self-assembled monolayers and small-molecule inhibitors, are commonly used to inhibit material growth. However, significant inhibition greater than 20 nm is rarely achieved with these types of inhibitors, which limits their use for certain applications. A possible alternative is to use photosensitive polymers as inhibitor, which are widely used in microelectronics and in high-volume manufacturing. This approach greatly simplifies integration schemes by combining the precision of photolithography with the advantage of an etch-free process, which is very beneficial in the case of highly sensitive materials. However, the use of these inhibitors has received little attention in the literature.

In this work, commercial photoresists with different properties and chemical compositions were used to inhibit the growth of oxides deposited by low-temperature atomic layer deposition (ALD). These include a poly(hydroxystyrene)-based photoresist (PHS), which is a positive chemical amplified photoresist (for 248 nm deep-UV lithography), a positive Novolak resin and a negative polyimide (PI) photoresist. Both are sensitive to wavelengths of 365 nm (i-line) and 436 nm (g-line). Their inhibition potential was characterized using atomic force microscopy (AFM), ellipsometry and X-ray fluorescence (XRF). Significant inhibition of ZnO was achieved using $\text{DeZn}/\text{H}_2\text{O}$ as precursors, with inhibition of up to 15 nm on the PI and the Novolak resins, and up to 45 nm on the PHS resist. No

inhibition of SnO_2 is observed when using TDMASn and H_2O_2 on these photoresists. However, using H_2O as the co-reactant enables inhibition up to 7 nm of SnO_x on the PHS resist. These results can be compared to those obtained with PMMA, which provides the best selectivity by far, with inhibition of at least 60 nm for both oxides. In addition, photoresists patterned using different sizes and shapes reveal that inhibition loss varies between them.

Interestingly, a very good selectivity is achieved with a PHS-based photoresist, which contains reactive hydroxyl groups. This is counterintuitive, given that passivation molecules currently in development are usually selected for having non-reactive functions to avoid reactions with precursors and lead to a hydrophobic surface. Therefore, the inhibition mechanism was carefully studied by using FTIR, XPS, and ToF-SIMS analyses. By comparing with PMMA results, this work allows to better understand the origin of the inhibition by these photoresists and how the loss of selectivity is likely to be induced.

2:15pm ASD1-TuA-4 Progress Toward Multi-Material Area Selective Deposition, Jeremy Thelven, Woonkyu Youn, Gregory Parsons, North Carolina State University

An outstanding challenge in the field of area selective deposition (ASD) is the demonstration of “bottom up” construction incorporating multiple materials in a sequence of orthogonal ASD steps. To date, a few reports examine methods to integrate multiple ASD materials,¹⁻⁴ but processes that fully repeat multimaterial ASD sequences are not known. Previously, we reported an ASD sequence of TiO_2 (or ZnO) on SiO_2 followed by ASD of W (or MoSi_x) on Si-H.^{1,2} Recently Poonkottil et al. demonstrated a sequence of ASD SnO_x on SiO_x vs. PMMA followed by co-located TaO_x on SnO_x vs. PMMA.³

In this study, starting with a previously reported CVD-ASD process for PEDOT on SiO_2 vs Si-H,^{4,5} we worked to develop an orthogonal ASD sequence shown in Figure 1. Starting with SiO_2 and Si-H, the addition of PEDOT and MoSi_x requires four distinct ASD steps: 1) PEDOT ASD on SiO_2 vs. Si-H; 2) MoSi_x ($\text{MoF}_6/\text{SiH}_4$, ALD) ASD on Si-H vs. PEDOT; 3) PEDOT ASD on PEDOT vs. MoSi_x ; and 4) MoSi_x on MoSi_x vs. PEDOT.

For the “ASD-1” step, we deposited ~10 nm of ASD PEDOT on SiO_2 vs. Si-H where the PEDOT shows inherent inhibition on Si-H. Using this starting surface, we explored ALD of MoSi_x using MoF_6 and SiH_4 as “ASD-2”. This MoSi_x process was successful, showing inherent inhibition on PEDOT vs Si-H, enabling more than 10 nm of MoSi_x ASD before the onset of substantial nucleation on PEDOT. Then, for “ASD-3”, we repeated ASD-1 and found that the MoSi_x showed no inherent inhibition. Therefore, we examined potential growth inhibitors to selectively passivate MoSi_x . Using water contact angle for initial screening, we examined MoSi_x exposed to octyl phosphonic acid (OPA), octadecyl phosphonic acid (ODPA), methane sulfonyl chloride (MSC), and methane sulfonic acid (MSA). From these results, we performed PEDOT CVD on MoSi_x samples treated with ODPA, OPA, and MSC, and initial results suggest ODPA may effectively passivate MoSi_x for PEDOT ASD. After this, we began studies of “ASD-4” by repeating the ALD of MoSi_x used for ASD-2. Initial results show that remnants of the ODPA passivation layer present on MoSi_x after ASD of PEDOT act to inhibit further MoSi_x ALD, indicating more work is needed to realize the integration scheme presented above. In this presentation, we will provide details of ASD processes and mechanisms and describe expected means to further advance the understanding of multimaterial ASD.

(1) H. Oh, et al., *Adv Funct Materials* **2024**

(2) S.K. Song, et al., *ACS Nano* **2021**

(3) N. Poonkottil, et al. *Journal of Vacuum Science & Technology A* **2026**

(4) H. Oh, et al. *Chem. Mater.* **2023**

(5) J.-S. Kim, et al. *Journal of Vacuum Science & Technology A* **2022**

2:30pm ASD1-TuA-5 Area-Selective Deposition as a Solution to Edge-Induced Shunting in Solar Cells, Nilesh Nilesh, Indian institute of Technology Madras, India; **Namitha Dsouza, Jatin Kumar Rath, Somnath Chanda Roy,** Indian Institute of Technology Madras, India

The advancement of photovoltaic technologies relies on high-quality thin films and precise interface engineering to improve charge transport, suppress recombination, and enhance device stability. Atomic layer deposition (ALD) is highly attractive for solar cell fabrication due to its atomic-scale thickness control, excellent uniformity, and exceptional conformality over complex surfaces; however, ALD growth requires a functionalized surface. These advantages are critical for emerging device architectures, where accurate control of hole-transport layers (HTLs),

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electron-transport layers (ETLs), passivation layers, and transparent conductive oxides (TCOs) directly affects performance.

A key limitation of conventional ALD is its non-line-of-sight nature caused by precursor diffusion, which results in unwanted deposition on wafer edges and the backside. In solar cells requiring single-side deposition, such uncontrolled growth can create parasitic shunting paths by electrically connecting front and rear layers at the wafer perimeter, making edge isolation extremely challenging and often leading to negligible photovoltaic output.

To address this issue, we developed an area-selective ALD (AS-ALD) approach based on patterned functionalized surfaces with selective precursor wetting. This method selectively inhibits deposition within a few millimetres from the wafer edge while maintaining uniform growth in the central region. The approach preserves the intrinsic advantages of ALD and does not require lithography or physical masking, relying instead on a simple process modification. PMMA is used as a growth-inhibitor surface.

In this study, two silicon solar cell devices were fabricated on commercial Cz wafers using identical material stacks. Both devices incorporated V_2O_5 as HTL, TiO_2 as ETL, Al_2O_3 for passivation, and AZO as TCO. The sole difference between the devices was the deposition method: conventional thermal ALD was used for one device, whereas AS-ALD with PMMA acting as a growth-inhibitor surface was employed for the other to suppress edge deposition.

The device fabricated using conventional ALD exhibited severe shunting, with parasitic edge conduction dominating its electrical characteristics and suppressing the open-circuit voltage, resulting in the absence of a photovoltaic response. The AS-ALD-based device showed stable and functional photovoltaic behaviour. By effectively preventing edge-related shunt pathways, the device achieved a proof-of-concept efficiency of 2.51%. Although this efficiency is modest, the results clearly demonstrate the critical role and effectiveness of selective deposition in enabling functional ALD-based solar cells.

2:45pm ASD1-TuA-6 Accelerating Future Logic Devices with Precision Area Selective Deposition, Yamato Tonegawa, TEL TTS, Japan INVITED

The semiconductor industry has entered a new phase driven by advances in device architectures featuring three-dimensional nanoscale structures, demanding innovative film deposition technologies that offer precision, scalability and sustainability.

Area Selective Deposition (ASD) is innovative technique that enables direct thin film formation only on specific regions of a substrate without the use of masks.

ASD not only contributes to the simplification of process steps but is also critically important for achieving the precise thin-film technology necessary for improving device performance.

In order to apply ASD to device manufacturing processes in the future, several challenges must be addressed. Besides requiring excellent selectivity, it is also essential to enable various types of film deposition, avoiding damage to adjacent areas and precisely control the growth direction and the morphology of the films.

This presentation explains the latest trends in ASD technology and provides examples of selective deposition of dielectric and metal films aimed at next-generation device applications.

Additionally, new process technologies and initiatives addressing these challenges will be introduced.

Area Selective Deposition

Room ETEC Atrium - Session ASD2-TuA

AI and Machine Learning for ASD

Moderators: Kayvan Kashefi, Applied Materials, Tania Sandoval, Universidad Tecnica Federico Santa Maria

3:45pm ASD2-TuA-10 ALD Precursor Design Through Atomic-Level Simulation, Yusuke Asano, Matlantis corporation, Japan INVITED

The integration of machine learning (ML) into atomic layer deposition (ALD) research offers a promising pathway to accelerate materials discovery. However, establishing reliable workflows that link atomic-level simulations with macroscopic process parameters remains a challenge. In this talk, we propose a comprehensive computational approach using a universal machine learning interatomic potential (uMLIP), Matlantis (PPF), to explore the potential of "inverse design" for Area-Selective ALD (ASD) precursors. First, we present a methodology for exploring surface selectivity

through high-throughput screening. Utilizing the universality of PPF, we calculated adsorption energies for varying Cobalt and Ruthenium precursors on growth (Si) and non-growth (Alkyl-SAMs) surfaces. By coupling these calculations with descriptor-based regression (LASSO) and Bayesian optimization, we established a workflow to extract ligand features that contribute to selectivity (e.g., piperidine derivatives) and to analyze the impact of steric bulk on reaction barriers. While these findings are preliminary, they demonstrate how data-driven approaches can guide the search for optimal molecular structures. Second, we discuss an emerging approach to predict precursor volatility from atomic simulations. We investigated the correlation between the enthalpy-related term derived from calculated adsorption free energy (ΔG_{ads}) and the Antoine equation's B parameter (heat of vaporization). Our initial model suggests a physical link between microscopic adsorption behavior and macroscopic volatility, showing a promising correlation for Co precursors. Although further validation with expanded datasets is required, this method indicates the possibility of predicting vapor pressure curves directly from computational results. By unifying reactivity analysis and property prediction within a single framework, this work highlights the capabilities of universal MLIPs as a tool for continuous methodology research. We will discuss current limitations, such as data scarcity, and the future outlook for refining these models to achieve high-precision, purpose-driven precursor design.

4:15pm ASD2-TuA-12 AI-Enabled Screening Framework for Precursor and Inhibitor Selection in Area-Selective Deposition, Han-Bo-Ram Lee, Bonwook Gu, Incheon National University, Republic of Korea

Area-selective deposition (ASD) critically depends on whether precursors and inhibitors can selectively adsorb and react on specific substrate surfaces. In practice, identifying suitable precursor-inhibitor-substrate combinations remains challenging, as it is difficult to experimentally verify the full range of chemical and process variables. This challenge is further amplified when exploring new molecules or previously unreported combinations, where experimental guidance is scarce.

In this work, we propose a data-driven screening framework that integrates large language models (LLMs), atomistic representations, and machine learning to support precursor and inhibitor selection for ASD. LLMs are used to analyze the ASD literature and automatically extract structured information, including precursor and inhibitor chemistry, substrate materials, process temperatures, and reported deposition outcomes. Based on this information, molecular structures of precursors and inhibitors are generated and then relaxed using machine-learning force fields (MLFFs). These relaxed structures, together with substrate descriptions and process parameters such as deposition temperature, are used to construct feature sets describing precursor-substrate and inhibitor-substrate interactions. Rather than focusing on detailed property prediction, the framework treats ASD outcomes as a classification problem (e.g., selective adsorption vs. non-selective/no adsorption) to assess whether selective adsorption and subsequent film formation are likely under specific conditions. The framework is modular, allowing flexibility in the choice of atomistic representations and machine learning models as the dataset evolves. To assess its applicability, the framework is being applied to an initial set of precursors and inhibitors not included in the training dataset, and the resulting predictions are used to guide subsequent ASD experiment design. By organizing existing knowledge and enabling rapid pre-screening of unexplored molecules, this approach provides a practical pathway toward more systematic and efficient development of area-selective deposition processes.

4:30pm ASD2-TuA-13 Computational Modeling Set in Motion: A Dynamic & Statistical View on SMI Layer Blocking Events Powered by Machine-Learned Potentials, Philipp Wellmann, Leipzig University, Germany

With the ability to process well-defined, uniform patterns at the nanometer scale, humanity has entered the era of atomic crafting. Whereas ALD is the pinnacle engineering technology to control the arrangement of features on the atomic scale, computational material science is a high-resolution window to monitoring, understanding, and fine-tuning of the various manufacturing processes. [1] Besides the steady increase of computing power, it is the rise and maturing of machine learning methods that provides material science with a myriad of uncharted possibilities left to explore for the ALD community. The most tangible of the recent improvements is the ascent of machine-learned potentials (MLPs), that tick most boxes on a computational material science method wish list: speed & accuracy paired with robustness & universality.

In inhibitor-based AS-ALD, where the systems of interest are rather large, the calculation of stationary quantities is computationally very demanding

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for the typical *ab initio* workhorse methods. Yet, these optimized glimpses of the system may only provide a limited understanding of the highly dynamic AS-ALD processes. MLPs now offer the possibility to calculate the forces and energies of the AS-ALD systems with comparably small error margins at a cost reduction factor of well over 1000. [2] Hence, the current generation of MLPs paves the way for exploring the dynamic view on AS-ALD, where the models' capabilities ultimately depend upon the quality of the training data.

We show how to compose data sets for the training of MLPs over a variety of ALD systems, while minimizing the amount of the time determining the DFT calculations. Equipped with these MLP models, we have the means to obtain statistical information on the blocking performance of an SMI layer in the event of a precursor impact by conducting tens of thousands so-called "molecular gun" dynamics simulations, with many process parameters (e.g. precursors, SMI density, temperature, degree of SMI layer deterioration, etc.) being adjustable at will. This novel, dynamic view on inhibitor-based AS-ALD furthers the understanding of experimental results and has also consequences for interpreting static modelling experiments.

References

F. Pieck, R. Tonner-Zech, *Chem. Mater.***2025**,*37*, 2979-3021, DOI: 10.1021/acs.chemmater.4c03477

H. Weiske, R. Barret, R. Tonner-Zech, P. Melix, J. Westermayr, *Digit. Discov.***2025**, DOI: 10.1039/D5DD00420A

4:45pm **ASD2-TuA-14 Establishing Boundaries: Using Machine Learning to Design Aminosilane SMIs**, *Marshall Atherton*, Carleton University, Canada; *Jiyeon Kim*, *Dennis Hausmann*, Lam Research Corporation; *Sean Barry*, Carleton University, Canada

Area-selective atomic layer deposition (AS-ALD) exploits surface chemistry to confine deposition to specific surface regions, minimising the need for lithographic steps. This work presents a systematic study of the structure-function relationships in amino-substituted silanes designed for use as AS-ALD inhibitors, with an emphasis on thermal volatility and surface selectivity. The goal is to improve the environmental impact of aminosilane production scale-up by exploring alternative synthetic pathways.

A more environmentally benign nucleophilic substitution route to the synthesis of disubstituted amines with chlorosilanes was undertaken using triethylamine as a sacrificial base, enabling access to a diverse inhibitor library while avoiding pyrophoric reagents and metal-containing intermediate chemistry. Thermal behaviour was evaluated by thermogravimetric analysis, as well as by measuring pressures at which 1 Torr of vapour is produced, and by determining decomposition temperatures using differential scanning calorimetry. Surface coverage of viable aminosilanes was assessed in an Anric ALD reactor equipped with an in-situ quartz crystal microbalance to measure adsorption and selectivity on metal and dielectric surfaces. Compounds exhibiting selective adsorption were subsequently assessed for growth inhibition of diethylzinc/water ALD relative to the bare surface on patterned metal/dielectric wafers.

The thermal data generated from this study were used to train structure-property machine learning (ML) models that map Si precursor structure and composition to relevant thermophysical properties, such as volatility and thermal stability. A commercially available chemistry-informed molecular property prediction engine (DeepAutoQSAR by Schrödinger) was leveraged to select the most accurate ML model to predict Si precursor properties. This ML model was then used to predict the physical properties of several additional Si precursors not included in the original training data. The predicted properties were compared to the experimentally determined properties to evaluate the model's performance.

5:00pm **ASD2-TuA-15 Surface Reaction Analysis of Area-Selective Co ALD Using a Machine-Learning Potential**, *Naoki Tamaoki*, *Jun Yamaguchi*, *Noboru Sato*, *Atsushi Tsukune*, *Yukihiro Shimogaki*, The University of Tokyo, Japan

As interconnect dimensions continue to scale, the current density in semiconductor wiring increases, and the resulting electromigration-induced degradation of Cu interconnect reliability has become a critical concern. Introducing a metallic Co capping layer is expected to enhance adhesion between interconnects and dielectrics, thereby extending the lifetime of Cu lines. In Co atomic layer deposition (ALD) using CCTBA (cobalt carbonyl tert-butyl acetylene) as the precursor, an incubation period exists on SiO₂ dielectric surfaces compared with Cu surfaces, enabling inherent selectivity in nucleation and growth. Here, we report an atomistic surface-reaction analysis of this area-selective Co-ALD process using simulations based on a

machine-learning potential (PPF; Preferred Potential by Preferred Networks, Inc.).

Our previous calculations indicate that CCTBA readily undergoes dissociative chemisorption on Cu surfaces via an exothermic pathway. In contrast, chemisorption on OH-terminated silicon oxide is endothermic and accompanied by an activation barrier of approximately 1.5 eV, making adsorption kinetically unfavorable and thereby contributing to selectivity. In this work, we further evaluated possible gas-phase decomposition pathways of CCTBA and found that a reaction involving CO-ligand dissociation can occur with an activation energy of ~1.3 eV. The resulting activated intermediate (CCTBA with one CO ligand removed) can physisorb with an adsorption energy of ~0.64 eV and then proceed to chemisorption by forming a Co-O bond with surface oxygen over a small barrier of ~0.2 eV. These results suggest that gas-phase decomposition may promote initial nucleation on non-growth surfaces, potentially degrading selectivity.

To explore a mitigation strategy, we considered the role of NH₃, motivated by prior reports on selective CVD using Co₂(CO)₈, where co-feeding NH₃ strongly suppresses growth initiation on non-growth surfaces. Consistent with this concept, our calculations confirm that NH₃ preferentially adsorbs on OH groups that otherwise serve as adsorption sites for Co precursors. This site-blocking effect may reduce nucleation on dielectric surfaces and help maintain high selectivity in area-selective Co deposition.

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

References

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5:15pm **ASD2-TuA-16 Understanding NHC Blocking Efficiency on Copper and Gold: From Surface Assembly to Precursor Inhibition**, *Franz Thiemann*, *Patrick Melix*, Leipzig University, Germany; *Emmett Desroche*, *Francesco Tumino*, *Cathleen Crudden*, Queen's University, Canada; *Ralf Tonner-Zech*, Leipzig University, Germany

In area-selective atomic layer deposition (ASD), the development of thermally robust and chemically specific blocking layers remains a key challenge for achieving defect-free patterning. N-heterocyclic carbenes (NHCs) have emerged as versatile small-molecule inhibitors with exceptional affinity for transition-metal surfaces, providing a tuneable molecular platform for surface passivation. In this work, we investigate the blocking efficiency of NHC monolayers on copper substrates using density functional theory (PBE+D4) combined with periodic slab models, thereby extending previous findings from analogous Au(111)-NHC systems.^[1] The resulting adatom-mediated dimer pattern forms a compact organic overlayer that effectively inhibits precursor adsorption during subsequent ALD half-cycles. Energy decomposition analysis for the extended systems^[2] reveals the origin of the overlayer stability: strong σ -donation to the surface and π -backdonation, together with dispersion interactions between the NHC backbones. Simulated STM images reproduce experimentally observed patterns at surface coverages of approximately 1.8 NHC nm⁻².^[3] The blocking efficiency of this layer against common ALD precursors was validated using an innovative machine-learning-based molecular dynamics workflow.^[4] This approach, referred to as the molecular gun method, reveals not only the statistical blocking efficiency but also the underlying mechanisms governing surface blocking and precursor breakthrough. Collectively, these results reveal the atomic-scale origins of NHC-based blocking in ASD and provide a foundation for the rational design of next-generation NHC architectures with optimized binding strength, packing order, and blocking performance.

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[2] Raupach et al. *J. Chem. Phys.***2015**, *142*, 194105.

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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, Cathleen Cruden*, 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 of high- κ dielectric on SiO₂ over Au bands. The selective adsorption behavior 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.

References:

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- [2] Nat. Commun. 2016, 7, 12654.
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- [4] Chem. Sci., 2024, 15, 2480-2485
- [5] J. Am. Chem. Soc. 2025, 147, 7, 5624–5631

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 SiO₂ and TiN surfaces. The simulations indicate a preference for EtOH adsorption on hydroxyl terminated SiO₂ 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 SiO₂. 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 SiO₂ 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.

References

1. F. Pieck, R. Tonner-Zech, *Chem. Mater.* **2025**, *37*, 2979-3021, DOI: 10.1021/acs.chemmater.4c03477.

ASD-TuP-7 Integrating Catalytic PMMA Etching with PMMA-Inhibited ASD of HfO₂, *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 O₂ 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/SiO₂ via catalytic O₂ 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 ZrO₂ in ZrO₂-based DRAM capacitors can promote ZrO₂ 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 °C. 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, Seo Eun 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 with MoO_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 electrode on 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 O_3 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.

References

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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 $<0.5\text{\AA}$) 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

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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 AlGaIn/GaN surface promotes faster nucleation, thereby, higher cycle rate than AlN/Si. Moreover, this wurtzite nature of the immediate substrate surface of AlGaIn 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 $\sim 2.07@75\text{nm}$ on Si, while bulk AlN is 2.1 & thick epi-layer is 2.095. At 350°C AlN on AlGaIn/GaN has n of $2.096@80\text{nm}$, indicating a nice cohesive high-quality AlN by TEL ALPHA 8SE™. 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 $Mo(CO)_6$, Yukihiko Shimogaki, Souga Nagai, Jun Yamaguchi, Noboru Sato, Naoki Tamaaki, Atsuhiko 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 ($\leq 400^\circ\text{C}$ for logic and $\leq 600^\circ\text{C}$ 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 $10\times 10\text{mm}$ 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 semiconductor technology advances toward sub-5 nm nodes, ruthenium (Ru) area-selective atomic layer deposition (AS-ALD) is of growing interest as 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 $200\text{--}300^\circ\text{C}$. Cross-sectional scanning electron microscopy (SEM) with surface coverage analysis reveals that both surfaces exhibit intrinsically delayed nucleation, with different extents correlated 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 *in situ* 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.

Acknowledgement

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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 Al₂O₃ ALD with trimethylaluminum (TMA), a small and highly reactive precursor.⁵

In this study, a perfluoroalkylpolyether (PFPE)-substituted alkoxy silane inhibitor (inhibitor 1) was developed, exhibiting high inhibition performance for Al₂O₃ 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/O₃-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, H₂O 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 SiO₂, Pt, TiN, Co, Cu, HfO₂, and ZrO₂ surfaces. These surfaces were subjected to 8 exposures of a 10 s pulse of pinacolborane and 30 s of N₂ purging, followed by Ru film deposition using bis(cyclopentadienyl)ruthenium (RuCp₂) and O₂ at 340°C. The results from energy dispersive X-ray spectroscopy indicate that the Ru film growth is inhibited on native SiO₂, TiN, Co, Cu, HfO₂, and ZrO₂ 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 HfO₂ 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 (TiSi₂) 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-TiSi₂ phase exhibits the desired beneficial properties; yet it is the metastable, high-resistivity C49-TiSi₂ 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-TiSi₂ 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-TiSi₂ 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 SiO₂ versus Al₂O₃ surfaces using an aldehyde-based inhibitor, butyraldehyde (BTA), and a new Ru precursor, C₄H₆Ru(CO)₃. The results reveal selective Ru growth on SiO₂, but not on the BTA-inhibited Al₂O₃ 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-Leonart, 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 $\text{MoS}_2/\alpha\text{-MoO}_3$ heterostructures with precise spatial control and excellent pattern fidelity. Raman spectroscopy confirms MoS_2 formation and reveals that amorphous MoO_3 crystallizes to $\alpha\text{-MoO}_3$ 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 MoO₃ on Gr/Ru(0001) and HOPG, Buddhika Alupotha 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, MoO₃ 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 MoO₃ 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 MoO₃ 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 MoO₃ 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 MoO₃ islands and their order increase with increasing annealing temperature. A distinct height difference of MoO₃ is observed on these two substrates. The height of MoO₃ islands on Gr/Ru(0001) corresponds to single layer of MoO₃, whereas the height of the MoO₃ island on HOPG corresponds to double layer. XPS data show that Mo

on 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 MoO₃ stoichiometry on both substrates, indicating a substantial charge transfer between MoO₃ 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 MoO₃ on graphene-based supports, providing a pathway to tailor 2D TMO heterostructures for electronic and catalytic applications.

Figure 1. Height differences of MoO₃ 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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