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 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 N_2H_4 instead of NH_3 in SiN AS-ALD was examined. First, the dependence of the SiN film thickness on the ALD cycles was investigated for both NH_3 and N_2H_4 at 600°C. The results showed that using the more reactive N_2H_4 rather than NH_3 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 SiO_2. Additionally, the SiN film thickness grown on the growth area (Si) was evaluated when growth began on the nongrowth area (SiO_2). In these measurements, the SiN film thickness on the growth area was found to be 1.3 nm with N_2H_4, while 1.5 nm with NH_3. This indicates a trade-off: using N_2H_4 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 N_2H_4 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 N_2H_4 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*; Akhilesh 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 SiO_2, and the reaction between this SMI and the SiO_2 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 SiO_2 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,* Standford 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-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/Al_2O_3 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/TiO_2 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/Al_2O_3 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 Aklanethiol Chain Length on Area Selective Deposition of Aluminum and Hafnium-Containing Films***,* ***Nicholas Strandwitz,*** Lehigh University

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

The stability and impermeability of monolayer-based blocking layers is critical to preventing film growth in certain regions.Few reports explicitly studied the affect 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 affect 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.

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