Area Selective ALD
Room Tamna Hall A - Session AS-TuA

Area Selective Deposition I

Moderators: Stacey Bent, Stanford University, **Mikko Ritala**, University of Helsinki

4:00pm **AS-TuA-11 Surface Chemistry Characterization for Area-Selective Atomic Layer Deposition of Ruthenium***, **Eun-Hyoung Cho,*** 2D Device TU(SAIT)/Samsung Electronics, Republic of Korea*; Young Min Lee, Yunseong Lee, Youngchul Leem, Giyoung Jo, Jeong Yub Lee, Kyung-Eun Byun, Jung Yeon Won, Bongsu Kim, Byeong Gyu Chae,* Samsung Advanced Institute of Technology, Republic of Korea*; Kyeongmin Min, Han-Bo-Ram Lee,* Incheon National University, Republic of Korea*; Iaan Cho, Myeong Kyun Nam, Bonggeun Shong,* Hongik University, Republic of Korea **INVITED**

Achieving atomic-scale precise control over material layering is critical for the development of future semiconductor technology. Area-selective deposition (ASD) has emerged as an indispensable tool for crafting semiconductor components and structures via bottom-up pattern transfer. The most widely used approach for ASD relies on self-assembled monolayers (SAMs) to deactivate specific surfaces. However, alternative strategies are being explored to better align with the requirements of high-volume device manufacturing and address the limitations of the SAM method. One promising alternative involves the application of small molecule inhibitors (SMIs). However, limited research has been conducted to elucidate the mechanisms governing their adsorption and inhibition of deposition. Additionally, research on elucidating the ASD mechanism, in which precursors are blocked rather than chemically adsorbed on SMIs, has predominantly relied on simulations such as density functional theory (DFT) calculations or Monte Carlo (MC) simulations. By closely investigating these interfacial phenomena using precise surface analysis techniques, a deeper understanding of the role that SMI composition and structure play in adsorption and inhibition can be achieved, ultimately contributing to the design of SMIs for future ASD systems. Recently, it was confirmed that by controlling the crystal orientation of metal grains, atomic layer deposited ruthenium (Ru) thin films on amorphous dielectric substrates exhibit electrical resistivity comparable to that of single crystal Ru. However, the oxidative counter-reactants such as O2 often used for atomic layer deposition (ALD) of metallic Ru films result in a considerable increase in contact resistance because of substrate oxidation, limiting the applications of both ALD and ASD of Ru. In this study, Ru ASD is demonstrated using two-step ALD with the sequential use of H2 and O2 as counter-reactants and dimethylamino-trimethylsilane (DMATMS) as a precursor inhibitor. Both theoretical and experimental results demonstrate that in the two-step Ru ALD, the oxide layer can be eliminated via the reduction of the oxidized substrate metal surface by the H2 counter-reactant. This mechanism simultaneously facilitates the adsorption of the Ru precursor (tricarbonyl-(trimethylenemethane)-ruthenium) and removal of the surface oxide layer. Consequently, Ru growth is suppressed on the DMATMS-inhibited SiO2 surface during ASD, enabling exclusive deposition of Ru on the Mo surface. The currently proposed Ru ASD scheme using two-step ALD is highly promising for driving advancements in interconnect technology for commercial applications.

4:30pm **AS-TuA-13 Dopant-Selective Atomic Layer Deposition (DS-ALD) for Fabrication of Electronic Devices***, **Daniel Aziz,** Nishant Deshmukh,* Georgia Institute of Technology, USA*; Ryugo Shimamura,* University of Tokyo, Japan*; Amy Brummer,* Georgia Institute of Technology, USA*; Kaifan Yue,* University of Michigan, Ann Arbor*; Siddharth Kurup,* Georgia Institute of Technology, USA*; Kira Barton,* University of Michigan, Ann Arbor*; Eric Vogel,* Georgia Institute of Technology*; Michael Filler,* Georgia Institute of Technology, USA

Area-selective atomic layer deposition (AS-ALD) methods promise bottom-up approaches for device fabrication, yet it remains difficult to achieve high selectivity with subtle surface chemical differences. In this work, we demonstrate dopant-selective ALD (DS-ALD) for the patterning of differently doped silicon surfaces. Our approach enables orthogonal patterning which can direct ALD to either heavily or lightly doped silicon. As a result, we can fabricate a metal oxide semiconductor field effect transistor (MOSFET) gate [1] on lightly doped silicon and a semiconductor-metal contact [2] on heavily doped silicon. In each of these patterning approaches, an organic surface-initiated mask is grafted from the surfaces of dopant modulated silicon structures. An etchant (aqueous KOH) then diffuses through the mask and selectively attacks the underlying silicon surface, thus degrafting the mask only in targeted regions. This process yields features to which ALD chemistries can deposit compatible metal or dielectric thin films. We characterize the process through a combination of X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), and Current-voltage (IV) measurements.

To direct ALD of gate dielectric and metal to the lightly doped silicon typically in the channel of a MOSFET, a hydrosilylation and subsequent polymerization results in the appropriate pattern after applying the selective etchant. We characterize the doping contrast required to enable this approach as well as the minimum achievable feature sizes. Notably, we observe an increase in etching selectivity as etching progresses which mimics the mechanism of aqueous KOH etching of bare silicon. ALD of the gate dielectric and metal results in working field effect devices.

To direct ALD of contact metal towards heavily doped silicon, as might be needed for the source/drain regions of a MOSFET, we leverage undecylenic acid's bifunctional nature which results in different attachment chemistry on differently doped silicon surfaces. Treatment with KOH removes the mask from the heavily doped silicon surface allowing the deposition of Pt metal via ALD on that same region. Current-voltage measurements demonstrate a metal semiconductor silicide contact.

In summary, by combining different organic mask materials with differently doped semiconductor surfaces, we can direct patterning and the subsequent AS-ALD. Our findings establish guidelines for novel approaches to nanoscale patterning and set the stage for fabricating a variety of high-performance electronic devices.

4:45pm **AS-TuA-14 ALD Outstanding Presentation Award Finalist: High Temperature Area Selective ALD SiN by in-Situ Selective Surface Fluorination***, **Haonan Liu,** Ken Okoshi, Hiroki Murakami, Yamato Tonegawa,* Tokyo Electron Technology Solutions Ltd., Japan

Presently, research on area selective atomic layer deposition (AS-ALD) is attracting strong interest. AS-ALD simplifies the process of deposition on patterned substrates and high aspect ratio (AR>70) structures, holding promise for various applications in semiconductor manufacturing. Inhibitors such as self-assembled monolayers (SAMs) and (dimethylamino)trimethylsilane (DMA-TMS) are typically used to passivate non-growth areas.[1] However, the deterioration of selectivity at temperatures exceeding 500℃ limits their applications in high temperature deposition processes. Fluorination is regarded as a candidate for overcoming these problems.[2] In this study, we present a novel approach to achieve high selectivity in high temperature AS-ALD on SiN versus SiO_2 through effective surface-selective fluorination without damage to the substrates.

Experiments were conducted with a batch furnace capable of treating over one hundred 300 mm wafers simultaneously. A wide range of substrates were utilized including 300mm wafers with blanket SiN and SiO_2 films and various nanostructured samples. Prior to inhibition, samples were precleaned by dilute HF to remove native oxides. An HF gas passivation was employed at 630℃ for 10 minutes to selectively inhibit the SiO_2 surface. ALD SiN was deposited with dichlorosilane (SiH_2Cl_2) as the precursor and NH_3 as the co-reactant at 630 ℃.

The initial AS-ALD sequence involved performing ALD cycles following HF passivation, resulting in AS-ALD of up to 6 nm SiN on SiN while maintaining good within-wafer non-uniformity (Win Unif.) of <3%. We then developed the area-selective-deposition-Loop (ASD-Loop) technique, consisting of alternating 10-minute HF passivation with ALD cycles, as shown in Figure 1. We achieved an AS-ALD of 28 nm on SiN blanket wafers with high selectivity while keeping excellent Win Unif. of <2% and high film quality, as confirmed by the wet etching rate. The ASD-Loop has also been successfully applied to SiN/SiO stripe-patterned substrates (Figure 2), resulting in a maximum ASD thickness of 21 nm; and to high-AR holes on SiO_2/SiN stacks (Figure 3), resulting in AS-ALD with high conformality of >90%. Thus, we have demonstrated high-temperature AS-ALD on 300 mm wafers and complex nanostructures with high selectivity, superior uniformity, and reliable quality. This offers a new pathway for the integration of AS-ALD into nanofabrication schemes, showing significant potential for advancing high-performance semiconductor applications including DRAM and 3D NAND manufacturing.

References

1. R. Khan et al., *Chem. Mater.* **2018**, 30, 7603.

2. H. Oh et al., *Adv. Funct. Mater.* **2024**, 34, 2316872.

5:00pm **AS-TuA-15 Mutifunctional Ru/ZnO Bilayer for Sustainable Cu Interconnects using Area-Selective Atomic Layer Deposition of barrier with Small Molecule Inhibitor***, **Minwoo Kim**, Yeseul Son, Sang Bok Kim, Soo-Hyun Kim,* Ulsan National Institute of Science and Technology (UNIST), Republic of Korea

With the scaling of semiconductor devices, the increase in via resistance, which constitutes a significant portion of the Cu interconnect resistance, has emerged as a critical issue. To reduce via resistance, studies [1, 2] have been conducted on forming bottomless barriers using area selective deposition (ASD), where a high-resistivity barrier layer is selectively deposited only on the via/trench sidewalls, SiO_2-based dielectrics without being deposited on the via bottom, Cu. In these studies, self-assembled monolayers (SAMs) with long alkyl chains were used as inhibitors for preventing the adsorption of the precursor on metallic surfaces. However, SAMs are typically adsorbed onto surfaces through solution-based processes, which pose compatibility issues with semiconductor processes and, due to their relatively long molecular structure, cannot form a uniform inhibitor layer within 3D nanostructures. To prevent these issues, this study used a small molecule inhibitor (SMI) to form a bottomless barrier. Additionally, based on previously reported studies [1], the Ru/ZnO bilayer, with ZnO for the bottomless barrier and Ru for the liner and seed layer, was applied for the sustainable Cu interconnects [Figure 1]. The ZnO ASD process is carried out using an amine-based SMI that selectively absorbs on Cu, with diethylzinc and H_2O used for the ZnO ALD process. After the ZnO ASD process and the removal of the inhibitor, the Ru film was deposited using an ALD process with tricarbonyl(trimethylenemethane)ruthenium and O_2. By controlling the conditions of the ZnO ASD process, we confirmed and analyzed the selective deposition of ZnO on the SiO_2-based dielectric substrate not on Cu one using TEM, XPS, and XRD etc. The detailed results will be presented in the conference.

References

[1]Mori, Yuki, et al. Small 19.34 (2023): 2300290.
[2]You, Shi, et al. "Selective Barrier for Cu Interconnect Extension in 3nm Node and Beyond", IITC (2018)

Acknowledgements

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5:15pm **AS-TuA-16 Technological Promise of a Frustratingly Elusive Ni(^{tbu2}DAD)$_2$—Yet the Challenge is Part of the Breakthrough***, **Gabriele Botta**,* Nanogune, Italy

Over the past decade, research into the area-selective behavior of M-(^{tbu_2}DAD)$_2$ compounds has highlighted the significant potential of these precursors. [1,2] The low-temperature AS-ALD deposition of metallic nickel and cobalt films on various metallic surfaces has demonstrated its technological relevance. However, while Co(^{tbu_2}DAD)$_2$ continues to be the focus of many studies, [3][4] Ni(^{tbu_2}DAD)$_2$ has seemingly received less attention. Despite their similar thermodynamic properties, handling Ni(^{tbu_2}DAD)$_2$ has proven more challenging than its cobalt counterpart.

In this study, we further investigate the delivery characteristics of Ni(^{tbu_2}DAD)$_2$ and expand the range of growth and non-growth materials for its selective deposition. We also examine the loss of selectivity on silicon-based surfaces, which are typical non-growth areas. This undesirable material nucleation can arise from several factors, but in the case of Ni(^{tbu_2}DAD)$_2$, it is especially pronounced on hydroxyl groups of silicon oxide substrates. After identifying the nature of these nucleation sites, we developed a method to deliberately create growth regions using focused ion beam (FIB) irradiation. This approach enables direct patterning of growth areas on non-growth substrates, such as SiO_2. Our findings demonstrate that both induced selectivity (achieved through FIB area activation) and the inherent selectivity of Ni(^{tbu_2}DAD)$_2$ for metallic surfaces can coexist, offering new potential strategies for advanced nanofabrication.

References:

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[2]Klesko, Joseph P., Marissa M. Kerrigan, and Charles H. Winter. "Low temperature thermal atomic layer deposition of cobalt metal films." *Chemistry of Materials* 28.3 (2016): 700-703.

[3]Breeden, Michael, et al. "Proximity effects of the selective atomic layer deposition of cobalt on the nanoscale: implications for interconnects." *ACS Applied Nano Materials* 4.8 (2021): 8447-8454.

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