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

Area Selective Deposition IV

Moderator: Jeffrey W. Elam, Argonne National Laboratory

2:00pm **AS-WeA-3 Area Selective Deposition of SiAlO$_x$ Films for Self-Aligned Dielectric-on-Dielectric Application***, **Eryan Gu**, Wang Li, Kun Cao, Rong Chen,* Huazhong University of Science and Technology, China

Area selective deposition (ASD) is a high-precision atomic-level manufacturing technology that enables the development of bottom-up manufacturing methods in the future semiconductor field. As the feature size decreases, the parasitic capacitance increases, and the RC delay limits the propagation speed of the signal, while increasing the power consumption of the chip. This study investigates the SiAlO$_x$ film via atomic layer deposition (ALD) process, focusing on the catalytic reaction mechanisms of various aluminum precursors on silicon. Trimethylaluminum (TMA) molecules, which are highly reactive, easily interact with Bis(ethylmethylamino)silane (BEMAS), resulting in relative lower k value. In contrast, dimethyl isopropylaluminum (DMAI) molecules exhibit lower reactivity, resulting in a slower catalytic reaction rate. Additionally, n-octadecanethiol (ODT) is used to inhibit nucleation on the metal surface, and the interaction between aluminum and silicon precursors and ODT is studied. The high catalytic activity of TMA on BEMAS will decrease selectivity, while the DMAI system can achieve high selectivity with 10nm on growth area of SiO$_2$ with minimal growth on non-growth area of Cu. This approach not only reduces the k value further but also offers a promising pathway for advancing semiconductor nodes.

References

1. Effect of Al precursor’s properties on interactions with self-assembled monolayers for area selective deposition. Eryan Gu, Jin Yan, Boxuan Li, Huilong Zhou, Zhuhui Lu, Yanwei Wen, Kun Cao, Rong Chen, J. Vac. Sci. Technol. A 42, 062403 (2024)

2:15pm **AS-WeA-4 Control of Three-Color Area-Selective Deposition of PEDOT Conjugated Polymer on SiN vs SiO2 and Si-H by Adjustment of Pre-Treatment Sequence***, **Jeremy Thelven**, Nicholas Carroll, Gregory Parsons,* North Carolina State University

Most research in area-selective deposition (ASD) focuses on deposition of one material on a growth surface while avoiding deposition on a non-growth surface. However, for many steps in manufacturing, the exposed surface is “multi-color”, consisting of three or more materials. This means that any desired ASD process must be tuned to deposit on more than one growth surface while simultaneously inhibiting deposition on more than one non-growth surface.

To analyze “three-color” ASD, we studied ASD of poly(3,4-ethylenedioxythiophene) (PEDOT) conjugated polymer by molecular layer deposition (MLD) and CVD using ethylene-dioxythiophene monomer and SbCl$_5$ as reactants for oxidative polymerization.[1–2]As a three-color substrate, we use blanket samples of silicon nitride, silicon dioxide, and silicon.Initially, we treat all three surfaces with dilute HF solution producing Si-NH, Si-OH, and Si-H surface termination, respectively.As shown in Figure 1, PEDOT CVD at 150°C results in “inherent” selectivity of more than 30 nm on SiN and SiO$_2$, with no substantial deposition on Si-H. This selectivity has been ascribed to Si-H reacting with the SbCl$_5$ oxidant, preventing subsequent monomer oxidation on that surface.

To control selectivity, three surface treatments were explored: 1) one cycle of MoF$_6$/N$_2$ gas for 1s/30s, respectively, at 250°C; 2) N,N-dimethylamino-trimethylsilane (DMATMS) vapor for 15 s at 250°C; and 3) DMATMS for 15 s at 250°C followed by liquid water for 15 minutes at room temperature. Figure 1 shows the resulting PEDOT thickness (from ellipsometry) vs deposition time. The MoF$_6$ vapor had minimal influence on growth on SiN but converted the SiO$_2$ from growth to non-growth, due to conversion of reactive Si-OH to non-reactive Si-F, while simultaneously converting the Si-H from non-growth to growth, ascribed to the presence of some Mo on the Si-H. Additional control was achieved using DMATMS and liquid water. The DMATMS vapor inhibited deposition on Si-OH but had no effect on Si-H, and minimal effect on SiN, consistent with DMATMS reacting preferentially to consume Si-OH groups to produce a hydrophobic Si(CH$_3$)$_3$ surface. After DMATMS, we find that exposure to liquid water selectively “actives” the Si-H via surface oxidation, with little change to the DMATMS-modified SiO$_2$, allowing ASD on SiN and Si-H regions vs SiO$_2$.

Overall, these results demonstrate the concept of selectivity control for ASD of one material on “multi-color” substrates, thereby providing insight into means to adjust selectivity for a variety of future applications.

1. Kim, J.-S. et al., *Chem. Mater.* **2021**, 33, 23, 9221-9239
2. Carroll, N. M. et al., *Chem. Mater.* **2024**, 36, 8, 3655-3665

2:30pm **AS-WeA-5 Annealing PEDOT Thin Films to Generate a Selectively Deposited Etching Hard Mask Layer***, Nicholas Carroll, Carwynn Rivera, Man Hou Vong, Hannah Margavio,* North Carolina State University*; Hwan Oh,* Brookhaven National Laboratory*; **Gregory Parsons**,* North Carolina State University

As feature sizes in contemporary device architectures aggressively shrink, enhanced understanding of area-selective deposition (ASD) is critical to support advanced patterning and feature alignment. In recent years, new strategies have been developed for ASD of poly(3,4-ethylenedioxythiophene) (PEDOT) conjugated polymer by molecular layer deposition (MLD) and chemical vapor deposition (CVD) on SiO$_2$ vs. Si-H,[1] orthogonal ASD of W and PEDOT,[2] and inverted “dual-tone” ASD of PEDOT on Si-OH vs. SiO$_2$-TMS.[3]

Hard masks for etching are a key application for ASD materials. However, conjugated polymers are expected to etch quickly during plasma exposure. In this work, we describe the effect of post-deposition annealing on the etch rate of PEDOT during O$_2$ plasma and demonstrate means to “reactivate” the film to convert it from non-etching to etching. In their as-deposited form, the materials etch readily, as expected. As shown in Figure 1(a), the etch rate decreases by 50% upon annealing at 250 °C and decreases to near zero after heating to 350 °C. XPS analysis in Figure 1(b) shows an increase in the concentration of the Sb oxidant after annealing. Also, Figure 1(c-e) shows HAADF STEM images and an EDS elemental map of a film after annealing 350 °C. The EDS indicates that upon annealing, Sb segregates to the film surface. We hypothesize that this Sb layer contributes to the observed reduction in etch rate. This is consistent with XPS after etching in Figure 1(f) showing Sb present in the film.

Interestingly, we find that after treating the annealed PEDOT in deionized liquid H$_2$O at 80 °C for 10 minutes, the films readily etch in O$_2$ plasma, as indicated by XPS in Figure 1(g). The ability to enable plasma etching resistance for a selectively deposited conjugated polymer film opens innovative avenues and strategies for protecting surfaces during plasma deposition or selective etching steps. These findings bolster the significance and versatility of ASD for modern manufacturing methodologies.

[1] J.-S. Kim et al., *Chem. Mater.* **33**, 23 (2021).

[2] H. Oh et al., *Chem. Mater.* **35**, 11 (2023).

[3] N. Carroll et al., *Chem. Mater.* **36**, 8 (2024).

2:45pm **AS-WeA-6 Ring-Opening Enhanced Etching of Cyclosiloxanes for Area-Selective MLD of SiOC(H) Thin Films***, **Xiaocheng Huang**, Weiwei Du, Yuanhao Shen, Pengzhe Cai, Delong Liu, Junjie Zhao,* Zhejiang University, China

As the feature sizes of semiconductor devices continue to shrink, edge placement errors caused by the overlay variations in lithography will lead to dramatically increased failure probability and durability issues. Area selective deposition (ASD), a technique that enables precise deposition on specific material surface, is promising for the fabrication of fully self-aligned vias (FSAV) for solving above challenges. ASD processes relying on inherent surface differences circumvents additional processing steps for surface pre-functionalization. However, these methods often suffer from a loss of selectivity after extended number of deposition cycles due to inevitable nucleation on the non-growth surface. Here, we report a novel ASD strategy for SiOC(H) thin film based on etching enhancement achieved through selective ring-opening of cyclosiloxane precursor. *In-situ* DRIFT spectra reveal ring-opening of 1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane (V$_3$D$_3$) precursor on cobalt oxide surfaces. Furthermore, we demonstrate that ring-opening promotes the plasma etching rate. Based on these findings, we developed an etching-enhanced ASD which integrates molecular layer deposition and plasma etching in A-B-C supercycles. We obtained an exceptionally high area selectivity for SiOC(H) thin films on Co/SiO$_2$ patterns even after extended number of cycles. Cross-section TEM and high-resolution EDX mapping images confirm negligible nucleation on the CoO$_x$ surface. Our work pioneers the exploration of precursor isomerization for etching-enhanced ASD and offers a new strategy for self-aligned SiOC(H) patterns.

3:00pm **AS-WeA-7 Area-Selective Molecular Layer Deposition of Polymer Thin Films for Contact Hole/Trench Shrinking***, **Pengzhe Cai**, Junjie Zhao,* Zhejiang University, China

With the rapid advancement of integrated circuit technology nodes, the demand for critical size shrinking in nano-fabrication has been growing. The traditional lithography-etching method struggles to achieve the desired pitch size while maintaining cost efficiency. Contact hole/trench shrinking is a post-processing step applied before or after etching transfer, enabling patterns that exceed the lithographic resolution limit. However, when used in back-end-of-line fabrication, contact hole/trench shrinking faces the limitations of conventional wet chemistry, which restricts its full potential. Here, we report an area-selective deposition (ASD) method for contact hole/trench shrinking. We developed a plasma-enhanced initiated molecular layer deposition (PEiMLD) process that selectively grows polymer thin films onto previously defined photoresist patterns. In this all-dry PEiMLD process, remote plasma activation on the polymer backbones of the photoresist initiates radical polymerization, grafting molecular layers to the photoresist. In contrast, common dielectric surfaces (e.g. SiO_2) are inert to such activation and thus maintained as non-growth surfaces. Thereby, we achieved an area selectivity as high as 95% on PMMA/SiO_2 substrates and demonstrated contact hole/trench shrinking by reducing the trench diameter from 126 nm to 24 nm. Moreover, attributing to the versatile options of monomers for radical polymerization, this PEiMLD method can also be applied to interfacial engineering, enabling potential applications beyond contact hole/trench shrinking. Our method paves the way for alternative nanofabrication strategies that are promising for reducing the demand for lithography and lowering manufacturing costs.

3:15pm **AS-WeA-8 Catalytic Oxygen Dissociation for Area-Selective HfO_2 Deposition on Cobalt through Selective PMMA Etching***, **Enzo Novoselic**, Christophe Vallée, Natalya Tokranova,* University at Albany-SUNY

Area-selective deposition (ASD) of thin films is critical for advanced semiconductor manufacturing, yet conventional methods often suffer from "mushrooming" defects due to poor selectivity at feature edges and lateral expansion of the isotropic growth. This work presents an alternative approach to ASD on cobalt (Co) substrates while avoiding mushrooming, leveraging catalytic dissociation for both polymer etching and selective deposition. The use of selective catalytic dissociation has been demonstrated for the etching and deposition steps. As an example, Zhang et al. [1] demonstrated selective etching on Pt/Ru/Cu/Ti, while Joseph et al. [2] demonstrated selective deposition on Pt. In this work, a polymethyl methacrylate (PMMA) material is non-selectively deposited on all exposed surfaces (Co and silicon). Through catalytic O_2 dissociation, PMMA atop Co is selectively etched in an atomic layer deposition (ALD) tool, while PMMA on silicon remains intact. Subsequently, the ALD step is performed in the same chamber at the same surface temperature, and under catalytic conditions, enabling selective growth on Co while suppressing nucleation on PMMA. Finally, PMMA is stripped, yielding structures exclusively on Co with sub-nanometer precision and vertical sidewalls.

We expect to show results demonstrating that the catalytic processes achieve near-complete selectivity and eliminate lateral overgrowth, addressing the mushrooming effect common in ASD. The use of catalytic dissociation for both etching and deposition steps simplifies integration into existing fabrication workflows. This approach offers a scalable pathway for advanced node patterning, particularly in back-end-of-line (BEOL) metallization and gate oxide applications where material selectivity and feature definition are paramount.

[1] Zhang, C.; Leskelä, M.; Ritala, M. Self-Aligned Thin-Film Patterning by Area-Selective Etching of Polymers. Coatings 2021, 11, 1124. https://doi.org/10.3390/coatings11091124

[2] Joseph A. Singh, Nick F. W. Thissen, Woo-Hee Kim, Hannah Johnson, Wilhelmus M. M. Kessels, Ageeth A. Bol, Stacey F. Bent, and Adriaan J. M. Mackus. Chemistry of Materials 2018 30 (3), 663-670. https://doi.org/10.1021/acs.chemmater.7b03818

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