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 Jousseaume,* 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 $DeZn/H_2O$ 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) $MoSi_x$ (MoF_6/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 MoSix 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), 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.

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