Area Selective Deposition
Room ETEC Atrium - Session ASD1-MoA

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**, ***Francois 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 SiO_2 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 NH_3 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 (SiH_2Cl_2) and NH_3 at 630 °C.

Our results show COR effectively removes native oxide without substrate damage, while selectively fluorinating and inhibiting SiO_2. 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 SiO_2. 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

1.H. Liu et al., presented at AVS 25th International Conference on Atomic Layer Deposition, Jeju, Korea, June 22-25, 2025.

2:15pm **ASD1-MoA-4 Selective Deposition of HfO_2 Films**, ***Rachel Nye de Castro***, *Francisco Freire-Fernandez, Elham Mohimi,* Lam Research

Area-selective deposition (ASD) of hafnium oxide (HfO_2) thin films is of interest for high-k or high etch resistant layers in logic applications. Development of selective HfO_2 films has been less well-reported in literature compared to other metal oxide and dielectric films (AlO_x, ZnO, TiO_2, SiO, SiN, etc).[1,2] In this work, we evaluate HfO_2 selective deposition with inhibition on SiO and similar surfaces using inhibitor molecules. First, we characterize thermal HfO_2 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 HfO_2 film on various metal and dielectric substrates.

HfO_2 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 HfO_2 is demonstrated on native SiO_2 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. HfO_2, 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 HfO_2 ALD process and our inhibitor molecules are compatible with 300mm tool processing under HVM conditions to enable selective HfO_2 deposition on metals or metal oxides while inhibiting SiO and similar surfaces. Future work is needed to evaluate additional HfO_2 precursors to maximize selectivity, film quality, and deposition rate.

References

1. Lee, Y.; Seo, S.; Shearer, A.; Werbrouck, A.; Kim, H.; Bent, S. F. *Chem. Mater.* **2024,** *36,* 9, 4303-4314.
2. Stevens, E.; Tomczak, Y.; Chan, B. T.; Altamirano Sanchez, E.; Parsons, B. N.; Delabie, A. *Chem. Mater.* **2018**, *30,*10, 3223-3232.

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 $GeCl_2.C_4H_8O_2$ and $Te(Si(CH_3)_3)_2$. 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 SiO_2 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 SiO_2 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 SiO_2 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.

References

1. J. Sinha, L. Gallis, J.-W. J. Clerix, M. van der Veen, J. Innocent, A. Illiberi, M. Givens, L. Nyns, and A. Delabie, *Chem. Mater.* 36, 5943 (2024).
2. J. Sinha, N. M. Carroll, M. van der Veen, L. Nyns, G. N. Parsons, and A. Delabie, *Chem. Mater.* accepted for publication.

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 Merkx, 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 SiO_2 ALD on planar Al_2O_3 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 mm 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.

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