

Monday Afternoon, November 4, 2024

Atomic Scale Processing Mini-Symposium

Room 116 - Session AP1+EM+PS+TF-MoA

Area Selective Deposition (ASD) II

Moderators: Satoshi Hamaguchi, Osaka University, Japan, Richard Vanfleet, Brigham Young University

2:30pm **AP1+EM+PS+TF-MoA-5 Area Selective Deposition: Advances, Challenges and Future Technology Enablement, Kandabara Tapily, J. Smith, A. deVilliers, G. Leusink**, TEL Technology Center, America, LLC INVITED K. Tapily, J. Smith, A. deVilliers, G. Leusink

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To achieve higher performance, higher density, and lower cost, for decades the semiconductor industry has relied on aggressive scaling of the device feature size using top-down lithography. Additionally, scaling is driving the need for new materials introduction, new processes and new device architectures increasing the integration complexity. As a result, the industry has introduced several scaling boosters such as high k / metal gate, stress engineering, air gaps and recently area selective deposition to meet the power performance area cost or PPAC requirement.

Advanced device architectures such as gate-all-around (GAA) and complimentary field-effective transistors (CFET) require additional design / technology co-optimized (DTCO) solutions to continue the device scaling roadmap. Selective deposition of materials is fundamental not only for the reduced cost and complexity of manufacturing these advanced devices, but also as fundamental solutions to promote power / performance / CPP scaling of these advanced device architectures.

Surface engineering is key in successfully realizing defect free area selective deposition. Surface sensitive and reaction driven processes such as atomic layer processes (deposition and etch) will be key enabler in some of the required selective deposition processes (1).

This talk will discuss the status and approaches of area selective deposition technology and challenges the industry is facing in implementing future technology nodes. We will go over multiple examples of how novel selective deposition processes can accelerate the industry roadmap in terms of PPAC scaling.

References:

1. G. N Parsons, R. D Clark, *Chem. Mater.*, 32(12), 4920 (2020).

3:00pm **AP1+EM+PS+TF-MoA-7 Examining UV-Induced Functional Group Formation on 2D Nanomaterials for Patterned ALD, Azeez O. Musa, A. Werbrouck, N. Paranamana, M. Maschmann, M. Young**, University of Missouri-Columbia

In our previous work, we employed a focused electron beam (e-beam) within an environmental scanning electron microscope (eSEM) to break down water vapor, allowing for the precise creation of hydroxylated patterns on highly oriented pyrolytic graphite (HOPG) surfaces. These patterns facilitated subsequent atomic layer deposition (ALD) in patterned areas, offering exceptional control over spatial resolution (exceeding 42 nm), and surface selectivity (ranging from 69.9% to 99.7%). However, despite its precision, the use of an e-beam is time-consuming and lacks industrial scalability due to the limited functionalization area on the substrate. In this study, we aim to explore the feasibility of patterning large areas of 2D material using UV irradiation in the presence of water vapor. Specifically, we seek to understand the impact of the direct UV ionization of water vs. ionization of water from secondary emitted electrons. Our experimental setup utilizes a custom-built hot-walled viscous-flow ALD reactor equipped with a vacuum ultraviolet (VUV) source unit with a peak emitted wavelength of 160 nm. This UV source incorporates a compact deuterium lamp with a MgF₂ window and UV photons are focused onto the sample using a convex MgF₂ lens to enhance photon flux density. We posit that the UV irradiation induces the formation of hydroxyl defects on the HOPG surface. To verify this, we employ spectroscopy including X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), and Raman spectroscopy (RS), assessing the formation of functional groups on 2D material surfaces. We also examine the impact of UV-functionalization on ALD nucleation and growth onto 2D materials. Our studies inform the applicability of this method for patterned thin-film deposition for semiconductor manufacturing.

3:15pm **AP1+EM+PS+TF-MoA-8 ASD of Low Temperature Cu Capping Layers for Polymers-Based 3D Technologies, Silvia Armini**, IMEC Belgium; A. Brady Boyd, Aberystwyth University, UK; E. Chery, IMEC Belgium

With the constant increase of complexity in integrated systems, more and more connections are required between adjacent chips. Advanced packaging technologies using heterogeneous integration rely heavily on the interconnects redistribution layer (RDL) for this routing.

The most promising option to further reduce the interconnect dimensions relies on a dual-damascene process using photo-sensitive polymers as dielectric.

Unfortunately, using a polymer as a dielectric presents serious reliability challenges as polymers are generally unable to block the diffusion of oxygen, resulting in copper oxidation even at temperatures below 200 °C. Additionally, copper oxidation is not self-limiting.

As the critical dimensions of the lines are scaled down, high rates of oxidation are therefore a major reliability concern.

Recently the possibility of protecting the copper lines from oxidation through very thin ALD layers was demonstrated. For example, HfO₂ films as thin as 9 nm have been shown to effectively prevent copper oxidation during aggressive corrosion stress tests. Nevertheless, despite their minimal thickness, these dense films, deposited on the full surface of the wafer, are known to lead to mechanical stress. Ultimately, this stress can result in delamination and fracture during the next process steps.

To overcome this issue, area-selective deposition of TiO₂ and Al₂O₃ capping layers on Cu with respect to polymers are studied and their reliability performance investigated

3:30pm **AP1+EM+PS+TF-MoA-9 SiO₂ Fluorination/Passivation for Area-Selective Deposition of TiO₂, ZnO, and Polymer on Metal and SiN_x vs. SiO₂, Jeremy Thelven, H. Oh, H. Margavio, G. Parsons**, North Carolina State University

Challenges related to nanoscale pattern alignment are motivating research in chemically-directed patterning by Area-Selective Deposition (ASD) for future 3D devices. Recently, we have begun to explore the growth and inhibition mechanisms of metal oxide ALD materials (Al₂O₃, ZnO, and TiO₂) on hydroxylated and fluorinated SiO₂, and hydroxylated and fluorinated silicon nitride, SiN_x. The ability to selectively react and deposit on an oxide vs nitride surface is recognized as a key problem due to the wide use of SiO₂ and SiN_x in electronic device processing, and because of the chemical similarity of these surfaces. To explore ASD on SiN_x and SiO₂, we exposed blanket SiN_x and SiO₂ wafers to multiple doses of molybdenum hexafluoride, MoF₆, at low temperature (~200°C). Based on XPS analysis, the MoF₆ exposure leads to fluorination of both surfaces. Then, we performed polypyrrole (PPy) oxidative-CVD using pyrrole monomer and SbCl₅ as a surface oxidant. For the oxidative CVD process, 15 seconds of CVD produced ~50 nm of deposition on receptive surfaces. We found that PPy deposited readily on SiN_x surface after some nucleation delay, but on SiO₂, only isolated nuclei were formed. Control experiments using SiN_x and SiO₂ substrates without the MoF₆ exposure step showed uniform deposition on both substrates. To extend this demonstration of ASD of SiN_x vs SiO₂ to other materials and substrates, we tested ALD of TiO₂, ZnO, and Al₂O₃ SiO₂, SiN_x and Mo metal after exposure to MoF₆. We find that this selective fluorination passivation of the SiO₂ surface allows for selective growth of TiO₂ and ZnO on Mo vs SiO₂, whereas ALD Al₂O₃ using TMA/H₂O showed uniform, non-selective deposition. Moreover, after exposing SiO₂ and SiN_x to MoF₆, TiO₂ ALD using TiCl₄/H₂O deposited on SiN_x after some delay, whereas a much longer delay was observed on SiO₂. The mechanisms behind selectivity, and the extent of metal-fluoride exposure needed to achieve passivation is currently under investigation. Direct comparisons between metal oxide ALD nucleation on SiO₂, SiN_x and metal after exposure to MoF₆ will give insight into mechanisms necessary to achieve high selectivity, as well as provide options for advanced multi-material ASD schemes.

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