Area Selective Deposition
Room ETEC Atrium - Session ASD1-MoM

ASD and Inhibitors I

Moderators: Annelies Delabie, imec and KU Leuven (University of Leuven), **Rachel Nye de Castro**, Lam Research

8:15am **ASD1-MoM-1 Welcome and Sponsor Thank Yous***,*

8:30am **ASD1-MoM-2 From Concept to Reality: The Evolution and Impact of Area Selective ALD***, **Stacey Bent**,* Stanford University **INVITED**

The continued downscaling of electronic device dimensions requires the development of new, precise patterning methods that are compatible with high-volume manufacturing. Area selective atomic layer deposition (AS-ALD) continues to gain attention as an important method to achieve nanoscale features at the sub-10 nm length scale. It is known that tuning the surface chemistry of the substrate can be used to either inhibit or enhance ALD nucleation, leading to selective deposition. Since proof of concept of AS-ALD was introduced more than 20 years ago, a key strategy has been the use of inhibitors that can alter the native surface reactivity to block nucleation. Initial studies used long-chain self-assembled monolayers as inhibitors, evolving more recently to also include small molecule inhibitors and other surface functionalization chemistries. This inhibition approach enables good selectivity in AS-ALD of thin films on a variety of substrate materials, including dielectrics and metals, and is in use today. As the field advances, additional process parameters will need to be tuned if we are to meet future AS-ALD application requirements, which are now dictating a wide breadth of materials systems (including dielectric/dielectric, metal/dielectric, carbon/dielectric, multicolor patterns, etc.) as well as a high degree of selectivity. I will start with a historical perspective and then introduce some of the approaches currently under development, including tuning the ALD precursor in concert with the inhibitor, and development of AS-ALD for new applications. Ultimately, developing molecular design rules for both inhibitors and ALD precursors will be critical for applying AS-ALD more widely to future challenges in nanoscale fabrication.

9:15am **ASD1-MoM-5 NHC 2.0: Surface-Dependant NHC Activation***, **Sean Barry**,* Carleton University, Canada*; Zeng Rong Wong, Emmett DesRoche, Francesco Tumino,* Queen's University, Canada*; Shengzhuo Wang,* University of Minnesota*; Eden Goodwin,* Carleton University, Canada*; Alastair McLean,* Queen's University, Canada*; Matthew Neurock,* University of Minnesota*; Cathleen Crudden,* Queen's University, Canada

N-heterocyclic (NHCs) are highly selective small molecule inhibitors (NHCs) for metal surfaces, while leaving dielectric surfaces free for deposition. Generally, NHCs are persistent, but they are not easily isolated due to a pathway that allows them to dimerise into ene-tetraamines. To prevent this, NHCs are delivered by the controlled thermal disassembly of the imidazolium bicarbonate salt, to produce one equivalent each of NHC, CO_2, and water. This can be a problem in sensitive workflows where an equivalent of water can interfere with surface chemistry.

We have recently synthesised an adduct of an N-heterocyclic carbene (NHC) and H_2, a novel molecular precursor to deliver NHCs in the gas phase. This NHC precursor undergoes volatilisation at 120°C without loss of H_2, unlike the imidazolium bicarbonate that generates free NHC before reaching the surface. Scanning tunnelling microscopy was used to discover the difference of surface chemistry on gold and copper metal surfaces: On Au (111) surfaces, surface-enabled dehydrogenation occurs selectively only at edge and kinked sites of the surface reconstruction. On a more reactive Cu (111) surface, ordered carbene monolayers form at room temperature on the crystal terrace, with a second deposition at 50°C resulting in extensive coverage of (111) faces. Density functional theory (DFT) calculations were used to interrogate the mechanism of the C-H activation: this occurs by sequential surface C–H activations.

9:30am **ASD1-MoM-6 Area Selective Ruthenium Deposition with Dual Inhibitors***, **Kai-Hung Yu**, Tarek Dinar,* TEL Technology Center America*; Ryota Yonezawa, Yuji Otsuki, Takumi Nishinobo,* TEL Technology Center America, Japan*; Joshua Mayersky, Gyana Pattanaik,* TEL Technology Center America*; Hirokazu Aizawa, Hidenao Suzuki,* TEL Technology Center America, Japan*; Cory Wajda,* TEL Technology Center America

Area-selective deposition (ASD) has been pursued for decades in semiconductor manufacturing to cut reliance on costly masks and mitigate misalignment from wafer distortion. Self-aligned and self-limited ASD schemes are integrated to protect electrical performance and preserve yield under aggressive scaling. In back-end-of-line (BEOL) processes, Cu interconnect scaling is becoming increasingly constrained at advanced nodes. Combining ASD techniques helps maintain Cu performance and reliability; selective barriers lower via resistance, and selective metal caps extend electromigration (EM) lifetime.

Building on the dual-inhibitor method reported at ASD 2024, we apply sequential surface treatments that widen the window for selective Ru deposition on Cu while suppressing nucleation on interlayer dielectrics (ILD). The approach employs two small-molecule inhibitors (SMIs) to passivate both Cu and low–k surfaces after chemical mechanical planarization (CMP). Under Ru deposition conditions, the passivation is lifted on Cu but retained on the ILD, enabling selectivity without additional masking. Inline tests (ILT) show reduced leakage current and an enhanced ability to extend queue times without degradation. This addresses queue-time control at fine pitches where the Cu/low–k spacing approaches critical dimensions. The ILT results illustrate delayed leakage degradation with either one SMI or both of two SMIs, and the SEM images and TEM cross sectional images confirms Ru selectivity on Cu with negligible ILD nucleation, indicating a path toward Cu interconnects with Ru wrap–around caps and improved electrical yield.

9:45am **ASD1-MoM-7 Blocking the Atomic Layer Deposition of Al2O3: Combined Effects of Precursor, Co-reactant, Blocking Molecule, and Reactor Temperature***, Jay Swarup, James Jensen, Burke Combs, **James Engstrom**,* Cornell University

As semiconductor device dimensions shrink toward the atomic scale, area-selective deposition has become a critical technique for overcoming the alignment and scaling limitations of conventional top-down lithography. This bottom-up approach enables precise material placement by preventing growth on non-growth surfaces, typically through the use of blocking molecules that passivate reactive sites. The success of this process depends on the combined effects of the specific chemistry of the ALD precursor and co-reactant, the choice and method of application of the blocking molecule, and reactor temperature. We report a systematic examination of the combined effects of these variables for blocking deposition of Al_2O_3 on SiO_2. We compare the conventional trimethylaluminum (TMA) to BDMADA-Al, a non-pyrophoric alternative precursor containing only Al-N bonds and no Al-C bonds **[1]**. For co-reactants, we compare H_2O versus *t*-BuOH. For blocking molecules, we evaluated a solution-phase self-assembled monolayer octadecyl trichlorosilane (ODTS) and a smaller, vapor-phase blocking molecule dimethylamino trimethylsilane (DMATMS). Growth was monitored at two different temperatures *in situ* and in real-time via quartz-crystal microbalance (QCM), with deposited films characterized *ex situ* using X-ray photoelectron spectroscopy (XPS) and other techniques. While we have shown that pristine ALD runs (without inhibitors) between BDMADA-Al and TMA produce comparable film density, stoichiometry (C incorporation), and growth rates, significant differences emerged during blocking studies. Specifically, the bulkier BDMADA-Al was more effectively inhibited than the smaller TMA across all tested conditions. Similarly, for single-dose applications, the larger, solution-phase ODTS provided more robust blocking than the vapor-phase DMATMS, suggesting that larger precursor and blocking molecules improve blocking performance through steric hindrance. We also find that higher temperatures improved blocking efficacy under similar process chemistries. Additionally, the dosing sequence in the ALD cycle is a critical factor; repetitive pulsing of DMATMS in an “ABC” cycle provided superior inhibition compared to a single pre-exposure, ultimately outperforming ODTS in some tested conditions.

[1]J. V. Swarup, H.-R. Chuang, J. T. Jensen, J. Gao, A. L. You and J. R. Engstrom, J. Vac. Sci. Technol. A **43**, 022404 (2025).

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