Area Selective ALD
Room Tampa Bay Salons 3-4 - Session AS1-WeM

ASD Process I

Moderators: Sumit Agarwal, Colorado School of Mines, **Stacey Bent**, Stanford University

8:00am **AS1-WeM-1 ALD Outstanding Presentation Award Finalist: Triazolylidene Small Molecule Inhibitor for Area-Selective Atomic Layer Deposition of High *k*-Dielectric Materials***, Giang Hoang Pham,* Western University, Canada*; Jordan Bentely,* Wesleyan University, Canada*; Dana Nanan, Cathleen Crudden,* Queen's University, Canada*; **Paul Ragogna**,* Western University, Canada

High selectivity in area selective atomic layer deposition (AS-ALD) requires the effective performance of an inhibitor that must exhibit selectively binding mode on non-growth areas as well as strong thermal, and chemical stability to prevent degradation or decomposition during the semiconductor manufacturing process. N-heterocyclic carbenes (NHCs) have emerged as promising next-generation alternatives to conventional small-molecule inhibitors (SMIs) due to their strong *σ*-donor character and preferential binding to metal surfaces over a dielectric region. We have prepared and developed *triazolylidene* NHC (Tz) derivatives as a novel class of NHC inhibitor for selective high-k dielectric growth on SiO_2 over metallic bands reaching a selectivity factor of 93% after 50 dielectric deposition cycles. The selective adsorption behavior and dielectric blocking efficiency were systematically evaluated using time-of-flight secondary ion mass spectrometry (ToF-SIMS), and X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM). The practical applicability of the Tz inhibitor is further demonstrated through bottom-up fabrication of a working field-effect transistor, in which the NHC selectively protects metal electrodes during the deposition of metal oxide dielectric and semiconductor layers. This work paves an innovative pathway for exploring novel class of SMIs toward advanced AS-ALD applications.

Selected references: (1) D.A.R. Nanan, J.T. Lomax, J. Bentley, L. Misener, A.J. Veinot, W-T Shiu, L. Liu, P.J. Ragogna**,** C.M. Crudden *J. Am. Chem. Soc.***2025**, *147*, 5624–5631; **(2)**J.T. Lomax, E. Goodwin, M.D. Aloisio, A.J. Veinot, I. Singh, W-T Shiu, M. Bakiro, J. Bentley, J.F. DeJesus, P.G. Gordon, L. Liu, S.T. Barry, C.M. Crudden, P.J. Ragogna *Chem. Mater.***2024**, *36*, 5500–5507; **(3)** P.J. Ragogna, C.M. Crudden, D.A.R. Nanan, J.T. Lomax, A.J. Veinot, J. Bentley, "Method of Selective Deposition of Triazolylidenes on Metallic Surfaces", International Patent Application No. PCT/CA2025/051508, filed: Nov. 12, 2025

8:30am **AS1-WeM-3 Maintaining Healthy Boundaries – Machine Learning Design of SMIs***, **Sean Barry**, Marshall Atherton,* Carleton University, Canada*; Dennis Hausmann, Jiyeon Kim,* Lam Research Corp.

Machine learning–guided molecular design is important for accelerating materials discovery, and we have applied it to area-selective atomic layer deposition (AS-ALD). In this work, we integrate machine learning with systematic experimental characterization to guide the development of amino-substituted silane small-molecule inhibitors (SMIs) to optimize volatility, thermal stability, and surface selectivity. By prioritizing data-driven structure–property relationships, this study helps establish a predictive framework for identifying viable SMIs while limiting experimental trial-and-error.

A diverse library of aminosilanes was synthesized using an environmentally benign nucleophilic substitution route involving disubstituted amines and chlorosilanes, with triethylamine as a sacrificial base. This approach avoids pyrophoric reagents and metal-containing intermediates, supporting sustainable scale-up. Thermal properties were evaluated using thermogravimetric analysis, vapour pressure measurements, and differential scanning calorimetry. Surface adsorption and selectivity were quantified using in situ quartz crystal microbalance measurements.

The experimentally derived thermophysical dataset was used to train ML models to map molecular structure and composition to key properties governing AS-ALD performance, including volatility and thermal stability. A chemistry-informed molecular property prediction platform (DeepAutoQSAR, Schrödinger) helped identify optimal model architectures. The resulting ML models were used to predict properties of previously untested silane precursors, enabling targeted selection of candidates for experimental validation. Comparison of predicted and measured properties demonstrates the effectiveness of this ML-guided workflow for accelerating inhibitor design.

8:45am **AS1-WeM-4 Role of Precursor and Aklanethiol Chain Length on Area Selective Deposition of Aluminum and Hafnium-Containing Films***, **Nicholas Strandwitz**,* Lehigh University

Area selective atomic layer deposition (AS-ALD) enables the selective placement of material based on differences in surface chemistry and is thus a promising strategy for device manufacturing by avoiding addition patterning steps and alignment issues.Key developments that are being sought include achieving high selectivity (near 100%) at high film thicknesses on growth surfaces, and expanding the palette of materials (such as new low-k materials) that can be grow in AS-ALD.In this talk I will explore two aspects of our work that work toward these developments: Examination of the role of alkanethiol chain length and examination of the role of alternative metal and co-reactant precursors on selectivity.

The stability and impermeability of monolayer-based blocking layers is critical to preventing film growth in certain regions.Few reports explicitly studied the effect of alkane chain length and temperature on selectivity, so we sought to do so with a series of alkanethiols of various alkane chain length on copper surfaces.We found that longer chain lengths achieved higher selectivity and all chain lengths to be unstable to the highest temperature investigated (180 °C).To isolate the precise breakdown mechanisms, we separately subjected the alkanethiol monolayers on copper to various individual ALD steps including elevated temperature, metal precursor exposure, or water exposure.We found that trimethylaluminum at elevated temperature induced alkanethiol desorption, whereas amido-based Hf precursors did not, thus demonstrating a chemical effect on monolayer stability.

To further investigate the role of film precursor, we studied an array of metal and non-metal precursors including alkyl aluminums, amido aluminum, aluminum alkoxide, and ethylene glycol.Importantly, we found that precursor size, rather than reactivity, was the prime determining factor in realizing high sensitivity.We found that molecular layer deposited films (using ethylene glycol) did not show significantly higher selectivity than traditional ALD growths with the same metal precursor.With certain combinations of large metal precursors and water, we were able to achieve high selectivity (>90%)at alumina film thicknesses greater than 15 nm on the growth surface.Thus, this work builds on existing reports from other groups that the precursor chemistry has a massive role in determining selectivity.

9:00am **AS1-WeM-5 Surface Blocking Effect of NH_3 in Selective Co-ALD with CCTBA Precursor***, **Naoki Tamaoki**, Jun Yamaguchi, Noboru Sato, Atsuhiro Tsukune, Yukihiro Shimogaki,* The University of Tokyo, Japan

As semiconductor devices continue to scale down, current densities in interconnects increase, leading to serious reliability degradation of Cu interconnects due to electromigration. The introduction of a metallic Co cap layer is expected to enhance adhesion between interconnects and dielectric layers, thereby extending the lifetime of Cu wiring. In Co atomic layer deposition (ALD) using CCTBA (Cobalt Carbonyl Tertiary-Butyl Acetylene) as a precursor, an incubation period exists in which film nucleation on SiO_2 dielectric surfaces is delayed compared with Cu surfaces, enabling selective growth [1]. In this study, the inhibitor effect of NH_3 was evaluated as a method to further enhance selectivity, motivated by previous reports on selective CVD using $Co_2(CO)_8$, where simultaneous NH_3 supply suppresses growth initiation and improves selectivity [2].

Deposition experiments were performed on Si substrates with a 300 nm thermally grown oxide layer at 120 °C using alternating CCTBA and H_2 pulses for 500 cycles, with in-situ monitoring by spectroscopic ellipsometry. Under standard conditions, no incubation period was observed and a growth-per-cycle (GPC) of 0.016 nm/cycle was obtained. When NH_3 was co-supplied during the CCTBA pulse, an incubation period of approximately 75 cycles appeared and the GPC decreased to 0.0099 nm/cycle, demonstrating that NH_3 functions effectively as an inhibitor.

Furthermore, surface reaction calculations using a machine-learning potential (PFP: Preferred Potential by Matlantis Corp.) suggest that NH_3 selectively adsorbs on OH groups on oxide surfaces, which serve as potential adsorption sites for CCTBA molecules, thereby blocking these reactive sites. These results indicate that NH_3 can act as a small-molecule inhibitor in Co-ALD using CCTBA, providing a promising approach for enhancing selective growth in Co capping processes for advanced interconnect applications.

The authors gratefully acknowledge Daikin Industries, Ltd. For their support and valuable discussions.

References

[1] J. Yamaguchi et al., AVS 24th International Conference on Atomic Layer Deposition, AA1-TuM-7 (2024).

[2] Z. V. Zhang et al., J. Vac. Sci. Technol. A 38, 033401 (2020).

9:15am **AS1-WeM-6 Fluorination Passivation for Area-Selective Deposition: Selective Passivation of SiO_2 vs SiN_x for Highly Selective TiO_2 Deposition using Water-Free $TiCl_4/Ti(^iPrO)_4$.**, ***Jeremy Thelven***, *Gregory Parsons,* North Carolina State University

There is an acute need for new memory and computing device structures that are more energy efficient.[1] To minimize energy loss, new complex 3D architectures are needed with precisely aligned features. To address inherent alignment limitations in lithographic patterning, area selective deposition (ASD) is an attractive process because, in principle, the alignment between the starting pattern and the deposited feature is determined by differences in reactivity for the molecules on the desired growth and non-growth surfaces. Therefore, when the growth and non-growth surfaces have similar active surfaces sites, such as SiO_2 and SiN_x, identifying reactants that preferentially deposit on one surface versus another is particularly challenging. Recently, we found that when a patterned SiO_2/SiN_x surface was exposed to a fluorinating agent (such as MoF_6), the SiO_2 surface became preferentially passivated for deposition of TiO_2 ALD using $TiCl_4/H_2O$, allowing selectivity >93% for ~9.6 nm of TiO_2.[2] We hypothesized that as ALD proceeds, a primary reason for the observed loss of SiO_2 passivation was unwanted oxidation during the water exposure step.

To address this, we reconsidered a previously studied "waterless" TiO_2 ALD process using $TiCl_4$ and titanium isopropoxide (TTiP) at 210℃.[3] Using $TiCl_4$/TTiP ALD on blanket SiO_2 and SiN_x substrates, we found (Figure 1a and b) that after pre-treating the SiO_2 and SiN_x with only a brief dip in dilute $HF_{(aq)}$, the $TiCl_4$/TTiP process showed delayed deposition on both surfaces. However, the extent of delay was much more substantial on the SiO_2 vs SiN_x, allowing several nm of ASD. Subsequently, we tested the same SiO_2/SiN_x surfaces after dilute $HF_{(aq)}$ followed by exposure to MoF_6 for 1 second at 210℃. As shown in Figure 1c and d, initial results indicate substantially improved selectivity for the fluorine-passivated water-free TiO_2 ALD, enabling ~ 25 nm of TiO_2 on SiN_x vs. SiO_2 with exceptionally high selectivity. The lines in the figures correspond to fits obtained from an analytical nucleation model.[4] Confirmation of these findings will require testing the process on nanoscale patterned substrates. Overall, these results demonstrate how the combination of pretreatment and precursor selection can help achieve chemical contrast for ASD, even on starting surfaces with similar chemical structure and composition.

1.Datta, S.; Chakraborty, W.; Radosavljevic, M. Toward. Science 2022, 378 (6621), 733–740.
2.Thelven, J. M.; Parsons, G. N. et al., Adv Materials Technologies 2025, 10 (23), e00284.
3.Atanasov, S. E.; Kalanyan, B.; Parsons, G. N. JVSTA 2016, 34 (1), 01A148.
4.Parsons, G. N. JVSTA 2019, 37 (2), 020911.

9:30am **AS1-WeM-7 Chemical Selectivity in Atomic Layer Selectivity (ALD) via Gas-Phase Silylation using N-(trimethylsilyl)dimethylamine (TMSDMA)**, *Mohammed Sadam Alam,* ***Francisco Zaera***, University of California at Riverside

The effectiveness of the silylation of both silicon oxide and copper surfaces using N-(trimethylsilyl)dimethylamine (TMSDMA) as a passivation agent in atomic layer depositions (ALDs) was evaluated and contrasted by using x-ray photoelectron spectroscopy (XPS). It was determined that on SiO_2 such silylation does indeed block the nucleation centers where the ALD precursors are activated and therefore inhibit film growth, but only temporarily; after a few ALD cycles, deposition becomes evident. By testing this chemistry on two types of SiO_2 surfaces, prepared by plasma-enhanced chemical vapor deposition (PE-CVD) and by chemical (RCA) treatment of Si(100) wafers, it was concluded that the nature of the initial substrate does not play a crucial role in the silylation or ALD blocking processes. The material being deposited, on the other hand, does make a difference: TiO_2 film growth can be blocked for almost 10 ALD cycles, whereas HfO_2 starts building up on the surface after less than 5 ALD cycles. Moreover, the steady-state deposition rate for TiO_2 was determined to be lower than for HfO_2. One of the key findings of this work is that the silylation can be carried out using either gas- or liquid-phase treatments. It was found that the extent of silylation and the inhibition of the subsequent ALD were comparable in both cases, but the gas-phase method was determined to be cleaner and to deposit less carbon contaminants.

On copper, by contrast, virtually no effect on the ALD of either TiO_2 or HfO_2 was observed upon silylation with TMSDMA. A slow but detectable initial rate of oxide deposition was observed either before or after treatment, similar in both cases: approximately 0.15 Å/cycle in the case of TiO_2, about 0.25 Å/cycle for HfO_2. On SiO_2, by contrast, these rates were measured to be ~0.6 and 1.2 Å/cycle, respectively, on the clean substrate, but only ~0.08 and 0.4 Å/cycle after silylation. Consequently, it is concluded that gas-phase silylation using TMSDMA can be used to selectively allow for the ALD of oxides on silica in the presence of copper, that is, for area-selective ALD (AS-ALD), albeit with limited contrast. It should be added that in some cases an induction period was observed before the start of the film growth. We speculate that this, and the non-zero deposition rates seen on Cu and silylated SiO_2, may be due to the possible existence of defects on the substrates acting as nucleation centers.

9:45am **AS1-WeM-8 Mechanistic Criteria for Area Selective Deposition of Multicomponent Al_xSi_yO Oxide Dielectrics**, *Eryan Gu, Zilian Qi, Kun Cao,* ***Rong Chen***, Huazhong University of Science and Technology, China

As integrated circuit technology continues to evolve towards three-dimensional architectures, device density and interconnect layers are constantly increasing. Area selective deposition (ASD) offers significant advantages as a bottom-up approach for such patterning. In this talk, an ASD process and selectivity criterion for multicomponent oxide of AlxSiyO is presented. Combined experimental and mechanistic analysis, the interactions between Al and Si precursors and their interactions with inhibitor modified surfaces were revealed. A selectivity criterion driven by penetration depth of precursors into inhibitors and the reaction barrier of multiple precursors was established, enabling selective deposition through precursor selection and composition regulation. The growth of AlxSiyO films is controlled by the synergistic effect of catalytic activation, precursor ratio and temperature, and has tunable dielectric properties, which is expected to improve the RC delay problem. Inhibition of ligand elimination at low temperatures leads to moderate carbon incorporation, thereby enabling the film dielectric constant to reach 4.3. Highly selective growth of 10 nm AlxSiyO films was achieved on Cu/SiO2 patterned, demonstrating a viable strategy for integrating AlxSiyO into next-generation interconnect technologies.

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