## Area Selective Deposition
## Room ETEC Atrium - Session ASD2-TuA

### AI and Machine Learning for ASD

**Moderators:** Kayvan Kashefi, Applied Materials, Tania Sandoval, Universidad Tecnica Federico Santa Maria

3:45pm **ASD2-TuA-10 ALD Precursor Design Through Atomic-Level Simulation**, ***Yusuke Asano,*** Matlantis corporation, Japan **INVITED**

The integration of machine learning (ML) into atomic layer deposition (ALD) research offers a promising pathway to accelerate materials discovery. However, establishing reliable workflows that link atomic-level simulations with macroscopic process parameters remains a challenge. In this talk, we propose a comprehensive computational approach using a universal machine learning interatomic potential (uMLIP), Matlantis (PFP), to explore the potential of "inverse design" for Area-Selective ALD (ASD) precursors.First, we present a methodology for exploring surface selectivity through high-throughput screening. Utilizing the universality of PFP, we calculated adsorption energies for varying Cobalt and Ruthenium precursors on growth (Si) and non-growth (Alkyl-SAMs) surfaces. By coupling these calculations with descriptor-based regression (LASSO) and Bayesian optimization, we established a workflow to extract ligand features that contribute to selectivity (e.g., piperidine derivatives) and to analyze the impact of steric bulk on reaction barriers. While these findings are preliminary, they demonstrate how data-driven approaches can guide the search for optimal molecular structures.Second, we discuss an emerging approach to predict precursor volatility from atomic simulations. We investigated the correlation between the enthalpy-related term derived from calculated adsorption free energy (ΔGads) and the Antoine equation's B parameter (heat of vaporization). Our initial model suggests a physical link between microscopic adsorption behavior and macroscopic volatility, showing a promising correlation for Co precursors. Although further validation with expanded datasets is required, this method indicates the possibility of predicting vapor pressure curves directly from computational results.By unifying reactivity analysis and property prediction within a single framework, this work highlights the capabilities of universal MLIPs as a tool for continuous methodology research. We will discuss current limitations, such as data scarcity, and the future outlook for refining these models to achieve high-precision, purpose-driven precursor design.

4:15pm **ASD2-TuA-12 AI-Enabled Screening Framework for Precursor and Inhibitor Selection in Area-Selective Deposition**, *Han-Bo-Ram Lee,* ***Bonwook Gu,*** Incheon National University, Republic of Korea

Area-selective deposition (ASD) critically depends on whether precursors and inhibitors can selectively adsorb and react on specific substrate surfaces. In practice, identifying suitable precursor–inhibitor–substrate combinations remains challenging, as it is difficult to experimentally verify the full range of chemical and process variables. This challenge is further amplified when exploring new molecules or previously unreported combinations, where experimental guidance is scarce.

In this work, we propose a data-driven screening framework that integrates large language models (LLMs), atomistic representations, and machine learning to support precursor and inhibitor selection for ASD. LLMs are used to analyze the ASD literature and automatically extract structured information, including precursor and inhibitor chemistry, substrate materials, process temperatures, and reported deposition outcomes. Based on this information, molecular structures of precursors and inhibitors are generated and then relaxed using machine-learning force fields (MLFFs). These relaxed structures, together with substrate descriptions and process parameters such as deposition temperature, are used to construct feature sets describing precursor–substrate and inhibitor–substrate interactions. Rather than focusing on detailed property prediction, the framework treats ASD outcomes as a classification problem (e.g., selective adsorption vs. non-selective/no adsorption) to assess whether selective adsorption and subsequent film formation are likely under specific conditions. The framework is modular, allowing flexibility in the choice of atomistic representations and machine learning models as the dataset evolves. To assess its applicability, the framework is being applied to an initial set of precursors and inhibitors not included in the training dataset, and the resulting predictions are used to guide subsequent ASD experiment design. By organizing existing knowledge and enabling rapid pre-screening of unexplored molecules, this approach provides a practical pathway toward more systematic and efficient development of area-selective deposition processes.

4:30pm **ASD2-TuA-13 Computational Modeling Set in Motion: A Dynamic & Statistical View on Smi Layer Blocking Events Powered by Machine-Learned Potentials**, ***Philipp Wellmann,*** Leipzig University, Germany

With the ability to process well-defined, uniform patterns at the nanometer scale, humanity has entered the era of atomic crafting. Whereas ALD is the pinnacle engineering technology to control the arrangement of features on the atomic scale, computational material science is a high–resolution window to monitoring, understanding, and fine–tuning of the various manufacturing processes. [1] Besides the steady increase of computing power, it is the rise and maturing of machine learning methods that provides material science with a myriad of uncharted possibilities left to explore for the ALD community. The most tangible of the recent improvements is the ascent of machine–learned potentials (MLPs), that tick most boxes on a computational material science method wish list: speed & accuracy paired with robustness & universality.

In inhibitor–based AS–ALD, where the systems of interest are rather large, the calculation of stationary quantities is computationally very demanding for the typical *ab initio* workhorse methods. Yet, these optimized glimpses of the system may only provide a limited understanding of the highly dynamic AS–ALD processes. MLPs now offer the possibility to calculate the forces and energies of the AS–ALD systems with comparably small error margins at a cost reduction factor of well over 1000. [2] Hence, the current generation of MLPs paves the way for exploring the dynamic view on AS–ALD, where the models' capabilities ultimately depend upon the quality of the training data.

We show how to compose data sets for the training of MLPs over a variety of ALD systems, while minimizing the amount of the time determining the DFT calculations. Equipped with these MLP models, we have the means to obtain statistical information on the blocking performance of an SMI layer in the event of a precursor impact by conducting tens of thousands so–called "molecular gun" dynamics simulations, with many process parameters (e.g. precursors, SMI density, temperature, degree of SMI layer deterioration, etc.) being adjustable at will. This novel, dynamic view on inhibitor–based AS–ALD furthers the understanding of experimental results and has also consequences for interpreting static modelling experiments.

**References**

F. Pieck, R. Tonner–Zech, *Chem. Mater.***2025,***37,* 2979-3021, DOI: 10.1021/acs.chemmater.4c03477

H. Weiske, R. Barret, R Tonner–Zech, P. Melix, J. Westermayr, *Digit. Discov.* **2025**, DOI: 10.1039/D5DD00420A

4:45pm **ASD2-TuA-14 Establishing Boundaries: Using Machine Learning to Design Aminosilane SMIs**, ***Marshall Atherton,*** Carleton University, Canada; *Jiyeon Kim, Dennis Hausmann,* Lam Research Corporation; *Sean Barry,* Carleton University, Canada

Area-selective atomic layer deposition (AS-ALD) exploits surface chemistry to confine deposition to specific surface regions, minimising the need for lithographic steps. This work presents a systematic study of the structure-function relationships in amino-substituted silanes designed for use as AS-ALD inhibitors, with an emphasis on thermal volatility and surface selectivity. The goal is to improve the environmental impact of aminosilane production scale-up by exploring alternative synthetic pathways.

A more environmentally benign nucleophilic substitution route to the synthesis of disubstituted amines with chlorosilanes was undertaken using triethylamine as a sacrificial base, enabling access to a diverse inhibitor library while avoiding pyrophoric reagents and metal-containing intermediate chemistry. Thermal behaviour was evaluated by thermogravimetric analysis, as well as by measuring pressures at which 1 Torr of vapour is produced, and by determining decomposition temperatures using differential scanning calorimetry. Surface coverage of viable aminosilanes was assessed in an Anric ALD reactor equipped with an in-situ quartz crystal microbalance to measure adsorption and selectivity on metal and dielectric surfaces. Compounds exhibiting selective adsorption were subsequently assessed for growth inhibition of diethylzinc/water ALD relative to the bare surface on patterned metal/dielectric wafers.

The thermal data generated from this study were used to train structure-property machine learning (ML) models that map Si precursor structure and composition to relevant thermophysical properties, such as volatility and thermal stability. A commercially available chemistry-informed molecular property prediction engine (DeepAutoQSAR by Schrödinger) was leveraged

to select the most accurate ML model to predict Si precursor properties. This ML model was then used to predict the physical properties of several additional Si precursors not included in the original training data. The predicted properties were compared to the experimentally determined properties to evaluate the model's performance.

5:00pm **ASD2-TuA-15 Surface Reaction Analysis of Area-Selective Co ALD Using a Machine-Learning Potential**, ***Naoki Tamaoki***, *Jun Yamaguchi, Noboru Sato, Atsuhiro Tsukune, Yukihiro Shimogaki,* The University of Tokyo, Japan

As interconnect dimensions continue to scale, the current density in semiconductor wiring increases, and the resulting electromigration-induced degradation of Cu interconnect reliability has become a critical concern. Introducing a metallic Co capping layer is expected to enhance adhesion between interconnects and dielectrics, thereby extending the lifetime of Cu lines. In Co atomic layer deposition (ALD) using CCTBA (cobalt carbonyl tert-butyl acetylene) as the precursor, an incubation period exists on $SiO_2$ dielectric surfaces compared with Cu surfaces, enabling inherent selectivity in nucleation and growth. Here, we report an atomistic surface-reaction analysis of this area-selective Co-ALD process using simulations based on a machine-learning potential (PFP; Preferred Potential by Preferred Networks, Inc.).

Our previous calculations indicate that CCTBA readily undergoes dissociative chemisorption on Cu surfaces via an exothermic pathway. In contrast, chemisorption on OH-terminated silicon oxide is endothermic and accompanied by an activation barrier of approximately 1.5 eV, making adsorption kinetically unfavorable and thereby contributing to selectivity. In this work, we further evaluated possible gas-phase decomposition pathways of CCTBA and found that a reaction involving CO-ligand dissociation can occur with an activation energy of ~1.3 eV. The resulting activated intermediate (CCTBA with one CO ligand removed) can physisorb with an adsorption energy of ~0.64 eV and then proceed to chemisorption by forming a Co-O bond with surface oxygen over a small barrier of ~0.2 eV. These results suggest that gas-phase decomposition may promote initial nucleation on non-growth surfaces, potentially degrading selectivity.

To explore a mitigation strategy, we considered the role of $NH_3$, motivated by prior reports on selective CVD using $Co_2(CO)_8$, where co-feeding $NH_3$ strongly suppresses growth initiation on non-growth surfaces. Consistent with this concept, our calculations confirm that $NH_3$ preferentially adsorbs on OH groups that otherwise serve as adsorption sites for Co precursors. This site-blocking effect may reduce nucleation on dielectric surfaces and help maintain high selectivity in area-selective Co deposition.

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).

5:15pm **ASD2-TuA-16 Understanding NHC Blocking Efficiency on Copper and Gold: From Surface Assembly to Precursor Inhibition**, ***Franz Thiemann***, *Patrick Melix,* Leipzig University, Germany*; Emmett Desroche, Francesco Tumino, Cathleen Crudden,* Queen's University, Canada*; Ralf Tonner-Zech,* Leipzig University, Germany

In area-selective atomic layer deposition (ASD), the development of thermally robust and chemically specific blocking layers remains a key challenge for achieving defect-free patterning. N–heterocyclic carbenes (NHCs) have emerged as versatile small-molecule inhibitors with exceptional affinity for transition-metal surfaces, providing a tuneable molecular platform for surface passivation. In this work, we investigate the blocking efficiency of NHC monolayers on copper substrates using density functional theory (PBE+D4) combined with periodic slab models, thereby extending previous findings from analogous Au(111)-NHC systems.[1]

The resulting adatom-mediated dimer pattern forms a compact organic overlayer that effectively inhibits precursor adsorption during subsequent ALD half-cycles. Energy decomposition analysis for the extended systems[2] reveals the origin of the overlayer stability: strong σ–donation to the surface and π–backdonation, together with dispersion interactions between the NHC backbones. Simulated STM images reproduce experimentally observed patterns at surface coverages of approximately 1.8 NHC $nm^{-2}$.[3] The blocking efficiency of this layer against common ALD precursors was validated using an innovative machine-learning–based molecular dynamics workflow.[4] This approach, referred to as the molecular gun method, reveals not only the statistical blocking efficiency but also the underlying mechanisms governing surface blocking and precursor breakthrough.

Collectively, these results reveal the atomic-scale origins of NHC-based blocking in ASD and provide a foundation for the rational design of next-generation NHC architectures with optimized binding strength, packing order, and blocking performance.

[1] Furlan et al. *Chem. Mater.***2025**, 37 (15), 5753.
[2] Raupach et al. *J. Chem. Phys.***2015**, 142, 194105.
[3] DesRoche et al. in Preparation
[4] Weiske et al. *arXiv***2025**, arXiv:2509.14828.

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