ALD Fundamentals: Growth and Characterization
Room HB Plant Ballroom - Session AF1-WeA

Modeling for ALD Processes I

Moderators: Ashley R. Bielinski, Argonne National Laboratory, **Alex Martinson**, Argonne National Laboratory

1:45pm **AF1-WeA-2 A Framework Bridging Generative AI Models and Atomic Layer Deposition for HfxZr$_{1-x}$O$_2$**, ***Han-Bo-Ram Lee***, *Bonwook Gu,* Incheon National University, Republic of Korea

As atomic layer deposition (ALD) is increasingly applied to complex, multicomponent materials, selecting appropriate compositions and phase windows in practice still relies heavily on trial-and-error. This becomes a serious limitation for functional oxides, where small changes in composition can strongly affect phase formation and electrical properties under thin-film growth conditions. In this work, we present an inverse-design framework for ALD, a general approach that connects recent advances in data-driven artificial intelligence (AI) models for inorganic materials with experimental ALD process development. We first generate many candidate crystal structures by using an AI-based structure generator (a model that proposes plausible crystal structures from composition). This generator prioritizes physically reasonable inorganic structures and compositions, as well as thermodynamically stable candidates (i.e., structures likely to form). These structures are relaxed with machine-learning interatomic potential (a fast surrogate for DFT) to obtain consistent formation energies and the energy above the convex hull (E_{hull}), enabling fast thermodynamic screening across composition. Based on this thermodynamic screening, graph neural network models are used to estimate key electronic properties, allowing composition–structure–property trends to be mapped without extensive first-principles calculations. The framework is demonstrated using the Hf–Zr–O dielectric system. The model captures a clear trade-off between band gaps and dielectric response across composition and highlights an intermediate composition range where low-energy tetragonal and orthorhombic phases are frequently predicted. Guided by these results, $Hf_{1-x}Zr_xO_2$ thin films were deposited by atomic layer modulation (ALM; an ALD sequencing method that tunes the Hf/Zr ratio cycle-by-cycle), which enables atomic-scale control of cation ratios within a single ALD sequence. Structural, electrical, and optical measurements show that the predicted phase evolution and property trends are reproduced experimentally, confirming that the model-guided design window remains meaningful under realistic ALD conditions. Overall, this framework provides a practical way to reduce empirical trial-and-error in ALD by focusing experiments on the most promising composition and phase regions. Although demonstrated here using a Hf–Zr–O system, the framework is not material-specific and can be readily applied to other complex oxides, doped systems, and emerging ALD materials.

2:00pm **AF1-WeA-3 Analysis and Design of Nb PE-ALD using Neural Network Potential Molecular Dynamics Simulation**, ***Noboru Sato***, *Akimasa Nakashima, Jun Yamaguchi, Naoki Tamaoki, Atsuhiro Tsukune, Yukihiro Shimogaki,* The University of Tokyo, Japan

Niobium (Nb) is a promising material for semiconductor interconnects, pMOS contacts, and superconducting components for Cryo-CMOS in quantum-computing applications. However, as a group-5 transition metal, Nb is difficult to reduce to the metallic state, and low-temperature CVD/ALD processes remain limited. We have been developing a low-temperature plasma-enhanced ALD (PE-ALD) process using $NbCl_5$ as a precursor and hydrogen plasma as a reducing agent. The resulting Nb films still exhibit high resistivity (~200 μΩ·cm), likely due to residual impurities and small grain size, compared with the bulk value (~15 μΩ·cm). In this study, we analyze the reaction mechanisms of $NbCl_5/H_2$ PE-ALD and explore process-design guidelines using molecular dynamics (MD) simulations based on neural network potentials (NNPs).Reaction analyses were conducted using NNP-based MD simulations implemented in MatlantisTM. The NNP was trained on PBE-based density-functional-theory data with empirical dispersion corrections. First, we examined saturated adsorption of $NbCl_5$ on the Nb(110) surface of body-centered cubic (bcc) Nb, a representative stable surface of metallic Nb. At low coverage, Nb and Cl atoms were largely dissociated on the surface; as coverage increased, Nb atoms aggregated, and at later stages chain-like $NbCl_4$ species formed on the surface.Next, we modeled plasma exposure by injecting H and Ar atoms onto the $NbCl_5$-saturated surface while varying acceleration energy and incident angle. For H atoms, low acceleration energy (0.1 eV) yielded a high probability of reaction with surface Cl to form volatile HCl; this probability decreased as acceleration energy increased. H incorporation into the Nb substrate was most likely at normal incidence (0°) and decreased at higher incident angles. For Ar atoms, $NbCl_4$ desorption was observed when the acceleration energy exceeded 10 eV, whereas surface structural collapse occurred above 100 eV. In contrast to H, Ar showed no strong dependence on incident angle.Experimentally, Nb PE-ALD was performed at 175 °C using an H_2/Ar plasma step with substrate bias. Comparing two bias conditions, (a) 60 W for 7 s and (b) 60 W for 3 s followed by 30 W for 4 s, the lower-bias sequence reduced residual Cl as quantified by XPS from 0.98% (a) to 0.33% (b). The combined simulation/experiment results suggest that suppressing excessive ion energy while maintaining sufficient hydrogen-driven chlorination removal is key to lowering halogen impurities in low-temperature Nb PE-ALD.

2:15pm **AF1-WeA-4 Study of Pd Ald as a Growth Enhancer for Ultrathin CoW Liner/Barrier Layer ALD**, *Noboru Sato, Wataru Mori, Souga Nagai, Yichen Zou, Yuxuan Wu, Yubing Deng, Jun Yamaguchi, Naoki Tamaoki, Atsuhiro Tsukune,* ***Yukihiro Shimogaki***, The University of Tokyo, Japan

Cu interconnects in advanced ULSI employ a bilayer liner/barrier stack to ensure adhesion to Cu and to suppress Cu diffusion. As scaling progresses, however, the effective resistivity of Cu line increases, motivating the use of a single-layer CoW liner/barrier that can provide both adhesion and barrier functions while improving the Cu volume fraction. A major challenge in forming an ultrathin (1–2 nm) continuous CoW film on dielectric surfaces by ALD is the intrinsically low nucleation density of metal ALD on insulators ($<10^{10}$ cm^{-2}), whereas $>10^{14}$ cm^{-2} is typically required for immediate film continuity.

To address this nucleation bottleneck, we explore Pd as a catalytic growth enhancer (GE) for CoW ALD. We previously observed that Co ALD on PVD-Pd/SiO_2 increases the Co nucleation density to ~10^{12} cm^{-2}, i.e., ~100× higher than conventional nucleation on dielectrics [1]. Building on this concept, the present work aims to develop a Pd ALD process capable of forming Pd clusters with nucleation densities ≥10^{13} cm^{-2} on dielectric surfaces, thereby further enhancing the initial nucleation of CoW.

First, we investigated the chemisorption behavior of the Pd precursor $Pd(hfac)_2$ using neural-network-potential molecular dynamics (NNP-MD). The NNP was trained to reproduce dispersion-corrected PBE (Perdew–Burke–Ernzerhof) reference data using Matlantis^{TM}. NNP-MD simulations at 450 K showed no chemisorption of $Pd(hfac)_2$ on hydroxyl-terminated SiO_2, whereas adsorption was observed on hydroxyl-terminated α-Al_2O_3 within 100 ps. These results suggest that creating an Al_2O_3-like hydroxylated surface is essential to enable high-density Pd nucleation on insulating substrates.

Guided by the simulation, we experimentally performed Pd ALD on SiO_2 and Cu substrates after surface modification with trimethylaluminum (TMA) at 145 °C to form an Al_2O_3-like overlayer. We compared (a) no treatment, (b) TMA treatment followed by air oxidation, and (c) TMA treatment followed by H_2O exposure. On SiO_2, Pd uptake increased after surface modification. On Cu, a marked increase in Pd uptake was obtained only for condition (c). The higher effectiveness of (c) over (b) is attributed to differences in Al_2O_3 surface termination; notably, our MD simulations also indicated that $Pd(hfac)_2$ does not adsorb on gibbsite-like Al_2O_3 surfaces. These combined computational/experimental results provide a practical route to engineer dielectric surfaces for high-density Pd nucleation as a growth enhancer toward ultrathin, continuous CoW liner/barrier ALD.

Reference

[1] Deng et al., Advanced Metallization Conference 2025, #4-3, Oct. 9-10, 2025, Toyo (2025).

2:30pm **AF1-WeA-5 Design and Performance of AI Agents Based on Large Language Models Interfacing with an Autonomous Atomic Layer Deposition Tool**, ***Angel Yanguas-Gil***, *Jessica Jones, Sungjoon Kim, Chi Thang Nguyen, Jeffrey Elam,* Argonne National Laboratory

In this work we introduce the design of an atomic layer deposition (ALD) reactor augmented with an AI interface for autonomous materials synthesis. Our modular interface encapsulates the particularities of the hardware behind a Python interface that communicates with the ALD control software via transmission control protocol (TCP). This interface is compatible with model context protocol (MCP) interfaces used in agentic frameworks. To evaluate its performance, we have integrated our tool with a simple AI agent that leverages a large language model to transform user-supplied queries into ALD processes that are then run in our reactor. Our approach uses a JavaScript object notation (JSON) schema to encode ALD processes. Our experimental results show that the AI interface does not impose a significant overhead to our control software, at least within our fastest 10 ms scale. We also carried out a detailed evaluation of the agent performance based on leading models in three types of tasks: basic instruction tasks and process discovery tasks, where the agent is presented with a target material and needs to identify the correct ALD process compatible with the reactor configuration, and process optimization. Despite the simplicity of our agent design, we observed that most of the advanced models excelled at the instruction tasks. However, only recent models such as o1, o3, GPT-5, and Claude Opus 4, with reasoning capabilities, performed well in process discovery tasks. While the results obtained are promising, we identify areas where AI research could help improve the performance of autonomous process discovery and optimization tasks involving atomic layer deposition.

2:45pm **AF1-WeA-6 Generalized Reaction Networks for Atomic Layer Deposition***, **Simon Elliott**,* Schrödinger, Ireland*; Thomas Ludwig,* Schrödinger*; Thomas Hughes, Chloe Luyet,* Schrödinger*; Jacob Gavartin,* Schrödinger, UK

ALD processes are defined in terms of their underlying chemistry, namely self-limiting gas-surface reactions. Much work has been done to determine the reaction mechanism in specific cases, but a general understanding is lacking regarding the criteria for ALD and the resulting limits on growth rates and sticking coefficients. In this work, we develop a generic reaction network for the deposition or etching of metal oxides by ALD or CVD and use microkinetic modelling (MKM) to compute these measurable process characteristics as a function of process parameters. We use ZnO, Al2O3 and HfO2 as illustrative examples that span a range of metal valences and restrict ourselves to water as the co-reagent, though the extension to sulfides or nitrides in similar Bronsted acid-base chemistry would be straightforward. Building on past mechanistic studies, we identify the elementary forward reactions that together comprise the reaction network as (i) precursor/co-reagent adsorption, (ii) ligand or proton exchange, (iii) elimination of protonated ligands as by-products and (iv) densification into solid film. The reverse of each reaction is also included in the reaction network. We streamline the network by omitting linearly dependent reactions. Since these elementary steps convert one surface intermediate into another, the size of the network scales in principle with the square of the number of intermediates. We therefore restrict the number of surface intermediates to the minimum for the number of ligands per precursor and number of protons per water molecule. Activation free energies for each elementary step would typically be computed with DFT, but here our interest is in how the pattern of relative activation energies across the network affects the overall process. Running MKM simulations of multiple pulse-purge cycles, we establish the bounds for ALD versus CVD behavior in terms of the reactivity of individual metals and ligands. The relative kinetics of ligand transfer and proton transfer are found to be the crucial factor.Having used MKM to identify the chemical spaces where ALD is viable, we then derive the corresponding ranges of growth/etch per cycle and sticking coefficients, which are measurable characteristics of the growth/etch process and can be used as inputs to higher-scale simulations. We present the dependence of these characteristics on precursor mass, metal valence, process temperature and pulse pressure.

3:00pm **AF1-WeA-7 Active-Learning PES Exploration: Fast Reaction Discovery in ALD Chemistry***, Nicolas Onofrio, Nestor Aguirre, **Fedor Goumans**,* Software for Chemistry & Materials, Netherlands

Understanding elementary reaction mechanisms of ALD precursors and plasma species is critical to predict nucleation, film microstructure, and process windows. We describe an automated, active-learning workflow that uses a foundation M3GNet interatomic potential to accelerate potential-energy-surface (PES) exploration and discover mechanistic pathways for ALD chemistries. Starting from a compact DFT seed set, the M3GNet model is fine-tuned and used to propose adsorption states, intermediates and transition-state candidates via ML-guided scans and NEB initializations. An uncertainty-aware query policy identifies high-value configurations for targeted DFT verification; verified results are fed back to the MLIP in iterative retraining. This loop expands PES coverage by orders of magnitude for a fixed DFT budget while maintaining DFT-level accuracy for kinetically relevant energetics. Verified elementary steps parameterize kinetic models (kMC) to evaluate nucleation, lateral growth and defect incorporation under varied pulse timing, temperature and co-reactant conditions. In ALD case studies (high-k precursor screening and Ru–H chemistries) the ML-augmented exploration uncovered low-probability dissociative channels and alternate TSs that materially affect predicted growth and electronic proxies. The approach enables faster, physics-grounded mechanism discovery and targeted DFT allocation, shortening precursor screening cycles and providing mechanistic insight for process engineers.

3:15pm **AF1-WeA-8 in-Silico, High-Throughput Exploration of Ald Reaction Mechanisms***, **Martin Siron**, Luis Pinto,* Entalpic AI, France*; Tristan Deleu,* Entalpic AI, Canada*; Alexandre Duval,* Entalpic AI, France

Understanding and ultimately controlling the elementary surface reaction steps that govern atomic layer deposition (ALD) remains a fundamental challenge for rational precursor design, growth selectivity, and process optimization. Although ALD is often idealized as a sequence of perfectly self-limiting half-reactions, practical film growth frequently proceeds through a complex interplay of competing ligand-exchange pathways, surface restructuring, precursor fragmentation, parasitic decomposition, and coverage-dependent kinetics. Quantitative prediction of reaction barriers, mechanistic branching, and rate-determining steps is therefore essential to connect molecular-scale surface chemistry with macroscopic deposition behavior such as growth-per-cycle (GPC), conformity, and selectivity.

Recent advances in high-throughput in silico reaction discovery, automated reaction network construction, and machine-learning interatomic potentials (MLIPs) are enabling mechanistically informed exploration of ALD chemistry at unprecedented length and time scales. By combining algorithmic reaction enumeration, accelerated transition-state refinement, and ML-driven reactive sampling, emerging computational frameworks provide a systematic route to map ALD reaction landscapes, identify kinetic bottlenecks, and evaluate competing pathways across broad precursor–surface chemical spaces.

At Entalpic, we develop agnostic and scalable workflows for the automated construction of complete ALD reaction mechanisms by integrating state-of-the-art cheminformatics and quantum chemistry methodologies. Using bond–electron formalism–based reaction enumeration, we generate comprehensive sets of chemically plausible surface reactions, intermediates, and mechanistic pathways. Thermodynamic screening of reaction networks is rapidly performed using MLIPs, enabling efficient evaluation of large chemical spaces beyond the limits of conventional density functional theory.

To characterize kinetic accessibility, we compute activation barriers through a combination of transition-state sampling strategies, including advanced methods such as Popcornn, alongside generative approaches for transition-state structure proposal and refinement. Through the LeMaterial initiative, we are assembling the largest curated database of transition-metal–organic complex reaction pathways, which directly supports the training of predictive and generative models for mechanistic inference. In parallel, we have benchmarked key elementary reactions for technologically relevant ALD precursors, establishing mechanistic descriptors that correlate with experimentally observed growth-per-cycle trends.

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