ALD Fundamentals: Growth and Characterization
Room HB Plant Ballroom - Session AF-MoA

ALD Precursor Design I

Moderators: Rick Chen, The Electronics business of Merck KGaA Darmstadt, **Atsushi Sakurai**, ADEKA CORPORATION

4:00pm **AF-MoA-11 Bridging Code and Chemistry: The Origin of Precursor Decomposition***, **Seungjin Song**, Ga Youn Lee, Dexter Dimova, Sean Barry,* Carleton University, Canada

Yttrium (Y) and scandium (Sc) play critical roles in high-k material by forming Y_2O_3 and Sc_2O_3 high-k dielectric oxides, so that they can suppress leakage current and improve thermal stability in advanced semiconductor devices. Conventional Cp- and β-diketonate-based precursors suffer from limitations such as high deposition temperatures, low surface reactivity, and carbon contamination. Therefore, the development of next-generation Y and Sc precursors with high volatility, strong reactivity, and low impurity incorporation is essential for future nanoscale device fabrication.

Our group uses a silicon-containing ligand to prepare the homoleptic Y and Sc precursors and investigates the origin of thermal decomposition in precursors containing highly basic ligands. We synthesized the homoleptic group 3 precursor using salt metathesis and acid-base reaction. Our product was characterized through nuclear magnetic resonance (NMR) spectroscopy and single-crystal X-ray diffraction (SC-XRD). We investigated the thermal properties of the complex by thermogravimetric analysis and, using flame-sealed samples in a glass tube, revealed the origin of the thermal decomposition mechanism by NMR spectroscopy and density functional theory (DFT) calculations with Eyring analysis.

Our DFT calculations and Eyring analysis allow us to identify the key structural point in the precursors to prevent thermal decomposition. This talk will focus on connecting the experimental observations and DFT calculations through the Eyring analysis. The presentation will show a detailed synthesis and characterization, and mechanistic thermal decomposition pathways for a representative methodology on how we connect the DFT calculations and experimental observations.

4:15pm **AF-MoA-12 Multi-Objective Discovery of New Precursors for ALD with Steerable Generative AI***, **Tristan Deleu**,* Entalpic, Canada*; Alexandre Duval,* Entalpic, France

Advances in atomic layer processes are often constrained by the limited availability of precursors that satisfy an increasingly complex set of requirements for the deposition of specific thin films. The development of novel precursors for ALD poses unique challenges in organometallic chemistry, where ideal candidates must balance multiple objectives simultaneously. For example, they must be stable at room temperature for safe storage in liquid form and possess a volatility range that matches the optimal ALD temperature window, all while guaranteeing proper reaction with the substrate to avoid contamination. While historically the design of new compounds has often relied on experience and chemical intuition, there is now an opportunity to leverage modern tools from artificial intelligence (AI) to navigate this massive chemical space at scale and accelerate discovery.

At Entalpic, we are building a platform that applies cutting-edge generative AI to find a wide range of new candidate precursors. Our approach integrates a collection of prediction models, each of them targeting desirable properties for ALD, to steer our generative models towards molecules of interest within a multi-objective optimization framework. We first train a general-purpose model capable of generating organometallic complexes, based on open-data available through initiatives such as LeMaterial. Depending on controllable settings, the model can either construct new molecules from an existing library of ligands available for purchase, or discover new ligands altogether while ensuring synthesizability of the final complexes.

Recognizing that ligands in transition metal complexes play an essential role in determining their properties, we train a variety of machine learning (ML) models, such as transformers, graph neural networks (GNNs), and machine learning interatomic potentials (MLIPs), to accurately predict vapor pressure and other critical parameters, while ensuring robust generalization to new ligands. These predictive models then provide a feedback signal to guide our pre-trained generative model with reinforcement learning (RL). Finally, these molecules suggested by the fine-tuned generative model undergo a series of thermodynamic screening steps to narrow down the set of promising candidates that can be submitted to the lab for evaluation.

4:30pm **AF-MoA-13 First-Principles Screening of Precursors and Inhibitors to Achieve Enlarged-Grain MoS_2 Through Area-Selective Deposition***, **Bram van der Linden**,* KU Leuven and Imec, Belgium*; Geoffrey Pourtois, Sergiu Clima,* IMEC, Belgium*; Ian Campbell,* IMEC*; Pierre Morin, César Javier Lockhart de la Rosa,* IMEC, Belgium*; Ageeth Bol,* University of Michigan, Ann Arbor*; Annelies Delabie,* KU Leuven and Imec, Belgium

MoS_2 is a promising channel material for field-effect transistors, owing to its superb intrinsic carrier mobility at nanoscale dimensions. While Atomic Layer Deposition (ALD) enables conformal deposition of MoS_2, it typically yields nanocrystalline layers with low mobility due to grain-boundary scattering. Enlarged MoS_2 grain sizes are essential to obtain the mobility needed for nano-electronic devices. This may be achieved through inhibitor molecules that passivate part of the reactive groups at the initial surface, thus reducing the number of sites available for nucleation. The vast number of possible precursor-inhibitor combinations makes experimental assessment too time-consuming and costly. We therefore use first-principles thermodynamic simulations to evaluate the two most important criteria for achieving large MoS_2 grain sizes using surface inhibitors: highly reactive molybdenum precursors and sulfur co-reactants, and effective surface inhibitors that block adsorption of the molybdenum precursors and sulfur co-reactants.

To enable efficient screening of precursors and inhibitors, we developed a three-step first-principles thermodynamic approach. Using this framework, we assess the reactivity of 14 molybdenum precursors reported for the growth of various molybdenum-based materials, with H_2S as the sulfur source. The precursor reactivity is evaluated in combination with 15 SiO_2 surface (passivation) chemistries under typical low–temperature ALD conditions (200°C, 0.1Torr). First, we evaluate the thermodynamic driving force for each precursor to form monolayer-thin MoS_2 crystals of various sizes. $Mo(NMe_2)_4$ is the only precursor that exhibits strong thermodynamic driving forces for forming all tested grain sizes, consistent with the low ALD growth temperature (60°C) reported for this precursor[1]. For all precursors, reactivity improves with increasing grain size. In addition, we could identify new promising precursors for MoS_2 ALD, such as $MoCl_4O$. Second, we use a SiO_2 cluster model to calculate the reaction energies of molybdenum precursors and H_2S with the reactive surface hydroxyl groups and candidate surface-passivation groups. -Si-F emerges as one of the most promising surface passivation groups, as precursor reactions yield largely endothermic reaction energies, suggesting strong inhibition of MoS_2 growth. Third, to verify the results of the SiO_2 cluster approach, we compute the reaction energies for selected precursor-inhibitor combinations using a periodic SiO_2 surface slab model. The combined use of cluster and slab models enables efficient screening of precursors and inhibitors, ultimately identifying promising ALD process conditions that yield films with enlarged MoS_2 grains.

(1) T. Jurca et al. Low-Temperature Atomic Layer Deposition of MoS_2 Films. *Angew Chem Int Ed* **2017**, *56* (18), 4991–4995.

4:45pm **AF-MoA-14 Molecular–Level Insight Into Thermal Stability and Substrate–Dependent Nucleation of DDAP for Platinum ALD***, **Tomohiro Tsugawa**, Hideaki Nakatsubo, Yohei Kotsugi, Ryosuke Harada,* TANAKA PRECIOUS METAL TECHNOLOGIES Co., Ltd., Japan

Platinum (Pt) thin films are widely utilized in advanced semiconductor devices due to their low resistivity, high work function, catalytic activity, and excellent thermal stability. Atomic layer deposition (ALD) of Pt is essential for achieving film thicknesses below 20nm with superior conformality in high–aspect–ratio 3D structures. However, stable and uniform Pt–ALD remains difficult because conventional precursors exhibit limited thermal stability, insufficient volatility, and substrate–dependent nucleation behavior that is not yet fully understood.

In this work, we investigate the Pt precursor DDAP (Dimethyl-(3,4–*η*)-*N,N*–dimethyl–3–butene–1–amine–*N*)platinum(II), $C_8H_{19}NPt$), which has demonstrated high ALD growth rates and low–resistivity Pt films using O_2 as a reactant [1, 2]. Despite its promising performance, the molecular–level origins of its thermal stability and substrate–specific growth characteristics have remained unclear. We present a combined experimental and simulation study such as density functional theory (DFT) to clarify these mechanisms.

DFT analysis identifies intrinsic thermal decomposition pathways and activation barriers consistent with the experimentally observed onset of precursor decomposition near 275 ℃, providing mechanistic insight into the established ALD process window. Furthermore, adsorption energetics were evaluated on technologically relevant surfaces including Pt, Cu, TiN, and oxide substrates such as OH–terminated SiO_2, Al_2O_3, and ZrO_2. DDAP exhibits weaker adsorption on oxide surfaces compared to metals, correlating with delayed nucleation and non–uniform initial Pt growth observed experimentally on SiO_2.

By linking ALD behavior directly to DFT–derived energetics, this study provides a molecular–level explanation for DDAP's thermal properties and substrate–dependent nucleation phenomena. These insights offer guidance for designing next–generation Pt precursors optimized for highly conformal and substrate selective ALD processes.

References

[1] Se-Hun Kwon et. al., *Chem. Mater.* **2019**, *31*, 5056-5064.
[2] Soo-Hyun Kim et. al., *J. Vac. Sci. Technol. A* **2020**, *38*, 032404.

5:00pm **AF-MoA-15 Theoretical Analysis on Organic Sulfur Sources for Atomic Layer Deposition of MoS_2**, ***Myeong Kyun Nam,*** Hongik University, Republic of Korea*; Bonggeun Shong,* Hanyang University, Republic of Korea

Molybdenum disulfide (MoS_2) is widely recognized as a promising two-dimensional semiconductor material. Atomic layer deposition (ALD) can provide a scalable route for the controlled synthesis of MoS_2. Conventional ALD processes of sulfides often employ H_2S as the sulfur source; however, its extreme toxicity has motivated development of benign alternative sulfur sources. Previous studies have reported MoS_2 ALD processes using organic sulfur precursors such as diethyl sulfide (DES) and diethyl disulfide (DEDS), in combination with $Mo(CO)_6$ as the molybdenum precursor [1]. Experimental results indicate that DEDS achieves higher growth rates and more efficient nucleation than DES [1]. In this work, density functional theory (DFT) and machine learning interatomic potential (MLIP) calculations are employed to elucidate the chemical reaction mechanisms and fundamental origins of the distinct reactivities of DES and DEDS during MoS_2 ALD. MoS_2 edge models with thermodynamically stable hydrogen coverages are constructed under appropriate temperature and pressure conditions. Adsorption of $Mo(CO)_6$ on these surfaces exhibits self-limiting behavior, consistent with the characteristics of ALD processes. Subsequent reactions with DES and DEDS are investigated with emphasis on the removal of residual CO ligands bound to surface Mo. Our results reveal that the cleavage of the S-S bond, present only in DEDS, is relatively facile in contrast to the cleavage of the C-S bonds. Current research could contribute to a deeper understanding of the chemistry behind sulfide ALD, and provides insights into utilization of organic reactants in ALD.

References [1] Adv. Mater. 29, 47, 1703031 (2017)

5:15pm **AF-MoA-16 A Data-Science Approach to the Analysis of Temperature-Dependent Alumina Atomic Layer Deposition Growth Per Cycle*, Raymond Adomaitis,*** University of Maryland

Temperature-dependent alumina atomic layer deposition (ALD) growth per cycle (GPC) data were collected from nearly 40 studies of the trimethylaluminum (TMA)/water ALD process. The data were used in multiple regression approaches based on fitting the data to globally defined polynomials in temperature T, and two linear piecewise-continuous representations of the fitted data, each patterned after the hypothesized existence of an ALD window exhibiting constant or linear GPC(T) dependence. All three regression approaches identified a low-T region characterized by rising GPC with T, reaching a maximum of approximately 1.1 A/cycle slightly below 200 deg. C, followed by a slower decline in GPC with T after this point. The results indicate that a temperature-independent ALD window for the TMA/water system may be relatively small (with lower and upper limits of 177 and 208 deg. C, respectively), if it exists at all. Multiple approaches to statistical analysis of the validity of observed trends will be presented.

Reference

Adomaitis, R. A., "Regression analysis of temperature-dependent alumina atomic layer deposition growth per cycle using trimethylaluminum and water as precursors," J. Vac. Sci. Technol. A 43 062406 (2025) DOI: 10.1116/6.0004738

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