ALD Fundamentals
Room Halla Hall - Session AF2-TuM
Mechanism and Theory II

Moderators: Seung-Min Chung, Hoseo University, **Atsushi Sakurai**, ADEKA CORPORATION

10:45am **AF2-TuM-12 Screening Volatile Metal Complex for ALD Precursor by Modified COSMO-SAC Method and Estimating Its Reactivity by Atomistic Simulator Using Neural Network Potential***, **Noboru Sato,*** The University of Tokyo, Japan*; Naoyuki Hoshiya, Akiyoshi Yamauchi, Shigehito Sagisaka, Yosuke Kishikawa,* DAIKIN INDUSTRIES, LTD., Japan*; Yuxuan Wu, Jun Yamaguchi, Atsuhiro Tsukune, Yukihiro Shimogaki,* The University of Tokyo, Japan

The film growth characteristics of ALD vary greatly depending on the precursors; therefore, there are many attempts to develop novel metal complexes. We are developing a method to predict and measure metal complexes' vapor pressure and adsorption equilibrium constants for the ideal ALD precursor. As ALD utilizes the saturated chemisorption of the precursor, high vapor pressure and equilibrium constant are required. We established a method for accurately estimating the vapor pressures of metal complexes by modifying the COSMO-SAC (COnductor-like Screening MOdel - Segment ACtivity) method proposed by Lin et al [1, 2]. In this presentation, we report the results of predicting and developing metal complexes with high vapor pressures, and we analyze the reactivity of candidate compounds using an atomistic simulator based on neural network potential (Matlantis™). Calculations were performed using the PBE+D3 level of theory.

When investigating the conditions for high-vapor-pressure complexes, we found that the lower the polarizability and dielectric constant, the higher is the vapor pressure (Figure 1). Accordingly, we predicted the vapor pressure of Co complexes with a polarizability of 220 or less and a dielectric constant of 2.1 or less, the results are shown in Figure 2. When we synthesized $CpCo(C_2F_4)CO$ and measured its vapor pressure, we found it to be 8 Torr at 85°C, which is sufficiently high for ALD applications (Figure 3). Thus, by utilizing the COSMO-SAC method, it is possible to design metal complexes with high vapor pressures.

To evaluate whether $CpCo(C_2F_4)CO$ can be used for ALD, we used Matlantis™ to calculate the chemisorption process on the Cu(111) surface, which served as the growth substrate (Figure 4). The metal complex physisorbed with an energy of 90kJ/mol, and the Cp ligand dissociated with a low activation barrier of 10–25kJ/mol, suggesting that it can be readily adsorbed on a clean Cu(111) surface at 200–300°C. When calculating the adsorption energies of the CO, C_2F_4, and Cp groups, we found that while the CO and C_2F_4 groups have adsorption energies of 90kJ/mol, the Cp group exhibits a very high adsorption energy of 245kJ/mol. This indicates that removal of the Cp group is likely to be the rate-determining step. The effective removal of Cp groups from the surface remains a challenge for future work.

References

1. Lin S.T., et. al., *J. Phys. Chem. A*, **108** (2004) 7429-7439.
2. Sato, N., et. al., AVS 24th International Conference on Atomic Layer Deposition, Helsinki, Finland (2024), AF1-TuM-2.

11:00am **AF2-TuM-13 Ion Effects on Plasma-induced Surface Composition Changes during SiCN Atomic Layer Deposition: A Combined Ab-Initio and Monte Carlo Approach***, **Ting-Ya Wang,*** University of Texas at Austin, Taiwan*; Hu Li,* Tokyo Electron America, Inc., China*; Peter Ventzek, Jianping Zhao,* Tokyo Electron America, Inc.*; Gyeong Hwang,* University of Texas at Austin

Plasma-enhanced atomic layer deposition (ALD) is an effective method for reducing deposition temperatures, particularly during nitridation. However, plasma can also introduce adverse effects, such as altering chemical composition and causing densification, which significantly influence key material properties like the dielectric constant. Understanding plasma-induced changes in surface morphology and composition is therefore critical. While experimental techniques for surface analysis face inherent limitations, theoretical methods also present challenges, particularly in modeling ALD processes where primary surface reactions are rare events.

Integrating kinetic Monte Carlo (kMC) with density functional theory (DFT) offers a powerful approach for simulating ALD. However, a key challenge in kMC lies in the need for a predefined list of permissible events. Traditionally, researchers manually compile a set of reactions deemed most significant. Yet, the vast number of possible events on a surface, combined with the importance of rare events in ALD, raises concerns about the authenticity and completeness of outcomes derived from manually curated reaction lists.

We developed an atomistic, off-lattice, three-dimensional simulator that integrates kMC with DFT. We employed a strategic approach to construct a comprehensive event list, capturing a broad spectrum of potential surface reactions. Our study focused on investigating the effects of ions in N_2 plasmas on silicon carbonitride (SiCN) materials, with particular emphasis on the roles of ion energy and flux.

SiCN is a low-k material critical for semiconductor manufacturing, where low dielectric constants are essential to minimize capacitive coupling in integrated circuits. The dielectric properties and mechanical strength of SiCN are strongly influenced by the elemental composition, bond types, and bond orders. Variations in these parameters can lead to significant differences in film quality and functionality, highlighting the importance of understanding and controlling these characteristics. By utilizing our simulator to model surface reactions and the evolution of SiCN films during ALD, we aim to validate and refine our approach while identifying strategies to optimize the material's properties for industrial applications.

11:15am **AF2-TuM-14 Atomistic Insights into the Surface Chemistry Driving ALD of IGZO Films from First-Principles and Machine-Learning Simulations***, **Alex Watkins,*** University of Warwick, UK

The quaternary oxide semiconductor In-Ga-Zn-O (IGZO) has gained attention in recent years due to its promise in key properties: high optical transparency, high electron mobility, and low fabrication costs. These properties make it an exciting candidate for several applications including thin-film transistors (TFTs) in next-generation OLEDs, flexible electronic devices, advanced CMOS, and AI hardware.[1] One technique that has become indispensable for thin-film fabrication such as this is ALD, due to its exceptional conformality and control. The ALD process of IGZO requires a complex supercycle consisting of three single-component steps, each requiring a three-step process. This complexity requires significant optimisation to have success, this is where understanding the underlying surface chemistry is key, and atomistic simulations can provide great assistance.

In ALD the initial nucleation of a precursor on a target substrate is key to the overall quality of the deposited film, this requires effective precursor binding to the surface. Molecular dynamics (MD) simulations and minimum-energy reaction pathway analysis, enabled by *ab initio* Density Functional Theory (DFT) offer valuable insights into reaction chemistry, shedding light onto kinetics and thermodynamics factors.[2,3,4,5,6,7,8] Most recently machine-learned interatomic potentials (MLIPs) offer a major boost to the capabilities of these simulations, in bridging the gap between atomistic simulations studying binding of a single precursor and the kinetic Monte Carlo simulations studying larger scale properties such as rates of deposition and surface coverage.

In this contribution, we will present key atomistic insights into the ALD nucleation and growth mechanisms of IGZO on silicon oxide (SiO_2) substrate, as predicted by DFT and MLIPs, considering the different ALD sub-cycles, e.g. InOx, GaOx and ZnOx depositions. In particular, we will discuss the effect of simultaneous substrate binding of multiple precursors/co-reactants on the nucleation and growth behaviour, and the effect of temperature on the adsorption and surface coverage properties.

[1] *ACS Applied Electronic Materials* **2024,** 6 (8), 5694-5704; [2] *ACS Nano* **2017**, 11, 9, 9303–9311; [3] *Chem. Mater*. **2019**, 31, 4, 1250–1257; [4] *Chem. Mater*. **2017**, 29, 3, 921–925; [5] *Nanoscale*, **2021**, 13, 10092-10099; [6] *Chem. Mater*. **2017**, 29, 5, 2090–2100; [7] *Nanoscale*, **2016**, 8, 19829-19845; [8] *Solar Energy Materials and Solar Cells* **2017**, 163, 43-50.

11:30am **AF2-TuM-15 Adsorption State Study of Trimethylaluminum Using Neural Network Potential Computation and High Accuracy in-situ Quartz Crystal Microbalance***, **Yuxuan Wu,*** The University of Tokyo, Japan, China*; Jun Yamaguchi, Noboru Sato, Atsuhiro Tsukune, Yukihiro Shimogaki,* The University of Tokyo, Japan

Atomic layer deposition (ALD) is primarily applied in ULSI fabrication because of its characteristics of alternately supplying the precursor and reaction gas, relying on saturation of surface adsorption. This results in excellent uniformity and stability of the film thickness against fluctuations in fabrication conditions. Detailed results from previous studies have constructed a well-defined adsorption and reaction pathway for TMA ALD by in-situ characterization and computational simulation. The growth of

Al_2O_3 could be understood by the adsorption amount and structures of TMA and H_2O at each step, where the $-CH_3$ and -OH densities on the surface significantly determine the characteristics of deposition. Understanding such termination on the surface can reveal the thermodynamic and kinetic factors for the reaction, where the quality and efficiency of the reaction can be controlled.

Conventional methods, such as Density Functional Theory (DFT) and Quartz Crystal Microbalance(QCM), examine the surface adsorption and reaction of precursors. However, the challenges of time-consuming and inapplicable for the steric hindrance prediction with a large slab size remain for DFT, and the insufficient accuracy of QCM (1 ng/cm^2) limits the measurement of small molecule adsorption. These limitations influence the analysis of the surface adsorption of TMA.

Using a state-of-the-art simulator (Matlantis^{TM}) with the Preferred potential (PFP) and high-accuracy in-situ QCM with a calibrated frequency counter and resonator, we explored the adsorption and reaction of TMAon the Al_2O_3 surface. Because of the precise neural network potential (PFP) developed by advanced machine learning-based techniques, it can easily predict the adsorption behavior of precursors on large adsorption surfaces in an extremely short time (minutes). We calculated the adsorption state and energy for TMA using Matlantis^{TM} and found good agreement with previous DFT calculations, as shown in Fig.1 (<0.07 eV). The adsorption calculation later expanded to multiple TMA molecule adsorption on the surface and predicted surface coverage for TMA by the steric hindrance effect due to the methyl group as 0.75, compared with the reference predicting surface coverage of 70%–80%. The adsorption amount of TMA on the Al_2O_3 surface with predicted surface coverage is 34.7 ng/cm^2, which is close to the experimental results from modified in-situ QCM, which shows 40 ng/cm^2 with a crystal roughness of 15%. The results from jMatlantis^{TM} were predicted well and precisely compared with both experiment results from QCM and computational DFT.

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