

ALD Fundamentals

Room Hall 3A - Session AF2-TuA

Precursors and Chemistry: Simulation, Modeling, and Machine Learning for ALD

Moderators: Michael Nolan, University College Cork, Ralf Tonner-Zech, Leipzig University

4:00pm AF2-TuA-11 Machine Learning Assisted Surface Reaction Study of Al(Me)₃ and Water on OH/Si(111), H. Nakata, Cheol Ho Choi, Kyungpook National University, Republic of Korea

INVITED

Knowledge of the detailed mechanism behind the atomic layer deposition (ALD) can greatly facilitate the optimization of the manufacturing process. Computational modeling can potentially foster the understanding; however, the presently available capabilities of the accurate *ab initio* computational techniques preclude their application to modeling surface processes occurring on a long time scale, such as ALD. In this talk, we propose an iterative protocol for optimizing machine learning (ML) training data sets and apply ML-assisted *ab initio* calculations to model surface reactions occurring during the ALD process on the semiconductor surfaces. The protocol uses a recently developed low-dimensional projection technique, greatly reducing the amount of information required to achieve high accuracy (1 kcal/mol or less) of the developed ML models. Hence, the proposed protocol furnishes a very effective tool to study complex chemical reaction dynamics at a much-reduced computational cost.

4:30pm AF2-TuA-13 Quantum Chemical Investigation on the Reaction Mechanism of Atomic Layer Deposition of ZrO₂ from Heteroleptic CpZr(N(CH₃)₂)₃ Precursor and Ozone, Rabi Khanal, R. Joe, A. Dip, Tokyo Electron America, Inc.

High-k oxides, such as ZrO₂, are being studied as alternatives to SiO₂ due to their advantageous properties for scaling down semiconductor devices. They have lower leakage current, consume less power, switch faster, and are thermally stable. Moreover, they can maintain a high capacitance at thinner film thickness, which is ideal for achieving higher packaging density and increasing memory cell integration on a single chip.

Heteroleptic precursors containing amido and cyclopentadienyl (Cp) ligands exhibit adequate thermal stability for the atomic layer deposition (ALD) of ZrO₂. In ALD, ozone (O₃) can be used as an oxidizer instead of water (H₂O). Ozone has a higher oxidation potential than H₂O. This higher oxidation potential allows for more surface reactions, faster growth, uniform deposition, and reduced impurities. It is worth noting that different ligands in heteroleptic precursors have unique reaction paths depending on their ligand exchange reactions, unlike homoleptic precursors. It is crucial to understand the detailed surface reaction mechanism of ALD to enhance the quality and performance of thin films by reducing impurities incorporated during film growth.

In this study, we have employed quantum chemical calculations at the density functional theory (DFT) level and *ab initio* molecular dynamics (AIMD) to investigate the detailed reaction mechanism of ZrO₂ ALD with the precursor CpZr(N(CH₃)₂)₃, and O₃ as an oxidizer. Our findings suggest that when the precursor is adsorbed onto a hydroxylated Si surface, the elimination of the amido ligand is preferred over that of the Cp ligand. During the oxidation process, all remaining ligands on the adsorbed precursor are eliminated through the adsorption of O₃ in two subsequent processes, each consisting of multiple intermediate reaction mechanisms.

In addition, the energy barriers associated with the oxidation of Zr-Cp bonds are higher (about 12 kcal/mol) than those of the Zr-N bonds. The higher energy barrier indicates that the release of the Cp ligand occurs after the amido ligand. When the Cp ligand remains on the surface during the ALD cycle, it increases the adsorption energy for incoming molecules and acts as a blocking group to reduce impurity incorporation during film growth. Our study provides a fundamental understanding of the reaction mechanism of various ligands with O₃ at the Si surface, which has yet to be reported. We believe this knowledge can be extended to the deposition of other high-k oxides, such as HfO₂. Also, it can serve as a basis for tuning film properties using feature and reactor scale simulations.

4:45pm AF2-TuA-14 Microkinetic Modelling to Reveal How the Atomic-Scale Mechanism of Deposition or Etch Plays Out at Feature and Reactor Scale, Simon D. Elliott, Schrödinger, Ireland; T. Hughes, T. Ludwig, Schrödinger; J. Gavartin, Schrödinger, UK

Microkinetic modelling is a technique for determining the turnover of a gas-surface process by solving the coupled kinetic rate equations of its constituent elementary reaction steps [1]. It is widely used in the field of heterogeneous catalysis. Here we present a microkinetic model of the atomic layer deposition (ALD) of alumina from trimethylaluminium (TMA) and water and discuss its utility in investigating growth at macroscopic length and time scales.

We first outline the computational scheme, where elementary steps and their activation energies have been computed with density functional theory (DFT), averaging across a wide variety of geometries. We emphasize the importance of converting the DFT energies to free energies at the temperatures and pressures of interest. The resulting microkinetic model for alumina-on-alumina growth yields measurable quantities (relative growth per cycle and sticking coefficients) as a function of temperature and pressure, which are validated against experiment. For instance, the values of sticking coefficient from the model, $s_0(\text{TMA}) = 7 \times 10^{-3}$ and $s_0(\text{H}_2\text{O}) = 3 \times 10^{-4}$ at 1 Torr and 300°C, compare well with experiment [2]. Sticking coefficients are crucial inputs for computational fluid dynamics simulations at feature-scale and reactor-scale.

We then show results for how microkinetic modelling can be used in specific scenarios. By adding appropriate elementary steps, the model can reveal the contribution from continuous CVD-style growth under given conditions, or under what conditions ALD can be flipped over into ALE. Alternatively, activation energies can be modified to account for the different chemistry that may exist during nucleation on a substrate, without explicitly modelling any one substrate at the atomic scale. This can be used to test which chemistries are effective in tuning area-selectivity of a process towards various substrates. Finally, we show how a microkinetic model can be used to study the variation of sticking coefficient with pressure and thus account for penetration depth and conformality within high aspect ratio features.

These examples illustrate how existing mechanistic data from atomic-scale DFT can be leveraged in computationally-inexpensive higher-scale models to allow 'what-if' experiments to be carried out that link directly to measurements.

[1] Iwao, T.; Yang, T.-H.; Hwang, G. S.; Ventzek, P. L. G.; *J. Vac. Sci. Technol. A* **2023**41, 032410

[2] Arts, K.; Vandalon, V.; Puurunen, R. L.; Utraiainen, M.; Gao, F.; Kessels, W. M. M.; Knoops, H. C. M.; *J. Vac. Sci. Technol. A* **2019**37, 030908

5:00pm AF2-TuA-15 First-Principles Based Comprehensive Surface Kinetic Modeling for Molybdenum ALD Film Growth, Toshihiko Iwao, K. Lee, J. Cha, J. Hong, J. Son, S. Kang, Etch/CLN Equipment R&D Team, Samsung Electronics, Republic of Korea

As a design rule of semiconductor device fabrication reaches near tens of angstrom scale, interconnect metallic materials require not only lower bulk resistivity but also smaller electron mean free paths which cause an increase in the effective resistivity of nanometer-scale structures due to interface electron scattering phenomena. Consequently, there is an increasing demand for nanoscale wiring formation using materials with short electron mean free paths, such as molybdenum (Mo), ruthenium (Ru), and cobalt (Co). Among them, the development of Mo micro-wiring formation technology using atomic layer deposition (ALD) is being actively pursued, but further acceleration of productivity is required. In this study we have established a surface reaction model using first-principles analysis to identify the rate-limiting factors of Mo growth mechanism. The construction of reaction models consists of three elements: calculating the activation energy through first-principles surface reaction analysis, determining the reaction pathway, and analyzing real-time coverage using the activation energy. This analysis demonstrates that the temperature dependency of Mo growth-per-cycle (GPC) is caused by the 1.27eV of desorption energy of surface adsorbed hydrogen site Mo-H(s) desorption. During the molybdenum dichloride dioxide (MoO₂Cl₂) precursor dose step, decomposed chlorine and oxygen atoms from the precursor molecule remain on the molybdenum surface and inhibit further precursor molecule adsorption by creating Mo-O-Mo(s), and Mo-Cl(s) surface. This phenomenon describes the monolayer saturated adsorption of the precursor and reveals the necessity of hydrogen flux to remove these inhibitors from the surface. We also analyzed the reaction barrier of

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removing surface inhibitor by both molecular hydrogen and surface stuck hydrogen site Mo-H(s). By combining these reaction path into surface kinetic model we have successfully reproduced the GPC tendency with over 90% accuracy on various process parameters based on these reaction barrier energy and surface kinetic model, which analyzes the surface coverage in actual process timescale. These film growth analysis scheme provides the detailed and quantitative film growth mechanism for various novel materials and processes.

5:15pm **AF2-TuA-16 Modelling the Ligand Exchange Process for the Atomic Layer Deposition of Metal and Metal Oxide Thin Films**, *Ji Liu*, Tyndall National Institute, University College Cork, Ireland; *H. Sønsteby*, University of Oslo, Norway; *M. Nolan*, Tyndall National Institute, University College Cork, Ireland

Atomic layer deposition (ALD) is widely used in microelectronics and semiconductor industry to deposit metal and its oxide and nitride thin films as part of device fabrication in nano- or subnano-dimensions. The key advantages of ALD are the conformality and precise thickness control at the atomic scale, which are difficult for physical or chemical vapor deposition methods. The atomic scale understanding of ALD is vital and essential to design and optimize the deposition process, and density functional theory (DFT) calculations play an important role in providing detailed reaction mechanism, theoretical screening of suitable precursors and estimated growth-per-cycle (GPC).

In this presentation, I discuss our recent work on the detailed first principles simulation of ligand exchange process for thermal ALD of a range of technologically relevant deposition chemistries. 1) Co thin film deposition using $\text{CoCl}_2(\text{TMEDA})$ and reducing agent $\text{Zn}(\text{DMP})_2$; 2) FeZn thin film deposition using FeCl_3 and $\text{Zn}(\text{Et})_2$; and 3) BaO/Ba(OH)₂ using $\text{Ba}(\text{acac})_2$ and oxygen-containing reactants as part of depositing BaTiO_3 (BTO). We first focus on gas-phase precursor chemistry and apply DFT calculations to identify plausible ligand elimination pathways, which allow us to assess the most favourable chemistry for each film deposition. Then we explore the surface chemistry in the two half reactions for the ALD process. For Co deposition we show that a pathway involving initial ligand exchange of DMP and Cl on Co(111) surface with CoCl_2 termination and Zn is removed via $\text{ZnCl}(\text{DMP})$ formation and desorption, resulting $\text{Co}(\text{DMP})_2$ termination on the surface. The two DMP ligands are removed via C-C bond formation in a straightforward way. In intermetallic alloy deposition we show that the FeCl_3 precursor is found on the surface as an FeCl_2 and -Cl fragment and the reaction with DEZ follows mixture of butane and subsequent EtCl formation and desorption. Finally, for BaO/Ba(OH)₂ ALD, we explore how the $\text{Ba}(\text{acac})_2$ precursor reacts on Bi-O terminated surfaces and how this can impact on the preferred deposition chemistry. These works showcase how we can apply DFT calculations to elucidate the ligand exchange mechanism during metal or metal oxide thin film growth and give some insights on how the selection of precursors and reducing agent or co-reactant affects the growth behavior.

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