ALD Fundamentals
Room Auditorium - Session AF2-MoA
Simulation, Modeling, and Theory of ALD I

Moderators: Hannah Margavio, North Carolina State University, Bonggeun Shong, Hongik University

4:00pm **AF2-MoA-11 A User Experience Feedback on Numerical Simulation for CVD/ALD Precursor Design & Development***, **Romain Gaillac**,* Air Liquide **INVITED**

Molecular modelling has been a widely used tool in biochemistry or catalysis for decades. More recently, its application to CVD/ALD precursors has been suggested as a way to improve their design and development. We have explored its potential, especially through ab-initio molecular simulations.

In particular, we investigated the relevance of such simulations for the assessment of synthetic pathways and reactions occurring during Atomic Layer Deposition processes. We also assessed the interest of assisting analytical efforts with molecular simulations, for example for substance identification via spectra simulation.

Our work showed that molecular simulations are a useful tool for the development of new ALD precursors. They can be used to different degrees of accuracy to understand:

1. Intrinsic molecule stability, either isolated or in a condensed phase
2. Reaction thermodynamics and reaction paths
3. Surface adsorption/desorption and reactivity

However the predictive power remains to be improved, and at this point, it should be seen as a useful companion to experimental work. Effective collaboration between the synthetic chemists, ALD/CVD practitioners and molecular modeling theorists accelerates the acquisition of a chemical and mechanistic comprehension of ALD Precursors. Such learning can bring an acceleration to the design and development process.

4:30pm **AF2-MoA-13 From Monolayers to Crystalline Materials in ALD: Simulation and Comparison With Experiments***, **Angel Yanguas-Gil**, J. Elam,* Argonne National Laboratory

Controlling the microstructure of ALD materials is key for many different applications. In some cases, like gate dielectrics in microelectronics, the goal is to achieve materials with good interfaces and that lack grain boundaries to improve leakage and avoid the onset of breakdown. In other cases, applications require the growth of materials with good crystalline quality.

One of the key characteristics of ALD is that its growth conditions (low temperature and pulsed, self-limited nature) are far from those considered in traditional growth models, where the growth of crystalline materials is promoted by either large surface mobilities that allow relaxation or reversible processes close to thermodynamic equilibrium that tend to self-correct defects randomly occurring during growth. In this work, we present a model that explores the evolution of crystallinity and microstructure under self-limited and kinetically limited conditions characteristic of ALD. This model, based on a generalization of the Potts model, tracks the evolution of local coordination environments as a function of the number of ALD cycles, and differs from traditional approaches in the literature by considering the following assumptions: 1) microstructure relaxation takes place only through local rearrangement of atoms 2) relaxation is kinetically limited so that only transitions that lower the energy of the systems are allowed 3) growth takes place in a two-step process involving adsorption of a precursor and reaction with a co-reactant. When these are separated in time, the process is fully self-limited.

The simulation of the evolution of the medium range order, captured in the average size of locally ordered domains, agrees well with experimental results, both ex-situ and in-situ, obtained for a wide range of oxide materials including ZnO, Al_2O_3, and TiO_2. When the probability of local relaxation is high, the material grows from an amorphous interface into crystalline domains of increasing size, demonstrating that local relaxations are sufficient for crystallinity to emerge. This transition can take place in as few as 10 ALD cycles. On the other hand, if the relaxation is too slow or the growth rate is too large, the film reaches a metastable configuration composed of very small domains. These results open up the question of how to use ALD surface chemistry to promote crystallinity by enhancing such relaxation mechanisms. They can also explain some interesting phenomena observed in the ALD literature, such as explosive crystallization.

This research has been funded through Argonne's LDRD program.

4:45pm **AF2-MoA-14 What Is the Reactivity of a Precursor in ALD? - Simulation of Growth and Etch Rates***, **Simon D. Elliott**, A. Chew, Y. An,* Schrödinger, Inc.

In atomic level processing, the most important requirement is reactivity of a precursor towards deposition or etching of the target material; however, it is difficult to quantify reactivity. One possible experimental measure is the growth per cycle (ALD) or etch per cycle (ALE) under conditions where the chemistry is self-limiting. Experimentally measuring reactivity for all possible precursors and target materials is prohibitively expensive, necessitating alternative ways to explore the large design space.In this talk, we examine how to compute precursor reactivity with atomistic modeling.

We discuss long-standing models [1] that use density functional theory (DFT) to simulate ligand exchange in the precursor molecule itself as a measure of reactivity. Advantages of these models are conceptual simplicity, ease of computation and suitability for processing large sets of molecules [2]. Furthermore, these models can extend from oxides/nitrides to metals, approximate temperature effects and deliver formation energies.

However, more information about the multistep reaction mechanism is required to calculate the growth/etch rate of the process.We examine the thermodynamic basis that dictates how many reaction steps the precursor can undergo at the surface, i.e. the 'extent' of the reaction [3].The reaction extent can be converted into a growth/etch rate per cycle if additional information about ligand size and material density is calculated.We propose a high-throughput approach for computing surface reactions with DFT and hence quantifying the reaction extent and the growth per cycle.We then validate our approach against experimental data for commonly used precursors for the ALD of dielectrics.

Finally, we explore the capabilities of machine learning models (ML) to accurately predict the DFT reactivities using structure-property relationships. Since the computational time for running machine learning models is significantly lower than for DFT, an ML approach can enable thousands of ligands to be screened quickly.

These automated modeling approaches enable the quantification of precursor reactivity in terms of growth/etch rates, which will open new opportunities for *in silico* design and process understanding.

[1] P. Hirva et al., Surf. Sci. 220, 137–51 (1989); S. D. Elliott, Surf. Coat. Technol. 201, 9076–81 (2007); T. P. Holme et al., J. Phys. Chem. A 111, 8147–51 (2007); I. Kazadojev et al., Chem. Vap. Depos. 19, 117–124 (2013).

[2] RASIRC® ALD Oxide/Nitride Wizards™ https://www.rasirc.com/ald-oxide-wizard/ https://www.rasirc.com/ald-nitride-wizard/

[3] S. D. Elliott, Comput. Mater. Sci. 33, 20–5 (2005).

5:00pm **AF2-MoA-15 Random Sequential Adsorption and the Consequences for the Growth-Per-Cycle of Atomic Layer Deposition Processes***, **Ilker Tezsevin**, S. Deijkers, M. Merkx, E. Kessels, A. Mackus,* Eindhoven University of Technology, The Netherlands

Atomic layer deposition (ALD) processes are known to deposit a sub-monolayer of material per cycle due to (*i*) steric hindrance effects and/or (*ii*) limited availability of surface sites.[1, 2] Another contributing factor, which has not been addressed in detail, is that molecules arrive one by one at the surface and adsorb at random surface sites, such that the saturation coverage of precursor ligands substantially deviates from closed packing. In this work, the effect of the random sequential adsorption (RSA) mechanism on the saturation of precursor adsorption and hence on the growth per cycle (GPC) of ALD processes is investigated. By systematically varying the precursor radius and the precursor binding sites in the RSA simulations, the surface densities of the adsorbed precursor molecules are modelled. It is found that the random sequential adsorption of the precursor molecules results in a 25% to 68% lower surface density than the (unrealistic) reference case of closed packing of ligands. Moreover, RSA simulations are also used to model the growth-per-cycle values based on the precursor shape and size. Using this RSA model for metallocene precursor adsorption, GPC values of Co, Os, and Ru ALD processes are calculated as 0.28, 0.38 and 0.37 Å/cycle, in agreement with the experimental findings with accuracy of ± 0.08 Å/cycle. [3-5] Therefore, this work clearly demonstrates the importance of the random sequential adsorption mechanism on the ALD growth.

[1] R.L. Puurunen, Chem. Vap. Depos. 9, 249 (2003).

[2] R.L. Puurunen, Appl. Surf. Sci. 245, 6 (2005).

[3] J. Hämäläinen, T. Sajavaara, E. Puukilainen, M. Ritala, and M. Leskelä, Chem. Mater. 24, 55 (2012).

[4] T. Aaltonen, A. Rahtu, M. Ritala, and M. Leskelä, Electrochem. Solid-State Lett. 6, (2003).

[5] J. Yoon, H.-B.-R. Lee, D. Kim, T. Cheon, S.-H. Kim, and H. Kim, J. Electrochem. Soc. 158, H1179 (2011).

5:15pm **AF2-MoA-16 Machine Learning Based Atomistic Modeling of ALD Processes***, J. Schneider, **Suresh Kondati Natarajan**, V. Arcisauskaite, U. Martinez,* Synopsys Denmark*; A. Blom,* Synopsys Inc.

Atomic layer deposition (ALD) of materials has been a key enabling technology for atomically fine-tuned manufacturing of semiconductor devices in the past two decades. As the future brings continued down-scaling of electronic devices, extreme fabrication limits require optimization of existing and development of new deposition setups for maximum process capability and yield, enabled by physical modeling with topography tools, such as Sentaurus Topography.

In this talk, we will show how machine learning (ML) based atomistic simulations of ALD processes can efficiently provide important parameters for topography simulations, which have been historically extracted from experiments. This multiscale modeling approach can be of particular importance when developing new deposition processes where experimental data are unavailable or expensive and time-consuming to obtain. We will demonstrate how to efficiently obtain ALD parameters such as sticking coefficient and maximum precursor coverage by simulating the $HfCl_4$ precursor pulse in the ALD of HfO_2.

ALD atomistic simulations can be computationally very demanding or even unmanageable if performed using *ab initio* density functional theory (DFT) molecular dynamics (MD), whereas computationally cheaper conventional Force Fields are often not available and require a long and error-prone process to be developed, as in the case for $HfCl_4$-HfO_2. This can be overcome by generating and using ML based interatomic potentials (MLIPs). In this work, we efficiently developed and used moment tensor potentials (MTPs), which provide high accuracy with lower computational cost when compared to other MLIPs [1,2]. MTP was trained using reference data from DFT simulations to reproduce *ab initio* quality potential energy surface of the $HfCl_4$-HfO_2 system. MD simulations with such trained MTPs give us DFT quality MD trajectories at a significantly (100x) reduced computational effort. Automated MTP training and MD simulations were performed using the QuantumATK software [3,4] developed by Synopsys.

MD simulations of $HfCl_4$ molecules impacting the HfO_2 (111) substrate reveal that Hf atoms bind to O atoms on the surface as expected, with binding energies being consistent with DFT results. Finally, we show that the sticking coefficient of the precursor decreases as its surface coverage increases and becomes 0 after attaining a maximum coverage at 0.3 monolayers.

[1] A. V. Shapeev, Mult. Model. Sim., 14, 1153 (2016).
[2] Y. Zuo et al., J. Phys. Chem. A, 124, 731 (2020).
[3] S. Smidstrup et al. , J. Phys.: Conden. Matter 32, 015901 (2019).
[4] QuantumATK version T-2022.03, Synopsys QuantumATK (https://www.synopsys.com/silicon/quantumatk.html)

5:30pm **AF2-MoA-17 Modelling Ruthenium Deposition in Atomic Layer Deposition of Ru-doped TaN***, **Rita Mullins**, M. Nolan,* Tyndall National Institute, Ireland

The downscaling of semiconductor devices has led to critical issues with the widely used Cu interconnect such as diffusion into the substrate dielectric layer. A Ru-doped TaN surface is a promising combined barrier and liner material that has the liner properties of Ru and barrier properties of TaN. Ru has good adhesion strength with Cu, high thermal stability and can promote direct electrodeposition of Cu. A previous first principles density functional theory study found that Ru doping of TaN produces nucleation sites for Cu growth and promotes formation of conducting Cu films.

Atomic layer deposition (ALD) allows the fabrication of ultra-thin films for a wide range of applications and offers excellent conformity and thickness control. ALD is a self-limiting film growing process distinguished by exposure to alternating precursors that are introduced sequentially. Similar to thermal ALD, plasma-enhanced ALD (PE-ALD) provides potential advantages such as improved film purity and the facility for deposition at reduced substrate temperatures. To avoid oxygen contamination in PE-ALD process for metals, non-oxidative reactants are chosen. Furthermore, PE-ALD of Ru using oxygen plasma can lead to lower growth or even the absence of growth due to oxygen plasma competitive etching of Ru. Replacing oxygen plasma with NH_3 plasma leads to the formation of smooth Ru films.

In this contribution, the chemistry of NH_x (x = 1,2) surface terminations of TaN and their reaction with Ru precursors is studied using first principles density functional theory (DFT) using the $RuCp_2$ precursor. NH_x-terminations of TaN for the post plasma surface are studied to test their coverage and stability. The TaN surface consists of 24 N (1 ML) and 24 Ta (1 ML) sites that could be H/H_2 and NH/NH_2 terminated respectively. Stable coverages of 1 ML H and 0.5 ML H/0.5 ML H_2 terminated were found for the 24 N sites. For the 24 Ta sites, stable coverages of 0.04 ML NH_2/0.46 ML NH and 0.67 ML NH_2 terminated were found. The adsorption of precursor $RuCp_2$ to the stable NH_x terminated TaN surfaces is then examined. The Cp ligands are lost through hydrogen transfer from the NH_x-terminated surface to the Cp ligand in this mechanism. No spontaneous hydrogen transfer was observed on any of the NH_x-terminated TaN upon adsorption of $RuCp_2$. Therefore the hydrogen transfer step must overcome activation barriers which are computed using the nudged elastic band method.

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