ALD Fundamentals
Room Grand Ballroom E-G - Session AF1-WeA

Computational ALD I

Moderators: Prof. Dr. Michael Nolan, University College Cork, Atsushi Sakurai, ADEKA CORPORATION

1:30pm **AF1-WeA-1 Effect of Inhibitor Adsorption on the Mechanisms for Selectivity Loss*, Tania Sandoval,*** Technical University Federico Santa Maria, Chile **INVITED**

Area selective atomic layer deposition (AS-ALD) addresses some of the challenges that can occur in nanofabrication of complex multilayers structures, where different surfaces require patterning and alignment at the atomic scale. In this case, AS-ALD allows ALD to occur only on the surface that is desired through different strategies that include the use of inhibitor molecules. For the past few years, the use of small molecule inhibitors (SMIs) has gained attention as they show promise for implementation in high-volume manufacturing. However, selectivity values continue to be low, which could be attributed to the challenges in achieving suitable selective adsorption, and the need for understanding of the mechanisms behind selectivity loss.

In this presentation, theoretical studies on the fundamental understanding of the mechanism for selectivity loss will be discussed. Using a combination of both static and dynamic density functional theory (DFT) calculations, insights into t he displacement of acetylacetone by trimethylaluminum (TMA) and dimethylaluminum isopropoxide (DMAI) were studied. The results revealed the dependence between the inhibitor adsorption configuration, temperature, and selectivity loss. Due to the high reactivity and small size, TMA shows a higher probability to displace adsorbed Hacac than DMAI. We found that the adsorption mechanism for the SMI influence the probability of displacement, as the energetics determines the driving forces of the process. Moreover, by calculating thermochemistry it is possible to determine the extent of how much the selectivity can be improve with temperature within the AS-ALD process.

Overall, these results are keen in helping with proper selection of inhibitor molecules for AS-ALD.

2:00pm **AF1-WeA-3 Electronic Structure of ALD Al_2O_3/TiO_2 Heterointerfaces: A First-principles Study*, Hyobin Eom,*** *C. Ahn, J. Park, B. Shong,* Hongik University, Republic of Korea

Two-dimensional electron gas (2DEG) is a group of free electrons that is localized at thin region at an interface. 2DEG often exhibits high anisotropic carrier mobility along the in-plane horizontal direction, and large charge concentration. Because of such advantages, 2DEG can be applied to semiconductor devices such as high-electron-mobility transistors (HEMTs). Recent studies show that quasi-2DEG can be manifested at Al_2O_3/TiO_2 heterointerfaces formed via atomic layer deposition (ALD) [1]. Such low-lying donor states originate from the oxygen vacancy on the TiO_2 surface chemically formed by trimethylaluminum (TMA) [2]. In this work, various continuous bulk heterojunction structures of Al_2O_3 and TiO_2 with buried oxygen vacancies are studied through density functional theory (DFT) calculations. Analyses of density of states (DOS) along with local charge distribution show that the donor states are localized at the two-dimensional interface between Al_2O_3/TiO_2 where the oxygen vacancies are located. The structural stability of the heterojunction interface structures is confirmed using ab-initio molecular dynamics (AIMD) simulations. Non-equilibrium Green's function (NEGF) simulations prove high anisotropicity in electron transport of these structures. Current work provides atomistic understanding on electronic properties of ALD-formed emergent interfacial structures.

References [1] Chem. Mater. 2020, 32(18), 7662; [2] Mater. Today Adv. 2021, 12, 100195.

2:15pm **AF1-WeA-4 Reaction Mechanism of Bifunctional Organic Reactants and Diethylzinc for Atomic and Molecular Layer Deposition*, Miso Kim,*** *H. Oh, B. Shong,* Hongik University, Republic of Korea

In molecular layer deposition (MLD) processes, bifunctional organic reactants often show different growth behaviors depending on the chain length of their molecular backbone. For example, MLD using 1,2-ethanediol (1,2-ED) and diethylzinc (DEZ) results in organic-inorganic hybrid thin film of "zincone" containing stoichiometric amount of carbon.[1] In contrast, in a process using 1,5-pentanediol (1,5-PD) and DEZ, atomic layer deposition (ALD) of ZnO thin film without carbon impurities is reported.[2] Also, MLD thin films of Mo-thiolates shows decreased C content when dithiol with longer chain is used.[3] However, the molecular mechanism for the governing factor for removal of the carbonaceous moieties from the MLD thin films is yet unclear. In this study, the chemistry of DEZ and bifunctional organic reactants (linear $HX\text{-}C_nH_{2n}\text{-}XH$, X=O or S, n=2-6) according to the length of the backbone of bifunctional reactants was investigated through density functional theory (DFT) calculations. Several intramolecular reaction pathways in which $Zn\text{-}C_nH_{2n}\text{-}XH$ on the surface is converted to Zn-OH were investigated. By comparing the reactivity according to the backbone length of the bifunctional reactant structures, it was confirmed that the activation energy for forming Zn-XH decreases as the number of carbon increases, possibly resulting in inorganic ALD thin films without C.

References

[1] Chem. Mater. 2009, 21 (5), 820; [2] Chem. Mater. 2017, 29 (8), 3371; [3] J. Vac. Sci. Technol. A 2022, 40 (1), 012402.

2:30pm **AF1-WeA-5 Simulated Conformality of ALD Growth Inside Lateral HAR Channels: Comparison between a Diffusion-Reaction Model and a Ballistic Transport-Reaction Model***, J. Järvilehto, J. Velasco, J. Yim, C. Gonsalves,* ***Riikka Puurunen,*** Aalto University, Finland

Atomic layer deposition (ALD) is known for its ability to produce films of controllable thickness, even in narrow, high-aspect-ratio (HAR) structures [1]. These films can be highly conformal, meaning that the structure is covered by a film of uniform thickness [1,2]. However, when the structure's aspect ratio is increased sufficiently, deposition becomes limited by the diffusion of the reactants into the deep end of the structure, potentially resulting in the formation of an adsorption front, followed by a region of lower coverage [3]. Theoretical models have been developed to predict film conformality in HAR structures, as reviewed in Ref. 2.

This work presents a comparison of a diffusion-reaction model (DRM) developed by Ylilammi et al. [4,5] (Model A) and a ballistic transport-reaction model (BTRM) by Yanguas-Gil and Elam [6,7] (Model B). For the comparison, saturation profiles were generated using both models with similar simulation parameters (Knudsen number Kn >>1).

Qualitatively, both models produced similar trends in terms of half-coverage penetration depth and slope at half-coverage penetration depth. The saturation profiles were similar in shape, except for the film growth observed at the channel end in Model B. Quantitative examination yielded consistently higher half-coverage penetration depths in Model B. Model A produced steeper slopes at half-coverage penetration depth. In Model B, the discretization resolution was found to affect the penetration depth.

While the models gave qualitatively similar results, quantitatively extracted parameters differed. This finding is consistent with a previous comparison of a DRM and BTRM in the context of low pressure chemical vapor deposition [8]. The quantitative differences are relevant, for example, when the models are fitted to experimental data for the extraction of kinetic parameters, such as the sticking coefficient.

References

[1] J.R. van Ommen, A. Goulas, and R.L. Puurunen, "Atomic layer deposition," in Kirk-Othmer Encyclopedia of Chemical Technology, John Wiley & Sons, Inc., 42 p. (2021).
[2] V. Cremers et al., Appl. Phys. Rev. 6 (2019) 021302.
[3] J. Yim and O.M.E. Ylivaara et al., Phys. Chem. Chem. Phys. 22 (2020) 23107-23120.
[4] M. Ylilammi et al., J. Appl. Phys. 123 (2018) 205301.
[5] J. Yim and E. Verkama et al., Phys. Chem. Chem. Phys. 24 (2022) 8645.
[6] A. Yanguas-Gil and J.W. Elam, Theor. Chem. Acc. 133 (2014) 1465.
[7] A. Yanguas-Gil and J.W. Elam, (2013) https://github.com/aldsim/machball, accessed Feb 13 2023.
[8] M.K. Jain et al., J. Electrochem. Soc. 140 (1993) 242.

2:45pm **AF1-WeA-6 Simulated Conformality of ALD in Lateral High Aspect Ratio Channels: Impact of Knudsen Number on the Saturation Profile*, Christine Gonsalves,*** *J. A. Velasco, J. Järvilehto, J. Yim, V. Vuorinen, R. L. Puurunen,* Aalto University, Finland

Due to its unparalleled conformality, atomic layer deposition (ALD) is often the method of choice for coating nanostructures having complex geometries with atomic level precision [1]. However, conformality in high-aspect-ratio (HAR) surface features evolves with time and depends on process parameters and chemistry [2,3]. Different models have been

developed to simulate ALD growth in HAR structures [2,3]: diffusion–reaction models, Monte Carlo models and ballistic transport–reaction models.

Studies of ALD growth in HAR (AR ≥ 100) features typically assume free molecular flow conditions (Knudsen number $Kn >> 1$), with the molecule's mean free path much larger than the feature size. However, depending on the limiting feature size and pressure, the free molecular flow assumption may not be fully valid in real ALD processes.

In this work, we mapped the evolution of conformality in lateral high-aspect-ratio (LHAR) channels in terms of the Knudsen number from free molecular flow governed by Knudsen diffusion ($Kn>>1$) through the transition regime ($Kn \sim 1$) to continuum flow conditions governed by molecular diffusion ($Kn<<1$). The mapping was done by varying the LHAR channel height and reactant partial pressure; Knudsen number was varied by 13 orders of magnitude. Thiele modulus was kept above one, so that diffusion-limited conditions prevailed and the simplified model by Ylilammi et al. [4] re-implemented earlier [3], could be used for the simulations. Reactant exposure was kept constant.

When $Kn>>1$, regardless of the partial pressure of the reactant and the channel height, the same characteristic saturation profile was obtained. When $Kn \sim 1$ and $Kn<<1$, the penetration depth decreased and the steepness of the adsorption front increased with decreasing Knudsen number.

The slope method by Arts et al. [5] was used to back-extract the sticking coefficient from simulated saturation profile, up to demonstrating how the slope method breaks when conditions deviate from free molecular flow. Using the slope method for conditions where the Knudsen diffusion assumption is not valid, would lead to an incorrect (too high) interpretation of the sticking coefficient (even unphysical values above one).

References

[1] J.R. van Ommen et al., "Atomic layer deposition," in Kirk Othmer Encyclopedia of Chemical Technology, John Wiley & Sons, Inc. (2021).

[2] V. Cremers et al., Appl. Phys. Rev. 6 (2019) 021302.

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[5] K. Arts et al., J. Vac. Sci. Technol. A. 37 (2019) 030908.

3:00pm **AF1-WeA-7 Atomistic Modeling of Thin-Film Deposition with Carrier Gases**, *S. Natarajan, P. Khomyakov, J. Wellendorff,* Synopsys Denmark*;* ***Baiyu Zhang****, A. Blom,* Synopsys, Inc.

Advances in thin film deposition techniques are at the core of atomically fine-tuned manufacturing of next-generation semi-conductor devices. Extreme fabrication limits require optimization of existing and development of new thin film deposition setups for maximum process capability and yield. In silico modeling approaches can be of particular importance when developing new deposition processes where experimental data are unavailable or expensive and time-consuming to obtain. We have previously shown how machine learning based atomic-scale modeling of ALD processes, e.g., ALD of HfO_2, [1] with Synopsys QuantumATK software [2,3] was used to simulate energetics, dynamics, and mechanisms of precursor molecule interaction with a substrate material, and provide important parameters, such as sticking probabilities and growth rates, for further physical modeling with topography tools, such as Sentaurus Topography.

In this talk, we will present an enhancement of this deposition simulation workflow by including the effect of carrier gases. The impact of carrier gases becomes critical at higher pressures, as carrier gas molecules collide with precursor molecules and alter growth rates. We will demonstrate the enhanced complete workflow in QuantumATK, including density functional theory-based thermochemistry, reaction kinetics and classical molecular dynamics, and show results for Si deposition using disilane precursor and hydrogen carrier gas at varying pressures.

In the first step, we identify the most probable reactive gas phase species and evaluate their equilibrium concentrations in gas mixtures, which are present in the reactor at the process conditions. This is achieved by comparing Gibbs free energy profiles of many possible gas phase decomposition reactions. Since the above results do not include kinetic information, they are usually valid only when the activation barriers of the considered reactions are fully breached by thermal energy. Thus, in the second step, we compute reaction kinetics which involves obtaining rates and branching ratios of the most probable reactions from step 1 to identify the flux ratios of the reactive species. These flux ratios inform us of the fractions of the dissociated species in the reactor along with the intact precursor molecules at the process conditions. In the final step, we perform molecular dynamics simulations with the flux ratio from kinetic studies to compute the sticking probabilities and growth rates.

[1] J. Schneider et al., ALD 2022.
[2] S. Smidstrup et al. , J. Phys.: Conden. Matter 32, 015901 (2019).
[3] QuantumATK version V-2023.09, Synopsys QuantumATK.
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3:15pm **AF1-WeA-8 Chemistry of Plasma-Enhanced and Thermal Atomic Layer Deposition of Metal and Intermetallic Thin Films: The Role of Substrates and Reducing Agent***,* ***Ji Liu****, M. Nolan,* Tyndall National Institute, University College Cork, Ireland

Atomic layer deposition (ALD) is widely used in microelectronics and catalysis to deposit metal thin films. The key advantages of ALD are the conformality and precise thickness control at the atomic scale. Cobalt (Co) is an interesting material in the semiconductor industry due to its attractive electrical and physical properties. The replacement of Cu with Co as contacts or interconnects in semiconductor devices serves as an illustrative example and is an ongoing process driven by large device manufacturers.

In this presentation, I will present our recent work on the plasma enhanced (PE) and thermal ALD growth of Co from first principles calculations. For PE-ALD of Co using $CoCp_2$ and N-plasma, we first addressed the surface reaction mechanism in the metal precursor pulse and plasma half-cycle on NH_x-terminated Co surfaces, which corresponds to the steady growth for the PE-ALD. The reactions at the initial stages on a series of Si surface terminations are investigated to gain detailed atomic insights on the effect of different substrates on the elimination of Cp ligands.

For thermal ALD of Co, our collaborators have shown that Co thin films deposited with ALD are metallic and Zn-free. We modelled the reaction mechanism of $CoCl_2$(TMEDA) and a reducing agent, $Zn(DMP)_2$. Our DFT calculations indicate that the reactions proceed via initial ligand exchange of DMP and Cl on Co(111) surface with $CoCl_2$ termination and Zn is removed via ZnCl(DMP) formation and desorption, resulting $Co(DMP)_2$ termination on the surface. The two DMP ligands are removed via C-C bond formation in a straightforward way.

Further, we presented our recent collaborative work of a new type of ALD process for intermetallic FeZn thin films, where diethyl zinc (DEZ) serves as a coreactant. The $FeCl_3$ + DEZ process yields in situ crystalline Fe_4Zn_9 thin films. DFT calculations indicate that the favorable pathway of eliminating the Cl group and the Et ligand is via butane and subsequent EtCl formation and desorption.

Our DFT studies show that substrate terminations and reducing agents have significant impact on ALD deposited metallic thin films.

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