ALD Fundamentals
Room Van Eyck - Session AF-TuM2

Simulation, Modeling, and Theory of ALD II

Moderators: Simon Elliot, Schrödinger, Inc., Michael Nolan, University College Cork

10:45am AF-TuM2-1 Theoretical Understanding on the Chemical Principles of Atomic Layer Deposition, *Bonggeun Shong,* Hongik University, Korea (Republic of)   **INVITED**
Atomic layer deposition (ALD) is a vapor phase thin film deposition technique based on sequential, self-limiting surface reactions. Through ALD, exceptional conformality on high-aspect ratio structures, thickness control at the Angstrom level, and tunable film composition are achievable. Furthermore, area-selective ALD (AS-ALD) has recently emerged as a possible alternative bottom-up approach for nano-patterning. With these advantages, ALD is gaining interest as a powerful tool for many industrial and research applications, especially in microelectronic fabrication. Since the entire ALD process should be based only on the surfaces of the substrates, it is important to understand the surface chemical reaction mechanisms during ALD, in order to improve the process conditions and material quality of ALD. With development of modern simulation tools, utilization of quantum mechanical calculation is becoming increasingly useful toward deeper understanding and design of such chemical reactions. In this talk, fundamental principles governing the surface chemistry of ALD processes will be discussed. Especially, the talk will focus on the recent examples that theoretical analysis of various surface reactions together with experimental approaches could be synergistically enhance the research and development of ALD.

11:15am AF-TuM2-3 A Study of Area-Selective TiO_2 Deposition Using First Principles Based Thermodynamic Simulations, *Yukio Kaneda,* Sony Semiconductor Solutions Corporation, Belgium*; E. Marques,* Katholieke Universiteit Leuven, Belgium*; S. Armini, A. Delabie, M. Setten, G. Pourtois,* IMEC, Belgium
Recent transistor developments consider not only dimensional scaling but also design device structures in the vertical direction to reduce the active footprint. Consequently, the structures and process steps are becoming increasingly complex. In that context, area-selective deposition (ASD), which enables film formation from the bottom-up in a specific area, has been attracting attention. In this field, a lot of work aims to improve selectivity and to increase the material variations that make ASD possible to suit the different target applications [1]. Understanding the atomic-scale physics and chemistry during ASD processes is essential for interpreting the results, as well as for enabling further developments and new applications.

Here, we propose a simulation technique to analyze chemical reactivities based on first-principles calculations and statistical thermodynamics as a method to gain insight into atomic-scale physics. In this framework, we will show how we can investigate the effects of chemical reactivity, and hence selectivity, on many chemical species and process conditions.

In this presentation, we report the results of the analysis performed on the ASD of TiO_2 on substrates patterned with end groups including OH and alkyl-silyl groups. First, we evaluated our method by comparing with experimental results of TiO_2 ALD using $TiCl_4$ and $Ti(OMe)_4$ as precursors, whose selectivity was already confirmed [2]. The theoretical results demonstrate better selectivity with $TiCl_4$ as precursor, consistent with experiment. The impact of the process temperature and purge times during ALD was also qualitatively consistent with the experimental results. Moreover, the theoretical results also indicated that the mechanism of selectivity degradation may be due to the desorption of inhibitors during ALD at the higher process temperature. Therefore, we used this technique to investigate whether the precursors and coreagents referred in [3] and inhibitors with altered ligand size, which are the end groups of the non-growing surface, are effective in improving the selectivity. In conclusion, we confirmed that the best performance had been obtained by combining $TiCl_4$ as a precursor and trimethylsilyl termination as an inhibitor.

[1] Gregory N. Parsons and Robert D. Clark, Chem. Mater. 2020, 32, 12, 4920–4953

[2] Job Soethoudt, et al., The Journal of Physical Chemistry C 2020 124 (13), 7163-7173

[3] Janne-Petteri Niemelä et al., Semicond. Sci. Technol. 2017 9 (32), 093005

11:30am AF-TuM2-4 Chemistry of Plasma Enhanced Atomic Layer Deposition of Co using CoCp2 and Nitrogen/Hydrogen Plasma, *Ji Liu, M. Nolan,* Tyndall National Institute, University College Cork, Ireland
The copper interconnect issue that has arisen with the downscaling of semiconductor devices is a major challenge in the nanoelectronics industry. One solution is to find alternate materials that do not suffer these issues to replace Cu. Transition metal cobalt has attracted much attention due to low resistivity, particularly at small dimensions, and good physical and chemical stability. The deposition of metals onto the typical high aspect ratio structures in nanoelectronics devices is difficult and the atomic layer deposition (ALD) is applied due to the resulting conformality and precise thickness control at the atomic scale. Plasma-enhanced ALD (PE-ALD) is used for low-temperature thin film growth by alternating exposures of metal precursors and plasma reactants. The PE-ALD of Co has been experimentally investigated using Cp-based precursors. However, the reaction mechanism is not clear and theoretical studies on the reaction mechanism is entirely lacking.

In this presentation, we study the PE-ALD growth of Co by first principle calculations. The following central questions will be addressed: (Q1) what is the coverage and stability of the NH_x-terminated Co surfaces? The (001) surface, with a hexagonal structure, is the most stable and the (100) surface with a zigzag structure is less stable but has high reactivity. These two surfaces allow the study of the influence of the surface facet. The surface NH_x saturation coverage is studied by considering co-adsorption of NH and NH_2 terminations on both surfaces. (Q2) What is the reaction mechanism for the elimination of Cp ligands in $CoCp_2$ on these NH_x-terminated Co surfaces? A plausible reaction pathway includes: precursor adsorption, hydrogen transfer, CpH formation and desorption. The barrier for hydrogen transfer is calculated and the results show that (100) surface has higher activity than (001) surface. The final terminations after metal precursor pulse are determined. (Q3) What is the role of plasma radicals in the plasma cycle? Here, we focus on two parts: (1) how the remaining Cp ligands and surface NH_x terminations are eliminated with plasma generated radicals N_xH_y; and (2) how the metal surface is recovered with NH_x terminations at the post-plasm stage. Our DFT results highlight the importance of NH_x species to deposit high-quality and low-impurity Co thin films.

11:45am AF-TuM2-5 Adsorption Mechanics of Trimethyl Metal Precursors on AlN, GaN and InN, *Karl Rönnby, H. Pedersen, L. Ojamäe,* Linköping University, Sweden
Aluminum nitride (AlN), gallium nitride (GaN) and indium nitride (InN), collectively known as the group 13 nitrides (13Ns), are important materials in many semiconducting applications, for example in optoelectronics as the range of band gaps, 6.3 eV for AlN to 0.7 eV for InN, ranges from UV to IR.

The standard ALD approach for growth of 13Ns is to use a trimethyl metal (TMMe, Me=Al, Ga or In) precursor together with ammonia as co-reactant. Although similar to the typical ALD process of Al_2O_3 from TMA and water, the growth of the 13Ns is much more challenging. This can be attributed to a much lower reactivity of nitrogen compared to oxygen. The badly tuned chemistry is evident by the non-stoichiometric ratios between the precursors in continuous CVD and the need to utilize plasma-enhanced processes, especially for InN, to achieve good growth rates. Theoretical investigations into the growth mechanism would yield a possibility to understand the limitations and apply targeted improvements to the process.

In this work, we modeled the adsorption mechanisms of the TMMe precursor by density functional theory (DFT) on a periodic surface slab. TMMe molecules were placed in proximity to possible adsorption sites and their structures were optimized. Further surface decomposition mechanisms were then explored. Transition states along the reaction paths were investigated by the nudge elastic band method (NEB). Investigations of the lateral interactions between adsorbed precursor molecules were performed by introducing multiple molecules into the simulation cell. A kinetic model was then derived, showing how the surface evolve over time during the metal pulse.

When introduced to a NH_2-terminated surface, the first TMMe precursor adsorbs by forming a Lewis adduct to a surface NH_2 group by donating its empty p-orbital to the electron pair on the surface nitrogen. From this position, the adsorbed precursor could decompose, reaching an end state

with all methyl ligands removed. A second TMMe shows preferred adsorption close to an already adsorbed metal atom, indicating a nucleation effect. As not enough hydrogen atoms are cleared by the absorbing molecules, the surface will reach a saturation at a much lower coverage than 1 ML.

We also investigate how the different rates of adsorption, diffusion, and decomposition affect the separation of initial nucleation points and the rate of cluster growth during the ALD half-cycle.

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