ALD Fundamentals
Room Halla Hall - Session AF1-TuM
Mechanism and Theory I

Moderators: Christophe Vallée, University of Albany, **Charles H. Winter**, Wayne State University

8:00am **AF1-TuM-1 The Mechanism of Thermal ALD of Silicon Carbonitride from Chloroalkylsilanes and Ammonia – Theory Meets Experiment***, **Simon Elliott**,* Schrödinger, Ireland*; Jiyeon Kim, Paul Lemaire, Dennis Hausmann,* Lam Research

Carbon-doping of silicon nitride or silicon oxide results in a lowering of the dielectric constant and etch rate. The C-doped derivatives are therefore being used to replace the parent films in many applications in FEOL semiconductor manufacturing, such as for spacers and gap fill. Traditionally these C-doped films are deposited by CVD methods, but recently ALD methods have been formulated using silicon precursors with Si-CHx bonds. Maintaining the Si-CHx bond has been challenging due to its propensity to cleave under plasma conditions or at high temperatures. For these reasons, precursors that can be used in a low temperature thermal ALD process are highly desired.In this work we investigate whether ammonia is viable as a thermal ALD co-reagent for this application and what mixture of chloro and alkyl ligands are most favorable in the silicon precursor.

We use density functional theory (DFT) to compute the atomic-scale structure of surface intermediates and the mechanism of potential ALD reactions and complement this with detailed characterization during substrate exposure experiments.

Looking first at the co-reagent, we investigate the kinetics of proton transfer from ammonia to a model silyl fragment on an aminated surface. Four proton transfer pathways are obtained for HCl elimination, all with high barriers (>1.2 eV) that are indicative of low Bronsted acidity and suggest that side-reactions will compete with the ALD process. Three pathways are obtained for CH4 elimination with even higher barriers (>2.5 eV). Therefore, up to moderate temperatures, terminal-CH3 is likely to survive ammonia treatment and be incorporated into the film, and this could be a route to C-doping. Residual gas analysis (RGA) and quartz crystal microbalance is used to monitor whether HCl or CH4 is in fact evolved during each half reaction.

The second part of the study looks at the effect of various combinations of chloro and methyl ligands in candidate Si precursors, both monomers (SiCl4, SiHCl3, SiCl3Me, SiH2Cl2, SiHCl2Me, SiCl2Me2) and dimers (Si2Cl6, Si2Cl4Me2). Structural models are generated efficiently of the >100 surface intermediates that can potentially occur through physisorption, chemisorption via ligand elimination and etching by exchange with surface amines. For each precursor, DFT-based thermodynamics reveal that the most favorable intermediate is surf-SiCl3 up to about 250C, surf-Cl2 up to 450C and surf-Cl at higher temperatures, with associated predictions of ALD growth rate. Film composition and growth rate is then validated experimentally by ellipsometry (SE) and infrared red spectroscopy (ATR-FTIR), ex-situ but with an inert atmosphere glove box.

8:15am **AF1-TuM-2 Mechanistic Studies on Area Selective ALD of Iridium***, **Heta-Elisa Nieminen**, Matti Putkonen, Mikko Ritala,* University of Helsinki, Finland

The importance of self-aligned film deposition processes is obvious when considering the complexity of the devices being currently manufactured. Every process that can directly deposit only on selected areas may decrease the number of processing steps needed. When the growth is dictated by surface chemistry also issues related to pattern misalignment can be avoided. Finding new self-aligned thin film deposition processes becomes yet more important as the device dimensions are shrinking. Understanding the mechanism behind the selectivity helps in finding new process and surface combinations. In this work, the reason behind a selective growth of iridium on a set of substrates that are chemically alike is studied. The surface reactions and the selectivity mechanism are studied with ALD-UHV cluster tool by using *in vacuo* XPS, LEIS and TPD together with *in situ* QCM.

Excellent area selectivity in ALD of metallic iridium on a wide selection of substrates was initially found by Zhang et al. (*Chem. Mater.* 2022, 34, 8379-8388). The depositions were done with iridium(III) acetylacetonate, $Ir(acac)_3$, and O_2 as precursors. The growth is believed to start with a ligand exchange reaction between surface -OH group and the $Ir(acac)_3$ precursor. Initial hypothesis for the selective growth is that the weakly acidic byproduct formed in the ligand exchange reaction, Hacac, adsorbs preferably on more basic surfaces passivating them. In the current work, two surfaces on which iridium was deposited successfully, native SiO_2 terminated Si and *in situ* deposited Al_2O_3, are compared to two surfaces on which the deposition did not succeed, Al_2O_3 and HfO_2. The latter mentioned oxides as well as the native SiO_2 terminated Si were exposed to air and airborne hydrocarbons prior to the iridium deposition.

The passivation of the non-growth surfaces was clearly confirmed with the analysis methods used and details of the nature of the passivating compounds were resolved. Also, the possible role of the adventitious hydrocarbons in the beginning of the film growth was studied. The increased knowledge about the surface reactions can guide the thinking when selectivity is aimed on new process and surface combinations.

8:30am **AF1-TuM-3 ALD Outstanding Presentation Award Finalist: Like Boots or Hearts: The Kinetics of Precursor Decomposition***, **Sean Barry**,* Carleton University, Canada

One of the main differences between Chemical Vapor Deposition (CVD) and atomic layer deposition (ALD) is gas-phase reactivity: we anticipate precursors to react together or independently in the gas phase in CVD but generally expect ALD precursors to arrive at the substrate intact. However, thermal activation of a precursor in the gas phase can benefit ALD saturation by producing a more active chemical species.

Our group often uses an *in-situ* solution-phase method to discover thermal behaviour and track the kinetics of decomposition. Samples are flame-sealed in a glass tube with an appropriate solvent and monitored by nuclear magnetic resonance (NMR) spectroscopy. This characterization method is common in synthetic chemistry and can be used to analyse a variety of nuclei independently, and this technique can commonly and easily assess protons. Using this technique in conjunction with thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), we can build structure-function relationships to help design better precursors.

The framework $Mo(VI)(=N^tBu)_2Cl_2.(L\text{-}L)$ (where L-L is a chelating ligand) allows us to easily investigate the role of chelate ligands in precursor design due to the thermal stability of the imide/chloride core. This talk will center on measuring the thermodynamics of precursor thermolysis through Eyring analysis and detail the implications of β-H versus γ-H elimination, as well as differentiating *inter*-molecular vs. *intra*-molecular reactivity. The presentation will show detailed reaction coordinates and different mechanistic thermolysis pathways for a growing family of Mo(VI) compounds.

8:45am **AF1-TuM-4 Reaction Mechanism of Atomic Layer Deposition of Zirconium Oxide Using Tris(dimethylamino)cyclopentadienyl Zirconium***, **Yong Richard Sriwijaya**, Hye-Lee Kim, Okhyeon Kim, Khabib Khumaini,* Sejong University, Republic of Korea*; Romel Hidayat,* PT PLN, Indonesia*; Won-Jun Lee,* Sejong University, Republic of Korea

A promising strategy for the development of advanced atomic layer deposition (ALD) precursors is the design of heteroleptic metal-organic compounds in which multiple ligand types are attached to a metal center. These heteroleptic precursors offer advantages over homoleptic counterparts, such as improved thermal stability while maintaining high reactivity. A notable example is tris(dimethylamino)cyclopentadienyl zirconium ($CpZr(NMe_2)_3$), which has successfully replaced the homoleptic precursor tetrakis(ethylmethylamino)zirconium ($Zr(NEtMe)_4$) in the fabrication of zirconium oxide (ZrO_2) films for dynamic random-access memory (DRAM) devices. Compared to Zr(NEtMe)4, CpZr(NMe2)3 exhibits better thermal stability, enabling better conformality at high process temperatures of 300°C with a growth per cycle of ~0.9 Å [1]. However, the competition between the NMe_2 and Cp ligands during surface reactions complicates the identification of the final chemisorbed species, which is important for designing the precursor for high-temperature ALD. In this study, we investigated the reaction mechanism of ZrO_2 ALD using a combined approach of *ab initio* calculations and *in situ* characterization. Density functional theory (DFT) calculations were performed to model the stepwise surface reactions of $CpZr(NMe_2)_3$ on a ZrO_2 surface, while *in situ* quartz crystal microbalance (QCM) analysis was used to study the ALD process with alternating precursor and ozone (O_3) exposures. DFT results indicate that the first two NMe_2 ligands are readily released during chemisorption of the Zr precursor with low activation energies of 0.22 eV and 0.16 eV. In contrast, the release of the Cp ligand or the third NMe_2 ligand is thermodynamically unfavorable due to its endothermic nature and high activation energy. As a result, the final chemisorbed surface species is predicted to be $O_2ZrCp(NMe_2)^*$. QCM analysis confirms the release of two

NMe_2 ligands during the first ALD half-cycle, which agrees with the DFT results. This study demonstrates the effectiveness of integrating DFT calculations with QCM analysis to gain mechanistic insight into ALD reactions, especially when heteroleptic precursors are involved.

References [1] J. Niinisto et al., J. Mater. Chem. 18, 5243 (2008).

9:00am **AF1-TuM-5 A Study on the Correlation of Surface Chemistry to Electrical Properties of Ultra-thin Oxide Semiconductors by Atomic Layer Deposition: A Case Study of Indium Oxides Thin Films*, Joohyeon Lee,*** Ajou University, Republic of Korea*; Dohee Kim, Ja Yong Kim, Jong Young Lee, Seung Wook Ryu,* SK hynix, Republic of Korea*; Il Kwon Oh,* Ajou University, Republic of Korea

Atomic layer deposition (ALD)-grown ultra-thin In_2O_3 offers promising solutions with amorphous films at sub-3 nm thicknesses, allowing effective tuning of mobility and V_{th} based on thickness [1].

Materials and electrical properties of ultra-thin ALD films are significantly dependent on surface chemistry. For example, $HfCl_4$, with simple chlorine ligands, achieves a higher growth per cycle (~1.3 Å/cycle), lower interface trap density ($1.86×10^{11}$ eV^{-1} cm^{-2}), and reduced leakage current density ($3.94 × 10^{-7}$ A/cm^2 at $V_{FB} = -1V$). This is due to efficient oxidation and minimal steric hindrance, resulting in stoichiometric films with fewer oxygen vacancies. In contrast, $Hf(N(CH_3)_2)_4$, with bulky dimethylamino ligands, exhibits slightly lower GPC (~1.2 Å/cycle) and higher oxygen vacancy concentrations, leading to increased D_{it} ($8.96 × 10^{11}$ eV^{-1} cm^{-2}) and leakage current ($2.25 × 10^{-6}$ A/cm^2). Steric hindrance limits oxidant access, resulting in sub-stoichiometric HfO_{2-x} phases [2]. This highlights the critical role of ligand structure in determining film stoichiometry, defect density, and electrical performance, emphasizing the need for a comparative study for ultra-thin film formation using ALD.

In this study, we investigate the reaction mechanisms and surface chemistry of two indium precursors, [3-(dimethylamino)propyl]dimethyl indium (DADI) and trimethyl indium (TMI), for ALD-grown ultra-thin In_2O_3 films using O_3 as the reactant. DADI, containing dimethylamino and methyl groups, introduces greater steric hindrance compared to TMI, which has only methyl groups. This difference affects adsorption density, oxidizer accessibility, and oxygen deficiency during film growth, leading to variations in film composition, density, and electrical properties. To evaluate these differences, quadrupole mass spectrometry (QMS) will analyze ALD byproducts, X-ray photoelectron spectroscopy (XPS) will assess impurity levels and oxygen vacancies, and transmission electron microscopy (TEM) will confirm film uniformity. Physical properties such as morphology and density will be analyzed using atomic force microscopy (AFM) and X-ray reflectometry (XRR). Finally, a bottom-gate TFT will be fabricated to correlate these properties with electrical performance, providing a comparative evaluation of the precursors for BEOL integration into monolithic 3D devices.

References [1] Si et al., Nano Lett., 21, 1, 500–506 (2021) [2] Oh et al, J. Mater. Chem. C 6, 7367 (2018).

9:15am **AF1-TuM-6 Catalytic Role of Silane(SiH4) in Enhancing Titanium Nitride(TiN) Atomic Layer Deposition(ALD)*, Hu Li,*** Tokyo Electron America Inc.*; Taichi Monden, Masaaki Matsukuma,* Tokyo Electron Technology Solutions Ltd., Japan*; Jianping Zhao,* Tokyo Electron America Inc.*; Yoshitada Morikawa,* Osaka University, Japan*; Peter Ventzek,* Tokyo Electron America Inc.

Titanium nitride (TiN) films are crucial for microelectronics applications due to their exceptional electrical conductivity, thermal stability, and barrier properties. Atomic layer deposition (ALD) has emerged as a preferred method for TiN fabrication, offering precise thickness control and superior conformality, particularly important for nanoscale structures. In this study, first-principles calculations based on density functional theory (DFT) were employed to investigate the catalytic role of silane (SiH_4) in the $TiCl_4/SiH_4/NH_3$ ALD process, with a focus on the removal of chlorine (Cl) atoms from the substrate surface. The results demonstrate that SiH_4 effectively promotes Cl desorption by reducing surface-bound Ti–Cl species, thereby enhancing surface reactivity and increasing the availability of active sites for improved precursor coverage. Detailed analyses of reaction pathways, activation energy barriers, and adsorption energies reveal that SiH_4 significantly lowers the energetic cost of Cl elimination, leading to a more efficient ALD process with higher growth-per-cycle (GPC) rates. These findings provide valuable insights into the catalytic mechanisms of SiH_4 and underscore its critical role in producing high-quality TiN films with reduced impurity levels. This work offers practical guidance for optimizing precursor combinations and process parameters in ALD technology.

9:30am **AF1-TuM-7 Correlation of Hydroxyl Group and Growth Characteristics in Atomic Layer Deposition of Ternary Oxide Depending on Growth Temperature*, Sanghun Lee,*** Yonsei University, Republic of Korea*; Il-Kwon Oh,* Ajou University, Republic of Korea*; Hyungjun Kim,* Yonsei University, Republic of Korea

Atomic layer deposition (ALD) of doped or alloy materials has been intensively investigated with recent advances in nanotechnology applications. However, ALD of multicomponent materials is challenging because the growth characteristics often deviate from what is expected due to the difference in surface characteristics of heterogeneous and single materials, resulting in undesired thickness or properties. For metal oxides, the growth characteristics highly rely on the surface hydroxyl groups, which play a role as the reactive site. Thus, studying the reaction mechanism of a precursor on hydroxyl-terminated heterogeneous surfaces is important for understanding the nonideal growth of ternary oxide. This work provides understanding of how growth characteristics of ALD $TiSiO_x$ are deviated according to process temperature. Here, we investigated the correlation between hydroxyl and the growth of ALD $TiSiO_x$ depending on temperature, analyzing infrared spectra, and chemical compositions. The results show that large amounts of hydroxyl are detected in $TiSiO_x$ deposited at 100 °C, where the adsorption of H_2O on Ti–O–Si bonds is favorable. It leads to higher growth per cycle (GPC) than the estimated value. In contrast, hydroxyl disappears at 200 °C due to dehydroxylation, resulting in lower GPC. Differences in hydroxyl also influence the film density as revealed in x-ray reflection spectra, which is related to the film qualities (e.g., elastic modulus and dry etch rates). This work provides insight into how to control hydroxyl in the ALD of ternary oxides, which is susceptible to hydroxyl incorporation, leading to undesired growth characteristics.

9:45am **AF1-TuM-8 Atomistic Modeling of Oxygen Recombination Reactions in the ALD of SiO_2 and Al_2O_3***, Suresh Kondati Natarajan,* Synopsys Inc., Denmark*; Rafshan Ul Atik,* Synopsys India Pvt. Ltd., India*; **Yong-Ju Kang**,* Synopsys Korea Inc., Republic of Korea*; Jess Wellendorff, Søren Smidstrup,* Synopsys Denmark ApS, Denmark

Atomic layer deposition (ALD) has been a key enabling technology for atomically fine-tuned manufacturing of cutting-edge semiconductor devices. Depending on the underlying chemical mechanism of the ALD process, growth rates can vary significantly from process to process. In semiconductor gate stacks, Al_2O_3 is considered as interface dipole inducer and SiO_2 has been used as gate oxide. It has been shown that plasma enhanced ALD (PEALD) growth rate of SiO_2 is orders of magnitude larger than that of Al_2O_3 [1]. In these processes, O_2 plasma is used as the source of oxygen. O_2 plasma includes reactive species such as O radicals which can, in principle, recombine with the previously deposited O species on the growth surface and form O_2 gas. It has been proposed that the growth rate difference between SiO_2 and Al_2O_3 can be attributed to the differences in the oxygen recombination rates at the respective growth surfaces [1].

In this talk, we present evidence from atomic scale modeling in terms of thermochemical, kinetic and dynamic analysis of reactions taking place at the SiO_2 and Al_2O_3 growth surfaces using industry-grade simulation frameworks within the QuantumATK software [2,3] developed by Synopsys. Dynamic simulations with Synopsys QuantumATK have been previously utilized to get insights and determine mechanisms of ALD of HfO_2 [4] and ALE of 2D TMD materials [5].

In this study, we employed Density Functional Theory to calculate the thermochemical and kinetic properties of oxygen recombination reactions at both SiO_2 and Al_2O_3 growth surfaces. Using thermochemical modelling, we computed the free energy change associated with oxygen recombination. Using kinetic modelling, we extracted the activation barrier for the recombination reaction and derived the corresponding reaction rates. MACE universal machine learned force field is chosen for dynamic simulations as *ab initio* methods are very time-consuming for such studies. Using dynamic modelling, we explicitly simulated the plasma species-surface interaction and compared the probability of recombination at both growth surfaces. From the results generated at different levels of atomic-scale modelling, we provide a comprehensive understanding of the oxygen recombination leading to growth rate differences observed in the PEALD of the two materials.

[1] K. Arts et al., J. Phys. Chem. C, 123, 27030−27035 (2019).

[2] QuantumATK V-2024.09, Synopsys. (https://www.synopsys.com/quantumatk)

[3] S. Smidstrup et al., J. Phys.: Conden. Matter 32, 015901 (2020).

[4] J. Schneider et al., ALD/ALE 2022, Ghent, Belgium.

[5] S. K. Natarajan et al., ALD/ALE 2024, Helsinki, Finland.

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