Thin Films
Room 115 - Session TF1+AP-ThM

Thin Films: Fundamentals of ALD
Moderators: **Matthias Young**, University of Missouri, **Sarah Atanasov**, Intel

8:00am TF1+AP-ThM-1 AVS Medard W. Welch Award Talk: The Surface Chemistry of the Atomic Layer Deposition of Metal Thin Films, *Francisco Zaera*[1], University of California - Riverside   **INVITED**
The deposition of thin solid films is central to many industrial applications, and, thanks to the isotropic nature of the adsorption of chemical species (which affords even coverages on surfaces with rough topographies), chemical vapor deposition (CVD) methods are particularly useful for this task.Moreover, by splitting the overall film-depositing reactions into two or more complementary and self-limiting steps, as it is done in atomic layer depositions (ALD), film thicknesses can be controlled down to the sub-monolayer level.Thanks to the availability of a vast array of inorganic and metalorganic precursors, CVD and ALD are quite versatile and can be engineered to deposit virtually any type of solid material.However, the surface chemistry that takes place in these processes is often complex and can follow undesirable side reactions leading to the incorporation of impurities in the growing films.Appropriate precursors and deposition conditions need to be chosen to minimize these problems, and that requires a proper understanding of the underlying surface chemistry.

In this presentation we discuss the progress made in our laboratory toward that goal.Our focus has been on the deposition of late transition metals.We will comment on the general nature of the metallorganic complexes used as precursors for these depositions, and the uniqueness that solid surfaces and the absence of liquid solvents bring to the ALD chemistry and differentiate it from what is known from metalorganic chemistry in solution.We then delve into the adsorption and thermal chemistry of those precursors, highlighting the complex and stepwise nature of the decomposition of the organic ligands that usually ensued upon their thermal activation.We discuss the criteria relevant for the selection of co-reactants to be used on the second half of the ALD cycle, with emphasis on the redox chemistry often associated with the growth of metallic films starting from complexes with metal cations.Another consideration is the nature of the growing films, which rarely retain the homogeneous 2D structure often aimed for.We end with some general conclusion and with a personal outlook of this field.

8:30am TF1+AP-ThM-3 Effects of ALD Chemistry on Process Windows, Thin Film Composition and Modification of the Underlying Substrate Surface, *Jay Swarup, J. Engstrom,* Cornell University
In this work we have examined explicitly how the choice of ALD chemistry (precursor and co-reactant) can affect the process temperature window, composition of the deposited thin film, and possible modification of the underlying substrate.Growth of Al_2O_3 from $Al(CH_3)_3$ (TMA) and H_2O may be the most studied and robust ALD process.Here we consider two perturbations from this benchmark process by considering both a different precursor (a heteroleptic Al complex, void of halogens and Al-C bonds, L'_2AlL''), and a different organic oxidizing compound (RO_x).We have employed a quartz-crystal microbalance (QCM) to monitor ALD *in situ* and in real-time, and the deposited thin films have been characterized using X-ray photoelectron spectroscopy, spectroscopic ellipsometry, and X-ray reflectivity.Growth of thin films of Al_2O_3 using TMA and either RO_x or H_2O as the co-reactant at T = 285 °C produces thin films of similar physical properties (density, stoichiometry, minimal carbon incorporation), and the growth rate per cycle is similar for the two co-reactants at this temperature.At a lower temperature of T = 120 °C, the behavior is starkly different, where growth occurs with H_2O but not with RO_x.At either process temperature, we find no evidence for significant coverages of a long-lived intermediate from the reaction of RO_x. Growth from the heteroleptic Al precursor is similar to that observed with TMA—essentially stoichiometric Al_2O_3 is formed, and growth occurs readily with H_2O at T = 120 and 285 °C, while there are differences in the species formed at the end of the precursor half cycle.Growth with the heteroleptic precursor and the organic oxidizing species exhibits a similar dependence on temperature as observed with TMA—deposition at T = 285 °C, but not at T = 120 °C.Deposition of thin films of Al_2O_3 on metal surfaces of Cu and Co has been examined for evidence of interfacial oxidation.[1] While growth with either co-reactant (H_2O or RO_x) does not lead to the oxidation of the underlying Cu substrate, use of H_2O leads to the oxidation of Co, while use of RO_x as the co-reactant does not. We postulate that the size of the co-reactant in this case plays a role, where the diffusion of species through the deposited Al_2O_3 thin film could result in oxidation at the Al_2O_3|metal interface, a process that is strongly hindered in the case of RO_x due to its size.

[1]*ACS Appl. Mater. Interfaces* **16**, 16983−16995 (2024).

8:45am TF1+AP-ThM-4 Atomic Layer Deposition Chemistry – Trimethylaluminum on SiO_2 and Cu from a Surface Science Perspective, *Leonhard Winter, F. Zaera,* University of California, Riverside
Atomic Layer Deposition (ALD) is a chemical method used to grow thin films by sequentially employing complementary, self-limiting half-reactions. ALD offers the possibility to grow high-quality films on geometrically challenging substrates with sub-monolayer thickness control. An important development in ALD research is the ability to perform the growth selectively on specific areas.[1] For example, in the microelectronics industry, an ALD film often needs to be grown only on the dielectric (often SiO_2) or only on the electric contacts (often Cu) while avoiding the other material. Therefore, it is important to understand the surface chemistry of the ALD precursors on the competing surfaces. There has been some progress towards this goal,[2] but more mechanistic details are needed to tailor the selective ALD chemistry.
To this end, we have set to first study and contrast the surface chemistry of trimethylaluminum (TMA), a precursor commonly used to deposit Al_2O_3 films, on SiO_2 versus Cu surfaces by using X-ray photoelectron spectroscopy (XPS) and temperature-programmed desorption (TPD). On SiO_2, we have observed high chemical reactivity of this precursor at unexpectedly low temperatures and exposures, below the cryogenic temperatures required for multilayer condensation. This low-temperature chemistry appears to be complex, with desorption of Al-containing fragments being accompanied with changes in the relative Al/C atomic ratio on the surface. It was also determined that the initial sticking coefficient at room temperature is approximately 4-5 times smaller than at cryogenic temperatures, and that the TMA uptake is self-limiting. This high TMA reactivity on SiO_2 surfaces will need to be compared with that on Cu substrates, as the differences are expected to have significant implications for the selectivity of the ALD and for strategies to control it.

[1] A. J. M. Mackus, M. J. M. Merkx, W. M. M. Kessels, *Chem. Mater.* **2018**, *31*, 2-12.
[2] S. T. Barry, A. V. Teplyakov, F. Zaera, *Acc. Chem. Res.* **2018**, *51*, 800-809.

9:00am TF1+AP-ThM-5 Spatial Atomic Layer Deposition: Transport-Reaction Modeling and Experimental Validation of Film Geometry, *Daniel Penley, N. Dasgupta,* University of Michigan, Ann Arbor
Close-proximity atmospheric-pressure spatial atomic layer deposition (AP-SALD) is a powerful technique to control nanoscale surfaces and interfaces at scales relevant to large-scale manufacturing. To investigate the manufacturing tradeoffs in an AP-SALD system (film quality-throughput-cost-sustainability), many studies utilize computational modeling to gain insight into the difficult to observe process region that contains the isolated precursor zones. However, there is limited investigation into the effects of process parameters on the spatial separation and distribution of the precursor zones and their resulting impact on the deposited film. Additionally, few previous works have paired a computational model with an experimental system that has comparable, closed-loop control over the many system parameters, including gap size, relative alignment, gas flow rates, and substrate velocity.

In this work, we introduce a transport-reaction model to study how variations in process parameters affect the resulting deposited film. A finite element method model uses laminar flow fluid mechanics and transport of dilute species to give insight into the pressure, velocity, and partial pressure gradients within the process region. These outputs are then input into a surface reaction model that simulates the chemical reactions, yielding predicted film thickness maps. The model is validated and parameterized by comparing the simulated film geometries with TiO_2 films deposited using a mechatronic AP-SALD system. By coupling an experimental system with the transport-reaction model, process parameters can be tuned both physically and digitally to provide new insights into AP-SALD process control and optimization for thin film deposition at large scales.

---

[1] **Medard W. Welch Award Winner**

9:15am **TF1+AP-ThM-6 Deposition Efficiency Modeling according to Precursor Flow Rate in ALD Process with Fixed Chamber Pressure**, *Dongho Shin,* Samsung Electronics, Republic of Korea

Atomic Layer Deposition (ALD) is a key technology for achieving excellent thin film step coverage in a high aspect ratio structure. Therefore, many studies regarding various ALD technologies and ALD mechanism modeling in microstructure have been conducted. However, there are few studies of ALD technologies in terms of cost and environment, related to the efficiency of precursor used during ALD process. Deposition Efficiency (DE) is defined as the ratio of the thickness of deposited film to the volume of the precursor consumed. Research on ALD technologies that reduce precursor consumption by increasing DE of precursor is urgently needed considering cost reduction and ESG management. Therefore, in this paper, a new precursor supply model representing DE is established for ALD system with fixed pressure control. Based on the model, we found that precursor flow rate and DE are inversely proportional. Due to this characteristic, the decrease of the flow rate results in the higher DE. The feasibility of the model has been confirmed through CFD simulation and the model is finally verified through pattern evaluation. This proposed concept presents an additional direction to be pursued in ALD research in the future.

9:30am **TF1+AP-ThM-7 Time-Resolved Heat Generation of ALD MgO Surface Reactions**, *Ashley Bielinski, J. Xu,* Argonne National Laboratory; *S. Htun,* Northwestern University; *S. Hruszkewycz, C. Liu, A. Martinson,* Argonne National Laboratory

Many of the properties that are prized in films deposited with atomic layer deposition (ALD) such as precise control of composition and thickness, as well as conformal coverage on high aspect ratio structures, rely on the self-limiting nature of ALD surface reactions.A deeper understanding of the fundamental thermodynamics, kinetics, and mechanisms of ALD precursor reactions is essential to enable emerging applications such as site-selective ALD and area-selective ALD, which rely on chemical selectivity between precursor molecules, inhibitors, and the substrate surface.Differences in the surface composition and availability of reactive sites, as well as the precursor ligands can have a significant influence on the properties of the deposited film and the formation of interfaces, even within a given material system.

ALD pyroelectric calorimetry measures the in situ, time-resolved heat generated by ALD surface reactions under standard ALD conditions. Previously, we used this technique to measure the heat generation rates of trimethylaluminum (TMA), tetrakis(dimethylamino)zirconium (TDMAZr) and water to form Al_2O_3 and ZrO_2.Here we extend this technique to study the reaction between bis(ethylcyclopentadienyl)magnesium ($Mg(CpEt)_2$) and water to form MgO.To fully extract the heat generated by these ALD surface reactions over longer time scales, the data was fit to a calibrated model to account for cooling and electronic decay.These results were then compared to computational first principles models of various surfaces and reaction steps as well as calculations of the standard reaction enthalpies.Pyroelectric calorimetry provides a unique opportunity to quantitatively benchmark the values provided by computational models.This can help evaluate the accuracy of proposed processes and mechanisms.Heat generation rates provide new insight into ALD processes, helping us to untangle the thermodynamics, kinetics, and mechanisms of these heterogenous surface reactions.

9:45am **TF1+AP-ThM-8 In situ Stress Measurements During Tungsten Atomic Layer Deposition**, *Ryan B. Vanfleet, S. George,* University of Colorado at Boulder

In situ film and surface stresses were measured during tungsten (W) atomic layer deposition (ALD) using wafer curvature techniques. Tungsten was deposited at temperatures between 130 °C and 300 °C using tungsten hexafluoride (WF_6) and disilane (Si_2H_6) as the reactants on aluminum oxide (Al_2O_3) ALD surfaces. The stress was initially compressive during nucleation over the first 8-10 W ALD cycles as expected from a Volmer-Weber growth model. The stress was then tensile as the film became continuous.

Large tensile stresses were measured for the W ALD films. The film stress was ~2.0 GPa at a deposition temperature of 200 °C (Figure 1). For comparison, Al_2O_3 ALD films deposited at low temperatures have much smaller tensile film stresses of ~0.45 GPa. The large tensile stress in W ALD films may be generated at the grain boundaries. Atoms are too far apart at grain boundaries and experience an attractive force that wants to pull them together.

Surface stresses were also measured during the individual WF_6 and Si_2H_6 exposures (Figure 2). The WF_6 exposures produce a tensile stress of ~+2 N/m. This tensile stress is correlated with WF_6 reacting with SiF_2H^* sacrificial surface species to deposit WF_5^* surface species ($SiF_2H^* + WF_6(g) -> WF_5^* + SiF_3H(g)$). The Si_2H_6 exposures then partially release the tensile stress with a stress change of ~-1 N/m. The Si_2H_6 exposures redeposit SiF_2H^* sacrificial surface species ($WF_5^* + Si_2H_6(g) -> WSiF_2H^* + SiF_3H(g) + 2H_2(g)$).

The large tensile stress in the W ALD films can lead to film cracking and delamination. This phenomenon is clearly evidenced by the *in situ* stress measurements (Figure 3). A large reduction in tensile stress is observed during film failure. The film failure was also obvious by visual inspection of the W ALD films when the W films began to peel off the underlying wafer.

Additional in situ measurements have observed that the large tensile film stress in W ALD films may be reduced by occasional exposures to trimethylaluminum (TMA). The addition of Al breaks the crystalline continuity in the W ALD film and forces the W ALD film to re-nucleate. These observations suggest that film stress can be controlled by adding dopants during film growth.

Author Index

Bold page numbers indicate presenter