Thin Films Division
Room: 20 - Session TF-TuA

ALD Precursors and Surface Reactions
Moderators: Qing Peng, University of Alabama, Riikka Puurunen, Aalto University, Finland

2:20pm **TF-TuA1 Accelerated Searching of Potential Precursors for Silicon Carbide-atomic Layer Deposition from Ab-initio Machine Learning Methods**, ***Zhigang Mei***, *S. Bhattacharya, A. Yacout*, Argonne National Laboratory

Due to the superior thermophysical properties of silicon carbide at high temperature, silicon carbide (SiC) coatings have the potential to offer excellent resistance to both oxidation and hydriding of zircaloy-based nuclear fuel cladding used in light water reactors. Unfortunately, the current deposition technique for SiC using chemical vapor deposition (CVD) can be only achieved at relatively high substrate temperatures, which can severely degrade the performance of zircaloy cladding. As a comparison, atomic layer deposition (ALD) enables the growth of pinhole free films on large and convoluted substrates with nanometer precision that operates at low temperatures. Developing a new ALD process requires better understanding of how the film growth process takes place, which depends on the chemicals being used. The major obstacle to low-temperature ALD of SiC is to determine the right precursors. To this end, we use high-throughput *ab initio* calculations and state-of-the-art machine learning (ML) techniques to accelerate the precursor screening. The method involves two different types of prediction: the forward and backward predictions. The objective of the forward prediction is to train a set of machine learning models for the free energies of silicon and carbon-containing molecules from the high-throughput *ab initio* database. Inverting the trained forward models through Bayes' law, we quantitatively predict the free energies of all the possible silicon and carbon-containing molecules from the PubChem compound database. By calculating the Gibbs energy of reaction using the ML predicted energy, several potential silicon and carbon precursors are predicted to be promising for ALD of SiC at low temperature. We believe the present method will be helpful to develop novel ALD precursors for other applications.

2:40pm **TF-TuA2 Surface Chemistry of Ru Atomic Layer Deposition Precursors**, *X. Qin*, ***Francisco Zaera***, University of California

The thermal chemistry on nickel, silicon oxide, and aluminum oxide surfaces of tris(2,2,6,6-tetramethyl-3,5-heptanedionato)ruthenium(III), a precursor used for the growth of metallic ruthenium thin films via atomic layer deposition (ALD), was characterized by using a combination of X-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD), and reflection-absorption infrared absorption spectroscopy (RAIRS). Several intermediate steps were identified during the surface decomposition of this precursor on nickel, with the release of carbon monoxide into the gas phase, the formation of tert-butyl species on the nickel substrate, and the reduction of the metal center in stepwise fashion between approximately 300 and 500 K. ALD cycles with oxygen as the second reagent accomplish the efficient removal of all carbon contaminants from the surface and the reversible oxidation-reduction of the metal, indicating the feasibility of growing metallic films with such oxidizing reactant. However, the formation of volatile Ru oxides prevents the buildup of multilayers of the metal. Experiments with other oxidants (nitrous oxide) and other substrates show promise for finding a solution to this problem.

3:00pm **TF-TuA3 Mechanistic Aspects of ALD Ru Thin Film Growth based on Ru(DMBD)(CO)$_3$ and H$_2$O using Downstream Quadrupole Mass Spectrometry**, ***Zhengning Gao***, Washington University in St. Louis, *R. Kanjolia,* EMD Performance Materials, *P. Banerjee*, Washington University in St. Louis

The precursor 2, 3 - dimethyl butadiene Ruthenium tri-carbonyl (Ru(DMBD)(CO)$_3$), is a volatile molecule with favorable properties for the deposition of both Ru and RuO_2 films via ALD.[1] An intriguing aspect of this precursor is its asymmetric molecular structure with the DMBD ligand coordinated to one side of the Ru^{4+} center, while the 3 carbonyl groups are bonded to the opposite side. This makes the molecule an attractive candidate to study using *in situ* downstream quadrupole mass spectrometry (QMS) since, the release of DMBD vs. carbonyl groups during ALD half-reactions can provide a particularly descriptive view at the atomic level of how Ru(DMBD)(CO)$_3$ interacts with the substrate.

In this talk, we will discuss the mechanism of ALD of Ru thin films using Ru(DMBD)(CO)$_3$ and H_2O. The QMS signal of the Ru(DMBD)(CO)$_3$ consists of three distinct species. First, the mass-to-charge ratio (m/e) of 67 corresponds to the DMBD ligand dissociating from the molecule[2]. Second, a strong m/e = 16 is also observed as the DMBD further cracks into smaller fragments. Finally, m/e = 44 is observed and is related to CO_2 and HCOOH formation from the reaction of the tri-carbonyl groups with H_2O.[3] The QMS signal of these three species will be discussed in the context of varying process parameters such as Ru(DMBD)(CO)$_3$ and H_2O pulse times and the temperature of the ALD process. Additionally, *ex situ* film characterization including atomic force microscopy, transmission electron microscopy, X-ray diffraction, X-ray photoelectron spectrum and resistivity measurements will be presented to correlate the process signatures obtained via QMS to the film type, morphology and electrical properties.

References:

1. Austin, D. Z.; Jenkins, M. A.; Allman, D.; Hose, S.; Price, D.; Dezelah, C. L.; Conley, J. F., Atomic Layer Deposition of Ruthenium and Ruthenium Oxide Using a Zero Oxidation State Precursor. *Chem. Mater.* **2017**.

2. Chiang, C.-M.; Rowe, J.; Malic, R.; Sen, A.; Steigerwald, M.; Mills, A., A new CVD reaction for atomic layer deposition of silicon. *Applied surface science* **1996,***107*, 189-196.

3. Rosenberg, S. G.; Barclay, M.; Fairbrother, D. H., Electron beam induced reactions of adsorbed cobalt tricarbonyl nitrosyl (Co (CO) 3NO) molecules. *The Journal of Physical Chemistry C* **2013,***117* (31), 16053-16064.

3:20pm **TF-TuA4 Nucleation of Al$_2$O$_3$ Atomic Layer Deposition with Water or H$_2$O$_2$**, ***Adam Hinckley***, *A.J. Muscat*, University of Arizona

Aluminum oxide (Al_2O_3) is a suitable replacement for SiO_2 in electronic devices such as flash memory due to its wide band gap and higher dielectric constant. Atomic layer deposition (ALD) using sequential pulses of trimethylaluminum (TMA) and an oxidant is a leading method for the formation of nano-scale Al_2O_3 layers. Al_2O_3 layers grown by ALD have been demonstrated with leakage currents of less than 1 nA/cm^3. The quality of the layers depends on both the deposition temperature and choice of oxidant, which is commonly water or oxygen atoms generated using a plasma.

An oxidant more reactive than water, such as H_2O_2, could produce a denser Al_2O_3 film. The growth of Al_2O_3 on hydrogen-terminated silicon using TMA and H_2O_2 was compared to that using TMA and water as a reference. Spectroscopic ellipsometry was used to determine the growth per cycle (GPC), and *in situ* x-ray photoelectron spectroscopy (XPS) was recorded before and after each precursor dose. The O 1s XPS peak at 531.8 eV and the Al 2p peak at 75.5 eV were used to monitor the formation of the Al-O bond and the C 1s peak at 284.5 eV was used to monitor the persistence of the Al-C bond after each half cycle. A second state in O 1s XPS at 533.3 eV assigned to the O-H bond was used to estimate the number of reactive sites present after each oxidant pulse.

The growth-per-cycle (GPC) was equal to 1.2 Å at H_2O_2 pulse times above 0.3 s, which is similar to reported ALD growth rates using water. The Al 2p XPS peak appeared after 4 ALD cycles using anhydrous H_2O_2 and after 7 cycles using water. The aluminum coverage after 10 ALD cycles was 40 % greater for anhydrous H_2O_2 compared to water, although the GPC was similar for each co-reactant. The O-H coverage doubled with each pulse of H_2O_2. The O 1s peak assigned to O-H also broadened with subsequent ALD cycles due to the presence of additional surface states. Each pulse of water increased the O-H coverage by about 1.5 times compared to the subsequent pulse. The ratio between C 1s and Si 2p peak areas showed twice as much carbon present on the surface during H_2O_2 ALD. The C 1s/Si 2p ratio increased during pulses of TMA and decreased during pulses of H_2O_2 due to surface reactions that desorb CH_4. Greater OH densities and C coverages indicate that H_2O_2 activates more surface sites for the metal precursor than water, improving Al_2O_3 film density.

4:20pm **TF-TuA7 Direct Measurements of Half-Cycle Reaction Heats during Atomic Layer Deposition Provide Mechanistic Insights**, ***Charles T. Campbell***, *J. Lownsbury,* University of Washington, *K.S. Kim, A.B.F. Martinson*, Argonne National Laboratory

We introduce here a new high-temperature adsorption calorimeter that approaches the ideal limit of a heat detector whereby the signal at any time is proportional to the heat power being delivered to the sample, and prove its sensitivity for measuring pulse-to-pulse heats of half-reactions during atomic layer deposition (ALD) at 400 K. The heat dynamics of amorphous Al_2O_3 growth via sequential self-limiting surface reaction of trimethylaluminum (TMA) and H_2O is clearly resolved. Calibration enables quantitation of the exothermic TMA and H_2O half-reactions with high precision, -343 kJ/mol TMA and -251 kJ/mol H_2O, respectively. A time resolution better than 1 millisecond is demonstrated, allowing for the deconvolution of at least two distinct surface reactions during TMA micro-dosing. It is further demonstrated that this method can provide the heat of reaction versus extent

of reaction during each precursor's half-reaction, thus providing even richer mechanistic information on the surface processes involved. The broad applicability of this novel calorimeter is demonstrated through excellent signal-to-noise ratios of less exothermic ALD half-reactions to produce TiO_2 and MnO.

4:40pm **TF-TuA8 Cyclic Silane Precursors in Atomic and Molecular Layer Deposition**, ***Nicholas Strandwitz**, L. Ju*, Lehigh University

Cyclic azasilanes are a promising class of reactants for atomic and molecular layer deposition due to their volatility, reactivity, and diverse set of peripheral chemical functionalities. The reactivity of this class of molecules stems from ring strain and unstable Si-N bonding. Reaction with water or OH groups results in ring opening and Si-O bond formation and is a useful chemical step for controlled film growth. This work focuses on using and understanding this class of molecules for use in atomic and molecular layer deposition (ALD, MLD). The efficacy of the ring opening reaction and the diversity of functional groups on the cyclic azasilanes deem this precursor group highly promising for MLD. We report the growth of various MLD films based on reaction with anhydrides, metal-organics, and water. The film growth was found to be optimal near 100 °C. The two chemistries reported here are the sequential reaction of (1) a cyclic azasilane, maleic anhydride, and water and (2) a cyclic azasilane, maleic anhydride, trimethylaluminum (TMA), and water. Reaction 1 showed clear evidence of diffusion and reaction within the film as evidenced by large growth rates (~10 nm per cycle) after ~15 growth cycles, regardless of purge time. However, use of TMA in reaction 2 arrested this diffusion, presumably due to consumption of reactive groups or through densification of the film. Film properties were measured as a function of annealing temperature using ellipsometry, x-ray reflectivity, and infrared absorption measurements. These measurements indicate a densification of the films while maintaining low surface roughness. Porosity is evident after removal of organic components by a low dielectric constant for the films derived from reaction 1.These MLD chemistries offer a route to tunable hybrid thin films on high aspect ratio substrates and have potential applications in diffusion barriers, low dielectric constant layers, and passivation layers.

5:00pm **TF-TuA9 Area Selective Atomic Layer Deposition Via Precursor Selective Adsorption: Theory, Strategy, and Applications in Catalysis**, ***Rong Chen***, Huazhong University of Science and Technology, PR China **INVITED**

Atomic layer deposition (ALD) is a powerful thin film deposition method with precise thickness control, good uniformity, and high conformality on entire surface. While in catalysis applications, there are increasing interests for synthesis of catalysts with well-defined nanostructures, thus ALD has become a desired method for catalyst synthesis with precise control of size, composition, nanostructure, etc. Herein we report the area selective growth strategies via ALD precursor selective adsorption to obtain desired metal-oxide composite catalysts. Combining *in-situ* QCM, FTIR and DFT calculations, a series of oxide ALD precursors with $-(CH_3)_n$ $-(N(CH_3)_2)_n$, $-(Cp)_n$, and $–(thd)_n$ ligands are studied on their chemisorption and binding energies to metal surfaces. The selective growth behavior shows a strong correlation with different precursor ligands as well as the counter reactants. Thus with optimal precursor choice and reaction condition, desired nanocomposite structures could be achieved via area selective ALD.

5:40pm **TF-TuA11 AVS 2017 John A Thornton Memorial Award and Lecture: Atomic Layer Deposition: Highlights from the Last 25 Years**, ***Steven George****, University of Colorado at Boulder **INVITED**

The Thornton Memorial Lecture will discuss atomic layer deposition (ALD) highlights from the last 25 years. The lecture will trace the history of ALD starting with the earlier developments in atomic layer epitaxy (ALE). The presentation will recount the importance of semiconductor processing needs to the growth of ALD and the situation that led to the name change from ALE to ALD. The talk will also describe personal highlights in the development of ALD and acknowledge some of the people and circumstances behind those developments. In addition, the lecture will include commentary on the evolution of ALD. The presentation will conclude by looking ahead to the future of ALD.

* **John A. Thornton Memorial Award Winner**

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