ALD Fundamentals
Room Jan & Hubert Van Eyck - Session AF-TuA

Characterization I & II

Moderators: Jiyoung Kim, University of Texas at Dallas, Jin-Seong Park, Hanyang University

1:15pm **AF-TuA-2 Laterally Resolved Low Energy Ion Scattering Study of Selective ALD Model Samples*, Philipp Brüner*,** *T Grehl,* IONTOF GmbH, Germany*; A Mameli, F Roozeboom, P Poodt,* TNO/Holst Center, Netherlands

We present a low energy ion scattering (LEIS) study of various model samples for area-selective spatial ALD of SiO_2. The aim of the study is to assess SiO_2 selectivity and growth behavior on a number of different substrates intended as non-growth areas, including Al_2O_3, IGZO, Ta_2O_5, ZrO_2, SnO_2, and ZnO.The SiO_2 films were grown in a spatial ALD reactor, using a three-step approach consisting of successive doses of inhibitor (a carboxylic acid), silicon precursor (bis(diethylamino)silane, BDEAS) and O_2 plasma [1]. The rotary spatial ALD reactor design leads to varying dosing times of the ALD chemicals along the wafer radius, so that the different areas on the wafer are exposed to different deposition conditions [2]. Thus, laterally resolved surface analysis allows for investigating the effect of different exposure times on the selectivity on one and the same sample.

Due to the high surface sensitivity of just a single monolayer, coupled with simultaneous film thickness measurements, LEIS reveals important information about the early stages of film growth, such as surface coverage, layer closure, growth mode, and deposition rate. We show how LEIS spectra are analyzed to separate the measurement signal of the first monolayer ("surface signal") from contributions from deeper layers ("sub-surface signal"). The surface signal is evaluated to quantify the elemental composition of the outer monolayer of the sample, while the sub-surface signal contains information about elements below the surface and about film thickness.

A typical LEIS measurement probes a region of about 2x2 mm² of the sample surface. In combination with stage scanning, larger scale wafer mapping becomes possible, where small variations in film thickness and coverage across the wafer are detected with high precision. As a result, the film properties can be correlated to different exposure times of the spatial ALD process, and therefore derive optimal conditions for maximizing the selectivity.

[1] A. Mameli *et al.*, *ACS Nano*, 11, 9303-9311 (2017).

[2] F. J. van den Bruele *et al.*, *JVSTA*, 33, 01A131-1-7 (2015).

1:30pm **AF-TuA-3 In situ Characterization of Quantum Dot Photoluminescence during Atomic Layer Deposition: Towards Stable Cd-Free QD-Based Devices*, Robin Petit*,** *N Zawacka, J Kuhs, P Smet, Z Hens, C Detavernier,* Ghent University, Belgium

Quantum dots (QD) are emerging as optically active components in an increasing number of applications including solar cells and concentrators, light-emitting diodes and lasers [1-4]. This surge is attributed to the unique benefits QD provide resulting from their size-tunable opto-electronic properties and the possibility for solution-based processing. In order to compete with the current state-of-the-art in other technologies, the stability of the QD optical performance needs to be addressed. In many cases, the QD are embedded in a host matrix which can act as a barrier, shielding the QD from their immediate environment (and vice versa) [5, 6]. One of the most promising methods used for embedding is atomic layer deposition (ALD), a vapor-based deposition technique enabling layer-by-layer growth by adopting sequential exposure to precursor materials and suitable reactants. However, the embedding of QD with ALD has been shown to also affect the QD optical performance [7]. Here, we report on a novel method to preserve the QD optical stability during the entire ALD process.

Previously, we reported on the photoluminescence (PL) stability of CdSe/CdS/ZnS core/shell/shell QD during the ALD process [8]. Due to the toxicity of Cd, the use of Cd-based QD should be avoided as much as possible. In the current study, the Cd-free $CuInS_2$/ZnS core/shell QD and InP/ZnSe core/shell QD are investigated adopting a similar approach as before [8]. Using a home-built in situ PL setup the effect of different precursors (TMA, TDMAT, DEZ), reactants (H_2O, O_3), gases (O_2, H_2O, N_2, Ar) and plasma's (O_2, H_2O, H_2) on the QD PL is evaluated, elucidating the QD PL behaviour during complete ALD cycles (Al_2O_3, TiO_2, ZnO). We demonstrate that the QD PL intensity can be maintained by incorporating an additional QD encapsulation step prior to coating with ALD. In this regard, important progress is made towards stable Cd-free QD-based devices, suitable for a growing number of applications.

[1] *Nature Photonics* **6**, 133-135 (2012).

[2] *Semiconductors* **38**, 909−917 (2004).

[3] *Nature Photonics* **7**,13−23 (2013).

[4] *Science* **290**, 314−317 (2000).

[5] *The Journal of Physical Chemistry C* **120**, 4266-4275 (2016).

[6] *Chemistry & biology* **18**, 10-24 (2011).

[7] *Chemistry of Materials* **23**, 126-128 (2011).

[8] *ACS Applied Materials & Interfaces* **11**, 26277-26287 (2019).

1:45pm **AF-TuA-4 Capturing the Dynamic Atomic Structure in ALD Reactions with *In situ* XANES, *ab initio* Simulations, and Machine Learning*, Orlando Trejo*,** University of Michigan*; A Dadlani,* Norwegian University of Science and Technology, Norway*; F De La Paz, S Acharya, R Kravec,* Stanford University*; D Nordlund, R Sarangi,* SLAC National Accelerator Laboratory*; F Prinz,* Stanford University*; J Torgersen,* Norwegian University of Science and Technology, Norway*; N Dasgupta,* University of Michigan

In order to continue to improve our fundamental understanding of ALD growth mechanisms, we must build upon our model understanding of self-organization at the atomic scale. In particular, there is a need for a more detailed mechanistic understanding of the dynamic structural evolution of materials during thin-film growth. In this study, *in situ* X-ray absorption spectroscopy (XAS) measurements of the S K-edge during the growth of ZnS thin films on TiO_2 nanoparticles were collected and analyzed.[1] We built a modular ALD that can safely be used to deposit and characterize ALD of sulfide materials at the Stanford Synchrotron Radiation Lightsource. The two precursors used were H_2S and diethylzinc.

The experimental results show that sulfide and sulfate species form during the nucleation phase of ZnS on TiO_2. As the film growth proceeds, the S K-edge spectra of the *in situ* ZnS film converge to that of a representative *ex situ* ALD ZnS film. Through high-throughput screeningof *ab initio* simulations of the XAS spectra, we were able to observe the stage in the growth process during which the surface sulfur species transition into a four-fold coordination environment that resembles the bulk ZnS crystal structure. We simulated XANES spectra using the FEFF9 code and built a computational platform to enable high-throughput generation, modeling, and analysis of atomic configurations based on the simulated spectra. We used random forests and artificial neural networks to create a workflow for determining the structural changes of representative S moieties during ALD growth. The experimental and computational strategies presented in this study provide an example of how *in situ* synchrotron-based characterization can be leveraged using machine learning approaches to capture the dynamic atomic structure during thin-film synthesis.

1) Trejo, O.; Dadlani, A. L.; De La Paz, F.; Acharya, S.; Kravec, R.; Nordlund, D.; Sarangi, R.; Prinz, F. B.; Torgersen, J.; Dasgupta, N. P. "Elucidating the Evolving Atomic Structure in Atomic Layer Deposition Reactions with in Situ XANES and Machine Learning" *Chem. Mater.***2019**, *31* (21), 8937–8947.

2:00pm **AF-TuA-5 Atomic Layer Deposition of Erbium Oxide, Erbium Fluoride and Stoichiometrically-Tunable Erbium Oxyfluoride Films*, Neha Mahuli*,** *S George,* University of Colorado - Boulder

Rare earth metal oxides, metal fluorides and metal oxyfluorides have received attention as protective coatings in reactive plasma environments. Our recent work has developed the atomic layer deposition (ALD) of AlO_xF_y [1], HfO_xF_y and ZrO_xF_y oxyfluorides. This current study explored the ALD of erbium oxide (Er_2O_3), erbium fluoride (ErF_3) and erbium oxyfluoride(ErO_xF_y). Various deposition mechanisms were investigated to achieve tunable stoichiometry in ErO_xF_y films based on the HF exchange method and the nanolaminate method.

The depositions were performed at 250˚C using $Er(n\text{-}BuCp)_3$ as the Er source. H_2O and HF were used as the oxygen and fluorine sources, respectively. Initially, erbium oxide and erbium fluoride ALD were investigated using *in situ* quartz crystal microbalance (QCM) measurements. The Er_2O_3 ALD cycle consisted of alternating exposures of $Er(n\text{-}BuCp)_3$ and H_2O. Both reactions exhibited self-limiting behavior versus reactant exposure. The Er_2O_3 ALD growth rate was 64 ng/(cm² cycle) or 0.7 Å/cycle. The ErF_3 ALD cycle consisted of alternating exposures of $Er(n\text{-}BuCp)_3$ and HF. Both reactions again exhibited self-limiting behavior versus reactant exposure. The ErF_3 ALD growth rate was 32 ng/(cm^2 cycle) or 0.4 Å/cycle (Figure 1).

Erbium oxyfluoride ALD was then conducted using the HF exchange method and the nanolaminate method. The HF exchange method is based on the thermodynamically favorable F/O exchange reaction between HF and Er_2O_3. Compositional control was obtained by varying the HF exposure time, HF pressure and the thickness of the underlying Er_2O_3 film. In the nanolaminate method, sequential deposition of Er_2O_3 ALD and ErF_3 ALD nanolayers defined each supercycle (Figure 2). Compositional control was achieved by varying the ratio of number of Er_2O_3 ALD cycles to ErF_3 ALD cycles. X-ray photoelectron spectroscopy (XPS) and Rutherford Backscattering Spectroscopy (RBS) analysis were utilized to evaluate the ErO_xF_y ALD film composition. The ErO_xF_y ALD film stoichiometry could be varied from Er_2O_3 to ErF_3 using the HF exchange method and the nanolaminate method.

[1]Neha Mahuli, Andrew S. Cavanagh and Steven M. George, "Atomic Layer Deposition of Aluminum Oxyfluoride (AlO_xF_y) Thin Films with Tunable Stoichiometry", *J. Vac. Sci. Technol. A* **38**, 022407 (2020).

2:30pm **AF-TuA-7 From the Noise: Measuring Atomic Structure in Amorphous Thin Films Grown by Atomic Layer Deposition*,*** ***Matthias Young,*** University of Missouri-Columbia*; N Bedford,* University of New South Wales, Australia*; J Elam, A Yanguas-Gil, S Letourneau, M Coile, D Mandia, B Aoun,* Argonne National Laboratory*; S George, A Cavanagh,* University of Colorado - Boulder*; X He, A Jasim,* University of Missouri-Columbia*; Q Wyatt,* University of Missouri-Columbiai*; N Paranamana, T White,* University of Missouri-Columbia **INVITED**

The ability to successfully translate ALD coatings to applications is impaired by limited understanding of process-structure-property relationships for nanoscale ALD films, and especially by a lack of understanding of the structure of these films at an atomic or molecular level. Single-crystal materials are only rarely achieved by ALD. More often, ALD films form amorphous, polycrystalline, or defective structures. ALD process conditions such as precursor selection(s), precursor exposure(s), and reactor temperature are known to impact the properties of ALD films. The substrate also affects the properties of ALD films, especially for ultrathin film thicknesses. To date, the ALD community has had difficulty connecting the atomic-scale structure of ALD films with their performance, largely because of limited availability of techniques to determine the atomic-scale structure of ultrathin ALD films. In this talk, we summarize recent work and report new results employing high energy X-ray diffraction and electron diffraction, both coupled with pair distribution function analysis and Reverse Monte Carlo modeling, to reveal new understanding of the atomic structure of ALD films. The techniques we discuss can be applied broadly to understand the local structure of ALD films, including low-Z and amorphous films, and help tailor ALD coatings for a range of applications of emerging interest.

4:00pm **AF-TuA-13 Effects of Gas Phase Reaction Chemistry on Electronic Conductivity of ALD Grown TiO_2 Films*,*** ***Aein Babadi,*** *P McIntyre,* Stanford University

In situ monitoring of gas phase composition has been used to provide a link between changes in gas phase chemistry during ALD half-cycle reactions, and the electronic conductivity and metal:oxygen ratio of the deposited TiO_2 films. Dimethylamine ($(CH_3)_2NH$), DMA was probed as the main product of both the TDMAT and water vapor half-reactions during the TDMAT/H_2O ALD process. In-plane transport characteristics of the ALD grown films demonstrated that the presence of DMA significantly increases the conductivity and transiently reduces the TiO_2 films by its reaction with surface oxygen-containing species.

In this study, we show that relatively slight variations in ALD conditions can cause large changes in the electrical conductivity of TiO_2 films. The experiments were performed in a custom-designed ALD system with a load lock to ensure a low base pressure ($<1\times10^{-3}$ Torr) of the process chamber with the aim of minimizing the potential wall reaction/contamination during the wafer load and unload sequences. A residual gas analyzer (RGA) with the mass range of 1-300 amu was integrated with the ALD reactor to achieve real-time chemical diagnostic data of the TiO_2 ALD process. An adequate pressure gradient between the process environment 5×10^{-3} Torr and the RGA region 1×10^{-6} Torr was maintained through a differentially pumped sampling system. TiO_2 films were grown using half-cycle dosing of Tetrakis(dimethylamino)titanium (TDMAT) and water vapor on both p-type silicon single crystal substrates with resistivity of 0.001-0.005 Ω.cm and fused silica with resistivity of $\rho \sim 10^{12}$ Ω.cm @ 250℃. The silicon samples were used for physical characterization while all the electrical measurements were performed on the fused silica samples. Electrical conductivity of TiO_2 films deposited on highly resistive fused silica substrates was measured using transmission line method (TLM). TLM test patterns were defined by electron beam evaporation of Pt (200 nm thickness) through a shadow mask. TLM measurement results showed an increase in resistivity as TiO_2 films are deposited with longer purge time, suggesting that DMA has the potential to reduce the TiO_2 film during the deposition. Intentional dosing of DMA, at the end of TiO_2 atomic layer deposition was used to alter the resistivity of the film by reducing the TiO_2 film transiently resulting from the reaction of DMA with surface oxygen containing species. Angle-resolved X-ray photoelectron spectroscopy was used to test for evidences of reduction of the TiO_2 films as a result of DMA exposure under ALD and ALD-like conditions. The concentration of the Ti^{3+} defect states was investigated by angle-resolved XPS (see supporting info.).

4:15pm **AF-TuA-14 *In Situ* Reflection High Energy Electron Diffraction in Atomic Layer Deposition for Monitoring the Epitaxial Transformations*,*** *N Strandwitz,* ***Alexandra Howzen,*** Lehigh University

The maximum amount of thermal energy available during atomic layer deposition (ALD) is generally determined by the decomposition temperature of the precursors and also sets the maximum temperature in the "ALD window". This maximum temperature in some cases limits the structural perfection and extent of crystallization in resulting films. Intermittent annealing during the film growth in between ALD chemical exposures has been explored previously and shown to increase density and quality of ALD films.[1] However, without direct monitoring of one or more of the physical properties of the films, it can be difficult to determine the nuances of film transformation, such as crystallization temperature, surface roughening, and dependence on gas ambient.

In this work we integrate reflection high energy electron diffraction (RHEED) into a home-built ALD system to monitor structural and morphological transformations during ALD growth and thermally-induced structural transformations. RHEED is a surface sensitive diffraction technique that utilizes high energy (> 10 keV) electrons at a glancing angle, and is most commonly utilized in molecular beam epitaxy and pulsed laser deposition systems. The relatively high pressures associated with ALD are incompatible with RHEED due to filament instability and a short electron mean free path, necessitating differential pumping on the electron gun, and either 1) a short path length for electrons or 2) a pump down to high vacuum conditions. In addition to describing the system design, flow, and thermal modelling; we will show initial results of the deposition and annealing of ultrathin films (1-20 ALD cycles) focusing on transformations of polymorphic Ga_2O_3. The integration of RHEED with ALD offers a slow-motion picture of traditional epitaxial growth techniques by decoupling the deposition and crystallization steps with simultaneous monitoring of the surface structure.

[1] J.F. Conley, Y. Ono, and D.J. Tweet, Appl. Phys. Lett. **84**, 1913 (2004).

4:30pm **AF-TuA-15 In Situ Detection of the Reaction Heat Produced by ALD on High-Surface-Area Substrates*,*** ***Benjamin Greenberg,*** *K Anderson, M Wolak, A Jacobs, J Wollmershauser, B Feigelson,* U.S. Naval Research Laboratory

Many ALD reactions are highly exothermic, with some likely releasing hundreds of kJ/mol per cycle. In ALD on conventional substrates (e.g., wafers), this exothermicity is typically ignored, because the deposited mass is small compared to the substrate mass. However, in the case of high-surface-area substrates such as metal-organic frameworks (MOFs) or nanopowders, the coating/substrate mass ratio can be thousands or millions of times higher, raising the possibility of nonnegligible reaction heat. To understand the potential impact of this heat on the substrate and ALD process, we measure via pyrometry the surface temperature of a static bed of low-thermal-conductivity ceramic nanopowder undergoing particle ALD (pALD). Depositing Al_2O_3 from trimethylaluminum (TMA) and water on Y_2O_3-stabilized ZrO_2 (YSZ) nanopowder with an average nanoparticle (NP) diameter of 8 nm, we observe temperature gains, ΔT, around 20 °C above the baseline. Given that the pyrometer measures only surface temperature, we propose that within the nanopowder bed—or in a hypothetical fluidized bed—the maximum local ΔT may be significantly greater than 20 °C. This proposition is supported by a calculation of individual NP temperature based on literature reaction enthalpies and sticking coefficients. To complement our investigation of NP temperature, we also acquire high-speed videos of nanopowder agitated in a rotary pALD reactor and examine how cyclical changes in surface energy influence NP motion.

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