

Thin Films Division

Room A124-125 - Session TF+2D+AP+EL+SS-MoA

ALD and CVD: Nucleation, Surface Reactions, Mechanisms, and Kinetics

Moderators: Adrie Mackus, Eindhoven University of Technology, The Netherlands, Qing Peng, University of Alabama

1:40pm **TF+2D+AP+EL+SS-MoA1 ALD on Particles: What is Different from Wafers?**, *Ruud van Ommen*, Delft University of Technology, Netherlands

INVITED

Advanced materials, often relying on nanostructured particles as building blocks, are crucial in meeting grand challenges in energy and health. Atomic layer deposition (ALD) is an excellent technique to make such nanostructured particles: particles of which the surface is either covered by an ultrathin film or by nanoclusters. Although the underlying mechanisms are similar, there are quite some differences between ALD processing of wafers and ALD processing of particles. This presentation will discuss recent developments and insights in the field of applying ALD to particles, with an emphasis on reactor technology, precursor utilization, operating conditions, and scaling up. I will show that ALD is suited to produce nanostructured particles with very high precision. Moreover, it is scalable such that large amounts of such particles can be produced.

2:20pm **TF+2D+AP+EL+SS-MoA3 Insights into Particle ALD Peculiarities from In- and Ex-Situ Characterization**, *Benjamin Greenberg*, American Society for Engineering Education; *J.A. Wollmershauser*, *B. Feygelson*, U.S. Naval Research Laboratory

Particle atomic layer deposition (pALD) is an increasingly popular technique for mass production of core/shell nanoparticles (NPs). In a typical pALD process, NP powders are agitated in a fluidized bed or rotary reactor, and conformal coating of the entire powder surface—often > 100 m² in lab-scale reactors—is attempted via prolonged precursor exposures and purges. Over the past 2+ decades there have been many reports of highly encouraging results, including TEM images of NPs individually encapsulated by shells of uniform thickness. Nevertheless, several fundamental questions about pALD mechanisms and behavior remain challenging to answer. For example, how does the pALD growth per cycle (GPC) deviate from the corresponding ALD GPC on a flat substrate, and why? Or more importantly, what conditions are required to maximize the fraction of powder that attains an ideal core/shell structure (individual NP encapsulation) rather than a coated-agglomerate structure in which cores are glued together? In this work, using a commercial rotary pALD reactor to coat various NPs with oxide shells, we employ a wide array of characterization techniques to shed light on these issues and inform process optimization. *In situ*, we experiment with relatively uncommon techniques such as high-speed video analysis and pyrometry of the agitated NP powder, as well as conventional techniques such as mass spectrometry (RGA). High-speed videos in particular reveal aspects of the process often undiscussed (and sometimes difficult to convey) in the pALD literature, including changes in the powder motion as surface chemistry evolves. *Ex situ*, we characterize the coated NPs via TEM, XRD, SAXS, XPS, and N₂-adsorption surface area measurements (BET method).

3:00pm **TF+2D+AP+EL+SS-MoA5 Controlling the Nucleation of CVD Cobalt Films on SiO₂: Combining an Amido-based Nucleation Promotor with an Amine-based Growth Inhibitor to Afford Atomically-smooth Surfaces**, *Zhejun Zhang*, *G.S. Girolami*, *J.R. Abelson*, University of Illinois at Urbana-Champaign

Cobalt films are of interest for the back-end metallization and transistor contact in microelectronics because cobalt has a greater electromigration resistance and a lower diffusion rate in dielectrics compared with copper. However, few-nanometer thick Co films deposited by CVD on dielectrics are usually non-continuous – they consist of islands with pinholes and significant roughness – which renders them unsuitable for nanoscale device fabrication. A nucleation layer, such as TiN, can be pre-deposited to improve the area density of Co nuclei; this approach eliminates the problem of islanding, but it subtracts cross-sectional area from the plug or line, thus increasing the electrical resistance.

Here, we solve the Co nucleation problem in CVD using a two-pronged approach. First we expose the SiO₂ surface to a tetrakis(dimethylamido)(transition metal) precursor at low temperature. This affords a self-limiting, submonolayer coverage of an intermediate,

similar to the behavior of such molecules in ALD processes. The adsorbate layer then enhances the nucleation of cobalt from the Co₂(CO)₈ precursor, such that a large area density of nanoscale islands forms with essentially no nucleation delay. Using this approach, the rms surface roughness for a 1.5-nm-thick Co film decreases from 2.5 to 1.0 nm.

Second, we further improve the surface morphology by adding a co-flow of ammonia together with the carbonyl precursor; this serves as a growth inhibitor that reduces the steady-state growth rate of Co films by 50 %. The presence of the inhibitor does not alter the nucleation rate, however, the rms roughness of a 1.5-nm-thick film is further reduced to only 0.4 nm. We suggest that the roughness is due to a better valley-filling at low precursor reaction probability, consistent with the literature. In summary, our approach enables the use of CVD to afford excellent Co films for nanofabrication.

3:20pm **TF+2D+AP+EL+SS-MoA6 Plasma-assisted Atomic Layer Epitaxy of Indium Aluminum Nitride Studied Using *in situ* Grazing Incidence Small-angle X-ray Scattering**, *Jeffrey M. Woodward*, ASEE (residing at US Naval Research Laboratory); *S.G. Rosenberg*, American Society for Engineering Education (residing at US Naval Research Laboratory); *S.D. Johnson*, *N. Nepal*, U.S. Naval Research Laboratory; *Z.R. Robinson*, SUNY Brockport; *K.F. Ludwig*, Boston University; *C.R. Eddy*, U.S. Naval Research Laboratory

Indium aluminum nitride (InAlN) is an attractive material for power electronic applications. However, conventional methods of epitaxial growth of InAlN are challenged by a large miscibility gap and the significant differences in optimal growth conditions for the constituent aluminum nitride (AlN) and indium nitride (InN) binary compounds. Despite these challenges, the epitaxial growth of InAlN alloys throughout the entire compositional range has been demonstrated using plasma-assisted atomic layer epitaxy (ALEP)¹, a variant of atomic layer deposition in which relatively higher temperatures are utilized. In the ALEP growth of InAlN, the desired alloy compositions are achieved by forming ultra-short period superlattices of alternating InN and AlN layers, referred to as digital alloys (DA). In order to further advance these empirical efforts, significant research is needed to better understand the nucleation and growth kinetics of ALEP DA growth. To this end, we employ *in situ* grazing incidence small angle X-ray scattering (GISAXS) for the real-time study of the evolving ternary InAlN surfaces as has been done previously for binary InN² and AlN³.

Here we present *in situ* GISAXS studies of ALEP growth of InN, AlN, and a range of InAlN DAs on GaN (0001) substrates, which were performed at Brookhaven National Laboratory's NSLS-II using a custom reactor. The InAlN DAs studied include In_{0.19}Al_{0.81}N (3 AlN cycles and 2 InN cycles per supercycle), In_{0.5}Al_{0.5}N (1 AlN cycle and 3 InN cycles per supercycle), In_{0.64}Al_{0.36}N (1 AlN cycle and 5 InN cycles per supercycle) and In_{0.83}Al_{0.17}N (1 AlN cycle and 14 InN cycles per supercycle). Preliminary analysis of the data suggests that while the pure InN and AlN grew in 3D and 2D modes, respectively, the InAlN growth mode did not follow a simple trend as the nominal composition was tuned from InN to AlN. Instead, select compositions (50% and 83% In) exhibited predominantly 3D growth, while others (19% and 64% In) exhibited 2D growth. We also present complementary ALEP growth studies using a commercial Ultratech/Cambridge Nano Tech Fiji 200 and *ex situ* characterization methods, including high resolution X-ray diffraction, X-ray reflectivity, and atomic force microscopy.

¹ N. Nepal, V.R. Anderson, J.K. Hite, and C.R. Eddy, *Thin Solid Films* **589**, 47 (2015)

² J.M. Woodward, S.G. Rosenberg, A.C. Kozen, N. Nepal, S.D. Johnson, C. Wagenbach, A.H. Rowley, Z.R. Robinson, H. Jores, K.F. Ludwig Jr, C.R. Eddy Jr, *J. Vac. Sci. Technol. A* **37**, 030901 (2019)

³ V.R. Anderson, N. Nepal, S.D. Johnson, Z.R. Robinson, A. Nath, A.C. Kozen, S.B. Qadri, A. DeMasi, J.K. Hite, K.F. Ludwig, and C.R. Eddy, *J. Vac. Sci. Technol. A* **35**, 031508 (2017)

Monday Afternoon, October 21, 2019

4:00pm **TF+2D+AP+EL+SS-MoA8 Real-time Monitoring of the Surface Chemistry of Atomic Layer Deposition by Ambient Pressure X-ray Photoelectron Spectroscopy**, *Joachim Schnadt*, *P. Shayesteh*, Lund University, Sweden; *R. Tsyshkevskiy*, University of Maryland; *J.-J. Jean-Jacques*, *F. Bournel*, Sorbonne Université, France; *R. Timm*, Lund University, Sweden; *A.R. Head*, Brookhaven National Laboratory; *G. D'Acunto*, *F. Rehman*, *S. Chaudhary*, Lund University, Sweden; *R. Sánchez-de-Argas*, Uppsala University, Sweden; *F. Rochet*, Sorbonne Université, France; *B. Brena*, Uppsala University, Sweden; *A. Mikkelsen*, *S. Urpelainen*, *A. Troian*, *S. Yngman*, *J. Knudsen*, Lund University, Sweden

INVITED

Atomic layer deposition (ALD) and chemical vapour deposition (CVD) are very important methods that enable a highly controlled growth of thin films [1]. The surface chemistry of the underlying processes remains, however, little understood. While idealised reaction mechanisms have been developed, they represent postulates rather than models based on the factual identification of surface species and kinetics [2]. *New in situ* and *operando* methods offer the prospect of gaining a much more thorough understanding of the involved molecular and atomic surface processes and (dynamic) structures, which, in turn, means that a much better knowledge basis can be achieved for the future improvement of materials and growth recipes (see, e.g. [3,4]). One such *operando* method, which can be applied to the investigation of ALD and CVD, is synchrotron-based ambient pressure x-ray photoelectron spectroscopy (APXPS). While conventional x-ray photoelectron spectroscopy (XPS) is limited to vacuum pressures of 10^{-5} mbar and below, APXPS can be carried out at realistic pressure. Today, most APXPS machines can operate at pressures up to the 10 mbar regime, which is an ideal match to the pressure regime used in standard ALD reactors.

Here, I will report on our recent efforts to apply density functional theory (DFT)-assisted synchrotron-based APXPS to the ALD/CVD of oxides (TiO_2 , SiO_2 , and HfO_2) on semiconductor (InAs and Si) and oxide surfaces (TiO_2 , RuO_2) [3-5]. I will show that APXPS allows the identification of the surface species occurring during thin film growth and the real-time monitoring of their evolution with a time resolution of down into the millisecond regime. Here, DFT is an important tool for pinpointing the nature of the chemical species and for providing deeper insight in the surface chemical processes. I will also report on our efforts to further improve instrumentation with the goal of achieving a much closer match of the APXPS sample environment with the geometries used in conventional ALD reactors. The development will also open for the use of a wider range of precursors and growth protocols.

- [1] V. Miikkulainen et al., *J. Appl. Phys.* 113 (2013) 021301.
- [2] F. Zaera, *Coord. Chem. Rev.* 257 (2013) 3177.
- [3] B. A. Sperling et al. *Appl. Spectrosc.* 67 (2013) 1003.
- [4] K. Devloo-Casier et al., *J. Vac. Sci. Technol.* 32 (2014) 010801.
- [3] S. Chaudhary et al., *J. Phys. Chem. C* 119 (2015) 19149.
- [4] A. R. Head et al., *J. Phys. Chem. C* 120 (2016) 243.
- [5] R. Timm et al., *Nature Commun.* 9 (2018) 412.

4:40pm **TF+2D+AP+EL+SS-MoA10 Kinetics during TMA-H₂O ALD: The Possible Role of Cooperative Surface Reactions**, *Brent Sperling*, *B. Kalanyan*, *J.E. Maslar*, National Institute of Standards and Technology (NIST)

Until recently, the CH_3 groups produced by surface reactions of trimethylaluminum (TMA) during atomic layer deposition were widely believed to always be highly reactive toward H_2O , but *in situ* measurements have shown this is not the case below about 200 °C.[1] At these temperatures, some CH_3 groups react slowly, and a significant amount persists from cycle to cycle under typical growth conditions. Interestingly, these persistent CH_3 groups are not incorporated as carbon impurities. We have observed these CH_3 groups using *in situ* reflection infrared spectroscopy and have confirmed low carbon concentrations in our films using *ex situ* XPS. Furthermore, we have measured the kinetics of the reaction with H_2O and have found them to be well-described by a double-exponential decay function. A simple Monte Carlo simulation that incorporates cooperative effects by clustered surface reactants (as suggested by DFT calculations[2]) reveals that a double-exponential decay of coverage can result even when only one species of reactant is present. Furthermore, the short-range distributions of coverage that result in the simulation differ from purely random ones. This difference implies that measurements sensitive to dipole-dipole interactions when combined with an independent measurement of surface coverage could be used to confirm or disprove the cooperative reaction model.

[1] V. Vandalon and W. M. M. Kessels, *J. Vac. Sci. Technol.* A35 (2017) 05C313

[2] M. Shirazi and S. D. Elliott, *Nanoscale*7 (2015) 6311.

5:00pm **TF+2D+AP+EL+SS-MoA11 Atomic Layer Deposition of Metal Sulfides: Growth and Surface Chemistry**, *Xinwei Wang*, Shenzhen Graduate School, Peking University, China

Atomic layer deposition (ALD) of metal sulfides has recently aroused great interest, and many new sulfide ALD processes have emerged during the past several years. Surface chemistry plays a key role in ALD, but it remains yet to be investigated for many recently developed sulfide ALD processes. In this representation, I will report our study on the growth and surface chemistry of the ALD of nickel, iron, and cobalt sulfides, using various *in situ* characterization techniques of X-ray photoelectron spectroscopy (XPS), low-energy ion scattering (LEIS), quartz crystal microbalance (QCM), and quadrupole mass spectrometry (QMS). For instance, nickel sulfide (NiS) can be deposited from a Ni amidinate precursor ($\text{Ni}(\text{amd})_2$) and H_2S by ALD (*Chem. Mater.* (2016) 28, 1155), but the surface chemistry of this process is found to deviate from the conventional ligand-exchange ALD scheme, and a formation of a nonvolatile acid-base complex from acidic surface sulfhydryl and basic amidine is suggested during the H_2S half-cycle (*J. Phys. Chem. C* (2018) 122, 21514). The initial ALD growth of NiS on a SiO_2 surface is also intriguing, as the initial growth mechanism is found to be rather different from that in the later steady film growth. In the initial ALD cycles, the XPS results show a drastic cyclic variation of the signals for the Ni-O bonds, with prominently observable Ni-O signals after each $\text{Ni}(\text{amd})_2$ dose but almost negligible after the subsequent H_2S dose. These results suggest that the Ni-O bonds are first formed on the surface in the $\text{Ni}(\text{amd})_2$ half-cycles and then mostly converted to NiS in the following H_2S half-cycles. To describe this initial ALD growth process, a reaction-agglomeration mechanistic scheme is proposed (*Chem. Mater.* (2019) 31, 445). Surface thermolysis study of the Ni amidinate precursor further reveals the temperature-dependent behavior of the film growth.

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