Thin Films Division
Room 316 - Session TF1+AP-WeA
Manufacturing and Scale-Up of CVD and (Spatial) ALD

Moderators: Joe Becker, Kurt J. Lesker Company, **Marceline Bonvalot**, Grenoble Alpes University, France

2:20pm **TF1+AP-WeA-1 Optimizing Vapor Delivery of a Nickel Diazadienyl Complex for Nickel Metal Atomic Layer Deposition***, J. Maslar, **Berc Kalanyan**,* NIST-Gaithersburg*; V. Dwivedi,* NASA*; D. Moser,* EMD Electronics

Nickel metal films find applications in numerous areas, including microelectronics and heterogeneous catalysis.In the case of microelectronics in particular, a nickel metal thermal deposition process that can produce high-purity, thin, conformal films at low deposition temperature is highly desirable.Atomic layer deposition (ALD) is widely used to deposit thin, conformal films when suitable precursors are available.However, because nickel is an electropositive metal, many of the combinations of reducing agent and metal precursor classes employed in more traditional metal thermal ALD processes are not suitable for Ni ALD.In contrast, transition-metal diazadienyl complexes represent a class of precursors that has been used successfully for metal thermal ALD, with the deposition of nickel films achieved using bis(1,4-di-*tert*-butyl-1,3-diazadienyl)nickel [Ni(DAD)$_2$].[1]A complicating factor in the reproducible deposition of nickel metal films with Ni(DAD)$_2$ is that this precursor is a solid at typical delivery temperatures and, in general, delivering a constant flux of a solid precursor can be difficult.Flux variations may not be an issue for an ideal ALD process unless the total precursor dose is insufficient to saturate all surface reactive sites, however, it is not clear what delivery conditions are necessary to provide consistently saturating Ni(DAD)$_2$ doses.The goal of this investigation is to optimize Ni(DAD)$_2$ delivery for nickel ALD and to identify any factors that may lead to irreproducible delivery.To achieve this goal, the dependence of the flux of both Ni(DAD)$_2$ and the DAD ligand (the primary decomposition product under the conditions of this study) on delivery conditions was characterized.The flux of each species was measured simultaneously using a two-channel gas analyzer which employed a broadband ultraviolet-visible source, a beam splitter, bandpass filters for wavelength isolation, and avalanche photodiode detectors.While the results of this investigation specifically apply to Ni(DAD)$_2$ delivery, it is expected that these results should also provide insight into optimizing delivery of other transition-metal diazadienyl complexes, as well as solid precursors in general.

[1] Kerrigan, M. M.; Klesko, J. P.; Blakeney, K. J.; Winter, C. H. Low Temperature, Selective Atomic Layer Deposition of Nickel Metal Thin Films. *ACS Appl. Mater. Interfaces* 2018, 10, 14200−14208.

2:40pm **TF1+AP-WeA-2 Mechatronic Spatial Atomic Layer Deposition: Model-Informed Design for Scalable Manufacturing***, **Daniel Penley**, T. Cho, O. Trejo, K. Barton, N. Dasgupta,* University of Michigan, Ann Arbor

Spatial atomic layer deposition (SALD) holds promise to address the large-scale manufacturing needs of interfacial engineering at the nanoscale. However, the many SALD systems are limited in their ability to tune and dynamically control the full range of key process parameters, such as the depositor head and substrate gap size and parallel alignment. This lack of mechatronic control limits the ability to examine the coupled chemical, thermal, and transport phenomena as a function of SALD process parameters. Additionally, there have been several previous efforts to computationally model the SALD processes. However, there is a general lack of experimentally-validated models to verify the effects of systematically tuning the multitude of process parameters during SALD growth.

Herein we describe a customized SALD system that enables mechatronic control of key process parameters. A showerhead depositor design effectively delivers precursor to the substrate surface while stepper motors and capacitive probes maintain gap size and parallel alignment through multiple axis tilt and closed-loop feedback. Precision motorized stages control the substrate velocity and positioning, *in situ* monitoring actively controls the gas flow rates, and a thermal management system controls process temperature. We developed a three-dimensional COMSOL Multiphysics model to understand the pressure, velocity, and concentration fields of the precursor gas flow within the system geometry. The capability to tune process parameters both physically and digitally allows for the unique ability to experimentally validate and parameterize the computational model to gain further insight into the otherwise difficult to access process area of close-proximity SALD. Using this linked experimental and modeling approach, we demonstrate the model's ability to predict resulting films from the mechatronic SALD system. With the experimentally-validated model and system, we present a study of the impact of SALD process parameters on the uniformity and quality of deposited SALD films. We then broaden our findings to discuss design implications SALD system design on the manufacturing tradeoffs of quality-throughput-cost-sustainability.

3:00pm **TF1+AP-WeA-3 Atmospheric Pressure Spatial ALD of Al-Doped ZnO: Co-injection vs. Supercycles***, **Mike van de Poll**, B. Macco, E. Kessels,* Eindhoven University of Technology, Netherlands

Atmospheric pressure spatial atomic layer deposition (ALD) is particularly interesting for high volume, low cost applications, because of its exceptionally short deposition times compared to temporal ALD.

For doped and compound materials, such as transparent conductive oxides, the electrical and optical properties are typically closely related to their composition. This makes accurate compositional control essential for high quality films. Spatial ALD of doped and compound materials generally follows one of two approaches. Supercycles can be formed by alternating two ALD cycles with different precursors, where the ratio between both cycles determines the composition of the deposited film. Alternatively, in the so called co-injection approach, the precursors can be dosed simultaneously. Here, the composition is determined by the precursor flows ratio.

In this work, ZnO:Al thin films were deposited using spatial ALD, with diethylzinc (DEZ) and dimethylaluminum isopropoxide (DMAI) as zinc and aluminum precursors, respectively, and H_2O as co-reactant. The supercycle and co-injection approaches were used, and the cycle ratio and mixing ratio were varied to alter doping concentrations. The films were capped with a layer of Al_2O_3 to shield from the ambient, and to mitigate hydrogen effusion. Electrical and optical properties of the samples as-deposited, and after stepwise anneal, were extensively studied.

Co-injection and supercycles resulted in the successful deposition of ZnO:Al films with optical and electrical properties (e.g., resistivity = 1.73 mΩcm, mobility = 9.6 cm^2/Vs, carrier concentration = $3.75\cdot10^{20}$ cm^{-3}) similar to temporal ALD ZnO:Al. Furthermore, the extensive study of these approaches led to identification of their advantages and disadvantages. Co-injection results in films with low resistivity as-deposited, due to homogeneous distribution of dopants. However, obtaining low Al doping levels can be practically challenging because low DMAI flow is required. Meanwhile, supercycles give precise compositional control by changing the cycle ratio, but result in dopant planes with low doping efficiency, and post-deposition anneal is required. After annealing the results are similar to co-injection.

Currently, our work focusses on the innovative approach of co-injection supercycles. Here, pure DEZ and co-injection DEZ/DMAI cycles are alternated, allowing additional compositional control by tuning both the DMAI flow during the doping cycle, and the cycle ratio. With co-injection supercycles we aim to combine the advantages of both dosing approaches. Initial films have been deposited and the full study will be presented at the conference.

3:20pm **TF1+AP-WeA-4 Manufacturing of ALD-enhanced Li-ion Batteries via Particle ALD Coatings And R2R ALD on Separators***, **Markus Groner**, A. Dameron, B. Hughes, D. Lewis, J. Keene, M. Martinez, J. Burger, M. Rodgers, J. Ragonesi,* Forge Nano*; J. Li,* Oak Ridge National Laboratory, China*; W. Steenman, K. Livingston,* Oak Ridge National Laboratory

ALD processing equipment for coating anode, cathode, and separator materials at scale has been developed to demonstrate ALD-enhanced Li-ion battery manufacturing. The promising performance enhancements seem previously in coin cells for ALD coated anode and cathode powders are now being validated in pouch cells. Thin ALD coatings can stabilize graphite and NCM materials, yielding improved capacity retention and rate performance, especially at higher voltages. Particle ALD coating tools are available for coating powders at the tons-per-day scale, both in semi-batch and continuous ALD versions. Additionally, ALD coatings on separators enhance electrolyte wetting and thermal stability, which should lead to improvements in the time & energy intensive filling/formation/aging steps as well as safety. A true roll-to-roll ALD tool for coating separators with alumina ALD films has been designed and built. Over the next year, this R2R tool will be integrated with a slitter and a pouch cell stacker. The performance improvements of the ALD-coated anode and cathodes, combined with the benefits of R2R ALD-coated separator, promise reductions in the cost/time/energy of battery manufacturing via ALD-enhanced Li-ion batteries.

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