Thin Films Division
Room 316 - Session TF-TuM

Growth in 3D, High Aspect Ratio and Nanostructured Materials

Moderators: Adriana Creatore, Eindhoven University of Technology, Netherlands, **Richard Vanfleet**, Brigham Young University

8:00am **TF-TuM-1 Tailoring 3-D Nanomaterial Architectures Using ALD: Bridging Scales from Atoms to Bulk*, Neil Dasgupta,*** University of Michigan **INVITED**

As we move towards a vision of "materials by design" in the 21st century, the ability to rationally control hierarchical material architectures becomes increasingly critical. This is inspired by natural systems, which routinely achieve material properties that are not available in the bulk through precise ordering across several orders-of-magnitude in length scale. However, while there have been tremendous advances in self-assembly and additive manufacturing in three dimensions to create periodic structures such as meta-materials, as we move towards composite material architectures composed of multiple dissimilar materials, heterogeneous interfaces play an increasingly important role. In particular, integration of materials with significantly different mechanical, thermal, optical, and/or electronic properties into "bulk" hierarchical architectures requires atomically-precise and deterministic control of surfaces and interfaces.

In this talk, I will demonstrate examples of how Atomic Layer Deposition (ALD) is a key enabling technique to enable the rational design of hierarchical material systems. These atomically-precise surface modifications can be used to direct self-assembly processes, provide tunability of the optical, electronic, thermal, and mass transport properties of integrated material systems, and encapsulate structures to promote their stability in a wide range of environments. I will present examples of how ALD can enable hierarchically-structured materials by design, including three-dimensional solid-state batteries, photocatalysts for solar fuel conversion, multi-functional composites, and anti-fouling surfaces. I will further provide a perspective on how this versatile approach can lead to the design and scaled-up manufacturing of material systems with precision at length scales ranging from atoms to meters

8:40am **TF-TuM-3 Thin Film Technology and Diagnostics for Multilayered Solid-State Batteries*, Victoria Castagna Ferrari,*** *G. Rubloff, D. Stewart,* University of Maryland, College Park

Thin-film solid-state batteries (SSBs) can provide high-power performance with easy miniaturization and on-chip integration, but broader applications demand higher energy density. Thin film fabrication enables new cell architectures to achieve this. Using sequences of in-situ patterning and deposition, we were able to produce a multilayered battery in a 3D architecture like a prismatic pouch cell. The advantages of such unique design are: i) individual solid-state batteries can be small (µm to cm scale) and shaped to fit the application while providing faster charge and discharge; ii) a multilayered stack, where the cathode and anode layers are connected on either sides in parallel, minimizes passive structural material, thereby improving the total device energy density; and iii) applying multilayer shadow masking during sputtering avoids high-aspect ratio deposition challenges.

Prototypes of this prismatic battery with 1 and 3 layers were made using the sputtering tool to judge the scaling of discharge capacity and power performance. Thin films of silicon, LiPON, and lithiated vanadium oxide (LVO) were deposited as the anode, electrolyte, and cathode layers to produce a battery with tunable lithium content, without breaking vacuum during the entire fabrication sequence. As a final step, the whole SSB stack was post-annealed at 300 °C. A single-layer prototype device with area 0.15 cm^2 and total battery thickness 1µm was electrochemically active when cycled between 0 and 4 V. Charge-discharge testing showed an initial capacity of 50 mAh/g under fast rate (5C) with a Coulombic efficiency of 98 %.

Our initial multibattery device, comprising a three-battery stack, revealed rougher interfaces and susceptibility to delamination. SEM-cross-sectional images showed unexpected voids in the LVO/LiPON interface, suggesting side reactions and possible additional lithiation of the LVO from the LiPON layer. Clearly, understanding and controlling interfaces will be crucial to multilayered thin-film batteries. Hence, we have conceived a new diagnostic platform for developing multilayer SSBs comprised of new shadow masks configured to characterize properties of each active layer and interface, as well as the entire multibattery device, using electrochemical impedance spectroscopy (EIS) and equivalent circuit modeling of the full battery and its constituent components. As a preliminary result, we found that the LVO/LiPON interface represents the largest contribution to the total cell impedance. As simultaneous high power and high energy drive multibattery SSB architectures, revealing properties of individual interfaces and layers will be crucial to success.

9:00am **TF-TuM-4 Interface Mixing in Thin-Film Solid-State Sodium Batteries*, Blake Nuwayhid,*** *A. Kozen,* University of Maryland*; D. Long,* Air Force Research Laboratory, USA*; G. Rubloff, K. Gregorczyk,* University of Maryland

Nanostructured solid-state batteries (SSBs) are poised to meet the demands of next-generation energy storage technologies, with atomic layer deposition (ALD) being a powerful tool enabling high-performance nanostructured SSBs that offer competitive performance with their liquid-based counterparts. Furthermore, switching from lithium-ion batteries to those based on the more abundant sodium-ion charge carrier is an attractive route to decrease costs. Recently, we developed an ALD process for sodium phosphorus oxynitride (NaPON) as a solid-state sodium ion electrolyte.[1] NaPON proved to be an effective solid-state electrolyte (SSE) with an ionic conductivity of 1.0 x 10^{-7} S/cm at 25 °C and a wide electrochemical stability window of 0-6.0 V vs. Na/Na^+. In this presentation, thin-film solid-state sodium batteries are explored, in which NaPON is paired with a V_2O_5 cathode and a thermally evaporated Na metal anode. Electrochemical analysis of the SSB suggests intermixing of the NaPON/V_2O_5 layers during fabrication. We investigate this interfacial reactivity in three ways: with *in-situ* spectroscopic ellipsometry, time-resolved XPS depth profiling, and cross-sectional cryo-TEM. We characterize this reaction during the ALD NaPON deposition on V_2O_5 to be two-fold: (1) reduction of V_2O_5 to VO_2 and (2) Na^+ insertion into VO_2 to form Na_xVO_2. The Na metal evaporation process is found to intensify this reaction, resulting in the formation of irreversible interphases between discrete battery layers. Despite the mixed interphases formed during fabrication, the SSB can operate for over 100 cycles and represents the first demonstration of a functional thin-film solid-state sodium-ion battery. This work highlights the high reactivity of Na compared to Li-based battery chemistries, not only necessitating the need for interfacial coatings in Na-SSBs, but also helps to define design rules required during fabrication of Na-SSBs or liquid Na-ion batteries.

1. Nuwayhid, R. B.; Jarry, A.; Rubloff, G. W.; Gregorczyk, K. E., Atomic Layer Deposition of Sodium Phosphorus Oxynitride: A Conformal Solid-State Sodium-Ion Conductor. *ACS Applied Materials & Interfaces* **2020,***12* (19), 21641-21650.

9:20am **TF-TuM-5 Direct CVD Synthesis of MgH_2 Thin Films and Nanowires by Decomposition of the Novel Magnesium *Bis*-Diamidodiboranate Precursor*, Laurent Souqui,*** *C. Caroff, S. Shrivastav, G. Girolami, J. Abelson,* University of Illinois at Urbana-Champaign

MgH_2 is a wide-bandgap light-weight dielectric which can be fully dehydrogenized to form metallic Mg above 410 °C. For these reasons, it has been extensively studied as a potential material for switchable windows and for hydrogen storage and fuel cells, and as a passivation layer for Si-based photovoltaic devices. Compared to common synthesis routes to MgH_2, such as high energy ball milling and liquid phase nanoconfinement, chemical vapor deposition (CVD) allows reduced synthesis time and process scalability with precise control of grain size and distribution to afford ultrathin layers. Unlike sputtering and evaporation, CVD is not a line-of-sight technique; at low deposition temperature, limited precursor reactivity produces highly conformal deposition on complex morphologies and structures. In the present work, a new CVD precursor, magnesium *bis*-diamidodiboranate ($Mg[N(Me)_2\text{-}BH_2\text{-}N(Me)_2\text{-}BH_3]_2$, $Mg(NBNB)_2$), was designed for clean reactivity at low temperatures. We report the direct synthesis of α-MgH_2 thin films by CVD from $Mg(NBNB)_2$ in the range 80-350 °C and 10-60 mTorr, affording growth rates of 1.9 to 11.3 nm/min. In contrast with earlier works, which utilized the composition of the gas phase to infer the synthesis of MgH_2 from alkyl magnesium precursors, we document the formation of MgH_2 using thin film characterization techniques.

We found that only the mass-transport-limited regime could be accessed even at the lowest deposition temperature, indicating that the reaction

sequence of the precursor with the growing MgH_2 surface has relatively low energy barriers. This is in contrast with the interaction of the precursor with the substrate surface, as a significant nucleation delay was observed, lasting from 7 min at 170 °C to 20 min at 350 °C. We suggest that this delay is due to an increasing desorption rate of the precursor, an increasing instability of initial nuclei or an increasing diffusion rate of Mg into the substrate. The crystallinity of the films was found to be independent of the temperature and was mostly affected by the precursor partial pressure. Above 170 °C the morphology of the films changes from granular to a percolated network of islands and nanowires grew extensively above 200 °C. These nanowires were found to be 50 nm in diameter, which makes them interesting for application in hydrogen storage. The refractive index and absorption coefficient were found to be dependent both on deposition pressure and deposition temperature, this behavior is attributed to the tendency of MgH_2 to form H vacancies at high vacuum and high temperature conditions.

9:40am **TF-TuM-6 The Fabrication of Heterojunctions by Atomic Layer Deposition for Gas Sensing Applications***, **Nicola Pinna**, H. Raza,* Humboldt University Berlin, Germany

Material and methods for detecting a wide range of harmful species are becoming increasingly necessary as automation and industrial growth increase. Chemoresistive gas sensors using semiconducting metal oxides (SMOX) are fundamental for developing efficient gas sensors. The sensitivity and selectivity of these nanostructured SMOX can be boosted by combining them with other SMOX. Yet control over the thickness of the shell layer is crucial; particularly, a thin shell layer modulates the space charge layer at the interface, thereby influencing effectively the charge conduction channel. The engineering of heterojunctions with well-defined core and shell layers is required to better understand the sensing response of heterostructured nanomaterials. A comprehensive understanding of the role of semiconductor heterojunctions and the sensing response of core-shell heterostructures is achieved by synthesizing a series of well-defined and well-controlled heterostructures with varying core and shell layers. NiO- and SnO_2-based hierarchical coaxial core-shell heterostructures are therefore proposed to achieve this objective. The designed heterostructures exhibit sensing responses related to the NiO or SnO_2-shell layers, or in some cases to the heterojunctions between $_n$SMOX (SnO_2) and $_p$SMOX (NiO). A comparison of the sensing response in order to understand the transduction mechanism across the interfaces in atomic layer deposition grown heterojunctions will be presented.

11:00am **TF-TuM-10 Tunable ALD Infiltration into High-Aspect-Ratio Aerogels Enabled by Process Modeling for Solar Thermal Applications***, **Andrew J. Gayle***[1]*, Z. Berquist, Y. Chen, A. Davoodabadi, A. Hill, J. Hoffman, A. Bielinski, A. Lenert, N. Dasgupta,* University of Michigan, Ann Arbor

ALD provides a unique opportunity to impart conformal surface functionalization onto ultra-high-aspect-ratio structures, but depositions are complicated by precursor diffusion and dosing limitations. ALD modifications on substrates such as aerogels help enable their use in fields such as concentrated solar thermal (CST), catalysis, and filtration. SiO_2 aerogels possess a unique combination of desirable properties for CST applications, including high optical transparency and low thermal conductivity, but they suffer from poor stability at elevated temperatures. In this work, we investigate the ALD conditions needed to conformally modify SiO_2 aerogel monoliths (AMs) with aspect ratios >60,000:1 [1]. To minimize precursor waste during the long diffusion times necessary to conformally modify the AMs, we implemented a multi-dose-quasi-static-mode (multi-dose-QSM) deposition procedure. In standard QSM recipes, reactor pumping is halted during an “exposure step”, allowing precursor to diffuse into a structure without being purged. In the multi-dose-QSM technique, multiple doses and exposure steps of a single precursor are implemented prior to dosing the counter reactant. This was necessary due to the large surface area of the AMs.

To enable tunable ALD infiltration depths into the AMs, we developed a model of the multi-dose-QSM deposition process. Our model accounts for precursor depletion in the ALD chamber during an exposure step and the effect of multiple precursor doses. This model also allowed for the optimization of the ALD modification process, including precursor usage efficiency and total process time.

SEM-EDS was used to quantify the ALD infiltration depth to validate the model. ALD saturation was further confirmed using mass gain measurements. The ALD-modified AM also showed improved resistance to structural degradation at elevated temperatures, likely due to stabilization of the SiO_2 nanoparticles. These changes may be due to the formation of a ternary Al-Si-O phase at the interface between the SiO_2 backbone and Al_2O_3-based modification, as shown using XPS measurements. This leads to an improved retention of the low thermal conductivity and high transmittance following annealing, compared to bare SiO_2 AMs. This combination of properties makes the ALD-modified AMs a promising transparent insulating material for CST applications [2]. ALD-modified AM synthesis is currently being scaled up from ~25.4 mm-diameter discs to ~155 x 65 mm tiles for use in a prototype CST receiver.

[1] A. J. Gayle, Z. J. Berquist et al. *Chem. Mater.* **2021**, *33* (14), 5572-5583.

[2] Z. J. Berquist, A. J. Gayle et al. *Adv. Func. Mater.* **2022**, 32 (12), 2108774.

11:20am **TF-TuM-11 Ultra-thin, Conformal ALD Films for Reliable Corrosion Resistance in SLM Metal Additive Manufactured Surfaces***, **Timothy J. Gorey**,* Los Alamos National Laboratory

Metal additive manufacturing (MAM) is a valuable method for prototyping and circumventing the geometry constraints of conventional manufacturing methods, such as machining or extrusion. The field of MAM is still relatively novel, and aging properties, such as unpredictable corrosion resistance, hinder widespread application and reliable interchangeability with traditionally manufactured parts. Here, we utilize the self-limiting deposition method of atomic layer deposition (ALD) to apply ultra-thin, conformal anti-corrosion barriers onto monolithic 316L stainless steel surfaces. Substantial improvement in corrosion reliability was repeatedly obtained on single-surface, proof-of-concept coupon samples for thicknesses ranging from a few to hundreds of nanometers. This presentation will discuss the unique advantages and nuances of ALD and its relevance to MAM components. Corrosion results for coated and uncoated MAM 316L surfaces will also be discussed that predict ALD to be a viable post-manufacturing approach in MAM parts.

11:40am **TF-TuM-12 Atomic Layer Deposition of Superconducting Films for Through-Silicon-Via Structures and Photon Detection***, **John Femi-Oyetoro**, H. LeDuc, P. Day, F. Greer,* Jet Propulsion Laboratory (NASA/JPL)

Superconductors traverse to normal metal behavior in the millimeter-far-IR wavelength range as consistently described in the Bardeen-Cooper-Schrieffer (BCS) theory. This property has been explored and leveraged upon in Astrophysics, for detecting the early universe in the millimeter-far-IR spectrum, where radiation appears to be the strongest. The first light emitted after the Big Bang approximately 14 billion years ago can still be detected as the cosmic microwave background (CMB), and superconductors have aided this effort. Superconducting (SC) detectors are essential and have scientific opportunities in solving key problems in astronomy and cosmology. To buttress, at Jet Propulsion Laboratory, SC transition edge sensors have been deployed at the South Pole, including the Background Imaging of Cosmic Extragalactic Polarization (BICEP) telescopes and the Keck Array. These instruments have performed CMB polarization measurements with great sensitivity to the signatures of the early universe. In addition, kinetic inductance SC detectors are been utilized in future missions and concepts such as the Terahertz Intensity Mapper (TIM) balloon experiment and Galaxy Evolution Probe (GEP) for integral field spectroscopy. In this work, we demonstrate the deposition of high-quality SC films such as titanium nitride (TiN) with high transition temperature and kinetic inductance for high-density through-silicon-via (TSV) structures for large photon detectors arrays. SC films provides outstanding sensitivity, mature fabrication, and large array sizes, for multiplexing and hybridization techniques. However, while conventional sputtering technique have been useful in fabricating SC detectors, atomic layer deposition (ALD) has provided an advantage of spatial uniformity and conformality. These properties are absent in sputtering techniques. We employed ALD to control the repeatability, composition and thickness, which plays a role in the transition temperature of SC films. These possibilities have an advantage to explore different SC materials for specific detection application in future science observations. We also explored different precursors and deposition conditions, including temperatures as low as 200 °C. In a nutshell, we are interested in TSV SC films with spatial uniformity, high-aspect-ratio and high transition temperature, that will overcome the challenges of interconnect density using 3D integration. We believe that, extending these integration techniques to SC detectors are very crucial in the 3D hybridization of high-density pixel detector arrays with outstanding sensitivity. Results aiding these TSV structures for SC detectors will be discussed.

[1] **TFD James Harper Award Finalist**

12:00pm **TF-TuM-13 Reliable RF and DC Plasma-Power Solutions Supporting Today's Demanding Industrial Applications***, **Mike Meyer**, P. Maloney,* Advanced Energy Industries, Inc., USA

Process stability, reliability, and repeatability are key to optimizing yield in advanced plasma-based applications. As these processes become more complex, involving numerous steps and rapid plasma transitions, accurate control of the power to ignite, maintain, and manipulate the plasma becomes increasingly critical. This presentation describes developments in RF and DC power-delivery technologies and techniques that enable these demanding manufacturing applications, including bipolar DC pulsing with customizable waveforms, and RF-power phase synchronization, real-time impedance management, customizable arc management, and waveform controls. It also explains how real-time access to power-delivery data and analysis provides intelligence that engineers and operators can apply immediately to refine process performance, as well as to predict and perform maintenance. Ultimately, combining the described power hardware with these critical insights can maximize yield and minimize downtime – crucial capabilities for today's semiconductor, glass, FPD, solar, and industrial applications.

Presenters:

Mike Meyer is a senior product manager at Advanced Energy with 23 years of experience in the precision thin-film industry, including eight years with RF and DC power systems for PVD, PECVD, and a variety of industrial, plasma-based, thin-film deposition applications. He also spent 15 years in the precision optical-coating industry specializing in ion-beam sputtering technology and complete optical coating system solutions.

Paul Maloney has four years of experience in the precision thin-film industry working with Advanced Energy plasma power products. He currently leads the DC Product Management team and is developing next-generation DC and pulsed-DC power supplies. He previously worked in the defense industry and has an educational background in nuclear engineering.

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