Thin Film
Room 105A - Session TF+EM-MoA
ALD for Energy Conversion and Storage
Moderators: Virginia Wheeler, U.S. Naval Research Laboratory, Angel Yanguas-Gil, Argonne National Laboratory

1:40pm TF+EM-MoA1 Fabrication of Nano-power Generators using Thin Atomic Layer Deposited Films, Giovanna Scarle, H.S. Mann, B.N. Long, James Madison University; V.D. Wheeler, Naval Research Laboratory; B.C. Utter, Bucknell University

Infrared power generation is emerging as a useful method to harvest infrared (IR) light and transform it into usable energy available day and night. So far, this method is implemented using bulk power generator (PG) devices, neglecting any effort to improve the materials employed as their active element. Here we initiate this effort by fabricating thin thermoelectric TiO$_2$/TiN multilayer films via atomic layer deposition (ALD) and focusing on the exploration of the effects of film resistance on the voltage produced by nano-PG devices with these films as their active elements. By changing the number and thickness of the TiO$_2$/TiN layers, we control the sheet resistance ($W/\Omega$) over three orders of magnitude. We observe that the voltage produced by nano-PG devices linearly increases with the thin multilayer films resistance, especially in the $W/\Omega$ range. On the contrary, we measure an almost constant voltage jump versus film resistance when we excite the nano-PG device through Joule heating. The observed behavior suggests that the nano-PG device works effectively when mimicking the mechanism of a capacitor, similar to the case of a bulk device. Our studies pave the way to improving the properties of nano-PG devices by improving the properties of the active materials in the form of thin films fabricated via ALD.

2:00pm TF+EM-MoA2 Ultrafast Triggered Transient Energy Storage by Atomic Layer Deposition Into Porous Silicon for Integrated Transient Electronics, Anna Douglas, N. Murudhiran, R.E. Carter, K. Share, C.L. Pint, Vanderbilt University

We demonstrate the first on-chip silicon-integrated rechargeable transient power source based on atomic layer deposition (ALD) coating of vanadium oxide (VO$_x$) into porous silicon. A stable specific capacitance above 20 F g$^{-1}$ is achieved until the device is triggered with alkaline solutions. Due to the rational design of the active VO$_x$ coating enabled by ALD, transience occurs through a rapid disabling step that occurs within seconds, followed by full dissolution of all active materials within 30 minutes of the initial trigger. This work demonstrates how engineered materials for energy storage can provide a basis for next-generation transient systems and highlights porous silicon as a versatile scaffold to integrate transient energy storage into transient electronics.


One of the most economically viable methods for solar power uses an array of mirrors to concentrate sunlight onto a central receiver tower. The receiver surface heats up, and this heat is used to drive turbines that generate electricity. To improve the efficiency of these “power tower” facilities, the receiver must operate at higher temperatures and this requires developing high performance coatings. These coatings must be spectrally selective in order to absorb all of the visible light while emitting as little infrared radiation as possible (low emissivity). In addition, these coatings must be refractory to endure decades of high temperature operation under ambient conditions. We are pursuing a novel strategy to develop refractory solar selective coatings using ALD. Our strategy uses thin film nanocomposites composed of conducting metallic nanoparticles in a dielectric matrix. These films are prepared by combining the ALD processes for a metal (e.g. W using SiH$_4$/WF$_6$) with that of an oxide (e.g. Al$_2$O$_3$ using TMA/H$_2$O$_2$). The resulting nanocomposites have tunable optical properties that can be adjusted to achieve a high solar selectivity. In addition, we use these ALD coatings to infiltrate inverse opal scaffolds which serve as photonic crystals to further enhance the spectral selectivity. In this presentation I will discuss our ongoing work synthesizing and characterizing these refractory solar selective coatings. In particular, I will describe in situ quartz crystal microbalance, mass spectrometry, and infrared spectroscopy measurements performed to elucidate the unusual surface chemistry for these ALD nanocomposites, and discuss the relationships between the composition and the optical/ electrical properties of these films. I will also describe the results of finite difference time domain modeling to understand how the photonic scaffold modulates the spectral selectivity, and finally I will report on the high temperature performance of these coatings.

2:40pm TF+EM-MoA4 Sequential Infiltration Synthesis of Doped Polymer Films with Tunable Electrical Properties for Efficient Triboelectric Nanogenerator Development, Yanhao Yu*, X.D. Wang, University of Wisconsin-Madison

Triboelectric nanogenerator (TENG) is rising as a promising technology for converting mechanical energy into electricity with merits of high output, simple design and low cost. The working principle of TENG is based on the combined effect triboelectrification and electrostatic induction. According to this mechanism, controlling the charge density on the triboelectric surface is the most fundamental strategy for improving the performance of TENG. Noting that a surface modification of triboelectric polymer is the predominant approach to regulate the charge density. However, operation of TENGs requires intimate contact and sometimes friction between triboelectric materials, which inevitably induces wearing of surface. In this regard, surface modification/engineering yields little contributions toward the performance gain in long-term operation. Therefore, one essential solution is to extend the property engineering from mere surface to the bulk of material.

Atomic layer deposition (ALD) is a powerful thin film growth technique on the basis of sequential self-limiting surface reactions. When implemented to certain polymers, the large permittivity of metalorganic precursors allows deep infiltration of inorganic compounds during ALD process, leading to inorganic/organic hybrid materials. This process is known as sequential infiltration synthesis (SIS). It has been successfully used to convert block co-polymer nanopatterns into more durable inorganic patterns and to improve the polymeric lithography resistance to subsequent etching. Inspired by these developments, we expect SIS could effectively tailor the internal composition and electrical properties of polymer films, which may provide an ultimate solution for triboelectric material design in the development of high-performance TENGs. Here, we report an internal ALD doping of several polymers via SIS, including polydimethylsiloxane (PDMS), polyimide (Kapton) and poly(methyl methacrylate) (PMMA).[1,2] We showed that SIS can introduce ALD, molecules $\sim$3 $\mu$m deep into these polymers, which effectively tuned the bulk electrical property of the film. TENG devices using the modified polymer films exhibited enhanced power output; and this enhancement remained effective after the surface of polymer film was polished off for more than 2 $\mu$m. This polymer doping approach opens a new route to bulk electrical property modification of polymer films, demonstrating a promising strategy for improving the performance of functional polymer based devices, such as TENGs.

Reference

3:00pm TF+EM-MoA5 ALD for Interfacial Engineering of Energy Conversion Devices, Neil P. Dasgupta†, University of Michigan, Ann Arbor

INVITED

Recently, there has been a dramatic increase in research of nanoscale materials for energy conversion and storage applications due to several advantageous features such as high surface areas, short transport distances, novel optical phenomena, and tunable material properties. However, with these benefits come challenges. In particular, the ability to precisely control the properties of surfaces and heterogeneous interfaces at the nanoscale limits the performance of many of these devices, and requires novel approaches. This problem becomes increasingly important as dimensions decrease, as the surface-to-volume ratios continually increase with decreasing feature size.

One technique that has been increasingly explored for surface and interfacial engineering of nanostructured energy conversion and storage devices is Atomic Layer Deposition (ALD). This gas-phase process allows for highly conformal deposition of a wide variety of materials with sub-nm precision in material thickness and tunable chemical composition. A wide range of materials, including oxides, sulfides, and metals can be deposited by ALD. The combination of conformality and thickness control of ALD

† TFD James Harper Award Finalist
‡ Paul Holloway Award Winner
facilitates precise tuning of the electronic, optical, thermal, and chemical properties to optimize their interfaces in energy conversion devices. This talk will present several examples of using ALD to fabricate highly-controlled interfaces for energy conversion and storage devices. Examples include batteries [1], photovoltaics [2-3], and photoelectrochemical cells [4-5]. The key theme linking these studies is that through deterministic control of interfacial layer composition, thickness, crystallinity, and morphology, we can “program” properties such as charge transfer resistance, catalytic activity, and chemical stability. This control enables interfacial materials engineering to optimize both device efficiency and lifetime. The importance of fully understanding ALD surface chemistry will be discussed from a theoretical and experimental perspective. The talk will conclude with a perspective on future directions and challenges for widespread commercial adaption of these technologies.


4:00pm TF+EM-MoA8 Anchoring Down Soluble Polysulfides for Lithium and Sodium Sulfur Battery Cathodes using Atomic Layer Deposition, Rachel Carter, A.P. Cohn, L. Oakes, N. Muralidharan, A.E. Douglas, K. Share, C.L. Pint, Vanderbilt University

Among the most significant challenges for practical lithium or sodium sulfur batteries is polysulfide shuttling, where intermediate discharge products (e.g. Li$_2$S, M_xS_y and M_S) dissolve into the electrolyte lowering active sulfur mass and fouling the metal anode. To overcome this, we demonstrate the use of atomic layer deposition (ALD) to produce thin oxide coatings on cathode materials to stabilize these soluble polysulfides and mitigate active material loss. We specifically focus on V$_2$O$_5$ (vanadium pentoxide) due to its demonstration in recent theoretical studies to exhibit strong polar interaction with soluble polysulfides that exceeds other oxide materials. With the application of the V$_2$O$_5$ binding interlayer the initial discharge capacity of the sulfur cathodes is enhance by 20%, which is a direct result of anchoring the soluble species for optimal complete discharge of the sulfur. The capacity retention of the sulfur cathode is enhanced to 87% capacity retention over 100 cycles, in comparison to less than 50% retention without ALD binding layer. The binding effect was also probed using UV-Vis analysis, since there are distinct absorption peaks for the soluble S$_2^{2-}$ state in the electrolyte. Solutions of Li$_2$S and Na$_2$S we studied before and after exposure to ALD binding layers with dramatic decrease in the S$_2^{2-}$ signature in solution observed proving the binding interactions between the polysulfides and V$_2$O$_5$ binding interlayer. Overall, our work shows how ALD is a versatile tool to atomically engineer surfaces to sustain excellent performance without compromising the gravimetric performance needed for practical battery applications.

4:20pm TF+EM-MoA9 Hybrid Inorganic-Organic Thin Films by ALD/MLD for Emerging Energy Technologies, Maarit Karppinen, Aalto University, Finland

INVITED

For hybrid inorganic-organic materials it is in principle possible to realize properties not seen for conventional materials. An elegant, yet industrially feasible way to link the inorganic and organic entities via strong chemical bonds to form coherent multi-layered hybrid materials is to combine the ALD (Atomic Layer Deposition) technique originally developed to deposit high-quality thin films of simple inorganic materials with MLD (Molecular Layer Deposition) cycles based on organic precursors. This enables the atomic/molecular layer-by-layer production of inorganic-organic hybrid thin films through sequential self-limiting gas-surface reactions with high precision for the film thickness and composition.

In this talk I will discuss our recent efforts towards synthesizing new functional materials by the combined ALD/MLD technique. In particular, we have fabricated oxide-organic thin-film superlattices in which the periodically introduced single/thin organic layers between oxide layers are designed to hinder phonon transport and substantially enhance the thermoelectric properties of (Zn,Al)O$_2$ and (Ti,Nb)O$_4$ films. Other exciting application areas foreseen for the ALD/MLD hybrid thin films include the flexible and transparent Li-ion microbattery materials and so-called metal organic framework (MOF) materials.
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