Thin Films Division
Room 104B - Session TF2-MoM

IoT Session: Thin Film Processes for Energy Storage
Moderators: Virginia Wheeler, U.S. Naval Research Laboratory, Paul Poodt, Holst Centre / TNO

8:20am **TF2-MoM-1 Thin Films for Next Generation Batteries**, *Brecht Put*, Imec, Belgium; *S Hollevoet, N Labyedh,* KULeuven & Imec, Belgium; *M Debucquoy,* Imec, Belgium; *E Kessels, M Creatore,* Eindhoven University of Technology, The Netherlands, Netherlands; *P Vereecken,* KULeuven & Imec, Belgium INVITED

Li-ion batteries are enabling the increase in electrical vehicles, local energy storage systems and the recent revolution in portable electronics. In this talk we will focus on the application of atomic layer deposition (ALD) in two different battery systems, namely: the (3D) thin film battery and the all-solid-state bulk battery system. Each of these systems has its own specific advantages and limitations.

Thin film batteries are required for on chip energy storage. They are expected to fuel the onset of the internet of things, wireless sensor networks, etc. The ion storage capacity of such a battery is limited due to the usage of thin electrode films (<1µ m), however they can be recharged rapidly (within minutes). To increase the Li-ion storage capacity, a high aspect ratio structure can be employed. Clearly, the coating of such structure must be done in a conformal, pin-hole free way. We will discuss the latest developments in the usage of ALD to coat such structures. In addition, we will show that nanoscaling of different electrode materials can increase the Li-loading by removing kinetic limitations seen in bulk materials. Among the materials that will be discussed are TiO_2, LiPON, $LiMn_2O_4$, and their respective planar and 3D half cells.

When considering bulk energy storage systems, the focus is shifting from 'wet' Li-ion cells to the all-solid-state batteries. These all solid cells are expected to improve safety and energy density. The elimination of the flammable organics, present in the commonly used liquid electrolyte, removes the threat of leakage and reduces the fire hazard. The energy density on the other hand is increased by introducing high voltage electrode materials or a lithium metal anode. However, currently no electrolytes exist that can provide durable cell cycling when using such electrodes. This is attributed to the limited electrochemical voltage window of most electrolytes, leading to reaction at the interfaces. To avoid such unwanted side reactions, a protective coating can be applied. Protective coatings or buffer layers have already been widely explored in batteries with liquid electrolytes. The deposition of such layers can be considered the most common application field for ALD in batteries. The thin-film buffer coatings on the electrodes prevent reaction between the electrode material and the electrolyte. At present, fully electron and ion blocking layers like Al_2O_{-3} are used. We will show that the ideal buffer coating should be selected based on the required stability window, ionic and/or electronic conductivity, and uniformity. We will discuss the deposition of protective coatings like e.g. TiO_2, Al_2O_3 and LiPO(N).

9:00am **TF2-MoM-3 Radical Enhanced Atomic Layer Deposition of Cobalt Oxide Based Electrodes for 3D Lithium-ion Battery Applications**, *Ryan Sheil, J Lau, B Dunn, J Chang,* University of California at Los Angeles

Lithium-ion batteries have been an enabling factor in the success of consumer electronics and have the potential to offer energy storage solutions for microelectromechanical systems (MEMS). Current thin film battery technology consists of a two-dimensional planar stack of materials characterized by poor volumetric utilization where large areal footprints are required to supply the needed energy and power for device operation. Moving away from these traditional two-dimensional batteries towards next generation three-dimensional battery architectures (e.g. cylindrical arrays, interdigitated plates, etc.) allows for an effective decoupling of the areal energy and power density resulting in improved areal footprint utilization. In 3D architectures, the short distances between the anode and cathode improve the transport properties allowing for high areal power densities and the high aspect-ratio nature of the electrodes promotes high areal energy densities. Integration with these 3D architectures presents a challenge—requiring the synthesis of conformal thin films of both the electrolyte and counter-electrode, where optimization of the solid electrode/electrolyte interface is crucial for optimal device performance. Cobalt oxide is a potential candidate as a high capacity thin film anode

material demonstrating lithiation capacities of 716 and 891 mAh/g for CoO and Co_3O_4, respectively.

The atomic layer deposition of cobalt oxide thin films was explored via a radical enhanced process employing the use of the metalorganic precursor, cobalt(II) (tmhd=2,2,6,6-tetramethylheptane-3,5 dione) and atomic oxygen, in addition to a thermal process involving H_2O. The growth rate of the radical enhanced CoO_x films was determined to be 0.3Å/cycle demonstrating a stable ALD temperature window from 190-230°C. The as-deposited cobalt oxide thin films demonstrated polycrystalline character on Pt(111)-Si substrates and a post deposition annealing treatment was utilized to further promote crystallization of the Co_3O_4 phase. A 75 nm CoO_x thin film demonstrated lithiation capacities ranging from 3,200 to 2,500 mAh/cm³ at C/6 to 2C rates with a voltage cut-off of 0.4V vs. Li/Li⁺. The discharge capacity and rate-ability were explored as a function of film thickness and post deposition annealing treatment conditions. Crucial in the realization of the all solid state 3D lithium-ion batteries is the optimization of the solid electrode/electrolyte interface. A solid electrolyte material, $Li_xAl_ySi_zO$, synthesized via a thermal ALD process utilizing H_2O as the oxidant source was integrated with the cobalt oxide electrode materials and their electrochemical properties explored.

9:20am **TF2-MoM-4 Fast-charging 3D Battery Electrodes with High-Capacity Materials Using Large Area Atmospheric Pressure Spatial ALD**, *Lucas Haverkate, S Unnikrishnan, D Hermes,* Holst Centre / TNO, The Netherlands; *F Roozeboom,* Eindhoven University of Technology, The Netherlands, Netherlands; *F Zorro, F Grob, E Balder,* Holst Centre / TNO, The Netherlands; *P Poodt,* Holst Centre / TNO and SALDtech B.V., Netherlands; *M Tulodziecki,* Holst Centre / TNO, The Netherlands

The key challenges in next-generation all-solid state Li-ion battery technology development are related to the required energy and power densities, fast charging constraints, battery lifetime & safety hazards, and at the same time keeping the cost low by high-volume production. Such technology criteria require superior electrode as well as electrolyte materials (pinhole-free), and processing techniques enabling even advanced 3D designs. Apart from enabling fast-chargeability, 3D electrode architectures pave the way for the use of high-capacity materials without long-term cycling challenges.

However, newer architectures demand newer processing techniques, especially for conformal coating over three-dimensional structures. An technology researched fundamentally a lot in this respect is the Atomic Layer Deposition (ALD), which is well-known for its superior material quality and layer conformality over ultrahigh aspect ratio topology. But, in applications outside the advanced micro- and nanoelectronics industry, ALD technology is impeded by the economics of the low film deposition rates. Here, the scalable atmospheric pressure Spatial ALD (sALD) holds the best promise for sufficient deposition rates and large-area roll-to-roll processability, which is key to battery industry.

We will present about high-rate 3D Li-ion battery electrodes with sALD, which show charging speeds of 12 mins or less. Highlighted will be the development of new high performance battery electrode materials (in-situ doped titanate based) by engineering material properties at the nanoscale. Next to it, we will present about the *first-ever* sALD based LIPON electrolyte material (<100nm thick) exhibiting Li-ion conductivity > 10^{-7} S/cm. Such electrolytes are also relevant for development of protection layers in wet electrolyte-based Lithium ion batteries, as well as for enabling thin-film planar & 3D solid state batteries with ultrathin electrolyte layers (few 10s of nanometers thick). Other improvements aimed at stabilizing the solid-electrolyte interphase especially in wet Li-ion cells, maximizing ease of manufacturing and battery lifetime, will be part of the discussion as well.

9:40am **TF2-MoM-5 Thin Film Technology - Opening New Frontiers for Solid State Batteries**, *Gary Rubloff, K Gregorczyk,* University of Maryland, College Park; *A Pearse,* Control Electron; *S Lee,* University of Maryland, College Park; *A Talin,* Sandia National Laboratories, Livermore INVITED

Solid state batteries (SSBs) offer several major advantages over the lithium ion rechargeable batteries that dominate today - most notably safety, design versatility that broadens the application space, and potentially higher performance. The safety benefit is largely ensured by avoiding flammable organic liquid electrolytes. Design flexibility is derived from the thin film processing approaches naturally employed in solid state batteries, accommodating various form factors consistent with patterning approaches at the heart of microelectronics manufacturing. A major step toward enhanced performance has recent emerged in 3D SSBs that deliver high power and energy, enabled by structures which extend to high aspect ratios. The promise they show is exemplified in SSBs based on thin film

sputter deposition and more recently on atomic layer deposition (ALD), achieving a fully conformal 3D SSB with ALD multilayers serving as electrodes, solid electrolyte, and current collecting layers over high aspect ratio features. The resulting interdigitated 3D architecture exhibit the profound performance improvements expected. We consider the potential of this and other promising architectures, along with their pros and cons with respect to process sequence complexity and manufacturability.

10:40am **TF2-MoM-8 Atomic Layer Deposition: A Scalable Process for Enabling the Next Generation of High Performance Materials**, *Arrelaine Dameron,* Forge Nano   **INVITED**
Atomic Layer Deposition (ALD) is a platform technology that has been widely demonstrated throughout the semiconductor industry, but is not yet widely accepted for modification of high surface area materials. However, R&D literature has shown ALD to impart significant processing and performance gains in all areas of advanced materials. For energy applications like energy storage and fuel cells, it has been perceived as slow and too expensive to consider as a realistic process for commercial adoption. However, Forge Nano has patented, constructed, and demonstrated a high throughput ALD capability at manufacturing scales, unlocking new potential for lower cost integration of ALD into products.

For example, in energy storage, as the mobility and portability requirements grow, so does the need for higher energy density materials, higher power density systems, and enhanced lifecycles of devices, all of which create additional stresses at interfaces within energy storage modules such as lithium-ion batteries, fuel cells, and supercapacitors. It is now widely accepted that the interfaces of lithium-ion battery electrode materials can be highly dynamic in nature, and are the source of detrimental effects such as electrolyte decomposition, particle fracturing, crystal phase transformations and other causes of performance fade. The next generation of energy storage devices will be designed and engineered with tailored interfaces to overcome some of these materials challenges. ALD is a critical tool for anyone attempting to modify interfaces at the R&D scale. Therefore, ALD should also be at the manufacturing scale to maintain an edge in a competitive market. This talk will discuss ALD as a means of controlling surface phenomena and its application for powder modification for a spectrum of technologies ranging from batteries to catalysis.

11:20am **TF2-MoM-10 A Facile CVD Route for the Large-scale Fabrication of Silicon-graphite Core-shell Composites**, *Giorgio Nava,* J Schwan, L Mangolini, University of California, Riverside
Over the last decade, the research community engaged in significant efforts to investigate novel anode materials for Li-ion batteries with the goal of increasing the storage capacity of these devices. Among several candidates, silicon-carbon nanocomposites represent one of the most promising choices, featuring the highest theoretical gravimetric storage capacity. The small size of the silicon -Si- structures tackles the volume expansion undergone by the semiconductor upon lithiation, which causes pulverization of bulk Si electrodes, and promotes a robust cycling. The carbonaceous coatings, on the other hand, improve the electrical conductivity of the composite and prevent the direct interaction of Si with the electrolyte which in turn enhances the stability of the solid electrolyte interphase. Although a wide range of different Si-C nanocomposites have been investigated, these structures are often produced with methods characterized by questionable scalability, hence hindering the immediate introduction of these materials into actual manufacturing. In this contribution, we describe a facile and scalable-by-design approach for the fabrication of Si-core graphite-shell nanoparticles -NPs. Commercial Si NPs with an average size of 100 nm are introduced into a hot-wall furnace with an alumina combustion boat. The NPs are wrapped with a conformal coating of amorphous carbon resulting from the dissociation of acetylene -C_2H_2- at 650 °C. After removing C_2H_2 from the reaction zone, the furnace is ramped up to 1000°C in Argon -Ar- yielding a controlled graphitization of the C-shell, as highlighted by Raman and TEM analysis, with no detectable presence of silicon-carbide. The as-produced composites are introduced into a slurry with no addition of conductive additives, coated onto a copper substrate and studied as pure anode material in Li-ion battery half-cell assemblies. The amorphous-C-coated Si NPs exhibit a high first cycle coulombic efficiency – CE – in the order of 87% and a capacity of 1800 mAh g^{-1} which rapidly decays below 1000 mAh g^{-1} during the first 40 cycles. The

graphitization of the C-shell, achieved through the high-temperature step in Ar, significantly improves the cycling stability of the material showing a capacity above 1500 mAh g^{-1} over more than 100 cycles. Finally, the silicon-graphite composite is tested as a simple drop-in additive in graphite anodes. The addition of small amount of the Si-based active material (10% in wt) enables the fabrication of electrodes with a gravimetric capacity 30% higher than the one of the pure graphite electrodes used in commercial batteries, a first cycle CE of 90% and stable cycling over 100 cycles.

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