ALD Applications
Room Plaza ABC - Session AA-TuM

Batteries I (8:00-10:00 am)/Emerging Apps II (10:45 am-12:00 pm)

Moderators: Christophe Detavernier, Ghent University, Belgium, Christophe Vallee, LETI-LTM, France, Gary Rubloff, University of Maryland, Tero Pilvi, Picosun Oy

8:00am **AA-TuM-1 Designing of Surface and Interface of Electrodes for Highly-stable Li Ion Batteries, Li-S Batteries and Metal-Air Batteries***,* ***Xueliang Sun,*** University of Western Ontario, Canada **INVITED**

The poor cell lifetimes of Li/Na batteries are rooted mainly in side reactions occurring at the electrode-electrolyte interface. The use of surface coatings to control of the electrode-electrolyte interface is an important strategy to design new electrodes. This talk will include two parts:

In the first part, we will report our work on the applications of atomic layer deposition (ALD) in Li ion batteries [1] including synthesis of coating materials such as Al_2O_3, ZrO_2, TiO_2, $AlPO_4$and LiTaO3 [2,3,4] as well as the ALD coating materials to modify the anode ($Li_4Ti_5O_{12}$, SnO_2) [5] and the cathode (commercial $LiCoO_2$, NMC) [6].

In the second part, we will discuss MLD coating on Li-S batteries operating at 55C [7].

In the third part, we will discuss our recent results on ALD Al_2O_3 coating on Na metal for Na ion batteries and Na-Air batteries [8].

Reference:

[1] X. Meng, X.-Q.Yang, X. Sun. ***Adv. Mater.***2012, 24, 3589-3615.

[2] J. Liu, X. Meng, Y. Hu, D. Geng, M.N. Banis, M. Cai, R. Li, X. Sun. ***Carbon*** 2013, 52, 74-82.

[3] J. Liu, Y. Tang, B. Xiao, T.K. Sham, R. Li, X. Sun. ***RSC Adv***. 2013, 3, 4492-4495.

[4] J. Liu, M. Banis, X. Li, A. Lushington, M. Cai, R. Li, T.-K. Sham, X. Sun, **J. Phys. Chem. C** 117 (2013)

20260-20267

[5] X. Li, X. Meng, J. Liu, D. Geng, Y. Zhang, M. Banis, Y. Li, R. Li, X. Sun, M. Cai, M. Verbrugge, **Adv.**

Funct. Mater. 22 (2012) 1647-1654.

[6] X. Li, J. Liu, M. Banis, A. Lushington, R. Li, M. Cai, X. Sun*,* **Energy Environ. Sci.** 7 (2) (2014) 768-778

[7] X. Li, A. Lushington, Q. Sun, W. Xiao, J. Liu, B. Wang, Y. He, K. Nie, Y. Hu, Q. Xiao, R. Li, J. Guo, T.-K. Sham and X. Sun, **Nano Lett.,** 16 (2016) 3545-3549.

[8]Y. Zhao, L. Goncharova, A. Lushington, Q. Sun, H. Yadegari, B. Wang, W. Xiao, R. Li, X. Sun., **Adv. Mater.,** (2017) In press

8:30am **AA-TuM-3 ALD Vanadium Oxides for 3D Thin-film Lithium Ion Batteries***,* ***Felix Mattelaer,*** Ghent University, Belgium*; K Geryl,* Ghent University*; T Dobbelaere,* Ghent University, Belgium*; G Rampelberg,* Ghent University*; J Dendooven, C Detavernier,* Ghent University, Belgium

Several pathways are investigated to obtain high power and high energy density thin-film lithium ion batteries. The high power aspect can be obtained by scaling down the film thickness, which unfortunately decreases the films actual capacity. By coating thin-film electrodes onto 3D-structured substrates, the high power inherent of thin-film electrodes can be achieved while the energy density per footprint area can be increased.

In addition to 3D structuring, materials selection is of key importance for achieving high power and high energy density in thin-film lithium ion batteries. Traditional electrode materials such as $LiCoO_2$ are limited to a reversible range of lithium insertion, which leads to capacities of 550-700mAh/cm^3 for commercialized electrode materials. Traditionally, battery research mainly focuses on crystalline electrodes. Indications exist that higher energy density and higher power density can be achieved using amorphous materials. ALD is uniquely suited to deposit amorphous materials at low temperatures in a conformal way onto 3D structured substrates, validating the investigation of this class of materials.

In this work, crystalline and amorphous ALD vanadium oxides are deposited and examined as electrode materials. We demonstrate the deposition of amorphous V_2O_5 and two 'flavors' of VO_2 (water-based ALD and ozone-based ALD). By careful tuning of the post-ALD annealing conditions, the influence of initial ALD process, atmosphere, temperature and substrate on the crystallization and oxidation of the VO_2 films is revealed. Using this knowledge, the whole range of vanadium oxides can be obtained (VO_2–V_6O_{13}–V_4O_9–V_3O_7–V_2O_5), which are all displaying storage capacity with very high energy densities (e.g. 1380mAh/cm^3 for V_4O_9). The amorphous initial states (amorphous VO_2 and V_2O_5) on the other hand also display very high capacities, and much better kinetics than their crystalline counterparts. Moving from crystalline to amorphous vanadium oxides more than doubles the storage capacity for a given film thickness. Finally, the conformal deposition is demonstrated on silicon micropillar arrays, which demonstrates the transfer of the thin-film kinetics to a higher energy density per footprint area electrode.

In conclusion, a wide range of ALD vanadium oxides was demonstrated as potential thin-film cathode. In particular, amorphous vanadium oxides, and VO_2 (B) show promise thanks to their high energy density and good kinetics, enabling a much higher storage capacity than the stable range of V_2O_5.

8:45am **AA-TuM-4 PE-ALD of Transition Metal Phosphates as Lithium-Ion Battery Electrode Materials***, T Dobbelaere, F Mattelaer, J Dendooven,* Ghent University, Belgium*; P Vereecken,* Imec, Belgium*;* ***Christophe Detavernier,*** Ghent University, Belgium

In today's power-hungry society, lithium-ion batteries are the current state of the art of electrochemical energy storage. Their usage ranges from applications on large scales (e.g. off-grid storage) to medium (e.g. electric vehicles) and small ones (e.g. smartphones). For certain applications, e.g. chip-scale integration, the goal is to make them also on the microscopic scale. Although thin-film batteries have been demonstrated, mostly using planar, sputter-deposited films, their capacity is necessarily low because of the small amounts of active material. By using 3D microstructured substrates rather than planar ones, the capacity can be drastically increased. However, coating these substrates requires a conformal deposition method, leading to ALD as a promising technique.

Using a trimethyl phosphate (TMP) plasma as the phosphorus source, we are able to deposit three well-performing electrode materials: iron phosphate[1], titanium phosphate[2], and vanadium phosphate[3]. The process sequences are similar, with each one consisting of three steps: TMP plasma exposure, followed by O_2 plasma exposure, followed by a metal precursor exposure. The metal precursor is either tert-Butylferrocene (for iron phosphate), titanium isopropoxide (for titanium phosphate), or tetrakisethylmethylamido vanadium (for vanadium phosphate).

Each of the three processes shows ALD-type growth at a substrate temperature of 300 °C, with properties including linearity and (slow) saturation. They all have high growth rates, resp. 1.1, 0.7, and 0.8 nm/cycle, as shown in Fig. 1 (a,c,e). This is attractive for depositing thicker films in a time-efficient manner. They have low impurity levels, with ERD-measured stoichiometries of resp. $FeP_{1.5}O_{4.7}$, $TiP_{1.7}O_{5.6}$, and $V_{1.1}PO_{4.3}$.

Although each material can be crystallized by post-deposition annealing, this is not necessary (nor beneficial) because the as-deposited amorphous forms can be directly electrochemically lithiated and subsequently cycled. They yield capacities of resp. 0.7 µAh/cm^2 between 2.3-4.3V, 1.0 µAh/cm^2 between 2.3-3.2V, and 2.2 µAh/cm^2 between 1.4-3.6V, as shown in Fig. 1 (b,d,f). They can be used as practical electrodes, given that their coulombic efficiencies are close to 100% and that they show good capacity retention upon extended cycling.

[1] Dobbelaere et al., Chem. Mater. 2016, 28, 3435-3445

[2] Dobbelaere et al., J. Mater. Chem. A 2017, 5, 330-338

[3] Dobbelaere et al., In preparation

9:00am **AA-TuM-5 Comparing Temporal and Spatial Atomic Layer Deposition for Enhanced Performance of Li Ion Battery Electrodes***,* ***Alexander Yersak****, A Dameron,* University of Colorado - Boulder*; X Li, Y Yang,* Colorado School of Mines*; K Hurst, R Tenet,* National Renewable Energy Laboratory*; S George,* University of Colorado - Boulder

Ultrathin atomic layer deposition (ALD) coatings on Li Ion battery (LIB) electrodes can improve the capacity stability for both anodes and cathodes. The remaining challenge is to scale-up the ALD on LIB electrodes for commercialization. This work focused on comparing temporal and spatial ALD methods for coating the LIB electrodes. If the temporal and spatial ALD methods deliver comparable LIB performance, then the next step will be to extend the spatial ALD to roll-to-roll (R2R) spatial ALD.

The experiments utilized our spatial ALD rotating cylinder reactor [1]. Using this reactor, we have already demonstrated uniform ALD coatings in nanoporous anodic aluminum oxide (AAO) membranes with aspect ratios of 250 at an equivalent web speed of 10 m/min [2]. Porous battery electrodes have an estimated aspect ratio of ~50. Based on Monte Carlo simulations of ALD in the nanoporous AAO membranes, uniform ALD coatings should be possible in the porous battery electrodes at an equivalent web speed of 100 m/min.

We first examined the capacity stability for $LiCoO_2$ (LCO) cathode electrodes that were uncoated or coated with 4 Al_2O_3 ALD cycles using either temporal ALD or spatial ALD. The temporal ALD coatings were deposited using trimethylaluminum (TMA) and water at 120ºC. The spatial ALD coatings were deposited using TMA and ozone at 60ºC and a rotation speed equivalent to a web speed of 10 m/min. The cathode electrodes were taped to the inner drum of the rotating cylinder reactor for the ALD coating. For electrochemical testing, the LCO electrodes were cycled at 3.3-4.5V and charge/discharge rates of 1C and C/3.

The electrochemical testing results are shown in the supplemental figures. For the uncoated LCO electrodes, a significant capacity fade was observed after 10 and 94 charge/discharge cycles for rates of 1C and C/3, respectively. The ALD-coated electrodes show much better capacity stability especially for the 1C rates. The performance of temporal ALD and spatial ALD coated LCO electrodes is also comparable. We are now extending our rotating cylinder spatial ALD reactor to full R2R operation. We hope to have results from this R2R spatial ALD reactor by the ALD2017 conference.

[1] K. Sharma et al., *J. Vac. Sci. Technol. A* **33**, 01A132 (2015).

[2] K. Sharma et al., *J. Vac. Sci. Technol. A***34**, 01A146 (2016).

9:15am **AA-TuM-6 All-Solid-State Thin-Film Battery with a Novel Organic Cathode Material by Atomic/Molecular Layer Deposition***, **Mikko Nisula,** M Karppinen,* Aalto University, Finland

The miniaturization of electronic devices creates demand for energy storage systems of the same length scale. As the downsizing of conventional liquid electrolyte cells is difficult, the current focus is on all-solid-state thin-film batteries. In order to increase the energy density while preserving the power density of the cells, various 3D architectures have been proposed to enhance the effective surface area. Such an approach places an apparent need for a thin-film deposition method capable of manufacturing the electrode and electrolyte materials on high-aspect-ratio substrates. A strong candidate for the task is the atomic layer deposition (ALD) technique and the recent years have seen the emergence of a number of ALD processes for both electrode and electrolyte materials.

An interesting choice for the electrodes is the group of organic electrode materials such as quinones and conjugated carboxylates. While impractical for conventional batteries due to conductivity and dissolution issues, these downsides can be circumvented by applying the organic electrode material in all-solid-state thin film batteries. Recently, we demonstrated that these materials are attainable using the combined atomic/molecular layer deposition (ALD/MLD) by depositing the lithium terephthalate anode material.[1] Compared to the more conventional inorganic materials, the ALD/MLD approach yields a number of advantages such as simple binary deposition processes, low processing temperatures (<200 °C) and no need for a post-deposition anneal. Moreover, given their environmentally benign constituents, organic electrode materials would be well suited for the emerging *transient electronics* technology.[2]

In this contribution, we present an all-solid-state thin-film battery based on a novel lithium-bearing organic cathode material by ALD/MLD combined with ALD-made LiPON[3] as the solid electrolyte. As well as investigating the electrochemical performance of the solid-state battery by cyclic voltammetry and galvanostatic charging/discharging, we discuss the aspects of device fabrication such as the effect of electrode and electrolyte layer thicknesses on the device performance as well as the role of the interfaces and methods for controlling them.

1. M. Nisula, M. Karppinen, *Nano Lett.***16** 2016 1276 – 1281

2. K. K. Fu, Z. Wang, J. Dai, M. Carter, L. Hu, *Chem. Mater.***28** 2016 3527 – 3539

3. M. Nisula, Y. Shindo, H. Koga, M. Karppinen, *Chem. Mater.***27** 2015 6987 – 6993

9:30am **AA-TuM-7 Atomic Layer Deposition of Hierarchical CNTs@FePO₄ Architecture as a 3D Electrode for Lithium-Ion and Sodium-Ion Batteries***, **Jian Liu,*** The University of British Columbia, Canada*; B Wang, Q Sun, R Li, T Sham, X Sun,* University of Western Ontario, Canada

Three-dimensional (3D) microbatteries hold great promise as on-board energy supply systems for microelectronic devices [1]. The construction of 3D microbatteries relies on the development of film deposition techniques that can enable coatings of uniform electrode and electrolyte materials in high-aspect-ratio substrates [2]. Herein, a 3D $FePO_4$ on carbon nanotubes (CNTs@$FePO_4$) structure is fabricated by coating $FePO_4$ on CNTs/carbon paper substrate using atomic layer deposition (ALD) [3]. Compared to $FePO_4$ on a planar substrate, the 3D CNTs@$FePO_4$ electrode exhibits significantly increased areal capacity and excellent rate capability for lithium-ion and sodium-ion storage. The 3D CNTs@$FePO_4$ maintained areal capacities of 64 µAh cm^{-2} and 33 µAh cm^{-2} after 180 cycles for LIBs and SIBs, which are 16 and 33 times higher than those of planar $FePO_4$ electrode, respectively (Figure 1). Moreover, hybrid 3D CNTs@$FePO_4$@Li_3PO_4 structure is fabricated by coating Li_3PO_4 solid-state electrolyte on 3D CNTs@$FePO_4$. The CNTs@$FePO_4$@Li_3PO_4 electrode shows stable cycling performance in lithium-ion batteries. Hard X-ray Photoemission Spectroscopy analysis discloses that Li_3PO_4 coating prevents the formation of undesirable LiF in the solid-electrolyte interphase layer, which is believed to be responsible for the performance degradation in CNTs@$FePO_4$ (Figure 2). It is expected that this work will pave the way to building reliable 3D nanostructured electrode and electrolyte architecture for high areal capacity microbatteries.

References

[1] J. F. M. Oudenhoven, L. Baggetto, P. H. L. Notten, Adv. Energy Mater. 2011, 1, 10.

[2] J. Liu, X. Sun, Nanotechnology, 2015, 26, 024001.

[3] J. Liu, B. Wang, Q. Sun, R. Li, T.-K. Sham, X. Sun, Adv. Mater. Interfaces 2016, 1600468.

9:45am **AA-TuM-8 Unravelling The Role of ALD Al_2O_3 and TiO_2 Protective Coatings on Lithium-Ion Battery Electrodes.***, **Felix Mattelaer,*** Ghent University, Belgium*; M Kurttepeli,* University of Antwerp*; S Deng,* Ghent University, Belgium*; D Cott, P Vereecken,* IMEC, Belgium*; J Dendooven,* Ghent University, Belgium*; S Bals,* University of Antwerp*; C Detavernier,* Ghent University, Belgium

Nanoscaling of lithium-ion battery electrodes enhances the kinetics and footprint capacity, but also sensitively increases the electrode-electrolyte interfacial area. While this is beneficial for fast lithium-ion diffusion, most capacity fading mechanisms are also related to interface phenomena, such as solvent decomposition and metal dissolution. Interface stabilization by ALD coatings has been heavily investigated since 2010. Partially thanks to the ease of deposition, the main part of research has been devoted to ALD of Al_2O_3 as protective coatings. However, it is a poor lithium-ion conductor, and other ALD films can both provide enhanced cycle life while maintaining the excellent thin-film battery kinetics.

In this work, we use two thin-film lithium-ion battery electrodes as model systems to benchmark ALD Al_2O_3 and ALD TiO_2 as interfacial modifiers for lithium-ion batteries. On a near-ideal electrode (lithiated thin-film TiO_2), the lithium-blocking nature of ALD Al_2O_3 is revealed. Al_2O_3 films beyond 3nm are completely blocking, while thinner coatings impose an impedance of >10^{12} Ωcm. ALD TiO_2 does not pose a kinetic bottleneck and is never blocking. On a less-than ideal model system (overcharged thin-film $LiMn_2O_4$), it is shown that 5nm ALD TiO_2 can prevent solvent decomposition, which more than 10 better capacity retention at 100C.

Finally, ALD is used to decorate a CNT forest with both a V_2O_5 film as a lithium-ion battery cathode, and an amorphous TiO_2 coating as a protective coating to extend cycle life. The dual-layer conformality is confirmed using EDX-STEM tomography. The electrode is cycled with two lithium-ions per V_2O_5 unit cell. A high areal capacity and excellent kinetics are found for the V_2O_5-coated CNTs, but a fast capacity degradation is observed and associated to vanadium dissolution during cycling. Coating the V_2O_5/CNTs with 5 or 25 cycles of ALD TiO_2 retained the excellent kinetics, but almost completely alleviated the vanadium dissolution issue, improving the cycle life dramatically. Furthermore, the coating was found to aid in the cycling-driven amorphisation of the V_2O_5.

In conclusion, ALD Al_2O_3 was identified as a very resistive coating towards lithium, using thin-film electrodes as model systems. ALD thin-film V_2O_5 on CNTs was demonstrated a high-power lithium-ion cathode. The deterioration mechanism of deep charging of the V_2O_5/CNTs is shown to be related to vanadium dissolution. ALD TiO_2 coatings improved the cycling performance by alleviating this dissolution issue, while maintaining the excellent thin-film battery kinetics.

10:45am **AA-TuM-12 ALD Layer Opportunties for Reversible Bonding of Ultrathin Glass Substrates***, **Messaoud Bedjaoui**, S Poulet,* LETI, France

Over the past few years, we are witnessing to a rapid development of flexible electronics leading to a number of promising devices in the area of energy sources and advancing displays (e.g microbatteries, organic state lighting, liquid crystals displays…) especially with the emergence of ultrathin and flexible glass substrates (<100µm). However, handling of ultrathin substrates is a great challenge for front-end and back-end processes. On the other hand, wafer bonding techniques are being increasingly used to achieve innovative stacking structures. In order to bond ultrathin substrates containing temperature-sensitive devices, a bonding process that yields high bond strengths operating at a moderate temperature (<600°C) is needed.

The purpose of this work is to present a new cost reduction concept of handling for ultrathin glass substrates covering both bonding and debonding processes. In order to elaborate flexible thin film components using this kind of ultrathin substrates, their bonding based on intermediate atomic layer deposition (ALD) as well as debonding from thick carrier has to be studied. First of all, we investigate the bonding behavior of glass/Al_2O_3, glass/TiO_2 and glass/Al_2O_3-TiO_2 layer structures submitted to room temperature up to 600°C annealing. Surface and bonding energies are measured in an anhydrous atmosphere and bonding defectivity is analysed using scanning acoustic microscope (SAM). Layers deposited by ALD onto glass carrier are suited for direct bonding.

This work is also focused on the debonding process by demounting the interface layer fabricated using atomic layer deposition in humid atmosphere conditions (>80%RH and T°>90°C). Spontaneous debonding phenomena occurred solely for low temperature (80°C to 150°C) Al_2O_3 layers on thick glass carrier even after annealing treatment. This debonding, unobservable for TiO_2 and Al_2O_3-TiO_2 bilayer bonding structures, may be explained by chemical or structural modification such as internal stress, pinholes formation or stoichiometry instability. The intermediate bonding layers have been also characterized using infrared spectroscopy, scanning electron microscopy (SEM) and complementary analysis (spectroscopic ellipsometry, X-ray photoelectron spectroscopy) before and after exposition to humid atmosphere (Figure 1, Figure 2, Figure 3 in supplemental document). Based on these results, an Al_2O_3 debonding mechanism is proposed. These studies demonstrated that the approach of this work provides a method to fabricate temperature-sensitive devices on bonded ultrathin glass and to achieve a low cost solution of debonding from glass carrier which can be repeatedly reused after simple cleaning.

11:00am **AA-TuM-13 Atomic Layer Deposition and Precursor Development for Chemoresistive Gas Sensing Materials***, **Rachel Wilson**, C Blackman, C Carmalt,* University College London, UK

Chemoresistive gas sensors are simple to use, have low cost, small size and high sensitivity. The performance of such sensors is defined by the composition, morphology and structure of the sensing materials. This work demonstrates the use of Atomic Layer Deposition (ALD) to engineer *n*- and *p*-type metal oxide films for gas sensor applications.

A major drawback of using *n*-type materials for gas sensing is their sensitivity to moisture and humidity. *P*-type gas sensing materials however, are believed to be less moisture sensitive, making them attractive materials within the semiconductor industry. However, *p*-type metal oxides have received relatively little attention compared to their *n*-type congeners, which may be ascribed to their apparently low sensitivities, limiting their potential applications. ALD provides atomic level control of film growth, allowing fabrication of materials with defined thickness, making it an ideal tool for exploring the fundamental sensing properties of these materials.[1] The long term goal is to identify the most promising new materials and provide key information regarding the optimization of the materials synthesis to obtain gas sensing materials with maximum sensitivity and selectivity.

Metal oxide thin films have been deposited using a flow-type ALD reactor which was built in house. TiO_2 films have been deposited using titanium isopropoxide and water precursors. Nickel and copper complexes have been synthesized for use as potential ALD precursors for the deposition of nickel (II) oxide (NiO), and copper (I) oxide (Cu_2O) using water as the co-reactant. These include but are not limited to; alkoxides, guanidinates and amides. NiO has been deposited via ALD and CVD methods. Metal oxide films have been deposited onto alumina sensors, which have been exposed to different concentrations of gases. By measurement of the films electrical resistance the gas sensitivity can be determined and hence we can define the thickness which gives the maximum sensor response (and see if this is comparable with the Debye length). Although the use of TiO_2 as a gas sensor material is widely known, we have manged to obtain responses at very high resistance values with excellent kinetics of response. We have shown that the pattern responses of the electrical resistance towards certain gases indicate typical *n*-type semiconducting behavior. The TiO_2 film thickness plays a dominant role within the conduction mechanism. Gas sensitivity testing of *p*-type NiO films is currently underway.

References

[1] Kim, H. ALD of metal & nitride thin films: Current research efforts & applications for semiconductor device processing, J. Vac. Sci. Technol., 2003, 21: 2231

11:15am **AA-TuM-14 Physics with and Physics of Atomic Layer Deposited Nanofilms***, **Neal Sullivan**,* Arradiance*; A Lehmann,* Universitat Erlangen-Numberg*; A Brandt,* University of Texas at Arlington

In high energy physics (HEP), the need for precise timing (pico-seconds), was established by the inability to extract all measurable information (i.e. 4-vectors) from multi-TeV particle collisions at the Fermilab Tevatron in 2003[1] Psec-resolution requires a detector that is small enough that variations in the fastest transit times of the photons or electrons correspond to a time jitter smaller than the resolution. Microchannel plates (MCP) possess this requisite timing dimension, but MCP-based photodetectors, were not considered for these applications due to the high-cost / area, and poor lifetime – typically less than one month under use conditions. While photomultiplier tubes (PMTs) are the workhorse devices for photo detection, microchannel plate-based PMTs (MCP-PMT) significantly advance the state-of-the-art achieving more than 100-fold improvements in spatial and temporal resolution. This work presents the development of ALD-functionalized MCPs that have improved MCP-PMT performance and extended lifetimes by more than 40x.

ALD process development for both secondary emissive and conductive layers as well as the integration of these ALD nanofilms with the MCP device at Arradiance will be discussed in detail. The tradeoffs required and the overall device performance is compared to the standard reduced silicate lead glass (RSLG) MCP. Application lifetime and MCP-PMT performance results, collected by Dr. Lehmann at the PANDA experiment over the last 5 years and at Professor Brandt's lab at University of Texas Arlington, will be presented and the implications for high energy physics will be examined. Analytical studies, assessing the role of each of the functional ALD films in lifetime improvement will be presented, with an eye towards understanding the underlying physics of the nanofilm in the MCP-PMT

High speed photodetectors with micron space resolution and temporal resolution less than 10 picoseconds (psec) represent a disruptive technology across the physics frontiers of energy, intensity, and cosmic with the capability to support experiments addressing the origin of mass, neutrino physics and proton decay, and the nature of dark matter and energy. Additional technology and commercial areas such as: homeland security, astronomy, space instrumentation, remote night time sensing, TOF mass spectrometry, and medical imaging (PET scanning) all stand to benefit from this technology.

[1] Henry J. Frisch, et. al., A Brief Technical History of the Large-Area Picosecond Photodetector (LAPPD) Collaboration, http://arxiv.org/abs/1603.01843 March 2016

11:30am **AA-TuM-15 Highly Resistive ALD Coatings for Microchannel Plates Operating at Cryogenic Temperatures***, **Till Cremer**, B Adams, M Aviles, J Bond, C Craven, M Foley, A Lyashenko, M Minot, M Popecki, M Stochaj, W Worstell,* Incom Inc.*; J Elam, A Mane,* Argonne National Laboratory*; O Siegmund, C Ertley,* University of California, Berkeley

We report on the structure-property relationships of highly resistive nanocomposite films synthesized by atomic layer deposition (ALD). These nanocomposites are composed of metal nanoparticles dispersed in a dielectric matrix, resulting in an amorphous material with semiconductor-like electrical properties characterized by a negative thermal coefficient of resistance (TCR) . The material's (thermo-) electrical properties depend on film thickness, composition, nanostructure, and the chemical nature of the dielectric and metal components. We show how the structure-property relationships developed in this work can be used to design coatings with improved thermo-electrical properties.

Atomic layer deposition (ALD) has enabled the development of a new technology for fabricating microchannel plates (MCPs) with improved performance performance that offer transformative benefits to a wide variety of applications. Incom uses a “hollow-core” process for fabricating glass capillary array (GCA) plates consisting of millions of micrometer-sized glass microchannels fused together in a regular pattern. The resistive and secondary electron emissive (SEE) functions necessary for electron amplification are applied to the GCA microchannels by ALD, which – in contrast to conventional MCP manufacturing– enables independent tuning of both resistance and SEE to maximize and customize MCP performance.

Incom is currently developing MCPs that operate at cryogenic temperatures and across wide temperature ranges. All MCPs exhibit a negative TCR: when the MCP is cooled, the resistance increases, and when heated, the resistance drops. Consequently, the resistance of each MCP must be tailored for the intended operating temperature. This sensitivity to small temperature changes presents a challenge for many terrestrial and space based applications including for detectors capable of operation either at room temperature or at cryogenic temperatures. Our results demonstrate how the structural and compositional changes (dielectric-to-metal ratio and elemental composition) affect the resistivity and, specifically, the TCR of the nanocomposite. Developing structure-property relationships for the resistive material enables us to develop highly resistive materials with a) improved TCR characteristics, and b) fabricate MCPs optimized to operate at cryogenic temperatures.

11:45am **AA-TuM-16 Reactions on ALD TiO_2, ZnO, and Al_2O_3 Metal Oxides during Nucleation of UiO-66-NH_2 MOF Thin Films as Hydrolysis Catalysts for Chemical Warfare Agent Simulants.***, **Dennis Lee**, J Zhao, C Oldham,* North Carolina State University*; G Peterson,* Edgewood Chemical Biological Center*; G Parsons,* North Carolina State University

Highly toxic compounds such as chemical warfare agents (CWAs) (e.g., sarin (GB), soman (GD), VX), ammonia or chlorine gas, or NO_x-based pollutants can pose a severe chemical threat. Recently, highly crystalline, stable, and microporous metal-organic frameworks (MOFs), in particular UiO-66-NH_2 MOF, have become active materials to effectively degrade deleterious chemicals. These MOFs are readily formed as powders, but for effective application, new means are needed to create controllable and conformal MOF thin films, especially on high aspect ratio textiles and fibrous substrates. We recently reported that ALD metal oxides act as suitable nucleation agents for UiO-66-NH_2 thin films, but nucleation mechanisms and how they are driven by ALD oxide composition were not well understood.

Here, we describe surface reaction mechanisms on ALD Al_2O_3, TiO_2, and ZnO during nucleation of UiO-66-NH_2 MOF. The MOFs are excellent quality, with high crystallinity and net surface area exceeding 1000 m^2/g_{MOF}. We find that ALD Al_2O_3 and TiO_2 layers are fairly stable under solvothermal MOF growth condition. On the other hand, crystalline ALD ZnO surface partially dissolves in the synthetic environment. The chemical instability of ZnO promotes MOF nucleation in the liquid phase, likely via reaction on Zn^{2+} ions, creating a significant amount of MOF crystals, up to 145 $m^2/g_{fiber+MOF}$, but limiting MOF thin film growth. The stability of ALD Al_2O_3 and TiO_2 enables good MOF coatings, but the density of nucleation sites is markedly larger on TiO_2 vs Al_2O_3, resulting in 65 $m^2/g_{fiber+MOF}$ on TiO_2 vs 34 $m^2/g_{fiber+MOF}$ on Al_2O_3. Accordingly, we find the MOF-fabric formed with TiO_2 performs better than those with Al_2O_3 for hydrolysis of dimethyl 4-nitrophenyl phosphate (DMNP), a chemical warfare agent simulant, allowing the half-life for degradation to be in the range of 10 minutes versus several days measured for control metal oxide samples without the conformal MOF thin film.

We will discuss how ALD surfaces with different composition can impact on the MOF mass loading, which correlates with DMNP destruction performance, and how functionalized textiles can be also utilized for removing hazardous gases, such as ammonia, chlorine, and hydrogen sulfide.

Author Index

Bold page numbers indicate presenter