

# Tuesday Morning, November 1, 2011

## Thin Film Division

Room: 107 - Session TF+EN-TuM

### ALD for Energy

**Moderator:** W.M.M. Kessels, Eindhoven University of Technology, the Netherlands

8:20am **TF+EN-TuM2 Controlling the Dispersion and Size of Platinum Nanoparticles Using Pt Atomic Layer Deposition and Surface Treatments**, V.R. Anderson, University of Colorado, Boulder, N. Leick, Eindhoven University of Technology, Netherlands, K.E. Hurst, National Renewable Energy Laboratory, A.S. Cavanagh, University of Colorado, Boulder, S. Kocha, K. Jones, A.C. Dillon, National Renewable Energy Laboratory, S.M. George, University of Colorado, Boulder

Platinum nanoparticles are used as the catalyst on the cathodes of proton exchange membrane (PEM) fuel cells. Controlling the dispersion and size of the Pt nanoparticles is important for efficient and cost-effective fuel cells. When Pt atomic layer deposition (ALD) is performed on oxide or carbon substrates, nucleation difficulties and the high surface energy of Pt lead to Pt nanoparticles rather than continuous films. This research explored strategies to control the dispersion and size of Pt nanoparticles using Pt ALD together with various surface treatments. Pt ALD was performed using Pt hexafluoroacetylacetonate Pt(hfac)<sub>2</sub> and formalin as the reactants. Titanium oxide (TiO<sub>2</sub>) and tungsten oxide (WO<sub>3</sub>) were explored as the substrates. We used *in situ* transmission Fourier transform infrared (FTIR) spectroscopy to monitor the surface species during Pt ALD. Surface poisoning by hfac species was observed during the nucleation of Pt ALD on TiO<sub>2</sub>, in agreement with our previous studies of Pd ALD [1]. Trimethylaluminum (TMA) was able to remove the hfac species from TiO<sub>2</sub> and promote more facile nucleation of Pt ALD, also as expected by our earlier work on Pd ALD [2]. We then used hfacH adsorption prior to Pt ALD to block surface sites, delay Pt ALD nucleation and decrease Pt nanoparticle dispersion. In addition, we used TMA exposures after Pt(hfac)<sub>2</sub> exposures to facilitate Pt ALD nucleation and increase Pt nanoparticle dispersion. The Pt nanoparticles were detected by the rising absorbance baseline of the FTIR spectrum, and transmission electron microscopy images of Pt nanoparticles on TiO<sub>2</sub> and WO<sub>3</sub> particles. The size of the Pt nanoparticles was dependent on the number of ALD reaction cycles.

1. D.N. Goldstein & S.M. George, *Thin Solid Films* (In Press).
2. D.N. Goldstein & S.M. George, *Appl. Phys. Lett.* **95**, 143106 (2009).

8:40am **TF+EN-TuM3 Nucleation & Growth of Continuous and Ultrathin Pt ALD Films for Improved Oxygen Reduction Activity in Fuel Cells Using W ALD Adhesion Layers**, L. Baker, A.S. Cavanagh, S.M. George, University of Colorado, Boulder, A. Kongkanand, F.T. Wagner, General Motors Research & Development

Transition metals, such as Pt, are important as catalysts in fuel cells. The cost of Pt requires that this metal be utilized as efficiently as possible. Previous studies have demonstrated that flat, continuous Pt surfaces have an activity for the fuel cell oxygen reduction reaction (ORR) per surface Pt atom that is 5-10 times larger than the activity of 3 nm Pt nanoparticles on carbon-supported electrocatalysts. Consequently, very thin continuous Pt layers are needed to achieve high activity per mass of Pt and favorable economics.

Pt has a high surface energy and does not readily wet low surface energy oxide and carbon material surfaces. Instead, Pt nanoclusters are formed during the nucleation of Pt ALD on these low surface energy supports. A continuous Pt film is possible only after the coalescence of the nanoclusters when the film thickness is >5 nm. One possible route to obtain a continuous and ultrathin Pt film is to deposit on an adhesion layer that has a higher surface energy than Pt. In this case, the Pt will wet the adhesion layer because the deposited Pt film will lower the surface energy. One material that has a higher surface energy than nearly all other metals, including Pt, is tungsten (W).

W ALD using WF<sub>6</sub> and Si<sub>2</sub>H<sub>6</sub> is known to nucleate and grow rapidly on Al<sub>2</sub>O<sub>3</sub> ALD surfaces [1]. The surface chemistry of W ALD is able to form chemical bonds to the underlying Al<sub>2</sub>O<sub>3</sub> substrate that overcome the surface energy differences. In this study, Pt ALD is performed using MeCpPtMe<sub>3</sub> and H<sub>2</sub> plasma on W ALD adhesion layers grown on Al<sub>2</sub>O<sub>3</sub> ALD films. X-ray photoelectron (XPS) and x-ray reflectivity (XRR) studies have demonstrated that Pt ALD nucleates nearly immediately on the W

ALD adhesion layers. The XPS and XRR data are consistent with a layer-by-layer growth model. Pt ALD films can be deposited that are 1 nm thick, conformal and continuous. Initial electrochemical measurements on these thin films have yielded a large proportion of the anticipated ORR activity benefit.

[1] R.A. Wind, F.H. Fabreguette, Z.A. Sechrist and S.M. George, "Nucleation Period, Surface Roughness and Oscillations in Mass Gain per Cycle during W Atomic Layer Deposition on Al<sub>2</sub>O<sub>3</sub>", *J. Appl. Phys.* **105**, 074309 (2009).

9:00am **TF+EN-TuM4 Engineering Li<sub>1</sub>Al<sub>1</sub>Si<sub>2</sub>O Ion Conducting Thin Films by Atomic Layer Deposition for Lithium-ion Battery Applications**, Y.-C. Perng, J. Cho, D. Membreno, N. Cirigliano, B. Dunn, J.P. Chang, University of California Los Angeles

Lithium (Li)-ion batteries have drawn much attention for their outstanding performance in portable electronics applications. However, formation of the solid electrolyte interphase (SEI) layer on the surface of electrodes during the charge-discharge cycling can reduce battery capacity and the long-term reliability of current battery technology. The use of solid electrolyte layers can effectively suppress formation of the SEI. Another application for thin solid electrolytes is in microbatteries, especially those based on the engineering of electrodes into 3D architectures involving high aspect ratio pillars. To realize this potential, an ultra-thin and highly conformal electrolyte layer is needed to coat the 3D electrode array. The ionic conductor lithium aluminosilicate (LiAlSiO<sub>4</sub>) synthesized by atomic layer deposition (ALD), is a promising candidate for these battery applications. The material exhibits high ionic conductivity along its c-axis because of channels formed by the alternating tetrahedra of aluminum-oxygen (Al-O) and silicon-oxygen (Si-O).

The self-limiting characteristic of ALD allows for precise control of thickness and composition of complex oxides and results in a highly conformal and pinhole-free coating suitable in 3D micro-battery applications or electrolyte surface coatings. The metal precursors used in this work are tetraethyl orthosilicate (TEOS), trimethylaluminum (TMA) and lithium t-butoxide (LTB). These precursors, along with water vapor as the oxidant, were used to deposit SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Li<sub>2</sub>O, with deposition rates in the range of 0.8~2 Å/cycle, respectively. The deposition rate of stoichiometric LiAlSiO<sub>4</sub> was ~5 Å/cycle at a temperature of 290°C. The concentration of each metal element in Li<sub>1</sub>Al<sub>1</sub>Si<sub>2</sub>O (LASO) thin films is found to correlate closely to ALD cycles and the associated incubation times. Complex impedance measurements show that the ionic conductivities of as-deposited LASO films are in the range of 10<sup>-7</sup> to 10<sup>-8</sup> S/cm and directly related to the lithium content in the film. The LASO ALD coating on 3D features, such as NWs and nanoparticles (NPs), were confirmed to be conformal and uniform by transmission electron microscopy (TEM) imaging. Further electrochemical tests to check pinhole-free coatings on 2D and 3D features were performed as well. The crystallinity of the films after post-deposition rapid thermal annealing (RTA) was a function of cation concentration. The epitaxial relation of LASO to silicon, a potential anode material, was found to be β-LiAlSiO<sub>4</sub> (-1 2 -1 0) || Si (400) and β-LiAlSiO<sub>4</sub> (1 0 -1 0) || Si (004).

9:20am **TF+EN-TuM5 ALD: Enabling Designer Nanostructures for Energy Applications**, G.W. Rubloff, University of Maryland **INVITED**

Nanostructures will dominate next-generation energy technologies. Progress in nanofabrication increasingly allows design flexibility control of structural geometry and material combinations to achieve high performance multifunctional 3-D nanostructures for energy harvesting and storage. Such designs derive advantage from high surface areas, ultrathin films, structures with high aspect ratios, heterogeneous materials combinations, and control over 3-D profiles of material compositions and nanostructure shapes. Self-assembly, self-alignment, and self-limiting reactions enable both nanofabrication of desired energy nanostructures and their scaling to unprecedented levels of integration.

Atomic layer deposition (ALD) plays a pivotal role in this paradigm because of its intrinsic attributes: thickness control at the atomic scale; exceptional conformality to apply this control in the most demanding of nanogeometries; and a growing portfolio of ALD materials choices from new precursors and processes. As a result, ALD is becoming common, even pervasive, in nanostructure-based energy research, spanning applications from heterogeneous nanowires to passivating electrochemical layers and high-efficiency catalytic nanostructures.

Two primary challenges will determine whether ALD's potential is realized in next-generation energy technology.

First, integration of ALD with other processes into suitable process sequences determines how well nanostructure designs can be fabricated and tailored for the energy application. For example, in high aspect ratio trenches, pores, or aperiodic porous materials, ALD films can be highly conformal or tapered "top-down" to thinner layers deeper in the structure, while electrodeposited films can be grown "bottom-up" from a working electrode at the bottom, together offering more design flexibility in vertical profiles than does either process alone.

Second, scaleup of ALD equipment, processes, and control is required for cost-effective ALD manufacturing. Significant efforts are already underway to develop these technologies, notably including roll-to-roll and other high throughput approaches, as well as atmospheric pressure ALD to circumvent the cost and complexity of vacuum-based equipment.

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10:40am **TF+EN-TuM9 Functionalized Quartz Fibers by Atomic Layer Deposition for Dye-Sensitized Solar Cells**, *D. Kim, H.J. Koo, M. Woodroof, J.S. Jur, B. Kalanyan, K. Lee, C.K. Devine, G.N. Parsons*, North Carolina State University

Dye-sensitized solar cells (DSCs) are a promising alternative to Si-based photovoltaic cells because of their high efficiency, low cost, and simple processing. To improve the efficiency, the light harvesting properties of the DSC photoanode structure should be improved.

This work shows the ability to improve DSCs efficiency by the incorporation of quartz fiber mats functionalized by ALD with a conformal nanoscale TiO<sub>2</sub> coating for the photoanode. The TiO<sub>2</sub> atomic layer deposition allows precise nanoscale thickness control throughout the quartz fiber mat. In addition, thermal stability of the quartz fiber also enables the annealing of TiO<sub>2</sub> films at high temperatures in order to obtain anatase crystallinity, which is the preferred TiO<sub>2</sub> phase in DSCs due to faster electron transfer kinetics. As a result, we obtained very stable anatase TiO<sub>2</sub> on quartz fibers by annealing at as high as 1050 °C. The micro-sized randomly oriented structure of coated quartz fibers caused high light scattering effect inside the photoanode, so that it increased the photon adsorption. At the same time, TiO<sub>2</sub>-coated quartz fibers were successfully sensitized by more dye molecules compared to bare quartz fibers.

The use of the dye-sensitized quartz fiber mats in a DSC framework produces devices with overall efficiency exceeding 7% in our laboratory, compared to ~ 6% for similar devices without the coated fiber scattering layer. We will present X-ray diffraction, morphological changes, and optical properties of TiO<sub>2</sub>-coated quartz fibers, as well as I-V and IPCE data for the DSCs. The effects of various integration schemes for introducing quartz fibers into the DSC photoanode will be discussed. Moreover, it is believed that the combination of quartz fiber and ALD is very attractive especially to energy research fields where they need finely tuned nanostructures to meet intricate requirements.

11:00am **TF+EN-TuM10 Angle Dependent Electromotive Force in an Al<sub>2</sub>O<sub>3</sub>/Al/Thermoelectric Power Generator System Interacting with Infrared Radiation**, *A.J. Vincent-Johnson, K.A. Vasquez*, James Madison University, *A.E. Masters*, Custom Thermoelectric, *X. Hu, G. Scarel*, James Madison University

We present a fundamental study of the interaction between infrared radiation and an Al<sub>2</sub>O<sub>3</sub> film on Al sheet placed on a thermoelectric power generator (system 1). We compare the results with those obtained for a system consisting in an Al sheet on a thermoelectric power generator (system 2). The Al<sub>2</sub>O<sub>3</sub> film in system 1 is prepared using atomic layer deposition, which provides smooth and well defined air/film and film/substrate interfaces. Infrared spectra show that Al<sub>2</sub>O<sub>3</sub> films on the aluminum foil absorb an increasing amount of infrared radiation at increasing angle of incidence. This behavior, known as the Berreman effect, is caused by the radiative surface polaritons excited close to the frequencies of longitudinal optical phonons by the infrared radiation at the interfaces of Al<sub>2</sub>O<sub>3</sub>/Al. Our work demonstrates that a similar trend occurs when infrared radiation is absorbed by system 1: as the infrared radiation starts illuminating system 1 in its initial condition, the electromotive force jumps up to a maximum (EMF<sub>max</sub>) and then decays exponentially. The EMF<sub>max</sub> value and its amplitude increase with the increasing incidence angle of the infrared radiation. Since system 2 exhibits only a weak dependence of the EMF<sub>max</sub> value and amplitude on the incidence angle of the infrared radiation, we conclude that the behavior of the electromotive force during

the transient in system 1 is caused by radiative surface polaritons in Al<sub>2</sub>O<sub>3</sub>/Al. This research is at a seminal stage and needs further understanding. However many routes can be investigated to enhance the efficiency of the electromotive force production. The results are relevant to energy generation from radiation, sensors, and electromagnetic wave detectors.

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