Wednesday Afternoon, August 1, 2018

ALD Applications

Room 116-118 - Session AA1-WeA

Energy: Catalysis and Fuel Cells

Moderators: Myung Mo Sung, Hanyang University, Yongfeng Mei, Fudan University, China

1:30pm **AA1-WeA-1 Oleo Sponge: Reusable Sorbent for Oil Spill Cleanup Fabricated using Sequential Infiltration Synthesis**, ***Jeffrey W. Elam***, *A Mane, E Barry, S Darling, J Avila, J Libera,* Argonne National Laboratory

Crude oil spills in the ocean can be devastating to the environment and extremely expensive to mitigate. Furthermore, while oil on the surface can be removed by skimming or burning, there are currently no technologies for the cleanup of subsurface oil droplets in the ocean. To address this need, we have developed a reusable sorbent material, Oleo Sponge. To synthesize this material, we begin with commercial polyurethane foam, and first treat the foam using sequential infiltration synthesis (SIS). SIS is similar to ALD in that it uses alternating, self-limiting exposures between gaseous precursors and a substrate. However, whereas the ALD substrate is a solid surface, in SIS the substrate is a polymer, and the precursors react on organic functional groups within the polymer to seed the nucleation of metal oxide clusters. We performed in situ infrared spectroscopy and mass spectrometry to elucidate the mechanism for metal oxide SIS within the polyurethane foam, and we have studied the effects of temperature, time, and partial pressure on the resulting SIS deposits. The next step is to graft an oleophilic monolayer onto the SIS-treated foam, either through gas-phase or solution phase treatment. The resulting material is simultaneously hydrophobic and oleophilic, and is able to rapidly extract oil from water. We have performed extensive bench-scale testing using 1" cubes of the Oleo Sponge and found that it absorbs >40x its weight in oil, and can be simply squeezed out and used again. Next, we performed a 10,000 scale up, and tested the material at the Ohmsett facility in Leonardo, New Jersey, using the largest outdoor saltwater tank facility in North America. The Oleo Sponge performed very well in extracting subsurface crude oil and diesel fuel from seawater under realistic conditions.

1:45pm **AA1-WeA-2 Evaluation of Zinc Oxide Fabricated by Atomic Layer Deposition as an Antibacterial Coating under UV Light**, ***Gwon Deok Han***, *K Park, M Kim, H Choi, J Koo, H Park, J Shim,* Korea University, Republic of Korea

Zinc oxide (ZnO) is widely used as a promising antibacterial agent in environmental remediation processes such as water disinfection and air purification [1]. This is because ZnO has a wide band gap energy (approximately 3.3 eV) which is favorable for photocatalytic reaction. In aquatic environments, ZnO produces reactive oxygen species (ROS) such as superoxide anion, hydroxyl radical, and singlet oxygen based on photocatalytic reaction promoted under UV irradiation. The photo-generated ROS exhibits antibacterial activity against microorganisms such as gram-negative bacteria and gram-positive bacteria. Recently, the improvement of the antimicrobial effect through application of nanoparticle ZnO having a high active surface area has been verified [2]. However, the ZnO nanoparticles have a problem in that the antibacterial ability is lowered due to agglomeration between nanoparticles and weak adhesion to the continuous flow-through reactor in wastewater treatment. Accordingly, immobilization of ZnO on reactor surface is essential.

In this study, we successfully demonstrated that thin-film ZnO fabricated by atomic layer deposition (ALD) exhibits comparable levels of antibacterial activity to commercially available ZnO nanoparticles [3]. We observed that the as-deposited ZnO consisted of closely packed nano-sized grains and firmly attached to the underlying substrate. As an alternative to the particulate photocatalysts, it was confirmed that the thin-film ZnO efficiently adsorbed UV light of 380 nm or less and continuously generated ROS even in repeated use in an aqueous environment. *Staphylococcus aureus* (*S. aureus*) was used as a gram-positive model bacterium for antimicrobial activity evaluation. Finally, we demonstrated that the photo-generated ROS from the thin-film ZnO damage cellular membrane and contribute to the death of *S. aureus*.

References

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[2] Y. Li, W. Zhang, J. Niu, Y. Chen, ACS nano, 6 (2012) 5164-5173.

[3] K.-H. Park, G.D. Han, K.C. Neoh, T.-S. Kim, J.H. Shim, H.-D. Park, Chem. Eng. J., 328 (2017) 988-996.

2:00pm **AA1-WeA-3 ALD Enabled Non-linear Optical Properties at Substrate-film Interfaces**, *Z Gao,* Washington University, St. Louis*; M Hussain,* University of Dayton*; D Ceglia,* Aegis Technology Group Inc.*; M Vincenti,* University of Brescia, Italy*; A Sarangan, I Agha,* University of Dayton*; M Scalora,* US Army AMRDEC*; J Haus,* University of Dayton*;* ***Parag Banerjee***, Washington University, St. Louis

Metal-insulator and metal-semiconductor interfaces are a technologically important class of interfaces, given their ubiquitous presence in advanced materials and devices. ALD is an enabling synthesis tool for studying such materials systems as the first few monolayers deposited during ALD provide superb control over film thickness and nuclei morphology. Together with theoretical calculations and experimental nonlinear optical measurements, interfacial electronic properties at the nanoscale can be unraveled.

In this talk, the unique nonlinear optical signals generated from Au-Al_2O_3 and Au-ZnO systems will be described and correlated with predictions from hydrodynamic model for free electrons, incorporating quantum tunneling effects. Al_2O_3 and ZnO provide vastly differing nucleation behavior on Au substrates. Further, whereas Al_2O_3 is not known to be a nonlinear optical material, ZnO is strongly non-linear. The nucleation and growth of Al_2O_3 and ZnO on Au are studied using x-ray photoelectron spectroscopy (XPS) and Kelvin-Probe Force Microscopy (KPFM). The results show a clear nucleation followed by growth mechanism for ALD Al_2O_3 on Au, whereas for ALD ZnO on Au, a conformal layer-by layer growth is observed.

Second harmonic (SH) generation and third harmonic (TH) generation of incident light were measured on metal/insulator (MI): Au/Al_2O_3 & Au/ZnO; and metal/insulator/metal (MIM): Au/Al2O_3/Au & Au/ZnO/Au. The MIM was fabricated by coating the surface with gold nanoparticles. Both Al_2O_3 and ZnO films show a common feature for the SH signal in both MI and MIM structures. SH signals monotonically decreases and saturate once the Au surface is fully covered by the ALD film. In the case of Au/Al_2O_3, this allows us to develop a new phenomenological model[1] that estimates the occupancy of delocalized electrons in metal-induced-gap-states (MIGS) at 44%. On the other hand, the TH signal for the MIM case has a maximum that reaches a peak when the ALD film has a sub-nanometer thickness and is fully consistent with the electron quantum tunneling theory. Thus, ALD enables us to measure and understand interfacial electronic properties at the nanoscale for designing and fabricating future nonlinear optoelectronic devices.

References:

1. Gao, Z.; Hussain, M. M. R.; de Ceglia, D.; Vincenti, M. A.; Sarangan, A.; Agha, I.; Scalora, M.; Haus, J. A.; Banerjee, P., Unraveling delocalized electrons in metal induced gap states from second harmonics. *Appl. Phys. Lett.* **2017,***111*, 161601.

2:15pm **AA1-WeA-4 Bottom-up Fabrication of X-ray Optics using ALD**, ***Umut Tunca Sanli***, Max Planck Institute for Intelligent Systems, Germany*; C Jiao,* Thermo Fisher Scientific, Netherlands*; M Baluktsian, G Schütz, K Keskinbora,* Max Planck Institute for Intelligent Systems, Germany

The interest in X-ray microscopy has gained a rapid momentum especially in the last decade with the emergence of third- and fourth-generation synchrotrons, free electron lasers and new laboratory size X-ray sources. These new advanced X-ray sources require high-performance X-ray optics to study nano-scale structures. One of the most popular X-ray optic is the Fresnel zone plate (FZP), owing to its high-performance, monolithic structure and versatility. A FZP consists of alternating opaque and transparent co-axial annuli, which are the zones of the FZP. The resolution of the FZP is defined by the width of the outermost zone. Fabrication of the FZPs have been mostly relied on e-beam lithography, achieving resolutions down to 20 nm. However, efficient focusing of hard X-rays and resolutions beyond 20 nm requires structures that are extremely challenging to achieve *via* e-beam lithography or any other top-down subtractive method.

In this study, we follow a bottom-up approach and exploit the conformality and precision of ALD to manufacture the extremely challenging FZPs to achieve ultra-high resolution, highly efficient FZPs. Our method consists of three-steps: i) the fabrication of a micro-pillar array using a Plasma Focused Ion beam milling (PFIB), ii) the deposition of the multilayer zones of the FZP *via* ALD on the micro-pillar array and iii) the lift-out of individual FZPs using a FIB lift-out technique. The fabrication of FZPs requires using the ALD at the extreme. We deposit several hundred layers of ceramic materials, with thicknesses of 20-40 nm. The total deposition thickness reaches 6 µm. Due to its conformality, ALD allows multiple pillars to be deposited simultaneously. Hence, virtually unlimited number of FZPs can be fabricated out of one successful deposition. ALD is essential here as it

provides the needed precision in zone positions through sequential, self-limiting reactions.

ALD-FZPs resolved 15 nm structures, the best resolution ever obtained via a multilayer FZP. For even higher resolutions, a better control of the interface sharpness, the microstructure, the volumetric mass density, and the chemical composition of the deposited layers become essential. In this study, characterization of the ALD layers via High-resolution Transmission Electron Microscopy (HR-TEM), Electron Energy Loss Spectroscopy (EELS), Energy dispersive X-ray Spectroscopy (EDX) Wavelength-Dispersive X-ray spectroscopy (WDX), X-ray Photoelectron Spectroscopy (XPS) and X-ray reflectometry (XRR) will be presented. Our results confirm that high-quality layers and interfaces are achieved through our ALD processes, required for sub-10 nm resolutions.

2:30pm **AA1-WeA-5 Thickness Optimization of Aluminum Oxide for High Secondary Electron Emission Deposited via Atomic Layer Deposition**, ***Baojun Yan,*** Institute of High Energy Physics, Chinese Academy of Sciences, China

The performance of traditional electron multipliers, such as microchannel plate and channel electron multipliers, can be improved by coating high secondary electron emission (SEE) layers such as aluminum oxide via atomic layer deposition (ALD). The gain, peak to valley ratio and energy resolution of coated electron multipliers have been greatly improved by our previous study. As we all know, the SEE coefficient is depend on the material thickness if other conditions are fixed. In this study, the thickness optimization of aluminum oxide have been investigated. The aluminum oxide with varied thickness were deposited by ALD, and by comparing the performance of MCPs without and with aluminum oxide, the optimal range of SEE thickness can be obtained.

2:45pm **AA1-WeA-6 Effect of Deposition and Annealing Condition on Atomic Layer Deposited SnO_2 for Environmental Ozone Monitoring**, *S Mills, V Misra,* ***Bongmook Lee,*** North Carolina State University

Portable and wearable systems to continuously monitor environment pollutants over long periods of time is great interest to correlate an individual's exposure levels to personal health. For example, Asthma is a lifelong respiratory ailment causing wheezing, breathlessness, chest tightness, coughing and degrades the quality of life for the patient. The impact of certain environmental exposures such as ozone and particulate matter are also known to be critical triggers in asthma attacks. Solid-state based thin film sensors are favorable for real-time and long-term environmental monitoring. Among various types of gas sensors, metal-oxide based thin film sensors are widely used but detection of gases relies on high temperatures (>300^{o}C) for sensitivity and selectivity to various gases at the cost of many mW of power. Development of nanoscale metal oxide gas sensors which operate at room temperature is a promising strategy that leads to improved performance and reduced power consumption in the µW range. We have demonstrated that the high sensitivity and room temperature operated an ozone sensor based on atomic layer deposited (ALD) tin oxide (SnO_2). This work investigates the processing parameters such as deposition temperature and annealing time and its effects on tin dioxide sensor characteristics. Hall measurements were conducted on the SnO_2 films to evaluate the electrical properties as deposition and annealing conditions changed. It was found that the carrier concentration is generally increased with deposition temperature due to carbon impurities in the film at lower deposition temperatures. The electron mobility also increases strongly with deposition or annealing temperature resulting in lower resistivity of the film. It was also found that the SnO_2 deposited at 250^{o}C has a crystalline structure confirmed by the XRD but the orientation was not preferable for sensor application. Transient sensor response was conducted for different ozone concentrations varying from 25 parts per billions (ppb) to 100 ppb. Decreasing deposition temperature was found to be associated with decreasing film conductivity, increased ozone response, and increased carbon content. The carbon content was a result of steric hindrance during the deposition process and that the carbon is a substitutional impurity for oxygen in the crystal lattice. This results in the decreased electron concentration and increased ozone response. The effect of annealing temperature was also evaluated. 600C air anneal shows a maximum ozone response. By optimizing deposition temperature and annealing condition, a highly sensitive, selective and room temperature operated ozone sensor is realized.

3:00pm **AA1-WeA-7 Etch Behavior of Ti-based Oxide Grown by Atomic Layer Deposition for Spacer Application**, *H Kim,* ***Sanghun Lee,*** Yonsei University, Republic of Korea*; W Lee,* Pusan National University, Republic of Korea*; W Noh, S Gatineau,* Air Liquide Laboratories Korea*; S Kwon,* Pusan National University, Republic of Korea

Thin film grown by Atomic Layer Deposition has been enabled advanced nanopatterning technology such as spacer defined multiple patterning. The main scheme of this patterning technology is using sidewall spacer deposited by ALD as a hardmask.[1] However, usually the high aspect ratio and poor mechanical strength of spacers often causes its collapse problem and this phenomenon was also identified during multiple patterning process.[2] Therefore, the studies for spacer materials that have high etch selectivity and good mechanical properties are required, but there is lack of research on it. In this respect, TiO_2 is one of good candidate for spacer materials.[3,4]

Here, we studied on film properties of TiO_2 grown by ALD for spacer materials and further investigations for mixture with SiO_2 were followed. We observed growth of $Ti_xSi_{1-x}O_2$ (x=0~1) using $Ti(CpMe_5)(OMe)_3$, $Ti(O^iPr)_4$ and $H_2Si[N(C_2H_5)_2]_2$ and O_2 gas using PE-ALD at low temperature (100 °C). The chemical composition and carbon impurities of the films were analyzed by x-ray photoelectron spectroscopy (XPS), and the nanostructures of the films were analyzed by x-ray diffraction (XRD). And mechanical property of $Ti_xSi_{1-x}O_2$ films was investigated by nanoindentation. We compared the etch rate of $Ti_xSi_{1-x}O_2$ films using both dry and wet etching process. As a result, we obtained $Ti_xSi_{1-x}O_2$ films with various Ti/(Ti+Si) compositions and there was no Ti precursor dependency on dry etch rate which decreases as Ti composition increases. However, both pure TiO_2 films were not strippable by diluted HF solution due to its anatase phase. Furthermore, wet etch rate of mixtures were higher than even pure SiO_2 film when the films deposited by using $Ti(CpMe_5)(OMe)_3$.

Reference

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3:15pm **AA1-WeA-8 Scaling Atomic Layer Deposition to Astronomical Sizes: Low-temperature Aluminum Oxide Deposited in a Meter-sized Chamber**, ***David Fryauf,*** University of California Santa Cruz*; A Phillips,* University of California Observatories*; G Tompa,* Structured Materials Industries Inc.*; N Kobayashi,* University of California Santa Cruz

Atomic Layer Deposition (ALD) is attractive for producing transparent barrier films on metal-coated astronomical mirrors, but to date has been limited to relatively small-sized substrates. A new ALD tool has been designed, constructed, and tested to apply uniform protective coatings over a substrate with 0.9 m diameter. The new tool, nicknamed the Big ALD , employs a novel chamber design which isolates a large substrate surface to be coated by utilizing the substrate as a wall of the reaction chamber. Conceptual design and implementation of this new tool are discussed with potential applications to large astronomical telescope optics, specifically protective coatings for silver mirrors, and other future large structures. To demonstrate the potential of this new design, aluminum oxide was deposited by thermal ALD using trimethylaluminum and water at a low reaction temperature of 60°C. Growth rates, dependent on precursor pulse times and chamber purge times, show that the two half-reactions occur in a saturated regime, which demonstrates typical characteristics of ideal ALD behavior. It is found that uniformity in growth across the chamber, rather than growth rate at a single chamber position, must be studied and optimized to identify saturated growth mode in the Big ALD. Thickness uniformity across a 0.9 m substrate is within 3% of the average film thickness. Aluminum oxide deposition process parameters of the Big ALD are compared with those of a conventional 100 mm wafer-scale ALD tool, and saturated ALD growth over the 0.9 m substrate is realized with a simple scaling factor applied to precursor pulse and purge times. The

results show promising application of transparent robust dielectric films as uniform barriers across large optical components scaled to meter-sized and potentially larger substrates.

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