

## Thin Films Division

Room: 20 - Session TF-MoA

### Emerging Applications for ALD

**Moderators:** Mark Losego, Georgia Institute of Technology, Virginia Wheeler, U.S. Naval Research Laboratory

#### 1:40pm TF-MoA1 Probe the Reaction Chemistry during Atomic Layer Deposition onto $\text{CH}_3\text{NH}_3\text{PbI}_3$ , *Qing Peng, X.Z. Yu*, University of Alabama

The rapid development of organic-inorganic hybrid halide perovskites, represented by  $\text{CH}_3\text{NH}_3\text{PbI}_3$ , based solar cells is one of the major scientific breakthroughs of recent years. It is superior optoelectronic properties inspired applications beyond solar cells, including LEDs, transistors, and sensors. Thin metal oxide coatings are promising electron extraction layer, moisture barrier, electron injection layer, electron blocking layer, and high-k dielectrics for semiconducting  $\text{CH}_3\text{NH}_3\text{PbI}_3$ . Atomic layer deposition (ALD) is a promising method to directly put these metal oxides onto  $\text{CH}_3\text{NH}_3\text{PbI}_3$ . The pure heterogeneous reaction mechanisms provide ALD the capability to deliver conformal films on substrates of complex morphology with sub-nanometer control of the composition and thickness of the film. On the other hand, the heterogeneous-reaction-driven film growth mode in ALD process demands a molecular level understanding of the heterogeneous reaction chemistry. In this presentation, we will show the surface reaction mechanisms of ALD oxide on  $\text{CH}_3\text{NH}_3\text{PbI}_3$  by using a suite of in-situ and ex-situ analytic methods. Our results show that the heterogeneous reaction chemistries of ALD during the nucleation stage of ALD oxide on  $\text{CH}_3\text{NH}_3\text{PbX}_3$  is complex. Based on these fundamental understandings, we will further show that one can control the formation of the oxide layer by ALD through the careful control of the ALD chemistry and process conditions.

#### 2:00pm TF-MoA2 Digital Doping of ALD $\text{Nb:VO}_2$ Thin Films for Thermochromic Applications, *Alexander Kozen, M. Currie, B.P. Downey, C.R. Eddy, Jr., V.D. Wheeler*, U.S. Naval Research Laboratory

Vanadium Dioxide ( $\text{VO}_2$ ) is a thermochromic material that undergoes a first order crystalline phase transition at a critical temperature ( $T_c$ ) of 68°C. This structural phase transition is accompanied by major changes in electrical and optical properties, particularly in the infrared. As such,  $\text{VO}_2$  is suitable for many applications including microbolometers, adaptive thermal coatings, and passive spacecraft thermal shielding.

While the  $T_c$  of  $\text{VO}_2$  is appropriate for many current applications, it is desirable to modify the  $T_c$  to other values for improved performance of current applications or to address new emerging application needs. The  $T_c$  of  $\text{VO}_2$  has been shifted by doping with other transition metals on the order of 1-5%. [1], [2], however these doped  $\text{VO}_2$  films were deposited by PLD, MBE, and sputtering, all line of sight physical vapor deposition techniques.

We demonstrate digital doping of ALD  $\text{Nb:VO}_2$  by incorporation of ALD  $\text{Nb}_2\text{O}_5$  (TBTDEN +  $\text{O}_3$ ) into the conventional ALD  $\text{VO}_2$  process (TEMAV +  $\text{O}_3$ ). Inclusion of Nb into the ALD  $\text{VO}_2$  process in amounts between 1% and 5% makes minimal impact on as-deposited film morphology. After annealing, the  $\text{Nb:VO}_2$  films also exhibit minimal physical changes from their undoped analogues. We find that Nb doping can lower the  $T_c$  of the  $\text{VO}_2$  films by -13.5°C/Nb% while maintaining acceptable optical modulation behavior, critical for use of doped  $\text{VO}_2$  in emerging applications.

[1] W. Burkhardt, T. Christmann, B. K. Meyer, and W. Niessner, "W- and F-doped  $\text{VO}_2$  films studied by photoelectron spectrometry," *Thin Solid Films*, vol. 345, no. 2, pp. 229-235, 1999.

[2] X. Wu, Z. Wu, C. Ji, H. Zhang, Y. Su, Z. Huang, J. Gou, X. Wei, J. Wang, and Y. Jiang, "THz Transmittance and Electrical Properties Tuning across IMT in Vanadium Dioxide Films by Al Doping," *ACS Appl. Mater. Interfaces*, vol. 8, no. 18, pp. 11842-11850, May 2016.

#### 2:20pm TF-MoA3 Mechanisms in Organic and Hybrid Organic-Inorganic Molecular Layer Deposition, *David Bergsman\**, S.F. Bent, Stanford University

Molecular layer deposition (MLD) has seen increased interest in recent years for the deposition of organic and hybrid organic-inorganic ultrathin films. This vapor-phase, layer-by-layer technique, which relies on the same self-limiting precursor saturation as atomic layer deposition, has shown promise for the development of many applications that require conformal organic-

containing coatings, such as in photoresists, porous catalysts, and metal organic frameworks. Despite recent developments in MLD, there is a significant gap in our understanding of the mechanisms behind MLD and the microscopic properties of MLD-grown films, such as their molecular-level structure or degradation mechanisms. In this presentation, we will present results of our recent studies to understand such mechanisms, and discuss how that understanding can be used to better control the thermal, mechanical, electrical, and catalytic properties of these materials.

First, we discuss our exploration of the growth behavior of organic MLD films by examining trends in film properties as a function of backbone flexibility [1]. Our results suggest that changes in growth rate between the most rigid and most flexible backbones (4 Å/cycle vs 1 Å/cycle) are not caused by differences in length of molecular precursors, chain orientation (~25° on average for each backbone), or film density (1.0 - 1.2 g/cm<sup>3</sup>), but are instead caused by an increased frequency of terminations in the more flexible chemistries. Because of the physisorption of precursors, which reintroduce reactive sites, these terminations do not lead a complete cessation of film growth. We further elaborate on the structure of the films by examining crystal orientation and infrared absorption data, which suggest that films consist of a mixture of upward growing chains and horizontally aligned layers of paracrystalline polymer segments.

Second, we discuss manganese/ethylene glycol hybrid films, which have promise as nanostructured, earth-abundant catalysts for electrochemical water splitting. Time-dependent ellipsometry, infrared absorption, and x-ray photoelectron spectroscopy data indicate that the organic component of the films is unstable in air, as seen in other hybrid MLD materials. The degradation pathway will be discussed, based on the observation that the organic linkers primarily degrade into carboxylate ions. Thermal annealing and chemical treatments, such as exposure to oxygen and water, are further shown to affect this degradation and can be used to control the formation of nanoporous, catalytically active catalysts for the oxygen reduction reaction.

1. D. S. Bergsman, et. al., *Chem. Mater.*, 2017, 29, 1192

#### 2:40pm TF-MoA4 Inorganic Modification of Cellulosic Fibers for Enhanced Oil Sorption Capacity, *Andrew Short, S. Pamidi, Z. Bloomberg, M.D. Losego*, Georgia Institute of Technology

A few atomic layer deposition (ALD) cycles of metal oxides onto cellulosic fibers is known to modify the fiber's surface energy and make the fiber hydrophobic. In this research we use the trimethylaluminum-water chemistry to make cellulosic fibers highly hydrophobic (WCA ~160°) and oleophilic, transforming natural cotton into an ideal material for oil spill remediation. The ALD-treated cellulose floats on water for over 12 months and readily sorbs oil, whereas untreated cellulose preferentially sorbs water over oil (Figures 1 and 2). ALD-treated cellulose has a significantly higher oil sorption capacity (e.g., 20 g g<sup>-1</sup> vs. 0.11 g g<sup>-1</sup>) than raw cotton across a range of experimental conditions approximating those encountered in real-world oil spill remediation efforts (Figure 3). While studies in the literature report ultra-high oil sorption capacities (~200 g g<sup>-1</sup>), this study finds that reporting oil sorption capacity in terms of g g<sup>-1</sup> can be misleading, and recommends this measure be reported in tandem with the material's volumetric oil sorption capacity (g cm<sup>-3</sup>) because of its greater relevance to use-case effectiveness. The comparison of g g<sup>-1</sup> and g cm<sup>-3</sup> oil sorption capacities given in Table 1 demonstrate that the sorbent produced here is comparable to some of the best reports in the literature. This talk will detail how the oil sorption capacity of these new materials change with differing real-world conditions and explain the efficacy of  $\text{Al}_2\text{O}_3$  ALD applied to cellulosic fibers as a scalable, cost-effective method for creating biodegradable, on-demand materials for oil spill remediation.

#### 3:20pm TF-MoA6 Atomic Layer Deposition of Nano-Coatings on Fabrics for Antibacterial Applications, *Renee Puvvada, M. Bellavia, T.A. Sulchek, M.D. Losego*, Georgia Institute of Technology

About 1.7 million Americans contract hospital-acquired infections every year resulting in 99,000 inadvertent deaths and an estimated \$20 billion in healthcare costs. Here, we investigate the use of atomic layer deposition (ALD) to treat various fabrics (e.g., polyester, cotton, and blends) with antimicrobial inorganic materials to create unique antibacterial linens, scrubs, and hospital gowns. Our protocols include biological testing of the antibiotic performance of ALD-treated fabrics against DH5- $\alpha$ , a strain of *E. coli* that is engineered to be suitable for laboratory purposes. Antibacterial performance is tracked as a function of ALD cycle number at various deposition temperatures. Fabrics were exposed to *E. coli* and then incubated for 20 hours, after which cultures are serially diluted up to 7 times, spotted onto

\* TFD James Harper Award Finalist

Petri dishes, and incubated for another 20 hours. Colony counting is then used to quantify antibiotic effectiveness.

For ZnO ALD coatings of 0, 1, 10, and 100 cycles, we find that only the 100 cycle sample is sufficiently cytotoxic to kill all of the *E. coli* bacteria. Interestingly, for only a few cycles of ZnO (1, 3, and 10 cycles) the bacteria appears to grow more rapidly. We attribute this increased bacterial growth rate to the  $Zn^{2+}$  ions acting as a nutrient for the bacteria. It is known that in order to be an effective antimicrobial agent, ZnO must be "nano-sized" or larger; atomic forms of Zn and ZnO, which ionize into  $Zn^{2+}$  in nutrient broth, act instead as nutrients. A more detailed investigation of this transition from nutrient to antimicrobial will be discussed during this talk. We will also examine the effectiveness of other oxide materials including  $TiO_2$  and  $ZrO_2$  as well as compare the long-term performance of ZnO against common disinfectants like Lysol® and their stability in aqueous environments of varying pH.

4:00pm **TF-MoA8 ALD-based Functionalization of Biomaterials: Recent Developments and Future Challenges**, *Christos Takoudis*, University of Illinois at Chicago **INVITED**

Biomaterials are engineered to interact with biological systems for therapeutic and diagnostic clinical applications. Biomaterials can be synthesized in a lab or can directly be obtained from natural resources, and they constitute whole or part of a biomedical device or a living structure that can be utilized to execute, improve, enhance or restore a natural function. The surface of a biomaterial controls the interactions occurring at the interface between the biomaterial surface and its surrounding living environment. Hence, successful performance of a biomaterial relies on its appropriate surface properties. Many biomaterials do not have appropriate surface functions and properties to cater to specific needs and applications. Therefore, surface modification and functionalization leading to significantly improved performance of biomaterials would be highly desirable and sought after.

In modern surface science and engineering, bio-nanotechnology is a potent tool to functionalize surfaces incorporating nanometer size thin films and nano-structural features into materials. Among the available deposition techniques, atomic layer deposition (ALD) offers unique advantages in yielding conformal thin films of metal oxides or metals (from a few Å to hundreds of nm thick), uniformly, with precise control at atomic or molecular level; in this manner, the performance and functionality of functionalized biomaterials could be selectively altered, optimized and controlled as needed.

ALD is a relatively new technique for optimizing materials in bio-nanotechnology. Here, after a brief review of the more widely used modes of ALD, ALD's potential in bio-nanotechnology is presented with a few of its latest developments in biotechnology. ALD is promising means in tuning the hydrophilicity/hydrophobicity characteristics of biomedical surfaces, forming conformal ultra-thin coatings with desirable properties on high aspect ratio biomedical substrates, tuning the anti-bacterial properties of substrates surfaces of interest, and yielding multifunctional biomaterials for medical implants and other devices.

Recent developments on ALD at low (room or near room) temperature to functionalize the surface of heat-sensitive biomaterials with complex nanostructures are presented and discussed. Surface characterizations are done to investigate the morphology, chemical composition, crystallinity and wetting behavior of ALD-nanofilm coated biomaterial surfaces. The bioactivity of ALD  $TiO_2$ -coated surfaces, for example, is presented using in-vitro and in-vivo biocompatibility and biomineralization studies. Future challenges of ALD-based functionalization of biomaterials will be discussed.

4:40pm **TF-MoA10 Titanium Nitride ALD using Ultra-high Purity Hydrazine at Low Temperature**, *Dan Alvarez, J. Spiegelman, R. Holmes, S. Allanson, RASIRC, A.C. Kummel, S. Wolf, M. Kavrik*, University of California, San Diego, *K. Andachi, RASIRC*

Overview

New channel materials such as SiGe, Ge and InGaAs create challenging thermal budgets (<400°C) for metal nitride deposition. TiNx metal gate electrodes in particular need new low temperature ALD methods.

Hydrazine has shown viable reactivity in previous studies but practical use has been limited due to purity concerns, especially water contamination [1-3]. Commercially available anhydrous hydrazine typically has a water concentration ranging from 0.2-2.0%. In addition to this low purity issue, oxygen concentration in metal-nitride films made using hydrazine is a high 4-15% for SiNx and TiNx.

Previous reports detail the safe delivery of gaseous hydrazine using a solvent-based formulation and membrane delivery system [4]. This presentation details studies on water measurement and removal, plus low resistivity films resulting from hydrazine-based low temperature TiNx ALD.

Hydrazine Purification, Measurement

Studies show that water contamination levels can be reduced to <50 parts-per-million (ppm) using new hydrazine source purification methods as measured by Karl-Fischer and GC-MS methods. Gas phase output of the ultra-dry materials was measured below the FT-IR moisture measurement method lower detection limit of 0.83ppm (Figure 1). Standard commercially available hydrazine has a comparatively high gas phase moisture measurement of 31ppm.

Titanium Nitride Deposition

Sequential pulsing of  $TiCl_4$  and  $N_2H_4$  precursors at substrate temperatures of 275°C-350°C achieved atomic layer deposition TiNx. Initial measured resistivity at 350°C was a low  $R_{average} = 130$  ohm,  $R_{sheet} = 50$  ohm. Growth rate is approximately 0.5Å per cycle. Films were characterized by XPS (Figure 2), AFM, KPFM, TEM and four-point sheet resistance. Little to no oxygen was present in the TiNx film, which had a near stoichiometric ratio of Ti/N. The presentation will include additional optimization to reduce residual chlorine content at lower temperatures. In addition, a correlation with regards to residual Chlorine content/Resistivity versus deposition temperature will be discussed.

References

- [1] S. Wolf, M. Edmonds, T. Kent, D. Alvarez, R. Droopad, A. C. Kummel, AVS (2015) EM+NS+PS-MoA7.
- [2] K. Bernal-Ramos, T. Chen, R. Kanjolia, Y. J. Chabal, AVS ALD (2014).
- [3] B. Burton, S. Kang, S. Rhee, S. George, J. Electrochem. Soc. 155(7) (2008) D508-D516.
- [4] D. Alvarez Jr, J. Spiegelman, E. Heinlein, R. Holmes, C. Ramos, M. Leo, Sean Webb, ECS Trans. 72(4), (2016), 243-248.

5:00pm **TF-MoA11 ALD Barriers for Protection of Electronic Devices in Biological Environment**, *Ankit Singh, K. Adstedt, S. Graham*, Georgia Institute of Technology

Encapsulation plays a significant role in the protection and lifetime enhancement of electronic devices. Devices like OPVs, OLEDs, biological implants, and thin film solar cells are susceptible to rapid degradation on exposure to the surrounding media containing moisture and ionic species. Encapsulation barriers hermetically seal the devices and thus, prevent the ingress of moisture or any other fluid that can affect the function and stability of the devices. It involves use of inorganic barrier layers deposited using vacuum deposition processes. Out of several vacuum deposition techniques used for this purpose, atomic layer deposition (ALD) has shown an outstanding performance by producing films which have water vapor transmission rate less than  $10^{-4}$  g/m<sup>2</sup>/day. However, the performance and reliability of ALD barrier films is subject to their stability and resistance to corrosion in the surrounding environment.

Recently, miniaturized medical devices have gained popularity because of their new treatment and monitoring capabilities, ease of application and enhanced portability. These devices include artificial pacemakers, cochlear implants, artificial heart valves, etc. These devices are exposed to different bodily fluids that have varying pH and salt concentrations. Any electronic device cannot be expected to last for long enough time to be used as an implant with any protective covering. Thus, it becomes imperative to look for a robust solution.

In this work, we explore the use of different metal oxides deposited using ALD at 100°C in biological environment. The materials include  $Al_2O_3$ ,  $HfO_2$ ,  $TiO_2$  and  $ZrO_2$ . Chemical stability of the ALD films is determined by using electrochemical impedance spectroscopy (EIS) whereas, biocompatibility of the ALD films is determined using MTT cell proliferation assay measurements. For chemical stability test using EIS, a 3 electrode setup was used to understand the mechanism of material degradation. The ALD deposited materials were exposed to phosphate buffer saline (PBS) solution, simulated sweat and saliva, and Dulbecco's Modified Eagle Medium (DMEM) for 21 days. Besides ALD  $Al_2O_3$ , other metal oxides have demonstrated enhanced corrosion resistance and stability in different solutions. ALD  $HfO_2$  has better stability as compared to ALD  $Al_2O_3$  but tends to develop crack with long exposure time. However, ALD  $TiO_2$  and  $ZrO_2$  were found to be most stable in all the biological solutions used for testing. All the ALD materials used during the test have been found to be biocompatible using MTT cell proliferation test. Finally, we demonstrate the application of these ALD materials for protection of active implantable devices.

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