Thin Films Division
Room 104B - Session TF+PS-ThM

Deposition Processes for 3D and Extreme Geometries

Moderators: Richard Vanfleet, Brigham Young University, AnnaMaria Coclite, Graz University of Technology

8:00am TF+PS-ThM-1 ALD and Diffusion in High Aspect Ratio Carbon Nanotube Forests, *David Kane, R Davis, R Vanfleet,* Brigham Young University

Very high aspect ratio or nanostructured materials have numerous applications. In many of those applications, the surface is decorated by atomic layer deposition or other vapor phase deposition techniques. In these extreme geometries the uniformity of deposition is a function of the interplay between transport (diffusion) and reaction rates. The A-B cycling in Atomic Layer Deposition (ALD) separates the deposition reaction from the transport. We have observed a limited penetration depth which decreases with cycle number in ALD on vertically aligned multiwall carbon nanotube (MWCNT) forests with an effective aspect ratio of 1000. Models of ALD in high aspect ratio features based on Knudsen diffusion transport combined with a simple geometric model of nucleation and growth on surfaces with a low nucleation site density can qualitatively reproduce the observed deposition. Fitting the models to the data allows extraction of the diffusion coefficients for these confined geometries.

8:20am TF+PS-ThM-2 Nanoporous Reference Substrates for ALD on High Aspect Ratio High Surface Area Materials, *Dmitri Routkevitch,* InRedox

Deposition of conformal and uniform coatings onto high aspect ratio high surface area substrates and materials is a unique domain of ALD impacting many important applications, including energy generation and storage, semiconductor device manufacturing, chemical and biosensing and many others. However, ALD process development on such substrates is hindered by complex material geometry leading to poorly understood transport conditions and high cost of real substrates, such as large Si wafers at later staged of processing. In addition, modern ALD reactors, designed and optimized for high speed processing of flat substrates, require validation of uniformity and conformality of ALD coatings both inside the pores and laterally across the high surface area substrates with complex multiscale topology.

Nanoporous Anodic Aluminum Oxide (AAO) – a self-organized material resembling nanoscale honeycomb – is a controllable, well-defined, inexpensive and convenient nanomaterial platform to support the development and validation of high surface area ALD. The combination of ALD with AAO enables control of both the nanoscale geometry and chemistry with unprecedented precision to provide new avenues for design and engineering of functional materials and devices.

Some of the benefits of AAO as a reference ALD substrate are:

1. Highly uniform and parallel cylindrical pores, complex pore structures (modulated, branched, etc) available to emulate different pore size distributions of other materials.
2. A broad spectrum of transport conditions (pore diameters from 2 nm to 500 nm and pore lengths from <100 nm to >300 μm for aspect ratio (L/D) from 1 to as high as 50,000) that could be tested to aid better understanding and rapid development of new ALD processes.
3. Reproducible and well-understood surface chemistry of alumina makes it nearly universally suitable for many binary reactions involved in ALD.
4. High pore densities (10^{12} to 10^7 cm^{-2}) allow straightforward characterization of elemental depth profiles by EDS even for very thin (5-10 nm) coatings.
5. Available in different form factors and on different substrates (flexible foils and tapes, rigid plates, Si wafers, glass blanks, etc) to accommodate different types of ALD reactors, such reel-to-reel reactors for coating battery electrodes or reactors designed to process stacks of Si wafers or PV substrates. Scaleable to large sizes, low cost.

Several case studies will be presented where AAO was used as a reference substrate to aid the development of ALD for high surface area materials.

8:40am TF+PS-ThM-3 Fine-tuned Resistive Coatings for Detector Applications, *Maximilian Gebhard, A Mane, D Choudhury, S Letourneau, D Mandia, Y Zhang, J Elam,* Argonne National Laboratory

An important building block for detector devices are amplifiers, such as microchannel plates (MCPs). Due to the geometry of several periodically arranged microchannels, incident electrons or irradiation can be amplified by several orders of magnitude, making MCPs highly efficient in several applications such as neutron detectors and night-goggles. The efficiency of state-of-the-art MCPs is strongly related to functional coatings, acting as resistive coating and secondary electron emission (SEE) layer. While the SEE material (*e.g.* Al_2O_3 or MgO) should exhibit a high SEE coefficient, the resistive coating must facilitate a uniform and stable electrostatic field along the pores and during operation. It was shown previously that atomic layer deposition (ALD) is capable to produce highly efficient SEE coatings (MgO) as well as a fine-tuned resistive coating directly on the MCP substrate, thereby improving the overall performance of the detector devices.[1,2] By producing highly conformal thin films over large areas and on large aspect ratios, ALD is the method of choice to produce functionalized MCPs.

One challenge in manufacturing reliable MCPs for advanced applications are external conditions like ambient temperature. With temperature gradients of 100 K or higher, the thermal coefficient of resistance (TCR) of the resistive coating plays a major role with respect to electrical transport phenomena. Positive TCRs can cause increased resistance at elevated temperatures and in due turn a collapse of the MCP's performance. Similar determining factors are on hand for strongly decreased temperatures. A second challenge is the fluorine-based chemistry, which is currently often employed to produce ALD-functionalized MCP coatings.

We present here the development of ALD-fabricated materials, being free of fluorine chemistry and exhibiting tailored electric resistance over a broad temperature range as well as promising performance as resistive coating in MCPs. Apart from thorough process development, those transition metal-based materials were analyzed regarding their composition, structure and electrical behavior employing XPS, SEM, XRD and extended IV-measurements. Furthermore, the coatings were applied to MCPs, which were tested for their performance.

[1] A. U. Mane and J. W. Elam, *Chem. Vap. Deposition*, **2013** (19), 186-193

[2] M. J. Minot, B. W. Adams, M. Aviles, J. L. Bond, C. A. Craven, T. Cremer, M. R. Foley, A. Lyashenko, M. A. Popecki, M. E. Stochaj, W. A. Worstell, A. U. Mane, J. W. Elam, O. H. W. Siegmund, C. Ertley, H. Frisch and A. Elagin, *Proceedings Volume 9968, Hard X-Ray, Gamma-Ray, and Neutron Detector Physics XVIII*, **2016**, DOI: 10.1117/12.2237331

9:00am TF+PS-ThM-4 Tungsten Atomic Layer Deposition on Vertically Aligned Carbon Nanotube Structures, *Ryan Vanfleet, R Davis, D Allred, R Vanfleet,* Brigham Young University

Carbon Nanotubes (CNTs) can be grown from 2D patterns into high aspect ratio, 3D MEMS structures. These porous structures can then be filled solid with different materials in order to impart specific and unique properties to the MEMS device. Tungsten, with its conductivity, high density and high temperature resistance, could be of special interest for many MEMs devices. Due to the high packing density and high aspect ratios of vertically aligned CNT forests, it is difficult to uniformly deposit films throughout the entirety of the structure. Atomic Layer Deposition (ALD) has been shown to uniformly coat structures with extreme geometries using sequential, self-limiting surface reactions. This in an inherently slow process, especially on geometries where the deposition is diffusion-limited such as in CNT forests. Approximately 50 nm of tungsten is required to fill a CNT-patterned structure solid where the individual CNTs grow roughly 100 nm apart. The tungsten ALD process has been shown to be able to deposit more than a single atomic layer per cycle so that the necessary number of cycles to fill the CNT structure is reduced. The process parameters that facilitate this increased deposition rate will be discussed. Tungsten-filled CNT beams were subjected to three-point bending tests to determine material properties of the composite structures. Preliminary tests on beams with about 35 nm of as-deposited tungsten give an ultimate strength of 11 MPa and a Young's Modulus of 1.7 GPa. The microstructure of the as-deposited tungsten is extremely fine and annealing studies will also be addressed.

9:20am TF+PS-ThM-5 ALD in Metal Organic Frameworks: Toward Single Site Synthesis and Sinter-Resistant Catalysts, *Alex Martinson,* Argonne National Laboratory   **INVITED**

Reproducibly and homogeneously synthesizing single-site transition metal catalysts on exceedingly high surface area supports with stability under

catalytic conditions remains a grand challenge. To address this challenge, we utilize atomic layer deposition (ALD) in metal-organic frameworks (MOFs), a process we call AIM. Here, ALD provides a straightforward gas phase route to access a wide variety of small precision clusters with spatial and dimensional homogeneity. The well-defined structure of MOF NU-1000 framework and nodes allows for detailed characterization of their size and uniforming as well as insight into their inherent stability. This talk will discuss several classes of ALD precursors and processing conditions that have been identified to be compatible with few-atom cluster deposition in Zr-based MOF NU-1000.

11:00am **TF+PS-ThM-10 Alumina Deposition by Atomic Layer Deposition (ALD) on Flat Surfaces and High Aspect Ratio Structures**, *Dhruv Shah, D Patel, D Jacobsen, J Erickson, M Linford,* Brigham Young University

Atomic layer deposition (ALD) involves layer-by-layer deposition due to sequential exposure of two precursors to as substrate . ALD was developed in the late 1970s by Suntola and co-workers as a modification of chemical vapor deposition (CVD). In ALD, the dosing and purging steps are separated to ensure that each precursor saturates the surface before the other precursor enters the chemical reactor. ALD is widely used in the semiconductor and microelectronics industry to deposit thin films of various oxides on different substrates. ALD can be operated in two modes: plasma assisted and thermally assisted. Thermally assisted ALD has been widely used due to its high uniformity and conformality in depositing thin films on a variety of substrates.

Here we report alumina deposition by ALD using trimethylaluminum and water as precursors on silicon substrates. We optimized the process on flat surfaces like silicon shards, and extrapolate the process to high aspect ratio devices and powders, ultimately confirming the deposition on these high aspect ratio materials. Achieving high degrees of consistency and uniformity for deposition on powders through a frit using ALD has been difficult. We tried multiple recipes for alumina deposition, optimizing the dose time, purge time and effective exposure of the precursor on the substrate to achieve uniform results. Our thin films are characterized by spectroscopic ellipsometry (SE), water contact angle goniometry, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and/or transmission electron microscopy (TEM). The thin films we have obtained on planar substrates using ALD vary in thickness from 0.5 – 41.0 nm. These thin films were used to conduct a multiple sample analysis (MSA) in SE to obtain the optical constants of alumina. Since alumina is one of the most commonly used material in microfabrication, its optical constants will be useful in the field.

11:20am **TF+PS-ThM-11 Resistivity of the Alumina Diffusion Barrier in Catalytic Carbon Nanotube Growth**, *Berg Dodson, G Chen, R Davis, R Vanfleet,* Brigham Young University

By using photolithography techniques and catalytically grown carbon nanotubes (CNTs) it is possible to fabricate high aspect ratio structures that can be used as scaffolds for MEMS devices. The drawback of making CNT structures this way is it is difficult to electrically connect to them since they are grown on an insulating alumina layer. However, previous work demonstrates that the alumina layer becomes conductive during CNT growth. Two-point probe measurements from tungsten to a CNT post in a 100 nm tungsten/alumina 50 nm/CNT stack yielded 580 ± 65 Ω. I present TEM based data showing how this change in conductivity correlates with iron and carbon diffusing into the alumina layer during CNT growth. I will also show how the observed diffusion in these samples compares with what is predicted by diffusion models as well as how the change in resistivity compares to what is expected in doped alumina.

11:40am **TF+PS-ThM-12 High Temperature Active CeO_2 Nanorods Generated via Diffusion Limited Atomic Layer Deposition**, *Haoming Yan, X Yu, Q Peng,* University of Alabama

CeO_2 has attracted lots of attention due to its superior oxygen storage and donating ability as a catalyst support. CeO_2 nanorods has the best donating ability than all the other types of CeO_2 materials. However, the nanorods change its morphology and lose its activity at 400°C or above. Therefore, improving the thermal stability of CeO_2 nanorods can unlock the potential applications of CeO_2 nanorods in the high temperature applications. In this work, we introduce a diffusion-limited Al_2O_3 atomic layer deposition to selectively passivate the surface site of CeO_2 nanorods, largely enhancing its thermal stability and its oxygen storage capacity simultaneously.

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