Wednesday Morning, November 9, 2016

Thin Film
Room 105A - Session TF+MI+NS-WeM

ALD and Nanostructures

Moderators: Sean King, Intel Corporation, Mariadriana Creatore, Eindhoven University of Technology, Netherlands

8:00am **TF+MI+NS-WeM1 Scalable Manufacturing of Nanostructured Materials by Gas-Phase Deposition Techniques***, **Ruud van Ommen**,* Delft University of Technology, Netherlands **INVITED**

Core-shell nanoparticles and other nanostructured particles have high potential in applications such as catalysis, energy storage and pharma. However, a hurdle in their utilisation is that typically large amounts of such materials are required. Current liquid-phase and gas-phase synthesis methods often lack the high precision required or do not lend themselves to large-scale production. Gas-phase coating can be used to provide the surface of a particle with either a thin continuous coating or a decoration of nanoclusters. Coating techniques that can be used are chemical vapour deposition (CVD) [1], atomic layer deposition (ALD) [2], and molecular layer deposition (MLD) [3].

When carried out in a so-called fluidized bed, gas-phase coating is an attractive way of producing nanostructured particles with excellent scale-up potential. In such a system, the particles are suspended in an upward gas flow. We can do this both for nanoparticles and micron-sized particles. Nanoparticles – contrary to what is typically observed for larger particles – are fluidized as very dilute agglomerates with distinctive fluidization characteristics. I will discuss the challenges related to coating of nanoparticles using CVD, ALD, and MLD with such a system. Moreover, I will give a number of examples of the applications of nanostructured particles produced in this way.

[1] Valdesueiro, D., Meesters, G., Kreutzer, M., and van Ommen, J.R., 'Gas-phase deposition of ultrathin aluminium oxide films on nanoparticles at ambient conditions', Materials 8: 1249-1263 (2015).

[2] Goulas, A. and van Ommen, J.R., 'Atomic layer deposition of platinum clusters on titania nanoparticles at atmospheric pressure', Journal of Materials Chemistry A 1(15): p. 4647-4650 (2013).

[3] Vasudevan, S.A., Xu, Y., Karwal, S., van Ostaay, H.G.M.E., Meesters, G.M.H., Talebi, M., Sudhölter, E.J.R., and van Ommen, J.R., 'Controlled release from protein particles encapsulated by molecular layer deposition', Chemical Communications 51: 12540-12543 (2015).

8:40am **TF+MI+NS-WeM3 Surface Passivation of InP Nanowires by Atomic Layer Deposition***, **Lachlan Black**, Y. Cui, A. Cavalli, M.A. Verheijen, E.P.A.M. Bakkers, W.M.M. Kessels,* Eindhoven University of Technology, Netherlands

III/V semiconductor nanowires offer a variety of novel properties that make them of interest for electronic and optoelectronic device applications, including enhanced light trapping/concentration, reduced material use, and relaxation of lattice-matching constraints, which enables novel heterostructures and growth on inexpensive substrates. However, the greatly increased surface-to-volume ratio of nanowires compared to planar devices significantly increases the importance of surface recombination and hence of effective passivation of the nanowire surface.

In this work, we focus on nanowires of InP, a material of particular interest for optoelectronic devices. In contrast to the situation for GaAs, the bare or natively oxidised surface of InP presents relatively few electronically active defect states to facilitate surface recombination. However, in order to form InP device structures it is necessary to deposit an insulating dielectric layer on part of the InP surface, and this tends to result in significant depassivation of the surface, to the extent that the performance of InP devices is commonly limited by surface recombination.

Atomic layer deposition (ALD), as a relatively “soft” deposition technique capable of forming well-controlled, high-quality dielectric layers, would seem to offer the best chance of successfully passivating InP nanowire surfaces. ALD can be performed at low substrate temperatures, which is important to avoid phosphorus out-diffusion and resulting damage of the InP surface, while its excellent conformality allows for uniform deposition on nanowire surfaces. Nevertheless, previous attempts to passivate InP surfaces by ALD have encountered similar difficulties to other techniques in achieving low surface recombination for deposited dielectric layers of appreciable thickness.

In this work, we demonstrate successful dielectric passivation of InP planar and nanowire surfaces in the presence of a relatively thick (>10 nm) ALD Al_2O_3 layer deposited from trimethylaluminium (TMA), through the use of a thin phosphate interlayer deposited at low temperature in the same system from trimethyl phosphate (TMP), in both cases using an O_2 plasma oxidant. Time-resolved photoluminescence measurements show that carrier lifetimes are increased relative to the native surface for both planar and nanowire InP samples (e.g. from 1.6 to 2.4 ns for one nanowire sample), in contrast to a strong depassivation observed following ALD of Al_2O_3 and other dielectrics on the bare InP surfaces. X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) are used to elucidate the composition and structure of the deposited phosphate layers.

9:00am **TF+MI+NS-WeM4 Selectivity and Nucleation Effects in Atomic Layer Deposition of Copper for Plasmonic Nanostructures***, **Jie Qi**, B.G. Willis,* University of Connecticut

Plasmonic nanostructures made of conducting metals such as copper, silver, and gold have been intensively investigated due to their capability for enabling optics beyond the diffraction limit and making it possible to manipulate visible and near-IR radiation at the nanometer scale. The interaction between metallic nanostructures and incident light induces large enhancements of the local electromagnetic fields via the excitation of localized surface plasmon resonances (LSPRs). These confined and enhanced fields have many exciting applications in optical detection, cancer therapeutics, biological and chemical sensors, spectroscopy, catalysis, and photovoltaics. A key feature of nanoscale plasmonic materials is a strong dependence of the plasmon resonance on size, shape, composition, and surroundings of the nanostructures. Selective area atomic layer deposition (SA-ALD) offers a promising nanofabrication technique to further tune the properties of plasmonic nanostructures with composition and thickness control at an atomic level. Successful application of SA-ALD requires good control of nucleation and surface morphology evolution, as well as good selectivity. Unfortunately, there are very few studies that report selectivity and/or nucleation characteristics, and their dependence on growth conditions.

In this work, we investigate the growth characteristics of Cu SA-ALD for tuning plasmonic nanostructures. Pd nanostructures are fabricated by electron-beam lithography and used as template layers. Samples are analyzed by AFM, high-resolution SEM, and image processing to investigate nuclei size and density, and morphology evolution. It has been found that nucleation is greatly affected by deposition temperature and co-reactant H_2 partial pressure. Poor nucleation leads to a rough surface with randomly distributed nanoparticles, while good nucleation leads to smooth, conformal growth over the entire feature. Sample surface pretreatments are found to be more critical for initiating growth on nanostructures compared to planar films, which might be related to residual impurities from photoresist layers or other contaminants from nanofabrication processing. Several preparation cleaning methods have been investigated for their effects on Cu film nucleation and growth selectivity including: UV-Ozone, O_2 plasma, annealing in H_2, annealing in He, boiling in water, and dipping in dilute HF.

9:20am **TF+MI+NS-WeM5 Metal Oxide Aerogel Patterning by CO_2 Laser Etching of ALD-coated Carbon Nanotube Macro-Structures***, C. Aksu, P.D. Bradford, **Jesse Jur**,* North Carolina State University

Patterning techniques of metal oxide foam architectures embedded within an ALD-coated carbon nanotube interconnected matrix are defined. Three dimensionally interconnected networks of carbon nanotube are produced from spinnable vertically aligned CNT arrays in which CNTs make. Atomic layer deposition is used to functionalize the surface of the CNTs in the array. Prior work has demonstrated that the CNT networks can be sacrificially removed to form aerogel architectures of the ALD material. In this study, we present a simple and scalable method to fabricate macro-sized structures of ALD alumina foams embedded in the carbon nanotube foam architecture via a CO2 continuous wave laser etching. Specifically, we have demonstrated the ability to ALD modify the CNT in large macro-structures (>1 cm2) and subsequently remove the CNT from specified areas, leading to the complex hybrid alumina-CNT periodic structures. The effects of ALD coating thickness are inspected by in-situ heating transmission electron microscopy methods and by high resolution scanning electron microscopy. Factors relating to manufacturability (i.e. etching speed and power) and dimension stability (i.e. laser etch size) are defined to identify scale-up opportunities.

9:40am **TF+MI+NS-WeM6 Tungsten ALD in Porous Carbon Nanotube Forests***, K. Hinton, N. Hollingworth, D.D. Allred,* ***Richard Vanfleet,*** Brigham Young University

We have deposited tungsten on carbon nanotube (CNT) forests by CVD (WF$_6$ & H$_2$) and ALD -the silane reduction of WF$_6$. Resulting structures are studied by scanning electron and transmission electron microscopy. We observed that the CNT forest provides a scaffolding for the nucleation and growth of the tungsten. Such structures may be a useful avenue for metal MEMS that does not require extensive etching. The present study may provide insight into the mechanisms of ALD in highly porous structures. In conventional ALD on surfaces which are largely planar, the amount of reactants needed to completely cover the surface does not change much from step-to-step. In contrast the surfaces of carbon nanotube forests consist of cylindrical tubes largely oriented perpendicular to the sample surface. Thus, the surface area increases with deposition. This is in addition to the changes in surface area associated with incubating early stage nucleation sites. When beginning with adequate tungsten or silane one might expect to move to starvation mode as the number of cycles increases if the amount of each reactant is kept constant. We see evidence for tungsten starvation in our research results. For low number of cycles the CNT fibers have a spatially uniform nucleation of tungsten. For low amounts of WF$_6$ or low "soak" times, as cycles increase, growth on the top surface and sidewalls of the carbon nanotube forest outpaces growth within the structure. Post deposition cross-sections show distinct bands witnessing the starvation of tungsten growth in the interior as more of the tungsten is deposited on regions that have direct access to the WF$_6$ gas. EDX analysis across such a cross-section shows distinct plateaus in the amount of tungsten present corresponding to the bands.

11:00am **TF+MI+NS-WeM10 Rational Design of Hyperbranched ZnO Nanowire Systems for Superomniphobic Surfaces Enabled by ALD***,* ***Ashley Bielinski,*** *M. Boban,* University of Michigan, Ann Arbor*; Y. He,* Pacific Northwest National Laboratory*; E. Kazyak,* University of Michigan, Ann Arbor*; C. Wang,* Pacific Northwest National Laboratory*; A. Tuteja, N.P. Dasgupta,* University of Michigan, Ann Arbor

Semiconductor nanowires (NWs) are powerful 1D building blocks for a range of technologies including electronics and optics, sensors, mechanical resonators, and energy conversion [1]. NW arrays are synthesized with careful control of morphology and composition using both top-down and bottom-up approaches. However, the hierarchical assembly of these NWs into heterogeneous systems remains challenging, largely due to lack of deterministic control of feature size, shape and position in 3D assemblies. Here we demonstrate that Atomic Layer Deposition (ALD) is a powerful tool for modifying interfaces to control the fabrication of ordered hyperbranched NW systems. Hierarchical branched NWs bridge the nano and micro length scales, while providing an exponential increase in surface area. Examples have been synthesized for a variety of applications, but the ability to tune the morphology along a spectrum in order to optimize the structure requires development.

Nanoscale patterning techniques for NW placement, while slow and costly on planar substrates, often become impossible on high aspect ratio structures. Solution-based techniques offer scalability and lower cost, but the results are often disordered and difficult to tune. Our approach uses ALD to catalyze the nucleation of NWs on the substrate during hydrothermal growth. ALD is essential for this approach because it deposits conformal films on ultra-high aspect ratio substrates, with atomic-scale control of film composition and structure. We've demonstrated that by varying the thickness of ALD ZnO films, their crystallographic orientation, roughness, and surface stress can be controlled [2]. These catalyst seed layers allow us to tune the NW array morphology, including density and orientation, over a range of substrate materials and geometries.

We further show that ALD can overcome challenges that arise when transitioning from simple NW arrays to complex branched structures [3]. First, amorphous ALD TiO$_2$ over-layers are used to reduce nanowire density creating space for subsequent levels of hierarchy. Next, ALD interlayers are used to block the crystallinity of the previous level of ZnO NWs to allow for non-epitaxial deposition of the subsequent ALD seed layer, forming core-shell NWs. These new techniques were used to grow hierarchical branched NW arrays, which were shown to be superomniphobic (repellent to high and low surface tension liquids) with tunable contact angles for different liquids using ALD to control the array properties.

[1] Dasgupta, N. P.; et al. *Adv. Mater.***2014**, *26* (14), 2137–2184.

[2] Bielinski, A. R.; et al. *Chem. Mater.***2015**, *27* (13), 4799–4807.

[3] Bielinski, A. R.; et al. *Submitted***2016**

11:20am **TF+MI+NS-WeM11 Bio-Templated *Morpho* Butterfly Wings by ALD for Photocatalysis***,* ***Robin E. Rodriguez,*** *D. Das, S.P. Agarwal,* University of Michigan, Ann Arbor*; W. Shang, T. Deng,* Shanghai Jiao Tong University, China*; N.P. Dasgupta,* University of Michigan, Ann Arbor

Hierarchical nanostructures found in biology have unique properties that inspire bio-mimetic engineering. These natural nanostructures present design principles of bottom-up nanomanufacturing for materials with tunable properties. For example, structural coloration is a phenomenon observed in a wide range of natural materials that take advantage of nanoscale hierarchical structures to tune their reflection and absorption properties through periodic diffraction and photonic resonances. Here we demonstrate *bio-templating* via Atomic Layer Deposition (ALD) as an approach to manufacture atomically-precise synthetic materials that manipulate the natural structural coloration found in *Morpho* butterfly wings for enhanced photocatalytic activity.

Until recently, conventional approaches to bio-templated nanomaterial synthesis have been limited in their ability to create highly conformal 3-D interfaces between temperature- and chemically-sensitive bio materials and functional thin films. ALD is uniquely suited for scalable and conformal bio-templating, which allows us to use the nanoscale structural complexity that nature provides to tune the interfacial properties of natural systems by coating them with functional materials. By varying the geometric and optical properties of the surface, ALD is able to tune structural coloration to manipulate the light absorbing and photocatalytic properties of natural materials with nanostructured surfaces.

Morpho butterflies are particularly interesting examples of structural coloration, which occurs due to hierarchical nanostructures on their wing surfaces. The combination of strong photonic resonances and high surface area in these wings represent an ideal template for photocatalysis. To demonstrate this, proof-of-concept tests were performed on *Morpho* wings coated by ALD of TiO$_2$ and ZnO. Electron microscopy images showed conformal coating of the wing geometries at the nanoscale. The structural coloration of the butterfly wings could be tuned using this approach, which was modeled using finite-difference time-domain simulations of the modified wing geometry. The viability of this approach was further demonstrated in the photocatalytic degradation of methylele blue dyes in water, which led to an increase in photocatalytic activity relative to planar thin film samples. The ALD deposited materials show superior photocatalytic activity which was attributed to enhanced light absorption and increased surface area from the butterfly's hierarchical structures.

Author Index

Bold page numbers indicate presenter