Wednesday Morning, October 20, 2010

Thin Film
Room: Ruidoso - Session TF-WeM

ALD: Nanostructure, Magnetics and Biological Applications

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

8:00am **TF-WeM1 Magnetic Nano-Objects Based on Atomic Layer Deposition: Switching Modes in Nanotubes and Core-Shell Nanowires**, ***J. Bachmann***, *K. Nielsch*, University of Hamburg, Germany **INVITED**

Atomic layer deposition (ALD) is uniquely suited to the conformal deposition of magnetic thin films in pore structures of high aspect ratio, while offering precise tuning of the layer thickness and high uniformity. Combining one or several layers of ALD with self-ordered porous anodic alumina membranes used as templates yields arrays of magnetic nanotubes with diameters tunable between 20 and 200 nm, wall thicknesses from 2 to 40 nm, and lengths set anywhere between 0.1 and 100 microns. The magnetic properties of such nanotubes strongly depend on their geometry, as evidenced on the ensemble and single-object levels by SQUID and MOKE magnetometries, respectively. The structural parameters can be chosen so as to favor a certain mechanism of magnetization reversal or another.

Further structural complexity can be created by introducing additional preparative steps. Interference lithography can be exploited for sculpting tubes with controlled modulations in diameter. Electrodeposition enables us to synthesize wires in which a core and a shell of two distinct magnetic materials are separated by a non-magnetic spacer layer. In those cases, the geometric parameters are still accurately controlled and tunable. The particular geometric characteristics of the system directly transpire into their magnetic properties: diameter modulations may hinder the propagation of magnetic domain boundaries, whereas core-shell structures may give rise to two distinct magnetic reversal events.

8:40am **TF-WeM3 Structural and Magnetic Properties of Anatase Mn-doped TiO_2 Film Synthesized by Atomic Layer Deposition**, ***M.C.K. Sellers***, *E.G. Seebauer*, University of Illinois at Urbana-Champaign

Transition metal doped semiconductors exhibiting room temperature ferromagnetism are intensely investigated for spintronics applications. Devices leveraging the spin-dependent effects of these materials would allow for increased data processing speeds, decreased power consumption, and improved integration densities in comparison to standard charge-based electronics. In the past ten years, experimental and computational studies have demonstrated room temperature ferromagnetism (RTFM) for several TiO_2-based dilute magnetic semiconductors (DMSs) namely TiO_2 doped with Mn, Cr, Fe, and Co. Most DMS TiO_2 films are synthesized via sol-gel, pulsed laser deposition (PLD), and plasma-assisted molecular beam epitaxy (PAMBE). Atomic layer deposition (ALD) of DMS TiO_2 has never been demonstrated, although this method has been used to deposit Mn-doped ZnO with DMS properties. ALD circumvents complications with solvent and byproduct removal and with calcination-induced shrinkage that arise during sol-gel synthesis. PLD and PAMBE are ill-suited to the high throughput requirements of commercial manufacturing. In addition, PLD can result in high particulate composition and uneven coverage, while PAMBE films suffer from thickness-dependent morphologies. ALD avoids such problems. The present work involves the synthesis of Mn-doped anatase TiO_2 (0 to 5 at% Mn) thin films on Si(100) via ALD at 200°C and 400°C. $Ti(OCH(CH_3)_2)_4$ and H_2O are utilized as ALD precursors and $Mn(DPM)_3$ as a dopant source. The effect of substrate temperature, number of cycles, precursor and oxidant injection times, purge time, and distance between sample and delivery tube on film thickness and uniformity have been investigated. X-ray photoelectron spectroscopy measurements indicate that Mn is successfully doped in the TiO_2 matrix and reveal information about film composition and elemental chemical states. Microstructure, crystallinity, bulk density, and roughness were investigated with scanning electron microscopy, x-ray diffraction, and x-ray reflectivity. SQUID magnetometry was used as a probe of RTFM; the bulk density, microstructure, and magnetic moment of the TiO_2 vary with the concentration of Mn. The results provide insight into the properties of DMS TiO_2 synthesized via ALD and underscore the advantages of the technique - precise thickness, compositional control, and higher process throughput - in comparison to alternative techniques of DMS growth.

9:00am **TF-WeM4 Fabrication of Refractory Nanoporous Structures by ALD of Tungsten on High Surface Area Silica Aerogels**, ***A.U. Mane***, Argonne National Laboratory, *U. Sampathkumaran, T. Owen, R. Winter*, Innosense LLC, *J. Nolen, J. Greene, J.W. Elam*, Argonne National Laboratory

Refractory nanoporous materials with high porosity could serve as efficient catchers for the fast release of unstable nuclei in rare isotope accelerators. The unique, self-limiting capability of atomic layer deposition (ALD) offers an attractive synthetic route for fabricating refractory nanoporous materials. Here we demonstrated a method using high surface area silica aerogel monoliths as templates for the growth of conformal thin films by ALD. Static mode ALD of W using Si2H6 and WF6 at 200oC was employed to coat the inner surfaces of the low density, nanoporous silica aerogel monoliths. To facilitate nucleation and improve adhesion of the ALD W, the aerogels were coated with 2Å Al2O3 using alternating exposures to Al(CH3)3 and H2O prior to the W ALD. After coating, scanning electron microscopy revealed a porous microstructure in which the ALD W completely encapsulates the silica aerogel. The porosity of the aerogels was preserved during the first ~10 W ALD cycles allowing the density to be controlled by adjusting the number of W ALD cycles and values as high as 5 g/cc were obtained. BET surface area measurements revealed a gradual decrease in the surface area of the silica aerogel with increasing numbers of W ALD cycles consistent with a gradual filling of the aerogel voids. Next, we heated the W-coated aerogels to 1500oC in an inert atmosphere and observed that they maintained their integrity and porosity with almost no loss in density. These results are very encouraging for the deployment of these materials as isotope catchers.

9:20am **TF-WeM5 Nucleation and Ultra-Thin Film Formation during ALD on Multiwall Carbon Nanotubes**, ***C. Devine***, *J.S. Jur, C. Oldham, J. Bonner, G.N. Parsons*, North Carolina State University

Atomic layer deposition is widely studied as a means to coat and encapsulate polymers to impede diffusion of water, oxygen or other species. ALD is also a viable means to coat and surface functionalize carbon nanotubes and other nanostructured materials. Previous work suggests that ALD nucleation proceeds differently on single and multiwalled carbon nanotubes, where the more defective nature of multiwalled tubes allows more rapid nucleation and film growth. In this work, we are interested in using ALD to encapsulate multiwall carbon nanotubes with as thin a layer as possible, to modify the chemical signature of the nanotubes while maintaining their advantageous mechanical and physical properties. Our motivation for this work is to explore means to alter potential toxic inhalation effects that carbon nanotubes may present, for example, in manufacturing facilities producing nanotube-based products. We have worked with multiwall nanotubes from Helix Materials Solutions as well as from Mitsui. The Mitsui tubes are 30-50 nm in diameter and contain many concentric nanotubes. TEM analysis shows that ALD using TMA/water at 90 C proceeds slowly at first, producing isolated nuclei for the first 15 cycles. Films are smoother after 25 cycles, and continuous film coatings are observed after 80 cycles, corresponding to film thickness of 3.8 nm. After complete film coverage, the film growth rate increases to values close to that expected for TMA/water at this process temperature. We will present results regarding how these coatings affect physical properties of the nanotubes, including surface wetting, as well as possible new means to coat large numbers of nanotubes in a conventional viscous flow reactor system.

9:40am **TF-WeM6 Chemical Vapor Deposition of Sandwiched Antibacterial Layers**, ***F. Schamberger***, *T.H. Huber, G. Franz*, Hochschule Muenchen, Germany

To deposit organic polymers on three-dimensional, even rugged surfaces, (pe)cvd is the method of choice. Thickness and film quality are mainly controlled by the number density of the precursors and their mixing ratio which determine the equilibrium of polymerization between reactions in the gas phase at high densities or at the surface for low densities. In most cases, MFCs can be used. Since MFCs can be heated only up to about 80 °C, precursors with low vapor pressure cannot be discharged into the reactor by this method, and the flow is mainly controlled by vapor pressure which limits the controlled deposition of thin layers.

We have recorded the vapor pressure curves for diparylene N and diparylene C applying a dynamic and a static method, resp. [1], and correlated flow and deposition rate with vapor pressure. To meet the demands for exact layer thickness even for values below 1 µm, an almost digital grow method is required. We introduce such a simple, low-cost method for the coating of antibacterial layers which have been deposited by subsequent wet chemical methods and galvanic plating. For very thin layers, the increase in pinhole density with shrinking film thickness has

been investigated as functions of total pressure and process time by qualitative visual inspection (sem) and quantitative measurements by comparing the permeability of thin films against water vapor and oxygen. For swiss cheese layers, the antibacterial film below is but partly protected, however, the antibacterial action can be prolonged over years. Eventually, the change in mechanism from polymerization at the surface to volume polymerization has been investigated by varying the doping levels of the ambient gas (argon or oxygen), and has been correlated in-situ by mass spectrometry and ex-post to some film properties; among them are surface roughness and surface energy and the refraction index as well as the ir spectrum which has been modeled for the dimeric and the polymeric species applying a Gaussian method.

[1] Council Regulation (EC) No 440/2008 of 30 May 2008 laying down test methods pursuant to Regulation (EC) No 1907/2006 of the European Parliament and of the Council on the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) (Text with EEA relevance), Official Journal L 142 , 31/05/2008 P. 0001 - 0739

10:40am **TF-WeM9 ALD for Nano and Micro Electro-Mechanical Systems**, ***V.M. Bright***, University of Colorado at Boulder **INVITED**

Atomic Layer Deposition (ALD) can be effectively used to deposit custom-designed, multi-material layers with atomic resolution on any micro- or nano-scale device surfaces. The nano-scale ALD coating can protect the devices from electrical short, charge accumulation, moisture-induced adhesion, wear, corrosion, creep, fatigue or anodic oxidation during prototyping or long-term product life. ALD films for N/MEMS achieve these goals similar to what CVD Si_3N_4 has been for CMOS. As MEMS scales further shrink toward nano-electro-mechanical systems (NEMS), ALD processes offer a new strategy for depositing conformal and precise films that may have important applications as a novel dielectric, a sacrificial layer for gap control in nanofabrication, or as a structural layer for NEMS realization.

ALD relies on sequential, self-limiting surface reactions to deposit ultra thin, conformal films. The following characteristics of ALD films and processes make them flexible and multifunctional, and represent their appeal for N/MEMS: ALD film thicknesses can be precisely deposited from a few Å to hundreds of nm; ALD films can be deposited at temperatures ranging from 33ºC to over 200ºC; ALD films are pinhole-free, dense, smooth and highly conformal; ALD films can be deposited on silicon, polysilicon, silicon nitride, metals, polymers, and ceramics; ALD films can be conformally deposited on any size or shape device or any substrate; ALD can coat high surface area to volume ratio structures with complex geometries; ALD can deposit dielectric or conductive layers; ALD can deposit hydrophobic or hydrophilic layers covalently bonded to the surface; ALD can deposit on lithographically defined selective areas; ALD films can be micromachined to create nano-scale gaps and free standing structures; ALD coating process' deposition rate can be high, e.g. 0.5 nm/min at 177°C for Al_2O_3.

These ALD techniques for N/MEMS, pioneered at the University of Colorado – Boulder, represent breakthrough in nano-scale processes that can be used to fabricate custom-designed, multi-material layers with atomic resolution. The ALD processes developed are proven, mature, and are available to serve the N/MEMS community.

References

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11:20am **TF-WeM11 Understanding Plasma Enhanced Chemical Vapor Deposition for the Production of Composite Nanomaterials with Biomedical Applications**, ***J.C. Shearer***, *E.R. Fisher*, Colorado State University

Fe_2O_3 and other magnetic nanoparticles are becoming key components of both chemical and biological applications, including drug delivery schemes and magnetic resonance imaging contrast agents. Nanoparticles coated with organic and inorganic films have distinct properties and enhanced functionalities over those of uncoated nanoparticles. Plasma-enhanced chemical vapor deposition (PECVD) was employed to conformally coat Fe_2O_3 with SiO_2 or polyallyl alcohol films, thereby creating composite nanomaterials. Comparisons will be made between composite nanoparticles created with an in-house atmospheric pressure plasma system and similar composite materials created in a traditional low-pressure PECVD system. In other studies, surface sites were activated with O_2 and Ar plasmas to plasma graft SiO_2 and polyallyl alcohol monolayer films onto the nanoparticles. Compositional and morphological data demonstrate that conformal SiO_2 and polyallyl alcohol coatings were achieved and that the use of PECVD methods allowed specific tailoring of the film structure, composition, and growth characteristics. The performance of the composite materials was explored through dispersion, UV-vis spectroscopy, and chemical functionalization studies. Further insight into the deposition process is provided by actinometric optical emission spectroscopy (AOES) and laser induced fluorescence spectroscopy (LIF), which allow characterization of the gas-phase species and their energetics (i.e. internal and kinetic energies) for each system. Preliminary data from our Imaging of Radicals Interacting with Surfaces (IRIS) technique provides additional information on the molecular-level chemistry that occurs at the interface between gaseous plasma species and nanoparticle substrates.

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