

# Tuesday Afternoon, October 16, 2007

## Nanomanufacturing Topical Conference

Room: 615 - Session NM+TF-TuA

## Nanomanufacturing of Materials

**Moderator:** M. Tuominen, University of Massachusetts, Amherst

**1:40pm NM+TF-TuA1 Nanoscale Patterning with S-layer Proteins and Area Selective Atomic Layer Deposition, J.R. Liu, C.M. Tanner, E. Lan, B.S. Dunn, J.P. Chang, University of California at Los Angeles**

Nano-sized crystalline bacterial cell surface layer (S-layer) proteins have the intrinsic property to reassemble into two-dimensional arrays with ordered pores of identical size onto solid supports,<sup>1</sup> ideal as a template for nanoscale patterning. In this work, we demonstrated that, when combined with area selective atomic layer deposition (ALD), the reassembled S-layer proteins can be effective nanotemplates to pattern nano-sized dielectrics. S-layer proteins were reassembled on Si wafer from the solution containing protein units and  $\text{CaCl}_2$ . Atomic force microscopy (AFM) and transition electron microscopy (TEM) images showed that the protein unit size and the pore diameter are about 10 nm and 5 nm, respectively. Octadecyltrichlorosilane (ODTS) was used to modify the more hydrophilic protein surface since ODTS has been demonstrated to be an effective monolayer resist on a hydrophilic  $\text{SiO}_2$  surface toward ALD of  $\text{HfO}_2$ .<sup>2</sup> High-k oxides were only deposited in the pores built by the protein units by an area selective ALD after the S-layer nano-template was modified by ODTS. Attenuated total reflection-fourier transform infrared spectroscopy (ATR-FTIR), contact angle measurement, and x-ray photoelectron spectroscopy (XPS) were employed to analyze the reassembling, modification, and removing process of S-layer proteins. FTIR analysis of the reassembled S-layer proteins before and after ODTS treatment revealed NH ( $3297\text{ cm}^{-1}$ ),  $\text{CH}_3$  ( $2968$  and  $2866\text{ cm}^{-1}$ ),  $\text{CH}_2$  ( $2922\text{ cm}^{-1}$ ), CO ( $1645\text{ cm}^{-1}$ ), and CN ( $1525\text{ cm}^{-1}$ ) from S-layer proteins, while the intensity of  $\text{CH}_2$  increased after modified by ODTS, due to the 17  $\text{CH}_2$  groups in ODTS. The ODTS treated S-layer proteins surface became more hydrophobic, evident by a contact angle change from  $59^\circ$  to  $84^\circ$  for 2h and  $101^\circ$  for 40h. After cleaning, the peaks of NH ( $3297\text{ cm}^{-1}$ ),  $\text{CH}_3$  ( $2968$  and  $2866\text{ cm}^{-1}$ ),  $\text{CH}_2$  ( $2922\text{ cm}^{-1}$ ), CO ( $1645\text{ cm}^{-1}$ ), and CN ( $1525\text{ cm}^{-1}$ ) from S-layer proteins disappeared, confirming that S-layer proteins have been removed completely. The current-voltage (I-V) of oxide nanopatterns is characterized by a conductive AFM.

<sup>1</sup> U. B. Sleytr, P. Messner, D. Pum, and M. Sara, *Angew. Chem. Int. Ed.*, 1034-1054, 38, 1999.

<sup>2</sup> R. Chen, H. Kim, P. C. McIntyre, and S. F. Bent, *Appl. Phys. Lett.*, 4017-4019, 84, 2004.

**2:00pm NM+TF-TuA2 Plasmonic Nanoparticle Complexes for Diagnostics and Therapeutics, N.J. Halas, Rice University INVITED**

The combination of metallic nanostructures and molecular adsorbates provides a broadly adaptable route to the development of optically addressable, functional nanocomplexes. In particular, nanostructures based on this approach can be designed to sample, and, via Raman scattered light, report on specific aspects of their chemical environment. Combining this sensing functionality with photothermal heating of the local environment of the nanocomplex provides an important strategy for functional therapeutics for cancer and beyond.

**2:40pm NM+TF-TuA4 Conduction Nature of Nanochannels of Track Etched Polymeric Membranes, K. Awasthi, University of Rajasthan, India**

The nanopores are developed by using one side etching of swift heavy ion irradiated polymeric membrane. In an electrolytic cell, the chemical solution serves as well as etchant and as an electrolyte. In the moment breakthrough of a track the beginning and increasing electrical current supplies information of the birth and growing of the track. The membranes used can be seen as model systems acting as interconnects between two separate liquids. There is a significant difference in the electrical conduction behavior of the electrolytes having common anion. It is clear from the voltage current characteristics that electrical conduction through the etched membrane of polycarbonate is dependent on size of cation.

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**3:00pm NM+TF-TuA5 Laser Sintering of Nano-Silver coated Polyetheretherketone Powder, D. Pohle, C. Damm, University Erlangen-Nuremberg, Germany, T. Rechtenwald, BLZ, Bavarian Laser Center gGmbH, Germany, A. Rösch, H. Münnstedt, University Erlangen-Nuremberg, Germany**

The effectiveness of silver as oligodynamic bactericide is proven and well investigated. The silver ions inhibit vital activities of the bacteria, such as breathing and metabolism. Elemental silver particles provide a large reservoir of antimicrobial silver ions, as in contact with water and dissolved oxygen they release small amounts of silver ions, only. The oxidation occurs on the surface of the particles. Accordingly the ion concentration and the rate of silver ion release are dependent on the surface to volume ratio of the elemental silver particles. The polymer matrix used in this investigation is polyetheretherketone. PEEK is a high performance thermoplastic with melting temperature of  $345^\circ\text{C}$ , very good mechanical properties and outstanding stability against chemicals and radiation. Its water uptake is below 0.5%. Because of this an antimicrobial equipment of the bulk material by use of silver is difficult. Silver nanoparticles were generated. Polyvinyl alcohol was dissolved in distilled water and silver nitrate was added. Sodium borohydride was used as reduction agent. Formation of elemental silver nanoparticles occurred, which were stabilized by the PVA. PEEK powder (PEEK 150 PF, Victrex, UK) was coated with silver nanoparticles by giving the polymer powder into the silver dispersion for 24h. The coated PEEK powder was used in a laser sintering (LS) process to generate antimicrobially equipped polymer specimens. LS of PEEK is a challenge because of its very high melting temperature and the irregular shape of the polymer particles. A modified laser sintering machine (EOSINT P 380, EOS, Germany) was used to obtain powder bed temperatures up to  $350^\circ\text{C}$ . After a pre-treatment of the polymer powder, including sieving and adding a small amount of carbon black to increase the flow ability, it was possible to manufacture discs with a diameter of 10mm and a height of 3mm. By use of LS specimens with open porosity are generated, so water can easily infiltrate the polymer parts. Stripping voltammetry showed that the sintered specimens released much more silver ions than hot pressed dense PEEK specimens. The silver release as function of time plot indicates that the release is governed by diffusion. To investigate the antimicrobial efficacy of the polymer specimens *Escherichia coli* was used. The antimicrobial tests were made by use of a solid agar plate method. As expected by the silver ion release test the specimens are active against *E. coli*.

**4:00pm NM+TF-TuA8 TEM-Based Metrology and Structural Characterization of  $\text{HfO}_2$  ALD Films Formed in Anodic Aluminum Oxide Templates, I. Perez, E. Robertson, L. Henn-Lecordier, P. Banerjee, S.J. Son, S.B. Lee, G.W. Rubloff, University of Maryland, College Park**

A broad variety of nanotechnology applications are poised to exploit the self-assembly that occurs in forming anodic aluminum oxide (AAO) films, which can be structured to comprise cylindrical nanopores with uniform dimensions (15-300nm diameters) spaced closely and regularly in AAO films microns in thickness. Such AAO films comprise templates for manufacturing of energy devices (capacitors, batteries, solar cells), electrochromic displays, or – if released by AAO dissolution - nanoparticle systems for targeted, imageable drug delivery, in which ultrathin highly conformal layers are formed in the nanopores by atomic layer deposition (ALD) or electrochemical deposition (ECD). Nanomanufacturing of such structures relies on the availability of fairly rapid metrologies and material characterization techniques which are precise at the nanoscale. We have achieved this goal based on transmission electron microscopy (TEM) methods, demonstrated here for ALD  $\text{HfO}_2$  nanotubes formed in AAO templates. The  $\text{HfO}_2$  nanotubes are first released by dissolution of the surrounding AAO template, then captured on standard TEM grids for observation in the TEM, whose high spatial resolution readily allows determination of nanotube diameters and wall thicknesses as a function of distance along the nanotube. We have developed image analysis codes to extract this metrology information in semi-automated fashion, so that ALD deposition profiles can be readily compared with ALD and AAO process parameters to optimize nanostructure manufacturing and to validate further models for process conformality. Furthermore, we have used HRTEM to identify  $\text{HfO}_2$  crystal phases at different locations along the nanotubes upon annealing, carried out on nanotubes either while embedded in the AAO template or after release. For annealing at  $650^\circ\text{C}$  for 30 minutes, we find the expected monoclinic phase of  $\text{HfO}_2$  is formed. These results demonstrate that the ability to release nanotubes from the AAO template, coupled with rapid HRTEM characterization and metrology, comprises an effective means to support AAO-based nanodevice manufacturing.

4:20pm **NM+TF-TuA9 Nano-Manufacturing of Materials at Oak Ridge National Laboratory's NanoApplications Center, S.M. Robinson,** Oak Ridge National Laboratory

The NanoApplications Center (<http://nanotech.ornl.gov/>) at Oak Ridge National Laboratory (ORNL) employs state-of-the-art facilities and multidisciplinary R&D capabilities to transition the discoveries of nanoscience to innovative technologies for energy environment, and economic competitiveness. It fosters innovation of new energy-related nanotechnologies and helps transform industry by enabling the responsible development of processes for mass production and application of nano-scale materials, structures, devices, and systems that provide unprecedented energy, cost, and productivity benefits. Capabilities within the NanoApplications Center include 1) materials processing and fabrication, 2) characterization, and 3) responsible nanomanufacturing, and 4) rapid prototyping for development and deployment. This paper describes example nano-manufacturing projects for materials processing and real-time measurements for process control. These include investigation of infrared-based processing for high temperature processing of metals to enhance metallurgical and mechanical properties by controlling grain size and development of coating processes that infuse alloys several hundred nanometers deep into the surface of a metal to create enhanced durability. To better enable nanomanufacturing, researchers at ORNL have developed and applied novel real-time characterization techniques to process monitoring and control. A commercial differential mobility analyzer is being used to sample and characterize nanoparticles in real time.

4:40pm **NM+TF-TuA10 Nanometrology: A Key Element for Successful Nanomanufacturing, M.T. Postek,** National Institute of Standards and Technology **INVITED**

Nanomanufacturing is the essential bridge between the discoveries of nanoscience and real world nanotech products - it is the vehicle by which this Nation will realize the promise of major technological innovation across a spectrum of products that will affect virtually every industrial sector. For nanotech products to achieve the broad impacts envisioned, they must be manufactured in market-appropriate quantities using reliable, repeatable, and commercially viable manufacturing processes. In addition, they must be manufactured so that environmental and human health concerns are met, worker safety issues are appropriately assessed and handled, and liability issues are addressed. Critical to this realization of robust nanomanufacturing is the development of the necessary instrumentation, metrology, and standards. This will allow the physical dimensions, properties, functionality, and purity of the materials, processes, tools, systems, products, and emissions that will constitute nanomanufacturing to be measured and characterized. This will in turn enable production to be scaleable, controllable, predictable, and repeatable to meet market needs. If a product cannot be measured it cannot be manufactured. This presentation will discuss some of the challenges confronting the effective development of the nanometrology needed for the success of nanomanufacturing.

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