

SYMPOSIUM AA

Dynamic, Self-Organizing Systems in Multifunctional Nanomaterials and Nanostructures

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particles. However, we will demonstrate that the method allows facile fabrication of nanoparticle coatings with a range of other useful properties. Two types of nanocoatings that will be presented are conductive metallic films from metal nanoparticles, and antireflective (AR) films from silica microspheres. Uniform nanocoatings were deposited in minutes directly from aqueous suspensions by convective assembly at high volume fraction. No additional substrate or particle preparation is required. The deposition process allows control over the coating thickness, optical properties, and the electric conductance of the films (in the case of the gold nanocoatings). For the gold nanocoatings, a rapid post-deposition annealing step was used to further tune their electronic, optical and structural properties. Scanning electron microscopy (SEM) observations and electrical conductance measurements showed that heating leads to a transition from a near-percolated nanoparticle structure to a discontinuous insular structure. The surface plasmon resonance peak could be tuned by heating to any value from 800 nm to 565 nm. The control over film structure and thickness via convective assembly also provides an excellent means for making AR coatings from silica particles. The refractive index required for AR materials is difficult to achieve in homogeneous materials (either natural or synthetic), but can be achieved with porous or composite films. In a single step, the reflectance of glass and silicon substrates was easily and reproducibly reduced by up to 75 percent relative to the bare substrates. Microstructural investigations using SEM, AFM, profilometry, and ellipsometry provided good correlations to the observed macroscopic optical properties imparted by the silica nanocoatings.

2:15 PM AA7.3

Large-scale Fabrication of Ordered TiO₂ Nano-Bowl Arrays. Xudong Wang, Elton Graugnard, Jeffery S. King, Zhong L. Wang and Christopher J. Summers; Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia.

The monolayer self-assembly (MSA) of polystyrene (PS) submicron spheres is an effective and economical technique for fabricating patterns on a relatively large scale. Atomic layer deposition (ALD), in which film growth is a cyclic, multi-step process of alternating surface-limited chemical reactions, has been demonstrated to be a powerful technique for fabrication of high-quality and multifunctional thin films on various substrates. We report a process that utilizes MSA and ALD for the large-scale fabrication of ordered TiO₂ nano-bowl arrays. The process starts with a self-assembled monolayer of polystyrene spheres, which was used as the template for atomic layer deposition of TiO₂. The top half of the TiO₂ coated PS spheres were then removed with an ion milling machine. In the final step, the PS hemispheres left on the substrate were etched away by toluene, resulting in a highly-ordered array of TiO₂ nano-bowls. Annealing at 850°C for 2 hours transformed the amorphous film into polycrystalline anatase TiO₂. SEM studies showed that the periodic structure of the PS monolayer was well preserved during the entire process. The TiO₂ walls are ~25 nm in thickness and no distortion was observed after the PS hemispheres were removed. The nano-bowls exhibit smooth interior and exterior surfaces and uniform size and thickness, which were not changed after the annealing process. TEM studies confirmed their anatase phase and showed that the TiO₂ bowls have a polycrystalline structure with a fairly large grain size, typically ~50 nm. As one of the important functional semiconductors, TiO₂ exhibits promising applications in solar cell, photocatalytic, photonic crystal and photovoltaic technology. The robust and highly-ordered anatase TiO₂ nano-bowl arrays with large surface area are expected to significantly increase the efficiency of surface related phenomena. The bowl size can be adjusted by using different sized PS spheres during the formation of the templates and this fabrication technique could also be applied to different substrates with smooth and hydrophilic surfaces, such as silicon, glass, metals or even polymers. The nano-bowl arrays have been demonstrated to be useful for selecting particles smaller than their inner diameter and could be a good candidate as a size separator and container for fine particles, or even for bio species, such as cells, if the interior surface is coated with proper functional groups. [1] For more information, please visit: www.nanoscience.gatech.edu/zwang

2:30 PM AA7.4

Si-based Nanoscale Island Array and its Related Nanostructures for Nanoelectronics and Nano-Optoelectronics. Y. F. Mei¹, G. G. Siu¹, Ricky K. Y. Fu¹, Paul K. Chu¹, Z. M. Li² and Z. K. Tang²; ¹Physics & Materials Science, City University of Hong Kong, Kowloon, Hong Kong; ²Physics, Hong Kong University of Science & Technology, Clear Water Bay, Kowloon, Hong Kong.

Porous anodic alumina (PAA) with highly ordered pore arrangement, controllable pore diameter, channel length, and fine insulating property is widely used as a template to grow nanowires or nanotubes since the pioneering work of Martin et al. The self-organization mechanism to achieve an ordered nanopore arrangement is still a

problem and a better understanding is vital to applications such as self-assembled nano-electronic quantum computers. Si-based nano-island arrays were fabricated on porous anodic alumina (PAA) by two methods. In the first method, a thick silicon film was deposited onto the surface with a highly ordered bowl array prepared by anodization of an Al foil, followed by the formation of a polycrystalline silicon nano-island array on the surface close to the bowl array after aluminum dissolution. In the second method, porous anodization was performed on an Al thin film on Si and a SiO₂ nano-island array was subsequently formed electrochemically. Time-resolved atomic force microscopy (AFM) and photoluminescence (PL) were used to investigate the growth process as well as mechanism. Two applications of the nanoscale islands are presented. A novel nano-MOS array: metallic carbon nanotube connected with nanoscale SiO₂ island inside insulated alumina nanochannel based on silicon substrate was fabricated via a Si-based PAA template. The electrical properties were determined by I-V and C-V measurements. The lower work function of the multiwalled CNTs induces lower flat-band voltages (VFB) compared to the conventional behavior of MOS. This structure is important for CNTs and PAA template via the self-assembled mechanism in nanoelectronics. The second example is Cu oxide nanowire array fabricated on Si-based SiO₂ nanoscale islands via nanochannels of a Si-based porous anodic alumina (PAA) template at room temperature under a pulse voltage using copper electrodeposition. X-ray diffraction and photoelectron spectroscopy show that the oxide nanowire is Cu₂O. The nanowires exhibit a preferential growth direction (111) and are interconnected with the nanoscale SiO₂ islands as confirmed by transmission electron microscopy (TEM). The formation of Cu₂O is due to the alkalinity of the anodized solution. However, the oscillations of the potential and current during the experiment tend to result in a small amount of copper and CuO in the nanowires. The cathodoluminescence (CL) data show that the energy level is larger than the bandgap of Cu₂O because of quantum confinement effects.

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Conjugated Oligomer Self-assembly: Correlation between Molecular Architecture, Microscopic Morphology and Optical Properties. Mathieu Surin¹, Philippe Leclerc¹, Prashant Sonar², Andrew C. Grimsdale², Klaus Mullen², Steven De Feyter³ and Roberto Lazzaroni¹; ¹Chemistry of Novel Materials, University of Mons-Hainaut, Mons, Belgium; ²Max Planck Institute for Polymer Research, Mainz, Germany; ³Laboratory of Molecular Dynamics and Spectroscopy, Katholieke Universiteit Leuven, Leuven, Belgium.

Conjugated materials offer new opportunities as active layers in optoelectronic devices. In particular, fluorene-based oligomers and polymers (PFs) are of major interest, since their blue luminescence offers new opportunities as active materials in optoelectronic devices, in particular to achieve full-color light-emitting diodes. Moreover, those polymers combine high fluorescence quantum yield, good charge transport properties and the ease of controlling the film forming properties via the facile substitution.[1] Understanding and exploiting the relationships between morphology and optoelectronic properties is of paramount importance in order to control the device performances. In this context, we study the microscopic morphology of a variety of fluorene-based oligomers. Tapping-Mode Atomic Force Microscopy (TM-AFM) is used to investigate the microscopic morphologies of thin deposits made from these molecules and to understand the results in terms of supramolecular organization, comparisons with molecular modeling simulations of chain assemblies are performed. For fluorene-based systems, we show that self-assembly of compounds substituted with linear alkyl groups leads to regular pi-stacks into long nanoribbons. In contrast, aryl-based substituted compounds lead to homogeneous, featureless films due to the steric hindrance imposed by bulky substituents that prevents a dense, regular packing of the molecules into well-defined nanostructures. A clear correlation is established between the degree of order in the deposits and the solid-state photoluminescence properties, which can be useful for light-emitting applications.[2] The microscopic morphology of various co-oligomers of fluorene with thiophene is also investigated. Due to their improved stability (compared to commonly used oligo- and polythiophene), these compounds are particularly interesting for field-effect transistor (FET) devices with high FETs performances.[3] We show that various types of nanostructures can be obtained, due to the specific interactions between the different segments. Using confocal optical microscopy at the sub-micrometer scale, the characterization of the optical properties of the structures is determined. We also apply an original soft lithographic method to orient the self-assembled nanostructures in a confined space delimited by the stamp features.[4] References [1] Neher, D. *Macromol. Rapid Commun.* 22 (2001), 1365. ; Scherf, U.; List, E. W. *J. Adv. Mater.* 14 (2002), 477. [2] Surin, M. et al. *Chem. Mater.* 16 (2004), 994. [3] Sirringhaus, H. et al. *Science* 290 (2000), 2123 ; Meng, H. et al. *Chem. Mater.* 15 (2003), 1778. [4] Cavallini, M.; Biscarini, F. *Nanoletters* 3 (2003), 1269.