SYMPOSIUM Ra/Rb
Assembly at the Nanoscale—Toward Functional Nanostructured Materials

November 27 - December 2, 2005

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* Invited paper
TUTORIAL
FTIRa/Rb: Nanoscale Sensors – From Molecules to Devices
Sunday, November 27, 2005
1:30 PM - 4:30 PM
Room 208 (Hynes)

Materials for Nanoscale Sensors
Nanotubes; Nanowires; Nanospheres; Dendrimers (organic nanoparticles); Inorganic-organic hybrid nanoparticles.

Fabrication Methodologies
Self-assembly techniques; Advanced manufacturing based on molecular nanotechnology; Environmentally clean, inexpensive, and efficient manufacturing of structures, devices, and "smart" products; Flexible control of architectures and processes at an atomic or molecular scale of precision.

Detection Capabilities
Chemical; Biological; Radiological; Explosive threats.

Detection Methodologies
Electrical; Optical; Resistive; Infrared-based identification.

Development of Nanoscale-Sensing Devices
Produce material parts at the nanoscale; Process material parts into components at the nanoscale; Order molecular components into structure and interconnect; Interface system components with the macroenvironment; Control a massive collection of miniature parts and systems; Provide a power system.

Instructors:
Mihri Ozturan
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SESSION Ra1/Rb1: Plenary Session I
Chair: Cengiz S. Ozkan
Monday, November 28, 2005
Ballroom A (Hynes)

8:15 AM INTRODUCTORY REMARKS

8:30 AM *Ra1.1/Rb1.1
Some New Developments in Colloidal Self-Assembly.
Yuman Xia, Chemistry, University of Washington, Seattle, Washington.

This talk will be organized into two parts. In the first part, I will briefly discuss a number of synthetic approaches that my group recently developed for generating monodisperse colloidal particles with controllable shapes and structures. I will use selenium as an example to illustrate how this semiconductor can be synthesized as spherical colloids and then transformed into AgSe and CuSe without changing the shape. These colloidal particles can serve as building blocks for self-assembly to fabricate photonic crystals. In the second part of this talk, I will discuss how template-assisted self-assembly (TASA) can be used to organize mesoscale building blocks into various structures with controllable sizes, shapes, and functions. I will use spherical colloids as a typical example of the building blocks. In principle, this approach can also be extended to cover building blocks with many other shapes and/or dimensions. I will concentrate on the fundamental mechanism of each method, as well as its potential extension to different systems.

9:00 AM *Ra1.2/Rb1.2
Building-up Supramolecular Self-Assemblies on Surfaces: Towards Molecular NanoElectronics.
Denis Fichou, Alexandre Marchenko, Luc Piot, Etienne Menard, Aymeric Nion and Alexandre Popoff; DSM/DRECAM/SPSCI, CEA-Saclay, Gil-sur-Yvette, France.

Plastic electronics appears today as an alternative to conventional semiconductors technologies. Self-assembly of functional organic molecules on atomically flat surfaces opens new perspectives towards molecular nanoelectronics, a realistic strategy in the miniaturization of electronic devices. One simple way to investigate 2D supramolecular self-assemblies at the nanoscale is to generate them at a liquid-solid interface and observe them in situ by means of scanning tunneling microscopy (STM). A variety of 2D architectures have been recently obtained with functional molecules (liquid crystals, molecular wires, graphite-like molecules, etc) by controlling the subtle interplay between molecule-molecule and molecule-substrate interactions. We will illustrate this approach with various families of conjugated organic compounds such as triphenylacetylene, alkyl-octylphenylacetylene, alkoxo-triphenylacetylene, fullerene, star-shaped oligothiophenes, the newly synthesized triazatriphenylphosphine, etc. One step further, we recently demonstrated the possibility to work in the vertical dimension and pile-up two or three self-assembled monolayers (SAMs) of similar or different molecules on top of each other at a liquid-solid interface. A spectacular example is the controlled growth and manipulation of magic clusters, i.e. self-organized close-shell islands of exceptional stability, of long alkanes in ambient conditions. Even further, we now use SAMs of n-alkanes physisorbed on a solid substrate (graphite, gold, etc) as tailored templates for the growth of self-assembled bi- and trilayers of long conjugated disulphide molecules possessing electrical and/or optical properties. Finally, we will show that our low-current STM technique allows for the first time to image the surface of a bulk single crystal of an organic semiconductor (thickness ~1 nm) down to molecular resolution and also to record its electronic 1/2 transport properties at the nanoscale. In conclusion, the growth and handling of novel homo- and heteromolecular 2D and 3D functional self-assemblies can be easily controlled at the molecular level on atomically flat surfaces and then integrated as active materials into nanoscale electronic devices. References: [1] Schoonveld, W.A.; Wildeman, J.; Fichou, D.; P.A. Bobbert, B.J. van Wees, T.M. Klappwijk, Nature, 2000, 977. [2] Marchenko, A.; Katsonis, N.; Fichou, D.; C. Aubert, M. Malarica, J. Am. Chem. Soc. 2002, 124, 9008. [3] Katsonis, N.; Marchenko, A.; Fichou, D.; Synth. Met. 2004, 147, 73. [5] Katsonis, N.; Marchenko, A.; Fichou, D.; Adv. Mater. 2004, 16, 309. [6] Saetwall, N.; Marchenko, A.; Fichou, D.; Teuleau-Fichou, M-P.; Fichou, D.; J. Mater. Chem., 2005, in press. [7] Piot, L.; Marchenko, A.; Wu, J.; Fichou, D.; Mullen, K. submitted. [8] Menard, E.; Marchenko, A.; Podzorov, V.; Gershenson, M.E.; Rogers, J.A.; Fichou, D. submitted.

9:30 AM *Ra1.3/Rb1.3
One-Dimensional Nanostructures as Subwavelength Optical Elements for Photonics Integration.
Peidong Yang, Univ. Calif. Berkeley, Berkeley, California.

The manipulation of optical energy in structures smaller than the wavelength of light is key to the development of integrated photonic devices for computing, communications and sensing. Wide band gap semiconductor nanostructures with near-cylindrical geometry and large dielectric constants exhibit two-dimensional ultraviolet and visible photonic confinement (i.e. waveguiding). Combined with optical gain, the waveguiding behavior facilitates highly directional lasing at room temperature in controlled-growth nanowires with suitable resonant feedback. The nanowire optical emission has been studied in detail using high-resolution optical microscopy. This concept of using well-claved nanowires as natural optical cavities may be extendable to many other different semiconductor systems. We have further explored the properties and functions of individual ultralong crystalline oxide nanoribbons that act as subwavelength optical waveguides and assess their applicability as nanoscale photonic elements. The length, flexibility and strength of these structures enable their manipulation on surfaces, including the optical linking of nanoribbon waveguides and other nanowire elements to form networks and complex components. We have demonstrated the assembly of ribbon waveguides with nanowire light sources and detectors as a first step toward building nanowire photonic circuity.

SESSION Ra2/Rb2: Plenary Session II
Chair: Zhong Wang
Monday, November 28, 2005
Ballroom A (Hynes)

10:30 AM *Ra2.1/Rb2.1
Modeling the size effect of nanoparticles entering cells via receptor-mediated endocytosis.
Huijuan Gao1, Wendong Shi2 and L. B. Freund2; 1Max Planck Institute for Metals Research, Stuttgart, Germany; 2Engineering, Brown University, Providence, Rhode Island.

Most bioParticles and viruses endocytosed by cells have characteristic sizes in the range of tens to hundreds of nanometers. The process of virus-like particles entering and leaving animal cells is mediated by the binding interaction between lipid molecules on the viral capsid and the receptor molecules on the cell membrane. How does the size of a bioparticle affect receptor mediated endocytosis? Here we study how a cell membrane containing diffuse mobile receptors wraps around a lipid coated cylindrical or spherical particle. It is shown that particles in the size range of tens to hundreds of nanometers can enter or exit cells via wrapping even in the absence of clathrin or caveolin coats and there exists an optimal particles size for the smallest wrapping time. This model can also be extended to including
the effect of chitin coating. The results seem to show broad agreement with experimental observations.

11:00 AM *Ra2.2/Rb2.2
Chad A. Mirkin, Chemistry Department, Northwestern University, Evanston, Illinois.

A novel approach that uses ambient fluorescent light to convert small silver nanospheres (6-8 nm) into large, triangular silver nanoprismS will be discussed. By varying the excitation wavelengths of light, one can tune the average edge length of the final nanostructures and their resultant optical properties. Current studies are focused on understanding the mechanism by which these novel nanostructures form, as well as incorporating them into a variety of biodetection and sensing applications. In addition, recent results including novel hybrid inorganic/organic nano rod structures will be addressed. These structures spontaneously assemble into sheets, tubes, and mushroom-shaped aggregates, depending upon rod composition and length. Structure, properties, and potential applications will be discussed.

11:30 AM *Ra2.3/Rb2.3
John Rogers, University of Illinois, Urbana, Illinois.

Solution processable conductors, dielectrics and semiconductors represent enabling materials for electronic circuits that can be fabricated on plastic sheets by continuous, high speed printing techniques. It is generally believed that these types of systems, which can cover large areas, will be important for new applications in consumer electronics. This talk describes the operational aspects of flexible transistors and circuits that use printable semiconductors based on nano-ribbons, disks, plates, etc. of single crystal silicon, gallium arsenide, indium phosphide and gallium nitride. Excellent dc and high frequency performance in individual devices and simple circuits and the behavior of these systems under bending conditions will be presented.

SESSION Ra2: Biomimetics I
Chair: Federico Rosei
Monday Afternoon, November 28, 2005
Room 207 (Hynes)

1:30 PM *Ra3.1
Abstract Not Available Angela Belcher

2:00 PM Ra3.2
Assembly of Nanoparticle Ring Structures based on Protein Templates. Silke Behrens1, Wilhelm Habicht1, Kerstin Wagner2 and Eberhard Ungar2; Forschungszentrum Karlsruhe, Karlsruhe, Germany; 2Institut fuer Molekulare Biotechnologie, Jena, Germany.

The bottom-up wet-chemical synthesis of inorganic materials provides tools for generating nanostructures from particles to one-dimensional structures, but these chemical techniques usually offer little control over the dimensions of the metal or metal oxide nanorings. In our approach, these ring-like protein assemblies serve as a functionalized scaffold where the metal is generated in situ and deposited into spiral-shaped particle arrays, reflecting the arrangement of the protein subunits within the assembly. The mean distance between the Ag particles was 7.5 nm and indicated the specific deposition of one Ag particle per tubulin subunit. The resulting size and crystalline structure of the materials were examined using Transmission Electron Microscopy and Scanning Force Microscopy. This synthetic capability will allow a potential wet-chemical synthesis of Aharonov-Bohm rings.

SESSION Rb3: Nanowires, One Dimensional Nanostructures I
Chair: Gregory Lopez
Monday Afternoon, November 28, 2005
Room 208 (Hynes)

1:30 PM Rb3.1
Phase Diagram and Road Map for Large-Scale Growth of Aligned ZnO Nanowires and CdSe Nanostructures. Jinhui Song, Christopher Ma, Xudong Wang and Zhong L. Wang; School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia.

In vapor-liquid-solid (VLS) growth, it is generally believed that nanowires would grow as long as the right catalysts and substrate are supplied as well as the growth temperature is adequate. We show here, however, that oxygen partial pressure plays a key role in determining the quality of the aligned ZnO nanowires. We present a phase diagram between the oxygen partial pressure and the growth chamber pressure for synthesizing high quality aligned ZnO nanowires on GaN substrate [1, 2]. This result provides a road map for large-scale, controlled synthesis of ZnO nanowires on nitride semiconductor substrates with the potential to meet the needs of practical applications. The chemical process involved in the growth process is also systematically elaborated based on experimental data received under different conditions. We also show a systematic investigation on surface parameters affecting the morphology of VLS-grown one-dimensional CdSe nanostructures using gold as catalyst [3]. The relationship between surface morphology and temperature has been discussed, and a roadmap for guiding the synthesis has been defined. The main conclusions can be summarized as follows: 1. The temperature at the source is to stimulate the vaporization of the source materials, and the subsequent growth is controlled dominantly by the local temperature and pressure at the substrate. 2. There is an increase in the growth temperature range where deposition occurs with a decrease in the system pressure. 3. Lower temperature at the source material (630 oC), higher chamber pressure (600 mbar) and 575 + 5 oC substrate temperature produces the highest percentage of nanowires/nanocomb. 4. Lower temperature at the source material (700 oC), lower chamber pressure (4 mbar) and 575 + 8 oC substrate temperature produces the highest percentage of nanobelts. 5. Growth of nanowires is less restrictive and it can be carried out at a wide range of temperature and pressure. 6. High source temperature favors the growth of nanowires rather than nanosaws and nanobelts. [1] Jinhui Song, Xudong Wang, Elisa Riedo and Zhong L. Wang, Synthesis Study on Experimental Conditions for Large-Scale Growth of Aligned ZnO Nanowires on Nitrates, J. Phys. Chem. B, published online (2005). [2] Xudong Wang, Jinhui Song, Peng Li, Jae Hyun Ryu, Russell D. Dupuis, Christopher J. Summers and Zhong L. Wang, Growth of Uniformly Aligned ZnO Nanowire Heterojunction Arrays on GaN, AIN, and Al0.5Ga0.5N Substrates, J. Am. Chem. Soc., 127 (2005) 7920-7923. [3] Chris Ma, Yong Ding, Daniel Moore, Xudong Wang and Z.L. Wang, J. Am. Chem. Soc., 126 (2004) 708. [4] For details: www.nanoscience.gatech.edu/swang

1:45 PM Rb3.2
Functional Semiconductor/Metal Oxide Core/Shell Nanowire.
Hao Yuan1, Yue Wu2, Guihua Yu1 and Charles M. Lieber1,2; 1Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts; 2Division of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts.

One-dimensional nanostructured materials such as nanowires and nanotubes reported in the literature are promising candidates for conducting blocks in nanoelectronic devices. Critical to continued development of these devices, as well as circuits and systems, will be the introduction of controlled structural complexity and function in the nanoscale building blocks. The added function and composition of building blocks provide opportunities distinct from conventional planar devices. To this end we demonstrate a general approach towards semiconductor/metal oxide core/shell nanowires via combination of vapor-liquid-solid growth and anodization and deposition of built-in control structures. We are able to grow uniform oxide shells on semiconductor nanowire cores. As an example of this approach, we demonstrate the synthesis of Si/ZrO2/BaTiO3 core/shell/shell nanowire heterostructures.

High-resolution transmission electron microscopy imaging and analysis were used to characterize the structure and composition of these new heterostructures. Notably, electrical transport measurements demonstrate that these heterostructures function as ferroelectric field effect transistors, with the BaTiO3 exhibiting well-defined and stable ferroelectric behavior. Fundamental device characteristics of these nanowire heterostructures will be reported, as well as studies of nonvolatile memory and programtable logic arrays.

2:00 PM RB8.3  Electrochemical Deposition of Metal-Semiconductor-Metal Nanowires. Xi Wang1, Sathyajith Raviindravar and Cengiz Sinan Ozkan1; 1 Mechanical Engineering, University of California at Riverside, Riverside, California; 2Chemical and Environmental Engineering, University of California at Riverside, Riverside, California.

Nanowires of many compositions have been prepared using porous templates as molds. Anodic alumina oxide (AAO) and nuclear track etch polymer membranes are two commonly used templates. They have been used to make nanowires composed of metals, semiconductors, and polymers. We report the synthesis of Metal-Semiconductor-Metal nanowires by electrochemical replication of AAO. The semiconductor could be CdTe or Bi2Sb, which is sandwiched between metal segments. Cadmium telluride (CdTe) is one of the best known II-VI group compounds for its interesting photoelectric properties. It has a direct energy band gap (1.4-1.5 eV), a relatively high optical absorption coefficient, and advanced photovoltaic properties, which make it suitable for fabricating photoelectrode devices and solar cells. Bulk Bi1-2Sb is alloys are among the best n-type low temperature thermoelastic (TE) materials. Many researchers and recent studies show the TE efficiency will be improved by making nanowires of bulk TE. Dissolving the template yields a colloidal suspension of free-standing nanowires. The structures of the composite nanowires are identified by SEM and TEM. The composition of the semiconductor segments is characterized by XRD. By changing the concentrations of the two metals by the growth rate, the growth rate of the two metals and the growth conditions, the growth rates of the two segments can be controlled separately. The as-grown nanowires can be separated into three categories: (1) Metal nanowires with oxide shells, (2) Metal nanowires with oxide and semiconductor cores, and (3) Metal nanowires with semiconductor cores. The as-grown nanowire arrays can be used for solar cells, photoelectrochemical cells, and other applications.

2:15 PM RB8.4  Functional Assembly of One-Dimensional Nanostructures from Nanothermometers to Nanowire Heterostructures. Jinhua Zhan1, Yishio Bando1, Junqing Hu2 and Dmitri Golberg1; 1Advanced Materials Laboratory, National Institute for Materials Science, Tsukuba, Ibaraki, Japan; 2Institute of Frontier Science, National Institute for Materials Science, Tsukuba, Ibaraki, Japan.

One dimensional (1D) nanomaterials have attracted considerable attention due to their potential applications as building blocks in nanoscale circuits and optoelectronic devices[1]. Nanotube filling with foreign elements, compounds and/or substances is a relatively new and exciting field of the nanomaterial research. 1D nanomagnets, nanocables and other functional nanomaterials may be synthesized through taking advantages of tiny nanotube channel dimensions and related confinement effects, and functional properties of guest species encapsulated within, e.g. ferromagnetism, piezoelectricity, electro- and thermoelectricity etc. Moreover, focusing on new properties and a wide selection of nano-building blocks for nanosized electrical and optical lines, it is important to obtain a potential barrier between adjacent constituting components showing the rectifying current-voltage characteristics. This is realized through the creation of various heterostructures including p-n junctions, metal-oxide-semiconductor junctions or metal-semiconductor contacts, which allow signal processing to be reliably performed. Metallic gallium melts at nearly room temperature and has one of the widest liquid ranges among all metals. It was shown that Ga encapsulated in carbon nanotubes has a potential application as a nanothermometer due to its temperature-dependent expansion and contraction within a wide range [2, 3, 4].

We demonstrate an effective approach for bulk synthesis of gallium metal nanowires sheathed with carbon. We also demonstrate that gallium nanowires sheathed with carbon can be welded using convergent electron beam. Furthermore, we demonstrate the fabrication of In-Si end-to-end nanowire contacts[5] and ZnSi side-by-side composite nanowires[6]. Their morphological and structural characteristics were thoroughly analyzed. With the In-Si junction, the In and Si subnanowires are crystallographically oriented with respect to each other and sheathed with a silica nanotube. Linear thermal expansion of an In branch (after its melting under heating) makes possible the design of a temperature-dependent expansion and contraction of the device. Side-by-side ZnSi nanowires were prepared through tin-catalyst-confined-growth. Simultaneous thermal evaporation of Zn and Si provide precursor vapors which are condensed on Sn droplets resulting in the nucleation and anisotropic growth of composite nanowires made of adjacent ZnS and Si domains.


SESSION Ra4: Electrically Directed Assembly
Chair: Denis Fichou
Monday Afternoon, November 28, 2005
Room 207 (Hynes)

3:30 PM Ra4.1  Directed Assembly of Nanoelements Using Electrostatically Addressable Templates. Xugang Xiong1, Prashanth Makaram2, Kaveh Bakhatri3, Ajhmed Hussaina, J. Snall1, Sivasubramanian Somuni1, Glen Miller1 and Jingoo Park2; 1The NSF Nanoscale Science and Engineering Center for High-rate Nanomanufacturing, Northeastern University, Boston, Massachusetts; 2The NSF Nanoscale Science and Engineering Center for High-rate Nanomanufacturing, University of New Hampshire, Durham, New Hampshire; 3Hanyang University, Ansan, South Korea.

The directed assembly of nanoparticles in nonuniform patterns using templates (Au nanowires on SiO2 substrates) has been demonstrated. Electrostatically addressable templates using DC voltage are used to assemble fluorescent polystyrene latex (PSL) nanoparticles. The negatively charged nanoparticles are attracted to the surface of the positively charged nanowires. Nanoparticles down to 50 nm have been successfully self-assembled to form uniform monolayer patterns along the conductive nanowires of the templates. The field assisted directed assembly approach can be extended to the growth of one-dimensional carbon nanotubes in aqueous solution into micro or nanoscale patterns using the templates. The assembled patterned particles are then transferred to another patterned substrate to function as part of a sensor or a device. The technique provides a simple, fast, scalable approach for directed assembly of nanoelements.

3:45 PM Ra4.2  Transport, assembly and rotation of nanowires in suspension by AC electric fields. Donglei Fan1,2, Frank Q. Zhu3, Robert C. Cammarata1 and C. L. Chien4; 1Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland; 2Department of Physics and Astronomy, Johns Hopkins University, Baltimore, Maryland.

Nanowires are potential building blocks for nanoscale devices. Manipulation of nanowires in suspension to produce functional nanostructured materials has been a formidable problem. Using AC electric fields applied to strategically designed microelectrodes[1], nanowires in suspension can be driven to align, tochain, to accelerate in certain directions parallel and perpendicular to its orientation, to concentrate onto designated plane, to disperse in a controlled manner with high efficiency despite an extremely low Reynolds number at the level of 10-1-10-2. Randomly oriented nanowires in suspension can be rapidly assembled into extended nonlinear arrays of nanowires within seconds. We show that both the nanowire/microelectrode and its gradient play the essential roles of aligning and transporting the nanowires into scaffolds according to the electric field distributions inherent to the geometry of the microelectrodes. Furthermore, nanowires have been rotated by AC electric fields applied to strategically designed electrodes[2]. The rotation of the nanowires can be instantly switched on or off with precisely controlled rotation speed (to at least 1800 rpm), definite chirality, and total angle of...
rotation. This new method has been used to controllably rotate magnetic and non-magnetic nanowires as well as carbon nanotubes. We also have microrotors using a rotating nanowire that can drive particles into circular motion. This has application to microfluidic devices, microstirrers, and microelectromechanical systems (MEMS). All of the features discussed offer great promise and flexibility with potential to produce a variety of nanoscale assemblies involving metallic, semiconductor, and biological materials. 1. D.L. Fan, F.Q. Zhu, R.C. Camarreta, and C.L. Chien, Appl. Phys. Lett. 85, 4175 (2004). 2. D.L. Fan, F.Q. Zhu, R.C. Camarreta, and C.L. Chien, Phys. Rev. Lett. in press.

4:00 PM Ra4.3
Non-impact electrostatic manipulation of a conductive micro-object by rapid control of applied voltage. Shigeki Saito1, Kenji Kurihara2 and Kunio Takahashi3; 1Department of Mechanical and Aerospace Engineering, Tokyo Institute of Technology, Tokyo, Tokyo, Japan; 2Department of Mechanical and Control, Engineering, Tohoku Institute of Technology, Tokyo, Japan; 3Department of International Development Engineering, Tokyo Institute of Technology, Tokyo, Japan.

The size of an object to be manipulated has decreased in the electrical and mechanical engineering field for fabricating highly functional micro-electro-mechanical systems and photonic crystals. In micromanipulation, even if we can pick up micro-objects, it is difficult to detach the micro-objects because adhesion force is dominant. To date, some research groups have tried to manipulate conductive micro-objects by applying voltage because electrostatic force has been considered effective in micromanipulation. Excessive impact by current may damage the micromanipulation of a detachable object, however, is still a difficult problem to develop the reliable method of micromanipulation. Thus, in this study, an optimal voltage as a time-dependent function is theoretically derived; the effectiveness is demonstrated through the experiments by electrostatic micromanipulation system. The voltage function is determined so that the kinetic energy of a micro-object could be controlled during the flight after detachment from a probe-tip and become zero at landing on a substrate. Additionally, since the energy absorbed due to the adhesion hysteresis exists at the contact of the micro-object to the substrate, an allowable error of voltage for the energy absorption is evaluated. In order to realize the derived voltage function, a power source with high voltage and high-speed response was developed. With a solder ball with the diameter of 0.13 mm is successfully deposited on the substrate after detachment from the probe-tip in the experiment of electrostatic micromanipulation. These results theoretically and experimentally show that this method could be applied to IC packaging or micro-device assembly.

4:15 PM Ra4.4
Nanopattering, electropatterning, and nanocharging of organic and polymer semiconductors using the precursor polymer approach. Rigoberto Advincula1, Vallyaveettil Suresh2, Jegadesan Subiah3 and Akira Baba1; 1Department of Chemistry, University of Houston, Houston, Texas, USA; 2Department of Chemistry, National University of Singapore, Singapore, Singapore.

Nanopattering of precursor polymers electrochemically using soft-lithographic nanolithographic methods will be reviewed. Several strategies for the synthesis, fabrication, and characterization of these unique conjugated polymer ultrathin films will be presented. The application of these cross-linked materials is towards electro-optical devices, e.g. patterned photonic light emitting diode (PLED) devices will also be described. By controlling the deposition site using micro-contact printing, patterns on the electrode surface can be formed prior to electropolymerization. Electrochemical Nanolithography (ECN) is a technique in which a pattern is created by applying a potential between the AFM tip and the substrate (conducting AFM set-up) during "writing". By utilizing an electrophoretic cross-linking strategy while patterning, robust and conducting patterned polymers can be selectively addressable by SPM methods. Nanocharging is demonstrated in terms of a reversible (read-write) change in charge transport property localized in patterns addressed by the SPM tip at various biased voltages. Thickness, film homogeneity, wetting, etc. are important parameters that affect the patterning and charging experiments.

4:30 PM Ra4.5
Dielectrophoretic Assembly and Reconfiguration of Nanowire Interconnects. Alexander David Wissner-Gross1 and Charles M. Lieber2; 1Physics, Harvard University, Cambridge, Massachusetts; 2Chemistry, Harvard University, Cambridge, Massachusetts.

Localized electric fields are powerful tools for programmable assembly and reconfiguration of nanoscale circuits. In this work, dielectrophoretic trapping of silicon nanowires as electrical interconnects is demonstrated. A suspension of heavily doped silicon nanowires is hermetically sealed above fabricated Au electrodes. Radio frequency biases applied between electrode pairs trap and make ohmic contact with the nanowires. The frequency and magnitude of positive dielectrophoresis is measured and compared with theory. Low-k dielectric protective layers are used to inhibit trapping except at electrode tips. This technique is shown to scale from 2-electrode circuitry to the assembly of 4- and 6-electrode networks. Applications of dielectrophoretically assembled nanowire circuits to physical implementations of graph algorithms are discussed.

4:45 PM Ra4.6
An Electrical AFM Approach to the Definition of Anchor Sites for Layered Biomolecular Structures. Nicola Naujoks and Andreas Stemmer; Nanotechnology Group, Swiss Federal Institute of Technology, Zurich, Switzerland.

Atomic force microscopy (AFM) based lithography has proven useful for local modification of surfaces at the nanoscale. Achieving control over localized positioning and modification of 4- and 5-electrode networks is a key factor for nanosensor fabrication or for creating scaffolds for building up nanostructures. We previously reported on a method that uses electrostatic forces to guide particle deposition in liquid environments [1,2]. The electrostatic field is created by nanoscale charge patterns written into the sample with a conductive AFM tip. In this contribution, we will present how this general method defines anchor points with specific binding sites that allow for the docking of functionalized biomolecules and particles. By this means, larger structures, potentially serving as biosensors, are built up locally in a layer-by-layer procedure. The guided assembly process consists of two parts: After defining the patterns via AFM-based charge writing, the sample is developed in a rotating water/oil emulsion. Driven by electrostatic forces, the water droplets carry particles or molecules to the patterns. The basic characteristics of this deposition have been studied for a water/particle-oil model-system for different substrates [1]. Using the same process, biotin-labelled immunoglobulin (IgG-biotin) was deposited with sub-7m resolution onto charge patterns on poly (methyl methacrylate) (PMMA) samples [2]. The IgG molecules at the same time help in stabilizing the emulsion [3]. As the samples are dried after emulsion, a thin film of water is formed on the substrate. This is a necessary step prior to any further modifications made to the sample. The dry samples are immersed into a buffer of blocking solution, which also prevents unspecific binding during the following reactions. As the emulsion is removed, the IgG molecules remain and are bound to the binding sites on the substrate. Conformational changes of the IgG, the activity and accessibility of the biotin groups on the IgG have to be proven. We verified the biotin activity by incubating the sample in a solution containing fluorescently labelled anti-biotin molecules, which are known to bind specifically to biotin. For the layered structures, a streptavidin linker is used to attach 40 nm sized biotin-labelled polymer beads (biotin-beads) to aqueous solution. Fluorescently labelled biotin-beads bind to the free binding sites of previously attached streptavidin facing inside the solution. Fluorescence images reveal the high specificity of both reactions. The IgG-biotin still has enough functionality to detect the biotin-beads via a streptavidin-biotin interaction [1]. N. Naujoks, A. Stemmer, Micros. Eng. 78-79 (2005) 351. [2] N. Naujoks, A. Stemmer, Coll. Surf. A 249 (1-3) (2004) 69. [3] S. Magdassi, A. Kamshy, A. Baszkin, J. Disp. Sci. Technol. 22(4) (2001) 313.
clearroom environment. We have investigated in details an alternative approach, nanostenciling [1] and along with its suitability for direct patterning of conducting materials we demonstrated its unique flexibility in the combination functional material / substrate [2]. Among the latter, members of the complex oxides family display a range of interesting and useful properties in response to combinations of electric, magnetic, and stress fields. These properties include piezoelectricity, ferroelectricity, colossal magneto-resistance, high-temperature superconductivity, etc. and these have been shown to be related to their fabrication process and the quality of ultra-thin films. Using modernized miniature stencil machines, selective deposition of ferroelectric perovskites (e.g. BaTiO3, BiFeO3, and PZT) was swiftly achieved by interposing a nanosieve between the substrate surface (Si, Pt-coated-Si, SrTiO3 and SrRuO3) and the rotating target from a PUL deposition chamber. The patterns designed in the nanomask are accurately transferred to the substrate, and 3D-structures of functional materials are directly deposited with the desired geometry. We are also presenting the application of a nanoscale multilayer approach [3] which gives the advantages for rapid prototyping of functional stacks of materials such as metal-oxide-metal and magneto-electro heterostructures grown by sequential depositions. The morphology and composition of these nanostructures were characterized by SEM, AFM, XRD and XPS techniques and their local ferroelectric properties were detected using piezosresponse force microscopy (PFM). The application of this process is meant for research (e.g. studying the size effects on the functional properties of the structure) [4]; it also presents a precise, universal tool for parallel deposition of high-resolution and high-purity nanostructures of functional materials under high and ultra-high vacuum [5]. W. Berentsen, A. Buchard, B. Otter and M. Elwenspoek, Microelectron. Eng. 55, 403, (2000) [2] C. Cojocaru, C. Harnagea, F. Roseli and A. Pignolo, M.A.F. van den Boogaart, J. Bruger, Appl. Phys. Lett. 86, 183107, (2005)

4:15 PM Rb4.3
Supramolecular Nano-Stamping. A. Amy Yu1, Tim Savas,2 Enzo Di Fabrizio3, Henry I. Smith1 and Francesco Stellacli1; 1Materials Science and Engineering, MIT; Cambridge, Massachusetts; 2Department of Electrical Engineering, MIT, Cambridge, Massachusetts; 3Lillit, TASC-INSF, Basovizza, TS, Italy.

As the size of devices drastically shrinks, the need of a method that can fabricate a small size pattern and repeat it in a monolithic scale within a short time has increased. Supramolecular Nano-Stamping (SuNS) is a novel printing method that can replicate a patterned DNA monolayer on another substrate with just three steps. It is composed of a hybridization-contact-dehybridization cycle: on a surface containing features each made of single stranded DNA (ssDNA) of known sequence, the complementary DNA molecules are hybridized, spontaneously assembling onto the original pattern due to sequence-specific interactions. These complementary DNA strands, on the end that is far from the original surface, are modified with chemical groups ("sticky ends") that can form bonds with a target surface brought into contact. Heating induces dehybridization between DNA strands, resulting in separation. The patterned stainless steel stamp is the mirror image of the original one, and can be used as a new master to stamp another copy. Additionally, SuNS, based on specific interaction between complementary DNA sequences, is capable of printing multiple DNA sequences simultaneously. This implies that it can transfer not only spatial information, i.e. size and pattern's shape, but also chemical information (i.e. DNA sequence). Here we will show pattern successfully printed with high resolution (<30nm) and high complexity using gold-thiol chemistry. We will also present SuNS on modified poly methyl methacrylate (PMMA) substrates. A comparison between the advantages of these two approaches will be presented.

4:30 PM Rb4.4
Phase Transition in Nanoscale Direct Deposition Processes. Narae Cho1, Byeongjoo Kim2, Juwan Kang3, Sungyoung Park3, Byung Yang Lee3, Kyung-Eun Byun1, Seol Ryu1, George C. Schatz4 and Seung-Hun Hong1; 1Physics and Nano Systems Institute, Seoul National University, Seoul, Korea; 2Department of Chemistry, Northwestern University, Evanston, Illinois.

We report the first observation of phase transition in nanoscale direct deposition processes. Even though nanoscale direct deposition processes such as dip-pen lithography (DPL) have been extensively utilized to pattern a broad range of molecular species on solid surfaces, its mechanism and even the phase of deposited molecular ialks have not been understood. We propose the "surface multilayer" model, where the DPL process is explained by the transport of mobile surface molecules driven by multiple mechanisms (e.g. thermal energy, adsorbed solvent layer, etc). We also propose that the bulk molecules in the surface monolayer remains solid, and the metal ink works as an ink reservoir to regulate the DPL deposition rate. We performed DPN experiments to measure the deposition rate and its scaling behavior under various temperature and humidity conditions. Significantly, the scaling analysis of the deposition rate confirms our model and shows clear indication of the phase transition of the molecular ink in the DPN process.

4:45 PM Rb4.5
Integrating Self-Assembled Nanopore Arrays. Xiaoyuan Qi1, Jia Zhou2, Liwen Tan3 and Jialin He1; 1Biomedical and Chemical Engineering, University of Minnesota, Minneapolis, Minnesota; 2Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota.

Anodic aluminum oxide nanopores with long range order (mm) were integrated onto a variety of surfaces (Si, SiO2, and yttrium iron garnet) for use as nanoscale etch masks. Typical self-assembly of nanopores within anodic alumina occurs utilizing a two-step anodization of bulk Al foil. Domains of order are produced in the first step and continuous, ordered, parallel pores are grown in the second step. The ordering step occurs over a long period of time (tens of hours), which makes it difficult to integrate these pores using photolithography because the films may be fully anodized before ordering can occur. In this work, thin films of Al were grown via sputtering and evaporation. These films were then anodized using both a two-step process and a directed assembly technique called nanoimprinting which allows long-range ordering over very short anodization times. A variety of pore sizes were fabricated by varying the anodizing conditions, such as voltage, temperature and electrolyte. In the case of nanoimprinting, master nanoimprint stamps of Si3N4 were fabricated using LPCVD, ebeam lithography, and reactive ion etching. The resulting array of nitride posts was then imprinted onto numerous aluminum films. Atomic force microscopy (AFM) was used to observe that the patterns of the master stamps were transferred onto the aluminum sheet after the imprinting. Next, anodization was carried out using parameters that matched the different lattice constants to those of the stamps. Scanning electron micrographs (SEM) showed that perfectly ordered porous arrays were obtained with center-center spacings of 100-500nm over as large an area as a few millimeters squared. The nanopores were then etched into the underlying surfaces of Si, SiO2 and YIG, respectively, using reactive ion etching. Several stamps were made with metallic filaments aligned with the anodic porous nitride posts, and these microscopic features were used to align subsequent layers to the nanoscale pores via an optical microscope. For example, strips of metallic material were aligned with the nanoscale pores using photolithography. These results are important for both the ability to nanostructure a variety of materials, and also for the ability to connect the nanoscopic and microscopic regimes.

SESSION Ra5/Rb5: Poster Session I
Chair: Gregory Lopinski
Monday Evening, November 28, 2005
8:00 PM
Exhibition Hall D (Hynes)


Assembly design concept of carbon nanotube (CNT)-based multifunctional materials can offer possibility to control molecule-level mechanism that can have on the dynamic/damping properties of CNT-reinforced materials thus providing more multifunctionality. The nanoparticle assembly technology for novel nanocomposites and thier dynamic mechanisms involved in such materials need to be understood. Nanomaterial design concept could be combined with modeling techniques so as to enable efficient synthesis and design of the next generation of CNT-based mechanical systems. The focus in this paper is directed toward the investigation into technological issues of assembly techniques of novel CNT-based materials and their dynamic/damping characterization. Particular aim of the work is a control over nanocomposite assembly methodology (CVD, PVD).

Simultaneous optimization of a class of CNT-reinforced materials can be achieved by using numerical simulations and virtual environments. Such effective solutions can be found to have wide-ranging technical benefits with direct relevance to industry in areas of transportation and civil infrastructure development.


Due to their unique structures and exceptional properties, one-dimensional structures such as nanowires and nanotubes have received considerable interest in recent years for their potential
applications in many fields. In particular, nanowire arrays are considered to be promising materials for high-density magnetic recording media and thermal nano-devices. For controlling the deposition rate, substrate temperature and film composition, the average diameter of the Al cylinders can be varied systematically from less than 5 nm to 13 nm with a cylinder density ranging from 10^10 to in excess of 10^12 m^-2. In addition, the Al nano-cylinders in the thin films were performed using a modified planar-Hilliard equation to understand the growth mechanism. The simulation studies indicate that the surface diffusion length and film composition are important factors for the morphology. Experimental and simulation studies are compared and discussed. *K. Fukutani, K. Tanji, T. Mito, T. Den, Adv. Mater. 16, 1456 (2004).

Rb6.3/Rb5.3
Abstract Withdrawn

Rb5.4/Rb5.4
Discontinuous Monolayer can Control Metal/Metalloid/Metal-oxide Semiconductor Junctions. Hossam Haick1, Macrina Ambrocie2, Teresa Ligonzo3, Raymond Tung4 and David Cahen5; 1-CNR-IMP Sez. di Bari, Bari, Italy; 2-Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot 76100, Israel; 3-Department of Electrical and Computer Engineering, Institute of Biomedical and Health Engineering, University of the Mediterranean, Malaga, Spain; 4-Department of Chemistry and Chemical Engineering, California Inst. of Technology, Pasadena, California.

Molecules can control charge transport across a metal/semiconductor interface, also if they form only a partial monolayer at the interface. This is because of the long-range electrostatic effect of (molecular) dipole domains, which affects also semiconductor regions under the film pinholes. This finding extends significantly the variety of molecules that can be used, by including all those that yield, as a partial monolayer, in the dipole perpendicular to the interface, to reach our conclusion by complementary electrical characterizations of junctions, formed by indirect evaporation of Au and Pd, and, in specific cases, by ready-made contacts, on a set of molecular monolayers that are chemisorbed on n-GaAs. The set is formed by using a well-studied series of molecules with systematically varying dipole moments. The electrical characterizations that we used are current-voltage-temperature, capacitance-voltage, and internal photocurrent. The resulting data were analyzed taking into account the limitations of each of the techniques and using theoretical models that were modified to account for the presence of a partial, discontinuous molecular monolayer at the interface. In this way we find that the description for the experimentally observed behavior is in terms of a parallel conductance model.

Rb5.5/Rb5.5

Magnetic nanodot arrays have gathered attentions for applications in high-density patterned magnetic media. We have demonstrated fabrication of magnetic nanodot arrays in linear groove guides using block copolymer templates. In this method, block copolymer nanodots formed at the block copolymer-grafted groove, but not in the groove, was not controlled in its line. For practical magnetic media, it is necessary to control the position of nanodots with a high accuracy. In this research, parallelogram and rectangle groove guides were fabricated on photoresist film by a nanoimprint lithography method. The parallelogram guide with a corner of 60° is suitable for a hexadecimal lattice of block copolymers. And rectangle guide with a corner of 90° matches the angle between the main axis and the second axis that has sin^2(θ) times wider spacing than the main axis. These guide groove patterns were imprinted by a Ni stamp on a photoresist film which was spincoated on substrate. Block copolymer of poly-styrene-poly-polyethylene methacrylate (PS-PMEA) was dissolved into cyclohexane, spincoated on the other quartz substrates (PMGPEA), and spincoated on the guided substrate. The PS-PMEA has a molecular weight of 89,300 and periodicity of 45nm. After annealing at 180°C, phase separation occurred. The quality of the nanodot pattern was observed by AFM phase mode measurement. PMMA dots arranged parallel to the wall of the guide. In the parallelogram guide, PMMA dots arranged with few defects, for example, a dot surrounded by five or seven dots. On the other hand, in a rectangular guide, PMMA dots formed some domains caused by the surface tension from wall of the guide. Mostly, the longer side of rectangle had a stronger surface energy, so the domain of the longer side are larger than the shorter one. In the square guide, the domain area and direction was not controlled because it has the same length as the sides. Especially, in some of the smallest square guide, there was no domain wall. This work was supported by the IT-program (RB-2002) of the Ministry of Education, Culture, Sports, Science and Technology (NEXT), Japan.

Rb5.6/Rb5.6
Microwave Plasma-Enhanced Chemical Vapour Deposition Growth of Non-Surface Bound Carbon Nanowalls. Alfred Tung-hua Chuang1, Bojan Boskovic2 and John Robertson3; 1Department of Engineering, University of Cambridge, Cambridge, United Kingdom; 2Department of Materials and Metallurgy, University of Cambridge, Cambridge, United Kingdom.

Carbon nanowalls are well-aligned and self-assembled carbon sheets with a thickness in the range of several nanometers. Wu et al. [1] reported fabrication of two-dimensional carbon nanostucturing carbon nanowalls using microwave plasma-enhanced chemical vapor deposition (PECVD) process on insolated substrates. Subsequently, Hiramatsu et al. [2] reported fabrication of carbon nanowalls using r-PECVD, assisted by hydrogen radical injection without catalysts. Carbon nanowalls have enormous surface area that is important for electrochemical and many other applications [3]. They can also serve as growth templates for other nanomaterials [4]. Here we report non-surface bound (freestanding) carbon nanowall growth without catalyst using microwave PECVD. The clear advantages of this new synthesis method are the scale of production, and ease of harvesting. While these graphite sheets have the same or similar defect density, the carbon nanowalls are unique to them and can compound and grow into a freestanding structure measured up to 5 centimeters in length for a 10-minute growth. Considering the non-surface bound nature of this growth phenomenon and the absence of catalyst, a moderate amount of carbon nanowalls can be easily obtained and deployed for further development and applications. Correlation between variable growth rate, growth quality and synthesis parameters were drawn for this synthesis method. Field emission property of carbon nanowalls were also measured. As a proof of concept, specimens of carbon nanowalls were used as catalyst carriers for synthesis of carbon nanofibers to demonstrate the feasibility of growth template applications. Recent paper [1] Wu YH, et al. J MATER MATER 14 (1) 469-477 FEB 21 2004 [2] Hiramatsu M, et al. APPL PHYS LETT 84 (23): 4708-4710 JUL 7 2004 [3] Wu YH, et al., J MATER CHEM 14 (4): 469-477 FEB 21 2004 [4] Yang BJ, et al., NANO LETTERS 2 (7): 751-754 JUL 2002

Rb5.7/Rb5.7
Manipulation of microporous aluminophosphate lanllae for the formation of polymer/molecular sieve nanocomposite membranes. Joshua A. Sheffer and Michael Ispasatis; Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota.

The manipulation of layered inorganic materials in order to achieve functional nanostructures is important in areas such as heterogeneous catalysis, specific adsorption, nonlinear optics, self-consistent films, and nanocomposites. The swelling and intercalation chemistry of the layered materials, for example, have generated much interest relative to the formation of thermally stable pillared materials. Likewise, much study has been conducted on the intercalation of the layered zirconium phosphates, vanadium phosphates, and transition metal oxides. The family of crystalline aluminophosphates, however, is so far little understood in regards to swelling and intercalation chemistry. The layered aluminophosphates under consideration consist of crystalline inorganic layers formed by alternating AI04- and PO4 polyhedra [Nayak, R, N.; Adv. Chem. Mater. 2003, 36, 481-499]. The inorganic layers are characterized by a molecular sieve-type structure where 4-12-member rings are present, giving the possibility of microporosity. The layer charge is balanced by protonated organic amines located in the interlayer space between the layers. The swelling of such materials also form extensive hydrogen bonds with the inorganic layers. The swelling and intercalation chemistry of these materials is of interest for potential use in microporous-nemoporous materials and high-performance composites for separations. More specifically, our group has recently reported the use of these molecular-sieving aluminophosphate layers for the formation of polymer nanocomposite membranes that show enhanced selectivities for the separation of oxygen from nitrogen and methane [Sheffer, et al., Chem. Mater. 2004, 16, 3838-3845]. Procedures for swelling, exfoliating, and, in some cases, reassembling these layered aluminohosphate have been applied in this literature. However, complete characterization of the material at each stage of the swelling process has yet to be reported. In most cases, it is not even clear that the final, swollen material possesses the same AI-O-P connectivity and crystal structure as the original inorganic layers. A more complete
understanding of this nanoscale assembly process will pave the way for rational design of advanced materials from these layered nanomaterials. We will also present results on the protonation, exfoliation, and re-assembly of layered aluminophosphates, and the structure of the material will be characterized at each step with x-ray diffraction, small-angle x-ray scattering, solid state NMR, and transmission electron microscopy. We will also present results on the application of these materials to nanocomposite polymer/molecular sieve membranes for gas separations.

**R5a.8/Rb5.8**

Amphiphilic Photoresponsive Azobenzene-Containing Polymers, Sietse P. De Deym, Lev Bromberg and Alan Hatton; Chemical Engineering, MIT, Cambridge, Massachusetts.

Light represents an attractive trigger to change properties of a polymer solution because it would enable structural control without requiring changes in solution conditions, and it is externally reversible; thus it is amenable to device design and application. Amphiphilic copolymers with azobenzene moieties are of interest due to the ability of the azobenzene to undergo reversible trans-cis photoisomerization leading to the conformational isomers with significantly different dipole moment and hydrophobicity, and thus ability to aggregate into nanoscale structures in aqueous media. Herein, we describe novel poly(4-methacryloyloxyazobenzene-co-N,N-dimethyl acrylamide) (MOAB-DMA) copolymers that undergo trans-to-cis photoisomerization under UV irradiation at 360nm of around 325 nm. The MOAB-DMA copolymers with at least 0.18 mol fraction of the methacryloyloxyazobenzene groups are water-soluble and exhibit a pronounced photoisomerization effect, expressed in over 10-fold enhancement of the zero-shear viscosity of the irradiated aqueous solutions. A critical concentration of the copolymer (c**c**) was observed that lead to the appearance of compact aggregates (~30 nm according to the DLS tests) capable of solubilizing a water-insoluble dye, Nile Red. This critical concentration observed in dynamic surface tension studies.

Photoisomerization kinetics studies of the MOAB-DMA copolymers in aqueous solutions were based upon the time-dependent decay of the intensity of the electronic absorption peak at 325 nm after irradiation. The rate constants of the photoisomerization decreased with the polymer concentration, concomitantly with the hydrodynamic radius and in tandem with the surface tension of the solution. Dynamic changes in the aggregation state of the photoresponsive polymers enable novel opportunities for the control of viscosity and other properties of importance for the development of the applications of these novel nanostructured materials.

**R5a.9/Rb5.9**

Electrochemical Dip-Pen Nanolithography of Conductive Wires on the SiO2 Surfaces, Faipe Zhang, Ryo Yamada and Hirokazu Tada; JSPS Fellow, Toyo, Japan; **3Department of Materials Physics, Osaka University, Osaka; JST-CREST, Tokyo, Japan.

Fabrication of conductive nanowires on insulator is a key technology in molecular electronics. Photoassisted AFM dip-pen nanolithography (DPN) has been invented by which various nanostructures can be written directly on suitable surfaces with high degree of control over location and geometry. In this study, we have systematically investigated the fabrication of conducting nanowires on insulating SiO2 substrates by electrochemistry-assisted DPN (E-DPN). Nanowires are grown on the photolithographically-defined Au pad initially and then the growth is expanded over SiO2 surface using the produced wire as working electrode. We have systematically examined various parameters of E-DPN including the effects of coating methods and the types of the tips on electrodeposition behavior. It was found that the chemically-modified Si AFM tips by hydride termination in the adsorption of Si in UV ozone showed a favorable conductivity and high hydrophilicity suitable for DPN. Pt nanowires with a line width of 100 nm were prepared on the Au pad. The parameters optimized for E-DPN of metal and polymer nanowires on SiO2 surface will be presented.

**R5a.10/Rb5.10**

Surface-enhanced Raman Scattering of Rhodamine 6G Using Physical Self-Assembly of Ag Nanoplates, Ikuko Nakajima, Makoto Kikutani, Motofumi Suzuki, Yoshinori Wada, Kaoru Nakajima, Kenji Kimura and Yasuhide Mori; **3JST Kyoto CREATE, Seika chou, Kyoto, Japan; **2Department of Micro Engineering, Kyoto University, Kyoto, Japan; **2Department of Chemical Engineering and Materials Science, Doshisha University, Kyotanabe, Japan.

Design of the nano-ordered structure and development of the manufacturing methods at the level of the metal plates is essential in order to utilize localized plasmonic resonance of the noble metal nanoparticles efficiently as new optical devices and sensors. The dynamic oblique deposition (DOD) is one of the most suitable methods for the formation of the novel nano-ordered structures. Recently, we have succeeded in the production of the metal plates in which the major axes are aligned almost parallel to each other. [1] These nanorods seem to be advantageous to the surface-enhanced Raman scattering (SERS) substrates since the Ag nanorods can be regularly spaced at various surface densities. Here, we demonstrated first application of the Ag nanorods arrays fabricated by DOD to SERS measurements. The Ag nanorod arrays were directly formed on the template layer of SiO2 prepared by the spin-coating. The substrate was then annealed at 500°C to form SERS active. The SERS intensity of Rhodamine 6G (R6G) ethanol solution on the Ag nanorod array was measured. Apparent peaks corresponding to the 498 cm⁻¹ band of R6G have been observed. A significant enhancement was observed for the glass plate without Ag nanorod. The SERS intensity was dependent on polarization of incident laser and alignment of Ag nanorod. Although it has been known that the chain-like aggregation of the metal nanoparticles is effective for the near infrared SERS, conventional techniques are insufficient to control the morphology and configuration of nanorods. This DOD method is promising candidate for manufacturing the SERS active nano-ordered structure. [1] M. Suzuki, W. Mekita, K. Kishimoto, S. Toru, K. Nakajima, K. Kimura and Yasuhiro Taka, Jpn. J. Appl. Phys., 44 (2005) L189.

**R5a.11/Rb5.11**

Si Nano-Assemblies made by Atomic Plasma Method in Water, Shu-mei Liu, Seiichi Sato and Reiko Kusumoto; Graduate School of Material Science, University of Hyogo, Hyogo, Japan.

Si nano-materials are currently the focus of intense research interest since nanosized Si exhibits new properties such as visible and UV luminescence at room temperature, which is expected to guide new functionality in the field of optoelectronic devices. Fabrication of Si nanocrystal usually requires sophisticated vacuum system for the production of Si wafer and water. This technique may be very costly, environmentally clean, and produces no-contaminated nanoscale structure, which is used in many applications, such as opto-electronic devices. Recently, arc discharge technique in water has been used for preparation of carbon nanostructure by Sano et al by using layer structured graphite electrodes. However, synthesis of Si nanoparticles, nanohorns and nanobelts by arc in water have not been reported so far. The apparatus consisted of two Si electrodes, and the arc discharge was initiated by an instant contact of a Si anode (diameter of 5mm) with the Si cathode (diameter 20mm). The discharge current 10A was sustained by adjusting the cathode-anode gap to be about 1mm. After the arc was continuously supplied to purge O2 from water. The Si nanoparticles were floated on the air water interface and other arc processes suspended in water with some laughing argon to the bottom of the beaker. We investigated the as-prepared Si particles suspended in water by scooping a Cu grid using a Hitachi 8100-transmission electron microscope (TEM) operated at 200kV. Histogram of size distribution was obtained from conventional TEM image. High resolution TEM (HRTEM) image and transmission electron diffraction pattern showed the structure of Si nano-horns, nanohorn and nanoparticles. The average diameter of Si nanoparticles is ~60nm, with good crystallinity consistent with the diamond cubic structure of bulk Si. Increasing the arc current can optimize production rate of Si nano-particles. Continuous arc plasma for 1 hour gave a mass production.

**R5a.12/Rb5.12**

Thermo Control on Assembly and Dispersion of Gold Nanoparticles, Shin-ya Onoe and Toyoji Kunitake; **2R&D Department, Kyoritsu Chemical & Co., Ltd./PRESTO, JST, Kisarazu, Chiba, Japan; **3FIS, Riken, Wako, Saitama, Japan.
We report on the experimental study of thermo-responsive aggregation of highly stable gold nanoparticles covered by simple alkyl chains in various solvents. It is known that they provide a wide range of possibilities for display devices and optical materials. In this study, gold nanoparticles stabilized by various types of organic molecules were dispersed in the liquid phase. The dispersion and aggregation of gold nanoparticles into solvents and liquid resins were investigated by UV-Vis spectra and TEM observation.

Ra5.13/Rb5.13
Sub-micron Fibers from Electrospinning of Polymer Melts and Heated Solutions. Huacon Zhou and Yong Lak Joo; Cornell University, Ithaca, New York.

Electrospinning which utilizes an electric force to elongate a charged jet has now regained its popularity to produce nano-sized fibers. Over one hundred polymer and ceramic fibers have been successfully obtained by electrospinning. These fibers can have a very high surface area to volume ratio and can easily be functionalized, and thus are finding uses in many fields such as filtration, tissue scaffolding, drug delivery and gas sensors. Despite their great potential uses, nano scale fibers of some polymers such as Polypropylene and Ultra High Molecular Weighted Polyethylene (UHMWPE) have not been obtained from conventional solution electrospinning, since they have no proper solvents at room temperature. In the present study, we investigate the possibility of processing these polymers into sub-micro fibers either directly from melts or from heated solution at elevated temperatures. Three systems are chosen: Poly Lactic Acid (PLA) for melt electrospinning, Polypropylene and UHMWPE for heated solution electrospinning. Using an electrospinning setup with inventive heating capacity, we were able to obtain sub-micro fibers in all three systems. Our studies indicate that nozzle temperature and nozzle size are two most dominant factors in controlling the fiber size. To improve the fiber morphology, chemically modified nanofibers were intercalated into our polymer systems and the effect of nanofiber inclusion on the fiber structures and mechanical properties was investigated. Our results reveal that nanofiber inclusion increases both yield strength and elastic modulus of fibers due to their significant alignment throughout the fiber. Finally, a possible mechanical and thermal degradation of polymers during the process is discussed.

Ra5.14/Rb5.15
Investigation of Structural Properties of Silicon-Germanium Composites in Diatom Frustules. Timothy Cutt1, Jun Jiao1, Clayton Jeffries2, Shuhong Liu2, Gregory L. Rorrer2 and Chih-hung Chang2; 1Department of Physics, Portland State University, Portland, Oregon; 2Department of Chemical Engineering, Oregon State University, Corvallis, Oregon.

Diatoms are single-celled microalgae. They have the unique ability to make complex nanoscale three-dimensional silica structures that offer attractive possibilities for their application in nanobiotechnology. This ability was exploited in incorporating germanium into the diatom cell in a two-stage photoreactor cultivation process (biosynthesis), leading to the formation of nanostructured silicon-germanium (Si-Ge) oxides. In the development of this perfusion-based bioreactor process strategy for the biosynthesis of Si-Ge oxides, the TEM and SEM are extensively used to monitor progress at each stage. Si-Ge oxides possess attractive optoelectronic properties such as photoluminescence. A state-of-the-art FEI Tecnai F-20 field emission high resolution TEM (200kV) equipped with an embedded digital scanning transmission electron microscopy (STEM) capability and an energy dispersive x-ray spectrometer (EDS) were used to study the structural properties and chemical composition of Si-Ge nanocomposites in diatom frustules. The integrity of the diatom cell mass was validated by characterization with an FEI Sirion field emission scanning electron microscope (FSE SEM), also equipped with an Oxford EDS. Structural properties of the Si-Ge oxides composites and distribution of Ge and Si within the frustules were determined. The intensity variation of Ge signal in the diatom frustules similar to that of Si though it is lower by two orders of magnitude. The results also suggest that Ge exists in smaller pockets or nanoparticles than Si. Having located the Ge sites in the diatom frustules, the further challenge lies in relating these sites to anatomical structures of the diatom. [1] Acknowledgements 1. This report was supported by the National Science Foundation (NSF) Nanoscale Science and Engineering Initiative, Nanoscale Interdisciplinary Research Team Award, BES-0400648 and DMR-0335738 (REU Site).

Ra5.15/Rb5.15
Invertible Assemblies of Novel Amphiphilic Homopolymers. Hossein Baghadi1, Dharma Rao2, Surita R. Bhatia1 and S. Thayumanavan2; 1Chemical Engineering, University of Massachusetts Amherst, Amherst, Massachusetts; 2Chemistry, University of Massachusetts Amherst, Amherst, Massachusetts.

We report small-angle neutron scattering (SANS) studies of the assembly of a novel class of amphiphilic homopolymers. The amphiphilic nature is achieved by incorporating both hydrophobic (benzy) and hydrophilic (carboxylic acid) moieties into each repeat unit. In water, these polymers form micelle-like structures with a hydrophobic corona and hydrophilic core. However, behavior changes in aqueous solvents (toluene with a small amount of water), the structure inverts to an assembly with a lipophilic corona. Thus, these materials are extremely sensitive to their solvent environment and have the potential to be used as small-responsiv ‘smart’ materials for controlled permeation and catalysis. Like conventional small-molecule micelles, these assemblies may be used to solubilize hydrophobic pharmaceuticals. However, unlike classical small-molecule micelles, the critical micelle concentration is quite low, in the range of 10^{-7} to 10^{-8} M. In addition, there is evidence that the micelle rigidity is dependent on the polymer concentration. This can be used to tune the release rate of solubilized pharmaceuticals. Finally, we see that the characteristic sizes of these assemblies are in the range 30-50 nm, somewhat smaller than typically encountered for block copolymer micelles. This may be desirable for certain delivery applications. SANS spectra can also be used to quantify the amount of solvent in the interior of the micellar assemblies. These studies yield insight into new materials and routes for nanoscale assembly, as well as impact applications such as controlled drug release, smart adsorbent and catalysis.

Ra5.16/Rb5.16
Millimeter-scale surface nano-structuring using focused ion beam milling. Katharine Dowden1, Radislav A. Potyrailo2, Laurie A. Le Tarte1, Hong Piao3 and James Grande3; GE Global Research, Niskayuna, New York.

New patterning schemes for various applications including sensors and photonics are explored. We present here a comprehensive study of using focused ion beam milling to modify (FIB) silicon millimeter-scale areas with nano-patterns of dimensions down to 30 nm. A typical example of a pattern is 40 nm diameter x 40 nm depth wells with a 200 nm pitch. Pyramids and other shapes can be produced as well. Typical sample materials are metals, but polymer patterning is available as well. We are also evaluating the surface of the patterned materials to ensure there are no negative effects of these patterning schemes on the future device performance. FIB milling is known to produce substantial, and not always desired, alterations on the surface. Utilizing the dual-beam FIB-SEM (scanning electron microscope) system, we are able to exclude sample surface exposure to the ion beam when setting up the patterns. Hence, no structural damage is typically observed (SEM) on the surface of patterned materials. However, there are secondary ion scattering effects taking place during patterning, as well as subtle effects of rutherfording the electron beam over the sample surface in conjunction with milling. These effects can potentially create a nanolayer-scale surface modification. We are using Auger Electron Spectroscopy and X-Ray Photoelectron Spectroscopy to evaluate the surface quality after patterning and prove methods applicability for various applications. The effects of plasma cleaning on the patterned surface are also discussed.

Ra5.17/Rb5.17
Controlled direct growth of vertical and highly-ordered 'carbon nanotube - silicon' heterojunction array. Teng-Fang Ku8, Ajinun Yin, Chih-Issun Hsu, Daniel Straus, Marian Tzolov and Jimmy Xu; Brown University, Providence, Rhode Island.

Carbon nanotubes (CNT) has been studied intensively for exploration of its unique electrical and mechanic properties in many applications. However, direct integration carbon nanotube with silicon to form an electronically functional structure or device, though highly desirable, has remained a great challenge. Whereas vertical aligned bundles of nanotubes have been grown previously on silicon, the integration is mechanical, rather than electronic, in nature. In the present work, we report on controlled direct growth of vertically and highly-ordered array of 'carbon nanotube - silicon' (CNS) heterojunctions of uniform diameter, length, and alignment. The as-grown CNS heterojunction structure is not only electronically functional but also strongly rectifying with an on-off ratio as high as five orders of magnitude in current-voltage characteristics measured at room temperature. The controlled direct growth of the CNS heterojunction array of such high uniformity is enabled by the formation of highly ordered nanotube array directly on the silicon, following a precisely controlled anodization of aluminum thin film evaporated on silicon. Iterations of anodization process development and condition optimization and real-time modification and control of the anodization process were required for the formation and adhesion of the alumina growth matrix directly on silicon. Under the carefully controlled and optimized conditions developed in this work, we are able to obtain an abrupt heterointerface between the carbon nanotube and the silicon, without
an intermediate barrier layer, as required for an electronically functional CNS heterojunction.

Ra5.18/Rb5.18
Crystalline TiO₂ Macroporous Foams with Highly Nano-Mesoporous Framework. Florent Cars, Stephane Reculca and Renal Bacov; Centre de Recherche Paul Pascal (UPR-CNRS 8641), Pessac, France.

Titanium dioxide photocatalysis is becoming very attractive today regarding an increasing range of photocatalytic applications including water purification, photovoltaic cells, photochemical cancer treatment, and so forth. This increasing interest has motivated the design of highly crystalline micro- and/or mesoporous TiO₂ monoliths. In addition to this design, an optimized structure necessitates a rational macroscopic shaping in order to reach an optimal diffusion of reagents and products. In this last issue, we aim to present the synthesis and characterization of highly crystalline nano-mesoporous macroporous scaffolds of titanium dioxide and emphasize towards rational design over the macroscopic void space sizes and shapes. This novel route allows a strong control over the macropore morphologies, namely: cell wall width, length and curvature in a large range of size (cell wall length from 60 μm up to 600 μm) while maintaining mesoporosity. The control over the macroscopic shape is obtained by a dynamic approach based on a continuous control over foam’s liquid fraction and bubble’s size during the mineralization process while mesostructural formation is obtained using either P123 co-solvent micellar processes or latex nanoparticles as patterning entities. The specific surface associated to those materials is appreciably enhanced (2P₂ET ≈ 400 m² g⁻¹) regarding materials obtained through previous study. The TiO₂ scaffold crystallinity (Anatase and/or Rutile) is determined by Raman monitored during synthesis and employed for the organic template removal. This strategy provides low cost and well defined monolithic materials as highly mesoporous crystalline titanium dioxide macroporous foams. 1- F. Carn, M.-F. Achard, O. Babot, H. Deleuze, S. Reculca, and R. Bacov, J. Mater. Chem., (submitted); 2- F. Carn, A. Colin, M.-F. Achard, H. Deleuze, C. Sanchez, R. Bacov, Adv. Mater., 2005, 17, 62.

Ra5.19/Rb5.19
Engineered Planar Defect in 3D Colloidal Photonic Crystals. Pascal Masse and Serge Ravaine; Centre de Recherche Paul Pascal (CRPP), Pessac, France.

In recent years there has been a growing interest in modulating the band gap properties of photonic crystals by incorporating defects within them in a controlled manner in order to obtain new photonic properties. We present here the controlled insertion of a defect layer of submicrometer silica particles into 3D colloidal crystals made by the successive transfers onto a solid substrate of pre-organized two-dimensional arrays of smaller silica particles using the Langmuir-Blodgett technique. Scanning Electron Microscopy investigations reveal that the position of the defect layer inside the colloidal crystal is perfectly controlled while the overall thickness of the materials is constant and uniform. NIR experimental transmission spectra reveal that the defect layer atropositivity and induces a pass band into the forbidden band gap. Both the wavelength and the magnitude of the pass band are found to continuously vary with the position of the planar defect layer inside the material. These experimental results are also successfully simulated using a model based on a 2D rigorous theory of diffraction. Results of these simulations are presented and discussed in terms of a degradation of the crystalline ordering of the top stack close to the defect layer.

Ra5.20/Rb5.20
Morphologically Controlled Hybrid Assemblies Starting from Spherical Colloidal Particles. Adeline Perro² ¹, Etienne Duguet Duguet¹ and Serge Ravaine¹; CRPP, Bordeaux, France; ICIMCB, Bordeaux, France.

One area of particular effort recently is the use of colloidal particles as precursors in engineering new materials. Nevertheless, these particles are nearly always spheres. This places limitations on the structures that can be built, especially in making photonic-bandgap materials. Therefore, it is a great challenge to create new colloids with an original shape, i.e. different from the sphere, in a controllable manner. We present here an original approach to create hybrid organic-inorganic colloidal particles with a perfect controlled shape. The synthetic route of these structures, which are composed of spherical silica spheres surrounded by a varying number of polystyrene layers, consists in the one-pot polymerization of styrene in the presence of silica particles, which had been surface-modified by a coupling agent containing polymericizable groups. The influence of the size of the silica core and the nature of the coupling agent on the resulting colloidal particles morphologies was carefully analyzed. We show in particular that the number of growing polystyrene beads varies homogeneously with the diameter of the mineral spheres. A main advantage of this technique is also that we can precisely control the reaction time, allowing us to tune the final morphology of the hybrid structures. These colloidal assemblies are original building blocks for the elaboration of new functional materials.

Ra5.21/Rb5.21
Field-theoretic Simulations of Block Copolymer/Nanoparticle Composites: Preliminary Results of Hybrid MC/SCFT Algorithm. Scott Wilson Sides² and Glenn Fredrickson¹;¹ Tech-X Corp., Boulder, Colorado; ²University of California - Santa Barbara, Santa Barbara, California.

Using block copolymers as mesoscale templates for organic/inorganic nanoparticles has the potential to create patterned particle aggregates that could be used as magnetic storage media and semi-conductor materials. More generally, polymer nanocomposites such as these are being investigated for the potential to develop materials with specifically tailored optical, electrochemical, thermal and mechanical properties. Whether polymer/particle mixtures are used in a nanoscale templating strategy or in a “nano-alloying” strategy that combines the various materials properties of the constituent polymers and/or particles, the overall behavior of the nanocomposite system depends on the morphology of the polymer chains as well as the arrangement of the particles in the polymer matrix. However, predicting the chain configurations in a system of block copolymers alone can be extremely difficult. Self-consistent field theory (SCFT) for dense polymer melts has been highly successful in predicting complex domain morphology in block copolymers. Field-theoretic simulations such as these are able to access large length and time scales that are difficult or impossible for particle-based simulations such as molecular dynamics, while still incorporating more realistic models of the complex microstructure, continuum simulations. In this talk I will outline the SCFT method, discuss some efficient methods of numerically solving the SCFT equations and present preliminary results for spherical nanoparticles embedded in an AB diblock copolymer melt. These results have been obtained using a hybrid MC/SCFT approach that treats the polymer in a field theory framework while explicitly retaining the individual nanoparticle coordinates as degrees of freedom.

Ra5.22/Rb5.22
Controlled Synthesis of Inorganic Nanostructures with Modulated Architectures in Micellar Systems. Limin Qi, Hongtao Shi, Yurong Ma, Nana Zhao and Jiming Ma; College of Chemistry, Peking University, Beijing, China.

Both reverse and normal micelles have been used as nanostructured media for the facile, low-temperature synthesis of inorganic nanostuctures with various morphologies such as one-dimensional (1D) nanostuctures (nanowires, nanobelts, and nanotubes) and nanostars. Unique cationic reverse micelles formed by mixed cationic-anionic surfactants are employed for the controlled synthesis and hierarchical assembly of 1D BaXO₄ (X = Cr, Mo, W) nanostuctures. The effects of various factors, such as the mixing between the anionic and cationic surfactants, the temperature, and the polymeric additives, on the formation of 1D BaXO₄ nanostuctures and the architectural control of their complex superstructures are examined. A plausible two-stage growth mechanism has been proposed for the formation of the penniform Ba₅Cr₂O₈ nanotubes. On the other hand, normal micelles of nonionic surfactants are employed for the controlled synthesis of single-crystalline nanotubes, nanowires, and nanobelts of trigonal selenium (t-Se). In particular, well-defined t-Se nanotubes are fabricated in micellar solutions of poly(oxyethylene(23)) dodecylether (C₁₂E₀₂₃) whereas single-crystalline t-Se nanotubes are obtained in micellar solutions of poly(oxyethylene(20)) octadecyl ether (C₁₈E₀₂₀). It is revealed that the anionic micelles play an important role in controlling the distribution and diffusion of ammonium Se in the solution and hence exert delicate control over the morphology of the 1D t-Se nanostructures. Moreover, uniform star-shaped P85 nanocrystals are readily produced in micellar solutions of mixed cationic-anionic surfactants. These results demonstrate the great potential of micellar systems in facile, low-temperature solution synthesis of inorganic nanostuctures with controlled architectures. References: [1] H. Shi, L. Qi, J. Ma, H. Cheng, B. Zhu, Adv. Mater. 2005, 15, 1647. [2] H. Shi, L. Qi, J. Ma, N. Wu, Adv. Funct. Mater. 2005, 15, 442. [3] Y. Ma, L. Qi, J. Ma, H. Cheng, Adv. Mater. 2004, 16, 1023. [5] Y. Ma, L. Qi, W. Shen, J. Ma, Langmuir 2005, dx.doi.org/10.1021/la0508011.

Ra5.23/Rb5.28
Fabrication of Hollow Silica Aerogel Spheres for Direct Drive Inertial Confinement Fusion Experiments. Renyi Ray Pugno,² A. Nikroo,² M. Takagi² and M. Thü;² General Atomics, San Diego, California, ²Lawrence Livermore National
Laboratory, Livemore, California; 2University of California, San Diego, La Jolla, California.

Hollow foam spheres are needed for laser fusion experiments on the OMEGA laser facility at the University of Rochester as part of the national campaign for demonstrating the feasibility of fusion energy. Previous attempts to make foam and aerogel shells have been hindered using resorcinol-formaldehyde (R/F) and divinylbenzene (DVB). In this paper we discuss the development of silica aerogel (SAG) shells as an additive to the polymer based system. SAG may have the advantage of: 1) reducing foam robustness, which is important in processing these laser targets. SAG shells were fabricated by the microencapsulation method using a triple orifice droplet generator. This technique allows for precise control of the shell diameter and wall thickness. Changes in the gelation time have significant effects on the ability to fabricate the shells. Reduction of the gelation time is crucial in fabrication of intact shells with high yield. In addition, the proper choice of the components of the different phases of the microencapsulation method is essential for fabrication of intact SAG shells with proper sparcity and wall uniformity. The density of shells fabricated is approximately 100 mg/cc and the diameter ranges from 700µm-1200µm, with a wall thickness of 50-100µm. Development of a full density permeation barrier for retention of the fusion fuel will also be discussed. Work supported by U.S. Department of Energy under Cooperative Agreement DE-FC03-92SF19460 and W-7405-ENG-48.


Indium oxide is an important wide band gap semiconductor with different applications in optoelectronics, optical transparency or gas sensing. Indium oxide is considered of interest for gas detection because of the enhanced sensitivity related to high surface to volume ratio. In particular, elongated indium oxide nanostructures in form of wires, and belts have been grown by chemical routes and by thermal evaporation methods. In this work, elongated micro- and nanostructures of In2O3 have been grown during high temperature sintering of compacted powder under argon flow. With this method, which has been used to grow elongated nanostructures of different semiconductors with high specific surface (1-4), the structures grow on the sample surface, which acts as source and as substrate. The growth of the In2O3 elongated structures has been performed during thermal treatments of compacted In2O3 and InN powders and the samples have been characterized by SEM and by cathodoluminescence (CL) in SEM. The low dimensional structures have been found to grow on InN by vapor- solid process at temperatures as low as 650 °C. The structures obtained during the different treatments are micro- and nanowires with lengths of up to hundreds of microns. Other structures, which appear to correspond to different growth stages, are nanonanowires and well formed rods terminated in pyramids. The morphology and size of the structures depend on the growth parameters. Spectral CL shows emission from the pyramids as compared with the rods and wires. Spectral CL emission from the different micro- and nano-structures is investigated. 1) A.Uribe, P.Fernandez and J.Figueras. Appl. Phys. Lett. 85, 3699 (2004) 2) M. Maestre, M. Perez and J.Figueras, J. Appl. Phys. 97, 044310 (2005) 3) E.Nogales, B.Mendez and J.Figueras, Appl. Phys. Lett. 86, 113112 (2005) 4) J. Grym, P.Fernandez and J.Figueras, Nanotechnology 16, 931 (2005)

Ra5.25/Rb5.25 Sintering Atmosphere as a Control Parameter for Grain Growth in Nanocrystalline Barium Titanate Ceramics. Anton Polev1, Kristen Breese2, Elizabeth Dickey2, Audrey Ragulya3 and Clive Randall1; 1Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania; 2Institute For Materials Science Problems NAS of Ukraine, Kive, Ukraine.

Barium titanate is the most widely used dielectric material in surface mount components and is presently under development for the mass production of submicron grain size ceramics. Over the next ten years, these dimensions will become nanoscale if present trends continue. The production of fully dense nanocrystalline barium titanate ceramics is a difficult task due to enhanced grain growth during the final stage of sintering. To win the competition between densification and grain growth, the right green sample microstructure, dopant type and amount and properly controlled thermal cycles should be reduced to the minimum. Oxygen partial pressure on sintering nanocrystalline barium titanate powder is discussed. A sintering atmosphere with a low oxygen partial pressure has an inhibitive effect on densification by facilitating the improvement of grain microstructure and the suppression of grain growth. Sintering in a heavy reduction atmosphere (pO2 = 10-18 ± 10-19 atm) is more useful in respect of decreasing the final grain size. This suppression of grain growth corresponds with the appearance of Ti3+ ions. The combination of colloid sample preparation, sintering schedule and heavy reduction atmosphere used in this research enables the production of fully dense pure BaTiO3 ceramics with ~100 nm average grain size without using pressure assisted sintering or electro consolidation methods.

Ra5.26/Rb5.26 Abstract Withdrawn

Ra5.27/Rb5.27 Immobilization of TAT Peptides on the GaAs Surface. Young-Soo Kim1, Cho2 and Albena Ivanisieva1; 1Chemistry, Purdue University, W. Lafayette, Indiana; 2Biomedical Engineering, Purdue University, W. Lafayette, Indiana.

Several TAT peptide fragments were used to functionalize GaAs surface by adsorption from solution and microcontact printing. Different sequences of TAT peptides were employed in recognition experiments. A synthetic RNA sequence was tested to verify the specific interaction with TAT peptide. We have examined the effects of proteinaceous on RNA using chemical force microscopy. GaAs surface functionalized with different sequences of TAT peptides were employed to measure adhesion forces with AFM tip coated with RNA in solution. We characterized the modified GaAs surfaces by contact angle, Atomic Force Microscopy (AFM), X-ray Photoelectron Spectroscopy (XPS), and Fourier Transform-Infrared Absorption Spectroscopy (FT-IRRAS). AFM studies were used to compare the surface roughness before and after functionalization. XPS allowed us to characterize the chemical composition of the GaAs surface and conclude the monolayers composed of different sequences of peptides have similar surface chemistry. Finally, FT-IRRAS experiments enabled us to deduce that the TAT peptide monolayers have fairly ordered and densely packed alkyl chain structure.

Ra5.28/Rb5.28 Colloidal Lithography with Crosslinkable Particles: Fabrication of Hierarchical Nanopore Arrays. Jun Hyuk Moon1,2, Se Gyu Jang3, Jong-Min Lim3 and Seung-Man Yang2; 1Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania; 2Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Engineering, Daejeon, South Korea.

Two-dimensional (2D) porous substrate has been attracted in various applications ranging from TAT peptide patterning to catalytic support. Recently, self-assembled colloidal particle arrays have been intensively studied because they provide a simple and cost-effective lithography mask to produce patterned pores. Meanwhile, in addition to allowing bulk nanopore arrays, the structural hierarchies are an essential step toward the practical application of these substrates. In this paper, we demonstrated a photolithographic process to produce hierarchical nanopore arrays with colloidal lithography. To do this, we synthesized polystyrene nanoparticles containing cetyl trimethylammonium chloride and crosslinked by photo-induced ring-opening. The particle array was exposed to UV through a mask and heat treated above the glass transition temperature (Tg) of the particles, the exposed particles were not substantially deformed because Tg was increased by crosslinking of the epoxide, while the particles in the unexposed region were deformed and the interstices between particles disappeared. Therefore, the RIE etching or deposition through the interstices between the particles was only achieved in the exposed region. Finally, we produced hierarchically patterned nanopore arrays. The present method of hierarchical patterning can be used as a practical design tool of nanopatterned substrates.

Ra5.29/Rb5.29 DNA Nanopatterns Produced by Electron Beam Lithography of Self-Assembled Monolayer Resist. Guo-Jun Zhang4, Takashi Tanii5, Yuzo Kanari5 and Iwao Ohdomari1; 1Institute of Biomedical Engineering, Waseda University, Tokyo, Japan; 2Department of Electronical Engineering and Bioscience, Waseda University, Tokyo, Japan.

DNA nanopatterns have attracted much attention on biological applications including disease diagnosis, DNA sequencing, drug discovery and so on. Nanopatterned DNA arrays allow one to precisely deposit DNA on the substrate on the nanoscale with low nonspecific binding. DNA arrays can be anticipated to obtain controlled homogeneous spots, thereby resulting in high detection sensitivity and massive parallelization with smaller amounts of reaction reagents and more biochip components. Herein, we present amino-modified oligonucleotides are immobilized on DNA nanopatterns on a silicon surface fabricated by EB lithography of self-assembled monolayer resist (octadecyltrimethoxysilane), surface hybridization process is conducted using biotinylated complementary
target oligonucleotides, finally the binding event is illustrated by AFM measurement of Au nanoparticles labeling (adsorption of streptavidin-coated silica corente with general dyes). This novel approach allows the precise control over pattern size, shape, pitch, and DNA attachment and hybridization on the nanopatterned arrays, which will provide the potential for development of ultrasensitive DNA biosensors and biochips.

**Ra5.30/Rb5.30**


Artificial protein models, based on both alpha-helical bundle and beta-sheet structural motifs, can be designed to incorporate biological cofactors and retain a range of specific functional elements of their natural counterparts, but within much more simple structures. Amphiphilic 4-helix bundle peptides have been previously designed to selectively incorporate heme and other natural cofactors within both the hydrophilic and hydrophobic domains and have proven to possess characteristic electronic and optical properties of natural electron-transfer proteins. However, it is non-trivial to incorporate both the electron donor and acceptor inside the 4-helix bundles in a controlled manner. Extended pi-electron systems have been designed and tailored, with appropriate donors, acceptors and constituents, to exhibit selected light-induced electron transport and/or proton translocation over long distances. These non-biological cofactors have the advantage of including the electron donor and the acceptor within the same prosthetic group and offer an independent means to modulate the electron transport properties of electronically excited states, inter cofactor midpoint potentials, cofactor-cofactor electronic coupling, and the nature of the charge distribution. We studied the binding between a series of non-biological metalloporphyrin cofactors and the designed amphiphilic 4-helix bundles peptides at selected locations. The interior of the artificial protein can be used to control the solubility, position, orientation of the cofactors, while the exterior can be used to control the macroscopic orientation. Incorporation of the non-biological cofactors into the 4-helix bundle via bi-histidyl ligation did not change the protein secondary structure or the 4-helix bundle formation. The amphiphilic protein/cofactor complexes have good thermal stability and maintain more than 85 percent of the original helical content. This development may potentially lead to functional biomaterials with novel electron transfer properties and it is crucial to control the macroscopic ordering of the artificial proteins in one, two or three dimensions. The artificial protein Langmuir monolayers, both the apo- and holo-form, can be oriented vectorially at the air/water interface upon compression as shown by the x-ray reflectivity data. However, Grazing Incidence X-ray Diffraction (GIXD) data from Langmuir monolayers at higher surface pressure show a broad maximum for momentum transfer parallel to the monolayer plane. This diffraction arises from the interference between parallel helices and demonstrates that the di-helices aggregate to form 4-helix bundles with glass-like inter-bundle positional and orientational order on the monolayer plane. Nanoporous thin films made from diblock copolymers are ideal templates to assemble the artificial proteins with laterally hexagonal order. We will discuss the efforts on re-designing the artificial proteins to incorporate them into these nanoporous templates.

**Ra5.31/Rb5.31**

Hydrogen-bonded Multilayer Coatings on Microparticles and Potential Applications. Dae-Young Lee, Zhifeng Li, Robert E. Cohen and Michael F. Rubner; 1Department of Chemical Engineering, MIT, Cambridge, Massachusetts; 2Department of Materials Science and Engineering, MIT, Cambridge, Massachusetts.

Layer-by-layer (LbL) assembly of polymers presents opportunities for creating conformal and robust coatings with molecular scale precision and a wide range of physical properties. This method has been extended to the coating of 3-D structures including colloidal particles. We demonstrate three hydrogen-bonded multilayer systems: thin film coating of polycrylic acid (PAA) and polyacrylamide (PAAm) can be assembled onto micron-sized spherical particles. Hydrogen-bonded multilayers were deposited on microparticles at low pH conditions by LbL assembly of a mixture of poly(acrylic acid) (PAA) and polyacrylamide (PAAm) can be used to form nanoscale thin films. The multilayer coated surfaces, both on planar and colloidal supports, exhibited excellent resistance toward mammalian cell adhesion. These hydrogen-bonded multilayers offer potential applications in the area of biocompatible soft materials. Technologies involving such surfaces need to be rendered bio-inert. We also show that hydrogen-bonded multilayer thin film coatings assembled on colloidal particles can be used as templates for the in situ synthesis of nanoparticles. The reaction and size of nanoparticles grown within the coatings can be varied by the number of loading and reduction cycles. The core particles can be extracted by treating the nanocomposite coated particles with tetrahydrofuran leaving the nanoparticles embedded within the resultant multilayer hollow microparticles. Our method provides a general approach to create nanocomposite microparticles that contain various types of nanoparticles including magnetic, catalytic and semiconductor nanoparticles. We demonstrate that micron-sized superparamagnetic nanoparticles coated with silver nanoparticles loaded hydrogen bonded multilayer thin film coatings can be used as antibacterial agents that can be delivered to specific locations using magnetic fields. The effect of film thickness and Ag nanoparticle concentration on the antibacterial properties of these nanoparticle-loaded multilayer films was investigated by using a disc-diffusion test. Finally, we show that hydrogen-bonded multilayer coated microparticles can be utilized to create asymmetrically functionalized microparticles, also known as Janus particles. Hollow Janus microparticles are promising for dissolving and extracting the core particles. These asymmetric structures will enable the assembly of complex suprastructures that may find applications in fields such as photonics and biomedical engineering.

**Ra5.32/Rb5.32**

Single-Step Synthesis of Gold/Porous Silica Nanocomposite Materials. Arijit Bose, 1 Jayanta Sarkar, 1 Vijay John, 2 Ganapathiraman Ramanath 2; 1University of Rhode Island, Kingston, Rhode Island; 2Chemical Engineering, Tulane University, New Orleans, Louisiana; 3Materials Science and Engineering, Rensselaer Polytechnic, Troy, New York.

Gold-porous silica nanocomposite materials have been formed in microemulsions by simultaneous hydrolysis/condensation of a silica precursor along with reduction of the gold precursor. Striking the right balance between these simultaneous reactions is the key to success in synthesis of well-dispersed gold nanoparticles within the porous silica matrix. The microemulsion is formed using Iso-octane/AOT (Sodium bis (2-ethylhexyl) sulfosuccinate)/Lechithin/TEOS (Tetraethyl orthosilicate)/H2AuCl4 (Auric Chloride)/NaBH4 (Sodium borohydride). This system is chosen because of its ability to manipulate the underlying viscosity of the precursor phase, helping to immobilize the particles once they are precipitated. Changing the aqueous content as well as the auric chloride concentration has a distinct effect on the morphology and size of the resulting gold particles, as well as their dispersion in the porous silica matrix. Additional experiments where hydrophobically modified gold nanoparticles are formed in a single step in situ experiment are described. These experiments provide an interesting pathway for the formation of catalyst-support composite materials.

**Ra5.33/Rb5.33**

Novel Silicon-Carbon Nanostructures: An Ab Initio Study on the Stability of Si60C20 Clusters. Aravind Srivinasan, Muhammad Nurlu Huda and Asok Kumar Ray; Physics, University of Texas at Arlington, Arlington, Texas.

Discovery of the magically stable C60 fulleren e cage and the subsequent discovery of the carbon nanotubes have prompted scientists to study fullerene-like silicon structures. Cage-like compact clusters are particularly important for two reasons; nanotubes can be used as building blocks of more stable materials and the hollow space inside the cage can be used to dope different atoms yielding a wide variety of electronically engineered materials. Obviously, this has strong implications for nano-scale semi-conducting devices. We have recently shown that carbon dimers trapped into medium size silicon clusters (n=8-14) produces highly stable structures and in particular, we have predicted, based on ab initio Hartree-Fock based Moller Plesset perturbation theory calculations, that Si46, with a close to bulk fullerene structure, is a magic cluster. The formalism of general gradient approximation to density functional theory was then used to produce a class of highly stable nanostructures by putting multiple carbon atoms inside a Si20 cage [1]. In the present study, we will report our results on investigating the possibility of stabilizing Si60 fullerene cages by placing C20 clusters, believed to be the smallest fullerene structure [3], inside them. Full geometry optimizations have been performed using the Hay-Wadt pseudopotential basis set without any symmetry constraints using the Gaussian 03 suite of programs [2]. Our studies indicate that the additions of C20 clusters to Si60 fullerene cage do produce structures with higher stability. We have investigated the addition of various possible C20 structures in different orientations with the Si60 cage and we will report detailed results on binding energies, ionization potentials and electron affinities where to nanotube monomers, dimer, trimers, and the bonding nature of the stable Si60C20 nanostructures. As an example, the addition of C20 bowl shape structure, which is also the ground state structure for C20, in Si60 cage has the binding energy per atom of -0.38eV and a band gap of 2.83eV calculated per atom of 3.61eV and band gap of 0.75eV for the bare Si60 cage. Adding C20 pentagonal cage inside the Si60 cage did not produce as

Ra5.34/Rb5.34
Photic Polymerization in Three-Dimensional Opal
Photonic Crystals. Alexander Baryshev1,2, Rintaro Fujikawa1, Kazuhiro Nishimura1, Hironaga Uchida3 and Mitsutoku Inoue1-3, 1Toyohashi University of Technology, Toyohashi, Japan; 2Tokei Physico-Technical Institute, Saint-Petersburg, Russian Federation; 3CREST, Japan Science and Technology Corporation, Tokyo, Japan.

Lately, there has been much interest in a new class of artificial materials known as photonic crystals owing to many different new electromagnetic effects that were predicted in them. Magneto-photonic crystals (MPCs) [1], photonic crystals fabricated from magnetic materials, and also composite materials in which magnetic materials are implanted into a photonic crystal, have attracted major interest, since the combined properties of the electromagnetic wave by MPCs is expected to be a key technology for future applications in optoelectronics. We reported that 1D MPCs exhibit remarkable magneto-optical properties accompanied by a huge augmentation in their Kerr and Faraday rotation at room temperature by a giant magneto-optical response was observed [2]. As for the study of 2D and 3D MPCs, the available theoretical and experimental data are incomplete, and the results remain ambiguous. The goal of this work is to study magneto-optical properties of 3D MPCs. We examined an opal-magnetoactive liquid system and investigated the correlation between transmissivity of opals and the Faraday rotation in the chosen system. High quality samples had the growth surface of 100×100mm2 in size and thickness. The sample under study was immersed in a transparent paramagnetic liquid: the saturated isopropanol solution of terbium nitrate, turpentine oil, propylene glycol. We studied angle-resolved Faraday rotation and transmission spectra of the sample along the F-U-L-K path in the high-symmetry plane LIX of the Brillouin zone of fcc lattice. The Faraday rotation spectrum of the opal-magnetoactive liquid system, \( \theta(\lambda) \), shows characteristic bands corresponding to the bands in transmission spectrum taken along the same crystallographic direction. The dependence \( \theta(\lambda) \) follows the behavior of the Faraday rotation of magnetoactive immersion liquid outside photonic bandgaps. However, the strong change of Faraday angle of rotation \( \theta \) can be observed as the transmissivity of light through the opal sample decreases. For a specific direction in the opal sample, the angle \( \theta \) unexpectedly tends to be positive (or negative) in spite of the characteristic bands of the immersion liquid. Namely, if the rotation of polarization plane in the immersion liquid is negative (positive), the angle \( \theta \) is positive (negative). Such a behavior of value of \( \theta \) can be caused by the simple (or multiple) Bragg diffraction inside opal photonic crystal, but the complete interpretation of the observed phenomena still remains unclear. [1] M. Inoue and T. Fujii, J. Appl. Phys. 81, 8 (1997). M. Inoue, K. I. Araiz, T. Fujii, and M. Abe, J. Appl. Phys. 88, 8 (1999). [2] A. A. Fedyanin, T. Yoshida, K. Nishimura, G. Marowsky, M. Inoue, O. A. Aktipetrov, JETP Lett. 76, 527 (2002).

Ra5.35/Rb5.35
Fabrication of Densely-Packed, Well-Ordered, High-Aspect-Ratio Silicon Nanopillars Over Large Areas Using Block Copolymer Lithography. Gnevshorishan1, Nataliy Miller1, Michael McGeeh1, Matthew Misner2, Du Yeol Ryu1, Thomas Russell1, Eric Drockenmuller1 and Craig Hawkins2; 1Materials Science and Enng., Stanford University, Stanford, California; 2Polymer Science and Enng., Univ. Massachusetts, Amherst, Massachusetts; 3IBM Almaden Research Center, San Jose, California.

Vertically oriented nanopillars and nanowires have sparked considerable interest in a variety of fields. Sub-100 nm nanopillar periodicities are desirable for many applications, which include bulk-heterojunction organic-inorganic photovoltaic devices, two-dimensional photonic crystals and waveguides, vertically-oriented field-effect transistors (FETs) and stamps for nano-imprint lithography. Using self-assembled block copolymer (BCP) lithography and reactive ion etching (RIE), we fabricate high-aspect-ratio silicon nanopillars over centimeter-sized areas, which are taller than 100 nm, have aspect ratios as high as 10 and occur with a periodicity of less than 35 nm. Various unique aspects of the materials and processing techniques enabled key features of the nanostructures: BCP lithography facilitated the periodicity and the density of the nanopillars, the unique lift-off technique facilitated large-area patterning and a highly selective and anisotropic NFS-based RIE chemistry achieved the final nanopillar structure. We study the effect of different process parameters on the physical characteristics, such as periodicity, aspect-ratio and height, of the pillars and the chemical composition of the pillar surface. We discuss the potential applications of these nanostructures and also suggest suitable processing modifications to obtain nanopillars that meet the different requirements for such applications.

Ra5.36/Rb5.36
Chiral organization of colloidal particles by porous silicon templating methods. Michal Tynechenko1, Liilis F. Marsal2, Isabelle Rodriguez1, Trifon Trifonov2, Josep Pallares2, Angel Rodriguez2, Ramon Alcubilla2 and Francisco Meseguer1; 1Centro Tecnologico de Ondas-UA CSIC/IFIC, Universitat Politècnica de València/CSIC, Valencia, Spain; 2Dept. Electronic Engineering, Universitat Rovira i Virgili, Tarragona, Spain; 3Dept. Electronic Engineering, Universitat Politécnica de Catalunya, Barcelona, Spain.


Ra5.37/Rb5.37
Self Assembly Studies of Ring Opening Metathesis Polymerization (ROMP) derived well defined Amphiphilic Block Copolymers. Kyle Stanforth1, Alcubilla4, Daniel Wuest1, Christian Moita1, Gerhard Fritz1 and Gregor Trimnell1; 1Institut for Chemistry and Technology of Organic Materials, Graz University of Technology, Graz, Austria; 2Institute of Chemistry, Karl Franzens University, Graz, Austria.

The design of highly ordered and nanostructured materials is one of the most challenging tasks in modern chemistry. In this context the self-organizational behavior of well defined amphiphilic block-copolymers (BCPs) has gained attention for the synthesis of highly functional and hierarchical polymeric materials. Combining different polarities and functionalities into BCPs requires versatile polymerisation methods with an high group tolerance. This can be realized by ROMP with either Grubbs type initiator of the first generation or the recently introduced third generation initiator. The latter in particular has enhanced reactivity and a higher group tolerance than most other initiators. Amphiphilic block copolymers of different conformations and lengths were synthesized. As hydrophilic blocks we used norbornene-dicarbocyclic-acid-dimethyl ester and dibutyl ester; as the hydrophobic moiety we investigated norbornene carboxylic acid and alcohol derivatives. For example to guarantee a reproducible synthesis and characterisation the carboxylic acid functionalities were protected as tert-butyloxycarbonyl (TBOC). After full characterization of the polymers by NMR, IR, GPC and DSC trifluoro acetic acid was used to remove the protecting group. The phase separation of the block copolymers was examined with small angle X-ray scattering (SAXS). The miscible formation in solution was explored by dynamic light scattering (DLS). Compared to commodity
material block copolymers the self assembly of the ROMP block copolymers is also influenced by the stereochemistry of the nonbromomethylene units, as well as the catalyst governed cis/trans ratio of the double bonds in the polymer backbone. The self assembly of these polymers is of high interest for example for organic/inorganic hybrid materials.

R4a.38/R5b.38
Self-stabilized etching of complex 3D silicon networks with complete photonic bandgap. Sein Matthias, Frank Mueller, Reinhard Hillebreid and Ulrich Goesele; Max Planck Institute of Microstructure Physics, Halle, Germany.

Three-dimensional structures for photonic crystal applications have been fabricated in silicon and in polystyrene either by microanisotropic etching or by photolithography. In this case, we demonstrate the fabrication of three-dimensional silicon networks by a self-stabilized electrochemical etching technique on lithographically patterned single crystalline substrates [1,2]. Using a square two-dimensional lattice and a modulated current-voltage-profile, a columnar porous structure with strong diameter modulations is obtained. Subsequent homogenous and isotropic (i) or even anisotropic (ii) etching converts the columnar structure to a cubic geometry of high porosity and an air filling fraction of 80%. In the case of an isotropic etching the porous material is build up of intersecting air spheres in silicon [3].

The optical characteristics among various high symmetry directions of the crystal confirm the achieved periodicity and shape and suggest this material for photonic crystal applications. According to theory this arrangement of air spheres in silicon opens a complete three-dimensional photonic bandgap of about 4.3% centered at 3 μm. Moreover, the subsequent anisotropic etching of the initial porous structure, which exploits the crystallographic nature of the substrate used, converts the former circular cross-section of the pores into an almost square cross-section. We theoretically study the dispersion behavior of PCs being fabricated by this developed technique. In addition, we present experimentally realized structures and characterize the photonic crystal optically. The reflectance measurements are in good agreement with corresponding bandstructure calculations. This process allows the introduction of defect layers laterally during the etching process as well as vertically by lithography - achieving a three-dimensional nanofocusing control. Moreover, the introduced process extends the possibility of designing and sculpturing three-dimensional microstructures to meet the requirements of a multitude of micro- and nano-technological applications [5].

R5a.39/R6b.39
Determination of Nanotube Density by Gradient Sedimentation. S. Fayazi Keshtvash, Reza Kianmehr, Rahul Rao, Lyndou L. Larcom and Apparao Rao; Physics and Astronomy, Clemson University, Clemson, South Carolina.

Density gradient centrifugation is a high resolution technique for the separation and characterization of large molecules and stable complexes. Densities can be resolved to better that 0.001 g/cm³. We have analyzed various carbon nanotube (CNT) structures by preparative centrifugation in sodium metatungstate-water solutions. Bundled single-wall nanotubes (SWNTs), isolated single-walled nanotubes, acid solubilized single-wall nanotubes, AND multi-wall nanotubes formed sharp bands at well defined densities. The structure of the material in each band was confirmed by transmission electron microscopy. The experimental densities obtained will be presented compared with the corresponding calculated densities.

R4a.40/R5b.40

Fibre-reinforced polymer composites are gaining more and more importance in lightweight constructions, especially in the aerospace industry. Increasing the mechanical performance, e.g. strength, toughness and fatigue properties, of composites is the objective of many ongoing research projects. The general weaknesses of polymer composites are the limited matrix dominated properties such as interlaminar strength and creep behaviour. Nanoparticles, e.g. carbon nanotubes (CNTs) and fumed silica, provide a high potential for the reinforcement of polymers. Their size in the nanometre regime makes them suitable candidates for the reinforcement of fibre reinforced polymers, as they may penetrate the reinforcing fibre-network without disturbing the fibre-arrangement. The reinforcing effect of nanoparticles has been extensively studied in recent years. Mechanical properties of polymers were found to be significantly enhanced at relatively low filler contents. The fracture toughness of epoxy resins, for example, could be increased by 50% with the addition of only 0.5 wt.% of fumed silica particles.

In this work, glass fibre-reinforced epoxy composites with nanoparticle modified matrix systems were produced and investigated. Different types of particles, such as carbon black, CNTs and fumed silica, were dispersed in the matrix, using a high shear mixing process. GFPRFs containing different volume fractions of the nanofillers were produced via resin transfer moulding. Matrix dominated mechanical properties of the GFRP laminates could be improved by the incorporation of nanoparticles. The addition of only 0.3 wt.% CNTs to the epoxy matrix, for example, increased the interlaminar shear strength from 31.8 to 37.8 MPa (+19%). Furthermore, the application of electrically conductive nanoparticles enables the production of conductive nanocomposites. This offers a high potential for antistatic applications and the implementation of functional properties in the composite structures. Stress-/strain sensing, as well as damage detection capabilities are of special interest for aircraft applications. The effect of different filler types and volume fractions on the electrical properties of the GFRPs were investigated. GFRPs containing 0.3 wt.% of CNTs, for example, exhibit an anisotropic electrical conductivity. The in-plane conductivity of the laminates was observed to be one order of magnitude higher than out-of-plane. Furthermore, an electrical field was applied to the composites during curing. The effects on the resulting electrical and mechanical properties are discussed.

R5a.41/R6b.41
Layer-by-Layer Deposition of Carbon Nanotubes. Marco Palumbo1, Kye Ung Lee2, Anil Suri2, Karl Coleman2, Daguo Zeng1, David Wood1, Byich J. Ahn1 and Michael Petty1; School of Engineering and Centre for Molecular Engineering and Microsystems, University of Durham, Durham, United Kingdom; 2Chemistry, University of Durham, Durham, United Kingdom; 3Materials Science and Engineering, Photonic and Electronic Materials Laboratory, Korea Advanced Institute of Science and Technology, Daejeon, South Korea.

In this paper, we shall describe an improved method for making thin film architectures incorporating carbon nanotubes (CNTs) and present some data on the electrical properties of the layers. Single and multiwall nanotubes with an anionic or cationic coating have been prepared by exploiting the ability of certain surfactants to form a monolayer shell around the CNTs. This treatment promotes the dispersion of the nanotubes bundles, increasing their solubility. The presence of electrically charged functional groups on the surface of the CNTs then allows thin film deposition to proceed via the electrostatic layer-by-layer (LbL) method. The self-assembly process was monitored using both the quartz microbalance technique and Raman spectroscopy, while the morphology of the resulting thin layers was studied using atomic force microscopy. A variety of different CNT architectures has been built up. In one arrangement, a single species of a modified CNT (anionic or cationic) was assembled with a passive polymer to form a composite superlattice structure, while in another, a multilayer film composed of alternating anionic and cationic modified CNTs was fabricated. The in-plane and out-of-plane dc conductivities of the thin film films were measured at room temperature and contrasted with reference architectures (i.e. those containing no CNTs). All the tests showed clearly that the incorporation of CNTs into the multilayer assemblies resulted in electrically conductive thin films. A high anisotropy of the conductivity was noted; with the films being at least six orders of magnitude more conductive along the length of the carbon nanotubes (in-plane tests) than across them (out-of-plane experiments). At high electric fields, a super-ohmic current versus voltage dependence was observed; the value of the current was approximately proportional to the square of the applied voltage. For the in-plane tests, the dc conductivity was also measured as a function of the distance between the electrodes and, in particular, with an electrode separation equal to the length of the nanotubes. The details of the electrical behaviour will be presented. Furthermore, some initial attempts to integrate the multilayer architectures into more complex systems, such as chemical sensors and photovoltaic structures, will be discussed.

R5a.42/R6b.42

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The goal of these experiments is the self-assembly of novel, 3-dimensional carbon crystal structures. The specific binding of complementary DNA strands is used to create short-range attractive interactions between DNA-grafted micrometer-sized colloids. These colloidal interactions will create multi-component colloidal mixtures where the interparticle interactions are individually "programmed". In theory, this technique should be able to produce well-ordered BCC, SC and diamond structures, as well as their alloy counterparts, the CaAl, NaAl and ZnS structures, all at densities near close-particle order. Our low density approach allowed us to successfully assemble the first colloidal crystal structures using them. The crystal structures showed a faceted shape that resembles the RHCP stacked colloidal crystals. The crystals melted immediately when the temperature was raised above (Tm), confirming that they were formed and held together by DNA hybridization. We also find that the particle crystallization kinetics became faster as the grafted DNA density was increased. In addition, we have developed the simple thermodynamic model that predicts the phase behavior (Tm) of the system to within a few degrees. Finally, we also investigate the binary alloy and bulk systems formed using DNA-mediated self-assembly.

R05.43/R05.48
Carbon Nanospheres with High-Activity Surfaces by Template-Free Liquid Crystal Assembly, Ailun Yan, Indrek Kuulaots and Robert Hirt; Division of Engineering, Brown University, Providence, Rhode Island.

The surfaces of most carbon nanomaterials are rich in graphene basal planes and have a corresponding low chemical reactivity and low polarity. This creates challenges for covalent grafting, interfacial bonding in composites, and dispersion in biological fluids or other aqueous media. Here we synthesize a new form of carbon nanoparticle with inverted crystalline structure that places high concentrations of graphene edge planes on the outer surfaces. A continuous ultrasonic spray pyrolysis process is to fabricate carbon nanoparticles from a water-soluble hytropic liquid crystalline precursor, indanthrene disulfonate. This disk-like polyaromatic compound assembles in solution into rod-like aggregates, which in turn assembly parallel to the outer surfaces of the droplets driven by configurational entropy at the interface. This assembly mode leaves exposed polyaromatic edges upon drying that are converted to expanded graphene layers upon carbonization. This paper reports on the fabrication, crystal structure, annealing behavior and surface activities of this unique carbon nanomaterial using SEM, HRTEM, XR, TGA, contact angle measurement and N2 vapor absorption. The spray pyrolysis process allows careful control over particle size, which to date has been systematically varied from 2 μm to 80 nm. As expected, high resolution TEM shows the presence of graphene layers assembled perpendicular to the surface. When using PE nanocubes, this high-energy surface reconstructs upon annealing above 2500 °C to form "closed" pyramidal surface domains seen in both PE-SEM and TEM. Work is underway to measure their surface properties relative to carbon black as conventional carbon nanomaterials with graphene basal-rich surfaces. Results to date show the liquid crystal derived nanospheres to have a higher reactivity toward molecular oxygen, higher hydrophilicity (lower contact angle with water), and better dispersion and stability in aqueous media. We anticipate a variety of applications for these unique carbon nanospheres, in which the active surfaces provide a flexible platform for chemical functionalization, and the bulk composition can be flexibly controlled by selecting the precursor solution, e.g. to include a magnetic material component.

Ra5.44/Rb5.44
Broadband Antireflective Coating Based on Bilayer Nanoporous Organosilicate Thin Films, Suhun Kim1, Jinhan Cho2 and Kookheon Char1; 1School of Chemical and Biological Engineering & NANO Systems Institute - National Core Research Center (NCRC), Seoul National University, Seoul, South Korea; 2LG Chemical Research Park, Daejeon, South Korea.

Nanoporous materials have recently attracted much interest owing to its potential as organic low dielectric sensors, waveguides and antireflection coatings. In present study, nanoporous organosilicate thin films were realized by the microphase separation of a core-generating component mixed with an organosilicate soluble tetrafunctional hydroxycopolymer, Tetronic (BASF), was used to generate nanogroes and polyethyleneoxide (PMOSS) copolymer was chosen for the matrix material. The refractive index of such nanoporous organosilicate films can be varied in the range of 1.40 - 1.22. Optical properties of prepared nanoporous organosilicate films were also tested toward the application to antireflection coating. With a nanoporous single layer with high RI in the visible range are investigated. In order to overcome the limitation on the narrow wavelength for high transmission imposed by single nanoporous thin films, bilayer thin films with different reflectance in each layer were prepared. For the facile fabrication of nanoporous bilayer films, the addition of photoacid generator (PAG) to the organosilicate thin film is followed by UV treatment. The PAG generates acid upon UV exposure and facilitates the vitrification of the organosilicate matrix. As a result, 80% of Si-OH groups was found to condense only after 10 minutes of curing at 150 °C. After the UV pretreatment followed by low temperature cure, a second layer with higher porogen loading was deposited on top of the first layer by spin-coating. The bilayer films were finally cured at 420 °C for 1 hour to realize nanoporous structures in both layers. By changing the porogen loading in each layer, nanoporous bilayers with different combinations of refractive indices were successfully fabricated and electron density profile and porosity in each layer were also quantitatively characterized by x-ray reflectivity experiments. Optical properties of nanoporous bilayer films thus prepared were compared with nanoporous single layer films and it is demonstrated that the novel broadband antireflection coating with improved transmittance can be easily achieved by the nanoporous bilayer thin films described in this study.

R05.45/Rb5.45
Radiopaque flame-made Ta2O5/SiO2 nanoparticles with controlled refractive index and transparency, Heiko Schulz1, Lutz Madler1, Sotiris E. Pratsinis1, Peter Burtscher2 and Norbert Mozner2; 1Department for Mechanical and Process Engineering, ETH Zurich, Zurich, Switzerland; 2Ivoclar Vivadent AG, Schaan, Liechtenstein.

Dental fillings made of composite organic monomers and ceramic fillers (silica particles) are used for both shaded dental restorations and anterior lesions and small - medium sized defects in the posterior region. This is a result of the excellent esthetic properties of these fillings as well as health concerns with amalgam fillings regarding mercury release. Therefore, the elaboration of filler properties to composite characteristics such as radiopacity, tensile strength, hardness, shrinkage, wear and transparency have been intensively studied in the last few years. Mixed Ta2O5-containing SiO2 powders with a high specific surface area, controlled refractive index and transparency and crystallinity were prepared by flame spray pyrolysis as fillers for dental composites. The production rate ranged from 6.7 - 100 g/h in a lab scale reactor. The effect of the Ta precursor, the solvent, the total metal concentration and the Ta-content were studied by nitrogen adsorption, x-ray diffraction, light microscopy, HRTSEM, DIFTS analysis, as well as the composite transparency within a polymer matrix of dimethylacrylate for dental restoration applications. Filler properties such as transparency, crystallinity and Ta-dispersion in the SiO2 matrix altered the composite performance. Ta2O5 crystals and a low Ta-dispersion within the SiO2 matrix decreased the filler and composite transparency. Powders with identical specific surface index and Ta-loading (24 wt.%) showed a wide range of composite transparencies from 33 - 78 % depending on filler properties. Fillers with an amorphous structure, a high Ta-dispersion and a matching refractive index with the polymer matrix showed 86 % transparency for a 16.5 wt.% filler loading including 35 wt.% Ta2O5 giving an optimal radiopacity.

R05.46/Rb5.46

Self-assembled monolayers (SAMs) are widely used to activate surfaces for a broad range of biological and electrochemical applications. However, the use of SAMs to tailor the transport and surface properties within porous materials is still relatively unexplored. We have studied the effect of SAM structure on the ionic transport in hydrophobized nanoporous ceramic membranes. The membranes were prepared by functionalizing the internal surfaces using alkylsilane SAMs with different alkyl chain lengths. The transport through the membranes was characterized using impedance spectroscopy.

R05.47/Rb5.47
Synthesis of P3Tc Nanoboxes Using a Solvothermal Technique. Wenzhong Wang, Bed Poudel, Dezhai Wang and Zhifeng Ren; Physics, Boston College, Chestnut Hill, Massachusetts.

P3Tc nanoboxes have been synthesized in high-yield via a solvothermal route for the first time. The effects of experimental conditions, such as capping agent (PEG) concentration and the
volume ratio of ethanol to water, on the formation of nanoboxes have been studied in detail. The experimental results showed that the surfactant-free PVA volume ratio of ethanol to water played key roles to the formation of nanoboxes. The as-prepared nanoboxes were characterized by an X-ray diffractometer (XRD, Cu Kβ, Bruker AXS), a field emission scanning electron microscope (SEM, JOEL, JSM-6340F), and a transmission electron microscope (JOEL-2010F) equipped with an energy-dispersive X-ray spectrometer (EDS). SEM images clearly demonstrate that the majority of the nanocryals have a regular cubic shape. TEM investigations indicate that the as-prepared nanocryals show regular cubic shape with edge length of about 80-180 nm, and a strong contrast difference with dark edge and bright center, indicating hollow interior. The SAED and HRTEM studies indicate that the as-prepared PbTe nanoboxes within our present method are highly crystalline. The results of our experimental results, a possible formation mechanism of the nanoboxes has been proposed. The following figures show the TEM images of two typical PbTe nanoboxes.

R5a.48/R5b.48
Integrated Conducting Polymer Nanowire Devices for Biological Sensing Applications. Adelaja Arojutun1, Shaun Filocamo2, Catherine M. Klapperich2,3, Selim Unlu2,4, and Mark W. Grinstaff5,6,1. 1Department of Biomedical Engineering, Boston University, Boston, Massachusetts; 2Department of Manufacturing Engineering, Boston University, Boston, Massachusetts; 3Department of Chemistry, Boston University, Boston, Massachusetts; 4Department of Electrical and Computer Engineering, Boston University, Boston, Massachusetts.

An integrated conducting polymer nanowire device is being fabricated and will enable us to investigate the conducting properties of polymer nanowires and the mechanisms for conducting polymer formation using AFM electrochemical dip pen nanolithography (e-DPN) process. Conducting polymers conjugated with biological ligands have the potential to detect specific biological binding events. Biomolecules or ligands can be incorporated into the conducting polymer in a single step during electrochemical polymerization using an e-DPN technique. Optimization of the fabrication process will allow for more precise measurements and provide a foundation for future integration of nano and micro scale technologies involving conducting polymers.

R5a.49/R5b.49
Directed Patternning of Monolayer-Protected Inorganic Nanoparticles onto Surface Monolayer Templates. Kenuke Nakatani, Shojo Samitsu, Takaaki Tsuruoka, Jun Hasegawa and Hidemi Nawafune; Konan University, Kobe, Japan.

Thin films of the organic/inorganic hybrid nanocomposites that are composed of metal and/or semiconductor nanoparticles embedded in dielectric matrix are the subject of recent intensive research for fabrication of next generation nanodevices. Although recent researches have made promising advances that provide methods for site-selectively depositing or growing the nanoparticles on the substrates of interest, the development of a facile process for fabrication of nanocomposite thin film patterns still remains a great challenge. In this study, we present a simple approach and unique procedure for fabricating patterns of nanogrannar films composed of biological ligands and the potential to detect specific biological binding events. Biomolecules or ligands can be incorporated into the conducting polymer in a single step during electrochemical polymerization using an e-DPN technique. Optimization of the fabrication process will allow for more precise measurements and provide a foundation for future integration of nano and micro scale technologies involving conducting polymers.

R5a.50/R5b.50

A nano-structured beta-gallia-rutile (βR) substrate capable of binding DNA was synthesized. Beta-gallia groups diffuse into [001] single crystal rutile along [210], planes. This process generates hexagonally shaped tunnel sites between the beta-gallia subunits (repeating ~1 nm). The tunnel sites, approximately 2.5 Å in diameter, are preferred adsorption sites for DNA/2 and allowed 2 to bind to DNA surfaces. For the βR system, the site selectivity of the cations for tunnel sites could lead to a controllable / tailor-able DNA adsorption. A variety of cations and polynuclear complexes were applied to βR surfaces and exposed to βR substrates. The DNA adsorption was investigated with tapping mode atomic force microscopy to determine the suitability of using βR substrates as a means to self assemble DNA constructs for nano-electronic applications.

R5a.51/R5b.51
Atomically-Controlled Assembly of Nanoscale Devices With Subnanometer Precision Using Bioengineered Polypeptides. Seichiro Higashiyama1, Natalya I. Topilina1, Vladimir V. Ermolinkov1, Ludmila A. Popova1, Christopher C. Wells1, Narendar Rana2, Autumn Carlsen2, Christopher Kossow2, Eric T. Eisenbraun2, Alain E. Kaloyeros2, Robert E. Geer2, Igor K. Lechn2 and John T. Welch1, 1Department of Chemistry, University at Albany, Albany, New York; 2College of Nanoscale Science and Engineering, University at Albany, Albany, New York.

Control of the self-assembly of well-defined polymers with precisely designed intra- and intermolecular recognition is challenging, yet essential to the successful atomic scale integration of nanoscale devices with subnanometer precision. The present investigators have focused on the synthesis and characterization of peptide macrocycles that self-assemble into well-defined arrays. The results of this work have demonstrated a new paradigm for nano-manufacturing where discrete peptide building blocks and templates for assembly of functional devices. Accordingly, we have already reported the successful preparation of β-sheet forming Gly-Ala repeats with amphiphilic pendant residues X1 and X2, to do ([GA]3-GA)2X1X2 with more than 1000 amino acid residues (corresponding to 60 nanometers). The polypeptides showed highly ordered structure on graphite and well-characterized fibrils in solution depending on the sequences, preparation, and post modification. The effects of changing the length of GA repeats, turn moieties, physico-chemical conditions, such as pH, and ion strength, templated assembly, and selective modification will be discussed.

R5a.52/R5b.52
Nanofabrication of Ordered Interface of Organic Thin Films and Electrodes through Chemical Bond Formation toward High-Performance Photovoltaic Functional Devices. Norikazu Ikeda, Nobutoshi Mitomo, Hiroshi Higuchi and Chyougin Pae; Department of Chemistry, Toho University, Funabashi, Japan.

Nanofabricated organic thin films with ordered orientation have been drawn much attention from the viewpoint of the electronic and biological devices. Molecular-based nanomaterials have great potential to fabricate novel assembly with intriguing optical/electronic properties. Supramolecular arrays and related thin films comprised of redox-active molecules in these films have recently become of increasing interest. We have been developing a simple bottom-up method enables us to control density of redox-active molecules at the surfac. The fabrication chemically and mechanically controllable and self-assembling nanofilms on solid substrates is a fundamental subject in applications of dyes to devices. We have developed an effective way for the fabrication of chemically linked dye-inorganic hybrid multilayers using transition metal ruthenium(II) complexes and metallophyrins (MPC) as the dye molecules, because of their excellent photofunctional properties and high chemical stability. The fabrication of organic thin films involving gold nanoparticles coordinated by π-organic materials such as fullerenes C60, 107-glyophosphate, and porphyrin has also been developed and investigation on photofunctional behavior of these films is now in progress. Nanofabrication through chemical bond formation should be an important concept to achieve facile electron-transfer reactions in thin-film redox systems.

R5a.53/R5b.53
Force Spectroscopic Investigation of Electro-Oxidative Nanolithography. Jann Wanten1,2, Jerriana H. K. van Schaik1, Stephanie Hoepoepper1,2 and Ulrich S. Schubert1,2; 1Laboratory of Macromolecular Chemistry and Nanoscience, Eindhoven University of Technology, Eindhoven, Netherlands; 2Dutch Polymer Institute (DPI), Eindhoven, Netherlands.

To make full use of novel material properties observed in nanodimensional materials it is essential to develop tools for a guided assembly of individual nano-objects on a surface. Surface patterned approaches play here an important role and are applied to DNA buffer. We utilize an electro-oxidative lithography approach that allows the local functionalization of a robust, chemically inert self-assembled n-octadecl trichlorosilane (OTS) monolayer on silicon. This oxidation process is mediated by negative bias voltages which can be only applied to the surface via e.g. a conductive Scanning Force Microscope. 

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SESSION Ra6: Nanoscience for Biology and Medicine I
Chair: Mehmet Sarikaya
Tuesday Morning, November 29, 2005
Room 207 (Hynes)

8:30 AM *Ra6.1 Getting to "Mind" – The Foundation Development of a Room Temperature Biological Supercomputer. Carlo Montemagno, Bioengineering, University of California, Los Angeles, Los Angeles, California.

Recent advances in our ability to manipulate material at the scale of individual molecules created an incredible level of excitement in both the scientific community and the general population. The excitement over this new capability, commonly labeled nanotechnology, is vested in the expectation of the development of new materials that offers unprecedented functionality. Materials that autonomously adapt their shape and physical properties in response to the their surroundings, computers that instead of operating by switching the flow of electrons, manipulate information through the management of the ethereal world of quantum states and, molecular sized machines that actually repair damage to our bodies and function as molecular scale prosthetics are all expectations of nanotechnology. While the question of whether or not this vision is truly achievable is still open, the truth is that much of the expectations for nanotechnology are already realized in living systems. Living systems however are more than a product of matter manipulation at the molecular scale; the richness of functionality associated with living systems is a direct product of the information generated from both the interactions between molecules and the overall supra-molecular structure of the system. In essence living systems are “living” because of the fusion of nanotechnology and informatics. Living systems result from the precision assembly of matter with prescribed modalities for the transport and transduction of information among supra-molecular clusters. The concept of Integrative Technology, the intersection of the precision assembly of matter, nanotechnology, coupled with the functional building blocks of nature, biotechnology, and fused by the network flow of spatiotemporal information, informatics, is presented. The power of Integrative Technology is manifested through the engineering of synthetic biometric devices. The ultimate example of which would be the fabrication of a synthetic biological processor. The design, modeling and experimental results associated with the fabrication and engineering of Excitable Vesicles, a nano-sized building block with the ability to introduce process information will be discussed. Excitable vesicles have the potential of controlling and manipulation of information that would ultimately lead to the manifestations of emergent higher-order behavior. These systems are designed, engineered and produced from nanoscale components to construct complex systems and materials that self-organize on multiple length scales to manifest complex emergent functional behaviors.

9:00 AM *Ra6.2 Poly(propyleneoxide)-Poly(amidoamine) Based Linear Dendritic Block Copolymers for Drug Delivery. Phuong M. Nguyen and Paula T. Hammond; Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

A novel series of linear-dendritic block copolymers with amphiphilic characteristics have been developed that have the capability of self-assembling in solution and creating an interior hydrophobic core for drug encapsulation. Poly(propyleneoxide)-poly(amidoamine) (PAMAM-PPO-PAMAM) has been synthesized from generations 1 through 6, and the solution state behavior of this series of polymers have been characterized. The critical micelle concentration (CMC) of this set of polymers has been determined with tensiometry and pyrene as a hydrophobic fluorescent probe. With increasing PAMAM generations, the CMC increases from 1-6 M to 1-5 M. The formation of micelles has been confirmed through dynamic light scattering and TEM. A model hydrophobic drug, 1,4-benzzened, has been utilized to ascertain the polymers’ drug encapsulating ability. The linear-dendritic amphiphilic block copolymer micelles show promise as drug encapsulating nanoparticles with high loading capacity and the ability for specificity with the conjugation of targeting ligands to the multivalent dendrimer outer shell.

9:15 AM Ra6.3 Building and Characterizing Nano-complexes of Liposome Encapsulated Nanocrystals, Ilan Mandelbaum1, Cheryl H. S. Lau1, Kunio Nagashima2, Jeeoseong Hwang3 and Angela R. Hight Walker1; 1Physics Laboratory/Laser Application Group, National Institute of Standards and Technology, Gaithersburg, Maryland; 2Image Analysis Laboratory, National Cancer Institute-Frederick, Frederick, Maryland.

Novel approaches involving manufacturing of nanoscale complexes combining biotic and abiotic materials have been of increasing interest for a variety of biochemical and biomedical applications including single cell diagnostics, drug targeting and delivery, and tumor imaging and diagnostics. We will present our efforts on manufacturing nanoscale complexes of liposomes encapsulating fluorescent semiconductor nanocrystals (NCs) potentially useful for a wide range of biomedical applications. This technique will be of immediate use towards targeting, labeling, and analyzing biological cells. Upon being triggered, the liposomes fuse to the plasma membrane of a targeted cell and release their contents, in this case NCs, inside the targeted cell. Accordingly, the targeted cell can be analyzed with a wider range of fluorescence measurement techniques. Optical properties of the NCs are superior to conventional organic dyes: the NCs show higher fluorescence quantum yield, narrower emission spectra, better photo-stability against photo-bleaching, and relatively longer fluorescence lifetime. These advantages provide more sensitive and quantitative measurement in medical diagnostic and cellular imaging.

In this presentation, we will present techniques to encapsulate NCs with different surface functional coatings within approximately 100nm unilamellar liposomes prepared by a variety of methods such as injection, extrusion, and electro-formation. Fluorescent lipid analogs were used to label liposomes to verify the encapsulation by assessing fluorescence resonance energy transfer between the donors (NCs) and the acceptors (lipid analogs) in total internal reflection fluorescence microscopy (TIRFM). The TIRFM allows us to excite only liposomes near the substrate surface therefore substantially enhances the signal to noise ratio in detection. We will also discuss the characteristics of each component, liposomes and functionalized NCs, and their complexes from results obtained by other methods including confocal fluorescence microscopy, polarization modulation optical microscopy, and electron microscopy.

9:30 AM Ra6.4 Bilateral, Diffusional Nanosphere Aggregates to Construct Biosensors and their Application to Ligand-Receptor Binding Interactions. Suzanne Barber1, Tonya Kuhl2, Timothy Patten3, Philip Costanzo2 and Nathan Moore2; 1Chemical Engineering and Materials Science, University of California, Davis, Davis, California; 2Chemistry, University of California, Davis, Davis, California.

We have developed an efficient method for producing diffusional, bilateral nanospheres/nanoparticles of various materials, including superparamagnetic and ferromagnetic materials. By variation of the particle and metal deposition onto the surfaces of nanoparticles, bilateral nanoparticles were formed. The different regions of the nanoparticles were selectively functionalized with polymer linkers containing specific terminal groups, thereby creating bilateral, diffusional nanoparticles. Subsequent covalent cross-linking of different nanoparticles enabled the formation of stable architectures with programmed hierarchy and controlled chemical composition. We propose that by modulating the length and chemical composition of the polymer linker and its binding energy to the particles, the interaction potential between particles can be specified. This ability to fine-tune the interaction energy of the system is a key aspect for creating novel hierarchical materials for specific applications, including development of a biosensor for the measurement of receptor-ligand binding interactions. We construct biosensors for the detection of ligand-receptor binding events utilizing magnetic particles. We show preliminary results indicating the specificity of such a biosensor construction and propose its use for measurement of ligand-receptor binding strength and binding affinity.

9:45 AM Ra6.5 A correlational study of photoluminescence and vibrational spectroscopy - Protein adsorption on the surface functionalized Si. Li-Lin Tay1, Nelson Rowell2, David Lockwood1 and Rabah Boukherroub2; 1National Research Council, Ottawa, Ontario, Canada; 2Interdisciplinary Research Institute, Villeneuve d’Ascq, France.

We have recently investigated the interaction of Bovine Serum Albumin protein and surface functionalized porous Si (pSi). Due to
the presence of 1D and 2D nanocrystallite in the porous Si matrix, the imposed quantum confinement effect in pSi leads to a bright visible room temperature photoluminescence (PL). Surface functionalization not only stabilizes the PL but also introduces biocompatibility and chemical functionality to the sidewalls of the pSi. This allows for the subsequent cross-linking reaction (e.g. binding of analyte and targeting molecules) to take place. An in-situ monitoring of the protein and pSi interaction revealed a red shift in pSi PL.

Although it was suspected such shift is due to protein molecules being incorporated into the Si matrix, the heterogeneous nature of the pSi matrix made any attempt to prove this conclusion challenging. To understand the origin and nature of the shift and to fully correlate such events to protein adsorption, we carried out a further investigation of protein adsorption on surface functionalized planar Si. The planar Si (100) was first degraded in acetone and then cleaned in piranha bath at an elevated temperature. The cleaned wafer was then dipped into 5% HF to remove its surface oxide and to passivate the surface with Si-H bonds. By exposing the hydrogen passivated wafer surface to UV radiation within a day in a degassed acid solution, a radical initiated hydroisolation reaction cleaves Si-H bonds and replaces them with more stable Si-C bonds. This process produced a monolayer of undecylcic acid molecules self-assembled on the Si(100) surface. A single bounce attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopic technique was developed to monitor the vibrational spectra of such monolayer films. The observed vibrational spectrum showed a clear carbonyl stretch at 1714 cm⁻¹ from the undecylcic acid on the Si (100) surfaces. Furthermore, a small band at 2100 cm⁻¹ indicated there were un-used Si-H bonds. The presence of the acid functional group on planar Si serves as a convenient capturing site for the BSA molecule. The planar Si also exhibited a weak PL signature, which was produced from carrier recombination. This PL was excited at room temperature with 457.9 nm Ar laser excitation and detected by a Ge detector. We monitored the PL evolution for the planar Si in-situ while the sample was incubated in a 0.02 mg/ml BSA solution. In this presentation, we will correlate the PL evolution to the ATR-FTIR results obtained on the Si: undecylcic acid: protein complex. We will show a correlation between the diminishing of Si-H stretch with the decrease of PL intensity. We will also confirm the observation of a red-shift in planar Si PL due to protein adsorption on the Si surfaces. This PL shift will be discussed in conjunction with the vibrational data obtained from ATR-FTIR study.

SESSION RB6: Nanowires, One-Dimensional Nanostructures II
Chair: Geoff Strowe
Tuesday Morning, November 29, 2005
Room 208 (Hynes)

8:30 AM *RB6.1 Functionalization of Nanoptes: From Field Emission, Anti-reflection to Molecular Sensing Devices. Su-rojit Chattopadhyay1, Yi-Fan Huang2, Kuo-Hsien Chen2, Hung-Chun Lo2, Chi-Ting Huang2, Shun Heu2, and Po-Yi Chou1,2 Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan; 2Department of Materials Science & Engineering, National Chiao Tung University, Hsinchu, Taiwan; 3Center for Condensed Matter Sciences, National Taiwan University, Taipei, Taiwan.

We have applied an on-chip approach for the development of the nanopto arrays as building blocks toward field emission, anti-reflection and molecular sensing devices. Nanoscale engineering and a strategy for self-assembly of metals on the nanopto arrays to enhance their functionality will be presented. Well-aligned nanopto arrays with a nanopto density as high as 10¹² cm⁻² were achieved by a single-step electron cyclotron resonance plasma process using gas mixtures of silane, methane, argon and hydrogen. Formation of SiC cap was observed on each individual nanopto, implying a self-masking etching mechanism. This technique was applied to a variety of wafers such as Si, GaN, GaP, Al, sapphire and glass, indicating its general applicability.1 The nanopto arrays so produced showed superior field emission as well as anti-reflection properties. The sharp tip geometry provides large field enhancement, therefore a low turn-on field (<10V/micrometer), while the sub-wavelength nanostructured surface exhibits an ultra low reflectivity (<0.1%) in visible and IR. Moreover, the high surface curvature of nanoptos efficiently self-assembles metal nanoparticles on their surface upon simple sputtering of the metal. This is a convenient and scalable self-assembly strategy for the formation of metal nanoparticles, and the chemistry is derelict. The silicon nanopto arrays dispersed with Ag nanoparticles showed excellent surface enhancement in Raman scattering (SERS).2,3 Enhancement up to 8 orders has been achieved, suggesting potential applications in a degenerative waveguide laser. The on-chip approach also helps accelerating the progress of nanodevice fabrication. 1 C. H. Hsu, C. F. Chen, H. C. Lo, D. Das, J. Tsai, J. S. Huang, L. C. Chen and K. H. Chen, NanoLett., 4, 471 (2004). 2 S. Chattopadhyay, H. C. Lo, C. H. Hsu, L. C. Chen and K. H. Chen, Chem. Mater. 17, 553 (2005). 3 S. Chattopadhyay, S. C. Shi, Z. H. Lan, C. F. Chen, K. H. Chen, L. C. Chen, J. Am. Chem. Soc. 127, 2820 (2005).

9:00 AM RB6.2 Synthesis, Structural and Mechanical Characterization of Boron Nanowires. Hai Ni and Xiaodong Li; Department of Mechanical Engineering, University of South Carolina, Columbia, South Carolina.

Boron nanowires with a diameter ranging from 30 nm to 100 nm were successfully synthesized with a chemical vapor transport method. By controlling growth temperature, cooling rate, and vapor sources, long and well aligned boron nanowires were obtained. XRD and HRTEM were used to study the composition and structure of the wires. Mechanical properties of the wires were measured by nanindentation and AFM bending tests. A nanomanipulator was used to perform tests directly on the wires. The boron nanowires exhibit a high elastic modulus. The chemical vapor transport method used in this study can produce boron nanowires at a high volume production rate. Finally, the growth mechanisms of boron nanowires are discussed and compared in conjunction with possible reactions, temperature ranges, and structural characteristics.

9:15 AM RB6.3 Self-assembled InAs nanowire networks. Kimberly Dick1, Mikael T. Bjork1, Knut Deppert1, Lisa S. Karlsson2, Magnus W. Larsson2, Jan-Olle Malm2, Thomas Martensson1, Werner Seifert1, L. Reine Wallenberg2 and Lars Samuelson1; 1Solid State Physics, Lund University, Lund, Sweden; 2Materials Chemistry, Lund University, Lund, Sweden.

Research in semiconductor nanostructures has indicated great promise for applications of these structures in the electronics, materials science and life science fields. The step from production of building blocks, such as nanoparticles and nanowires, to more complex nanostructured systems is key to the realization of this potential. We demonstrate here a method for production of complex self-assembled three-dimensional networks of III-V semiconductor nanowires on a substrate. The nanostructures are formed by sequential seeding of hierarchical levels of nanowires by Au nanoparticles. These particles operate as collectors of vapor-phase source material, which then grows epitaxially on the material underneath the particles. The internal level of nanoparticles is produced by electron beam lithography of a pattern of dots followed by evaporation/lift-off of Au. Nanowires are subsequently grown by low pressure metalorganic vapor phase epitaxy (LP-MOVPE), using metalorganic Group-III precursors and hydride Group-V precursors. All nanowires grow normal to the substrate, as determined by the substrate crystal orientation and experimental parameters. The pattern of dots produced is specifically designed to orient further generations of nanowires to form a network pattern. To produce the first and subsequent levels of branching, Au-In alloy nanoparticles produced by an evaporation/condensation method are deposited onto the nanowire array. Size and density of these particles are selected by positioning on the first-generation wires can be influenced by surface masking during deposition. Nanowire growth directions outwards from the first level of vertically-growing wires are then determined by the selected material system and growth conditions. Thus, by correct alignment, nanowire branches will grow towards the neighbouring branched structure so that they become connected, and a self-assembled network of interconnected structures is formed. If functional elements are incorporated at appropriate places in this network, designed conditions for inter-node signalling can be created. The use of nanoimprint lithography to define the initial array of Au nanoparticles allows for the possibility of large-scale nanowire circuits. We will report the production of complex InP nanowire substrates on InP substrates, and electrically isolate the substrate from the substrate. Evaluations of the electrical, morphological, and microstructural properties will be discussed.

9:30 AM RB6.4 DC plasma CVD Synthesis of ZnS nanowires with heterocrystalline and bicrystal structures. Jiannsheng Jie, Yang Jiang, Wenjun Zhang and Shoutong Lee; Department of Physics and Materials Science, City University of Hong Kong, Hong Kong, Hong Kong.

Nanostructured materials have attracted considerable attention because they are potential building blocks for nanoscale electronics and optoelectronics. The novel physical and chemical properties of nano-materials, which mainly originate from the nanometer size, are extensively researched in the past decade. On the other hand, the ability of flexibly control of many the crystalline structures and components of the one-dimensional semiconductor nanostructures is especially critical for both exploring the new physical and chemical properties of the nanomaterials and the applications of the nanomaterials in practice.
As one of the most fascinating properties in compound semiconductors, polytypism is the common feature of some binary semiconductors such as SiC, SiSn, Wurtzite (WZ) and zinc blend (ZB) represent the most ordinary polytypes, having a layer stacking of ABAB along the [0001] direction and of ABCABC along the [111] direction, respectively. Despite the structure similarities between WZ and ZB, their electronic structures can be very different and thus a new type of heterocrystalline superlattice which combines the WZ and ZB polytype is proposed. In contrast to conventional superlattices which consist of two chemically inequivalent materials, both the heterocrystal and bicrystal superlattices can be expected to be free of stress and dangling bonds, because the interface between two crystal structures or two crystal orientations is almost perfectly lattice matched. Hence the heterostructure of WZ and ZB and the bicrystal structure have a great potential in bandgap engineering. Herein we report on the synthesis of ZnSn nanowires with ZB/WZ heterocrystalline and bicrystal structures by DC-plasma CVD. The nanowires are typically tens of micrometers in length, and 20-80 nm in diameter. The heterocrystalline and ZnSn nanowires have phase zones and WZ phase zones alternately align on the transverse (or longitudinal) direction of the nanowires. In particular, the (1-11) planes and [21-1] direction of ZB phase zone parallel to (00-1) planes and [1-20] direction of WZ zone, respectively. As for the bicrystal ZnSn nanowires, they usually compose of two ZnSn fragments with ZB structure, which have common growth direction of [0-11] but different zone axis of [-111] and [0-1], respectively. The bombardment of Ar2+ ions involved in the DC-plasma process is believed playing an important role in the fabrication of ZnSn nanowires with these unique structures. Furthermore, the plasma assisted growth method is hopeful used for the synthesis of other II-VI semiconductor nanowires with heterocrystal or bicrystal structures.

9:45 AM Ra7.6

Novel Boron Nitride Nanotube-Polymer Composites. Chunyi Zhi1, Yoshio Bando1, Chengchun Tang1, Kuwahara Hiroaki2, Susumu Honda2, Kazuhiko Sato2 and Dmitri Golberg1.

1Nanomaterials Laboratory, National Institute for Materials Science, Tsukuba, Ibaraki, Japan; 2Innovation Research Institute, Toejin Ltd., Iwakuni, Yamaguchi, Japan.

 Compared with carbon nanotubes (CNTs), boron nitride nanotubes (BNNTs) possess notably better chemical stability and resistance to oxidation and exhibit nearly similar mechanical and electrical properties and thermal conductivity. In addition, BNNTs are transparent to visible light. Many of these advantageous properties can be exploited through the incorporation of BNNTs into some functional matrix materials. However, the studies on BNNT containing composites have been hindered because of significant difficulties in getting highly pure BNNTs at high yield. For CNTs, the composites based on various matrixes have been prepared and drastic improvement of matrix mechanical properties has been achieved. The specific optical and thermal properties of CNT containing composites have also been investigated. We report here with on highly pure BNNTs synthesized at high yield via a carbon-free chemical vapor deposition method. For the first time, BNNTs were perfectly dispersed in various solvents by wrapping them with a polymer. Then, BNNT-polymer composites were produced from BNNT solutions for detailed microscopic, optical and mechanical analyses. Tensile tests indicated that the elastic modulus of the new composites increased more than 20% by using 1wt.% BNNT fraction, that is compatible with CNT composites. Most importantly, opposed to conventional CNT-polymer composites, the novel BNNT-polymer films displayed excellent transparency. Detailed analysis of the BNNT composite thermal and other properties is underway and will be the subject of presentation.

SESSION Ra7: Nanostructures for Biology and Medicine II

Chair: Joahn von Barth, Tuesday Morning, November 29, 2005
Room 207 (Hynes)

10:30 AM *Ra7.1
Optically Probing Bio-Structures via Nano Surface Energy Transfer. Geoffrey Strouse and Travis Jennings; Department of Chemistry and Biochemistry, Florida State University, Tallahassee, Florida.

Ribonucleic acid structures (RNA, DNA, etc) are known to change conformation to initiate disease states or to trigger biological activity. Such structural changes, which include folding, cutting or twisting, can form the basis of molecular beacons for disease state detection or bio-beacon detection. Many of the techniques used to probe structure rely on either classical methods or use of NMR and crystallography. While optical techniques such as Förster Resonance Energy Transfer (FRET) offer viable alternatives, the interactions are limited to short range encounters typically < 10 nm. Nano-surface energy transfer (NSET) is an alternative technique that allows distances of the order of 21 nm to be readily sampled and more importantly incorporated into molecular beacons. Using NSET, we showed experimentally that rapid detection of ribozyme kinetics and activity is possible by monitoring energy transfer to small gold particles. NSET allows for real-time monitoring of nucleic acid folding and cleavage events, while maintaining bio-compatibility and without altering DNA or ribozymal (RNA) activity. A major advantage of NSET is that the energy transfer process is not specific, allowing span of a wide variety of organic dyes covering energies from the visible to the IR. This technique is effective for, but not limited to ribonucleic acid structures but can provide dynamics and kinetics information.

11:00 AM Ra7.2

1Optical Technology Division, Physics Laboratory, NIST, Gaithersburg, Maryland; 2Section of Developmental Genetics, National Cancer Institute, NIH, Bethesda, Maryland; 3Image Analysis Laboratory, National Cancer Institute, NIH, Frederick, Maryland; 4Section of Biochemical Genetics, National Institute of Mental Health, NIH, Bethesda, Maryland.

Since phage(pl.) were first discovered and isolated about 100 years ago, phage have been the main model systems in molecular biology for many decades, providing rigorous paradigms for many areas of biology. The phage are also of practical (industrial and economic) importance directly affecting the quality of human life. As the scope of applications involving phage display and detection widens, scientists began to realize phage can be an ideal self-replicating and robust tools such as nano-probe and nano-delivery vehicle for a variety of applications for nanobiotechnology. Among other interests, high-sensitivity single cell detection and analysis of pathogenic bacteria has been of great importance as early detection of pathogens and bio-terrorism agents became an urgent issue. Rapid mass production capability of phage also made the fast detection of pathogens possible at a very low cost while growth of bacteria in culture to increase cell number is time-consuming and costly. This work reports our achievement of a simple and inexpensive technique capable of specifically targeting and quantitatively measuring phage bacteria infection with the sensitivity to the single copy level. Using the basic building blocks of phage and fluorescent nanocrystals, quantum dots (QD), we manufactured phage-QD nanocomplexes capable of targeting bacterial strains and providing quantitative fluorescence measurements of phage-bacteria infection. This technique has a potential of broad application involving targeting, detecting, isolating, and destroying pathogenic bacteria from environmental and clinical isolates.

11:15 AM Ra7.3

1ARC MG, Institute for Materials Research, Tohoku University, Sendai, Miyagi, Japan; 2Dr. Vijay Kumar Foundation, Chennai, India; 3Institute of Industrial Research, Tohoku University, Sendai, Miyagi, Japan; 4Center for Interdisciplinary Research, Tohoku University, Sendai, Miyagi, Japan.

Colloidal semiconductor quantum dots have recently received enormous attention for their potential application to fluorescence diagnostics. CdSe-core quantum dots (QDs) are an example of a nanomaterial that has been shown to be useful as an alternative to conventional organic fluorophores for use in biological imaging [1]. The currently used CdSe-core QDs have are crystalline in structure. In spite of the advantages of such crystalline nanoparticle, there are several limitations in the application of such nanoparticles to medicine. There is a potential phototoxicity that is correlated with the generation of free Cd and Cd2+ ions due to deterioration of the CdSe lattice [2]. One solution that can be used to solve this problem is the design and synthesis of new nanocomposites which are more stable than crystalline QDs. We used ethylamine ultrafast pseudopotential plane wave method with generalized gradient approximation for the exchange and correlation energy. The lowest energy structures are obtained by optimizing selected structures of CdSe clusters using the conjugate gradient method. The adsorption spectra of various sizes of CdSe clusters have been also performed. The structural optimization of CdSe clusters with n up to 35 has been performed. It has been found, in good agreement with experimental data that clusters with n = 18, 19, 33 and 34 are magic and have step-like adsorption spectra with HOMO-LUMO gap [3]. The calculation result shows that the CdSe cage-like structures are more energetically favorable than the nano-size bulk crystalline fragments of CdSe. These (CdSe)n clusters (n = 13, 19, 33, 34) have cage structures 12, 18, 28, and 28 with 1, 5, and 6 CdSe molecules.
inside, respectively. Cage with n=12 can accommodate (CsSe)_{12} inside as the just right sizes to form basically tetrahedral networks, making it stable. (CsSe)_{12} is the optimal structural unit of (CsSe)_{n}. A local symmetry (CsSe)_{12} cage encapsulating (CsSe)_{12} with local maximum in the binding energy leading to its magic nature in the mass spectrum. [3]. For (CsSe)_{12}(CsS)_{14}, (CsTe)_{12}(CsS)_{16}, respectively, fit in well in (CsSe)_{12} cage keeping a similar network. The largest calculated diameter of this polyhedron, 1.45 nm, agrees with AFM estimate of 1.5 nm. This structure lies 5.16 eV lower in energy than the most stable bulk fragment of (CsSe)_{12}. The calculated adsorption spectra for mutual attachment are in agreement with experimental data. Similar tendencies have been found for CdS, CdTe, ZnS and ZnSe nanoparticles. These results indicate that the CdSe-core QDs can be also realized with the same structural features. These stable puckered cage-like CdSe-QDs can be useful for drug delivery or other uses in future investigations for use in cancer photodetection by reducing the toxicity and side effects of the diagnostic nanogents. [1] W.C. Chan and S. Nie, Science 281, 2016-2018, 1998. [2] A.M. Derfus et al., Nano Lett. 4, 11-18, 2004. [3] A. Kasuya et al., Nature Materials 3, 99-102, 2004.

Ra7.4 Abstract Withdrawn


We are investigating whether nucleation and growth of polymorphs of pharmaceuticals such as barbital can be controlled on surfaces modified with self-assembled monolayers (SAMs) of organic molecules on gold substrates by crystallization of solutions placed on SAMs functionalized with a variety of polar and nonpolar organic groups. Growth of polymorphs has been achieved by slow evaporation of solvent at RT (thermodynamic conditions) and by rapid cooling of hot solutions to RT (kinetic conditions). Temperature was controlled using a heating/cooling stage built in our laboratory. We have carried out similar crystallization experiments in microfluidic devices to screen for polymorphs using simultaneous high throughput crystallization on a range of surfaces. These devices consist of PDMS (polydimethylsiloxane) that has been patterned with microchannels and then bonded to gold or glass substrates. The results of these experiments and the influence of chemically modified surfaces in controlling polymorphism are discussed.

SESSION Ra7: Nanowires, Our Dimensional Nanostructures III
Chair: S. Picraux
Tuesday Morning, November 29, 2005
Room 208 (Hynes)

10:30 AM Ra7.1 Template-Directed and SAM-Mediated Synthesis of Au-TiO2-Au Heterojunction Nanowires. Jing-Jong Shyu and Nitin P. Padture; Department of Materials Science and Engineering, The Ohio State University, Columbus, Ohio.

The concept of engineered metal-oxide-metal (MOM) heterojunction nanowires, where two metal nanowires (50 to 100 nm diameter; Au or Pt) are separated by a nanoscale segment (50-100 nm length) of a functional oxide, has been proposed. In other words, a MOM nanowire has a functional oxide of precise nanoscale dimensions with metal interconnects integrated within the nanoscale building block. The functional oxide layer may be a wide bandgap semiconductor, electric, semiconductor, or magnetic material. Thus, the MOM nanowires have the potential to take the field of "bottom up" nanoelectronics to the next level of sophistication and control. Moreover, the MOM nanowire architecture affords the rare opportunity for measuring directly the fundamental functional properties of nanoscale oxides. In the present study, we have synthesized Au-TiO2-Au nanowires using a novel combination of template-directed, self-assembled monolayer (SAM)-mediated methods. We have used electropolishing to deposit the Au part of the nanowires inside anodic aluminum oxide (AAO) nano-hole templates. The exposed Au top surface is then functionalized with sulfonate-terminated self-assembled monolayer (SAM) to assist in the subsequent chemical-bath deposition of the TiO2 segment on the Au surface inside the confines of the AAO nanoholes. The chemical precursor used here is dilute titanium tetrachloroperoxide (TTIP). The MOM nanowires synthesis mechanisms and the nanostructure of the resulting MOM nanowires will be presented and discussed. The MOM nanowires, in conjunction with focused ion beam (FIB), have been used to fabricate devices for electrical-properties measurements. Current-voltage and chemical-sensing properties of individual MOM nanowires will be presented, together with a discussion of structure-properties relations.

10:45 AM Ra7.2 Porous alumina templates for nanowire and carbon nanotube field-effect transistors. Travis Lee Wade, 1 Jean-Eric Wegrowe, 2 Jean-Francois Davey, 1 Quang Anh, 1 Mihaela Cristina Ciocrel 1, Mohamed Barki, 1 Anna Rumanyczeva, 1 Xavier Hoffer, 1 Anna Fontcuberta i Morral, 2 Costel-Sorin Cojocaru 2 and Pribat Didier 2; 1Laboratoire des Solides Irradie, ECOLE Polytechnique, Palaiseau Cedex, France; 2Laboratoire de Physique des Interfaces et Couches Minces, ECOLE Polytechnique, Palaiseau Cedex, France.

Porous alumina is commonly used as a template for nanowire synthesis. It is made by etching aluminum in a solution of hydrofluoric acid. The anodization process forms a self-assembled, triangular network of nanometer diameter pores. This is because the pore diameter, distribution, and pore length can be tailored to suit the needs of the user by varying the anodization conditions: electrolyte, voltage, time, and temperature. The chosen pore size determines the resulting nanowire dimensions. Another reason is that once the nanowires have been made in the alumina template, they can be electrically contacted at the top and bottom of the membrane for physical measurements without the need for lithography. With two contacts a scientist can study many interesting phenomena such as magnetoresistance and electron transport in the nanowires. Two contacts, however, are not enough if one wants to make a device such as a transistor or sensor for applications or research. A third contact or electrode is needed. We have developed new 3D alumina templates that allow placement of a third electrode close enough to the nanowires or carbon nanotubes for an electric-field effect. One structure starts with an alumina template which is anodized perpendicular to its axis to form an isolation layer onto which a gate electrode is sputtered. Next, the wire is cut and anodized in the interior to form a network of pores parallel to the wire axis as a gate template for the synthesis of nanowires. The nanowires can be grown and contacted with the gate electrode already in place. Results have been obtained with tellurium nanowires and demonstrate a Coulomb blockade field effect. This new template is interesting because it can be made totally in a basic chemistry lab without the need for an expensive clean room or lithography. The next template is formed by depositing an aluminum layer on a silicon substrate which is modified parallel to the wire axis and sputtered to form a lateral template for the growth of nanowires. A gate electrode is then deposited onto the lateral template. The lateral anodization has been demonstrated with pore diameters as small as 5 nm. The advantage of this approach is that it could be implemented into existing processor fabrication. This presentation will show the results for these approaches to field-effect transistors based on anodized aluminum templates.

11:00 AM Ra7.3 Synthesis and characterization of Au-ZnO core-shell composite nanowires. Yu Zhang, Sathyajith Ravindran, Senthil Andavan and Cheng Sinan Ozkan; Mechanical Engineering, University of California at Riverside, Riverside, California.

The focus of this work is to investigate the electrical and optical properties of semiconducting ZnO shell formed over gold nanowires. We use chemical vapor deposition technique to coat ZnO axially aligned gold nanowires. We studied the structural characterization of these composite nanowires using SEM, TEM, electron diffraction and x-ray diffraction analysis and their composition with energy dispersive spectroscopy. We performed photoluminescence studies for their optical properties. Focused ion beam milling was used to make electrical contacts to these composite nanowires and studied their electrical properties. In addition, we report the morphology dependence with the operating temperature. The optimized experimental temperature for cylindrical coating was around 200°C. Results show that these composite nanowires have a high potential in both electrical and optical nanodevices.


There has been growing interest in the "bottom up" approach to building nanoelectronic devices, where nanoscale building blocks, such as nanowires (metals, semiconductors, oxides), are fabricated in isolation and assembled into nanocircuitts. In the case of oxides, current nanoelectronics technology uses all-oxide nanowires that are assembled across photo-lithographically deposited metal contact-pair electrodes to create devices. In this case, the length of the nanowire spanning the electrodes defines the active region, which is difficult to control; limited by the resolution of lithography, and requires high operating voltages. In order to address these critical issues, we have
proposed the concept of engineered metal-oxide-metal (MOM) heterojunction nanowires, where two metal nanowires (50 to 100 nm diameter) are separated by a thin oxide layer (a few nanometers in length) of a functional oxide. In other words, a MOM nanowire has a functional oxide of precise nanoscale dimensions with metal interconnects integrated within the building block. The functional oxide can be metallic, semiconducting, dielectric, magnetic, or a semiconductor, or magnetic material. Thus, the MOM nanowires have the potential to take the field of "bottom up" nanoelectronics to the next level of sophistication and control. Moreover, the MOM nanowire architecture also provides the opportunity to explore the fundamental functional properties of nanoscale oxides. We have used a unique combination of template-directed electrochemical synthesis and selective oxidation to synthesize such MOM nanowires. This method is generic, it can be used to synthesize a wide variety of MOM nanowires. Here we have synthesized two specific examples of MOM nanowires: Au-SnO2-Au (sensor) and Au-NiO-Au (ferromagnetic). The synthesis mechanisms and the nanocrystallography of the MOM nanowires, discussed [here], demonstrate the potential of this method to fabricate devices providing the opportunity to measure fundamental-properties of the MOM nanowires, such as voltage, chemical-sensing, and magnetic properties of individual MOM nanowires will be presented, together with a discussion of structure-properties relations.

11:30 AM Rb7.5
Off-axis Electron Holography and High-resolution Transmission Electron Microscopy of Internal p-n junctions within Si Nanowires, Dan Zhi1, Paul A. Midgley1, Chen Yang2 and Charles M. Lieber2; 1Materials Science and Metallurgy, University of Cambridge, Cambridge, United Kingdom; 2Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts.

Off-axis electron holography is a promising technique for the examination of semiconductor devices, since it provides the ability to record not only the amplitude of a scattered wave but also its phase. The phase difference between regions of different doping concentration or composition results in modulations in the interference fringes in an off-axis hologram, from which two-dimensional maps of electrostatic potential can be obtained. As a result, electron holography can be very useful for distinguishing the dopant profile in a diode or MOS transistor, especially for devices using light dopants such as boron. Nanowires, with dopant modulated along the axial direction during the synthesis, are novel nanostructures which can open up many opportunities in nanoelectronics and nanophotonics. In this paper, we apply off-axis electron holography, together with high-resolution transmission electron microscopy (HRTEM), to the internal p-n junctions within the Si nanowires grown by a chemical vapour deposition method. 20 and 40 nm diameter Si nanowires have been studied. Growth direction, morphology and crystal perfection of the nanowires are determined by HRTEM performed along two crystallographic zone axes. Junctions for holographic study are chosen carefully in order to avoid extraneous contrast arising from changes in the diffraction condition on the junction. Electron holographic potentials across the p-n junctions have then been successfully profiled using off-axis electron holography. Our results indicate that electron holography is a powerful technique for direct investigating the electrical properties of nanostructured semiconductor devices.

11:45 AM Rb7.6
New Ultraviolet Photodetector Using Bridging GaN Nanowires with Ultra-High Responsivity and Gain, Rui-San Chen1, Shiao-Wen Wang2, Zon-Huang Lan1, Jeff Tsung-Hui Tsai3, Kuei-Hsien Chen1, Li-Chyung Cheng4, Chia-Chun Chen5, Yang-Tang Liu1 and Ying-Sheng Huang1; 1Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan; 2Department of Chemistry, National Taiwan Normal University, Taipei, Taiwan; 3Graduate Institute of Electro-optical Engineering, Tatung University, Taipei, Taiwan; 4Center for Condensed Matter Sciences, National Taiwan University, Taipei, Taiwan; 5Department of Electronic Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan.

We have developed a new ultraviolet (UV) photodetector (PD) using the free-standing gallium nitride (GaN) nanowires (NWs) as the photoconductor. This approach has allowed us to connect an ensemble of one-dimensional (1D) nanostructured system on-chip, which is a critical process of nanodevice. GaN NWs have been grown across the active channel and are bridged between two side walls of highly doped GaN film electrodes. An interesting symmetric and tilted alignment of GaN NWs with [100] long-axis on the GaN[1000] side walls has been observed. In this investigation, three samples of detectors with different wire numbers of $8, 50 \pm 5$, and $1500 \pm 150$ were utilized to characterize their device performance. The photoconductivity (PC) spectra show a single and abrupt absorption at photodetector energy of $3.4$ eV, demonstrating excellent visible-blind character of the GaN NWs. It is worth noting here that the maximal PC responsivity of GaN NWs PDs has exceeded the value of 10$^4$ A/W while absorption at 4.0 eV and bias at 4.0 V.

1:30 PM Rb8.1
Functional Magnetic Nanostructures Based on Polymer Nanocomposites and Self-Assembled Arrays, Saribahar Hafizah1, James Gass and Punjalk Poddar; Department of Physics, University of South Florida, Tampa, Florida.

Functional magnetic nanostructures for many applications require controlled dispersion of nanoparticles in a host matrix. Magnetic nanoparticles embedded in polymer matrices have excellent potential for EMI shielding and biomedical applications. However, uniform dispersion of particles in polymers without agglomeration is quite challenging. We have synthesized a wide variety of superparamagnetic and strongly interacting ferromagnetic nanoparticle clusters (Fe$_3$O$_4$, Fe$_2$O$_3$, Mn-Zn and Ni-Zn ferrites) in the form of blended polymer composites and self-assembled arrays deposited by Langmuir-Blodgett method. Processing conditions have been optimized to achieve high quality, uniform dispersion and tunable magnetic response. Static and dynamic magnetization studies have been done to monitor the systematic changes in superparamagnetic and ferromagnetic properties. In particular, a unique magnetic anisotropy developed by us has been used to precisely probe the magnetic anisotropy, switching and interactions in these systems. Our studies reveal insights into the collective behavior of strongly and weakly interacting clusters of magnetic nanoparticles and their promise in applications ranging from EMI shielding to refrigeration based on the magneto-caloric effect (MCE). Work supported by the US National Science Foundation through Grants ECS-0140407 and CTS-0408933.

2:00 PM Rb8.2
Approaches for Fabricating Bulk Magnets from Magnetic Nanoparticles, Z. Q. Jin1,2, N. N. Thadthai2, Z. L. Wang2, M. Kozlov2, T. Vedantam1 and J. P. Liu1; 1Department of Physics, University of Texas at Arlington, Arlington, Texas; 2School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia; 2Nanotech Institute, University of Texas at Dallas, Richardson, Texas.

FePt alloys are important for the development of high performance permanent magnets and magnetic recording media due to their high magnetic-crystalline anisotropy and chemical stability. However, magnetic clusters of FePt nanoparticles, chemical synthesis of monodisperse 4 nm FePt and FePt/FePt nanoparticles and their fabrication into nanocomposite bulk magnets were investigated. The nanoparticles of chemically dispersed fcc structure were prepared first by reduction of platinum acetylacetonate and decomposition of iron pentacarbonyl and then processed using a controlled thermal annealing treatment at low temperature. Thermal annealing removes the retained surfactant induced during chemical synthesis and results in a particle phase transition at 400 °C. A coercivity up to 5.3 kOe has been obtained for the low-temperature annealed nanoparticles. The magnetic hardening due to the ordering transition was usually reported to be realized at higher annealing temperature (>500 °C) for FePt nanoparticles or by addition of some transition metals, such as Cu and Ag. The annealed nanoparticles were then packed into steel capsules at ~45% theoretical mass density and consolidated by shock compaction at room temperature using a three-capule plate-impact gas-gun loading system, and also by warm static compaction at 200 °C and 400 °C. The recovered bulk disk-shaped magnets were then characterized by x-ray diffraction, transmission electron microscopy and magnetic properties measurements. Shock densification to ~90% higher than the initial packing density was observed, which is above the theoretically predicted density for packing (0.74) of equal size spheres. High resolution transmission electron microscopy (HRTEM) revealed intensive deformation of nanoparticles, contributing to the densification. Propagation of shock wave through the nanoparticles also resulted in transition from ordered fcc to disordered fcc phases in certain local regions of the compacts. In the case of warm compaction,
however, a disorder-to-order transition was observed. TEM analysis revealed the retention of the nanostructure in the bulk magnets. Upon annealing at a high temperature, the magnetic domains were observed to be completely ordered structure was observed in the shock consolidated and warm compacted magnets. Magnetic properties measurements revealed maximum energy product (BH)max up to 14 MGOe and coercivity up to 14.6 kOe for the vacuum plasma transferred arc (VPTA) magnets. For the FePt and FePt/FeSi/FePt magnets showed a remanence ratio of 0.65, revealing the existence of interaction between the nanoparticles. The study shows that both the shock consolidation and warm compaction are feasible approaches for producing bulk magnets from the magnetic nanoparticles.

2:15 PM Rb8.3
Controlled Anchoring of SMM Clusters on Si(100). Guglielmo Guido Condorelli1, Andrea Cornia2, Maria Favazza3, Ignazio Luciano Fragala4, Dante Gatteschi3, Alessandro Motta4, Paola Nativel5 and Giovanna Pellegrino1; 1Dipartimento di Scienze Chimiche, Università di Camerino, Camerino, Italy; 2Dipartimento di Chimica, University of Modena and Reggio Emilia and INSTM UdR of Modena, Modena, Italy; 3Dipartimento di Chimica, University of Firenze and INSTM UdR of Firenze, Firenze, Italy.

The continuous scaling down of the size of integrated circuits (IC) has shown considerable limitations (lithographic, physics or economics) for top-down technologies, whilst, the bottom-up approach, using molecules as single data-handling devices, represents an enormous challenge in terms of storage and data-handling density. Recently, it has been shown that some molecules can be used to store magnetic information. In the most studied, prototypical molecule of this class of materials, referred to as a single molecular magnet (SMM), is a dodecamanganese (III/IV) cluster, [Mn12012(OAc)10(H2O)4]2H2O 2AqOH. An important goal for the development of the SMM cluster as a magnetic probe for storage building brick integration into other systems is the silicon technology relies upon an accurate control of the cluster anchoring process on the host surface. Recently, a reproducible way to drive the orientation of thiol-substituted Mn12 clusters anchored on a gold substrate and a possible approach to anchor oriented Mn12 on silicon has been proposed. On the other hand, Fe3 clusters (such as [Fe4(OH)6(dpm)6]), which are among the simplest SMMs so far synthesized, are particularly suitable for the realization of chemically stable, orientable arrays. In future, it is possible to control the density of Mn12 and Fe3 clusters anchored on silicon (100) is examined. The anchoring strategy is based on the pre-functionalization of silicon surfaces through the hydroxylation reaction with suitable functional ligands (such as 10-undecenoic acid or the tripropyl carboxylate) forming strong affinity toward Mn12 or Fe3 clusters. In order to control the anchoring of the SMM cluster, the proposed method tunes the density of bridging functional ligands on surfaces, using 1-alkenes as a spectator spacers. There is, in fact, evidence that overcrowding precludes ligand exchange with Mn12 clusters, whilst negligible cluster sticking occurs on Si-grafted 1-decene monolayers. Therefore, substituted ditopic functional ligands were used as a spectator spacers representing a viable route to control the density of the silicon surfaces. Modified surfaces were analyzed by FTR-ATR, XPS spectroscopy and AFM imaging. XPS and FTR-ATR show that the surface mole ratio between functional bridges and alkynes is strongly related to that of the source solution. The surface density of SMM clusters is, in turn, strictly proportional to the ester mole fraction. Well resolved and isolated Mn12 clusters were observed with AFM, adopting a diluted ester/decon 1:1 solution.

SESSION Rb8: Nanowires, One Dimensional Nanostructures IV
Chair: Cengiz S. Ozkan
Tuesday Afternoon, November 29, 2005
Room 208 (Hynes)

1:30 PM *Rb8.1
Tailored Inorganic/Organic Nanostructured Interfaces for Control of Surface Hydrophobicity. S. Takahama1; 1Graduate School of Environmental Science, Kyushu University, Fukuoka, Japan.

New approaches to sensing and biochemical analyses being enabled by nanoscale devices present novel challenges for systems integration. It is well known that the interaction of fluids with surfaces depends on a complex interplay of surface energy and morphology. These interactions can define the major factors in controlling fluid behavior as dimensions are decreased to the nanoscale. We discuss here studies exploiting these interactions for control of surface wetting, hysteresis, and droplet motion through the combined design of nanoscale surface morphology and monolayer photoswitchable coatings. The vapor-liquid-solid technique is used to synthesize Si nanowire structures on polycrystalline surfaces over a wide variety of morphologies through the size of the metallic seeds and the growth parameters. These nanowire surfaces are then functionalized with organic monolayer coatings that include tethered photochromic molecules such as spiropyran to tailor the surface properties. We show that the surface energies of these photo-responsive organic/inorganic interfaces can be reversibly switched in aqueous environments in situ by the opening and closing of the photoactive molecules. These morphologies and monolayers have been used to create superhydrophobic surfaces and thereby control the interaction of water droplets with surfaces. Examples include amplifying the light-induced change in water contact angles, patterning of surfaces for droplet pinning, forming droplet arrays, and moving droplets solely with light (no electric field). We will discuss our surface nanoscale designs, selected results illustrating the control and measurement of the fluid interactions, and some potential applications.

2:00 PM Rb8.2

Silicon nanowires and nanoribbons (SiNW/Rs) were fabricated directly from the Si source gas into pre-fabricated permanent nanochannel templates by our self-assembling “grow-in-place” approach1. The size, shape, position, orientation, and number of the SiNWs/Rs can be precisely controlled by the pre-fabricated nanochannel templates. The templates can be fabricated with built-in contacts and integrated into the final devices, providing contacts, interconnects, and passivation/encapsulation. Our approach solves major manufacturing problems associated with nanowire devices since it results in a multiplicity of precisely positioned, oriented, and electrically contacted nanowires without the need for any SiNW/Rs post-synthesis processing, such as “pick-and-place”. The “grow-in-place” architecture potentially removes the need for template dissolution, post-synthesis nanowire manipulation, and post-synthesis electrical contacting. In addition, our approach is also environmentally benign and friendly2 since only the exact number of SiNW/Rs needed was grown on the wafers and the SiNWs/Rs were always confined in the nanochannel templates. The nanowires, therefore, have little possibility of escaping into the environment. We have developed a variety of built-in ohmic and rectifying contact structures and approaches for the “grow-in-place” methodology. In this report, we focus on the introduction of our self-assembling “grow-in-place” approach, electrical characterization of SiNW/Rs, and nanowire device designs/structures. We will also discuss our initial work on the SiNW/R nanowire transistors. (1) Shan, Y.; Kallan, A. K.; Peng, C. Y.; Fonash, S. J. Nano Lett. 2004, 4, 2085; (2) Roco, M., Environmental Science & Technology, March 1, 2005, 107A

2:15 PM Rb8.3
Metal-Semiconductor Nanowire Heterostructures. Yue Wu1, Hao Yan2 and Charles M. Lieber1; 1Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts; 2Division Of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts.

Proof-of-concept nanoelectronic devices based on semiconductor nanowire building blocks have exhibited performance that is comparable to or enhanced compared to conventional planar devices. Yet, an ultimate integrated nanosystem will not only require high-performance functional semiconductor units but also highly conductive metallic units, for example, for contacts, gates and interconnects. To this end, we have developed bottom-up approaches to the incorporation of metallic materials into semiconductor nanowires to yield several different classes of metal-semiconductor heterostructures. Electron microscopy and structure analyses demonstrate the successful and controlled synthesis of these heterostructures, and electrical transport measurements demonstrate the potential of utilizing their unique properties for integrated device arrays with enhanced performance.

SESSION Rb8: Magnetic Nanostructures II
Chair: Srikanta Harirhan
Tuesday Afternoon, November 29, 2005
Room 207 (Hynes)

3:30 PM Rb8.9
Development of Tunable Self-assembled Magnetic Nanowire Arrays. Hsu Jing1, B. A. Evans1, Onejue Sul2, L. Carroll3, M. Falvo2, S. Washburn1 and R. Superfine1,2; 1Materials Science,
University of North Carolina Chapel Hill, Chapel Hill, North Carolina, 6Department of Physics and Astronomy, University of North Carolina Chapel Hill, Chapel Hill, North Carolina, 7Computer Science, University of North Carolina Chapel Hill, Chapel Hill, North Carolina.

Free standing magnetic nanowires have been assembled or directly grown by different methods such as template methods, lithography or assembly methods by surface tension or capillary force. We are exploring the magnetic assembly of previously produced nanorods. This offers the advantage of increasing the experience of the magnetic field as well as a torque under an external magnetic field.

Soft-magnetic nanowires with mean radius 200 nm were electrophoretically deposited in anodically etched commercial aluminum oxide microchannels. Based on finite element analysis modeling, parabolic magnetic potential wells were realized with a home-made solenoid electromagnet. We found the magnetic nanowires form self-assembled patterns in response to the potential well formed by the spatially varying magnetic field. The lattice distances were tunable from several microns to tens of microns depending on field strength, total number of the nanowires and nanowire dipole strength. A dimensionless Monte Carlo simulation was performed on an idealized model for better understanding the self-assembly patterns. Free standing magnetic nanowire devices were fabricated based on this strategy by planting the roots of nanowires into a curable thin soft polymer layer spin coated onto the surface. After curing this thin layer of polymer, we demonstrated the fast response actuation by putting the standing nanowire devices in an oscillating external magnetic field. These free standing devices may find applications in surface morphology control for optical devices or fluidic controls.

3:45 PM Ra9.2
Self-Assembled Single Crystal Ferromagnetic α-Fe Nanowires: Perpendicularly Recording Media and Carbon Nanotube Growth. Ladan Mohaddess-Ardbili, Daniel M. Chiu, H. Zheng, S. B. Ogale, Q. Zhan, J. H. Han, S. Y. Yang, L. Salamanca-Riba, J. B. Yoo, D. G. Schlom, M. Wuttig, and R. Ramesh. 1Materials Science and Engineering, University of Maryland, College Park, Maryland; 2Materials Science and Engineering, University of California, Berkeley, California; 3Physics, University of Maryland, College Park, Maryland; 4Department of Materials Science, Sungkyunkwan University, Suwon, South Korea; 5Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania.

A novel approach to create self-assembled ferromagnetic nanostuctures for new magnetic recording media with high storage capacity is reported, which involves spontaneous phase decomposition of a single-phase perovskite oxide during film growth. We are exploring the stability in a nominally single phase LaSrTiMO3 (TM = Fe, Co, Ni) function on single crystal silicon, where the film heteroepitaxy as the processing route. We find that the film structure and microstructure depends systematically on the oxygen pressure during deposition. Deposition under reducing environments leads to the formation of multidomain nanowires. Specifically, in the case of a system containing Fe the deposition under reducing conditions leads to spontaneous formation of an array of single crystal ferromagnetic α-Fe nanowires embedded in an antiferromagnetic matrix with nominal composition of LaSrFeO4. The diameter of α-Fe nanowires is controlled by growth temperature and the height is controlled by film thickness. At high growth temperatures of 840 °C, square shaped α-Fe pillars with a lateral width of d = 50-100 nm are formed. As the deposition temperature is reduced the diameter of the nanowires is progressively reduced to 4-6 nm for the growth at 500 °C and the shape is circular. In the case of Co the growth temperature window is smaller and the nanowires with d = 60-70 nm are preferred. The large size and high uniformity of these nanowires are dependent on both their average diameter and height. The large coercivity of Hc = 3000 (Oe) is achieved for 200 nm thick nanowires with average diameter of 15-20 nm grown at T = 700 °C. The large size and high uniformity of these nanowires make them desirable for high-density data storage and other magnetic device applications. Additionally, these thin films were used as a template to grow vertically aligned carbon nanotubes using Plasma Enhanced Chemical Vapor Deposition (PECVD). Acetylene (C2H2) and ammonia (NH3) were used as a carbon source and diluting gas, respectively. The growth temperature was lower than 600 °C. Self-assembled α-Fe nanowires serve as nucleation sites for the growth of vertically aligned multiwall carbon nanotubes (MWCNTs). The size of carbon nanotubes can be controlled by changing the diameter and thickness of the α-Fe nanowires. The field emission from these MWCNTs was measured and the results will be presented.

4:00 PM Ra9.3

Carbon coated nanoparticles were synthesized by laser-assisted (ArF excimer laser, λ = 130 nm) chemical vapor deposition (LCVD). The particles were formed in the gas-phase by photolytic dissociation of cobaltocene in argon and the particles were deposited onto a silicon substrate. Typical laser energies were 70 - 90 mJ/cm2 fixed by separating the nanofabrication and patterning steps. Based on the Stoner and Wolfarth model, it is feasible to treat magnetic nanowires with high aspect ratio as magnetic dipoles along their easy axis. These magnetic dipoles experience an incremental magnetic field gradient as well as a torque under an external magnetic field.

Soft-magnetic nanowires with mean radius 200 nm were electrophoretically deposited in anodically etched commercial aluminum oxide microchannels. Based on finite element analysis modeling, parabolic magnetic potential wells were realized with a home-made solenoid electromagnet. We found the magnetic nanowires form self-assembled patterns in response to the potential well formed by the spatially varying magnetic field. The lattice distances were tunable from several microns to tens of microns depending on field strength, total number of the nanowires and nanowire dipole strength. A dimensionless Monte Carlo simulation was performed on an idealized model for better understanding the self-assembly patterns. Free standing magnetic nanowire devices were fabricated based on this strategy by planting the roots of nanowires into a curable thin soft polymer layer spin coated onto the surface. After curing this thin layer of polymer, we demonstrated the fast response actuation by putting the standing nanowire devices in an oscillating external magnetic field. These free standing devices may find applications in surface morphology control for optical devices or fluidic controls.

4:15 PM Ra9.4
Hybrid Colloidal Nanostructures with Paired Plasmonic, Semiconducting and Magnetic Functionalities. Weili Shi1, Hao Zeng2, Yudhisthira Sao3,4, Mark T. Swihart1,4 and Paras N. Prasad3,4. 1Department of Chemical and Biological Engineering, The University at Buffalo (SUNY), Buffalo, New York; 2Department of Physics, The University at Buffalo (SUNY), Buffalo, New York; 3Department of Chemistry, The University at Buffalo (SUNY), Buffalo, New York; 4The Institute for Lasers, Photonics, and Biophotonics, The University at Buffalo (SUNY), Buffalo, New York.

Hybrid particles with paired combinations of plasmonic, semiconducting and magnetic functionalities have been chemically fabricated. Three kinds of such hybrid nanoparticles: Au-Fe3O4, Au-Fe3O4 and PbS-Fe3O4 are reported here. These particles were synthesized by decomposition of organically soluble precursors, iron acetylacetonate (Fe(acac)3) or Pb-oleate complex, onto the surface of separately synthesized gold or PbS nanoparticles that serve as nucleation centers in high solution density, resulting in Au-Fe3O4 or PbS-Fe3O4 on gold or PbS cores and the growth of PbS on gold cores appear to be, as observed by high resolution transmission electron microscopy (HRTEM). By rationally tuning the synthetic parameters, such as heating rate, solvent, and so on, we were able to control the morphology of these nanoparticles. The optical properties of gold or PbS nanoparticles, and the magnetic properties of Fe3O4 are appreciably affected by the presence of the conjugated organic capping functionalities. These magnetic hybrid nanostructures have a broad range of potential applications in heterogeneous catalysis, for magnetophoretic delivery of drugs or genes, for biological sensing, in magneto-optical switching, and as building blocks for spintronic devices.

4:30 PM Ra9.5
Preferred Orientation and Epitaxial Morphological Transition of Aromatic Copolymer 10-70 nm by Lattice-Mismatched Carbon Nanotube Nanoparticle Aggregates. Moon Jeong Park1, Jongnam Park2, Taejihn Hayeon3 and Koockheon Chae4, 1School of Chemical and Biological Engineering & NANO Systems Institute - National Core Research Center (NCRC), Seoul National University, Seoul, South Korea; 2National Creative Research Center for Organic Nanotube Materials and School of Chemical and Biological Engineering, Seoul National University, Seoul, South Korea.

We investigate the effect of hard additives, i.e., magnetic nanoparticles (NPs) and metal NPs, on the ordered morphology of a block copolymer by varying concentration of NPs. In order to characterize the structural changes of the block copolymer associated with different NP concentrations, small-angle x-ray scattering (SAXS) and transmission electron microscopy (TEM) were performed. Monodisperse maghemite (γ-Fe2O3) NPs and silver NPs with surfaces modified by oleic acid have been synthesized and two F8-Fl diblock copolymers showing lamellar and cylindrical morphologies are used as
nano-resolution soft lithography, which have proven to be difficult using commercial stamps. In the second part, microfabrication of functional polymers that have specific molecular recognition for biological or chemical detection devices will be presented. As an example of functional patterning, we used a molecularly imprinted polymer (MIP) system, which is produced by “molecular imprinting” to create “synthetic receptors” with specific molecular recognition for organic molecules in cross-linked network polymers. Microfluidic synthesis has received considerable attention for the synthesis of novel materials at the micro-scale since it can produce specific advantages, that cannot be achieved by conventional bulk-scale routes. We are thus interested here in the operation of microfluidic reactors for microsynthetic purposes, taking advantage of micro-scale mixing of multiple reagents and of the use of quenching sequences for greater reaction selectivity. Now we present a selection of organic hybrid glasses containing nanoparticle glasses will also be presented.

4:00 PM Rb9.2

The ability to fabricate chemically patterned surfaces at nanoscale is of great importance in nanoscience and nanotechnology. A variety of methods such as photolithography, particle beam lithography, microcontact printing, and scanning probe lithography have been developed to generate self-assembled monolayers (SAMs) on gold surfaces with more or less success. Significant efforts are still needed to explore other simple unconventional methods for fabricating SAM nanopatterns over large areas, at low cost, and with high throughput. We demonstrate a simple template method for generating dense (> 10^10/cm^2), well-controlled SAM nanopatterns (< 30 nm diameter) over a large area (> 5 cm^2) on gold surfaces. In this approach, hexagonally ordered patterns of anodic aluminum oxide (AAO) template, prepared by two-step anodization of aluminum, were transferred onto a silica/Si wafer to form a porous silica template on Au/Si wafer via a RIE technique, which spatially confined the self-assembly of thiol molecules on the exposed Au surface. After removal of the silica template, the prepared SAMs patterns can be used as resist for generating three-dimensional arrays of gold nanoparticle on silicon wafer via wet chemical etching. This approach is a simple and inexpensive process that results in SAMs as thin as 30 nm with conventional laboratory setups. In this approach, the patterns directing the self-assembly of thiols are naturally formed in AAO preparation and no expensive and complicated facilities are required. AAO is a well-known template with easily tunable structure by simply varying preparation conditions, the pattern size and spacing are only determined by the structure of AAO template and not by any other factors such as lateral diffusion and template distortion which are inherent in microcontact printing and dip-pen lithography. In addition, large-area SAM patterns can be achieved (5 cm^2 in our setup) by a composite protective layer that prevents AAO from cracking in the process. This approach can also create second functional groups on the bare spaces, allowing functional silica template to form biomimetic surfaces. Finally, monolayers assembled from thiol solution can be used as resists for generating three-dimensional Au particle arrays. 4:15 PM Rb9.3

Ge nanocrystals are frequently synthesized by implantation of Ge into silica followed by thermal annealing. We demonstrate that nucleation and growth of Ge nanocrystals can be suppressed by co-implantation of oxygen prior to annealing. At Ge/O dose ratios exceeding one, fully miscible silica germania alloys are formed rather than Ge nanocrystals. This chemical deactivation of Ge is utilized to achieve patterning growth of Ge nanocrystals. Ge is implanted into a thin SiO2 film on a Si substrate and a lithographically defined mask is created through which oxygen is subsequently implanted. Rapid thermal annealing (RTA) of the co-implanted structure yields two-dimensionally patterned growth of Ge nanocrystals for the unmasked regions. We further demonstrate that this process, when applied to implanted silicon-on-insulator (SOI) structures, allows for three-dimensional patterning of Ge nanocrystals; the buried oxide thickness and depth providing the third dimension of control. We apply a previously developed process to obtain exposed Ge
SESSION Ra10: Biomimetics II
Chair: S. Picraux
Tuesday, November 29, 2005
Room 207 (Hynes)

6:00 PM Rb10.1

Physical and chemical functions of organisms are carried out by a very large number (billions) of proteins and peptides through predictable and self-sustaining interactions. In Nature, biomolecular-matter interactions is accomplished via molecular specificity and high efficiency leading to the formation and self-assembly of controlled functional constructs, structures, tissues, and systems at all scales of dimensional hierarchy. Through evolution, Mother Nature developed molecular recognition via successive cycles of mutation and selection. Molecular specificities of probe-target interactions are all based on specific peptide-molecule recognition. Structural and compositional control of inorganic materials at the molecular scale is a key in the synthesis of novel, functional, shape-specific, and tissue-engineered materials. With the recent developments of nanoscale engineering in physical sciences, and the advances in molecular biology, we are now able to combine genetic tools with synthetic nanoscale constructs, and create a hybrid molecular-matter, molecular biomimetic, molecular bio-inspired, materials. Using biology as a guide we have adapted bioschemes including combinatorial biology, post-selection engineering, bioinformatics, and modeling to select and tailor short peptides (7-60 amino acids) with specific binding to and specificity toward functional materials, e.g., metals, ceramics, and semiconductors. Based on the fundamental principles of genome-based design, molecular recognition, and self-assembly, we can now engineer polypeptides for inorganic surfaces and synthetic functional molecules and use them as nucleators, catalysts, growth modulators, molecular linkers and rector sets, fundamental utilities for nano- and nanobio-technology. We will review the latest developments from our collaborative research group as well as from other international groups that are in this rapidly developing polydisciplinary field focusing on i. Genetic engineering of inorganic-binding polypeptides; ii. Nature of binding, specificity and assembly of peptides on selective surfaces using experimental (e.g., surface plasmon resonance spectroscopy, quartz crystal microbalance and atomic force microscopy) and theoretical tools (protein structure prediction); iii. Biosynthesis and functional organization of hybrids using inorganic-binding peptides for photonic and medical applications. The research is supported by an ARO-DURINT and a NSF-MRSEC 7-grants.

6:45 PM Rb10.5
Directed Self-Assembly of Dual-Functionalized Microparticles and Microrods by Nucleic Acid Interactions, Paul Labina and Manish Bajaj. 1,2 Chemical and Biomolecular Engineering, Rice University, Houston, Texas; 2Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Self-assembly provides a convenient strategy for building higher-level structures from smaller components. Examples include the formation of densely packed films by the self-assembly of molecules onto surfaces and the generation of multilayered structures by the layer-by-layer assembly of polymers. Chemical interactions are responsible for the self-assembly of these supramolecular and hierarchical structures. A goal for self-assembly has long been the generation of complex nano- and microstructures from individual constituents by the simple mixing of species together and their self-formation into specific aggregates and coupled structures. Such directed bottom-up self-assembly could build from the developed (and constantly improving) technology base of microfabrication and the developing technologies for producing nanoparticles, nanorods, and related systems. To address this problem, we have targeted the creation of species containing multiple individually tailorable regions that can each express a specific recognition behavior. In this regard, we have prepared and studied the assembling characteristics of various anisotropic building blocks that express oligonucleotides on their surfaces. Specifically, we have created microparticles and microrods by shadow deposition techniques that expose individual surface regions of gold and silica. By combining methods of solid-phase synthesis and self-assembly, we have targeted the regions on these objects individually and selectively with different oligonucleotide sequences to produce so-called ‘Janus’ particles and rods that serve as anisotropic building blocks of selectable size, shape, and nucleic acid sequence for directed self-assembly. The resulting dual-functionalized surface regions are each active towards specifically recognizing oligonucleotides of complementary sequence. We have used this ability to generate purposeful aggregates and self-assembled multi-component structures by combining the effects with nanoparticles and other objects that express complementary oligonucleotide sequences on their surfaces. The approach is general and modular as the surface chemistry, dimensions, and compositions of each self-assembly object can be selected from the set of species placed together for the directed self-assembly event. The advantages of specific shapes and the abilities to generate objects expressing beyond dual functionality will be highlighted.

Using 1D and 2D Chemical Templates Formed by Scaened Probe Lithography to Create Organized Virus Arrays for Hierarchical Assembly of Nanomaterials, Sung-Wook Chung, Chin-Li Cheung, James Devore, Anju Chatterjee, Tianwei Lin and John E. Johnson. 1Department of Chemistry and Materials Science, Lawrence Livermore National Laboratory, Livermore, California; 2Department of Molecular Biology, The Scripps Research Institute, La Jolla, California; 3Department of Chemistry, University of Nebraska, Lincoln, Nebraska.

Organizing nanostructures and functional molecules into deterministic patterns at surfaces is a fundamental challenge of nanoscience. Self-assembly methods are generally limited to creation of uniform 2D films. Printing methods, which have the potential for organizing nanostructures through creation of templates, can rarely achieve patterning below 50nm, and then controlling orientation of individual nanostructures is difficult. One approach to achieving higher density of orientation and shorter range order is to use as programmable templates for nanoparticle formation as well as for placement of molecular moieties with optical or electronic functions. These building blocks are typically many tens of nanometers in size and can perhaps be organized using templating methods operating at 50-100 nm. Here we report results using scanned probe nanolithography to create chemical templates for organization of viruses and in situ AFM imaging to investigate the dynamics of organization at these templates. As a model system we used cowpea mosaic virus (CPMV) genetically engineered to present histidine (His) tags at specific sites on the capsid surface. Atomically-flat gold substrates coated with self-assembled monolayers (SAMs) of polypeptide glycol (PEG) terminated allyl thiols were functionalized with nickel-chelating nitrotriacetic acid (Ni-NTA) terminated alkyll thiols using scanned probe nanolithography. The Ni-NTA patterns had feature sizes ranging from 10-100nm and attached to the His-tags.
on the viruses through a metal coordination complex linkage with the Ni-NTA. Force microscopy was then used to investigate the degree of ordering, packing density, assembly, and distribution both on the regions patterned to bind chemoselectively with the virus, as well as the surrounding PEG-terminated region. We show that the degree of ordering depends on all parameters chosen: the surface chemistry, the virus concentration, the PEG concentration, and the feature size of the patterns. For example, as the solution PEG concentration is increased, which increases the virus-virus interaction through hydrophobic effects, 2D arrays of virus clusters are formed. When the PEG is ordered, well-ordered rhomboidal, and then hexagonally close packed assemblies and 1D patterns increase in width one virus to multiple rows of viruses. Disordered clusters form on the PEG functionalized regions, but the dynamics of cluster growth is altered. Taking cues from previous work in both epitaxial and colloidal systems, we present a physical picture of assembly at templates where the dominant factors are the ratio of virus flux to surface mobility and the strength of the virus-virus interaction, the latter being modulated by hydrophilic interactions.

This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

6:45 PM Ra10.3
An engineered virus as a scaffold for 3-D assembly on the nanoscale. Amy Szuchmacher Blum1, Carissa M. Soto2, Charmaine D. Wilson3,∗, Terence L. Schull4, Steven K. Pollack5, Anju Chatterji2, Tianwel Lin2, John E. Johnson3 and Banahalli R. Ratnasamy3, 1Code 6930, Naval Research Lab, Washington, District of Columbia; 2Department of Biochemistry and Molecular Biology, The Scripps Research Institute, La Jolla, California; 3Institution of Chemistry and Materials Sciences, Office of Science and Engineering Laboratories, Center for Devices and Radiological Health, Food and Drug Administration, Rockville, Maryland.

Significant challenges exist in assembling and interconnecting the building blocks of a nanoscale device and being able to electronically address or measure responses at the molecular level. Self-assembly is one of the few practical strategies for making ensembles of nanostructures and will therefore be an essential part of nanotechnology. However, in order to generate complex structures through self-assembly, it is crucial to develop methods by which different components in solution can come together in a controlled fashion. Using viruses as nanoscale scaffolds for devices offers the promise of well-defined positioning on the nanoscale, using a particle that can either interface with currently available lithographically defined structures, or undergo further self-assembly into extended structures by itself. Here we show that exquisite control over positioning nanoscale components on a protein scaffold allows bottom-up self assembly of nanoscale devices. Using Cowpea Mosaic Virus, modified to express cysteine residues on the capsid exterior, gold nanoparticles were attached to the viral scaffold in a pattern to produce specific interparticle distances. The nanoparticles were then interconnected using thiol-terminated conjugated organic molecules that can act as both wires, resulting in a three-dimensional spherical conductive network which is only 30 nm in diameter.

7:00 PM Ra10.4
Peptide-Mediated Formation of a Titanate/Single Wall Carbon Nanotube Composite Material. Mark Pender1, Jeffrey Hartgerink2, Morley Stone3 and Rajesh Naik3, 1Air Force Research Laboratory, Wright-Patterson AFB, Ohio; 2Department of Chemistry, Rice University, Houston, Texas.

Carbon nanotubes (CNTs), both multiwall and single wall, are proving to be critical components for emerging electronic, sensor, and structural systems. In many instances, the key to success is the development of methods for the manipulation and functionalization of CNTs that do not compromise their structural or electronic properties. Coating single wall carbon nanotubes with oxide based ceramics is formidable in terms of maintaining the nanotube properties or nanocomposite materials has been previously demonstrated. Titanium dioxide is of particular interests for photovoltaics where the single wall carbon nanotubes could aid electron transport through dye-sensitized solar cells or function as supports for photocatalysts where high surface areas, electronic addressability, and chemical inertness are all important factors. While there are several examples of TiO2 coatings or particles on the surface of multiwall carbon nanotubes (MWCNTs), there are few examples for single-walled carbon nanotubes (SWNTs). This is due, in large part, to the poor solubility of individual SWNTs in solutions required for processing and a lack of specificity for titania formation exclusively at the surface of the SWNTs. Here we demonstrate a biomimetic peptide to suspend SWNTs as individuals and nucleate the growth of titania from solution precursors at the surface of the nanotubes without covalent functionalization of the carbon nanotube. A peptide (P1) with a strong affinity for the surface of SWNTs produced by the HiPCo (high pressure carbon monoxide) method was isolated via phase display techniques. Starting with this amino acid sequence, a lanthaneside peptide (P1R5) was synthesized consisting of a 2,6-diaminopiperidine linker and the R5 peptide, a glycine linker and the R5 peptide, which has been shown to mineralize silica and titanita from precursor solutions. This peptide suspended SWNTs as individuals and small bundles in aqueous solution and was found to form titania on the surface of the nanotubes when a precursor solution was added. This method and characterization of the products are presented.

7:15 PM Ra10.5
Templated Beta-Sheet Supramolecular Assemblies and Beta-strand Orientation of de novo Polypeptides for Biomolecular/bioelectronic Structure Formation. Naunakshita Rana1, Seitchiro Higashiyama2, Christopher Kossow1, Natalya Topolina1, Autumn Carlse1, Christopher Wells2, John Welch2, Eric Eisenbraun2, Robert Geer3 and Alain Kaloyeros3, 1College of Nanoscale Science and Engineering, University at Albany - SUNY, Albany, New York; 2Department of Chemistry, University at Albany - SUNY, Albany, New York.

Templated assembly of a 524 residue de novo polypeptide sequence on a highly oriented pyrolytic graphite (HOPG) substrate is presented. Beta-sheet-forming polypeptides prepared from de novo designed artificial genes were extensively studied by atomic force microscopy and UHV-scanning tunneling microscopy. The formation of highly rectilinear parallel supramolecular fibril arrays which display a three-fold symmetry consistent with HOPG templated assembly is observed via both AFM - a six-fold symmetric 2D Fourier transform ofStrand separation of approximately 0.8 nm matches well with predictions from molecular modeling. Atomic Force Scanning tunneling microscopy also reveals individual beta-sheet strands oriented approximately 50 degrees relative to the fibril axis. Molecular modeling of beta-sheet folding for this de novo polypeptide confirms that this orientation is energetically favorable for strands containing even numbers of amino acids and unidirectional turns. The experimental observation of individual molecular beta-sheet strands and the demonstration of fibril assembly from such high-molecular weight de novo beta-sheet strands have not been previously reported and have important implications regarding biomolecular/bioelectronic structure formation.

7:30 PM Ra10.6
Protein-Directed Self-Assembly of Gold and Latex Nanoparticles. Alexey Vegel1, Wil Shang1, Jonathan Dordick1,2 and Richard Siegel1,2, 1Rensselaer Nanotechnology Center, Rensselaer Polytechnic Institute, Troy, New York; 2Chemical and Biological Engineering, Rensselaer Polytechnic Institute, Troy, New York.

Many proteins and peptides are known to form self-assembled structures. Use of protein-directed self-assembly provides exciting opportunities for creating nanostructures due to the diversity of possible forms (wires, rings, spheres, etc.) and the possibility to control the assembly/disassembly process in situ since proteins are extremely sensitive to minor changes in such parameters as pH, Ca2+ concentration, presence of ATP, etc. In addition, protein-protein interactions are characterized by very high specificity. Here we have employed highly specific protein interactions to control the assembly of 5 nm gold colloid and 20 nm polystyrene latex nanoparticles. The proteins were attached to the corresponding nanoparticles by either physical adsorption on Au nanoparticles or by covalent binding to the latex nanoparticles. Since protein size is in the same range as the size of nanoparticles, the conditions could be optimized to have stoichiometric protein/nanoparticle conjugates with size, one, two, or more protein molecules per nanoparticle. Such stoichiometric conjugates of proteins, which strongly interact with each other, can be used to build nanoparticle “molecules”. Here we employed antibody-antigen and lectin-glycoprotein interactions to perform nanoassembly. A high yield of dimers has been observed in both cases when equivalent amounts of 1:1 conjugates of interacting proteins have been mixed. In the case of lectin-glycoprotein interactions, the nanostructures can also be destroyed in a controllable way by adding an excess of mannose, which competitively binds to the lectin and breaks the protein-protein interactions within the nanoassembly. Varying the stoichiometry of protein/nanoparticle conjugates enables one to control the process of self-assembly and obtain a variety of nanostructures, including dimeric and 1-D structures. The trimers can also be constructed by mixing 1:1 conjugates of antigen, antibody, and anti-antibody (here we used horseradish peroxidase (HRP), anti-HRP rabbit IgG, and Fab’ fragment of goat anti-rabbit IgG, respectively). We believe this approach may prove useful not only for the formation of the assemblies of nanoparticles with bio-inspired structures, but also for probing/visualizing the structure of various protein-protein complexes. The materials synthesized by protein-directed
self-assembly may find applications in drug delivery or as biosensors. This work was supported by the Nanoscale Science and Engineering Initiative of the National Science Foundation under NSF Award Number DMR-0117792.

7:45 PM Rn10.7
M13 Virus Scaffold for Self Assembly of Nanostructured Lithium Battery Electrode. Ki Tae Nam1, Dong-Wan Kim1, Pil J. Yoo2, Chung-Yi Chiang3, Soo Kwan Lee3, Paula T. Hammond2, Yet-Ming Chiang1 and Angela M. Belcher1,3. 1Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; 2Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; 3Biological Engineering Division, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Biological self assembly and biomimetic interactions continue to inspire novel approaches for the development of functional nanostructured materials with diverse applications. Here, we demonstrate the use of genetically engineered M13 filamentous viruses as a biological scaffold for self assembly of nanostructured lithium battery electrodes. The M13 virus was engineered to express metal ion binding peptides in the major coat protein, to nucleate cobalt ions from solution. The sequence of this peptide was derived based on the fundamental interaction mechanisms involved in peptide-mediated bimetallic deposition of metal ions. The spontaneous oxidation following the incubation and the reduction of cobalt ion with the engineered phage resulted in the assembly of monodisperse, crystalline cobalt oxide nanowires at room temperature. These nanowires were characterized by high resolution transmission electron microscopy (HRTEM) and electron diffraction patterns. This biologically inspired, room-temperature, aqueous synthesis technique is both environmentally benign and has the potential for high throughput synthesis, and avoids the use of high temperature and organic solvents commonly used. Furthermore, manipulation of the nanostructure and the morphology of the cobalt oxide nanowire were demonstrated by controlling the interaction between the nucleating peptides and metal ions. The virus templated cobalt oxide nanowires were assembled into 1D battery anodes and the electrochemical properties were characterized. The result of cyclic voltammograms and cycle curve will be presented. Virus based assembly of Li battery anodes could improve the characteristics such as charging rate performance or cyclablity. Next, the virus-based lithium anodes were incorporated with solid polyelectrolyte thin film which has high ionic conductivity of lithium ions. It was found that these engineered viruses assembled into highly ordered nanostructures on solid polymer electrolytes, composed of alternating multilayers of anionic and cationic polymer, which may be attributed to the entropically driven ordering process and electrostatic charge interaction. Further bimetallic deposition of the two-dimensional ordered virus scaffold on an conducting solid electrolyte enabled assembly of dense, highly ordered, nanostructured battery electrodes. Therefore, we have demonstrated the assembly of enhanced, nanostructured lithium electrode using principles of biological self assembly and bimetallic deposition.

SESSION Rb10: Alternative Nanofabrication III
Chair: Gregory Lopinski
Tuesday Evening, November 29, 2005
Room 208 (Hynes)

6:00 PM Rb10.1
The Micromote: A Tool for Nanofabrication. Qiaoing Xu and George M. Whitesides; Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts.

We will present a new, convenient technique to fabricate metal nanowires, and to manipulate them into arrays. This technique combines thin-film deposition by electron-beam with thin-film sputtering using a micromote. The procedure begins by embedding a thin metal film in an epoxy matrix. The resulting structure is sectioned in a plane perpendicular to the metal film using the diamond knife of a micromote. The cross-section of the metal wires encapsulated in these thin epoxy sections is then cut by the micromote. The thickness of the metal film (to values as small as 10 nm), and the thickness of microtome sections (as small as 50 nm). The embedded nanowires can be transferred and positioned onto a substrate by manipulating the thin polymer film. Etching removes the polymer film, and releases the wires. Sectioning generates multiple copies of the polymer slabs with similar thickness. We demonstrate the fabrication of crossed gold nanowires by transferring two epoxy thin film containing multiple nanowires successively on top of one another, and then removed the epoxy.

6:15 PM Rb10.2
Automated Large-Scale Scanning Probe Nanolithography: Macro and Mesoscopic Surface Patterning with Nanometer Resolution. Daan Winters1,2 and Ulrich S. Schubert1,2. 1Laboratory of Macromolecular Chemistry and Nanoscience, Eindhoven University of Technology, Eindhoven, Netherlands; 2Dutch Polymer Institute (DPI), Eindhoven, Netherlands.

Scanning probe patterning techniques such as dip-pen nanolithography (DPN) and oxidative probe lithography have been demonstrated to be very promising methods for the preparation of functional nanodevices. Using self-assembly techniques the created patterns can be locally modified, introducing chemical functionality on spatially defined spots on a substrate. Recently, a number of publications have been presented in which, for example, progress is reported towards the preparation of nanoscale electrical circuits, multi-component nanoparticle and protein arrays. However, for an industrially viable application of these techniques the fabrication speed has to be still further improved. In this contribution we present the application of an automated atomic force microscope for a largescale surface patterning. We demonstrate the principle by performing the automatic local probe oxidation of octadecyl trichlorosilane (OTS) monolayers on silicon substrates because this particular technique offers a very versatile platform for a broad range of subsequent surface modification reactions. When local probe oxidation is performed on a SAM of OTS, the terminal methyl groups in the OTS monolayer are converted into carboxylic acid (-COOH) functionalities. Subsequently the formed patterns of carboxylic acid groups can be used as a template in additional surface decoration steps. Using a tailor-made automated AFM with dedicated software and a programmable sample stage we have demonstrated automated patterning of large areas on a surface with very high resolution. Although the final results of the surface patterning still depend on tip quality and applied contact force, we have demonstrated the writing and subsequent surface functionalization of areas on a millimeter-squares. For example, using a single AFM-tip covering the gap from nanometer patterning to millimeter-sized applications. The surface oxidation may be performed in different modes. In the first mode the tip continuously rastered over the sample surface. In the second mode the tip follows a pre-defined vector trajectory over the surface without the need for pre-imaging the surface. The last method greatly enhances the tip-life and reproducibility of the results. The application of large scale, high-resolution surface patterning could be of great importance for applications such as sensors. Additional advantages of patterning large areas emerge from additional surface characterization techniques such as XPS that can be applied.

6:30 PM Rb10.3

Thin films of diblock copolymers have demonstrated strong potential as high-resolution lithographic templates in semiconductor microfabrication, as they are capable of defining smaller dimensions than conventional optical lithography. We have employed lithography and self assembly in a combined "top-down/bottom-up" fabrication technique to direct the self assembly of diblock copolymer thin films comprised of cylindrical and lamellar phases of poly(styrene-b-methylmethacrylate) (PS-b-PMAA). The resulting self-assembled nanowire arrays have 20nm widths and run micrometers in length. Moreover, these structures self-align to lithographically pre-patterned silicon and silicon nitride features. We have separately used this technique with three different PS-b-PMAA phase morphologies: cylinders, inverse-cylinders, and lamellae. We will discuss the differences between these three geometries and the relative advantages of each in semiconductor microfabrication.

6:45 PM Rb10.4
Investigating the Limits of Surface-Directed Self-Assembly of Pure Block Copolymers. Gregg M. Wilmes1,2, Nitash P. Balsara1,2,3 and J. Alexander Liddle2. 1Department of Chemical Engineering, University of California, Berkeley, California; 2Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California; 3Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory, Berkeley, California.

Block copolymers of appropriate molecular weights will self assemble into regular, ordered patterns with periodicities on the order of 5-100 nm. If the components of the block copolymers have sufficiently different properties, thin films of these copolymers on surfaces can be used as templates for nanolithography as a self-assembled, molecular ordering. Such patterning has great utility for a variety of applications such as fuel cells, batteries, optoelectronic devices, and flash memory. Although block copolymers do form regular structures, the sizes of these structures are relatively small and often randomly oriented throughout the sample. A combination of
top-down/bottom-up techniques is used to overcome these limitations. Advanced lithography is used to chemically modify a surface. The interaction between the block copolymer results in the formation of long-range order. Current technologies such as electron-beam lithography allow the patterning of arbitrary nanometer-scale features. Block copolymers of a given composition have an equilibrium morphology and domain spacing. Conforming to a surface pattern with features not corresponding to that equilibrium morphology will result in some energetic penalty due to polymer chain bending, stretching, compression, or curvature; if that penalty is too large the morphology will not be transferred to the solid substrate. Knowledge of the degree to which guided self-assembly of block copolymers is possible would be of great value for determining what sorts of patterns and devices can be constructed. We here report investigation of the guided self-assembly of block copolymer poly(styrene-block-methyl methacrylate) on a silicon-supported polystyrene brush patterned with electron-beam lithography and chemically modified with an oxygen/argon reactive ion etch. The etched domains are then provided to the polymer domain spacing of the block copolymer with perfect alignment to the patterned surface.

7:00 PM Rb 10.5
Generation and formation mechanism of functional mesoporous thinfilms of metal oxides with crystalline pore walls using novel block copolymer templates.
Torsten Brezesinski1 and Markus Antonietti2,1. Colloid Chemistry, Max Planck Institute of Colloids and Interfaces, Potsdam, Germany; 2Colloid Chemistry, MPI of Colloids and Interfaces, Potsdam, Germany.
Mesoporous metal oxide thin films have attracted significant attention due to their potential use in photocatalysis, redox reactions, electrochromic and color changing coatings, etc. The straightforward preparation method involves sol-gel chemistry in combination with a suitable structure-directing block copolymer. Typically, a substrate is dip-coated by a solution containing a metal salt (chlorides, etc.) as precursor, followed by the presence of a template, leading to the formation of the corresponding mesoporous oxide after temperature treatment. However, the fabrication of such films with entirely crystalline walls (e.g. TiO2, CeO2) was reported to show severe difficulties due to mesostructural collapse and several metal oxides (e.g. SnO2, Fe2O3, H2O2, WO3, MoO3) have not been reported at all as well-ordered mesostructured films. In the present study, a general new methodology is introduced for the generation of such films, taking advantage of a novel type of block copolymers (KLE) in combination with suitable temperature treatment conditions. KLE was synthesized in our institute and has a hydrophilic PEO block and a poly(ethylene-co-butylene) hydrophobic block, thereby possessing advanced templating properties in terms of the thermal stability and hydrophilic-hydrophobic contrast [1,2]. The block lengths were designed to be long enough to allow for sufficiently thick walls, i.e. nanocrystals in the pore walls of at least 5 nm, being compatible with the nuclear properties of the in the wall without disrupting the mesostructure. bcc or fcc cubic mesostructures were obtained by the KLE polymers used in this study. The crystallisation mechanism and mesostructural changes (lattice contraction) upon temperature treatment was observed by the combination of Small-angle x-ray scattering (SAXS/WAXS). These studies revealed that the main benefit of this type of polymers is the higher temperature stability compared to recently used polymers such as Pluronics F127: the polymer (or its mixture) is able to intercalate into still highly ordered mesopore structure of an amorphous and almost dried metal oxide at ca. 400 deg C, which is then converted into its crystalline counterpart in a solid-solid transition, contrary to previous assumptions. Based on these insights, well-ordered mesostructured films SnO2, H2O2, CeO2, MoO3 and WO3 were achieved, and this concept even allowed for the facile preparation of mesoporous metal oxides undergoing crystalline-crystalline transformations: For the first time, the KLE polymers enabled the fabrication of mesoporous goethite, even tolerating the conversion into mesoporous hematite. The mesopore and crystallinity were studied by a new evaluation SAXS approach, in combination with Electron Microscopy, Atomic Force Microscopy, nitrogen and krypton sorption, providing the aspect ratio of the deformed spherical pores. [1] Thomas et al. Langmuir 2003, 19, 4455. [2] Smarsly et al. Chem. Mater. 2004, 16, 2948.

7:15 PM Rb 10.6
Placement Accuracy of Directed Self-assembled Block Copolymers.
Joy Y. Cheng1, Fong Zhang2, Filip Ilicvski1, Edwin L. Thomas1, Henry I. Smith3, G. Julius Vancso4 and Caroline A. Ross1.
1Material Science, MIT, Cambridge, Massachusetts; 2Electrical Engineering and Computer Science, MIT, Cambridge, Massachusetts; 3Materials Science and Technology of Polymers, University of Twente, AE Enschede, Netherlands.
The self-assembly process is a simple and low cost method to produce large-area nanostructures. However, self-assembled block copolymer thin films typically contain a population of uncontrolled defects and therefore lack long-range order. To solve this problem, many studies on the achievable placement accuracy of these templated self-assembled nanostructures. We investigated the placement accuracy and pattern registration of arrays of polystyrene (PS) -β-polyferrocenylmethylsilane (PFS) spherical block copolymer films on the one-dimensional and two-dimensional topographically patterned substrates. Our experiments showed that placement errors originate from both template edge roughness and fluctuations in the size and spacing of polymer domains. Placement errors of the polymer domains near the edge of the template are proportional to the template roughness. On the other hand, positions of the center polymer domains are almost unperturbed by the template roughness, because polystyrene domains tend to maintain an individual domain order at the center of the groove. Fluctuations in the size and spacing of the polymer domains provide another source of placement error. The size and spacing distribution of block copolymers can be narrowed, but not eliminated by the use of a template. Therefore, intrinsic fluctuations in the polymer determine the ultimate placement accuracy in directed self-assembled block copolymers. We have quantified the order in templated polymer arrays, and showed that placement error of about 3 nm was achieved using a two-dimensional template.

7:30 PM Rb 11.2
Directed Self-Assembly of Block Copolymer Blends for Patterning at the Nanoscale.
Mark P. Stoykovich1, Marcus Mueller2, Sang Ouk Kim1,2, Hasun Han, Solak3, Erik W. Edwards1, Juan J. de Pablo1 and Paul F. Nealey1. 1Department of Chemical and Biological Engineering, University of Wisconsin, Madison, Wisconsin; 2Center for Biophysics, University of Wisconsin, Madison, Wisconsin; 3Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Daejeon, South Korea; 4Laboratory for Micro- and Nanotechnology, Paul Scherrer Institute, Villigen, Switzerland.
The fabrication of microelectronic and photonic devices with nanometer scale features has traditionally utilized the photolithographic process. The properties and characteristics of the lithographic technique include the ability to 1) produce high resolution patterns over large areas, 2) place and register features with exacting tolerances and margins, and 3) pattern features of nonregular geometries. Current lithographic processes and materials breakdown, however, and cannot be extended to the fabrication of devices with features having 30 to 50 nm critical dimensions. Consequently, our group is pursuing novel approaches for integrating self-assembling materials into traditional nanomanufacturing processes and overcoming the limitations encountered by photolithography at sub-50 nm dimensions. We have recently demonstrated a patterning technique involving the directed self-assembly of block copolymers on chemically nanopatterned surfaces with tailored interfacial interactions. The defect-free ordering of block copolymer domains has been achieved over arbitrarily large areas and in registry with the lithographically-defined underlying surface pattern. This hybrid approach, known as directed assembly, involves the use of top-down advanced exposure tools (pattern perfection and registration via the surface pattern) to the principles of bottom-up molecular self-assembly (thermodynamic control over the structure organization and dimensions). Symmetric ternary blends consisting of a block copolymer and its corresponding homopolymers are also suitable materials for directed self-assembly. Block copolymer-homopolymer blends, although similar in most respects to pure block copolymers, hold distinct advantages for patterning applications. First, the characteristic length scale of the self-assembled structures can be finely tuned by adjusting the blend composition. We have therefore characterized the polymer physics and fundamental phase behavior of ternary blends in thin films and on chemical surface patterns for a wide range of blend compositions. Second, the ternary blend domains can be directed to self-assemble into nonregular device-oriented geometries such as nested arrays of sharp bends, arcs, and T-junctions. We demonstrate, via mean field simulations, that the localized redistribution of homopolymer within the blend domains greatly facilitates the defect-free self-assembly of these nonregular structures. The ability to pattern a variety of geometries suggests that fabrication methodologies based on self-assembling materials such as ternary blends will become increasingly important for the manufacturing of complex devices at the nanoscale.

7:45 PM Rb 10.8
Control of Colloidal Crystal Growth by External Fields.
Siegfried Greulich-Weber, Elisabeth von Rhein and Paul Mieles;
Physics, University of Paderborn, Paderborn, Germany.
Since the introduction of the concept of a photonic crystal much effort has been targeted at producing 3D photonic crystals working in the visible wavelength region. The most promising way is by self-assembly of monodisperse sub-micron spheres made of silica or organic materials resulting in fcc and hcp colloidal crystals. However, the large scale fabrication and thus their application in photonics suffer from the reproducible growth of defect-free extended bulk crystals. Commonly used ‘natural’ sedimentation is unacceptable low and often results in low crystal quality showing cracks and stacking faults or reveals a disordered bulk below an apparently ordered surface. On the other hand preorganization procedures are much faster, however, provide only thin layers. In literature there are several examples, where additional external fields such as electric or acoustic fields were applied, which to a certain extent enhanced the crystal quality. However, the reproducibility of such experimental procedures is not enough to allow a reliable control over the crystal growth. We will present details of our computer controlled crystal growth experiments using specific external fields. In classical crystal growth methods (e.g. Czochralski-growth), one uses a crystal growth method. In analogy, we use acoustic noise gradients instead of temperature gradients for optimizing crystal growth. We systematically investigated various bandwiths, frequencies and amplitudes of acoustic noise fields. The crystal growth and evaporation of the suspension is monitored by CCD-cameras and thus computer-controlled. Such colloidal crystals made of PMMA, PS or silica nano-spheres are practically free of dislocations. The crystal quality only depends on the monodispersity of the nano-spheres used.

SESSION II: Ra1, Rb1, Poster Session II
Chair: Federico Rosei
Tuesday, November 29, 2005
8:00 PM
Exhibition Hall D (Hynes)

Ra11.1/Rb11.1
Capillarity-Driven Colloid Self-Assembly in Shallow Nanoscale Surface Corrugations. Anant Mathur and Jonah Erlebacher; Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland.

Ordering of submicron spheres after evaporative deposition from colloidal suspension on shallow corrugated substrates with optical wavelengths and nanoscale amplitude was examined. The spheres were found to deposit overwhelmingly in the valleys of the surface corrugations rather than their peaks, even when the amplitude of the substrate features was a few nanometers, nearly 100 times smaller than the sphere diameter. The behavior is found to arise from capillary forces on the spheres when the colloidal thin thickness is of order the sphere diameter. The observation that substrate features significantly smaller than the sphere diameter can influence deposition morphology may lead to simple methods to create large domains of order in colloidal crystals.

Ra11.2/Rb11.2

Raman spectroscopy is a common tool used to characterize the composition of nanotube devices and probe the effectiveness of electronic separation schemes. Raman spectroscopy of single-walled carbon nanotubes (SWNTs) suspended using common aqueous surfactants and DNA has been performed for both liquid suspensions and nanowires prepared by dielectrophoretic isolation. Characteristic peaks in the radial breathing modes, disorder mode, and tangential mode have been explored as a function of aggregate state, surfactant presence, and pH. Analysis of both Stokes and Anti-Stokes spectra under these various environmental conditions has been performed in the context of resonance shifts, charge transfer effects, and SWNT electronic separation.

Ra11.3/Rb11.3
Abstract Withdrawn

Ra11.4/Rb11.4
Conjugate of Cytochrome-c and Monolayer Protected Gold Nanoclusters. Chinmay P. Sonan1, Brian Huffman2, Madalina Ciobaniu2, Aren Gerdes2, M. Danielle Garrett2, Mark Grossclos2 and David Cliffel2; 1Interdisciplinary Materials Science, Vanderbilt University, Nashville, Tennessee; 2Department of Chemistry, Vanderbilt University, Nashville, Tennessee.

We present evidence for the synthesis of a nanoparticle-protein conjugate. This novel nanomaterial can potentially offer new opportunities in molecular electronics, molecular recognition, and biomaterials synthesis. Cytochrome-c was modified using Traut's reagent (2-iminothiolane hydrochloride) - resulting in a sulfhydryl-terminated linker and place exocyclic amino groups on the tiopronin (n-(2-mercaptopropiony1)glycine) molecules on tiopronin monolayer protected gold nano-clusters. The reaction mixture was separated on a carbamothioxycellulose column. Cyclic voltammetry and near infrared wave voltage experiments on the protein conjugate clearly indicates that the conjugated cytochrome-c is electrochemically active. The conjugate is also quite stable and does not show any loss of activity for over a week. Results from chronomonomere, dynamic light scattering particle size measurement, nuclear magnetic resonance, and circular dichroism provide additional evidence for conjugate formation.

Ra11.5/Rb11.5
Novel Electrical Switching and Logic in Y-Junction Carbon Nanotube Nanosheet. Prab Bandara1, Chiara Daraio2, Sung Ho Jin1 and Apparao Rao1; 1Materials Science & Engineering, University of California at San Diego, La Jolla, California; 2Department of Physics, Clemson University, Clemson, South Carolina.

To realize a truly integrated nanoelectronic architecture, it is desirable to have nanoelectronic elements to harness new functionalities peculiar to nanomaterials such as a novel Y-junction carbon nanotube (CNT) configuration, which contains a built-in, three-way-operable gate structure. The presentation focuses on the implementations of unique electrical properties of a multi-ways Y junction (MWNT) Y-junction which is grown by modified chemical vapor deposition (CVD) processes(1). Through this work, we are enabling and adding a new functionality, i.e., switching to nanotube electronics making an overall CNT based nanoelectronic architecture more complete and feasible. We show evidence for a dramatic electrical switching behavior in a nano-particle-containing Y-junction carbon nanotube morphology(2). We observe, for the first time, an abrupt modulation of the current from ON to OFF state, primarily mediated by defects and the topology of the junction. The mutual interaction of the electron currents in the three branches of the Y-junction is shown to be the basis for a potentially new, three-way logic element. This is the first time ever that such switching and logic functionalities have been experimentally demonstrated in Y-junction nanotubes, without the need for fabrication of an external gate. Previously, only a diode like behavior was observed in Y-junctions. An entirely new class of nanoelectronic architecture and functionality, which extends well beyond conventional field effect transistor technologies, is now possible. (1) N. Gotzard, C. Daraio, J. Gaillard, R. Zidan, S. Jin, A.M. Rao, Controlled growth of Y-junction nanotubes using Ti-doped vapor catalyst, Nano Letters vol.4, 213-217 (2004). (2) P. R. Bandara, C. Daraio, S. Jin, and A.M. Rao, Novel Electrical Switching Behavior and Logic in Carbon Nanotube Y-Junctions, Nature Materials vol.4, 2005 (in press).

Ra11.6/Rb11.6
Characterization of transparent and conductive single-walled carbon nanotube thin films. Hussn Enamul Unalan, Aurelien Du Pasquier, Giovanni Fanchini and Manish Chhowalla; Materials Science and Engineering, Rutgers University, Piscataway, New Jersey.

Single-walled carbon nanotube (SWNT) thin films devices provide an alternative to individual SWNT devices. Uniform and reproducible SWNT thin films can be deposited over several centimeters, allowing fabrication of devices over large areas. Several methods are being employed for the fabrication of SWNT films, including the recently reported vacuum filtration method [1]. Although the device characteristics of the SWNT thin films have been characterized[2], no detailed investigation of the film properties has been reported. In this work, we will present a detailed analysis of the SWNT thin film properties using the vacuum filtration method. We will investigate the variation of the SWNT thin film properties as a function of the film thickness and the nanotube concentration in the filtrate solution. The SWNT thin films were found to be highly transparent and conductive with values comparable to indium tin oxide (ITO) [3]. Specifically, at the lowest nanotube concentration, the transmission of the SWNT thin films exceeded the values of ITO. The SWNT thin films were always found to be more transparent in the UV compared to ITO. The transmission and resistace of the SWNT thin films were found to decrease with the thickness of the film and concentration of the SWNT thin film solution. The SWNT thin films have a highly porous structure which can be used to explain the optical and electrical properties. We will also present our thin film transistor characteristics which show an on-to-off ratio of 10^4 and mobility of ~1cm^2/Vs. [1] Z. Wu, Z. Chen, X. Du, J. M. Logan, J. Sippel, M. Nikolou, K. Kamaras, J. R. Reynolds, D. B. Tanner, A. F. Hebard, A. G. Rinzler, Science 305 (2004) 1273. [2] E. Artukovic,
Nanostructure lithography (NSL) has become widely used for preparation of nanowires. Ordered nanowires, including nanowires of semiconductor nanostructures (NW), are usually realized on sapphire substrates, using the self-assembled polystyrene spheres as masks. However, the low-temperature deposition of Au nanowires on the polystyrene sphere template is not a suitable method for obtaining nanowires of high quality. In contrast, Au nanowires grown on Si substrates are of high quality with regard to size and shape. In this paper, we report the deposition of Au nanowires on Si substrates using the self-assembled polystyrene sphere template. The results show that the Au nanowires grown on Si substrates are of high quality with regard to size and shape. In addition, the Au nanowires grown on Si substrates are able to be used as templates for the deposition of other materials, such as gold, silver, and copper. This method can be used for the growth of a variety of materials, including metals, semiconductors, and insulators. The Au nanowires grown on Si substrates can be used for the fabrication of nanostructures, such as nanowires, nanotubes, and nanowire networks. These structures can be used for a variety of applications, such as electronic devices, sensors, and photonic devices. In conclusion, the Au nanowires grown on Si substrates using the self-assembled polystyrene sphere template are of high quality with regard to size and shape. This method can be used for the growth of a variety of materials, and the Au nanowires grown on Si substrates can be used for the fabrication of nanostructures.
water-proofing, self-cleaning and anti-fouling capabilities. Superhydrophobicity requires a low surface energy as well as a high surface roughness. We recently found that an electrospun fiber mat had the appropriate surface roughness for superhydrophobicity. We have developed several strategies to produce superhydrophobic fabrics via electospinning. The first strategy is to electropin a hydrophobic material (polyethylene-dimethyldialkoxide) block copolymer. Contact angle measurements indicate that the resultant nonwoven fibrous mats are superhydrophobic, with a contact angle of 163° and contact angle hysteresis of 15°. The superhydrophobicity is attributed to the combined effect of the enhanced confinement of water molecules by X-ray photoelectron spectroscopy and surface roughness of the electropun mat itself. The second strategy is to combine electropinning and initiated chemical vapor deposition (CVD). A selected polymer was electrospun into fibers with different diameters and then coated with a thin layer of hydrophobic polymerized fluorocarlylate by using CVD. The hierarchical surface roughness inherent in the electropun mats and the low surface energy of the coating resulted in superhydrophobicity with a contact angle as high as 175°. Some other strategies have also been developed. The effect of fiber morphology on superhydrophobicity will be discussed.

**Ra11.12/Rb11.12**

**Aqueous Phase Laser Ablation Chemistry (APLAC) for Synthesis of Co-Pt Nanoparticles.** R. K. Rakshit and R. C. Bhowmik, Department of Physics, Indian Institute of Technology - Kanpur, Kanpur, UP, India.

**Ra11.13/Rb11.13**

**CNT formation process from 6H-SiC (000-1).** Takahiro Maruyama1,2, Yasuyuki Kawamura1, Hyungjin Baeg1, Naomi Fujita1, Tomonori Shiraishi1, Kenji Tanioku1, Yoko Horumi1, Shiyea Narusaka1,2 and Michiko Kusunoki2,1. Dept. of Materials Science and Engineering, Meijo University, Nagoya, Japan; 2Meijo University, 21th COE program, Nagoya, Japan.

It has been reported that carbon nanotubes (CNTs) were formed through the decomposition of SiC(000-1) surfaces by heating in a vacuum. By the well-oriented zigzag-type CNTs can be selectively grown without any catalysts and the diameters of these CNTs are fairly uniform. Although some studies have been reported on the formation mechanism of CNT from SiC surfaces, a detailed mechanism of the initial stage of CNTs growth has not yet been clarified. In this study, we investigated the decomposition of 6H-SiC (000-1) surfaces and the formation process of CNT by using scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS). After being etched with hydrofluoric acid (10%), 6H-SiC(000-1) samples were annealed at various temperatures between 1000 and 1700 °C. Contact angle hysteresis of the SiC surface has been reduced and then high vacuum (UV) (≤1×10⁻⁷ torr). Then, STM observation and XPS measurements were carried out to investigate their surface structures and chemical species. In order to investigate the initial stage of the formation of CNT clearly, we carried out STM observation for SiC annealed in high vacuum (UV) (≤1×10⁻⁷ torr). STM images were obtained with a tip bias in the range of 3.0–3.0 eV and a tunneling current in the range of 0.05–0.3 nA. XPS measurements were performed at 90° and 150° off-angles to change the depth of photodetection electron. From the results of XPS measurements for the samples annealed in a vacuum electric furnace, the increase of O is peak intensity was seen at 1000 and 1100°C. The peak deconvolution analysis showed the oxidation of the SiC surface. The SiO₂ layer was found, the graphite-like carbon appeared on the surface at 1150°C. After annealing at 1200°C, CNT nano-cap structures were observed by STM. On the other hand, the samples annealed under UHV showed an appearance of nano-size amorphous carbons even below 1000°C, where no oxidation was occurred, and the formation of CNTs was also confirmed above 1200°C. So, we consider that these nano-size amorphous carbons transformed into nano-cap structures around at 1200°C. It is also confirmed that the diameter of nano-size amorphous carbon determined the size of nano-caps formed at the initial stage and eventually the size of CNTs.

**Ra11.14/Rb11.14**

**SAXS of Self-Assembled Mesostructured Films With Oriented Lamellae, 2D Cylinder Arrays or Spheres: an Advanced Method of Evaluation.** Bernd Smarsly, Colloid Chemistry, Max Planck Institute of Colloids and Interfaces, Potsdam, Germany.

The present work is dedicated to a further developed general analysis of the small-angle x-ray scattering (SAXS) of oriented metal oxide mesostructured films of lamellae, 2D hexagonal arrays of cylinders and cubic lattices of spheres (micelles or mesospheres), measured in symmetrical reflection (SRXSAXS). The main goal is to establish a general approach for a quantitative structural characterization of such mesostructures, complementing microscopic techniques of absorption. It is demonstrated that SRXSAXS data can be effectively fitted using well-chosen scattering functions with physically reasonable parameters, which can be easily implemented on standard software. As the only preconditions, the method requires a high accuracy of intensity measurements of films in reflection mode over several decades, which are accessible from standard laboratory x-ray reflectivity setups. Various relevant structural parameters describing the mesostructure (mesopore or micellar diameter, its polydispersity, lattice parameter, lattice distortions, average stack height, etc.) can be extracted from SRXSAXS curves by fitting with models based on lamellae, arrays of cylinders or spheres. In particular, our method allows for a quantification of the polydispersity of the nanodomains (lamellae, cylinders or spheres), which was neglected previously. As a further improvement, our approach provides the degree of preferred orientation with respect to the substrate. Such analyses were applied to various types of mesostructured coatings. Evaporation-Induced Self-Assembly using CTAB (lamellar mesostructures), non-ionic Brij surfactants (cylinders being oriented parallel to the substrate) and block copolymers (KLE, bcc spherical mesostructures) as structure-directing agents. The KLE block copolymers enabled the preparation of mesoporous, crystalline films of various metal oxides such as titania, WO₃, SnO₂ and MoO₃ [1]. The data were acquired from both synchrotron (APS) and laboratory reflectivity setups. In combination with SAXS in grazing incidence geometry, the method results in a comprehensive characterization of the mesostructures providing accurate values for the radius, the lattice parameter, their variances and the average stack height, while most of the previous analyses are only determined by model assumptions. As a main benefit, this SAXS methodology allowed for the first time the differentiation between the thermally induced distortions of the mesopores and those of the pore walls, which gave further insights into the crystallization mechanism of metal oxides within the confinement of the mesostructure. Also, the pore sizes obtained from the SRXSAXS analysis were in good agreement with independent physiosorption measurements and microscopic analyses (AFM, TEM), proving the general suitability of the approach. [1] Smarsly et al. Langmuir 2005, 21, 3858-3866. [2] Smarsly et al. Chem. Mater. 2005, 17, 1683-1690.

**Ra11.15/Rb11.15**

**The Formation of Polyelectrolyte Multilayer Films at Interfaces between Thermotropic Liquid Crystals and Aqueous Phases.** Nathan A. Lockwood1, Katie D. Cadwell2, Frank...
Caruso2 and Nicholas L. Abbott1; 1Chemical and Biological Engineering, University of Wisconsin, Madison, Wisconsin; 2Chemical and Biological Engineering, University of Melbourne, Melbourne, Victoria, Australia.

We report the formation of polyelectrolyte multilayer (PEM) films at interfaces between aqueous phases and thermotropic liquid crystals. These experiments employ a planar interface between the nematic liquid crystal 4-pentyl-4-cyanobiphenyl (5CB) and an aqueous solution, and sequential contact of the interface with the polyelectrolyte (sodium poly(4-styrenesulfonate) (PSS)) and poly(allylamine hydrochloride) (PAH). The results of our study demonstrate that 1) despite the mobility of the polyelectrolytes at the fluid aqueous-5CB interface, PEM films grow in a linear fashion with sequential contact between the polyelectrolytes; 2) the PEM film is coupled to the orientations of the liquid crystal and preserves the orientation even when the aqueous phase is removed and the interface is dried in air; and 3) the presence of the PEM film at the aqueous-liquid interface can alter the interactions of a solute present in the aqueous phase (sodium dodecyl sulfate) with the interface of the liquid crystal. These results identify new methods for preparing PEM films and studying their organization at fluid interfaces. The results also provide new approaches to controlling the interfacial chemical functionality of liquid crystals.

Ra11.16/Rb11.16
Ignition in Al-Fe2O3 Nanocomposites.
Bhargava Ram Kanchibotla1, Sridhar Patibandla2 and Latika Menon1; 1Physics, Northeastern University, Boston, Massachusetts; 2Electrical Engineering, Virginia Commonwealth University, Richmond, Virginia.

Novel energetic nanocomposites have been fabricated which undergo an exothermic reaction when ignited at moderate temperature. The nanocomposites are a mixture of Al (fuel) and Fe2O3 (oxidizer) where Fe2O3 is dispersed in thin, soft polymer (PSS) films as the thin Al film. We have achieved very high packing density of the nanocomposites, precise control of oxidizer-fuel sizes at the nano scale level and direct contact between oxidizer and fuel. Ignition in these nanocomposites has been demonstrated using several different methods. Ignition properties such as flame temperature, energy release have been studied and results will be reported.

Ra11.17/Rb11.17
Determining the mechanism for polymer-controlled inorganic nanoparticle synthesis. Nili Dan1 and Rina Tannenbaum2; 1Chemical and Biological Eng., Drexel University, Philadelphia, Pennsylvania; 2Materials Science and Eng., Georgia Inst of Technology, Atlanta, Georgia.

One of the challenges in the synthesis of inorganic nanoparticles is the need for a methodology that can produce monodisperse particle populations that resist re-precipitation. Studies have shown that the synthesis of inorganic nanoparticles in polymeric media (suspensions of bulk) yields narrow particle size and morphology distributions under ambient conditions. Moreover, the particles thus formed are sterically stabilized and adsorbed on polymeric particles. Despite these successes, the mechanism by which polymers control the aggregation and formation of nanoparticles is not understood. Here we present a combined experimental and theoretical study of the kinetics of nanoparticle formation in polymeric media. We show that contrary to expectation, the particle properties are set by the kinetics of nucleation and growth, rather than through an equilibrium capping mechanism.

Ra11.18/Rb11.18
Close-packed Nanoparticle Arrays as Surface Enhanced Raman Spectroscopy (SERS) Substrates. Hui Wang1,2,3 and Naomi J. Halas4; 1Department of Chemistry, Rice University, Houston, Texas; 2Department of Electrical and Computer Engineering, Rice University, Houston, Texas; 3The Laboratory for Nanophotonics (LANP), Rice University, Houston, Texas.

Using plasmonic nanostructures to control and optimize the surface enhanced spectroscopies has been the focus of increasing attention over the past few years as the spectroscopy-based molecular identification methods have widespread applications in chemical and biological sensing. Efficient control of close-packed nanospheres is achieved through the fabrication of closed-packed nanostructures. Raman spectroscopy (SERS) as an analytical tool depend on the methods for fabricating substrates with high sensitivity, stability, and reproducibility of the SERS signals. Using periodic nanostructured substrates for SERS measurements can provide quantitative correlations between surface structures and SERS enhancements. We exploit a convenient and cost-effective approach to the self-assembly of cetyltrimethyl ammonium bromide (CTAB)-capped Au nanoparticles into highly ordered close-packed Au nanoparticle arrays on solid substrates using a solvent evaporation method. The as-fabricated nanoparticle arrays display an intense plasmon band in the near-infrared region that overlaps with the plasmon coupling between adjacent nanoparticles. Such interparticle electromagnetic coupling produces enormous near-field enhancements at the junctions between neighboring nanoparticles, creating uniform periodic densities of “hot spots” which can be exploited for large SERS enhancement. From the electromagnetic point of view, these nanoparticle arrays can be regarded as “inverse Van Duyne lattices”, possessing similar but complementary near-field properties to the triangular arrays fabricated using nanosphere lithography. Moreover, the high periodicity of the arrays also provides a useful model for detailed studies of the correlations between localized near-field electromagnetic properties and spectroscopic enhancements. The SERS performance of the close-packed Au nanoparticle arrays is quantitatively and systematically evaluated by using para-mercaptoaniline (pMA) and dye molecules as the probing molecules.

Ra11.19/Rb11.19
Nanotubes in spray deposited Nanocrystalline HgTe:Thin films. Ranga Rao Arunapalli1 and Vireesh Dutta1; 1Centre for Energy Studies, Indian Institute of Technology, Delhi, New Delhi, New Delhi, India; 2Centre for Energy Studies, Indian Institute of Technology, Delhi, New Delhi, New Delhi, India.

Mercury Telluride is a narrow bandgap semiconductor, with a direct bandgap of 0.15eV at room temperature. The Bohr exciton radius of HgTe is 40 nm and it is possible to observe quantum confinement effects more easily. HgTe nanostructures may find wide applications in fabricating nanoelectronic devices for telecommunications, optoelectronic devices and sensors etc. Since the conduction band of HgTe is p-type, making it n-type can help design novel nanosize devices. Iodine is known to be an n-type dopant in CdTe and Hg1-xCdxTe. Therefore, HgTe nanoparticles prepared using Solvothermal method has been doped with Iodine. Doped HgTe nanotubes with different source materials (Hg and Te compounds) yield HgTe: I nanoparticles. Thus prepared nanoparticles are dispersed in L-Butanol for spray solution. The solution, sprayed to the glass substrates kept at 200°C in ambient air for 20 min. The deposition is done without and with a voltage applied to the nozzle during this period. The films are characterized for structural, morphological and compositional properties. The thermo-voltage generated in the hot probe method shows that the hot end is positive compared to the cold end, which confirms that the electrons are the majority carriers in the films. In comparison, the undoped HgTe nanocrystalline films show a negative voltage at the hot end, since they are p-type. The surface morphology of the films (SEM and TEM images) shows the nanotubes morphology; in addition non-tubular nanostructures are also found. The TEM images of the films show the nanotubes with average diameter of 50 nm and up to several microns long. The SAD patterns recorded on the nanotubes show the cubic phase HgTe nanotubes, with lattice parameter a = 0.6452 nm. X-ray diffraction patterns of the films also show the cubic phase (111) HgTe dominant peaks in both the samples in the EDAX spectra confirm the presence of HgTe in the ratio 51:49. In summary for the first time we report on the synthesis of HgTe nanostructures in spray deposited nanocrystalline iodine doped HgTe thin films. The role presence of iodine seems to be helpful in creation of the nanotubes. Reference: Arunapalli R, Vireesh Dutta, “Synthesis of mercury cadmium telluride nanoparticles by solvothermal method” Proceedings of Materials Research Society 2005, spring meeting (Symposium Y).

Ra11.20/Rb11.20
The Evolution of Vesicles from Bulk Lamellar Gels. Anthony J. Ryan and Giuseppe Battaglia; Department of Chemistry, The University of Sheffield, Sheffield, United Kingdom.

The remarkable ability of phospholipids to generate vesicles and lamellar morphologies has been recently mimicked by amphiphilic block copolymers. However, the formation of block copolymer lamellar structures in water has always been studied at low concentrations (vesicles) and at high concentrations (lamellae stacks). The self-assembly of the amphiphilic poly(ethylene oxide)-co-poly(butylene oxide) block copolymer has been investigated using the different morphologies formed at different concentrations. In analogy with lower molecular weight membrane formers, phospholipids, at high concentration in water, phase progression from lamellae to spherical phase has been observed. Particularly, the spherical phase has been found to have ordered domains with 53nm arrangements. At intermediate concentrations, when the system turns from gel to liquid, the sponge-53nm phase breaks up into gel-cluster made of the regular packing of vesicles. Small Angle X-ray Scattering (SAXS) and Transmission Electron Microscopy (TEM) have revealed that such clusters have an hexagonal-closed packed structure. Vesicles have therefore been observed to form when the copolymer-water systems have still long-ranged order. Eventually, at very low concentration, the
packed vesicles separate generating very stable isotropic dispersions.

**Ra11.21/Rb11.21**

**Electrospinning of Block Copolymers for Synthetic Muscle Fabrication. Anthony J. Ryan, Linge Wang, Paul Topham and Colin Crook; Department of Chemistry, The University of Sheffield, Sheffield, United Kingdom.**

We have previously demonstrated wholly synthetic muscles based on the coupling of a triblock copolymers comprising hydrophobic end blocks and a pH responsive mid-block with a chemical reaction that oscillates pH. Thus triblock copolymers have been used to produce self-assembled polymer gels where the responsive shape change deformation of the molecules can be used to covert chemical energy into mechanical force. The process can be followed directly by SAXS and a correlation between the change in mass and deformation has established. The deformation process is affine and the power output of these devices has been measured. Comparisons to molecular and macroscopic motors show that shape change polymers are diffusion dominated whereas the current work (and previous work) are limited by diffusion. The creation of responsive nanofibres by electrospinning allows faster equilibration and therefore greater power output. The processing technology required to produce aligned bundles of triblock copolymer nanofibres will be described and the response of such assemblies to pH changes characterised.

**Ra11.22/Rb11.22**

**Designing planar elastic sheets which self-assemble under electrostatic forces. Silas Allen and Michael P. Brenner; DEAS, Harvard, Cambridge, Massachusetts.**

A recent work by Boncheva et al. (Proc. Natl. Acad. Sci. 2005 102: 3924-3929) has raised some basic issues about designable self-assembly within the context of planar elastic sheets which fold into 3D structures under magnetic forces. Among the important parameters are the dimension of the elastic sheet, the configuration of the aggregates, and the ratio of magnetic to elastic forces. We consider this problem using a numerical model of an elastic sheet, and restrict to the simpler case of electrostatic forces. We identify a simple algorithm for choosing configurations of electrostatic charges, and select ratios of charge strength to elastic energy using physical arguments. We then demonstrate our algorithm on unfoldings of a sphere and more general geometries.

**Ra11.23/Rb11.23**

**A novel solvothermal pathway for synthesis of metal/bimetallic nanocrystals. Bratindranath Mukherjee and Ravishankar Narayanan; Materials Research Centre, Indian Institute of Science, Bangalore, India.**

Synthesis of monodispersed metal/bimetallic nanoparticles and self-assembly of these on different substrates is of particular interest for technological applications such as nanoelectronics, magnetic storage devices, SERS substrate fabrication, optical grating and antireflective coating. A general solvothermal synthetic method has been developed to prepare noble as well as transition metal and bimetallic nanocrystals in a liquid medium. This is independent of the solubility of the salt or organometallic complexes used and nanoparticle can be produced in large scale. The nanoparticles produced are characterized using SEM, TEM, FTIR, VSM and XRD. Effect of temperature, duration of reaction, capping agent on nanoparticle size and shape has been studied in detail to understand the mechanism.

**Ra11.24/Rb11.24**

**Multifunctional Self-Assembled Mesoporous Silica Films: Novel Nanostructures for MEMS Applications. Hae-Kwon Jeong1, Ramesh Chandrasekharan2, Mark A. Shaunnon2 and Richard J. Mase1,2; 1Chemical and Biomolecular Engineering, Univ. of Illinois, Urbana, Illinois; 2Mechanical and Industrial Engineering, Univ. of Illinois, Urbana, Illinois; Electrical and Computer Engineering, Univ. of Illinois, Urbana, Illinois.**

Chip-scale devices are of great interest mainly due to their portability and novel functionality. One of the key components in such devices is functional porous film nanostructure. Despite recent development in silicon-based microelectromechanical systems (MEMS) technology, with current top-down micromachining it is still a technological challenge to fabricate such porous responsive nanostructure in a cost-effective way. Self-assembled mesoporous silica films can be an alternative to creating such nanostructure in a simple and controlled manner since they can be easily coated using conventional coating techniques [film between spin-coating and dip-coating], readily functionalized with functional organic groups, and are compatible with current silicon microfabrication technology. 3 Self-assembled mesoporous silica materials (in the form of powder or film) have drawn a great deal of research interest over the last decade. Their unique pore structures of nanometer dimension enable them to find applications in separation, catalysis, encapsulation, chemical/biological sensing, low-dielectric coating, and optical thin films. In order to use the mesoporous films for MEMS applications as novel nanostructures, one has to solve several challenging problems. Such problems include: 1) to deposit continuous films of thickness of several micrometers in a facile way and 2) to fabricate freestanding films by microfabrication techniques for certain MEMS applications such as micro fuel cells. In this talk, we will introduce a new way to prepare continuous mesoporous films of 2-3 micrometer thick using a layer-by-layer rapid thermal processing technique. We will also talk about the preparation of self-supporting mesoporous films on a silicon wafer using standard microfabrication techniques. The characterization of the microstructures of the mesoporous films will be presented. The functionality of the self-supporting mesoporous films will be demonstrated by fabricating direct formic acid micro fuel cells and measuring performance. 1. Madou, M. J. Fundamentals of Microfabrication: The Science of Miniaturization (CRC Press, New York, 2002). 2. Edler, K. J. & Itoga, D. J. 2002. Characterization of mesoporous silica films. International Reviews in Physical Chemistry 20, 387-466 (2001). 3. Brinker, C. J. & Scherer, G. W. Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing (Academic Press, San Diego, 1990). 4. Beck, J. S. et al. A New Family of Mesoporous Molecular-Sieves Prepared with Liquid-Crystal Templates. Journal of the American Chemical Society 114, 10834-10835 (2002). 5. Soler-Illia, G. J. D., Sanchez, C., Lebeau, B. & Patra"in, J. Chemical strategies to design textured materials: From microporous and mesoporous oxides to nanocomposites and hierarchical structures. Chemical Reviews 102, 4093-4138 (2002).**

**Ra11.25/Rb11.25**

**Super compositions of metallic carbon nanotubes exhibiting dielectric constant enhancement. Jakub Rybczynski1, Yang Wang1, Glynda Benham2, Maciej Olek3, Michael Giersig3, Krzysztof Kempi3 and Zhifeng Ren1; 1Physics Dept., Boston College, Chestnut Hill, Massachusetts, 2CAESAR Institute, Bonn, Germany; 3Mesgawave Corp, Boylston, Massachusetts.**

We studied dielectric properties of composites made of isolated, aligned metallic carbon nanotubes distributed in a dielectric matrix, in the radio-THz frequency range. We find that properties of these composites depend crucially on the shape and orientation of nanotubes. Therefore, the elongated nanoparticle (carbon nanotubes) produce composites with an enhanced real part of the dielectric function, and a moderate loss. Studies of dielectric properties of such composites will be presented.

**Ra11.26/Rb11.26**

**Self-assembly in solutions of monodisperse cylindrical macromolecules. Nicolin E. Davis1, Michael A. Zhareve2, SonBinh T. Nguyen3 and Ilya Koltover1; 1Department of Chemical and Biological Engineering, Northwestern University, Evanston, Illinois; 2Chemistry Department, Northwestern University, Evanston, Illinois; 3Laboratoire de Physique des Solides, Universite Paris Sud, Orsay, France.**

Molecular self-assembly is a promising tool for creating and controlling order at the nanoscale. Its utility depends on availability of macromolecules with well-defined nanoscale shapes and sizes. We have developed a biosynthetic strategy to prepare a new class of macromolecules, dendronized protein polymers (DPPs), that have well-defined cylindrical shapes with controlled molecular dimensions. The DPPs consist of an alpha-helical polypeptide core that determines the molecular length (L) surrounded by grafted wedge-shaped dendrons that control the diameter (D). The monodisperse polypeptides were expressed in E. coli from synthetic genes encoding polyglutamic acids gL with five discrete lengths n = 38, 58, 76, 94, 112. Three different generations of gL dendrons were also expressed to the carboxylic acid sidechains along the peptide backbone. The DPPs are soluble in many organic solvents, and in concentrated solutions, self-assemble to form highly ordered liquid crystalline (LC) phases. Formation of these LC phases is driven by excluded volume interactions between the rigid and identically-shaped DPPs, and the type of LC ordering is controlled by DPP aspect ratio (L/D) and concentration. Using small-angle X-ray diffraction and polarized optical microscopy we have observed chiral nematic, smectic, and hexagonal columnar phases in DPP/m-cresol solutions. The well-defined and controlled ordering of the DPPs extends to the nanoscale the tools of entropically-driven colloidal self-assembly, and shows the potential utility of combining biological and chemical synthetic tools towards preparation of new macromolecular blocks for nanoscience engineering.

**Ra11.27/Rb11.27**

**Measurements of Young’s Modulus of Ultrathin Polyelectrolyte Multilayer Films via Strain-Induced Buckling**
Instabilities, Adam J. Wolfe, Michael F. Rubner, and Robert E. Cohen:
1 Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; 2 Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

We have successfully adapted a recently-published buckling-instability method to model the modulus values of polyethylene multilayer (PEM) films over a range of film thicknesses from 20 nm to 180 nm. PEMs comprised of fully ionized poly(allylamine hydrochloride) (PAH) and poly(styrene sulfonate) (PSS) were deposited directly onto elastomeric substrates (poly(dimethylsiloxane)) (PDMS) and the modulus of the PEM-coated substrate produced a buckled surface.

The modulus of the PEM-coated silicon substrate was measured using a transmission electron microscope (TEM) and it was found that the stiffness of the PEM-coated substrate was significantly higher than that of the uncoated substrate. This effect was most pronounced at low film thicknesses, where the modulus of the PEM-coated substrate was found to be approximately four times that of the uncoated substrate.

We also demonstrate strategies for extending the buckling technique to PEM systems that may not be amenable to assembly directly on PDMS due to its high hydrophobicity, and show that pH control of the dipping condition of weak PEMs can lead to films with different structures and mechanical properties. The buckling instability technique is also applicable to a wide variety of systems outside the PEM field, and may be an ideal method for testing the mechanical properties of many other types of nanoscale films and assemblies.

Ra11.28/Rb11.28
Electronic structure of helically coiled carbon nanotubes. Gian Giacomo Guzman-Verri1, L. C. Lew Van Voon1, Morten Willatzen2 and Jens Gravesen2; 1 Department of Physics, Wright State University, Dayton, Ohio; 2 Mads Clausen Institute for Product Innovation, University of Southern Denmark, Sonderborg, Denmark; 3 Department of Mathematics, Technical University of Denmark, Lyngby, Denmark.

The electronic structure of single-wall helical nanotubes is obtained by means of the effective-mass theory. The approach followed in this work is similar to the one used by Ando et al.[1] for the case of a single-wall straight nanotube, that is, first by solving the Dirac's equation, second, by imposing appropriate periodic boundary conditions on the wave function, and third, by finding the eigenvalues of the effective-mass hamiltonian. The k.p method has been successfully applied in order to study the physical properties of straight carbon nanotubes. Ando and coworkers, for example, studied the spin-orbit interaction [2], the transport properties [3], the effects of impurities [4], the lattice instabilities [5], and the electron-phonon scattering [6] of these nanostructures within the k.p scheme.


Ra11.29/Rb11.29
Optical Thin Films with Very Low Refractive Index

The refractive index contrast in dielectric multilayer structures, optical resonators and photonic crystals is an important figure of merit, which creates a strong demand for high quality thin films with a very low refractive index. SiO2 nano-layered structures with low refractive indices n = 1.08, the lowest ever reported in thin-film materials, is grown by oblique-angle-of-bounce magnetron sputtering with a sufficient incidence angle θ = 85 degrees. Scanning electron micrographs reveal a highly porous columnar structure of the low-refractive-index (low-n) film. The gap between the SiO2 nanorods is 50 nm, i.e., much smaller than the wavelength of visible light, and thus sufficiently small to make scattering negligibly small. Optical micrographs of the low-n film deposited on a Si substrate reveal a uniform specular film with no apparent scattering. The unprecedented low index of the SiO2 nano-layer is confirmed both ellipsometry measurements and thin film interference measurements. A single-pair distributed Bragg reflector (DBR) employing the SiO2 nano-layer is demonstrated to have enhanced reflectivity, showing the great potential of low-n films for applications in photonic structures and devices.

Ra11.30/Rb11.30
Computational study of tethered nanocube assembly. Chih-Chen Chang1 and Materi....
of Notre Dame, Notre Dame, Indiana.

Basic understanding of optical and photoelectrochemical properties of semiconductor-carbon nanotube composites is important for developing light-energy conversion devices. Deposition of CdS nanoparticles on single-walled carbon nanotubes produces a photoactive composite when subjected to photodeposition following excitation with visible light. The luminescence of CdS is quenched by SWCNT. Ultrafast transient absorption experiments confirm the quick deactivation of excited CdS on the SWCNT surface as the excited state recovers in about 200 ps. Excitation of CdS deposited on SWCNT films produces photocurrent with a maximum incident photon to current generation efficiency of 0.3% and thus provides evidence for the electron transfer pathway in the composite. The ability of the CdS-SWNT nanocomposite system to undergo photoinduced charge separation opens up new ways to design light harvesting assemblies.

Ra11.34/Rb11.34

Controlling the nanoscale morphology of polymer blends is important for applications in optoelectronics from organic optoelectronics to alternative lithographic strategies. We show how nanoscale templates generated via Dip-Pen Nanolithography (DPN) can be used to control the phase separation in several polymer blends for a variety of applications. The ability to control the pattern sizes, patterns chemistry, background chemistry, film thickness, and blend compositions are all shown to be important factors impacting the size and fidelity of the polymer patterns. Using scanning-probe microscopy, optical microcopy, x-ray photoelectron spectroscopy, and selective etching experiments, we contrast the templating effects of nanoscale DPN-patterns with those of larger-scale patterns generated by micro-contact printing. Optimized conditions for pattern replication in both conjugated, non-conjugated, and block-copolymer films are reported.

Ra11.35/Rb11.35
Proof-Reading and Error Removal in a Nanomaterial Assembly. Xie Lu, Juewen Liu and Daryl P. Wernette; Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois.

Recent progress in self-assembly of nanomaterials promises to revolutionize a number of science and engineering fields such as molecular electronics, photonics and computations. A key hurdle to realizing such a potential is the presence of imperfect structures or errors in the assembly process. To overcome this problem, major efforts have focused on optimization of the assembly process to minimize errors or to design devices that can tolerate errors. We argue that it could be equally valuable to investigate proof-reading and error removal during and after assembly, as demonstrated beautifully in a number of patterns in biology, such as in mRNA and ribosome-mediated protein synthesis. Here, we report the first experimental demonstration of proof-reading and error removal in nanomaterial assembly by using DNAzymes (DNA molecules with catalytic activity) to proofread and repair mis-assembled gold nanoparticle assemblies. We showed that error particles can be specifically removed from the system. The concept demonstrated here can be applied to assembly of other nanomaterials using other bio- or biomimetic molecules.

Ra11.36/Rb11.36
Ionic Complex Formed by DNA and Asymmetric Discotic Triphenylene Salts. Lei Zhu and Li Cui, Chemical Engineering, University of Connecticut, Storrs, Connecticut.

A series of asymmetric triphenylene imidazolium salts with different spacer length (C5, C8, C11) were synthesized and their complexes with DNA were prepared by ion interaction. The thermal behavior of these complexes were studied by differential scanning calorimetry (DSC), polarized light microscopy (PLM) and wide-angle X-ray diffraction (WAXD). It shows that complexation of the discotic salt onto the rigid DNA chain favors the liquid crystalline properties. WAXD shows that the complexes packed into lamellar structure: The complex with shorter spacer length (C5) packed into ordered lamellar structure with the long axis of the dye molecule parallel to the DNA helix. The complexes with longer spacers (C8 and C11) show reduced correlation due to more mobility of the discotic molecules provided by the longer spacer.

Ra11.37/Rb11.37
Controlled alignment of single-walled carbon nanotubes and study of their electrical properties. Lifeng Dong, Vachara Chirayos1, Jocelyn Bush2 and Jiao Jun1, Department of Physics, Portland State University, Portland, Oregon; 2Department of Biology, Portland State University, Portland, Oregon.

We present a floating-potential dielectrophoresis method used for the first time to achieve controlled alignment of an individual semiconducting or metallic single-walled carbon nanotube (SWCNT) between two electrical contacts with high repeatability. This result is significantly different from previous reports, in which bundles of SWCNTs were aligned between electrode arrays by a conventional dielectrophoresis process where the result is only collected from the control electrode regions. In this study, our alignment focus is not only on the regions of the control electrodes, but also on those of the floating electrodes. Our results indicate that bundles of carbon nanotubes along with impurities were first moved into the region between two control electrodes, while individual nanotubes without impurities were straightened and aligned between two floating electrodes. The measurements for the back-gated nanotube transistors made by this method displayed an on-off ratio and transconductance of 105 and 0.3 μS, respectively. These output and transport properties are comparable with those of nanotube transistors made by other methods. Most importantly, the findings in this study show an effective way to fabricate individual nanotubes from bundles and the impurities, and advance the processes for site-selective fabrication of single CNT transistors and related electronic devices.

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Ra11.38/Rb11.38
Synthesis of Nanocomposites: [NbSe2], [CrSe2], [FeSe2], [NbSe2], [CrSe2], [FeSe2] Formed from Modulated Elemental Reactants. Polly Botzum, Kristine Carlsen, Astrid Albertini, Ngoc Nguyen and David C. Johnson; Chemistry Department, University of Oregon, Eugene, Oregon.

Modulated elemental reagents were used to synthesize new nanocomposite superlattices, [NbSe2]×n[CrSe2]×n, containing layers of metastable CrSe2. Preliminary magnetic measurements suggest the CrSe2 layers are stabilized by electron transfer, presumably from the NbSe2 layers. X-ray reflectivity measurements were utilized to study the reactant interfaces as a function of annealing temperature; the nanocomposites form with gentle annealing and are stable to about 500 °C.

Ra11.39/Rb11.39
Fabricating Ordered Nanoporous Thin Films Using Block Copolymers. Kevin A. Cavicchi, Thomas P. Russell1 and Dorothy Buechel; Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts; 2Seagate Technology, Pittsburgh, Pennsylvania.

Ordered nanoporous thin films are useful as templates or scaffolds for addressable media applications. Block copolymers that self-assemble into periodic nanostructures are attractive for the bottom up fabrication of nanostructured materials. We have been studying thin films of poly(isoprene-b-lactide) (PI-b-PLA) copolymers where the PI cores form cylindrical cores in a polylactide matrix. When the ordered state, the PI can be crosslinked and the PLA degraded to generate a nanoporous material. These polymers are highly immiscible and therefore low molecular weight polymers with small domain sizes can be used for fabrication. For example, LbL film processing yielded cylinders oriented perpendicular to the substrate are desirable. However, preferential interactions at the substrate and air interface can dominate the morphological behavior resulting in a parallel cylinder orientation. We have been using solvent vapor to swell the films and anneal the impurities and control over the domain orientation in the film. We have found a complex relationship between the domain orientation and the choice of solvent, concentration of solvent, and thickness of the swollen film where both parallel and perpendicular orientations can be obtained. This technique is also attractive from the point of view of processing as the time needed for solvent annealing (30 min) is short.

Ra11.40/Rb11.40
Strong Charge Inversion and Layer-by-Layer Assembly of Flexible Polyelectrolytes from Self-Consistent Field Calculations. Qiang Wang, Department of Chemical Engineering, Colorado State University, Fort Collins, Colorado.

We have applied a continuum self-consistent field (SCF) theory to flexible polyelectrolytes on flat surfaces either uncharged or carrying opposite charges to the polyelectrolytes. We examined in detail the effects of various parameters on the polyelectrolyte adsorption and surface charge compensation by the adsorbed polyelectrolytes. The ground-state dominance approximation (GSDA) was used to explore
the large parameter space involved, including the charge distribution and degree of ionization of the polyelectrolytes, surface charge density, short-range (nonionic) surfactant interactions, transmission electron microscopy with selective staining and infrared spectroscopy (IR) has established that the peptide segments assemble on the periphery of the nannofibrillae commonly with β-sheet architectures. In this work we report on the use of polarization-modulation infrared reflection-absorption spectroscopy (PM-IrRAS) to characterize the organization of β-sheets within the nannofibrils. Based on the surface selection rules in PM-IrRAS and the controlled deposition of nannofibrils running parallel to the surface, we demonstrate that β-sheets are oriented parallel to the long-axis of the nannofibrils and packed radially from the nannofibril core. Based on this model, we also show that we can use polarization-modulation infrared spectroscopy in transmission mode to characterize the peptide orientations and stoichiometries of monolayer-thick nannofibrils fabricated using controlled draining of peptide amphiphile solutions.

Our laboratory has recently been studying the self-assembly of peptide amphiphile (PA) molecules into one-dimensional cylindrical nannofibrillae. Previous results from transmission electron microscopy have shown that these PA molecules are able to aggregate into nannofibrillae by electrostatic interactions and phase transfer reactions. We have also investigated the effect of the solvent composition on the formation of nannofibrillae. Based on the experimental findings on nannofibrillae layer-by-layer assembly.

**Ra11.41/Rb11.41**

**Abstract Withdrawn**

**Ra11.42/Rb11.42**

**Novel template-less Fabrication of Poly (ethyl-2-cyanoacrylate) Nanofibrils. Pratik Manikday, Henry Foley and Ramakrishnan Rajagopalan; Chemical Engineering, Pennsylvania State University, University Park, Pennsylvania.**

Nanomaterials such as nanowires and nanorods are typically fabricated by a template-based technique wherein the material is first filled or synthesized within the template and subsequently released by dissolution/destruction of the template. The dimension of the resulting nanowires is therefore constrained by the dimensions of the template it was made in. In this work we report a novel, template-less technique to fabricate nanofibrils of poly (ethyl-2-cyanoacrylate) (PECA). PECA, best known as an instant adhesive or superglue, is formed by rapid anionic polymerization of cyanoacrylate on contact with a nucleophile. The nanofibrils were grown on a substrate placed in a humidity chamber where it was exposed to monomer vapor. The humidity acts as the nucleophile for initiation of the polymerization. Interestingly, the orientation, and solubility on the thickness and the fiber is a function of the relative humidity in the chamber. Higher the humidity, thinner is the diameter of the fibers formed. Also as this polymerization has a living character the length of the fiber is a linear function of the time of polymerization and the amount of monomer in the vapor phase. Hence, the dimension of the nanofibril can also be controlled during the synthesis.

**Ra11.43/Rb11.43**

**Addition of CeO2 nanoparticle dispersions to enhance flux pinning in Y-Ba-Cu-O superconducting thin films. Jianhua Su1, Vamsee Chintamani2, Pratik Joshi3, Sharmila Mukhopadhyay1, Suvarna Songupta1, R. R. Revar3 and T. Fyles3; 1Molecular and Condensed Matter Physics, University of Dayton, Ohio; 2Alphatech, Columbus, Ohio.**

Nanoparticle centers are expected to enhance the critical current density (Jc) of high temperature superconducting films at high magnetic fields. In this study, CeO2 nanoparticles have been successfully introduced into YBa2Cu3O7-δ (YBCO) thin films by dispersing a trifluoroacetate (TFA)-based clear colloid of CeO2 with particle size below 10 nm into TFA precursor solutions of YBCO. Precursor films were spin-coated onto (100) LaAlO3 single crystal substrates and then converted to epitaxial YBCO films through a two-step heat treatment. The Jc value of CeO2 colloidal sol has been evidenced to be a key factor to avoid agglomeration of CeO2 nanoparticles. Microstructure analysis reveals well-formed YBCO films. An enhancement in the critical current density was observed with addition of CeO2. The relationship between the content of CeO2 and Jc-H behavior is being investigated and will be presented. Our study reveals that introducing nanoping centers by a solution-based method, i.e., a lower cost fabrication process, is a feasible solution to improve the performance of YBCO at high magnetic fields.

**Ra11.44/Rb11.44**

**Internal Structure and Alignment of Peptide Amphiphile Nanofibrils. Hidden Zhang1 and Samuel I. Stupp2 1,2; 1Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois; 2Department of Chemistry, Northwestern University, Evanston, Illinois; 3Feinberg School of Medicine, Northwestern University, Evanston, Illinois.**

Our laboratory has recently been studying the self-assembly of peptide amphiphile (PA) molecules into one-dimensional cylindrical nannofibrillae. Previous results from transmission electron microscopy have shown that these PA molecules are able to aggregate into nannofibrillae by electrostatic interactions and phase transfer reactions. We have also investigated the effect of the solvent composition on the formation of nannofibrillae. Based on the experimental findings on nannofibrillae layer-by-layer assembly.

**Ra11.45/Rb11.45**

**Controlled Synthesis of Heteropod-Structured Monodisperse Particles by Discontinuous Growth. Changdeuk Bae3, Hyunjung Shin3 and Jooho Moon1; 1School of Advanced Materials Engineering, Konkuk University, Seoul, South Korea; 2School of Advanced Materials Engineering, Yonsei University, Seoul, South Korea.**

We designed and demonstrated a new class of monodisperse colloidal nano-building blocks possessing heteropod structures in a variety of combinations on their surfaces. Our approach is based on sol-gel method for both particle synthesis and site-selective growth of additional heteropods. A series of processes were carried out: Firstly, monodispersed silica colloids were produced by Stöber process having the size and distribution of particles confirmed with TEM use; Secondly, synthesized colloids were controlled to crystallize into many different periodic structures, such as face-centered-cubic (FCC), body-centered-cubic (BCC), two-dimensional (2D) close-packed, and 1D chain structures; Thirdly, the entire area of colloidal surfaces was coated with octadecyltrichlorosilane (OTS) - self-assembled organic monolayers (SAMs) by immersing the substrate with colloidal crystals into OTS molecules containing medium for several hours; then, the OTS-coated colloidal crystalline films were oxidized to titania, rendered onto the exposed silica surfaces, not OTS-coated surfaces resistant to nucleation and growth, making heteropods of TiO2 less than 100-nanometers. SEM, EDX, and HR-TEM data testify successful synthesis of these novel building blocks. We are also under study on photonic properties of 3D colloidal crystals consisted of these heteropod-structured particles, and feasibility of selective bioconjugation on them.

**Ra11.46/Rb11.46**

**Nano-patterned Liquid Metal Electrodes for Prussian blue Nanotube Synthesis. Sathyajith Ravindra1, Chunglin Tsai2 and Congzg Sinan Ozkan3; 1Mechanical Engineering, University of California at Riverside, Riverside, California; 2Chemical and Environmental Engineering, University of California at Riverside, Riverside, California; 3Electrical Engineering, University of California at Riverside, Riverside, California.**

We report the fabrication of Prussian blue nanotubes via a novel technique wherein a liquid metal surface is nano patterned with a porous polycarbonate membrane used as a hard mask. Prussian blue as 1D nanowires and nanotube are excellent candidates for ultra low level sensing, optical wave-guides and model systems to test the one-dimensional living model. One of the most feasible techniques for nanowire fabrication is to use porous template. However, Prussian blue nanotubes in strong acids and decomposes in the presence of strong bases. Conventional procedures, which use porous alumina with a backside metal contact, need strong acids and bases in the various steps of the nanowire fabrication. We report a novel technique, which will pave the way for the facile synthesis of nanowires and nanotubes in materials that are sensitive to strong acidic or basic environment. Hence, nano patterning of a liquid metal (Hg that functions as a topside metal contact) with polycarbonate membrane instead of porous alumina membrane eliminates the use of strong acids and bases during the fabrication of nanowires. With this innovative technique, we report the synthesis of novel organic Prussian blue nanotubes and nanowires.

**Ra11.47/Rb11.47**

**Abstract Withdrawn**

**Ra11.48/Rb11.48**

**Size Effects on the Stabilization and Growth of Tetragonal ZrO2 Crystalites in Nanotubular Structure. Bokyung Ahn1;**

450
Hyunjung Shin¹, Jaeg Lee¹, Jiyoung Kim¹, Pil-Ryung Cha¹ and Myung M. Sung²
¹School of Advanced Materials Engineering, Kookmin University, Seoul, South Korea; ²Department of Chemistry, Kookmin University, Seoul, South Korea.

Nanotubular oxide materials have especially promising physical properties and potential applications in nanoelectronics. Even though Zirconium dioxide (ZrO2) is an interesting inorganic material, there are only a few reports of ZrO2 nanotubes in the literature. We investigated Nanosize effects on the stabilization of ZrO2 polymorphs and the growth behavior of their crystallites in 1-D nanotubular ZrO2. Polymeric nanotubular structures of ZrO2 with tetragonal nanocrystallites were fabricated using the nanoporous PC (poly carbonate) templates, AAO (anodic aluminum oxide) template and ALD (atomic layer deposition) processes. Characterization of the ZrO2 nanotubes was established by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), and high resolution transmission electron microscopy (HR-TEM). As-prepared ZrO2 nanotubes were all polycrystalline of stabilized tetragonal polymorph at room temperature. Wall thickness (5 < 50 nm in thickness) of the ZrO2 nanotubes is extremely linear relative to the number of ALD cycles. Faster growth of the tetragonal nanocrystallites was observed in the nanotubes of 50 nm in outer diameter, compared to the one of 200 nm. Possibly, Gibbs - Thompson relation could explain the observed nanosize effects on the growth of the tetragonal ZrO2 nanocrystallites.

Ra11.49/Rb11.49

Advanced Photonic Crystals by Holographic Lithography and Atomic Layer Deposition. Jeffrey S. King¹, E. Graugnard², O. M. Roche³, D. N. Sharp⁴, J. Scrimgeour⁵, C. J. Summers⁶, R. G. Denning⁷ and A. J. Turberfield¹
¹Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia, USA; ²Physics, University of Oxford, Oxford, United Kingdom; ³Inorganic Chemistry Laboratory, University of Oxford, Oxford, United Kingdom.

Holographic lithography [1] and direct optical writing using two-photon excitation [2] are promising fabrication methods for 3D photonic crystals. Both methods create sub-micrometer periodic microstructure in polymeric photosensitive materials that are usually too slow to create negative replica of the polymers by deposition of high-index dielectric in their pores must make allowance for the low thermal decomposition temperature of the resist; limiting the range of materials that can be deposited by high temperature (between 100°C and 200°C) atomic layer deposition (ALD) of titania has been demonstrated for formation of single [3] and multi-component inverse opals [4]. This technique yields low porosity, conformal films with sub-nanometer control, making it an ideal technique for polymer template infiltration. Here we report successful realization of 3D titania photonic crystals formed by infiltration and subsequent removal of holographically-defined polymer templates. Homogenous infiltration of amorphous titania (2.0 g) was a 2 mm thick sample, ~22 unit cells deep. The polymer template was subsequently removed by O2 plasma etching. We present optical spectra for titania and titania-air photonic crystals and correlate them with calculated photonic band structures. These results demonstrate an exciting coupling of two powerful techniques yielding unprecedented control at the nanoscale, and enabling previously unimaginable opportunities.


Ra11.50/Rb11.50

Bi-functionality of TBP-1 (Ti-binding peptide-1) facilitates nano-fabrication of heterologous multi-layers composed of inorganic nanoparticles. Ken-Ichi San¹, Hirokuni Sasaki¹ and Kiyotaka Shib¹
¹Bioengineering, The College of Engineering, CREST/JST, Tokyo, Japan.

Compared to existing methods for preparing thin films, micropatterning is an attractive technique for the fabrication of functional surfaces. Inorganic micropatterns with high aspect ratio have been fabricated by a variety of methods including the current research, which involves the assembly of thin films of inorganic nanocrystals. However, a key challenge in this field is the ability to control and manipulate the assembly process in a precise and reproducible manner. This is where TBP-1 (Ti-binding peptide-1) comes into play. TBP-1 is a polypeptide that specifically binds to titanium oxide surfaces, making it a valuable tool for the fabrication of inorganic micropatterns. By utilizing TBP-1, researchers can precisely control the assembly and alignment of inorganic nanocrystals, allowing for the creation of complex and functional surfaces. This technology has the potential to revolutionize the field of micropatterning and has applications in various areas such as microelectronics, biology, and material science.

Ra11.53/Rb11.53

Loading of Carbon Nanoparticles with Magnetic Particles. Gulya Korleva¹, Hailuo Xu², Yong Guo³, Yuehui Zhao², Derek Halverson³
¹Chemistry, Drexel

Fluorescent and magnetic silica microspheres were prepared by the incorporation of maghemite (γ-Fe₂O₃) nanoparticles (Mps) and CdSe/CdZnS quantum dots (QDs) into the shells of silica core/shell microspheres. The MP- and QD-doped silica shells were grown on pre-made silica cores according to a method previously developed in our laboratory. Briefly, the MPs and QDs, featuring ligands with alkoxysilane moieties, were included in a mixture of silica microsphere core, tetraethoxysilane, and water in ethanol. The addition of ammonium hydroxide resulted in the initiation of silica shell growth on the cores, with the alkoxysilane ligands on the nanoparticles enabling their incorporation into the silica matrix. The microspheres were characterized using a combination of TEM, magnetization measurements and fluorescence microscopy. MPs of 5-18 nm in size were incorporated into core-shell silica microspheres of 100-500 nm in diameter. The microspheres demonstrated approximately uniform incorporation of QDs and MPs into the shell, and additional imaging under a fluorescence microscope. The magnetic moment of these microspheres allowed them to be manipulated by magnetic fields produced by a microelectromagnetic device while their fluorescence was monitored in real-time imaging of their localization.
University, Philadelphia, New Jersey; 3Materials Science and Engineering, Drexel University, Philadelphia, New Jersey; 4Electrical and Computer Engineering, Drexel University, Philadelphia, New Jersey; 5Drexel University, Philadelphia, New Jersey.

In the poster, we show a relatively simple, inexpensive, reproducible, scalable and fast method of filling the carbon nanotubes with functional nanoparticles, in particular, with magnetic nanograins. This technique opens an opportunity for engineering magnetic nanotubes based on the phenomenon of spontaneous penetration of wetting fluids into capillaries. The magnetic behavior of magnetic CNFs is controlled by the number of encapsulated magnetic grains, thus the tubes can be made very magnetic. In our experiments, for example, the number of magnetic grains in the tubes varies between N ≈ 10000-100000. The filled nanotubes follow the applied magnetic field, thus manifesting their magnetic nature. We showed that the yield of magnetic nanotubes after wet filling was close to 100%. Controllable manipulation of the magnetic behavior of the nanotubes and micromanipulators points to a straightforward way for utilization of these nanoneedles in different nanofluidic and electronic devices. Generally, the paper provides a procedure of making nanotubes functional. Other particular fluids, emulsions, and polymer solutions can be used to fill nanotubes and transform them into multifunctional nanomaterials.

Ra11.54/Rb11.54
Fabrication of epitaxial perovskite nanostructures.
Chang Chun You1, Nils Vidar Rystad2, Yun Liu2, Anne Borg2 and Thomas Tybell1,3.
1Department of Electronics and Telecommunications, Norwegian University of Science and Technology, Trondheim, South-Trondelag, Norway; 2Department of Physics, Norwegian University of Science and Technology, Trondheim, Norway; 3NTNU NanoLab, Norwegian University of Science and Technology, Trondheim, Norway.

Perovskites are attractive for a variety of electronic applications, for example ferroelectric non-volatile random access memories. In order to fully exploit their properties it is important to understand how size affects the materials as the components are scaled down, and to develop appropriate nanostructuring methods. Here we present data on the fabrication of epitaxial perovskite nanostructures. The structures were fabricated using a two-step process, with initial e-beam lithography and subsequent dry etching followed by scanning tunneling microscopy (STM) lithography in order to create structures with lateral dimensions down to ~5 nm. Data on how voltage bias, tunneling current, and scan speed effect STM etching of SrRuO2 will be discussed in detail. Moreover, the possibility to grow epitaxial perovskites on top of pre-structured SrRuO2 templates will be assessed, with focus on the fabrication of ferroelectric memories.

SESSION Ra12: Semiconductor Nanostructures I
Chair: Eli Sutter
Wednesday Morning, November 30, 2005
Room 207 (Hynes)

8:00 AM *Ra12.1
Self-Organized Nanopatterning of Surfaces by Focused Ion Beam.
Wei Zhang1, Haixia Qian2, Gnjian Cher Lim2, Lumin Wang2 and Michael A. Koval1.
1Precision Engineering & Nanotechnology Centre, Nanyang Technological University, Singapore; 2Singapore Institute of Manufacturing Technology, Singapore.

We aim to use 30-50 kV Ga+ focused Ion Beam (FIB) as a tool to control nanoscale periodic structures in Si, Ge, ZrO, SiO2, InP, GaAs, GaSb, GaN and metals for various applications. The highly focused ion beam is programmed to e-erode materials in selected areas by sputtering, nanoscale surface structures may be fabricated directly. We demonstrate the successful use of bitmap to control FIB for one-step maskless nanofabrication of pillars, wells and gratings in some materials such as Si. However, use of the direct writing method in many other materials is affected by either anisotropic surface diffusion (in Sn and Ti), or ion-induced nano-explosion (in Ge and GaSb), or severe redeposition of sputtered materials (in GaAs, GaSb and GaN). One of the one hand, we explored various ways to get over the problems. On the other hand, we managed to make use of the phenomena to produce self-assembled nano-patterns of nano-dots or nano-rods. It is noteworthy that we obtained convincing evidence, through monitoring evolution of the surface patterns using in-situ real-time secondary ion and secondary electron imaging, to show that ion beam dwell time has a significant effect on surface patterns formation. The Ga-containing compounds are common in the sense that liquid-like droplets may form on the surfaces at high ion doses. EDS and TEM analyses showed the droplets to be amorphous Ga. We have found a way to control the Ga droplets to make them disappear or appear in certain orders on the surfaces.

8:30 AM Ra12.2
Directed Self-Assembly of Highly Periodic Arrays of SiGe Quantum Dot Molecules Via Heteroepitaxy on Patterned Si Substrates.
Jennifer L. Gray1, Robert Hull1 and Jerrold A. Floro2.
1Materials Science and Engineering, University of Virginia, Charlottesville, Virginia; 2Sandia National Laboratories, Albuquerque, New Mexico.

Heteroepitaxial growth of SixGe1-x on Si substrates patterned ex-situ using a focused ion beam (FIB) can result in the self-assembly of quantum dot molecules (QDMs) at precisely defined locations under specific growth conditions. Individual QDMs are composed of four self-assembled islands that coalesce into molecules at the tips of pits that form in the FIB modified sites. In order to obtain uniform, well ordered islands, the FIB milling parameters and Si buffer thickness must be tailored to produce pits in the strained SiGe film with dimensions equal to or smaller than the compositionally-dependent natural length scale of strain relieving morphology that forms intrinsically and randomly in strained films on un-patterned substrates. We obtain long-range periodic arrays of QDMs with uniform shapes and sizes when growth is done under kinetically limited conditions to suppress roughening from occurring at locations other than directly adjacent to the pre-patterned pit sites. We will show that FIB substrate patterns deeper than 5nm result in degraded nanostructure self-assembly, while too shallow patterns can result in missing features. The ability to produce island arrays at specific locations is important for applications such as quantum computer chips where QDMs must be aligned and arranged into logic structures. These methods provide a new route to hierarchical assembly of nanostructures with potential applications to novel electronic device architectures. This work was partially supported by the DOE Office of Science, Basic Energy Sciences. Sandia National Laboratories is a multiprogram laboratory of the United States Department of Energy operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy National Nuclear Security Administration under contract DE-AC04-94AL85000.

8:45 AM Ra12.3
Step erosion during nucleation of InAs/GaAs(001) quantum dots.
Emanuele Placidi, Fabrizio Arciprete, Violetta Sesli, Massimo Fanfoni, Fulvia Patella and Adalberto Balzarotti.
Physics, University of Rome Tor Vergata, Rome, Italy.

We have investigated, by means of atomic force microscopy, the complete evolution of InAs/GaAs(001) quantum dots as a function of deposited InAs. Direct evidence is found for step erosion by quantum dots nucleated onto the step edge and an estimate of the eroded volume is provided. The analysis of quantum dots position shows that the step is a preferential site for nucleation at the beginning of 3D islands formation, while, after the step erosion, quantum dots are mainly located below the steps and in the flat regions of the sample. A similar analysis shows that nucleation on step bunching starts in advance compared to nucleation on flat regions, due to different strain conditions on the surface. By studying the quantum dots volume as a function of InAs coverage, we show that the wetting layer contribution in quantum dots formation is confined within a narrow range of coverage around the 2D-3D transition.

9:00 AM Ra12.4
Surface Diffusion Processes and Nanostructure Growth.
Jian Wang1, Hanchen Huang2 and Timothy S. CalE3.

This paper reports a molecular statics study of Cu surface diffusion barriers, particularly the facet-facet and step-facet barriers, and explains the phenomena in nanostructure growth based on these kinetic processes. The study focuses on the diffusion barriers on flat surfaces or step edges, and the step-facet barrier is substantially larger than diffusion barriers on flat surfaces or down non-flat steps. Explanations for the barriers are given by the size of the ending surfaces or facets, Cu[111] and Cu[100]. Our results show that these two barriers are distinct from conventional step barriers and are independent of facet size once it is beyond three atomic layers. Usually, the facet-facet barrier is substantially larger than diffusion barriers on flat surfaces or down non-flat steps. In general, the step-facet barrier is substantially larger than diffusion barriers along or across monolayer steps. Exceptions do exist. When two Cu[100] facets are involved, the barrier decreases as the size of the ending surfaces increases from one layer to two layers, and then increase from two to three (or more) layers. As a result of the large facet-facet and step-facet barriers, surfaces of Cu thin films are on the order of 100 nm, and the small facet-facet and step-facet barriers of Cu[100] facets, when the ending facet is two to three layers, make it difficult to form another Cu[100] facet near one Cu[100] facet. For the same reason, nanowires along <100>/<100> on the Cu[100] is unlikely while nanowires along <110>/<111> are feasible. Based on

In order to cope with prerequisites for opto-electronic applications, it is desirable to maximize the island density in the fabrication of quantum dots (QDs). Dot diameters can, in principle, be reduced by lowering the growth temperature but addition of carbon during the process of QD growth opens additional possibilities to control the size and shape of the islands by modifying the strain field in the substrate. The works aimed at understanding the dependence of the density of C-induced QDs with temperature of material deposition. The increased Ge surface diffusivity with temperature leads to the transformation from small and dense domes to larger islands. In the present work we especially focused on the role of a Ge wetting layer (WL) before carbon deposition on the subsequent growth of C-induced Ge dots, in order to clarify the dynamics leading to the dot density reduction observed in presence of a pre-deposited Ge WL, compared to the case of a bare silicon substrate. A study of morphology of the different samples reveals a clear trend with the growth temperature chosen for the Ge WL deposition. At low temperature interdiffusion of silicon in the WL is kinetically quenched and carbon dots nucleate on the surface to form a Ge-C rich environment, characterized by Ge-C chemical repulsion leading to energetic instability of carbon clusters. Further studies are under way in order to achieve a complete understanding of surface dynamics and their correlation with observed morphology.

9:30 AM Ra12.6 Self-Assembly of Steps and Vacancy-Lines on Ge Films Grown on Si(001). Surfaces, Interfaces, Spin Physics, Electron and Voids. B. Sheu; Solid Mechanics, Brown University, Providence, Rhode Island.

During initial stages of deposition of Ge on Si(001) surface, defects such as steps and vacancies lead to steps self-assemble to create a structure which has highly correlated features [1]. Understanding the mechanisms for this correlation/order is necessary for the possible use of this patterned surface as a template for nanofabrication of 1D structures or to study the growth of pyramidal quantum dots. We have studied these structures with the help of atomic simulations using empirical potentials. In our simulations, we have studied correlation between the steps and the vacancy-line based on energetics arguments. Our study provides a theoretical basis for the interaction between vacancies and steps and agreement with the experimental and statistical observations made by Sutter et al.[1]. [1] P. Sutter, I. Schick, W. Ernst and E. Sutter, Phys. Rev. Lett. 91(2003), 176102.

9:45 AM Ra12.7 Real-time observation of self-assembling Ge nanostructures on clean and Ga patterned Si(113). Torben Clausen; Thomas Schmidt 1, Jan-Ingo Fiege, Andrea Locatelli 2, Tsvik Orner Mestres 1, Stefan Hein 1, Fangzhan Guo 2 and Jens Falka 1; 1 Institute of Solid State Physics, University of Bremen, Bremen, Germany; 2 SINcrotecnica Trieste, Trieste, Italy; 3 Spring-8/JASRI, Hyogo, Japan.

We report on a systematical temperature dependent low energy electron microscopy (LEEM) study of Ge nucleation and island growth on clean and Ga patterned Si(113), providing a detailed insight into the growth kinetics and the resulting surface morphology. The in-situ and ex-situ measurements and calculations were performed in an UHV system equipped with a spectrosopic photoemission and low energy electron microscope (SPELEEM) at the ultra-beamline 1.2 at ELETTRA. During Ge deposition on clean Si(113) a strong temperature dependence of the Ge island shape is observed. Starting from a rather circular appearance at 380°C it changes to a cigar-like shape for temperatures of 440°C to 500°C, elongated in [33-2] direction. With increasing temperature the Ge islands become more elongated and the average island size increases up to about one to five microns in length whereas the density decreases. From the arrangement of the islands, no indication for a strongly anisotropic diffusion is found. An increase of the anisotropy towards an anisotropically grown relaxation. However, if Ge is deposited on a Ga saturated Si(113) surface the shape and the arrangement of the Ge islands changes drastically. Ga pre-adsorption leads to the formation of substrate facets with a direction of about 45° to the [33-2] direction. Ge deposition on this surface leads to Ge islands which are arranged at the Ga facets and elongated in [1-10] direction. A strongly anisotropic diffusion is observed, which may explain the Ge island shape and arrangement. Thus, using a unified interpretation of different degrees of small and aligned Ge nanoislands in the order of about 100 nm in length with high density is enabled.

SESSION Rb12: Alternative Nanofabrication

Chair: Younau Xia
Wednesday Morning, November 30, 2005
Room 208 (Hynes)

8:30 AM Rb12.1 Integration of Top-Down and Bottom-Up Nanofabrication Techniques. Jurjane Hulstens; 1 Supramolecular Chemistry & Technology, University of Twente, MESA+, Enschede, Netherlands; 2 Strategic Research Orientation “Nanofabrication”, University of Twente, MESA+, Enschede, Netherlands.

Nanotechnology deals with enabling technologies for the fabrication and study of materials (atoms, molecules, particles, etc.) on the nanoscale. In order to study nanodevices, the fabrication of nanodevices is not enough: careful study of their individual properties usually requires anchoring to a substrate, and preferably to targeted or prepatterned areas of a substrate. Nanofabrication is the subdiscipline that deals with the development of general fabrication methodologies for the preparation of nanodevices as well as of patterned substrates and of assembly methods for the anchoring of the objects to the patterned areas. In general, nanofabrication methods fall into two classes, which are called top-down and bottom-up. The integration of top-down and bottom-up nanofabrication schemes is considered a key issue for the advance of nanotechnology. In this paper, we will show an elaborate example of such an integration attempt. We chose to use nanomirror lithography (NIL) as the top-down technique [1], because it is a technique that allows sub-10 nm resolution in pattern replication and has recently been put forward by the semiconductor industry as the most promising technique to be implemented in future chip fabrication processes. As the bottom-up technique, we chose layer-by-layer (LBL) assembly [2], since this allows the control over layer thicknesses with a nm accuracy. The full integration of these methods is therefore envisaged to lead to the fabrication of 3D nanoobjects of arbitrary shape and position in structures, where the x,y dimensions are determined by NIL and the z dimension by the LBL assembly. For the LBL assembly, we have used a polymeric approach [3], based on host-functionalized substrates (molecular printboards [4]) and nanoparticles [5] in combination with guest-functionalized dendrimers [6]. The whole procedure is shown to result in a multistep, high-fidelity process yielding 3D objects with all dimensions on the nanoscale. [1] P. Maaroy, M. Peter, V. Mahalingam, D. N. Reinholdt, J. Huskens, Adv. Funct. Mater. 2005, 15, 451. [2] G. Decher, Science 1997, 277, 1229. [3] O. Crespo-Biel, B. Dordi, D. N. Reinholdt, J. Huskens, J. Am. Chem. Soc. 2005, 127, 7594. [4] J. Huskens, M. A. Delj, D. N. Reinholdt, Angew. Chem. Int. Ed. 2002, 41, 4467; T. Auletta, B. Dordi, A. Mulder, A. Sartori, S. Onclin, C. M. Bruinink, C. A. Nijhuis, H. Beijleveld, M. Peter, H. Schoenherr, G. J. Vancso, A. Casnati, R. Ungaro, B. J. Ravoo, J. Huskens, D. N. Reinholdt, Angew. Chem. Int. Ed. 2004, 43, 3669; S. Onclin, A. Mulder, J. Huskens, B. J. Ravoo, D. N. Reinholdt, J. Am. Chem. Soc. 2004, 20, 5409. [5] O. Crespo-Biel, A. Jukovic, M. Karlsson, D. N. Reinholdt, J. Huskens, J. Chem. 2005, in press. [6] Michels, J. B.; Baars, M. W. P. L.; Meijer, E. W.; Huskens, J.; Reinholdt, D. N. J. Chem Soc. Perkin Trans. 2 2000, 1914.


Abstract High-aspect-ratio responsive polymeric nanostructures are receiving increasing interests for potential applications in biomedical devices, tissue engineering, MEMS, sensors, and micro-optical elements. However, it is challenging to fabricate polymeric nanostructures with high aspect ratios. When the aspect ratio is greater than 5 and the pitch is small, polymer nanostructures collapse because of the surface adhesive forces. The molded sharp corner deformations due to the equilibrium between surface tension and Young’s modulus of the cured polymer. Here we demonstrate the fabrication of high-aspect-ratio nanojet arrays (diameter of 350nm to 1µm) with an aspect ratio up to 20 using nanotrench molding (nTM) technique. We investigate several parameters that affect the fidelity of the nanotubes, including the feature dimension, pitch, viscosity of the precursor liquids, and the mechanical strength of the cured polymers. When the aspect ratio is as high as 20 and the pitch is 1µm, the Si
master with sharp corners are faithfully replicated in the rigid epoxy resins without deformation, while those from soft materials, such as PDMS and Norland, are not. Using this technique, we can incorporate carbon nanotubes and magnetic nanoparticles, respectively, into the nanostrips as nanactuators in response to external fields. Further, we observe a much improved mechanical properties in the nanosize particle in different types of substrates, which may lead for broader applications of PDMS nanostructures.

9:15 AM Rb12.8
Sub-Micron-Scale Cubic Patterning of Surfaces, Suresh Gupta and Thomas P. Russell; Polymer Science and Engineering, University of Massachusetts, Amherst, Amherst, Massachusetts.

Micron-scale patterns can be generated by the application of electric field across two fluid interface making use of result of electrohydrodynamic instabilities. These patterns are generally hexagonally packed features on the polymer surface. Patterns can also be generated with various symmetries on fluid surfaces when three fields are forced to vibrate normal to surface by means of Faraday instabilities. But, when ultrasonic vibrations are used with single frequency, cubic patterns are generated on the surface that are dynamic. These structures, observed using an optical microscope, were produced by vibrations up to 100 KHz in frequency. Kelvin's equation can be used to predict the wavelength of the pattern as a function of frequency where with increasing frequency the width of the pattern decreases. This process is used widely in anodization of fluids. It is argued that cavitation produces the fine mist of spray or that the droplets are formed at the crests due to surface waves. Here, we have used an electric field to stabilize the pattern on thin polymer films using different vibration frequencies in the MHz range and found that the cubic packed patterns are produced. These features are sub-micron in size and the size can be varied by the ultrasonic vibrations. These kind of features in surface waves are generated at frequencies higher than 100 KHz and that may cause the formation of droplets or a fine mist.

9:30 AM Rb12.4
Edge-Spreading Lithography: A Versatile Technique for Nanoscale Patterning, Joseph M. McLellan, Matthias Geissler and Younan Xia; Chemistry, University of Washington, Seattle, Washington.

We recently developed a simple and versatile technique for nanoscale patterning over large areas, which we call edge-spreading lithography (ESL). A typical ESL process utilizes a planar PDMS stamp to deliver ink molecules to a surface via a guide. Upon reaching the surface the ink molecules form a self-assembled monolayer (SAM) around the footprint of each guide. With a continuous supply of ink molecules the SAM can expand laterally until all areas not blocked by the guides are covered. In our initial demonstrations, we utilized monolayer arrays of silica beads on gold and silver substrates as the guides and alkanethiols as the inks. The circular footprints of the beads resulted in the formation of an array of SAM rings with a lattice constant that was consistent with that of the bead array. After lift-off of the beads, the SAM could then be used as an ultra-thin resist in order to transfer the pattern into the underlying gold or silver through a wet chemical etch. Additional features generated by ESL may find use in a variety of applications such as substrates for surface enhanced Raman scattering (SERS). I will give an overview of our ESL experiments including some limitations of the process, how we characterized the patterns, and how we were able to tune the widths of the resultant SAM rings down to a range of 30 nm. I will also discuss the formation of arrays of concentric rings, with several different functional groups (e.g. methyl, carboxyl, hydroxyl, or amine) next to one another through consecutive steps of ESL. Patterns generated through successive ESL are quite versatile in that the dimensions and order of the different functional groups can be varied independently. Finally I will discuss how we have overcome the geometric limitations imposed by bead array geometry. ESL resist features as guides, enabling us to fabricate patterns of much higher geometric complexity.

9:45 AM Rb12.5
Directed Assembly of Nanoparticles onto Polymer Imprinted or Chemically Patterned Templates Fabricated by Nanoimprint Lithography, Pascale Maury, Maryana Escalante, Marta Peter, David Reinhard and Jurriaan Husken; university, Eindhoven, Netherlands.

Several unconventional techniques have been employed to direct the deposition of nanoparticles in order to produce colloidal patterns that fulfill the requirements of order, generic design and functionality necessary for a wide range of applications. One method makes use of topographical templates, made up of silicon or a polymer, to confine non-functionalized particles within the pattern. Another employs self-assembled monolayer (SAM) templates to fabricate chemically patterned substrates. Here, we report on a novel multistep process for preparing chemically directed nanoparticle arrays by combining top-down and bottom-up techniques, namely nanoimprint lithography (NIL) with self-assembly of silanes on silicon oxide in the nm-and sub-nm range. The nanoparticles are assembled by vertical deposition employing the meniscus method to allow versatile patterning of nanoparticles on different types of substrates. In NIL, a thin polymer layer on a substrate is patterned by means of compression molding of the polymer with a hard stamp at a temperature above the glass transition temperature of the polymer. After a residual layer removal step, the substrate consists of a polymer relief pattern with exposed and unexposed regions of the substrate. Subsequently, a SAM is formed on the exposed areas of the substrate. Furthermore, these substrates can be converted to truly chemically patterned substrates by removing the polymer template and covering the bare silicon oxide areas with SAMs of a different functionality. Both types of substrates are used to attach functionalized nanoparticles. Hexagonal close packing on nm-size features, and typical confined nanostructures on larger features will be demonstrated in this work. It will be shown that this process is able of a resolution down to 60 nm for single particle-wide lines of functionalized nanoparticles topographically confined on 60 nm morphological evolvent SAM substrates. [P. Maury, M. Peter, V. Halingan, D. N. Reinhard, J. Husken. Adv. Funct. Mat. 2005, 15, 451]

SESSION Ra13: Semiconductor Nanostructures II
Chair: Kohei Itoh
Wednesday Morning, November 30, 2005
Room 207 (Hynes)

10:30 AM *Ra13.1
Self-Assembly of Electrically Isolated Epitaxial Ge Quantum Dots on Ultrathin Silicon-oxide Insulator (100), Eli Sutter, W. Ernst, Percy Zahn, Young-suk Choi and Peter Sutter; Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York.

Mainstream microelectronics has been based predominantly on bulk silicon substrates. Silicon-on-insulator (SOI), a composite material in which a thin monocrystalline Si ‘template’ is bonded to a crystalline Si ‘handle’ wafer via a layer of amorphous silicon, has recently been developed into a viable substrate for very-large-scale integrated circuits. As a result of these efforts, which were largely driven by the promise of substantial advantages of depleted SOI in high-speed and low-power applications, a first generation of state-of-the-art SOI-based microprocessors has become available commercially. The growth of heteroepitaxial materials on engineered composite substrates such as SOI opens a new route for controlling the structural and electronic properties of materials at the nanoscale. Lattice strain induced by Ge quantum dots grown coherently on SOI causes significant local distortion in the ultrathin Si template (< 8 nm) and can be used as a tool for nanoscale band structure engineering of the Si substrate.[1] The Ge islands themselves form on SOI initially as hills and then transform into domes, similar to the sequence of epitaxially constrained shapes they assume on bulk Si (100). In the case of Ge growth on the ultrathin Si template, the transformation from hills to domes initiates the template formation process. This transformation is then driven by the nanostressor induced dewetting. We use a combination of atomic force microscopy, transmission electron microscopy, and in-situ low-energy electron microscopy to study the morphological evolution of the dewetting which in turn leads to the controlled formation of an array of free-standing Ge quantum dots. We identify the microscopic mechanisms underlying both the nanostressor induced dewetting and the spontaneous formation of the electrically isolated epitaxial Ge islands.[1]

11:00 AM Ra13.2
Self-assembled Nanoline Template for Growth of Nanoparticles and Nanowires on Si(001).
James Hugh Gervase Owen1,2 and Kazushii Mikuriya1; 1International Centre for Young Scientists, National Institute for Materials Science, Tsukuba, Ibaraki, Japan; 2Nanomaterials Laboratory, National Institute for Materials Science, Tsukuba, Ibaraki, Japan.

Long, straight Bi nanowires have been used as a 1D atomic-scale template for the deposition of metals on Si(001). Bi nanowires are ca. 1.5 nm wide, and up to 500 nm in length, limited only by the substrate terraces.[1] We describe the method for formation of these templates, demonstrate strongly preferential adsorption of several different metals onto the Bi nanowire templates, and show examples of both non-wetting and wetting behaviour, which produce nanoclusters and nanowires respectively. Deposition of noble metals such as Ag produces arrays of metal nanoclusters with size distributions sharply
peaked at 0.7 nm, 1.1 nm and 1.4 nm, which correspond roughly to magic-cluster dimensions. Cluster formation suggests a weak interaction within the InGaAs nanofilms. For epitaxial layers such as In, we form highly uniform nanowires with single-nm lateral dimensions, which have an epitaxial relationship with the underlying nanowire, indicating a strong template interaction. [1] J. H. G. Owen, K. Mikk. H. R. R. H. W. Yeo, and D. R. Bowler. Phys. Rev. Lett. 88 (2002), 226104.

11:15 AM Ra13.3

The use of an array of nanomeshes has proved to be an attractive way to obtain, for adequate design parameters of the mesas, the growth of one quantum dot per mesa. This has been recently investigated, for Ge deposited on a 1 pm thick layer of Si nanowires, from both experimental [1] and theoretical [2] points of view. The first part of the work reported here focuses on mesas of the order of one hundred nm wide, obtained by classical lithography methods. Such InP mesas can include a stressor, either tensile (Ga rich InGaAs layer) or compressive (In rich InGaAs layer) which can modify InAs dots nucleation at the top of the mesa. By making use of continuous elasticity, and taking into account surface energy, some tendencies are investigated, in order to determine an optimal set of design parameters (thickness, location of the stressor, within a given panel of mesa sizes) for the best efficiency of the stressor. A very interesting result is that for too narrow mesas the elastic relaxation is insufficient that 3D islands will never nucleate and InAs will keep covering the top of the mesa. For wider mesas transition to 3D growth mode on the top of the mesa will occur, but will be either advanced or delayed, depending on the type of the stressor. Either the stressor is compressive or tensile will also rule the place 3D island will preferentially nucleate (edges or center of the considered square nanomesh). Whereas the mesas studied in the first part are of the order of one hundred nm wide, the second part of the work reported here focuses on mesas smaller than a few tens of nanometers and result from the selective etching of a layer twist-bonded to its substrate. In this case the quantum dots one gets are square base pals that cover the top of the mesa. We address here, from the theoretical point of view and by making use of an atomistic description, the question of capping such an array of nanodots: where will Si atoms preferentially deposit? We point out completely different behaviors for pure Si capping or SiGe capping. How long it takes for recovering a flat surface strongly depends on Ge availability during capping process. References [1] F. Leroj, J. Eynymy, P Gentille, F. Fournel, Surf. Sci. 545 (2003) 211 [2] M. Bavenecoffe, E. Houard and C. Priester. J. Growth 275 (2005)305.

11:30 AM Ra13.4
MOVC Growth of GaN and GaMn Multifunctional Nanostructures. Shalmi Gupta1, Hun Kang1, Martin Strassburg2, Ali Asghari1, Matthew Kane1, William E. Fenwick1, Nikolaus Dietz1, and Ian T. Ferguson1,2 1Electrical and Computer Engineering, Georgia Institute of Technology, Atlanta, Georgia; 2Department of Physics and Astronomy, Georgia State University, Atlanta, Georgia; 3School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia.

Quantum dots (QDs) are known improve the efficiency and optical properties of opto- electronic devices as compared to two dimensional quantum wells in the active region. The formation of self-assembled GaN nanostructures on aluminum nitride (AIN) by MOVC was explored to take advantage of QD structures in the UV spectral range. Further, this paper reports the first studies on the effect of in-situ activation in N2 atmosphere on MOVC-grown GaN nanostructures. The introduction of silane and, for the first time, manganese as an antisolvent was studied. Manganese is of great interest as it introduces ferromagnetic material, enabling the formation of multifunctional nanostructures. GaN nanostructures on AIN buffer layers were grown by MOVC on sapphire substrates. The growth temperature and notably the V-III ratio were found to strongly affect the growth mode of the deposited GaN nanostructures. A low deposition temperature of 815°C and an extreme V/III ratio of less than 20 were determined to favor nanostructure formation. An ‘activation’ step in N2 ambient was employed after GaN deposition to control the formation of nanostructures, as surface kinetics provides an avenue for controlling island growth. The strong impact of the activation temperature on the nanostructure density and dimensions is confirmed by nucleation studies applying temperatures between 820 and 970°C. The smallest island dimensions and highest island densities occurred at activation temperatures above 850°C. Nanostructures with lateral dimensions of 40nm and a height of 2nm were obtained with a typical V/III ratio of 4.5 followed by backfill activation show a transition from 2D to 3D growth above an initial critical thickness of 2 monolayers (ML). Ripening of these structures was observed above a second critical thickness of 12ML. The density of the nanostructures is determined to be a function of the growth temperature. The above results depict Stranski-Krastanow like growth for these structures. The crystalline quality of the GaN/AIN nanostructures was confirmed by micro-Raman spectroscopy that showed the presence of the GaN A1(I) mode despite the extremely metal-rich growth conditions at relatively low deposition temperatures. The intensities of the GaN-related Raman modes increases with deposition time. Initial nucleation studies on GaMn grown on AIN epi layers were performed to achieve multifunctional nanostructures that combine the advantages of quantum dot forms and diluted magnetic semiconductors.. The AFM analysis revealed that Mn acts as an antiferromagnetic (similar to the behavior of Si) and eliminates the need for an annealing step at a deposition temperature of 815°C. Activation temperatures above 880°C contributed to ripening processes that lead to islands of infinite size reflected by increased island densities and smaller island densities.

11:45 AM Ra13.5
Self-Assembled GaSi1 Nanostuctures Grown on Si(001) Studied by TEM and STM, Gangfeng Li1, Martin A. Crimp1 and Togami Jun2 1Department of Chemical Engineering and Materials Science, Michigan State University, East Lansing, Michigan; 2Department of Materials Science and Engineering, University of Toronto, Toronto, Ontario, Canada.

Rare-earth (RE) metal silicides have attracted recent interest because they can form self-assembled nanowires in the initial stages of epitaxial growth on the Si(001) surface. In general, two classes of nanostructures are seen: monolayer high nanowires with an atomic layer thick 3D islands. Some of the 3D islands have large aspect ratios that are usually in excess of 10:1 and can also be described as nanowires. Nanowire formation is due to an anisotropy in the lattice mismatch between the hexagonal crystal structure of the RE silicide and the substrate. Transmission electron microscopy (TEM), scanning tunneling microscopy (STM), and atomic force microscopy (AFM) are used to study the crystal structure and morphology of GaSi2 3D islands grown on Si(001). Cross-sectional TEM shows that both hexagonal and orthorhombic polymorphs of the silicide co-exist in these nanostructures. Moiré fringes observed in plan-view TEM shows that the morphology of the silicide islands is correlated with the crystal structure; the hexagonal phase forms islands with large aspect ratios (nanowires) while the orthorhombic phase forms islands with small aspect ratios. Nano-beam diffraction results support this observation. This behavior can be understood in terms of the difference between the lattice constants of the two silicide polymorphs. STM and AFM were used to study the morphology of the silicide nanostructures versus growth conditions. It was found that by adjusting the deposition conditions it was possible to control the ratio of nanowires to 3D islands, with nanowires becoming predominant at higher evaporation rates.

SESSION Ra13: Alternative Nanofabrication V
Chair: Cengiz S. Ozkan
Wednesday Morning, November 30, 2005
Room 208 (Hynes)

10:30 AM *Ra13.1
Soft Lithography and Nanofabrication. George Whitesides, Qionbing Xu and Brian Meyers; Department of Chemistry, Harvard University, Cambridge, Massachusetts.

Soft lithography has provided a range of simple methods useful in fabricating small systems (for fluidic, optical, and electronic applications) with dimensions down to ~ 1 micron; below this size, fabrication by soft lithography (and other lithographic techniques) becomes more complicated. This talk describes a series of techniques based on sectioning of polymers and formation of cracks in crystals that allow the formation of simple nanostructures. It thus extends soft lithography into new areas of nanofabrication.

11:00 AM Ra13.2
Synthesis and Characterization of Multifunctional Nanopatterned Surfaces Via Silica Imprinting. John D. Bax and Alexander Katz; Chemical Engineering, UC Berkeley, Berkeley, California.

A key capability for enabling several technologies and applications in the future is the nanoscale organization of two different chemical functional groups on a solid surface, such as silica. Covalent silica imprinting in principle offers a solution to this problem by using a molecular template for organizing chemical functional groups on silica surfaces, on length scales that are in general too small to achieve with conventional lithographic approaches (< 2 nm). The imprinting
process consists of immobilizing the imprint molecule, which consists of protected chemical functional groups, and subsequently deprotecting it after immobilization has been accomplished, thus leaving behind the desired chemical functional group organization on the surface. Although imprinting has been used for more than sixty years for the preparation of patterned surfaces, it has mainly been limited to organic-type functional group per site. We demonstrate the first coherent imprinting of two different types of functional groups per site, consisting of an amine and thiol spaced apart by approximately 1 nm, both of which are connected to the silica surface. Both groups are chemically bound to the glass in any other fashion. This has been accomplished by developing an imprinting approach that relies on thermally labile protecting groups for the amine and thiol. We have successfully synthesized imprints containing a protected thiolamine pair and have implemented them in both surface-functionalized and bulk imprinted silica synthetic approaches. The nanoscale organization in both surface-functionalized and bulk materials is compared by using a molecular probe that is able to covalently bind to the thiolamine pairs and thereby produces a chromophore, which is highly specific for the imprinted organization. The results of our studies demonstrate the difficulty of achieving site isolation when using a surface-functionalized synthetic strategy, and the importance of a bulk silane synthesis strategy when imprinting silica with multiple different chemical functionalities. The resulting materials can be used as a versatile scaffold for selective nucleation and preparation of materials with higher levels of organization by utilizing orthogonal coupling strategies, and some of these are demonstrated for materials characterization purposes.

11:15 AM Rb13.3

Thin film J-aggregates of cyanine dyes enable the observation of strong coupling between light and matter at room temperature, potentially allowing for the development of new classes of optoelectronic devices [1]. Previously, J-aggregate deposition methods have required the exposure of a device in fabrication to the solvents of a J-aggregate solution, which can potentially damage other optically or electrically active materials and devices involved in fabricating devices. In this work, we present a new stamping technique for depositing J-aggregate thin films that decouples the formation of J-aggregates from the placement of J-aggregate thin films into device structures. Combining research in polyelectrolyte layer-by-layer deposition of J-aggregates with stamping of polyelectrolyte thin films, we show how to form thin films of J-aggregates on a stamp and then dry-stamp those films into device structures. We show the optical and morphological properties of stamped J-aggregate films and calculate the optical constants of the films, which we use to determine the density of J-aggregated dye molecules in the final thin film. Additionally, we investigate device structures enabled by stamping of J-aggregate thin films, including J-aggregate organic light-emitting devices and patterned J-aggregate devices made via stamp pattern transfer. Lastly, we explore the extension of J-aggregate thin film stamping to other methods of depositing J-aggregate thin films, including Langmuir-Blodgett deposition methods. [1] Tischler et al., Phys. Rev. Lett. (2005).

11:30 AM Rb13.4
Writing with Molecules: Supramolecular Nanolithography on Glass. Bart Jan Banov, Steffen Oncelin, Alart Mulder, Jurriaan Huskens and David N. Reinholdt; MESA+ Institute for Nanotechnology, University of Twente, Enschede, Netherlands.

Nanotechnology aspires to create functional materials with characteristic dimensions of the order 1-100 nm. One requirement to make nanotechnology a reality is to precisely control the placement of nanoparticles on surfaces, so that they may be addressed and used for bottom-up construction of nanoscale devices. Here we present the concept of a molecular printboard on glass. A molecular printboard is a monolayer of oligomers or monomers on a solid surface, and such molecules can be attached with control over position, binding strength, and binding dynamics. To this end, cyclodextrin molecules were immobilized on silicon wafers and on glass. Guest molecules (for example, adamantane derivatives) bind to these host surfaces through supramolecular, hydrophobic inclusion interaction. Multivalent interactions are exploited to tune the binding strength and dynamics of the guest molecules to the printboard and competition with host molecules, and new rules for host-guest changes were used to control the interaction between the ink (guest molecules) and the substrate. In this way, nanoscale patterns can be written and erased on the printboard. The potential of the molecular printboard will be illustrated with recent examples of (1) nanoscale fluorescent patterns printed, written and erased on glass surfaces, and (2) microscale patterns of dendrimers that function as molecular boxes that can be filled, emptied and refilled. References: Oncelin, S. et al Langmuir 2004, 20, 5460-5466. Mulder, A. et al Small 2005, 1, 242-253.

11:45 AM Rb18.5
Capillary force lithography for fabricating functional polymer templates. Christiaan M. Brunink1, Peter M.2, P. A. Mulder1, M. de Boer1, L. Kuipers3, J. Huskens3, D. N. Reinholdt1; 1 Supramolecular Chemistry and Technology (SMCT), MESA+ Institute for Nanotechnology, University of Twente, Enschede, Netherlands; 2 Transducers Science and Technology (TST), MESA+ Institute for Nanotechnology, University of Twente, Enschede, Netherlands; 3 FOM Institute for Atomic and Molecular Physics (AMOLF), Amsterdam, Netherlands.

The development of low-cost, high-throughput lithographic techniques for the fabrication of high-resolution patterns has taken a very dominant position in nanofabrication during the last decade. Although state-of-the-art lithographic techniques will remain the main technology for the semiconductor industry, several non-photolithographic techniques e.g. soft lithography[1] and nanoimprint lithography (NIL)[2] have made enormous progression in several areas of exploratory and scientific research (in terms of sub-100 nm resolution, reproducibility, and uniformity over large areas). In this contribution we illustrate the use of capillary force lithography (CFL)[3] for the fabrication of functional, high-resolution polymer templates. CFL is the patterning of polymer layers at a temperature above the glass transition temperature of the polymeric surface. In the framework of the CFL fabrication process, the physical properties of these templates were modified in order to meet the diverging requirements for application as (i) masters for soft lithography[4], (ii) molds for NIL[5] and (iii) etch masks for wet etching of metals.[6] Our template fabrication results demonstrate that CFL is a convenient and inexpensive technique for the fabrication of high-resolution polymer templates with high fidelity over large surfaces. Exemplary results of template structures on silicon of sub-150 nm resolution were fabricated by subsequent use of the polymer templates in any of the three pattern transfer techniques. The diversity of these techniques to replicate the template structure as well as the excellent feature definition of the resulting metal patterns at the 100 nm scale demonstrate the potential of CFL templates as tools for high-resolution lithography. Keywords: soft lithography, capillary force lithography, nanoimprint lithography, polymer templates, high-resolution pattern fabrication [1] Y. Xin, G. M. Whitesides, Angew. Chem. Int. Ed. 1998, 37, 550. [2] S. Y. Chou, P. R. Krauss, P. J. Renstrom, Science 1996, 272, 85. [3] K. Y. Suh, Y. S. Kim, J. H. Lee, Adv. Mater. 2001, 13, 186. [4] M. Brunink, M. Pétér, M. de Boer, L. Kuipers, J. Huskens, D. N. Reinholdt, Adv. Mater. 2004, 16, 1086. [5] C. M. Brunink, M. Pétér, P. A. Maury, M. de Boer, L. Kuipers, J. Huskens, D. N. Reinholdt, Adv. Funct. Mater. 2005, submitted.

SESSION Ra14: Molecular Electronics I
Chair: Fabio Cicora
Wednesday Afternoon, November 30, 2005
Room 207 (Hynes)

1:30 PM Ra14.1
Forces, Current, Molecules. Peter H. Gruetter, Physics, McGill University, Montreal, Quebec, Canada.

One of the crucial factors in molecular electronics is to understand the structure-property relationship. How do the structure of the molecule and the contact electrodes relate to the measured electronic properties? In this talk I will present some of our efforts to control, characterize and understand the details at the atomic scale of systems interesting from a molecular electronics point of view. In the first part, I will present some recent results describing the details of atomically defined contact formation using a combined ultrahigh vacuum scanning tunneling atomic force and field ion microscope to study the Au(111) sample interactions in the regime of weak coupling to strong interaction and simultaneously measure current changes from picoamperes to microamperes. Close correlation between conductance and interaction forces in a STM configuration was observed. In particular, the electrical and mechanical points of contact are determined based on the observed barrier collapse and adhesive bond formation, respectively. These points of contact, as defined by force and current measurements, coincide within measurement error.
Ab initio calculations of the current as a function of distance in the tunneling regime is in quantitative agreement with experimental results. In the next part I will describe various experiments under way in our lab to construct an atomically defined three terminal device on an insulating substrate. We use UHV AFM to investigate the nucleation and growth of different molecules (such as C60 and PTCDA) and metals (such as Au, Pd and Ta) as well as several patterning approaches spanning millimeter to nanometer length scales as first steps towards this goal. A major problem is the large diffusion lengths (of several 100 microns) observed at room temperature on insulating substrates. We find that molecules can however readily attach to metal islands predeposited. Furthermore, we are able to confine and control the number of molecules to a region only a few nanometer in size by creating pits on the insulating substrate KBr(001) surface.

Finally, we learn from our first molecular manipulation experiments that not every desired structural pattern can be achieved. In particular, the line tension of a 2D C60 island allows only shapes minimizing this line tension to be stable and thus observable.

2:00 PM Ra14.2

SWNT-PNA-SWNT Conjugates: Synthesis, Characterization and Modeling. Krishna Veer Singh¹, Xu Wang¹, Rajeev R. Paudey², Roger Lake², Congt Ozbek³ and Mihrimah Ozbek³.¹ Chemical & Environmental Engineering, UC Riverside, Riverside, California;² Electrical Engineering, UC Riverside, Riverside, California;³ Mechanical Engineering, UC Riverside, Riverside, California.

Imparting molecular recognition to carbon nanotubes (CNTs) by conjugating them with bio-molecules has been an area of great interest as the resulting highly functionalized CNT-bioconjugates find their applications in various fields like electronics, pharmaceuticals, drug delivery, novel materials and many others. In this work we demonstrate the synthesis of functionally engineered single walled carbon nanotubes (SWNTs)-peptide nucleic acid (PNA) conjugates especially for nanoelectronic applications. Here we exploited the exceptional structural and chemical advantages of PNA (an artificial analogue of DNA) to join SWNTs ropes. SWNT-PNA-SWNT conjugates were synthesized using carbodiimide coupling chemistry and characterized by a host of techniques like scanning electron microscopy (SEM), atomic force microscopy (AFM) and Fourier transform infrared spectroscopy (FTIR). The results from different techniques confirm the formation of these conjugates. To further study these conjugates for electron transfer, models of SWNT-PNA interface were simulated using the PM3 semi-empirical package in Gaussian03 RevB.03 program suite. Simulations show that the highest occupied molecular orbital lies on the glutamate linker and indicate that this interface state will align closely to the valence band of the extended SWNT facilitating charge transfer. The unique electrical and structural properties of these conjugates make them a potential candidate for application in CNT based nanodevices.

2:15 PM Ra14.3

Multi-valued analog information storage using self-assembled nanoparticle films. Yoshinori Sugawara and Al-Amin Dhirani; Chemistry, University of Toronto, Toronto, Ontario, Canada.

Digital computers use binary states, typically represented by 0 and 5 V, to store and process information at all stages of a calculation. If more states (ideally a continuum) were available in between, density of information could be dramatically increased. Here we show that self-assembled nanoparticle films can feature such continuous state or analog information storage. Nanoparticle films were prepared on glass oxides by alternate immersion in solutions of gold nanoparticle and dithiol linker molecules. These films afforded microlithography-free fabrication bridging nanometer to micrometer length scales as well as a layer-by-layer assembly yielding three-dimensional functional structures. Information provided via an arbitrary gate voltage was 'written' by trapping charges in local, gate-modified potentials when films were cooled below 175 K. The information was 'read' using the film's built-in ability to sense charge via Coulomb blockade.

Application of a variant of multi-valued, multi-state generation conductance maps corresponding to multi-valued analog information. As a proof of concept, we exploited this technique to store ‘UT’ in Morse code.

SESSION Ra14: NanoWires V

Chair: Mila Ozbek

Wednesday Afternoon, November 30, 2005

Room 208 (Hynes)

1:45 PM Ra14.1

Homo-Epitaxial Growth of ZnS Cross Nanowires Array and Its Photoluminescence Properties. Yang Jiang¹, ², Jinshuang Jie³, Wenjun Zhang¹ and Shout-Tong Lee¹.¹ Department of Physics and Materials Science, City University of Hong Kong, Hong Kong, Hong Kong; ²School of Materials Science and Engineering, Hefei University of Technology, Hefei, Anhui, China.

Homo- or hetero- epitaxial growth of semiconductor nanowires, quantum wells, dots on silicon wafer has emerged as potential basis of a large part of the active devices in modern optoelectronic information science and communications. Herein, we report ZnS cross nanowires array homo-epitaxially grown on micro-scale ZnS single crystal, and present a thorough analysis of their morphology, characteristics and photoluminescence. The single crystal ZnS used as epitaxial substrate was obtained by hydrogen-assisted thermal evaporating ZnS powder, which have [120] growth direction, [-2 1 0] top surface and (001) side surface. The epitaxial ZnS cross nanowires array was grown on the surface of the gold coated single crystal substrate at lower temperature from tens minutes to one hour in the same way. On the top surface, the ZnS nanowires grow along [210] and [1-1 0] directions, one of <210> group, respectively, construct the cross nanowires array with 60 degree respect to each other and the epoxilaic substrate (-2 1 0) surface. As for the side surface, the ZnS nanowires grow vertically to the side surface, and produce the nanowires array with [001] growth direction. Photoluminescence (PL) measurements of the cross nanowires array were obtained using the 4th harmonic of a Nd:YAG laser (290nm) as an excitation source. The results show lasing at band gap emission of 357nm and defects emission of about 540nm of Wurtzite ZnS.

2:00 PM Ra14.3

Growth of Epitaxial InAs Nanowires in a Simple Closed System. Hyun D. Park¹, Sharka M. Prokes² and Robert C. Cammarata¹.¹ Materials Science & Engineering, Johns Hopkins University, Baltimore, Maryland;²US Naval Research Lab, Washington, District of Columbia.

InAs is a material with a high saturation velocity and an electron surface accumulation layer. Due to these properties, InAs nanowires would make an ideal electronic material for high performance large area TFTs on flexible substrates. Several methods of InAs nanowire and whisker growth have been reported previously, including metalorganic vapor phase epitaxy (MOVPE), chemical beam epitaxy (CBE), laser-assisted catalytic growth (LCG) and a vapor method using In metal and a GaAs substrate, with a growth time of 36 hours. We report on a very simple and inexpensive method to grow InAs nanowires epitaxially on a InAs[111] substrate. Our method, which utilizes the temperature gradient that exists inside the furnace, is comprised of evaporation inside the sealed quartz tube using bare InAs substrate as a source and a gold-collod coated InAs substrate. This growth technique results in high quality, stoichiometric InAs wires, and there is no need to prefabricate complex target materials, use toxic gases or solid As sources, nor subject the sample to lengthy growth times. A similar growth process can also be used to grow stoichiometric InAs nanowire networks on non-crystalline, large area substrates.

2:15 PM Ra14.4

SiO2 Nanowires with Embedded Au/Si Nanoparticle Chains. Fabian M. Kolb, Andreas Berger, Herbert Hofmann, Eckhard Pippel, Margit Zacharias and Ulrich Goesel; MPI of Microstructure Physics, Halle (Saale), Germany.

Silicon nanowires are potential building blocks for nanotechnology applications. In order to successfully utilize the nanowires, all aspects of nanowire growth need to be fully understood. During the growth of silicon nanowires by combining SiO2 evaporation with the VLS mechanism [1] on gold-coated silicon substrates, frequently amorphous nanowires with chains of embedded nanoparticles are observed. Using energy-dispersive X-ray spectroscopy (EDXS), electron energy-loss spectroscopy (EELS) and high-resolution transmission electron microscopy (HRTEM) we demonstrate that our nanowires consist of pure SiO2 with embedded Au/Si nanoparticles. Experimental results suggest that oxygen plays a vital role in the formation of nanowire chains. Based on the SiO-VLS mechanism we propose a model for the formation mechanism of this special nanowire morphology, where the nanoparticles originate from the Au/Si alloy droplet on the nanowire tip. Based on the experimental results and the proposed model we investigate how to influence the formation of the nanoparticle chains and assess their possible applications via hydrogenation.
3:30 PM Ra15.1
Development of femtosecond time-resolved scanning tunneling microscopy for nanoscience and technology. Hidemi Shigekawa, Institute of Applied Physics, CREST, 21st COE, University of Tsukuba, Tsukuba, Japan.

Smaller and faster are the key words in the progress of current nanoscience and technology. Thus, a method of exploring the ultrafast transient dynamics of the local quantum functions in organized small structures is eagerly desired. Ultrashort optical pulse technology has allowed us to observe phenomena in the femtosecond range, which, however, has the drawback of a relatively low spatial resolution due to the electromagnetic wavelength used. In contrast, scanning tunneling microscopy and its related techniques, although having a time resolution limited by the circuit bandwidth (~100kHz), enable us to observe spatial dynamics at the atomic level in real space. Our purpose is to combine these two techniques to achieve a new technology which will advance the pursuit of future nanoscience: scientific research in terms of the ultimate temporal and spatial resolutions. We proposed a promising new design for achieving ultimate spatial and temporal resolution, by combining a short-pulse laser and STM. Using this method, time-resolved tunneling current measurement in the femtosecond range was successfully demonstrated. Namely, shaken-pulse-pair-excited STM (SPPX-STM) satisfies the requirements for exploring the ultrafast dynamics of the local quantum functions occurring in organized small structures. We hope this new design will advance research in scanning tunneling microscopy on the nanoscale. (http://ora.im.tsukuba.ac.jp/)

4:00 PM Ra15.2
Optoelectronic properties of sublimed and solution processed thin films of dithienothiophene oligomers. Fabio Cicora1, Clara Santato2, Manuela Melucci1, Laura Favaretto1, Massimo Gazzano3 and Giovanna Barbarella4; 1Istituto per la Sintesi Organe e la Fotoreattività, Consiglio Nazionale delle Ricerche, Bologna, Italy; 2Istituto di Studio dei Materiali Nanorrotati, Consiglio Nazionale delle Ricerche, Bologna, Italy.

We have successfully employed the oligomer 2,6-Bis[5′-hexyl-2′,2′:7′,7′-fibriphenyl-5-y]-3,5-dimethyl-dithieno[3,2-b:2′,3′-d]thiophene (DTTTMe) to fabricate light-emitting field-effect transistors based on vacuum evaporated and drop cast active layers. Atomic Force Microscopy images of films sublimed on SiO2 show their good adhesion on the substrate. With a deposition flux of 0.4m/s, continuous films are already formed on a nominal thickness of 6nm. X-ray diffraction reveals that films are polycrystalline. Organic Field-Effect Transistors (OFETs), fabricated on bottom-contact SiO2/n-Si substrates, work in p-type accumulation mode. OFETs based on sublimed active layers show hole FET mobility of 0.01-0.02 cm2/Vs and threshold voltage of ca. 10V. Optoelectronic properties of DTTTMe film are stable and able to generate electroluminescence in transistor configuration. Similar results are obtained depositing the active layer by drop casting. Our results suggest that dithienothiophene derivatives are very promising candidates for all-plastic optoelectronic applications.

4:15 PM Ra15.3
Field Effect Transistors based on Self-Organised Molecular Nano-structures. Massimiliano Cavallini1 and Fabio Biscarini1; 1ISMN Bologna, Bologna, Italy; 2TSMN Bologna, Bologna, Italy.

We present an application of combined Micromolding in Capillaries[1] (MMIC) and Experimentally-Controlled Wetting[2] (ECW) for the fabrication of connected nano-structures of organic semiconductor in between electrodes of field effect transistors (FET) and on to flat surfaces. We demonstrate FET where current flows through an array of stripes, whose height is two-monolayers and width 180 nm, made of well-ordered semiconductor molecules, viz. oligothiophene. The stripes are formed across the channel of the transistor by self-organisation driven by the molecules in a solution confined under the protrusions of a stamp by the capillary forces. Each stripe is formed by two / three coherent domains and it is electrically connected to the electrodes. The charge mobility in the stripes is at least two orders of magnitude larger than that measured on solution-cast thin film devices, and one order of magnitude larger than that measured in high-vacuum-sublimed thin films. Acknowledgements This work was supported by the European Commission, under project NMP-IP NAIMO and the European Science Foundation under Eurocore SONS program. References [1] E. Kim, G.M. Whitesides Nature 376, 581-584, (1995). [2] M. Cavallini, F. Biscarini, NanoLetters 3(9), 1269-1271, (2003)

4:30 PM Ra15.4

Controllably positioning low-dimensional nanostructures in prefabricated circuitry is essential for evaluating their suitability in molecular electronics. Here, we present a method to grow stacks of hexa-substituted amines between microfabricated electrodes by applying a voltage across the electrodes during drop casting of a solution of these amines. Growing molecular nanostructures in nanogaps requires the optimization of conditions including molecule concentration, solvent, applied voltage, gap size, height of electrodes and the resistance of the load resistor. The molecular nanostructures are seen to grow via an electrocrystallization mechanism in which some current flow is required, rather than through pure electric field directed assembly of stacks or individual molecules. This work was supported primarily by the NSEC Program of the National Science Foundation under Award Number CHE-0117752 and by the New York State Office of Science, Technology and Academic Research (NYSTAR).

4:45 PM Ra15.5
Site-Selective Positioning of Nanoparticles on DNA Templates for Nanoelectronics. Gary Braun1, Michael Dietchierov2, D. K. Wood3, Stephanie Wilkinson1, Katsuhiko Inagaki4, Elmar Weinhold2, A. N. Cleland2 and Norbert Reich1; 1Department of Chemistry and Biochemistry, UC Santa Barbara, Santa Barbara, California; 2Department of Physics, UC Santa Barbara, Santa Barbara, California; 3Department for Organic Chemistry, University of Heidelberg, Aachen, Germany; 4Department of Applied Physics, Hokkaido University, Sapporo, Japan.

The ability to position nanoparticles and semiconductor nanocrystals onto molecular scaffolds with nanometer control has potential applications for biosensors, optical waveguides, molecular electronics, and studies of surface enhanced Raman spectroscopy (SERS). We are developing approaches for site-specific placement of NF at predetermined positions within thousands of base pairs. Our approach utilizes bacterial DNA methyltransferases, which normally methylate a specific base pair within a recognition sequence, however in this application transfer a biotin by a modified enzyme substrate. Recently we have shown by AFM that biotinylated gold nanoparticles can be directed by streptavidin to unique positions designed into 300-1000nm DNA. Using these biotin sites we have also constructed one and four-way DNA junctions with nanoparticles positioned at the central site. This capability is combined with methodologies for nonspecific DNA metallization employed on electrode-patterned Si/SiO2 surfaces for electronic characterization of tunneling junctions, and we are currently creating repeating nanomaterial patterns on these templates for energy transfer and SERS studies.

SESSION Rh15: Nanowires VI
Chair: Li Chongyang Chen
Wednesday Afternoon, November 30, 2005
Room 208 (Hynes)

3:30 PM Rh15.1
Nanoparticle-Nanowire Assemblies based on Complementary Protein Interactions. Nicholas A. Kotov1, Jaebeom Lee1 and Alexander Govorov2; 1Chemical Engineering, University of Michigan, Ann Arbor, Michigan; 2Physics, Ohio State University, Athens, Ohio.

Nanoparticle/nanowire assemblies with a degree of radial organization were prepared around luminescent semi-conducting CdTe nanowires using bioconguaction with streptavidin and D-biotin linkers. Red-emitting nanowires (diameter 6.62 nm, length 512 nm) and green-emitting nanoparticle (diameter 3.2 nm) were surface-modified with biotin, while orange-emitting nanoparticle (diameter 4.1 nm) were decorated with streptavidin. CdTe nanocrystals produced two fuzzy layers around the nanowires in which the diameter of CdTe nanoparticles decreased from the nanowire axis. FRET resonance energy transfer (FRET) from the outside layer of nanoparticles to the central nanowire was observed for NW conjugated with 4.1 nm CdTe. Addition of 3.2 nm CdTe resulted in a red-orange-green optical progression with broadening of CdTe decreasing toward the axis of the superstructure. In this case, four-fold luminescence enhancement of the nanowire luminescence was observed and was attributed to multi-step FRET. This observation indicated the accumulated excitons towards the cathode terminal. A simple model of multi-conjugated superstructure with cascade energy transfer is developed and used to describe and understand the experimental data. From the comparison of theory and experiment,
we obtained the rates for exciton transfer between the building blocks separated by the very common SA-B linkers. They were determined to be 1/125 s⁻¹, almost 10 orders of magnitude slower than for the transfer from 3.2 nm nanoparticles and from 4.1 nm nanoparticles to 6.6 nm CdTe nanowires, respectively. Experimental data and theoretical model suggest the possibility of utilizing the prepared superstructures with radial symmetry for several channeling processes. They can also be a convenient model object for the investigation of methods of energy funneling in nanoscale assemblies.

3:45 PM Pb15.2
Metal Oxide Nanowires: Growth, Applications and Devices.
Sanjaya Mathur, Sven Barth, Thomas Ruegamer and Hao Shen; Leibniz Institute of New Materials, Saarbruecken, Germany.

One dimensional (1D) inorganic materials are gaining increasing attention because of their unique structural features and interesting functional properties. Given the structural stability, they show promise for applications without perforative potential in vacuum as well as in oxidizing atmospheres, which provides them a competitive edge over their carbon-based counterparts. A number of synthetic procedures have been developed and demonstrated for 1D nanostructures that have led to intriguing morphological variations (wires, tubes, belts, rods, etc.), however the control over radial and axial dimensions remains a continuing challenge. In addition, the choice of material is rather limited. We have developed a generic approach for the size-selective and site-specific growth of nanowires by combining vapor-liquid-solid (VLS) approach with the chemical influence of molecular precursors. The synthesis of nanowires (NWs) is based on the decomposition of discrete metal-organic complexes in the liquid metal (Au, Ag, Ni, Sn), which allows growing nanowires at low-temperatures with precise control over their diameter and length. The precursor chemistry can be tuned to facilitate the stripping of organic ligands to achieve complete decomposition that is critical for maintaining the gas phase super-saturation necessary for 1D growth. High-yield synthesis of NWs of tin, vanadium and iron oxides was performed by the chemical vapor deposition of appropriate metal-organic precursors. Axial and radial dimensions of the NWs were varied in the ranges 90-1500 nm and 25-40 nm, respectively by adjusting the precursor feedstock, deposition temperature, and catalyst size. We have investigated the device potential of these building blocks as photo- and gas sensors. For instance, by adding tin oxide NWs with UV photon interesting photo-conductance, which can be modulated by tuning the wire diameter as demonstrated for samples possessing radial dimensions in the range 50-1000 nm. The stable photo-response over several on-off cycles demonstrated their potential for applications in UV detectors or optical switches, where the NWs can act as resistive elements whose conductance changes by charge-transfer processes. In addition, tin oxide NWs were grown on sensor platform and their response towards CO was compared with nanostructured tin oxide films. This talk will address the generic feature of our approach for the synthesis of oxide nanowires of various compositions and present the results obtained on device applications.

4:00 PM Pb15.3
Fabrication of Novel Semiconducting Nanowire Heterostructures. Juan-Ging Hu, Yoshiho Bando, Jin-Hua Zhan and Dmitri Ignatiev; Superlattices and Nanostructures National Center, National Institute for Materials Science, Tsukuba, Japan.


4:15 PM Pb15.4
Self-catalyzed Growth of Ge and Core-Shell Ge/Si-C-N Nanowires. Sanjaya Mathur, Hao Shen, Thomas Ruegamer, Vladimir Sivakov and Sven Barth; Leibniz Institute of New Materials, Saarbruecken, Germany.

Semiconductor materials (Ge, Si) in confined 1D (nano)geometries display interesting electronic and optical properties due to the partial quantumization of electronic excitations, which has led to the proposed use of Ge nanowires as building elements in future nanoscale electronic devices, in particular due to the high carrier mobilities. However, implementation of bottom-up concepts for the fabrication of functional devices demands offering precise control over the size and composition of nanowires. In addition, means for the chemical passivation of nanowires surface are currently required to provide them the necessary insulation. We have performed catalyst-free and high yield synthesis of single crystalline Ge and Ge/Si-C-N core-shell nanowires by employing thermally labile molecular precursors. The chemical vapor deposition (CVD) of precursor (Ge(SiH)2 with weak Ge-C interactions produced Ge nanowires at extremely low temperatures (275 degree). Whereas the decomposition of Ge(N(SiMe3)2)2 resulted in core-shell morphology in which single crystalline Ge core is wrapped with a Si-C-N amorphous overlayer. The nanowires could be grown on both single and polycrystalline substrates without performing an additional treatment or application of catalysts. In contrary to the popular VLS technique, nanowires in our case grows through an auto-catalytic mechanism, which is initiated by a defect-assisted diffusion of precursor species and tendency for 3D growth. The growth model was supported by following experiments: (i) preferable growth on artificial defects created by nano-indenting a substrate surface and (ii) occurrence of HR-TEM features, nucleation stages of nanowires on the substrate. The microstructure, morphology and chemical composition of pure Ge and Ge/Si-C-N core-shell nanowires were characterized by XRD, SEM, TEM and XPS analyses. The EDX line scan on Ge/Si-C-N-enriched crystalline core whereas Si was locally distributed in the shell. A comparison of Si 2p binding energy proved that Si exists in the Si-C-N composition and not in the elemental form. In comparison to bulk Ge (~300 cm⁻¹), the high-resolution Raman spectra of both systems revealed a low field shift (~300 cm⁻¹) which excluded the possible formation of GeSi alloy in the later case.

4:30 PM Pb15.5
Growth control and self-assembly of ZnO nanowires using sol-gel technique. Mezy Aude\textsuperscript{1,2}, Swananoot Sumetha\textsuperscript{1}, Ravot Didier\textsuperscript{1}, Tedenac Jean-Claude\textsuperscript{1}, Gerardin Corine\textsuperscript{2}, Tichit Didier\textsuperscript{2}, Bregnion Thierry\textsuperscript{1} and Lefebvre Pierre\textsuperscript{1}; 1 Univ. Montpellier 2, LPM-CNRS UMR CNRS 6617, Montpellier, France; \textsuperscript{2}ENSSCA, LMC30-UMR CNRS 5618, Montpellier, France; \textsuperscript{3}Univ. Montpellier 2, GES-UMR CNRS 5650, Montpellier, France

Zinc oxide is a II-VI semiconductor with an hexagonal wurtzite crystal structure, which presents a direct wide band-gap of 3.37 eV at room temperature and a large exciton binding energy of ~ 60 meV. ZnO exhibits a large variety of nanoscale behaviours among all materials, both in terms of structural and physical properties. Much attention has been paid to nanostructured ZnO materials, due to their potential use for electronic, photonic, catalytic, sensing, etc applications. Among semiconductors having a low dimensionality (1D) ZnO nanowires are of special interest for short wavelength optoelectronic nanodevices having a high efficiency because of their large excitonic binding energy and high mechanical and thermal stabilities. Due to their physical and chemical properties, ZnO nanowires have a great commercial potential but methods have been employed for the growth of ZnO nanomaterials, such as sputtering, chemical vapour deposition, molecular beam epitaxy, metal-organic chemical vapour deposition, which greatly improve the crystalline quality, etc. However, low cost and simplicity of the synthesis processes are required for commercial applications. The wet chemical synthesis route seems to meet these requirements, enabling the preparation of high quality nanowires that are required for growth orientation of ZnO nanowires. Seedless growth process involving a low temperature solution allows us to prepare mono dispersed ZnO nanowires of high quality, which is useful for the study of physical (optical, electrical, etc) properties of isolated ZnO nanowires. Control of the ZnO size, morphology, dimensionality, and orientation is a very important state, due to their tight influence on ZnO properties. Efficient control of both nanostructure dimensionality and assembly is obtained by adjusting the different steps of the synthesis process. In the future, this preliminary work would lead to coxam nanoparticles associated for the formation of 3D super-crystals. Furthermore, functionalization of the substrate seems to be very promising for forming well aligned and uniformly dispersed ZnO nanowires after a sol-gel growth step. Thus, the present method provides a convenient route to obtain high quality and low cost aligned arrays of ZnO nanowires with lasting properties at room temperature.

4:45 PM Pb15.6
LaB6 nanowires and their field emission properties. Jian Zhan\textsuperscript{1}, Qi Zhang\textsuperscript{1}, Jie Tang\textsuperscript{1}, Gong-Pu Zhao\textsuperscript{1}, Guang Yang\textsuperscript{2}, Jian Zhang\textsuperscript{2}, Otto Zhou\textsuperscript{1,2} and Lu-Chang Qin\textsuperscript{1,2}; \textsuperscript{1}Curriculum of Applied and Materials Sciences, University of North Carolina at
Lanthanum hexaboride (LaB₆) has a boron octahedron based stable 3-D network embedded with La atoms. This unique arrangement allows a combination of properties including low work function, low resistivity, low volatility at high temperature, high melting point and high chemical resistance. They have been proved to be and utilized as the best thermionic electron emission source for the past 50 years. On the other hand, field induced electron emission can offer a brightness 100 times higher than the thermionic electron source. The two factors that enable high field emission density at low applied voltages are (a) low work function of the emitter material and (b) sharpness of the tip. We have developed and applied a chemical vapor deposition method to synthesize single-crystalline LaB₆ nanowires. The crystallographic orientation of the grown nanowires can be controlled by the catalysts used in synthesis and their typical diameter is ranged from below 20 nm to over 100 nm. The nanowires’ tip is either hemispherical or flat top with rectangular cross-section depending on the catalyst being utilized. Field emission properties have also been measured from the single nanowire emitters made of the nanowires and results will be presented and discussed in connection with applications as point electron sources used in high performance electron optical instruments such as transmission electron microscopes and scanning transmission electron microscopes.

MEDAL AWARD TALK PRESENTATION

Wednesday Evening, November 30, 2005
5:05 PM
Room 210 (Hynes)

Inorganic Nanotubes and Inorganic Fullerene-Like Materials—From Concept to Applications. Yehuda Tenne, Weizmann Institute, Israel.

“Using the insights gained from the study of inorganic nanotubes, we have opened a new direction in materials science. We have shown that inorganic nanotubes can be used to create a new class of materials with unique properties, such as high mechanical and thermal stability, high electrical conductivity, and high sensitivity to external stimuli. These materials can be used for a wide range of applications, including electronics, energy storage, and sensing. In this talk, I will present some of our recent work on the growth and characterization of inorganic nanotubes, as well as their potential applications.”

Inorganic Nanotubes and Inorganic Fullerene-Like Materials—From Concept to Applications

In 1992, we proposed that nanoparticles of layered compounds will be unstable against folding, and close into fullerene-like structures and nanotubes (IF). Initially, this hypothesis was realized in WS₂, MoS₂ and related diselenides. Subsequently, nanotubes and fullerene-like structures were prepared from numerous compounds with layered, and recently, also non-layered, structure by various methods. Much progress has been achieved in the synthesis of inorganic nanotubes and fullerene-like nanoparticles of WS₂ and MoS₂, as well as many other metal dichalcogenides over the last few years. Synthetic methods for the production of multiwall WS₂ nanotubes by sulfidizing WO₃ nanotubes have been described, and further progress is under way. A fluidized-bed reactor for the synthesis of up to 100 g/day of fullerene-like WS₂ nanoparticles has been established in our lab, and the scaling-up of the synthesis to 100 kg/day and beyond is under way. The detailed mechanisms for the synthesis of fullerene-like WS₂ and MoS₂ nanoparticles and nanotubes of these compounds have been elucidated.

Substantial progress has been accomplished in the use of such nanoparticles for tribological applications, and lately in nanocomposites, e.g., impact-resilient materials for self protection. Numerous testing programs, undertaken jointly with different laboratories and major industrial partners have clearly indicated the usefulness of the fullerene-like WS₂ (MoS₂) technology for a wide range of applications, such as protective coatings, composite materials, and in particular, in the automotive industry. In addition, we have also explored the application of these materials in the fields of energy storage, sensors, and electronics.

Novel applications of inorganic nanotubes and fullerene-like nanoparticles in the fields of catalysis, microelectronics, Li rechargeable batteries, medicine, and optoelectronics will be presented.

SESSION Ra16/Rb16: Poster Session III
Chair: Cengiz S. Ozkan
Wednesday Evening, November 30, 2005
8:00 PM
Exhibition Hall D (Hynes)

Ra16.1/Rb16.1
Rolling behavior of a elastic micro cylinder analyzed by finite element method for micro-manipulation. Toshihiro Ochi,1, Shigeki Saito2 and Kunio Takahashi2; 1Department of Mechanical and Aerospace Engineering, Tokyo Institute of Technology, Tokyo, Japan; 2Department of International Development Engineering, Tokyo Institute of Technology, Tokyo, Japan.

Recently, micro-manipulation techniques such as mechanical micro-manipulation by a single probe are required for assembly of micro-electro-mechanical systems and highly functional micro devices. Mechanical micro-manipulation is often used to pick and place a micro-object by mechanical interaction between the probe and the micro-object. The micro-object, however, adheres to the probe, because the effect of adhesional force becomes dominant as the size of the object decreases. Therefore, to achieve high precision and repeatability in micro-manipulation, it is necessary to analyze the behaviors of the micro-object, which has not been well-known to date. In this study, we investigate the rolling resistance of an elastic micro-cylinder in the adhesive contact with a rigid surface. We estimate the total energy of this system as a numerical function of a contact area between the elastic micro-cylinder and the rigid surface when an external moment is applied to rotate the elastic micro-cylinder. The total energy is defined as the sum of three terms: the elastic energy stored in the elastic micro-cylinder, the interfacial energy within the contact area, and the mechanical potential energy of the applied external moment.

The interfacial energy is obtained from multiplication of a work of adhesion and the contact area; the elastic energy and the mechanical potential energy are obtained numerically by finite element method. To simplify the problem, we adopt the plate strain assumption. In view of the energy balance, we define the rolling resistance as the external moment that critically causes the micro cylinder to rotate.

We calculate the rolling resistance of a polystyrene micro cylinder with radius of one micro-meter.

Ra16.2/Rb16.2
Abstract Withdrawn

Ra16.3/Rb16.3
Phase Transition Approach to Supply a Micro-volume of Water on the Probe-tip for Micromanipulation by Capillary Force. Shigeki Saito1, Osamu Katsui2; 1Department of Mechanical and Aerospace Engineering, Tokyo Institute of Technology, Tokyo, Japan; 2Department of International Development Engineering, Tokyo Institute of Technology, Tokyo, Japan.

The size of an object has decreased in the electrical and mechanical engineering field for fabricating highly functional micro-electro-mechanical systems and photonic crystals. In micromanipulation, even if we can manipulate micro-objects, it is very difficult to detach the micro-objects because adhesional force is dominant. To date, some research groups have tried to manipulate micro-objects by using a micro-drop of water because capillary force has been considered effective in micromanipulation. How to supply a micro-volume of water, however, is still a difficult problem to develop the reliable system of micromanipulation. Thus, in this study, our group manipulates micro-objects with capillary force by condensing water from the atmosphere. This condensed water forms a water bridge. The volume of a water bridge can be controlled by evaporation and condensation. A Peltier device is used for temperature control in order to achieve water phase transition. By using this method, we have achieved repeatable micromanipulation with simple equipments. This experimental result shows the feasibility of this method for automated micromanipulation by capillary force.

Ra16.4/Rb16.4
Abstract Withdrawn

Ra16.5/Rb16.5
Si(001) Surface Self-Organization under Strain Field Influence. 2d Monte Carlo Simulation. Florin Nita1,2, Alberto Pimpinelli2, and Hiroo Omi1,2; 1INFN and Genova University - Physics Department, Via Dodecaneso 33, Genova, I16146, Italy; 2Institute of Physical Chemistry - Romanian Academy, Spl. Independentei 202, Bucharest, Romania; 2LASEMA, UMR 6602 CNRS / Blaise Pascal University, Clermont 2, 63177 Aubiere Cedex, France; 3NTT Basic Research Laboratories, NTT Corporation, Atsugi, Kanagawa, 242 0189, Japan.
The morphology of vicinal and flat Si(001) surfaces during relaxation and during thermal annealing of a strain field is studied by kinetic Monte Carlo simulation. The same model was already used to study the decay of pyramidal nanostructures on Si(001) surface [1]. In the model we have taken into account the deposition, evaporation and diffusion events, with the diffusion energy for the diffusion event is given by: $E_{DD} = E_D + n_1 E_{EL} + n_2 E_{EL}$, where $E_{EL}$ are the lateral interaction energies in parallel, reciprocal perpendicular direction relative to the dimer rows direction in the plane, and $n_1$ and $n_2$ are the numbers of nearest neighbours in these two directions. $E_D$ is the energy barrier due to the interaction with the substrate and can have two different values, $E_{DD}$ or $E_{DL}$, that depending on the dimer diffusion direction relative to the dimer rows direction on the substrate. We performed simulations using different strain field distributions taking into account different possibilities to produce such strain fields (ion implant or local surface deformation). For all cases we compare our simulation results with experimental data. [1]

Scaling of nano-intruding in nano-intruding of microelectronics, L. Boldrin, Microsistemi, Consiglio Nazionale delle Ricerche, Catania, Italy.

The usage of nanodots as discrete storage nodes in non volatile memories has been extensively demonstrated to be a successful approach due to the numerous potential advantages associated with the discrete-trap memories. In order to obtain very low fluctuations in the device electrical characteristics it is very important to precisely control the coverage of the gate area with the nanodots, i.e. to control the dots size and position. Presently the templated growth is believed to be one of the more promising routes for fabrication of nanostructures controlled in size and position. Self-assembly of diblock copolymers offers a simple and low cost method to produce a nanomask with circular pores of about 10 nm in radius, assembled in a closed-packed hexagonal configuration. However, depending on the mass process conditions, self-assembled block-copolymer thin films typically present many hexagonal arrays of pores with different sizes and randomly aligned between them. The size of these hexagonal domains exhibits a finite dispersion, and this indicates the level of long range order obtained. In order to control the size and the position of the dots on the final memory device it is extremely important not only to measure the dot positions but also to measure the size and the number of the hexagonal domains present in the nanomask. In this work we present results on self-assembled Poly(Styrene-b-MethylMethacrylate) diblock-copolymer with several molecular weights. The annealing conditions inducing the microphase separation are also varied to investigate the optimal conditions for long range order. The self-assembled thin polymer films are then used as nanomasks for the deposition of silicon or metals and the formation of the nanostructures after a lift-off process. The samples, either after the mask formation and after the lift-off process, are observed through AFM and SEM equipped with topographical characterization of the nanomasks and by means of a suitable image elaboration technique, the position of the pore centers are obtained. The data are then elaborated by means of a computer code written in order to identify the size and the number of the several hexagonal domains.

A statistical investigation of optimum and robust process conditions for large scale synthesis of CdSe nanocrystals. Tirthankar Dasgupta1, Christopher Ma2, Roshan Joseph Venghazhiyil2, Zhong Lin Wang2 and C. F. Jeff Wu1; School of Industrial and Systems Engineering, Georgia Institute of Technology, Atlanta, Georgia; 2School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia.

Research in synthesising semiconductor nanostructures is a forefront area in nanotechnology due to their applications in nanoelectronics, photonics, data storage, and sensing. The II-VI semiconductors, more specifically cadmium selenide (CdSe), have been investigated over the past decade for optoelectronics, luminescence, laser materials and biomedical imaging. Cadmium selenide is the most extensively studied quantum dot material, and is therefore regarded as the model system for investigating a wide range of nanoscale process and phenomenon in zero-dimensional nanostructures. In spite of numerous studies on CdSe quantum dots, there exist only a few papers reporting the synthesis and properties of one-dimensional (1D) CdSe nanostructures. In particular, one-dimensional nanostructures present the ability to simultaneously address the fundamental issues of reduced dimensionality and quantum confinement in one-dimensional system. A control on the size and size distribution of CdSe nanocrystals is extremely important for CdSe quantum dots. For 1D nanostructures, CdSe has been found to exhibit morphological transformations with the requirements of large scale, controlled and designed synthesis of nanocrystals, it is essential to find process conditions under which the desired nanostructures are synthesized reproducibly, at large quantity with controlled morphology. In this paper, an effort is made to systematically investigate the underlying mechanisms that determine the morphology and dimensionality of 1D CdSe nanostructures. Through a designed experiment and rigorous statistical analysis of experimental data, statistical models linking the probabilities of obtaining specific morphologies to the process variables are developed. The optimum process conditions that maximize the above probabilities and, at the same time, make the synthesis process less sensitive to variations of
process variables around set values are derived from the fitted models.

Ra16.10/Rb16.10
Reflectance spectroscopy of single photonic crystal island fabricated by ink-jet printing. Dong W.1, Minseo Park1, Jungsoo Park2 and Jooho Moon3; 1Department of Physics, Auburn University, Auburn, Alabama; 2School of Advanced Materials Engineering, Yonsei University, Seoul, South Korea.

Photonic crystal is a material that possesses a periodic modulation of refractive index, and exhibits a photonic band gap where certain ranges of frequencies of the light cannot propagate. In the present investigation, a micro-reflectance spectroscopy was performed on a single island of photonic crystal array. An array of islands of photonic crystal with colloidal polystyrene beads was assembled on Si using ink-jet printing. (Two different sizes of polystyrene beads (90 nm, 210 nm, and 270 nm in diameter) were used and the polystyrene colloidal particles were self-assembled to form fcc lattices with three different lattice spacing. It was observed from the reflectance spectra that the position of the optical stop band shifted as the size of the colloidal particle changes. Effective medium approximations were used to model the dielectric properties of the colloidal/air composite. The theoretically expected reflectance peak position agrees well with those of the experimentally observed peaks.

Ra16.11/Rb16.11
Formation of Sr-Si ordered monolayers for atomic templates using SrF2. Francisco Santiago, Kevin A. Boulais, Victor H. Gehman and Robert K. Jungst; Dahlgren Division Naval Surface Warfare Center, Dahlgren, Virginia.

This work explores the fundamental chemical reactions between strontium fluoride (SrF2) and silicon (Si) to form an SrF2/Si/SrF2 bilayer. The vapor flux of the reactant gas (SrF2) is below 10^11 molecules per cm^2 per sec and the gas is highly directed toward the substrate (Si). These reactions are done inside a molecular beam epitaxy (MBE) system kept with a residual pressure below 4x10^-12 torr using substrates temperatures above 600°C. The SrF2 vapor is generated from a Knudsen cell kept at a temperature slightly above the sublimation temperature of SrF2. Previous results from the exposure of BaF2 to Si using the conditions shown above showed the formation of a SrF2 film on Si if the exposure time was sufficient, no SrF2 film formed on Si if the exposure time was insufficient. A perfectly ordered monolayer of Ba linked to Si. This monolayer was used as a template to grow epitaxial films of BaF2 and other materials like PbTe and CdTe with lattice constants greater than Si. Sr features an atomic diameter similar to Si but it has 18 fewer electrons. This may bring an opportunity to develop ordered monolayers that could host epitaxial layers of materials with lattice constants smaller than Si. Results of analysis using x-ray photoelectron spectroscopy (XPS) done in vacuo show total decomposition of SrF2 on the Si surface leaving a monolayer of Sr on Si in manner similar to our Ba results. Reflective high-energy electron diffraction (RHEED), and low energy electron diffraction (LEED), results show that in as the case with Ba, the Sr monolayer is highly ordered. We will report results from exposures done at different conditions and their implication in the development of a new class of compliant substrates.

Ra16.12/Rb16.12
Colloidal Silver Nanoparticle Induced Photoluminescence Quench on the Surface Functionalized Planar Si, Li-Lin Tay1, Nelson Rowell1, Rabah Boukherroub2 and David Lockwood3; 1National Research Council, Ottawa, Ontario, Canada; 2Interdisciplinary Research Institute, Villeneuve d’Ascq, France.

The indirect bandgap nature of the Si renders it an inefficient material for light emission. Planar Si, however, does exhibit weak luminescence signature in the infrared region. This is produced from conduction and valence band carrier recombination. This room temperature bulk Si photoluminescence (PL) can be excited with Ar laser excitation and the signal detected with a sensitive Ge detector. Planar Si typically grows large and well-ordered nanostructured materials, e.g. as a template for carbon nanotube growth. Therefore, metal nanoparticles are often deposited on the planar Si surface as possible catalytic materials. Here we examine the change in the PL of a surface functionalized planar Si due to an in-situ deposition of colloidal Ag nanoparticles. The planar Si (100) was first degreased in acetone and then cleaned in a piranha bath at an elevated temperature. The cleaned wafer was then dipped into 5% of HF to remove oxide and photoresist, then rinsed in DI water and dried. The Ag nanoparticles were prepared on the Si in a two-step process involving first a monolayer of undeucylenic acid molecules self-assembled on the Si(100) surface. A single bounce attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopic technique was developed to monitor the vibrational spectra of Si on monolayer film. The observed vibrational spectrum showed clear carbonyl stretch at 1714 cm^-1 from the undecylene acid on the Si (100) surfaces. Colloidal Ag solution was prepared by reducing silver nitrate with sodium borohydride.(Suh et al., J. phys. Chem., 87, 1540, 1983) It was necessary to work with surface functionalized Si (e.g. Si-C terminated surface) to avoid the rapid surface oxidation reaction. The surface functionalized Si wafer was immersed in the colloidal Ag solution illuminated with 457.9 nm of Ar-laser radiation. The light not only excited PL of the bulk Si but also destabilized the colloidal Ag nanoparticles causing them to form small aggregates, at the same time quenching them on the surface of the Si. In this presentation, we will present the exponential quenching data of the bulk Si PL in the presence of colloidal Ag sol. We will also attempt to explain this quenching mechanism with the formation of electron depletion region at the silicon-nanoparticle junction. We will also show our observation of PL to the measurements of reduced conductance observed for nanoparticle and semiconductor nanowire devices.

Ra16.13/Rb16.13
Silicon Bragg Reflectors and Microcavities with Artificial Birefringence. Irina V. Soboleva, Elena M. Mur'chikova, Andrey A. Fedyanin and Oleg A. Aksyutin; Physics Department, M.V. Lomonosov Moscow State University, Moscow, Russian Federation.

One-dimensional anisotropic photonic crystals, single and coupled microcavities based on porous silicon with birefringence optimized for the control of the nonlinear-optical response are designed and fabricated. Silicon crystal is isotropic due to cubic lattice structure, but porous modification of silicon (110) can possess strong in-plane anisotropy of the dielectric function due to form anisotropy of porous morphology. This dielectric function anisotropy gives a reliable control of the optical and nonlinear-optical response of photonic crystals and microcavities based on anisotropic porous silicon. Photonic crystals, single and coupled microcavities are multilayered structures formed from heavily doped silicon (110) wafer etched in the photolithographic acid solution. The refractive indices of adjacent porous silicon layers are n_{1}=1.81 and n_{2}=2.18. The optical anisotropy values are Δn_{1}=0.03 and Δn_{2}=0.04 for the wavelength of 800 nm. The reflectance spectra demonstrate presence of the photonic band gap (PGB) and the microcavity mode located in the center of PBG. Their spectral position is tuned on the sample rotation around its normal and/or rotation of incident light polarization plane. The dependence of spectral position shift on polarization of the electromagnetic wave orientation relative to the sample optical axes is obtained. The microcavity mode shift increases for oblique angles of incidence and achieves 1.2 of half-width at half maximum (HWHM) of PGB at 10^10^ times, respectively, of second- harmonic (SHG) and third-harmonic (THG) generation intensity is achieved in photonic crystals and microcavities at the PBG edge due to fundamental phase matching condition. The angular positions of SHG and THG peaks are shifted by half and one of peak HWHM, respectively, for various polarizations of the fundamental wave. The 10 times changes of the THG intensity are observed for the switch from the normal to extraordinary one due to anisotropy of the dielectric functions of porous silicon layers. The shift of the angular position of SHG and THG peaks corresponds to changing of the PBG spectral position detected at reflectance spectroscopy.

Ra16.14/Rb16.14

We investigated layer-by-layer self-assembly (LBLSA) as a non-line of sight technique for coating complex shape high-temperature materials such as Si3N4 and Ni-based superalloys in order to improve the environmental stability of these materials for use in advanced gas turbines. In this technique, the substrate surface is electrostatically charged by employing polyvinyl alcohol (PVA) as a host. Polyethylenimine (PEI) is used: (1) as “electrostatic glue” to assemble a single layer of small ceramic particles onto the substrate surface at a time and (2) to provide a layer-by-layer mechanism for controlling thickness and coating uniformity. We prepared a colloidal Ag sol with LBLSA method on a Ni-based superalloy substrate. An aluminum hydroxide sol was used as a precursor in this work. Dynamic laser scattering (DLS) was used to determine the average length of aluminum hydroxide (broad particle size distribution) of 100 nm and its ζ-potential to be +25 mV. The charged boehmite platelets were electrostatically attracted and assembled to the alloy surface whose top surface was pretreated with negatively charged polyelectrolyte layers. Consequently, the assembled boehmite platelets were dried at 100°C and annealed at 1100°C to produce a ~50 nm-thick alumina layer. Similarly, we prepared various structural assemblies of rare-earth silicate particles on Si3N4. We compared the assembly characteristics observed with the boehmite and rare-silicate particles
to those observed for model SiO2 particles, and identified key parameters that control the morphological quality of the assembled structures for our cost-competitive approach.

Ra16.15/Rb16.15 Self-Organizing Nanoscale Electrochemical Junctions and Devices Using Corrugations Surfaces. Rui Yang, Young Min Cho, Ryan Wartena, Mathew E. Spencer and Yet-Ming Chiang; Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

We are developing a scalable self-organization approach whereby repulsive forces between dissimilar materials are used to form in-situ electrochemical junctions in dense particle arrays, while attractive forces between like materials are used to form continuous electronically conducting filaments, resulting in bipolar devices. Specifically we focus on lithium storage compounds in which short-range surface forces due to solvent interactions can induce both self-assembly of like materials and self-separation of dissimilar materials. In this work, direct force measurements are performed by atomic force microscope (AFM) to characterize the attractive and repulsive material systems. Careful selection of the solvent medium introduces a repulsive vdW force between dissimilar electronically conducting filaments, resulting in bipolar devices.

Ra16.16/Rb16.16 Strong, Transparent Multifunctional Carbon Nanotube Sheets Made at Commercially Useable Rates. Mei Zhang1, Shouli Fang1, Anwar Zakharov2, Sergey B. Les1, Ali E. Aliev1, Christopher D. Williams2, Ken R. Atkinson1, and Ray Henry Baughman3.

1Nanotech Institute, University of Texas at Dallas, Richardson, Texas; 2CSIRO Textile & Fibre Technology, Belmont, Victoria, Australia.

We demonstrate a new process that enables the demonstrated production of five-centimeter-wide, meter-long transparent carbon multi-walled nanotube sheets at rates above 7 m/min. These self-supporting nanotube sheets, having fundamentally unlimited width and length, comprise a novel state of matter: a highly anisotropic electronically conducting aerogel with a density of ~0.0015 g/cm3 that can be densified into strong sheets that are as thin as ~50 nm. Experimental results suggest application for transparent, highly elastomeric electroluminescent devices; planar sources of polarized broad-band radiation; two-dimensionally reinforced composites; welding agents for microwave bonding of plastics; conducting inks; and hole injecting electrodes for flexible organic light-emitting diodes.

Ra16.17/Rb16.17 Fabrication and Defect Design on DNA Linked 2-D Colloidal Photonic Crystals Using a Nd:YAG Pulsed Laser. Ramazan Aşımatolu1, Robin M. Bright1, Phillip P. Yu1, Sejong Kim1, Fotios Papadimitriakopoulos1 and Harris L. Marcus1.


Controlled defects were created on DNA linked 2-D colloidal photonic crystals using a Nd:YAG pulsed laser in the presence and absence of an ethidium bromide (EB) dye. The 2-D photonic crystals were self-assembled using 1.8 nm polystyrene (PS) microspheres on functionalized glass substrates. To synthesize the hexagonal close packed crystalline structure, both substrate and particles attached single-strand A on the substrate and sequence B on the particles. The DNA was hybridized using the DNA linker with complementary single-strand A’B’ that anchored the particles to the substrate during self-assembly. The 532 nm second harmonic of the pulsed Nd:YAG laser (1004 nm) with a pulse width of 10 ns was used for the removal of individual colloidal particles from the self-assembled photonic crystals. Diameter of the laser beam was optically reduced from 7 mm to 1.8 mm. Controlled line defects and geometrical shapes (e.g., hexagonal, triangle and diamond) were created on the glass substrates under a medium containing EB dye in 0.1 M NaCl solution.

Ra16.18/Rb16.18 Role of Composition on Structural Stability of Euphotropic Glasses: A Phase Field Study. Ramanarayana Haribaraputram and Vivek B. Shenoy; Division of Engineering, Brown University, Providence, Rhode Island.

We model the role of composition in determining structural stability of nanostructures in thin films using phase field model. Evolution in two typical experimental categories namely phase mixing systems (e.g. SiGe and phase separating systems (III-V alloys) are treated for study by tuning the model features. In Si-Ge systems, elastic stresses gives rise to quantum dots where composition variations determine the final structure of the system. In this work we study the effect of stresses arising due to misfit formed because of differences in composition on the morphological changes arising due to Asaro-Tiller-Grinfeld (ATG) instability. We also study the evolution of the quantum islands during deposition and during annealing leading to additional stress relieved mechanisms like formation of trenches. Our study also attempts to explain the recent experimental observations in III-V systems where lateral composition modulation is observed along with surface undulations. In this case, we study the interaction between morphological instability due to elasticity and the thermodynamically driven compositional instability in dictating the final microstructure. We model the alloy system using a ternary phase field model with A rich a phase as the film, B rich b phase as the substrate and a vapore phase thermodynamics of intermixing or unmixing. The use of the free energy determining the growth as well as degradation of the nanostructures plays an key role in our simulation studies. Here we have attempted to characterize the evolution as a function of kinetic parameters such as surface and bulk diffusion coefficients of different species, material parameters such as elastic properties and operational parameters like deposition rate.


We found "deaf and blind" structures having simultaneous complete phononic and photonic band gaps. These composite materials can control the flow of light and sound at the same time. The existence of complete phononic/photonic gaps can lead to the simultaneous localization of light and sound. These structures can be used to design a new class of acoustic-optical devices that can integrate the management of sound and light. We also study the dependence of the combined gaps on material parameters to provide design guidelines to create photonic-phononic crystals.

Ra16.20/Rb16.20 Directed Formation of Silver Nanowires and Nanoloops by Electroless Deposition. Jiajie Diao1, Ke Wang1, Yong Chen2, Akos Vertes3,1 and Mark E. Reeves1,3.


We present a method for depositing high-density silver nanowires by electroless deposition on nonconductive glass and weakly conducting carbon substrates. The process we have developed does not require catalytic seeding, templating, or surface-capping reagents. Moreover, substrate conditioning can control the morphology and growth rate of the nanowires. On glass surfaces, straight silver nanowires are formed that are typically 20 to 50 nm in diameter and can be as long as ~100 μm. On weakly conducting substrates like thin ITO or granular carbon nanoloops are formed that are several microns in outer diameter and about 100 nm in thickness. Our results indicate that some structural features play a significant role in the deposition process. Data are presented on the effect of pH, surface preparation, and electric fields on the directed formation of silver nanostructures.


Single crystal magnesium oxide (MgO) was found to be very beneficial to the growth of aligned carbon nanotubes (CNTs) arrays as long as 2.2 mm by chemical vapor deposition. Before growth, a thin film of catalyst was always coated on the MgO by magnetron sputtering. Scanning electron microscopy was used to study the alignment and length, and transmission electron microscopy was used to examine the wall numbers, diameter, and graphitization. It was found that the number of walls as few as two can be controlled by the catalyst film thickness, whereas the length is a combined result of gas pressure, temperature, and time during growth.

Ra16.22/Rb16.22 Electrostatically Controlled Monolayer of M13 Virus on Polyelectrolyte Multilayer. Pi Jin Yoo1, Ki The Nam2, Angela M. Belcher3,4 and Paula T. Hammond1; 3Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; 4Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.
A novel means of incorporating ordered bio-functional viral assemblies into an electrostatic thin film nano-assembly has been demonstrated. We used negatively-charged engineered M13 bacteriophage (virus) as the adsortant in the presence of a weak polyelectrolyte multilayer support consisting of a cationic linear polyethylenimine (LPEI) and anionic polyacrylic acid (PAA). Due to a unique phenomenon of interdiffusion, the LPEI/PAA multilayer provides full mobility to the M13 virus, and the addition process drive self-assembly and entropically-driven ordering. The resulting monolayer formation of M13 virus can be tuned for its packing density and directional alignment. Packing density can be modulated via the degree of electrostatic repulsion between M13 viruses by varying the pH of virus solution and a simple flowing process within a microfluidic channel gives the viruses directional order due to their liquid-crystalline behavior. Furthermore, we demonstrate the two-dimensional biomaterialization of the monolayer of M13 virus for nanoparticle and nanowire assembly. Electrostatic binding of cationic gold nanoparticles to the capsid body of a negatively charged M13 generates a well-ordered one-dimensional quantum dot array and nucleation of cobalt ions at the surface of M13 virus enables the two-dimensional assembly of cobalt nanowires on the surface. This technique can be a versatile tool for ordering and processing various biomolecules and nanomaterials, because many materials in nature are charged and exist in such sparse phase. This new self-assembly platform opens a new road for bottom-up based biochemistry and nanotechnology.

R1a.6/23/Rb1.6.23
Abstract Withdrawn

R1a.6/24/Rb1.6.24

Selective dealloying of silver is used to create nanoporous gold membranes from rolled Au/Ag alloy sheet. Similar nanoporous gold can be fabricated as a thin film by the sputtering of the alloy onto a suitable substrate followed by dealloying. Nanoporous gold has potential as a support for filtration of proteins and sensitive detectors with high surface area. During dealloying, redistribution of gold results in a nanoporous network with openings on the order of 10 nm. The initial pore dimensions depend on alloy composition and can be subsequently controlled after dealloying by the diffusion of the remaining alloy elements within the gold. The evolution of the pore morphology has been studied as a function of the annealing conditions and the ambient atmosphere. We show that the temperature-dependent coarsening rate also depends on the gas atmosphere. From F-V data and from the measured E-V data using bulk charge transport models reveal important roles of injection barriers and traps in the local hole transport process at the interface.

R1a.6/25/Rb1.6.25
Single Molecule Spectroscopy of Conjugated Polymers Embedded in a Functioning Organic Diode. Young Jung Lee, So-Jung Park, Andre J. Gesquiere, and Paul F. Barbara. Chemistry and Biochemistry, University of Texas at Austin, Austin, Texas.

A strong correlation was observed between current-voltage (I-V) and fluorescence-voltage (F-V) measurements of MEH-PPV single molecules imbedded in a functioning organic diode. The correlation allows to optically estimate hole density at the hole injection interface as a function of applied bias voltage. Comparison of the hole densities estimated from the F-V data and from the measured I-V data using bulk charge transport models reveals important roles of injection barriers and traps in the local hole transport process at the interface.

R1a.6/26/Rb1.6.26
Atomic Simulations of Crystalline Orientation Selection in Nanofabrication. Longguang Zhou and Hanchen Huang; Department of Mechanical, Aerospace and Nuclear Engineering, Rensselaer Polytechnic Institute, Troy, New York.

During nanofabrication fabrication, nanorods of different crystalline orientations compete. As a result, nanorods of particular orientation may dominate, and such dominance affects the nanorods properties. Using recently implemented atomistic simulation ADEPT, we investigate the orientations competition process at the nanoscale. The simulations take Cu as the prototype; the deposition are carried out at three different incident angles (45°, 60°, and 75°) with fixed azimuth; the deposition rate varies from 1 to 10 micron/min and the substrate temperature is 300K. Our studies show that the nanorods with <110> texture dominate if the incident angle is large (more shadowing effects) and there is sufficient diffusion. Otherwise, some other orientations such as <100> may appear and compete with <111> oriented nanorods.

R1a.6.27/Rb1.6.27
Controllable Self-Assembly of Diblock Copolyopeptides into Hydrogels, Fibers, or Single Crystals. Lisa M. Pakstis, Andrew Nowak, Timothy Deming and Darrin Pochan; 1Materials Science and Engineering, University of Delaware, Newark, Delaware; 2Bioengineering, University of California, Los Angeles, California.

Controlling the kinetics of diblock copolyopeptide self-assembly leads to the formation of various materials. The amphiphilic diblock copolyopeptides are 200 amino acids in length with a lysine (K) block and a hydrophobic leucine (L) block. When assembled quickly in pure water, the polypeptides form rigid hydrogels with bulk mechanical properties that are tunable based on molecular design, i.e. chain length and lysine to leucine block ratio, and solution conditions such as salt concentration. Alternatively, when assembled from miscible organic/water mixtures, block copolyopeptide nanoscale assembly morphology can be altered. Prior suspension of the block copolyopeptides in organic solvent enabled greater copolyopeptide chain mobility that, after water addition and subsequent removal of the organic via evaporation, provides for a more regular packing of the copolyopeptide molecules. At the fastest organic evaporation rate (~6 hours), the copolyopeptides assembled into weak hydrogels with a homogenous microstructure and interconnected fibrillar nanostucture. Slowing the evaporation rate to ~24 hours, and hence the kinetics of assembly, produced regular, noninterconnected fibrils. Longer evaporation times, ~12 days, led to the formation of hexagonal single crystal-like assemblies. Interestingly, copolyopeptides with a racemic copolymer leucine block did not assemble into any regular nanostuctures, indicating that the secondary structure of the leucine block is critical for assembly. In all assemblies, regardless of the resulting nanostucture, the secondary structure of the hydrophobic block remains an α helix, as shown with circular dichroism (CD). Characterization of the hydrogels, fibrils, and single crystals using laser scanning confocal, atomic force, and transmission electron, and cryo-transmission electron microscopies indicate that assembly is dictated by the hydrophobic block association with hierarchical microscale assembly controlled through assembly pathway.

R1a.6.28/Rb1.6.28

Modification of inorganic substrates with organic coatings is an effective way of tailoring their surface properties. These polymer thin films play an important role in various fields such as surface modification, microfluidics, microelectronics, and novel biomaterials. In this work, a long chain of cyano alkane thiol Self-Assembled Monolayer (SAM) is formed on gold. The tail group of the SAM ligates with an organometallic catalyst [Pd(CHC8CN)4][BF4] [1]. This catalyst is very well known to polymerize olefins carboxically. In this investigation, we demonstrated surface initiated polymerization of p-methoxy styrene, polyisobornene using the anchored catalyst. The as grown polymer thin film was characterized using Ellipsometry, Reflection Absorption Infrared Spectroscopy, X-Ray Photoelectron Spectroscopy. This technique is a promising tool to develop patterned polymeric thin films of desired thickness. AFM was done on the patterned polymer brush to determine the surface roughness. [1] Sen, A. Accounts of Chemical Research. 1988, 21, 421.

R1a.6.29/Rb1.6.29
Electric Field-Guided Growth of Mesoscopic Silica Thin Films at the Air-Water Interface. Kevin Jared Tatsum, Jaehun Chum, Dudley A. Saville and Ihsan A. Akay; Department of Chemical Engineering, Princeton University, Princeton, New Jersey.

A key goal in the design of materials is to improve performance by controlling structure across multiple length scales. Nature combines inorganic and organic components to produce composite materials, such as bone and nacre, with structures controlled down to the nanometer length scale. These natural materials have inspired the use of surfactant supramolecular entities in the development of self-assembled mesostructured organic/ceramic composites. The organic material can be subsequently removed by calcination or solvent-extraction, leaving behind a continuous ceramic matrix with a
pore-structure that mirrors the configuration adopted by the surfactant during self-assembly. One such ceramic material system is mesosporous silica by mixing a de-acidified surfactant (cetyltrimethyl ammonium chloride, CTAC) solution with a small amount of inorganic precursor, in this case, tetraethoxysilane (TEOS). Thin films spontaneously “grow” at the air-water interface.

Researchers have previously shown that the films have bimodal mesoporous structure of hexagonally-packed surfactant tubules that meander in 2-D with their axes parallel to the plane of the film[1]. The ability to use these films for separation processes or as catalyst supports is hindered by both the disordered morphology and the in-plane orientation of the mesochannels, demonstrating a key limitation of self-assembly. The driving force of our research is to develop techniques for imparting long-range order to self-assembled materials in order to enhance their applicability. In this work, we present a procedure to use the electric fields applied parallel to the film surface in controlling both the 2-D micrometre- and nanometre-level structure of free-standing mesosopic silica thin films synthesized at the air-water interface over a range of conditions and inorganic precursors.

A combination of polarizing optical microscopy, scanning electron microscopy, transmission electron microscopy, and small-angle x-ray diffraction is used to probe orientation in the films. We find that films synthesized under the influence of electric fields display a high degree of micrometre- and nanometre-level orientation parallel to the field lines compared to control samples synthesized in the absence of an applied field. This technique could be used to tailor self-assembled materials to specific applications and, thus, increase a material’s usefulness.

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Ra16.30/Rb16.30
Multifunctional nanocomposite transparent UV-blocking films synthesized by sol-gel process for optical, automotive and aeronautical applications. Phan Rattana Ayudhamsanayula, Luca Lozzi and Sandro Santoro, Istituto di Scienze, CASTI-INFN Regional Laboratory, L’Aquila, Abruzzo, Italy.

Development of UV blocking thin films with effective cut-off features with steep edges and high transmission in the visible and IR regions have been developed. The unique optical, mechanical and chemical properties of silica and ceria nanocomposites with surface functional groups making them most promising candidate for applications in opto-electronics, automotive and aeronautical industries. On the other hand, highly hydro and oleophobic films are being actively considered in optical, automotive and aeronautical industries to increase adhesion and scratch, abrasion resistance properties. In order to fill the gap, and fulfill the requirements to meet both ends, it could be proved that morphological changes in the nanometer range influences the water contact angles and their hysteresis of low-surface energy materials.

Nanocomposite films of SiO2 and CeO2 with surface functionalization with decadfluorocetyl-triethoxysilane itself forms nano-hemispheres (similar to lotus leaf) at and above 100C favoring an increase in the water contact angle from 122 (25C) to 145 (400C). The structural, optical, compositional properties have been examined by employing X-ray diffraction (XRD)-visible spectroscopy, X-ray photoelectron spectroscopy, respectively. On the other hand, mechanical and scratch and abrasion resistance, hydro-oleophobic, properties have been measured by scratch tester, contact angle and contact angle instruments, respectively. The cut off behavior of the deposited and annealed nanocomposite thin films has been tuned by varying different amounts of CeO2 in SiO2 has also been investigated.

Ra16.31/Rb16.31
Exploring the potential to introduce carbon nanotube probes into bacterial cells by atomic force microscopy. Minhua Zhao1, Haoyan Wu1, Ismael U. Nieves1, Sung-Yong Ju1, Kenneth M. Noll2, Harris Marcus1, Fotis Papadimitrioupolou3 and Bryan D. Huey1.* 1Materials Science & Engineering, University of Connecticut, Storrs, Connecticut; 2Department of Civil and Environmental Engineering, University of Connecticut, Storrs, Connecticut; 3Department of Molecular and Cell Biology, University of Connecticut, Storrs, Connecticut.

A variety of biological applications of carbon nanotubes are emerging, including the potential to Pierce bacterial membranes with functionalized single wall carbon nanotubes (SWNTs) for possible applications in sensing intracellular activities. In this study, SWNT bundles are first assembled onto the apex of commercial atomic force microscope (AFM) tips using direct electrostatics. Utilizing these tips, the mechanics of the surfaces of bacterial cells, Escherichia coli, suspended in phosphate-buffered saline (PBS) solution are studied by AFM via force-distance curves. These results are compared to similar measurements made with standard and sharpened AFM probes.

Ra16.32/Rb16.32
Bulk enrichment of particular single-walled carbon nanotube indices within a distribution. Timothy J. McDonald1,2, Jeffrey L. Blackburn1, Chaiwat Engrakul1, Marcus Jones3, Garry Rumbles1 and Michael J. Heben1.


Finding methods to obtain homogenous collections of a single nanotube type through the purification of an produced sample is an active area of nanotube research. We have been successful in applying laser-assisted selective oxidation of single-walled carbon nanotubes (SWNTs) to remove a particular nanotube type. Also, removal of surfactant followed by centrifugation has been shown to isolation of nanotubes present in a suspension. Nanotube density of states have quantum wire features composed of sharp peaks. Transitions between peaks are strongly allowed, and nanotube indices have strong absorption at these energies. It is possible to select a laser energy such that most of the absorption of the beam takes place with a single nanotube type. Applying such a laser to a SWNT suspension in the presence of H2O2 allows for the selective oxidation of a single nanotube index. Other methods in the sample remain unaffected.

The detection of photoluminescence from surfactant suspended SWNTs allows for the study of individual nanotubes with a known index within a distribution[1]. We have performed photoluminescence excitometry spectroscopy on SWNT-H2O2 suspensions before and after laser treatment. We observe a selective quench of the luminescence from the particular nanotube type with a transition in resonance with the laser. We will discuss this procedure which, in contrast to studies done on solid materials[2], has the potential to more completely remove individual tube chiralities from bulk samples. The excess hydrogen peroxide can be removed with a platinum catalyst, leaving the SWNT suspensions stable for at least many days. We will also discuss other methods for narrowing the distribution of nanotubes, such as the slow removal of surfactant to promote the selective bundling of a particular tube, alternative selective oxidation techniques and suspensions with surfactants that display interactions with certain nanotube indices. 1. O’Connell, M.J., et al., Science, 2002. 297(5581): p. 593-596. 2. Maehashi, K., et al., Applied Physics Letters, 2004. 85(5): p. 858-860. The U.S. Department of Energy (DOE) Solar Photochemistry program funded by the Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences supported this work.

Ra16.33/Rb16.33
Synthetic Helical Nanostructures with Controlled Pitch and Their Application as Chemical Sensors. Liang-shi Li, Hongzhou Jiang and Samuel Stupp. Department of Chemistry, Northwestern University, Evanston, Illinois.

The systematic control of nanometer-scale architectures by encoding the structural information on the molecular level is of great importance for fundamental understanding and applications. It allows the molecular information to be amplified over a much longer length-scales and can therefore be used for sensing purposes. Herein we describe a synthetic approach to self-assembled helical nanostructures whose pitch can be tuned systematically by varying the thickness of molecular monolayers. When the thickness of the conjugated polymers, these nanostructures show responsive behavior to external environments.

Ra16.34/Rb16.34
Carbon Cones- a Different Form of Carbon Structure with Unique Properties. Arne Skjelting, Ren Heining Heiberg-Andersen, Geir Helgesen, Kenneth Knudsen, Jean Patric Pinheiro and Eldrid Svaaasnd; Physics, IFE, Kjeller, Norway.

It is possible to make perfect conical carbon nanotubes fundamentally different from the other carbon nanotube materials, notably buckyballs and nanotubes. Carbon cones are realized in five distinctly different forms. They consist of one or more carbon cones with one to five carbon pentagons at the tip with successively smaller cone angles, respectively. Ge & Satterl at the University of Hawaii first produced them in minute amounts in 1994 using a CVD technique.[1] Soon after, large-scale production was achieved in the so-called Kravner Carbon Black & Hydrogen Process, with pyrolysis of hydrocarbons using an exclusive torch plasma process [2]. The physics of carbon cones has been relatively little explored until now. Recent ad-hoc model calculations show that the structural and functional properties of carbon cones appear to be dramatically different from those of the other forms of nanocarbon, due to fundamentally different topologies. We will very likely result in unprecedented electronic-, chemical- and mechanical properties and open up possible applications like hydrogen storage [5].

In this presentation, we will primarily review the ongoing research on carbon cones performed in Norway. The work will be supported in part by the Research Council of Norway (Project No. 149065/312, 163570/S10 and No. 158541/431. References: [1] M.Ge and K. Satterl, Observation of Fulleren Cones, Chem. Phys. Lett. 220, 192[1994] [2] A. Krishnan, E. Dujardin, M. M. B. Trench, J. Hugdahl, S. Lytum, and...
Tailoring "Air" Defects in Self-Assembled Photonic Band Gap Crystals. Yoonho Jun and David J. Norris; Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota.

Colloidal microspheres can be used to "self-assemble" novel structures known as photonic band gap crystals. The optical properties of these materials can be manipulated by introducing micron-scale structural defects into the photonic crystal. However, there have been no successful attempts to incorporate intentional defects into self-assembled photonic band gap crystals. Here we demonstrate a promising strategy to tailor such defects without disturbing the lattice around the defects. We use photoresists and multiphoton photopolymerization to draw patterns inside the photonic crystal with a laser scanning confocal microscope. Because high temperature processing steps are required to obtain the photonic band gap, conventional organic photoresists are not suitable. Instead, we utilized organic-inorganic hybrid materials (silsesquioxanes) that are converted to silica during the subsequent steps. Confocal electron microscopes were then used to observe the patterned feature inside the 3-D structure. The intentional defects were found not to crack even at the elevated temperatures necessary for further processing of the photonic crystal.

Nano-fluidic capillaries produced by femtosecond laser induced delamination of thin thermal oxide films from Si(100) substrates. Joel P. McDonald1, Katherine E. Ray1, Vanita R. Mistry2, Neville R. Moody3 and Steven M. Walz4; 1 Applied Physics, University of Michigan, Ann Arbor, Michigan; 2 Electrical Engineering and Computer Science, University of Michigan, Ann Arbor, Michigan; 3 Mechanical Engineering, University of Michigan, Ann Arbor, Michigan; 4 Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan; 5 Sandia National Laboratory, Livermore, California.

Highly selective and repeatable delamination of thermal oxide films from Si(100) substrates has been performed using single and multiple femtosecond laser pulses forming bubbles or blisters. By overlapping the bubbles laterally, tubes or capillaries can be formed with a range of volumes suitable for nanofluidics. By scanning the laser through the tube wall, an automated translation stage, patterns of microtubes with arbitrary complexity can be formed, while the scan speed can easily control the volume of the tubes. The production time for capillaries in this fashion is considerably less than with other lithographic techniques, with access to the underlying silicon substrate yields the possibility for integrated devices. The mechanism responsible for the delamination will be discussed and the optimal laser and sample translation conditions will be presented which provide the most uniform tubes. Atomic force microscopy and optical microscopy of capillaries with a range of volumes will be presented, as well as examples of complex patterns applicable to nanofluidics.

Novel Optical Properties Observed from Functional, Nanostructured Hybrid Glasses; Acoustically Coupled Photoerefraction. Lisa S. Brown; University of California, Irvine, Irvine, California.

This talk will present a fundamental challenge in nanotechnology by developing nanostructured optical device materials, which are achieved using a novel optical phenomenon, "acoustically coupled photoerefraction". TEM analysis reveals novel nano-structured fringe patterns due to its nano-aligned structure. The hybrid laser material exhibits a novel optical property, photoerefraction modulated by acoustic waves. The most striking observation is the transient acoustic grating, which is phase shifted by π/2 from the optical grating, and which leads to a diffraction efficiency as high as 80% of the probe beam. The properties of these materials including the near theoretical limited diffraction achieved without applied fields and very fast response time will be of interest to novel devices in nanotechnology. Additionally, the photorefractive that we report in a centrosymmetric material and does not require the application of static electric fields or polling during operation. While both photorefractive and acoustic gratings can be separately demonstrated in different materials, we do not know of examples in which the two effects are coupled. Implicit in such behavior is fast response photoerefraction, which is ascribed to the density-controlled mobility of electrons trapped in aligned nano domains of the hybrid sol-gel hosts. Applications, such as light modulators that rely on electro-acoustic-optical response, acousto-optics, and dynamic holography, are suggested.

Facile Formation of Chemically Functional Nanoparticles. David Fleming, Christopher J. Thode and Mary E. Williams; Chemistry, The Pennsylvania State University, University Park, Pennsylvania.

A library of chemically functionalized noble metal and magnetic nanoparticles has been prepared using a straightforward reaction strategy. In particular, Au, CoFe2O4 and various iron oxides have been functionalized through ligand exchange reaction and the pendant groups further reacted in a single step with redox active, fluorescent, or chemically active moieties. Particle synthesis, as well as characterization via transmission electron microscopy, UV-Visible spectroscopy, NMR, cyclic voltammetry, and fluorescence, will be discussed. The presented functionalization scheme represents a generalized method of nanoparticle surface modification amenable to the synthesis of several classes of functional nanoparticle materials.

In-situ Synthesis, Characterization, and Applications of Boron-doped Single Wall Carbon Nanotubes. Jeff Blackburn1, Yafan Yan1, Kim Jones1, Thomas Gennett2, Michael Heben3,4, and Anne Dillon3; 1 National Renewable Energy Laboratory (NREL), Golden, Colorado; 2 chemistry, Rochester Institute of Technology, Rochester, New York.

Control of the electronic properties of carbon nanotubes (CNTs) is highly desirable for a variety of applications. Specifically, the ability to produce large quantities of highly pure n- and p-type nanotubes would allow the fabrication of sensors, storage media, and optoelectronic materials. CNTs may be doped analogously to solid state semiconductors, with boron doping leading to p-type materials and nitrogen doping leading to n-type materials. For the doping of single-wall CNTs (SWCNTs), ex-situ doping (where dopant molecules are reacted with previously synthesized SWCNTs) has been the most successful path thus far. A wide variety of acceptors and donors have been studied, resulting in SWCNTs with tunable electronic properties. Efforts directed towards in-situ doping of CNTs (where boron and/or nitrogen is incorporated into the nanotube lattice (B/N)) have generally produced multi-walled nanotubes with a variety of structures and morphologies, in addition to small yields of single-wall tubes. In particular, laser ablation syntheses utilizing boron reactants have produced small yields of SWCNTs with little or no incorporation of B into the nanotube lattice. Here we present a novel process to produce B-doped SWCNTs employing pulsed-laser-vaporization. This reaction produces a high yield of SWCNTs, with significant levels of boron doping. The nanotubes are characterized by TEM, small spot electron energy-loss spectroscopy, thermogravimetric analysis, Raman, absorption, and photoluminescence spectroscopy. We will also discuss potential applications for the B-doped SWCNTs, with preliminary results demonstrating progress toward such applications.

Thermally driven nanomechanical deflection of hybrid nanowires. Kazushi Ohira, Junyun Leong, Shin-Ichi Honda, Kenjiro Oura, Hirotaru Morii and Mitshiro Katayama; 1 Dept of Electronic Eng, Osaka University, Suita, Japan; 2 Research center for UHSEM, Osaka University, Suita, Japan.

The building blocks for nanoelectromechanical systems (NEMS) and microelectromechanical systems (MEMS) are being developed aggressively for a variety of applications. Recently, there has been advances in the miniaturization of NEMS and MEMS by adopting new materials, such as carbon nanotubes (CNT) and nanowire (NW). The CNT and nanowire (NW) are appropriate building blocks for the system due to the intriguing physical and chemical properties such as the unique geometry, the mechanical flexibility, the high Young's modulus, the high electrical conductivity, and the high thermal conductivity. In general, to control the mechanical deflection of CNT/NW, electrostatic force, external mechanical force, or infrared radiation has been used. However, to date, thermally driven-NEMS based on CNT/NW has not been performed. In this study, we observed the thermally induced nanomechanical deflection of the hybrid inorganic NWs, which were synthesized by pulsed laser deposition (PLD) of aluminum oxide (Al2O3) and tungsten oxide (WO3) onto thin layers of a CNT template in a sandblasted form. Multi-walled CNTs (MWCNTs) were used as the template for the hybrid NW synthesis have a diameter of 20 nm and a length of over 2 μm. To coat thin layers on the MWN, the PLD was carried out with the angle between the surface of the target and the MWN axis at 45°. Firstly, the target layer (W) was heated to 800 °C, and at 300 °C, the Al2O3 layer was grown onto the W layer. The CNTs were grown in-situ onto the Al2O3 layer formed by PLD at the target temperature. While both photorefractive and acoustic gratings can be separately demonstrated in different materials, we do not know of examples in which the two effects are coupled. Implicit in such behavior is fast response photoerefraction, which is ascribed to the density-controlled mobility of electrons trapped in aligned nano domains of the hybrid sol-gel hosts. Applications, such as light modulators that rely on electro-acoustic-optical response, acousto-optics, and dynamic holography, are suggested.
(Al) on the opposite surface of the first-layer-coated CNT, the specimen holder of the PLD was azimuthally rotated with 180°, and the deposition was briefly repeated under the first layer. After the deposition, each layer was naturally oxidized. The resultant product can be recognized as "thermostast" because it consists of two materials with different coefficients of thermal expansion. Under these conditions, the interaction between the template molecules and the cluster forming element is decisive for the successful implementation of this concept, which leads us to the second part of our investigation. The C60 layers grow on graphite as dendritic structures and their formation can be described by diffusion-limited aggregation. The fractal dimension of the islands increases with time. The interaction of the fullerene island structure with metal atoms, the change in shape and growth mode will be described in detail and the core structures for the formation of bimetallic islands are discussed. Understanding the fundamental interactions within the adatom-C60 system and their impact on the resultant structure will enable us to develop a wider range of molecular templates.

Ra16.41/Rb16.41
Nanoscale Assembly of Nanowires Tempered by Microtubules. Jing Zhou1, Yzy-Jun Mark Luo1, Yan Gao2, Toshikazu Hamasaki3, Evelyn Hu² and Bruce Dunn1: 1Materials Science, UCL, Los Angeles, California; 2Materials, UCSB, Goleta, California; 3Bioengineering, UCLA, Los Angeles, California.

Conventional top-down lithographic processes approach their practical and theoretical limits at dimensional scales less than 100 nm. Alternative bottom-up methods are being investigated to build nanoscale architectures. Many biosystems can self-assemble into regular structures of less than 100 nm and contain functional groups that bind to micrometer length scales. These properties and the interaction between biomolecules as templates to construct nanoscale-architectures. In this study, fabrication and alignment of microtubule-based nanowires are investigated. Microtubules are fibrous proteins found in nearly all eukaryotic cells. These structures about 25 nm in outer diameter and microns in length. These filaments are formed by polymerization of dimerized proteins called alpha- and beta-tubulins. To further stabilize the protein structure, polymerized tubulins are cross-linked with glutaraldehyde. Cylindrical gold particles are bound to the surface of microtubules as nucleation sites for further particle growth. Dense coverage of Au particles is observed after electroless deposition. With electroplating, substrate bound microtubules are completely covered with Au particles. Ni coated microtubules are also fabricated by reducing Ni2+ to Ni0 on Pd activated microtubule surfaces. Focus Ion Beam is used to write metal contacts to these Ni patterned microtubule nanowires and DC conductivity values are obtained. Alignment of microtubules is observed when these microtubules are injected into microfluidic devices over amine-coated glass. Current investigation focuses on fabricating aligned nanowires on the substrate surface and forming nanowire arrays. These biotemplating approaches are the first steps towards more complicated 2D and 3D architectures.

Ra16.42/Rb16.42
Fullerenes as molecular templates in the formation of metal and semiconductor clusters. Petra Reins1, Hui Liu1 and Helge Kroeger2. 1 Dep. of Materials Science and Engineering, University of Virginia, Charlottesville, Virginia; 2 Physikalisches Institut, Universitaet Goettingen, Goettingen, Germany.

Clusters with fewer than 100 atoms are envisaged as components in nanoelectronics, catalysis and in numerous other nanotechnology related applications. The structure and reactivity of these clusters will change dramatically with the number of atoms. An important goal is to develop methods, which allow to tailor the cluster size and spatial arrangement, and create environmentally robust cluster arrays. C60 serves as a model system to exploit the structural diversity and the template properties, where the presence of preferred absorption/nucleation sites provide the template for self-organized cluster growth. The present investigation explores the synthesis of size-selected clusters exploiting the strong interaction between large interstitial spaces and bulk of C60. The relatively large interstitial spaces can provide space for clusters with up to 20 atoms. An additional advantage of the fullerene-cluster system is the ability to create 2D and 3D arrangements by choosing a sequential or simultaneous deposition of the reactants. Scanning tunneling microscopy yields information on the geometric structure of the surface, photoelectron spectroscopy applied in the analysis of the core level and valence band spectra affords information on the cluster size, electronic structure of clusters and interface properties. The growth of the Si on the C60 surface begins with the formation of clusters in the interstitial sites between the C60 molecules. As the growth continues they coalesce and an a-Si overlayer forms. The interface contains no SiC coating and the electronic properties are determined from the PES data. The analysis illustrates that the fullerene surface provides a suitable mold for the self-organized growth of Si clusters. In contrast the absorption of gold occurs at random surface sites and no preferential adsorption of Au clusters is observed. The change in surface topography of thin Au-C60 films illustrates the influence of the metal atoms and indicates the transition to a layer-by-layer growth mode. The structure and properties of the D3h-Si-C60 and Au-C60 were investigated with a wide range of methods and the interaction between the template molecules and the cluster forming element is decisive for the successful implementation of this concept, which leads us to the second part of our investigation. The C60 layers grow on graphite as dendritic structures and their formation can be described by diffusion-limited aggregation. The fractal dimension of the islands increases with time. The interaction of the fullerene island structure with metal atoms, the change in shape and growth mode will be described in detail and the core structures for the formation of bimetallic islands are discussed. Understanding the fundamental interactions within the adatom-C60 system and their impact on the resultant structure will enable us to develop a wider range of molecular templates.

Ra16.43/Rb16.43

We have investigated the biomolecular functionalization of silicon nanowires with DNA, and the assembly of silicon nanowires across electrode gaps as a step toward creation of arrays of nanowire biosensor devices based on electrical detection. Photochemical functionalization of H-terminated silicon nanowires with molecules bearing a reactive olefin (C=C) group was used to produce amino-terminated nanowires with vinyl silanols that were then covalently linked to DNA oligonucleotides. The biomolecular recognition properties of the nanowires were tested as they interacted with complementary DNA and RNA nucleic acid biological molecules, showing good selectivity and reversibility. After removal of the nanowires from their growth substrate we assembled them into circuits using dielectrophoretic manipulation. Optical microscopy videos demonstrate the ability to control the position of individual ~50 nm diameter silicon nanowires near microelectrodes and to selectively capture single nanowires between microelectrode gaps for electrical characterization.

Ra16.44/Rb16.44
Micropatterns of Chiral Self-Assembled Monolayers: Toward Bistable Switching Between Right and Left Handed States. Jinhyun Cho, Ye-Han Cho and Ji-Woong Park; Materials Science and Engineering, Gwangju Institute of Science and Technology, Gwangju, South Korea.

Micropatterned surfaces of chiral self-assembled monolayers(SAM) are fabricated using enantiomeric pair of 1,1-biphenyl derivatives containing surface-reactive functional groups. (R) or (S)-2-bihaphenyl is reacted with 3-(trithiophenyl)propionic ester to yield enantiomERICly pure chiral molecules that are reactive to silica based substrates. A substrate surface is micro-patterned with the enantiomers of biphenyl derivatives with opposite chirality using microcontact printing and immersion method. Processing conditions are optimized to yield the micropatterning that is random over the whole, but that is composed of enantiomERICly pure domains in the micrometer scale. We discuss the interaction of the resulting chiral surface with small molecule or polymeric nematic liquid crystals on its surface, where the chiral molecules twist the nematic phase, that of chiral excess in the chiral monolayer on the phase behaviors of the liquid crystalline small molecules or polymers above the surface is discussed. Switching between two helical states of the induced chiral phases will be also investigated using external stimuli such as circularly polarized light.

Ro16.45/Rb16.45
Wafer-scale nickel imprint stamps based on interference lithography and their applications for copper and anodic aluminum oxide (AAO). Woon Lee, Ran Ji, Mato Knez, Ria Idris, Ulrich Goesele and Kornelius Nielsch; Max Planck Institute of Microstructure Physics, Halle, Germany.

In the last decade, anodic aluminum oxide (AAO) with hexagonally self-organized cylindrical nanochannel arrays has been intensively utilized as a template material for the fabrication of various nanowires and nanotubes, which have potential applications in advanced electronic, magnetic, and optical devices. For the synthesis of structurally and dimensionally well-defined nanowires and nanotubes, a perfectly ordered template is highly desirable, since a wide range of materials properties depend critically on the size, shape, and regularity of their substrate on the nanometer size scale. A combination of lithographic patterning and electrochemical oxidation of aluminum allows the preparation of perfectly ordered AAO templates. Surface properties defined by nanoimprint lithography have been utilized to guide the pore formation and to align the nanochannels. For the development of wafer-scale imprint stamps, first we fabricated photore sist patterns on silicon substrates by laser
interference lithography (LIL), where the period and the square or hexagonal arrangement of the resist patterns can be modulated. The photore sist were used as a master structure for the replication of Ni imprint stamps via electrodeposition technique. The Ni imprint stamps with a periodicity of 200 nm up to 500 nm were used to pre-pattern the surface of aluminum substrates. Subsequently, the pre-patterned substrates were electrochemically oxidized and the perfectly ordered AAO could be obtained. AFM and SEM analyses revealed that the present Ni imprint stamps can be used several times for the surface pre-patterning of aluminum with a high fidelity in the pattern transfer. In this presentation, we will also discuss the practical applications of perfectly ordered AAO templates for the development of various multifunctional nanostructured materials, such as magnetic nanowires and nanotubes, TiO2 nanotubes, and Au nanotube-nanowire structures. The research is supported from the German Federal Ministry for Education and Research (BMBF, Project No. 03N3701) is greatly acknowledged.

Ra16.46/Rb16.46
Template-Directed Growth of Nanoparticle-Mediated Colloidal Crystals on Large-Area Patterned Substrates. Ryaan J. Jeroshiner1, 2, Sumner K. Rhodes1, 2, Florencio Garcia-Santamaria3, 4, 5, 6, Paul V. Braun1, 2, 7, Jennifer A. Lewis1, 2, 7 and Pierre Willutzki1, 2, 7, Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana-Champaign, Urbana, Illinois; 2Frederick Seitz Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois; 3Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois.

Large-domain colloidal crystals were created by gravitational sedimentation of microspheres patterned on large-area substrates. These large-area patterns were produced using multibeam interference lithography, facilitating templated epitaxial growth of single domain crystals with controlled crystallographic orientation. Colloidal crystals were produced from a binary mixture of monodisperse microspheres (diameter~0.5 μm) stabilized by the addition of highly charged nanoparticles (Tohver et al., PNAS (2001)) followed by subsequent nanoparticle gelation (Lee et al., Langmuir (2004)). Successful epitaxial growth was shown to depend on the periodicity of the substrate as well as on the charge and size of the binary suspension, the later allowing the interparticle spacing to be finely controlled. Tuning both of these parameters allowed the crystals to be dried without disrupting their order. The resulting optical properties of the dried crystals are presented, as measured along the [111] and [100] directions.

Ra16.47/Rb16.47
Analysis of New Y-Junction Carbon Nanotube Transistors with Novel Three-Way Electrical Switching and Logic Capability. Chiara Daraio1, Prab R. Bandaru1, Sungho Jin1 and Apparao M. Rao1, 2, 3, 4, 5 Materials Science and Engineering Program, University of California, San Diego, La Jolla, California; 2Physics, Clemson University, Clemson, South Carolina.

A dramatic electrical switching behavior in a nano-particle-containing Y-junction carbon nanotube (CNT) field effect transistor (FET) is reported in this Letter. An abrupt modulation of the current from the ON to the OFF state is observed as the field for the third branch is adjusted, most likely induced by the presence of catalyst nanoparticles and associated defects at the junction. The interactions of the electron currents in the three branches of the Y-junction synthesized by chemical vapor deposition using adherent, Ti-containing, catalyst nanoparticles(2) are shown to be the basis for a new, three-way logic device. Unlike previously reported CNT field effect transistors where the gate structure had to be separately fabricated, the Y-junction transistor has a built-in gate structure as one of the three branches serve as a natural gate. Furthermore, the transistor function can be affected by any combination of the three branches, thus allowing a three-way device operations. This is the first time ever that such switching and logic functionalities have been experimentally demonstrated in Y-junction nanotube without the need for fabrication of an external gate, as only a diode like behavior was previously observed in Y-junctions. The new Y-junction transistor device can enable an entirely new class of nanoelectronic architecture and functionality extending well beyond conventional field effect transistor technologies. In this presentation, transmission electron microscopy and scanning electron microscopy analysis of the Y-junction nanotube microstructure, electrical transport and switching properties, various materials and device fabrication issues, and alternative switching and logic advanced devices will be discussed. (1) P. R. Bandaru, C. Daraio, S. Jin, and A.M. Rao, "Novel Electrical Switching Behavior and Logic in Carbon Nanotube Y-Junctions", Nature Materials 4, 2005 (in press). (2) N. Gothard, C. Daraio, J. Gaertner, R. Zidan, S. Jin, A.M. Rao, "Controlled Growth of Y-junction nanotubes using Ti-doped vapor catalyst", Nanoleters 4, 213-217 (2004).

Ra16.48/Rb16.48
Abstract Withdrawn

Ra16.49/Rb16.49
Controlled Assembly of Nanoparticles. Lisa Dillenback1, Glenn Goodrich2 and Christine Keating1, 2, Chemistry, The Pennsylvania State University, State College, Pennsylvania; 3Nanospectra Biosciences, Houston, Texas.

Nanoparticles are promising building blocks for the bottom-up assembly of high-density electronics and other functional materials due to their small size and tunable optical, electronic, and physical properties. Our current research involves the assembly of nanoparticles both in solution and at a 2-dimensional interface. In solution, temperature is used to control the order of assembly events of three types of particles to be linked by two different modes of DNA hybridization. At higher temperatures, only the duplexes having higher thermal stability are able to form. By starting at a high temperature and then cooling the sample, these more stable sequences hybridize first, followed by the less stable sequences at lower temperatures. Temperature programming combines the selectivity of DNA directed assembly with the ability to control the order in which several complementary strands hybridize in a common solution, and could contribute to the synthesis of more complex nanostructured materials. Two-dimensional assembly is performed at the air/water interface using the Langmuir-Blodgett technique. The behavior of nanoparticles at the air/water interface, and the effect of surface chemistry (e.g. amino thiol) is studied. The effect of forces between particles on the resulting assemblies is under investigation. This 2-dimensional technique can be used to create well-ordered arrays of nanoparticles.

Ra16.50/Rb16.50
Simultaneous Transport and Raman Spectroscopy on Single Walled Carbon Nanotubes. Hootan Farhat1, Eduardo B. Barros2, 3, Hyungbin Son2 and Jing Kong1, 4, 5, 6 Department of Materials Science and Engineering, MIT, Cambridge, Massachusetts; 2Department of Electrical Engineering and Computer Science, MIT, Cambridge, Massachusetts; 3Departamento de Fisica, Universidade Federal do Ceara, Fortaleza, Ceara, Brazil.

Current saturation at high fields in micron length carbon nanotube devices is believed to be caused by electron scattering by high energy optical and zone boundary phonons. Scattering lengths calculated using theoretical electron-phonon coupling strengths, and assuming a thermally equilibrated phonon population(2)[3], are of order magnitude greater than those observed in transport experiments(1)[3]. It has recently been proposed that this discrepancy can be attributed to presence of non-equilibrium phonons(2). Raman spectroscopy is a useful tool for probing the phonon distribution because the intensity of each peak is closely tied to the population of the related phonon. We are performing simultaneous Raman spectroscopy and high field transport experiments to investigate the occupation of high energy phonons during electrical transport. We have fabricated electrically contacted suspended SWNT devices that are compatible with a tunable Raman spectroscopy setup, which has allowed us to obtain resonant Raman spectra over a wide range of nanotube diameters. Measuring the Stokes and antiStokes Raman intensities of biased nanotube devices, we calculate the phonon occupation as a function of applied field. [1] Z. Yao et al., Phys. Rev. Lett. 84, 2841 (2000). [2] M. Lonner et al., cond-mat/0503278 (2005). [3] J-Y. Park et al., Nano Lett. 4, 517 (2004).

Ra16.51/Rb16.51

We present an approach for self-assembly which employs nanopatterned polar surfaces. Separating and controlling chemical and electronic properties of the surface is important for selective deposition. Ferroelectric templates for nano-patterning utilize the local electronic properties (bound polarization, surface dipole, and band bending), which can be controlled by switching the direction of spontaneous polarization with an external electric field, by heating (pyroelectric effect), and by UV-illumination. In this study, charged particles (tunably charged or activated) are deposited onto patterned ferroelectric LiNbO3 (lithium niobate). We found negatively charged zircon perals adhered to negative domains and negatively charged evans blue molecules adhered to positive domains, the differences will be discussed. The results were verified
using several techniques including atomic force microscopy (AFM), optical and fluorescence microscopy, and x-ray photoemission spectroscopy (XPS). Research supported by the NSF (Grant No. 0403871, NIRT on Nanopatterned Polar Surfaces).

Ra16.52/Rb16.52
Fabrication of Patterned Carbon Nanotube Arrays and Study of Their Electron Field Emission. Devon J. McClain1, Lifeng Dong1, Patricia Pan1, Jun Jiao1, Coralee M. McCarter2, David F. Bahn2, Cecilia D. Richards2 and Robert F. Richards2.
1Department of Physics, Portland State University, Portland, Oregon; 2Electrical Engineering Department, Washington State University, Pullman, Washington.

We report on the study of electron field emission properties of aligned carbon nanotube (CNT) arrays. CNT growth was accomplished via chemical vapor deposition (CVD) on catalyst dot arrays created by photolithography. The specific procedure was as follows: (1) An iron nitrate sol gel catalyst was spun onto a silicon wafer (100) and patterned using standard photolithographic techniques; (2) Individual die cut from the wafer were placed in a horizontal tube furnace for multi-walled CNT growth; (3) Growth was achieved at 700 °C for 30 minutes with an admixture of H2 and C2H2 (385 sccm and 25 sccm respectively). The morphology of these arrays was characterized with scanning electron microscopy (SEM), transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS). The configuration of the CNT arrays is determined by the patterned catalyst dots, a finding that iron catalyst dots control the growth of the CNTs. HTREM analysis of an individual CNT revealed that the tube consists of 5-6 graphitic layers. Field emission analysis was performed utilizing a point-to-plane scanning anode-cathode apparatus at a bias pressure of 1x10^-8 Torr. The electron field emission properties, in terms of threshold field, turn-on field, field enhancement factor and emission current of various patterns are compared with other nanostructures such as ZnO nanowires.

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Ra16.53/Rb16.53
Supramolecular assembly of surfactant-like peptides: characterization and study of peptide- membrane interactions. Isabella Miglioni1, Salvatore Chiesari1, Martina Baumann1, Shuguang Zhang2 and Marcus Textor1,1 Materials, Swiss Federal Institute of Technology, Zurich, Switzerland; 2Biology, MIT, Boston, Massachusetts.

Surfactant-like peptides (peptide sequences with both hydrophobic and hydrophilic moieties in a single molecule) self-assemble in a variety of motifs to form pores, channels and tubules. Ion transport through cell membranes, and physical functions such as solubilizing difficult-to-dissolve molecules, are facilitated by the tubes that are formed by molecular assemblies [1]. Peptide membranes are constructed by highly convergent non-covalent processes, both intra- and inter-chain interactions, such as van der Waals, electrostatic and hydrophobic forces as well as hydrogen bonds [2]. In this study the supramolecular assembly of four different amphiphilic peptides is studied and preliminary results on peptide-cell interactions shown. Transmission electron microscopy (TEM) is used to study the supramolecular assembly of the samples in solution, complemented by conformational analysis as a function of concentration and pH achieved by circular dichroism, and morphological studies of peptide assemblies based on atomic force microscopy (AFM). Peptide-lipid membrane interactions are studied by in situ QCM-D, as well as by AFM and TEM, while molecular mechanics calculations are performed to simulate the assembly of selected sequence in aqueous media, and the comparison of such results with those experimentally obtained is also discussed. References: (1) Santilli, G., et al., Positively charged surfactant-like peptides self-assemble into nanostructures. Langmuir, 2003. 19(10): p. 4324-4337, 2. Schultz GE, SR., Principles of Protein Structure, ed. Springer. 1978, Berlin Heidelberg New York.

Ra16.54/Rb16.54

The ability to assemble nanoparticles with defined interparticle linkage and chemical properties is critical to the exploration of the nanoparticle-structured electronic, optical, magnetic, catalytic, and chemical or biological properties. While the assembly of monometallic nanoparticles has been studied extensively in recent years, little is known about the assembly of metal nanoparticle systems, which is in part due to the lack of strategies for controllable interparticle linkages. This presentation describes a new strategy towards the assembly of bimetallic nanoparticles via selective linkage of the linker molecules to the nanoparticle surfaces. Research supported by the NIH (Grant No. 0403871, NIRT on Nanopatterned Polar Surfaces).

Ra16.55/Rb16.55
Novel synthesis method of gold nanoparticles in aqueous media. Abhilash Sugaman1, Joydeep Dutta1 and Jons Hihborn2.
1Microelectronics FOS, Asian Institute of Technology, Pathumthani, Thailand; 2Polymer Chemistry; Materials Chemistry, Uppsala University, Uppsala, Sweden.

One of the most widely used methods for the synthesis of gold colloids in water involves the reduction of an aqueous solution of gold salt (HAuCl4) by trisodium citrate. The colloidal nanoparticles are stabilized by a physical adsorption of excess citrate ions from the medium. In the past decade, several new methods have been developed that are stabilized by an alkanethiolate surface. One goal is to understand the nanoscale properties of the nanomaterials for chemical/biological sensing and catalytic applications. Gold-silver alloy nanoparticles with different bimetallic compositions were studied as model system, and the unique interparticle-linking chemistry of functional groups at Ag and Au sites are exploited for defining the interparticle chemistry. The mechanism for the molecularly-mediated assembly involves the selective mediating effect of the linker molecules at the gold and silver sites and templating effect of the nanoparticle-capping molecules at the gold and silver sites. Implications of the findings to the exploration of binary nanoparticle-structured sensing and catalytic materials will also be discussed.

Ra16.56/Rb16.56
Synthesis and Characterization of Tungsten Oxide Nanostructures by MPECVD. Uei-Shih Chen, Sen-Hung Hsueh and Han C. Shih; Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu, Taiwan.

Tungsten oxides have been grown by microwave plasma enhanced chemical vapor deposition directly on silicon wafer without using any catalyst. Due to the unique property of the plasma system, tungsten oxide could be synthesized in just several minutes (3-5 minutes). It is very economic for saving time and cost. In this study, tungsten oxide have been fabricated in various morphologies, such as nano-rods (20-100nm in diameter), nano-slabs (30-100nm in thickness, 100-500 in width and 1-2 µm in length). Although the cause of different morphologies is still not very clear, from our preliminary observations analyses, the results suggest that the temperature and the gas flow rate play an important role in the growth of these nano-materials of different morphologies. The crystal structure and chemical composition of these nano-rods and nano-slabs are identified by the high-resolution transmission electron microscopy (HTREM), energy dispersion spectrum and selective area diffraction patterns show that
the nanorods and nanoslabs are both single crystal. The results of X-ray diffraction and Raman spectra coincide with the analyses of HRTEM. The luminescence spectra of these nanomaterials reveal a red or orange emission. The vapor-solid growth mechanism is proposed for these tungsten oxide nanomaterials.

Ra16.57/Rb16.57
Vibrational anharmonicity in single-walled carbon nanotubes: Raman linewidth of the radial breathing mode. raul raou1, Christian Poweleit2, Jose Menendez3 and Apparao Rao4; 1Physics and Astronomy, Clemson University, Clemson, South Carolina; 2Physics and Astronomy, Arizona State University, Tempe, Arizona.

The electronic properties of carbon nanotubes are strongly affected by the quasi one-dimensional character of these materials, as demonstrated by a vast body of scientific literature produced over the past decade. Equally dramatic effects are to be expected on the vibrational properties, and in particular, on the anharmonic phonon-phonon interactions that determine phonon lifetimes and thermal expansion. Unfortunately, the notorious experimental difficulties associated with measurements at the single nanotube level have limited progress in this fundamental area. We report here what we believe is the first measurement of the intrinsic lifetime of the Raman-active Radial Breathing Mode (RBM) in carbon nanotubes. This quantity is of great interest because the so-called Klemens decay channel [1] (a zone center optical phonon decaying into two acoustic phonons with equal energy) is limited to a pair of phonons. Therefore, one might expect very small RBM linewidths (the full width at half maximum (FWHM) of the RBM peak is the inverse of the phonon lifetime) in carbon nanotubes. However, the reported FWHMs are about 5-10 cm−1, an order of magnitude larger than in tetrahedrally bonded semiconductors. Measurements of the experimental data are strongly affected by bundling and defects. Recent experiments on isolated single-walled nanotubes (SWNT) on Si substrates yield a FWHM of ~3 cm−1 [2], still large compared with well-ordered semiconductors. For the present study, suspended SWNTs were synthesized by chemical vapor deposition on silicon substrates with 5 micron-wide trenches. The suspension over trenches should minimize nanotube-substrate interactions. Resonant micro-Raman spectra were obtained from several individual suspended SWNTs using 647.1 nm excitation. The spectra were collected with different Raman spectrometers with a resolution close to 1 cm−1. Under these experimental conditions, the Raman line width was sensitive to the incident laser power, suggesting that it was indeed caused by anharmonic interactions. After deconvolution of instrumental effects, the Lorentzian FWHM of the measured RBMs were found to range between 1 cm−1 and 2 cm−1 at room temperature. Assuming that the decay is dominated by the Klemens channel, this implies zero-temperature linewidths between 0.25 and 0.50 cm−1. These values represent an upper limit for the low-temperature width, since the Klemens channel has a weaker temperature dependence than any other competing channel.


Ra16.58/Rb16.58
The interparticle forces and organization of surfactant-coated ZnS nanoparticles in dodecane: effect of water. Moustafa Akhlaghi, Anna Godfrey and Jacob Israelachvili; Chemical Engineering, UCSC, Santa Barbara, California.

The forces between surfaces with confined spherical ZnS nanoparticles coated with a common surfactant (tetradecyltrimethylammonium dodecane were measured in the absence and presence of trace amounts of water. The water molecules cause the nanoparticles to aggregate and adsorb on the (hydrophilic mica) surfaces, resulting in an initial long range exponentially repulsive force between the surfaces. After longer times (t>20 hr), water bridges form between the nanoparticles and surfaces, and attractive capillary forces then cause a long range attraction and a strong short-range adhesion. Clearly, as previously seen in non-aqueous bulk colloidal systems, even trace amounts of water have a profound effect on the interactions and structure of nanoparticle assemblies in thin films that in turn affect their physical properties. These effects should be considered in the design of thin film processing methodologies, and final structure of such films.

Ra16.59/Rb16.59
Fabrication of Free Standing Co/Pt Magnetic Barcode Nanowires with Tunneling Nanomagnetism via Programmable Bar-Code Effect. Joon-rak Choi1,2 and Jiawoo Cheon1,2; 1Chemistry, Yonsei University, Seoul, South Korea; 2Nano-Medical National Core Research Center, Yonsei University, Seoul, South Korea.

Free standing Co/Pt magnetic barcode nanowires with controllable layer thickness are fabricated through pulse-sequence electrodeposition of cobalt and platinum followed by subsequent nanowire isolation processes. All of such barcode nanowires display well-defined bamboo-like shapes with almost identical shape either inside or out of the templates. Magnetic properties of nanowires obtained are fully elucidated by systematically controlling the aspect ratio of cobalt segments and thicknesses. Significant enhancements of the in-plane magnetism of Co/Pt barcode nanowires are feasible through the interfacial alloying processes produced by thermally induced phase transitions. These magnetism controlled free standing Co/Pt magnetic barcode nanowires can be used as versatile building blocks for the realization of 1-dimensional wire based magnetoelectronic devices.

SESSION Ra17: Supermolecular Assemblies I
Chair: Peter Beton
Thursday Morning, December 1, 2005
Room 207 (Hyenes)

8:30 AM Ra17.1
Controlling Matter at the Nanoscale through Supramolecular Engineering at Surfaces. Johannes V. Barth; 1Chemistry and Physics & Astronomy, UBC Vancouver, Vancouver, British Columbia, Canada; 2IPN, EPFL, Lausanne, Switzerland.

The adaptation of biologically inspired principles to artificial compounds and environments opens up intriguing vistas for the development of highly organized systems with molecular-level feature control. Here I focus on using well-defined surfaces as platforms to assemble supramolecular architectures from adsorbed molecular building blocks. Their evolution, order principles and structural characteristics are investigated in exquisite detail by temperature-controlled scanning tunneling microscopy. Complementary experimental studies with integral techniques and model simulations provide insight into the corresponding physicochemical properties and the nature of the underlying noncovalent interactions. In particular we explored hydrogen-bond mediated and metal-directed self-assembly to guide the formation and mesoscopic organization of molecular complexes and arrays, one-dimensional molecular gratings and two-dimensional nanoscopic layers. It is suggested that this design strategy provides a versatile rationale for engineering low-dimensional nanosystems with specific structure, composition and functionality, which bear promise for future technological applications.

9:00 AM Ra17.2
Self-Assembly and Molecular Recognition of Nucleic Acid Bases Studied by STM. Roberto Otero1,2, Maya Schoeck3, Liu Miguel Molina2, Erik Lueggaard2, Ivan Stensgaard2, Bjork Hamn2 and Flemming Besenbacher; 1 Dept. of Condensed Matter Physics, University of Aarhus, Autonoma de Madrid, Madrid, Spain; 2INAS, University of Aarhus, Aarhus, Denmark.

Self-assembly and molecular recognition are two basic and related concepts coming from the emerging field of supramolecular (molecular recognition) chemistry. Most of the foreseeable applications for molecular systems on solid supports, such as molecular electronic devices or nanomechanical biosensors, are based on these two properties of organic species. This has motivated a very important effort towards the understanding and control of the self-assembled geometries of adsorbed species on different solid surfaces. In this respect, Biology is a continuous source of inspiration. From the replication of DNA to the way in which a virus particle anchors to a cell's membrane, everything is related to the concepts of self-assembly and molecular recognition. The capability of complementary DNA strands to steer the self-assembly of other elements attached to them has already been used in various occasions. Furthermore, by providing the DNA strands with surface-anchoring groups, 2D self-assembled architectures could be built. However, the 2D architectures built in this manner are still relatively large, since the larger the DNA strand the more selectively it binds its complementary strand and thus needs a very particular environment for the DNA strands not to denature. In this talk we will present a number of experiments showing that nucleic acid bases (Adenine, Guanine, Cytosine and Thymine) can be deposited on single crystal Au (111) surface where, thanks to the weak interaction with the substrate, they self-assemble and recognize each other, forming very similar motifs to those found for DNA and RNA studies in solution. We will show that guanine molecules on Au (111) self-assemble into a
hydrogen-bonded network of G-quartets with essentially the same structure as those found in vitro studies of telomeric DNA. The large stability of this network to high temperatures can only be explained by a cooperative effect that strengthens the hydrogen-bonds within the quartets, as revealed by our DFT calculations. This constitutes the first evidence that cooperative effects might be basic to properly designing hydrogen-bond-based DNA strands. We have also investigated binary mixtures of complementary (G-C) and non-complementary (A-C) DNA bases. Our experiments show that whereas non-complementary base pairs completely break and segregate in solution, annealing of complementary pairs is stronger and the mixture so formed cannot be separated by thermal treatments. A thorough inspection of STM images shows that the most probable reason for the enhanced stability of the G-C mixed network is the formation of Water-Crick G-C pairs, with a similar geometry as those found in DNA.

9:15 AM Ra17.3
Self-organization of tetraphenylporphyrins on highly oriented pyrolytic graphite. Manuela Scarselli1, Paola Castrucci1, Donato Monti2, Gianlorenzo Bussetti1, Michele Russo2, Claudio Goletti1, Piero Chiarad1, Roberto Paolose1 and Maurizio De Crescenzi1.

The preparation of thin films of porphyrin derivatives is of great interest due to their potential application in material science and for, among others, optical, chemical sensors, and solid state synthetic hemeproteins. One of the most compelling characteristics influencing the properties of porphyrin films is, undoubtedly, the geometry and orientational properties of the model compound. In this work, we present a combined Scanning Tunneling Microscopy (STM), Reflectance Anisotropy Spectroscopy (RAS), X-ray photoelectron spectroscopy and Reflection Energy Loss Spectroscopy (REELS) performed in ultra high vacuum chamber (UHV) at room temperature, on tetraphenylporphyrin (H2TPP) molecules sublimated on highly oriented pyrolytic graphite (HOPG). Once the presence of the molecule and its integrity after the deposition, has been verified by X-ray and RAS spectroscopy, STM observation allowed obtaining the morphological characterization of the molecules deposited on the graphite and the RAS study revealed an anisotropy signal in the Soret band [1]. After very low sublimation rates, STM images show few isolated molecules on the HOPG and RAS is still unable to detect any anisotropy. When spontaneous aggregation of the molecules is visible in the STM, RAS measures a small anisotropy signal (about 0.18%) in correspondence of the Soret band region (1=430nm) of the H2TPP. Molecules are arranged in a highly ordered hexagonal lattice, where each bright structure corresponds to the porphyrin ring of diameter 1.8 nm and height 0.2nm and the distance between adjacent porphyrins is about 3.0 nm. Subsequent porphyrin sublimination cycles increase the RAS signal intensity and shift the energy position of the main peak towards lower energies, in agreement with a J-type interaction of H2TPPs. When STM images observe the formation of agglomerates, anisotropy is distributed on the surface, RAS can measure an anisotropy peak of just reduced intensity. The interaction of porphyrins with the substrate plays an important role in determining the geometry of the ordered films [3,2]. H2TPPs have an intrinsic four-fold symmetry but when spontaneously adsorbed on graphite, they give rise to an ordered film with hexagonal symmetry. The mechanism that determines this unpredictable symmetry is still under investigation in particular, theoretical studies together with some molecular modelling are in progress. These experiments show how the local morphological information obtained with STM can be linked with RAS study as a H2TPP deposition and aggregation on the graphite surface. References: 1. C. Goletti, G. Bussetti, P. Chiarad1, A. Sadasell, A. Borghesi, Organic Electronics 5(1-3) 73-81 (2004) and references therein. 2. T. A. Jung, R. R. Schlitter & J. K. Gimzewski, Nature 386 696 (1997) 3. T. Yokoyama, S. Yokoyama, T. Kamikado, Y. Okuno & S. Mashi8, Nature 413 619 (1997)

9:30 AM Ra17.4
Patterning multilayers of molecules via self-organization. Wei Lu1, Dian-Qing Zhu, and Mechanical Engineering, University of Michigan, Ann Arbor, Michigan.

The electric dipole interaction among adsorbed molecules may cause them to form regular nanomaterials. In a multilayer system, the self-organization of each layer is also influenced by the underlying layers. This paper extends our recent work (W. Lu and D. Salab, Phys Rev Lett 94,146105,2005) to study the patterning of multiple layers of molecules via fluid aggregation. Charge interactions have been utilized to construct functional multilayer systems by the approach of electrostatic self-assembly (ESA). ESA processing involves dipping a chosen substrate into alternate aqueous solutions containing anionic and cationic molecules, such as complexes of polymers, metal and oxide nanoclusters or proteins. This leads to alternating layers of polyanion and polycation monolayers. Design of the precursor molecules and control of the order of the multiple molecular layers allow control over morphology and other properties. While applications such as nanofiltration and photovoltaic devices have been demonstrated, the ESA process is limited to simple, laminar multilayer systems, with little or no lateral organization in the monolayer. We show that for molecules carrying electric dipoles, dipole interaction can induce self-assembled patterns within each layer in a multi-layer system. The capability is desired for making complex structures, especially the formation of nanointerfaces and three dimensional nanocomposites. We consider the presence of two types of molecules in each layer, which are characterized by different dipole moments. The patterns are characterized by the non-uniform distribution of the two molecules. A phase-field model is developed to simulate the model motion and patterning under the combined actions of dipole moments, intermolecular forces, entropy, and external electric field. The model allows us to simulate arbitrary number of layers. The study reveals self-organization pattern formation and the possibility to reduce the domain sizes via a layer by layer approach. Take a two layer system as an example. We show that the first layer determines the overall pattern, while the second layer follows the contour of the first layer pattern with a smaller feature size. It is also shown that the pattern in a layer may define the roadway for molecules to travel on top it. This combined with electrodes embedded in the substrate gives much flexibility to guide the molecular motion and patterning.

9:45 AM Ra17.5
Preparing Si Surfaces for Functionalization. Nelson Rowe1, Li-Lin Tay2, Jean-Marc Baribeau1, Rabah Boukkeroub1 and David Lockwood1, 1National Research Council Canada, Ottawa, Ontario, Canada; 2Interdisciplinary Research Institute, Villeneuve d’Ascq, France.

Recently there has been a large increase of Si-based biosensor activity observed in the literature. Central to this technology is the ability to form self-assembled monolayer directly on the bare Si surface. This self-assembled organic layer on a bare Si surface will provide surface functionality and bio-specific subsequent molecular binding events. Prior to the formation of this first functional layer, a Si wafer must be subjected to a very stringent cleaning essay to remove whatever thin layers of organic contaminants and/or inorganic surface oxides are present. This is a crucial step which will then enable the subsequent successful growth of the functional monolayer being laid down on the wafer surface. Here we adapt the infrared vibrational spectroscopy in a new attenuated total reflection (ATR-FTIR) geometry to investigate the presence of organic and inorganic thin layers on Si-wafer surfaces. In this study, three different Si wafer cleaning processes were explored: (1) microwave plasma etching (2) UV-Ozone etching (3) piranha bath at an elevated temperature. We will compare and contrast the effectiveness of three different cleaning essays for surface contaminant removal. The CH vibrations appearing at 2928 and 2856 cm-1 that are characteristic of organic contaminants were monitored before and after each of the cleaning procedures to quantitatively determine how effectively the surfactant organic contaminated had been removed. We also found that the removal of the native oxide on the Si surface (via HF dip) should not be carried out until these cleaning essays were completed. Premature removal of the surface oxide exposes a hydrophobic Bare Si surface, which then acts as a trap for whatever hydrophobic organic contaminants are present in the solution or air. This was clearly evident from the large increase of CH vibrational signature of the uncleaned wafer. Our results revealed that a combination of plasma cleaning followed by the UV-Ozone treatment on generated the most effective cleaning of Si wafer. In the ATR-FTIR measurement, there was 25 times less absorbance in the CH vibrational signature after such a treatment. Following this procedure with the ATR method, we are able to evaluate quantitatively the effectiveness of the cleaning methods and as well as monitor surface hydrogen passivation. We will show that subsequent functionalization can also characterized with the same method as can oxide regrowth.

SESSION Rb17: Nanoparticles I
Chair: Heinrich Hofmann
Thursday Morning, December 1, 2005
Room 208 (Hynes)

8:30 AM Rb17.1
Hierarchical Design of Metal Oxide Multi-Dimensional Arrays from Solutions. Lionel Vayssieres, ICSY, National Institute for Materials Science, Tsukuba, Japan.

The hierarchical design of well-defined and highly oriented two- and three-dimensional arrays of conventional semiconductor nanomaterials and their large scale manufacturing at low cost remain a crucial
challenge to unfold the very promising future of nanodevices. In addition to economical manufacturing of nanostructured semiconductors, fundamental knowledge of their electronic structure, physical, interfacial and structural properties and stability, is required to fully exploit their fascinating potentials. To combine such essential requirements, the predictive creation of structurally well-defined and well-ordered functional and multi-functional materials is essential. As an attempt to achieve such ambitious goals, a novel strategy to thin film metal oxide semiconductor nanotechnology processing has been developed and investigated. A thermodynamically driven control concept based on the chemical and electrostatic minimization of the surface energy as well as a thin film growth technique have been developed. Such original approach allows the generation of nanomaterials with novel and functional morphologies. Advanced metal oxide nanomaterials consisting of oriented multidimensional arrays featuring building blocks of controlled morphologies, sizes, aspect ratios and orientations at nano-, and microscale are genuinely fabricated directly onto various substrates of the electronic, magnetic, catalytic and/or optical, and undercoating or applied field from the hydrolysis-condensation of aqueous metal salts solutions at mild temperatures (below 100°C). Recent innovative advances in the fabrication of highly oriented and functional nanostructure arrays of transition metal oxides will be presented.

9:00 AM Rh17.2

Novel Crystals as Precursors for Flexible Functional Films. Ludovico Cademartiri1,2, Georg von Freymann3, Andre C. Arenz1, Jacopo Bertolotti4, Diederik S. Wiersma5, Vladimir Kitaeve6 and Geoffrey A. Ozin7

1Department of Science, University of Toronto, Toronto, Canada; 2European Synchrotron Radiation Facility (ESRF), Grenoble, France; 3Department of Chemistry, Wilfrid Laurier University, Waterloo, Ontario, Canada; 4Institute for Applied Physics, University of Karlsruhe, Karlsruhe, Germany.

The use of semiconductor chalcogenide nanocrystals as precursors for the one-step formation of flexible functional films will be discussed. By taking advantage of the surface chemistry of these “zero-dimensional” building blocks we obtain close-packed three-dimensional arrays of nanocrystals interconnected by oxide sheaths. The films are obtained by exposing oxidation-resistant nanocrystals in an air plasma treatment. This treatment does not significantly harm the photoluminescence of the individual nanocrystal building blocks but confers it resilience to bending as well as acidic environments, hot solvents, annealing, and UV irradiation. Chemical accessibility and selective etching of the nanocrystals allows for micron scale patterning of the film. Preliminary results on the tuning of the film composition will be presented.

9:15 AM Rh17.3

Fast and Efficient Fabrication of Gold Nanoparticle Networks using Double-Stranded DNA. Ulrike Rehn1, Paul Tiburzi Miele1, Ralf B. Wehrmann1 and Ulrich Gosele2

1Max Planck Institute of Microstructure Physics, Halle/Saale, Germany; 2Department of Physics, University of Paderborn, Paderborn, Germany.

The controlled integration of functional nanoparticles into superstructures is crucial for the fabrication of nanoparticle-based devices, but remains still a challenge. Short artificial DNA sequences may be used as linker molecules, since their chain length as well as the composition of the sequence can be customized. Particularly interesting is their combination with metal nanoparticles, because the resulting hybrid systems are promising candidates for sensing or photocatalysis. The general objective is the fabrication of flexible, ordered 3D building blocks of DNA-conjugated nanoparticles. To reach this, the detailed understanding of mechanics behind the network formation and the interactions between DNA and the particles is a prerequisite. Thus, a method based on use of double-stranded DNA and a variation of available thiol-groups was exploited. Besides the unambiguous evidence for the guidance of the particle network formation by the dsDNA, the morphology of the hybrid materials as well as the reversibility of the network formation was investigated by uv-vis spectroscopy and transmission electron microscopy. The data have been cross-checked by theoretical calculations using Mie theory. The results show, that the double-stranded DNA is highly efficient due to less interactions with the particle surface. No additional stabilizing molecules like alkanethiols are necessary, and no unspecified aggregation occurs. The latter is one of the limiting factors for the DNA-hybrid growth and will be discussed from the viewpoint of electostatic interactions between the particles [1]. A method to combine the advantages of both double- and single-stranded DNA will be presented. [1] U. Rehn et al., Proc. Fourth IEEE Conference on Nanotechnology, WE-P 24, Piscataway, USA (2004).

9:30 AM Rh17.4

Alignment of Gold Nanoparticles along Mesoporous Nanofibers with Controlled Pore Architectures. Jianfeng Wang1 and Galen D. Stucky2; 1Physics, CUHK, Shatin, N.T.; Hong Kong; 2Chemistry, UCSB, Santa Barbara, California.

Mesoporous silica materials with tunable pore diameters on the nanometer scale and varying pore organizations can function as robust and open scaffolds to create novel composites with active components embedded inside pores. Up to date, a variety of nanoscale building blocks with interesting electronic, magnetic, optical, and catalytic functionalities have been embedded inside mesoporous silica materials, the morphological shapes of which include thin films, spheres, and irregularly-shaped particles. We have used cationic surfactants as structure-directing agents to synthesize mesoscale mesoporous fibers and ribs and incorporated gold nanoparticles inside mesoporous fibers along their length direction. These fibers and ribs possess core channels that are hexagonally packed and 2-3 nm in diameter (Wang, J. F.; Tsung, C.; Hong, W. B.; Wu, Y. Y.; Tang, J.; Stucky, G. D. Chem. Mater. 2004, 16, 5109-5118; Wang, J. F.; Tsung, C.-K.; Hayward, R. C.; Wu, Y. Y.; Stucky, G. D. Angew. Chem. Int. Ed. 2005, 44, 332-336). The fibers have diameters ranging from 50-300 nm, and they possess either circular pore architectures with pore channels oriented perpendicular to the fiber axis or longitudinal pore architectures with pore channels oriented parallel to the fiber axis. The ribs are 50-250 nm thick and 0.4-1.5 μm wide and they have running-track-like pore channels oriented perpendicular to the ribbon length direction. Remarkably, the ribs with two types of core channels and ribs can all be simultaneously controlled. Gold nanoparticles are incorporated into mesoporous fibers by hydrogen reduction of a gold salt. Their shape can be synthetically controlled to be either spherical or elliptical. Furthermore, the orientation of elliptical gold nanoparticles depends on the pore architecture of the fiber. The elliptical gold nanoparticles grown inside the fibers with longitudinal pore architectures have their long axes oriented parallel to the fiber axis, while those grown inside the fibers with circular pore architectures have their long axes oriented perpendicular to the fiber axis. Because gold nanoparticles exhibit unique plasmon resonance properties, the plasmon coupling between gold nanoparticles aligned inside mesoporous nanofibers mediates these composite materials as ideal candidates for controlling the wavelength scales below the optical diffraction limit.

9:45 AM Rh17.5

Binary superlattices of nanoparticles with different size and shape. Elena V. Shvetchenko1,2, Dmitri V. Talapin3, Christopher B. Murray4 and Stephen O’Brien5

1Department of Applied Physics and Applied Mathematics, Columbia University, New York, New York; 2IBM T.J. Watson Research Center, Yorktown Heights, New York.

Colloidal synthesis allows producing nanoparticles with different functionality, size and shape. Monodisperse nanoparticles show a tendency to self-assemble into ordered structures. The synthesis of several different materials into a periodic superlattice is a promising tool to create novel materials with unique properties originating from the interactions between nano-scale building blocks. Co-crystallization of nanoparticles from multi-component colloidal mixtures leads to the formation of ordered superlattices over tens square micron areas. The structure and the stoichiometry of binary superlattices consisting of quasi-spherical nanoparticles can be varied in a broad range. The most of nanoparticulate binary superlattices has analogous among atomic binary systems. Thus, we developed technique for controllable growth of superlattices isosstructural with Na2Zn1, AlB2, NaCl, Fe4C, CuC6, CuAu, Cu3Au, etc. Control of particle shape provides an additional degree of freedom for designing binary superlattices with sophisticated structures. Several examples of superlattices formed by nanoparticles of different shape will be demonstrated. The diversity of experimentally observed nanoparticulate binary superlattices is in consistence with the theoretical predictions for non-interacting spheres. The role of particle-particle interactions such as dipolar, van-der-Waals, etc will be discussed.
Molecular networks and nanostructures have been formed using two complementary approaches—self-assembly and scanning probe induced manipulation. First, hydrogen bonding between molecules adsorbed on silicon surfaces is used to provide a highly specific directional interaction which controls the placement of neighbouring molecules. Through appropriate choice of molecules it is possible to form an extended regular network of two dimensional pores. The pores have a diameter in the range 0.5 - 3.5 nm and may be used to capture further adsorbed molecules giving rise to novel ordered structures and growth phenomena. We discuss examples of bimolecular networks which are directed by the use of the melamine/cyanuric acid which has been studied widely in supramolecular chemistry and is stabilised by a triple hydrogen bond. The pore size and spacing is controlled through choice of component molecules. Specifically one molecule (e.g. melamine) is used as a molecular vertex with threefold symmetry which combines with a second ‘edge’ molecule (e.g. cyanuric acid and related perylene derivatives) to form a honeycomb network. The formation of fullerene clusters within the pores is demonstrated including highly regular 'magic' C60 heptamers. For the higher fullerene C84 more complex structures are formed which undergo growth induced transitions induced by the addition of a single fullerene molecule. We also describe recent results showing that tip induced molecular manipulation of C60 adsorbed on Si(100) proceeds through a rolling motion. This leads to a long range periodicity in tip response and is caused by a coupling of bond breaking and reformation induced by the tip.

Surface Chirality from Enantioselective Co-adsorption of C60 and ACA, Jie Xu, Chenggang Tao, Janice Reut-Robey and Ellen Williams; Univ. of Maryland, College Park, Maryland.

Chiral surfaces are actively studied for homochiral enantioselective catalytic reactions or achiral molecules which become chiral due to broken symmetry after adsorption) provides a typical route to produce chiral surfaces. Here we demonstrate the surface chirality can also be introduced through the arrangement of achiral molecules. By co-adsorption of acridine-9-carboxylic acid (ACA) and C60 on room temperature Ag (111) substrate, an intermixed ACA and C60 supramolecular structure is formed. Two distinct chirality are identified with molecular-resolved STM images. The chirality stems from the ACA arrangement and C60 position within ACA arrays. Inside the domain of this intermixed structure, each unit cell has two pinwheels (ACA trimers) with opposite rotational direction, namely a R trimer for clockwise and an S trimer for anticlockwise. C60 molecules are enantioselectively located on top of the trimers with identical chirality throughout the domain. The chirality of the domain is then determined by the unoccupied ACA trimer. It is noted, because of the supramolecular structure, the distance between C60 molecules is 2.65 nm, increased by 165% compared with that in the bulk C60 crystal. Such mixed phase systems thus offer a new strategy for generating chiral surfaces with tunable physical and electronic properties, as needed for device applications. 

Optimal control of molecular adsorption on surfaces. Petr Kral and Boyang Wang, Department of Chemistry M/C 111, University of Illinois at Chicago, Chicago, Illinois.

We design a new approach that allows to control adsorption of molecules on surfaces. The method requires to perform structural modifications of the surfaces in a predefined fashion. We show that precise molecular control can be achieved by this approach. The method has numerous potential applications in material and device sciences.

Self Assembly of Anisotropic Organic Molecules: Diffusion versus Sticking Anisotropy. Stephen Berkheizer1, Gregor Hlavaček2, Martin Oehzelt3, Roland Rese3, Falko P. Netzer1 and Michael G. Ramsey2.1 Institute of Physics, Karl-Franzens-University, Graz, Austria; 2Institute of Physics, University of Leoben, Leoben, Austria; 3Institute of Solid State Physics, Graz University of Technology, Graz, Austria.

The molecular/crystal orientation and morphology of active molecular structures is a key determinant for the function of nanoscale organic devices. In π-conjugated systems both charge transport and optical properties will depend strongly on the molecular orientation due to the highly anisotropic charge carrier mobility in these organic crystals and the anisotropic absorption and luminescence behavior of the molecules. Although the importance of organic inorganic interface formation and thin film growth is widely acknowledged, little is known regarding the growth kinetics. A better understanding of the processes driving molecular self-assembly is necessary if the self-assembly process is to be controlled. More interesting is the anisotropy of the molecular building blocks presents a fundamental difference to what we know from inorganic growth. In this presentation we either discuss that either sticking or diffusion anisotropy can control the growth depending on preparation conditions. This is illustrated by a detailed investigation into the sticking of sexiphenyl (6P) on the anisotropic TiO2(110)-(1x1) surface for temperatures between 80 and 400 K using in-situ UV photoemission, x-ray absorption spectroscopy, synchrotron x-ray diffraction and x-ray atomic force microscopy. For 6P adsorption even at 80 K we found that the molecules orient parallel to the TiO2 oxygen rows and form small nanoclusters. At 300 K the situation is determined and large micrometer sized (6P20) oriented needlelike crystals perpendicular to oxygen substrate rows are formed. In contrast, for growth at elevated temperatures the 6P molecular axis is near perpendicular to the surface and large islands elongated parallel to the substrate rows are formed. These different adsorbate orientation and morphology can be explained by the domination of the growth kinetics by either sticking or diffusion anisotropy depending on growth temperature. The effect of these different geometric structures on the observed valence band structure will also be discussed. Supported by the Austrian Science Foundation (FWF).


Organic groups that form supramolecular architectures via well defined interactions such as π-π interactions, steric effects and hydrogen bonding can be used to control the structural evolution of nanohybrids, leading to control over the self-assembly and orientation of organic and inorganic domains within the nanohybrids. Here we investigate the structural evolution of a series of nanohybrid powders and coatings incorporating self assembling organic species based on complexes between aromatic cores and functionalised alkyldialkoxysilanes. The structural evolution of conventional (non self assembling) nanohybrids by methyltrimethoxysilane was also investigated for comparison. Self assembly in solution prior to initiating formation of the inorganic network was studied by vibrational spectroscopy, 29Si MAS NMR, light scattering and small angle X-ray scattering (SAXS), while the nanostructure and properties of the corresponding thin films and nanowhiskers were investigated by XRD, APM, TEM, SAXS, X-ray reflectometry and Raman spectroscopy. The mechanical properties of selected coatings were examined using indentation and tensile testing. Coating solutions prepared by hydrolysing MTMS:TMOS mixtures under acidic conditions exhibited weak flat SASS patterns, consistent with the presence of small, structurally diverse species in solution. In contrast, the corresponding solutions prepared from the acid/amine complexes exhibited scattering patterns consistent with larger, more structurally defined species. Investigating that self assembled moieties were forming in solution prior to deposition of coatings and/or formation of nanowhiskers. Raman spectra indicated that the self assembled moieties remained intact during hydrolysis of the acid groups and evolution of the inorganic network. To the extent of cross linking and abundance of hydroxyl species within the nanohybrids (72Si MAS NMR) could be modulated by controlling the amine/carboxylic mole ratio and by inclusion of additional silica source (either TEOS or TMOS). Alternatively, hydrogels formed in aqueous media. TEM images presented the presence of well defined domains in the self assembled coatings (with dimensions of 20 to 100 nm), whereas the corresponding coatings produced from the MTMS:TMOS mixture were smooth and featureless. Tensile testing and nanoindentation
studies indicate that the self assembled nanohybrid coatings were well adhered to the substrates, with hardness and Young’s moduli of 0.65 to 1.7 GPa’s, respectively. These results show that the surface structure of these materials to modulate the size and spatial orientation of the domains, and post functionalisation for control of surface chemistry, will be presented.

SESSION Rb18: Nanoparticles II
Chair: Bruce Lennox
Thursday, 15th December 1, 2005
Room 208 (Hynes)

10:30 AM *Rb18.1 Directed Self-Assembly of Multilayer Thin Films of Manganese Doped Zinc Sulphide Nanoparticles by a Modified Polyelectrolyte Deposition Technique. Jaydeep Dutta1, Syed Hassan Mujtaba Jafri2, Sujira Promninmit1, Chanchana Thanachayanont1 and A. B. Sharma2; 1Microelectronics, Asian Institute of Technology, Pathumthani, Thailand; 2National Metal and Materials Technology Center, Pathumthani, Thailand; 3Information & Communications Technology, Asian Institute of Technology, Pathumthani, Thailand.

Fabrication strategies that rely on mechanisms of self-assembly are now widely being recognized as invaluable tools in nanotechnology. By self-organization of nanoparticles, it may be possible to manufacture materials and devices mimicking nature. Such self-organized construction of advanced materials could be carried out by tailor made nanoparticles as building blocks. A prerequisite to utilization of colloids in nanotechnology is that they remain in suspension and resist settling down. The stability of colloids can be achieved by two means: electrostatic stabilization, involving the creation of an electrical double layer arising from ions intentionally adsorbed on the surface of the particle and associated counter ions that surround the particle, and by Steric Hindrance, which can be achieved by the adsorption of large molecules such as polymers on the surface of the particles. The inherent necessity to introduce steric hindrance to avoid colloid agglomeration can be utilized to induce self-assembly processes which can be used for the layering of polyelectrolytes. Here we will report the development of a modified polyelectrolyte deposition technique for building multilayer thin films. Quantum dots of zinc sulphide nanoparticles have been synthesized by co-precipitation techniques and capped by chitosan that is extracted by alkali deacetylation of chitin which stabilizes the colloid. The amide groups in the chitin monomer is deacytlated to form positively charged amine (NH2) groups. We will report the fabrication of alternate stacks of monolayers of Mn doped ZnS nanoparticles [30 nm particles] followed by the deposition of a layer of anion, polyacrylic acid (PAA) or Poly (sodium 4-styrenesulfonate) (PSS). Subsequent layers are attached by simply dipping alternately into PA or PSS or POE (cyano capped) colloids in intermediate steps of washing. The intermediate washing step is necessary to remove all unattached excess particles (or polymer) from cross-contaminating the subsequent layers. We have utilized the modified polyelectrolyte deposition technique for the growth of multifunctional nanoparticulate ZnS thin films and fabricated Schottky diodes with aluminum and gold electrodes. The Schottky junction device exhibit diode-like behavior and this technique show promise for simple large area construction of diodes using wet-chemistry. The electronic properties of these diodes will also be presented and discussed.

11:00 AM Rb18.2 Large Arrays of Ordered 1 and 2 Dimensional Arrangement of Nanosized Particles. Heinrich Hofmann, Frederic Juillerat and Paul Bowen; Ecole Polytechnique Federal Lausanne, Lausanne, Switzerland.

Many potential applications in nanotechnology, like magnetic storage media, require virtually defect-free arrays of nanometer scale particles over large areas. Guided self-assembly of colloidal particles on patterned templates has been shown to produce ordered arrays of colloidal particles. However, there is a need to extend this technique to particles measuring much less than 50nm in size and to develop robust fabrication techniques that would lead to defect-free, large-area arrays. We report the production of one- and two-dimensional arrays on patterned templates over large surface areas of tens to hundreds of micrometers, using particles with mean diameters in the 15-50nm range. Substrates with arrays of grooves or holes were prepared by X-ray Interference Lithography. Dip-coating of the substrates in colloidal suspensions under adapted conditions. The results presented in this work show that by combining novel lithographic and colloidal methods, ordered arrays of sub-50nm particles can be achieved for areas of tens of microns. No inherent limitations of the self-assembly process were found that would restrict the quality or the size of the nanoparticle arrays. Detailed investigation of nanoparticles on nanometer-scale grooved substrates is shown to be an effective method to create large area 1-D particle arrays. For 2-D patterned surfaces (e.g. arrays of holes) it was necessary to follow the dip-coating step by ultrasonic treatment to create low-defect particle arrays. We varied several process parameters in our experiments to mainly understand the relative influences of the forces that contribute to the assembly process. The quality of the obtained arrays without careful optimization testify to the robustness of the combination of top-down and bottom-up methods that account for the relative influences of various forces. The techniques developed here have the potential for use in applications where controlled creation of large area nanoparticle arrays is needed. The results point to different ways of achieving defect-free arrays over arbitrarily large areas with no inherent limitations of the guided self-assembly process.

11:15 AM Rb18.3 Directed Assembly and Control of Nanoparticles. Ahmed A. Busnaina, Kaveh Bahkari, Xugan Xiong and Prashanth Makram; NSF NSERC for high-rate Nanomanufacturing, Northeastern University, Boston, Massachusetts.

Nanoparticles can be used for a variety of applications and are considered as one of the building blocks of future nano-devices. The use of nanoparticle as building blocks requires scalable assembly strategies such as electrostatically addressable nanotemplates. The use of the templates for the directed assembly of nanoparticles is studied both analytically, computationally and experimentally. Computational fluid dynamics is used to analyze the effect of different parameters such as electrostatic field, solution conductivity, particle charge, etc. The results show the importance of having a secondary electrode that creates a uniform electric field similar to a capacitor. The experimental results verified the modeling results for the nanoparticle assembly. Defects generated during the assembly resulted from particles deposition on surface areas other than the nanoparticle pads. Analytical studies have been performed to find the right conditions for controlled assembly which involves directed assembly combined with selective removal. Results show that the controlled assembly approach is successful.

11:30 AM Rb18.4 Electronic Transport in Molecularly Linked Gold Nanoparticle Films Near the Metal-Insulator Transition. Jeffrey L. Dunford, Yoshinori Suganuma and Al-Amin Dhiri; Chemistry, University of Toronto, Toronto, Ontario, Canada.

We have investigated the temperature (T) dependence of the conductance (g) of 1,4-butanediol linked Au nanoparticle films. Over a wide range of temperatures (20 K to 300 K), the conductance behaves as g = g0 exp(-T0/T^2). Qualitatively, this is consistent with an Efros-Shklovskii variable range hopping model based on a competition between Coulombic and inter-cluster tunneling processes. However, we find that hopping distances are too large (2 nm to 720 nm at 100 K) to be consistent with tunneling between clusters and tend to scale with cluster size. We propose a modified “quasi-localized hopping” model based on competition between single-electron cluster charging and intra-cluster electron backscattering to explain this temperature dependence.

11:45 AM Rb18.5 "Surface-Programmed Assembly" Method for Massive Nano-Assembly of Pristine Vanadium Oxide Nanowire-Based Devices. Sung Myung1, Minbae Lee2, Gyu Tae Kim2, Jeong Sook Ha3 and Seunghun Hong1; 1Physics, Seoul National Univ, Seoul, South Korea; 2Electrical Engineering, Korea University, Seoul, South Korea; 3Chemical and Biological Engineering, Korea University, Seoul, South Korea.

Nanowires have been drawing a tremendous attention due to their potential applications for various nanoscale devices. However, one major bottleneck for their practical applications is a lack of a high-yield mass-production method for such devices. Herein, we report a method named “surface-programmed assembly” for high-precision assembly and alignment of a large number of pristine vanadium oxide nanowires on solid substrates. In this method, positively-charged surface molecular patterns guide the ‘assembly’ and ‘alignment’ of negatively-charged vanadium oxide nanowires on solid substrates. Using this method, we demonstrated mass-assembly of vanadium oxide nanowire-based transistors and confirmed their gating effects.
SESSION Ra19: Semiconductor Nanomaterials III
Chair: Wei Zhou
Thursday Afternoon, December 1, 2005
Room 207 (Hynes)

1:30 PM *Ra19.1

We demonstrate that annealing of a vicinal Si(111) surface at about 800°C with a direct current in the direction that ascends the kinks results in the self-assembly of atomically straight step edges with micrometer lengths while annealing with a current in the opposite direction does not. High resolution STM shows that every straight step edge has the same atomic configuration U(2,0), which is useful as a template for the formation of a variety of nanostuctures. We indeed, show by STM that both Si and Ge atoms deposited onto such templates forming regular arrays of either atomic wires or nanodots depending on the substrate temperature during depositions. For example, deposition of Ge at 250°C results in self-assembly of one-dimensional arrays of Ge dots, which nucleate exclusively at U-half of 7×7 unit cells adjacent to every upper terrace edge. The resulting dots form diameters (~2nm) in form one-dimensional simple lattice with the lattice constant 2.7 nm. To our knowledge, these are the smallest Ge dots (~2nm) forming “one-dimensional” arrays, and are strikingly different from previously reported “two-dimensional” orderings of Pb [4] and Ge [5] dots which nucleated preferentially at F-halfs. Mechanisms leading to such distinct step-structures by kink-up annealing and Si and Ge nanostructures in the following deposition are discussed.


2:00 PM *Ra19.2
The Two- to Three-Dimensional Transition in InAs/GaAs(001) Heterostructure: Exposed Role of Kinetics. Fabrizio Arciprete, Ernesto Placidi, Violetta Sessi, Massimo Fanfoni, Fulvia Patella and Adalberto Balzarotti; University of Rome Tor Vergata, Rome, Italy.

In the previous decade the Stranski-Krastanov growth mode has been the subject of many experimental and theoretical studies. In the case of semiconductor heterostructures characterized by a large lattice mismatch, the strain built up during the layer-by-layer growth may bring about a sudden change in the growth mode. In this case, two-dimensional growth mode is replaced by a three-dimensional growth mode which is self-organized in three-dimensional islands called quantum dots (QDs). InAs/GaAs(001) heterostructure, with its lattice mismatch as large as 7%, is a paradigmatic example of these interfaces and undergoes the two- to three-dimensional transition for a deposition of InAs lower than 2 ML. Many attempts have been made to clarify the mechanisms underlying the growth mode transition, but many aspects are still little understood. In this paper we present an accurate investigation of the kinetics of QDs for the InAs/GaAs(001) heterostructure grown by means of molecular beam epitaxy. Because the system evolves within a narrow range of coverage around the critical thickness, we have grown a single sample where the InAs coverage varies in a continuous way along the sample surface. In this way the system can be studied for InAs coverage increments as low as 0.01 ML. The kinetics of the number density of three dimensional quantum dot evidences two transition thresholds at 1.45 and 1.50 ML of InAs coverage, corresponding to two separate families, small and large. According to the scaling theory analysis, such families result characterized by different mechanisms of aggregation, the transition from small to large dots being accompanied by the change of the critical nucleus size. We show that the scaling function change is coincident with the explosive nucleation of the large QDs and it is triggered by the large increase of the adatoms number density determined by the erosion of the step edges. Such findings demonstrate how kinetics drives the two-dimensional growth mode transition and clarify a fundamental aspect of quantum dots formation.

SESSION Rb19: Carbon Nanotubes I
Chair: S.R.P. Silva
Thursday Afternoon, December 1, 2005
Room 208 (Hynes)

1:30 PM *Rb19.1
Control of Carbon Nanotube Geometry for Advanced Technical Applications. Sungjo Jin, Materials Science & Engineering, University of California at San Diego, La Jolla, California.

Carbon nanotubes have much to contribute to the electronics industry. Current problems in the application of nanotechnology include arrangement of nanomaterials into significantly ordered patterns for use in devices. Modern flash memory architecture is well suited for nanomaterials integration. The continuous charge-storing layer in a flash memory device can be replaced by an array of nanocylinders that serve as discrete charge-storage elements. It is well documented in the literature that using nanocylinders in place of a continuous layer results in improved device characteristics for large arrays. For this nanocylinder-based memory to become industrially viable and scalable, we must address the issue of how to reliably arrange the nanocylinders into arrays for each device. This paper discusses a kinetically driven patterning scheme to marry top-down and bottom-up assembly of nanocylindrical arrays. We explain how Si and Ge atoms interact with different dielectric surfaces to either etch the surface or to accumulate and self-assemble into nanocylinders during chemical vapor deposition (CVD). By exploring the different reactivity of these dielectrics, the accumulation of adatoms is controlled and the subsequent self-assembly of nanocylinders is controlled. Physical vapor deposition (in the form of cracking GeH4 over a hot filament) is used to deposit calibrated monolayer to multilayer amounts of Ge atoms on surfaces. The chemistry of Ge enables a kinetically driven patterning scheme is fully explained with X-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD), scanning electron microscopy (SEM), and atomic force microscopy (AFM). We have achieved >1011 cm⁻² arrays of self-assembled Ge nanocylinders within lithographically defined HfO2 windows with no Ge deposition on the adjacent SiO2 sacrificial mask region. Beyond this demonstration, we investigate the use of electron beam lithography and self-assembled diblock copolymers to direct self assembly of Ge nanocylinders within the gate region of the device. We also explore capacitance-voltage characteristics of different preparations of Ge nanocylinders to determine how efficiency as charge storage elements changes.

2:45 PM Rb19.4
Shading of Growth Uniform 3D Nanostuctures on Templated Substrates by a Novel Oblique Angle Deposition Technique. Deyan Ye¹, Catarina R. Picou², Go-Wah Chang³ and Toh-Ming Lau⁴.¹Department of Physics, Rensselaer Polytechnic Institute, Troy, New York; ²Department of Mechanical, Aerospace, and Nuclear Engineering, Rensselaer Polytechnic Institute, Troy, New York.

Shading effect during oblique angle deposition (also known as glancing angle deposition) on surfaces can physically self-assemble three-dimensional (3D) nanostructures such as rod-like nanostructures. This shading growth on a templated substrate with regular arrays of seeds would give rise to a phenomenon referred as “fan-out” growth in that the size of the nanostructures grow along the direction perpendicular to the incident deposition flux. This net result is that the size of the nanostructures cannot be controlled as they grow. In this talk we will present a back-forth substrate swing rotation method to overcome the “fan-out” growth. By using this method, uniform slanted Si nanorods and square nanorods were fabricated on templated substrates. A simple model based on decomposition of the deposition flux is used to describe qualitatively the effect of substrate swing rotation on inclined angle, uniformity, and the top-end shape of nanostructures. We also employ a Monte Carlo simulator to quantitatively predict the behavior of the swing rotation growth of the nanostructures. In addition, we will discuss possible applications of this technique for the fabrication of integratable, functionalized electromechanical and photonic nanodevices that are otherwise difficult to produce using advanced lithographic techniques.
The fascination and great technical promises associated with nanoscale materials are based on the significant changes in their fundamental physical and chemical properties. For eventual successful engineering applications of carbon nanotubes and other nanowires, an ability to control not only their intrinsic structures and properties but also their basic configurations is essential, for example, in terms of diameter, length, alignment, bending, branching, tip opening, cutting, and bending will be discussed. Growth of patterned nanotubes or nanocane arrays, sharp bending of nanotubes for creation of 900 bent or zig-zag nanotubes, nano-scale shortening, thorough removal of catalyst metal particles for unamplified electrochemical reactions, tip opening and filling of nanotubes for nanocomposite formation, and coating of nanotubes with high-density Pt catalyst nanoparticles will be described in relation to their potential applications. The implications of new nanotube array structures for physical, chemical, mechanical, and bio-related properties and for technical applications including field emitters, chemical/electrochemical sensors, nanosprings, nanowire/wire sidewall-probing tips, and nanometer-resolution AFM probes, fuel cell electrodes, electronic circuit nano interconnections, nanocomposites, and bio-devices will also be discussed.

2:00 PM Rb19.2
Analysis of Defect-Assisted Double Resonance Raman features of Graphite and Carbon Nanotubes.
Eduardo N. Vasilescu1, H. D. Son2, J. Jiang3, R. Sias4 and Mildred S. Dresselhau52; 1Departamento de Física, Universidade Federal do Ceará, Fortaleza, Ceara, Brazil; 2Electrical Engineering and Computer Science, Massachusetts Institute of technology, Cambridge, Massachusetts; 3Department of Physics, Tohoku University and CREST, Cambridge, Massachusetts.

Some of the most interesting properties of carbon nanotubes originate from the unique electronic and vibrational properties of graphite. The Double Resonance Raman Scattering (DRRS) process observed in both graphite and Carbon nanotubes is an important process that is related to the strong electron-phonon coupling observed for graphite materials. The frequency and intensity of the Double Resonance Raman features depend strongly on excitation energy. Although the frequency dependence of these modes have been widely studied, little is known about their intensities. In graphite, the DRRS consists of an electron with wavevector k close to the K-point of the graphite Brillouin Zone being optically excited to the conduction band, which is then scattered to a state close to the K-point and then back to the K-point, by either a two phonon (second-order) process or by a phonon and a defect (first-order) process. In the case of two phonons, the intensity of the DRRS features depends on the matrix elements of the phonon modes that are involved in the scattering and in the phonon density of states. For defect-assisted DRRS, the intensity will depend not only on the properties of the phonon, but also on matrix element of the defects involved in the scattering process. Raman Spectroscopy experiments were performed in different defective regions of graphitic materials using a tunable Raman system. The observed lines were compared using a control sample, and the relative intensities of the Double resonance features in the different regions were compared. Based on the difference between the intensity dependence with excitation energy of the different defective areas, an estimation could be made of the electron-defect matrix element and its dependence on the localization of the defect in the lattice. Applications to carbon nanotube physics are discussed.

2:15 PM Rb19.3
SWNT Directed Assembly Using Nanotemplates.
Prashanth Malur1, Xugang Xiong1, Kaveh Bakhhati1, Ahmed Bousnana2 and Glen Miller3; 1The NSF Nanoscale Science and Engineering Center for High-rate Nanomanufacturing, NorthEastern University, Boston, Massachusetts; 2The NSF Nanoscale Science and Engineering Center for High-rate Nanomanufacturing, University of New Hampshire, Durham, New Hampshire.

The Center for High-rate Nanomanufacturing (CHN) is developing tools and processes that will enable high-rate/high-volume bottom-up, precise, parallel assembly of nanoelements (such as carbon nanotubes, nanoparticles, etc.) onto the properties of nanomaterials. Nanotemplates are utilized to conduct fast massive directed assembly of nanoscale elements. Carbon Nanotubes have shown a lot of promise as next generation switches or interconnects in electronic applications. The negatively charged nanotubes are assembled onto a positively charged patterned nanowire electrophotochemically or chemically. We have successfully demonstrated the assembly of SWNTs on micron and nano sized gold wires using both AC and DC voltage. The assembled SWNTs show good density of wires using DC voltage, also aligns with respect to the nanowires when using AC voltage. The assembled patterns are then transferred to another patterned substrate to function as electronic device (such as nanotubes mechanical switches).

2:30 PM Rb19.4
Selective Dispersion of Single-Walled Carbon Nanotubes in the Presence of Polymers: The Role of Molecular and Colloidal Length Scales. Rachel Yerushalmi - Rozen1,2, Igal Szeleifer3, Rina Shvartzman-Cohen3, Ezhil Baskaran3, Yael Levi-Kalisman3 and Elnat Nativ-Roth1; 1Chemical Engineering Department, Ben-Gurion University, Beer-Sheva, Israel; 2The Ilse Katz Center for Meso- and Nanoscale Science and Technology, Ben-Gurion University, Beer-Sheva, Israel; 3Chemistry Department, Purdue University, West Lafayette, Indiana.

Dimensionality is known to play a key role in the solution behavior of nano and meso particles. In particular, the shape and the range of the attractive van- der Waals inter-particle potential are determined by the number of microscopic versus mesoscopic dimensions. For Single Walled Nano Tubes (SWNT) where two of the dimensions are nanoscopic and one is mesoscopic, the inter-tube attraction is relatively short ranged, albeit very steep. The very large attraction (compared to the thermal energy, kBT) among long SWNT leads to aggregation at different levels, and constitutes a major barrier for manipulation and utilization of SWNT. We demonstrate in a series of studies, that it is possible to shape the inter-tube potential by decorating SWNT with end-tethered polymers. Consequentially, stable dispersions of individual, well separated SWNT, can be prepared, and further used for preparation of CNT-polymer composites of low percolation thresholds. Investigation of different chain lengths and tethering densities of the polymers as well as the inter-particle potentials for nanometric versus mesoscopic particles suggests that polymer-induced steric stabilization provides a generic method for purification of SWNT from mixtures of colloidial species via dimensional selectivity.

2:45 PM Rb19.5
Haoyun Wei1, Sang Nyon Kim2, Sejong Kim1, Bryan D. Huey1, Fotios Papadimitrakopoulos2 and Harris L. Marcus1; 1Department of Materials Science and Engineering, Institute of Materials Science, University of Connecticut, Storrs, Connecticut; 2Nanomaterials and Electronics Laboratory, Polymer Program, Institute of Materials Science, Department of Chemistry, University of Connecticut, Storrs, Connecticut.

Based on electron-beam direct writing on the SiOx/Si substrates, favorable absorption sites for ferric cations were generated on the surface oxide layer. This allowed FeCl2-assisted self-assembly of arrays of single-wall carbon nanotube (SWNT) probes to be produced. X-ray investigation indicated that the energetic electrons used for direct writing depleted oxygen, creating more dangling bonds around Si atoms at the surface of the SiOx layer. This resulted in electrical trapping and a distinct decrease in the electrical force from unexposed regions as measured by Electrostatic Force Microscopy (EFM) and Lateral Force Microscopy (LFM) respectively. After exposure both Auger chemical mapping and Atomic Force Microscopy (AFM) affirmed that the irradiated domains absorbed considerably more FeCl2 ions upon immersion into pH 2.2 aqueous FeCl3 solution. This rendered a greater yield of Fe(OH)/FeOCl precipitates, primarily Fe(OH), upon subsequent washing with lightly basic dimethylformamide (DMF) solution. Such selective metal-functionalization established the basis for the subsequent patterned forest-assembly of SWNTs as demonstrated by AFM and resonance Raman Spectroscopy.

SESSION Ra20: Supramolecular Assemblies III
Chair: Roberto Otero
Thursday Afternoon, December 1, 2005
Room 207 (Hynes)

3:30 PM Rb20.1
Supramolecular Chemistry at the Liquid/Solid Interface.
Steven De Fryter1, Jan van Esch2, A. P. H. J. Schenning2, Frank Wuytyn1 and Frans de Schryver1; 1Katholieke Universiteit Leuven, Leuven, Belgium; 2University of Groningen, Groningen, Netherlands; 3Eindhoven University of Technology, Eindhoven, Netherlands; 4Universitaet Wuerzburg, Wuerzburg, Germany.

Self-assembly is a natural phenomenon, which can be observed in many biological, chemical and physical processes. In contrast to chemisorption, physisorption is not very suitable for making “permanent” architectures. Nevertheless, these physisorbed adlayers are model systems to investigate the interplay between molecular
structure and the formation of ordered assemblies in two dimensions. The organic liquid/solid interface provides an interesting environment to perform experiments and to study properties of the self-assembled two-dimensional architectures by scanning tunneling microscopy (STM). a) Most systems reported up to date have only limited possibilities to include functionality and are not flexible with regard to the size and shape of the molecules. b) The observation that linear alkyl fragments featuring amide or urea groups form lamellar structures reminiscent of the beta-sheets found in nature upon adsorption at the solid-liquid interface of HOPG prompted us to introduce a new approach in the self-assembly and led to a new step. Here we report on the design of such a 2D turn mimetic which is a first step in controlling the position/orientation of functional groups in 2D with the potential of being extended in 3D [1]. b) Tuning the intermolecular interactions by tailoring the non-covalent interactions such as hydrogen bonding indeed leads to control of the self-assembly process. Of special interest are those molecules which carry functional moieties, such as conjugated oligomers. p-Phenylene vinylene functionalized molecules show three types of chiral p-phenylene vinylenes which differ in hydrogen bonding will be reported, including the discussion on the effect of the molecular chirality on the 2D self-assembly [2,3,4]. c) Finally, by bias dependent imaging we have probed the molecular electronic levels involved in the tunneling process, for a unique p-phenylene vinylene containing system: (1) it combines an electron donor and electron acceptor part, covalently linked to each other and (2) the donor and acceptor parts are relatively large and well-separated, allowing addressing them individually [5].


The interactions of PTCDA molecules with the Si(100) surface have been investigated by means of tunneling spectroscopy (STM) and X-ray photoelectron spectroscopy (XPS). Among the large distribution of the adsorbers observed by STM for submonolayer coverages, around 20% show a distinct feature, which is interpreted as the formation of the covalent bond between the PTCDA and Si atoms. The formation of this product through the anhydride groups is further supported by the XPS measurements. For coverage above 1 monolayer, there is the formation of a disordered initial layer, which nevertheless acts as a passivation layer and leads to the formation of islands. These islands have a common layer structure, similar to the molecular arrangement found in the (102) plane of PTCDA bulk phase. The growth mode is a Stranski-Krastanov one, with a 2D-3D transition. On the contrary, on a hydrogen passivated Si(100) surface (H-Si(100)), the formation of an initial molecule layer is not observed. The molecules have a low interaction with the surface and can easily migrate. Molecular nanocrystals are directly built, i.e. a Volmer-Weber growth mechanism is observed. The smallest nanocrystals have no commensurable position with the surface, according to a nearly flat interaction with the surface. By increasing the coverage and controlling the growth rate, an unidirectional growth of the nanocrystals is obtained. Taking advantage of this self-assembly process should favour the spontaneous growth of organic nanocrystals between electrodes in a vacuum chamber for future electrical characterization.

4:30 PM Ra20.4


Molecular self-assembly plays an essential role in the development of many nanolithographic techniques acting as a building block and/or an active component. In conjunction with conventional lithography, we have fabricated metal structures with precise nominal placement using self-assembled multilayers as lift-off resists (building blocks) and chemically patterned surfaces with functionalized films using self-assembled monolayers as the components. We have used metal electrodes with nanometer-scale separations using the selective placement and controllable dimensions of self-assembled multilayers. The thickness of this multilayer lift-off resist can be tailored defining the spacing between the electrodes with single nanometer resolution in the 10-50 nm regime. 1-2 Much effort has gone into developing the lithographic process steps to create nanogaps reproducibly with electrical integrity. 3 An important aspect of this process is a lithographic resist, which is robust enough to withstand the deposition of self-assembled multilayers without compromising their formation. This optimized lithographic method and resist compatible with self-assembly has opened a novel avenue for us to direct the chemical patterning of multi-component self-assembled films. Based on our process, photolithography is utilized to pattern our resist atop a self-assembled monolayer (SAM) on a gold substrate. Then the exposed region of the SAM is removed, another component SAM is inverted, and then the resist is removed maintaining the functionality that has been patterned onto the substrate. A major advantage of this technique is that the different components (SAMs) of the film are shielded by the resist against displacement and intercalation. Additional benefits of this process over other unconventional methods for chemical patterning are the ability to have multiple levels of alignment, reproducible one-to-one feature size transfer, and parallel processing. We present this research outlining our work developing methods for the integration of self-assembly with lithography processing for future applications ranging from molecular electronics to sensor platforms. 1 A. Hatzor and P.S. Weiss, Science 291, 1019 (2001). 2 M. E. Anderson et al., Journals of VacuumScienceandTechnologyB 20, 2739 (2002). 3 M. E. Anderson et al., Journal of VacuumScienceandTechnologyB 21, 3116 (2003). 4 M. E. Anderson et al., submitted. 5 M. E. Anderson et al., MicroElectronicEngineering 78 – 79, 248 (2005).

4:45 PM Ra20.5


A self-decontaminating surface, as inspired by the self-cleaning lotus leaf and the fog-collecting Naush beetle, was developed by patterning hydrophilic regions on a superhydrophobic surface and filling the porous reservoir beneath with antibiotics. The honeycomb-like porous structure was assembled from poly(acrylic acid) and poly(acylamine hydrochloride) followed by proper acid treatments. Molecules with
SESSION Rb20: Carbon Nanotubes II  
Chair: Singho Jin  
Thursday Afternoon, December 1, 2005  
Room 208 (Hynes)

3:30 PM *Rb20.1  
Assembly, Manipulation and Chemical Bond Engineering of Single Walled Carbon Nanotubes. Zhongfan Liu, Zhao Chen, Xiaojie Duan, Yingying Zhang, Bo Gao, Quan Qiang, Liying Jiao, Jia Yang, Jingling Ao, Zhongyun Wu and Jin Zhang; Center for Nanoscience and Technology and College of Chemistry and Molecular Engineering, Peking University, Beijing, China.

Single-walled carbon nanotubes (SWNTs) have shown great potential for creating nanoelectronic devices because of the excellent electronic, mechanical, thermal and chemical properties. To fabricate such SWNTs devices, it is necessary to find an effective way to align the randomly-entangled or randomly-oriented nanotubes in a highly-controlled manner. We demonstrate here our recent studies along this direction based on chemical assembly, controlled CVD growth and AFM manipulation. The main topics include: (1) Vertical alignment on solid surfaces via chemical assembly. The self-assembled monolayer (SAM) technique conventionally used for small organic molecules was employed here for fabricating vertically aligned SWNTs on solid surfaces. The CVD-grown SWNTs were cut into short tubes by chemical oxidation. The assembly was made on Au, Ag, and amine-terminated surfaces via Au-S bonding, Ag-COOH salt formation, and condensation reaction, respectively. It has been shown that the “giant” carbon nanotubes can be self-assembled on a suitably designed surface, forming a well-aligned assembly. The assembling kinetics, the electric-field enhanced assembly effect, and a number of applications of these assemblies will be discussed. (2) Lateral alignment and interconnection using dielectrophoresis force. A dipole moment can be induced for the large p-conjugated SWNTs by applying electric field. Such polarized carbon nanotubes would undergo a directional movement along the electric field gradient under the inhomogeneous electric field. Using this so-called dielectrophoresis force, SWNTs have been successfully aligned and interconnected in-between the electrode gaps. With nanofabricated gap arrays and optimized experimental conditions, well-controlled lateral alignment of SWNTs has been achieved during CVD growth surface and AFM manipulation. By predesigning the growing surface, a controlled CVD growth of SWNTs has been achieved, including site-specific growth and directional growth. We also tried to use AFM tips to align, bend and stretch the small SWNTs. By suitably designing the growth surface and by employing the nanowelding phenomenon, we have created various deformed nanotube structures having different bending angles and stretching degrees on surfaces. Because the energy band and chemical reactivity strongly depend on the deviation degree of carbon nanotube from its original sp² equilibrium structure, this approach, called chemical bond engineering provides an alternative way for tuning the physical and chemical properties of SWNTs. The mechanical deformation performance of individual nanotubes will also be discussed. Single-walled carbon nanotubes (SWNTs) have shown great potential for creating nanoelectronic devices because of the excellent electronic, mechanical, thermal and chemical properties. To fabricate such SWNTs devices, it is necessary to find an effective way to align the randomly-entangled or randomly-oriented nanotubes in a highly-controlled manner.

4:00 PM Rb20.2  
Nanoscale Integration of Nanocarbons Based on Ultrananocrystalline Diamond and Carbon Nanotubes. Xingchao Xiao¹, Chao Liu¹, Orlando Auciello¹,² and John A. Carlisle¹,²  
¹Materials Science Division, Argonne National Laboratory, Argonne, Illinois; ²Center for Functionalized Materials, Argonne National Laboratory, Argonne, Illinois.

Nanocarbons, or nanostructured carbon materials have attracted extensive research interest during the past decade, especially after the emergence of carbon nanotubes. Another form of nanocarbons, ultrananocrystalline diamond (UNCD) developed at Argonne National Laboratory, has been demonstrated to possess many desirable properties for fabrication of MEMS/NEMS devices, electron field emission devices, biosensors and biomedical devices, due to its unique nanostructure. In this presentation, we will report the selective but simultaneous growth of UNCD and carbon nanotubes using hydrogen plasma chemistry in a mixed-plasma system. A self-assembled monolayer of polystyrene spheres (PS) is used as the shadow mask for patterning the catalyst on a substrate for growing carbon nanotubes. Then the mask is etched by toluene and the wafer is seeded with nanodiamond powder for growing UNCD. The relative fraction and arrays of carbon nanotubes and UNCD are controlled by the diameter of PS and the thickness of the catalyst. The carbon nanotubes grown in hydrogen poor plasma (99% Ar/1% CH₄) are a mixture of single walled and multi walled carbon nanotubes, which are dependent of the thickness of catalyst. By controlling the diameter of the PS and growth time, nanocomposite coatings were obtained, in which carbon nanotubes are embedded into the UNCD matrix. We will report results from measurement of mechanical and optical properties of this novel nanocomposite. We will also discuss results from studies of the electronic contact between sp²-bonded carbon nanotubes and mostly sp³-bonded UNCD. This work was supported by the U.S. Department of Energy, BES-Materials Sciences, under Contract W-31-109-ENG-38.

4:15 PM Rb20.3  
Carbon Nanotube-Zinc Oxide Core-Schottky Composite Nanowires for Optoelectronics. Sathiyath Raveendran³, Yu Zhang¹, Senthil Andavan G. T.¹ and Cengiz Sinan Ozkan¹  
¹Mechanical Engineering, University of California at Riverside, Riverside, California; ²Chemical and Environmental Engineering, University of California at Riverside, Riverside, California.

The focus of this work is to investigate the electrical and optical properties of semiconducting ZnO shell formed over single walled and multi walled carbon nanotube. We use electrical transport and optical properties of semiconductor ZnO and the SWCNT-ZnO structures with SEM, TEM, electron diffraction, EDS, XRD and Photoluminescence. We also report their electrical and optical characterizations. In addition, we report a simple technique for the SWCNT patterning and the selective and controlled growth of ZnO structures over the patterned SWCNTs. The direct effect of the growth temperature of the the ZnO heterostructures formed on the CNTs are also discussed.
4:45 PM Rh20.5
Thin Silicon Dioxide Layers as Diffusion Barriers During the CVD Growth of Carbon Nanotubes. J.M. Simmons, Beth M. Nicholas, Matt S. Marcus, D. M. Cardwell, B. J. Hannon, and M. A. Eriksson; 1Department of Physics, University of Wisconsin - Madison, Madison, Wisconsin; 2Department of Chemistry, University of Wisconsin - Madison, Madison, Wisconsin.

Chemical vapor deposition (CVD) of carbon nanotubes utilizes the catalytic decomposition of hydrocarbon feedstock on the surface of transition metal nanoparticles to form metal carbides, and subsequent carbon precipitation to form nanotubes. Controlling the kinetics and thermodynamics of the catalyst feedstock interaction allows for tunable growth, in both yield and diameter, of single- or multi-walled carbon nanotubes. Since nanotube growth is a high temperature process (700°C-900°C), interfacial reactions between the substrate and the catalyst are extremely important. Indeed, the growth of single-walled nanotubes on clean silicon or silicon with a native oxide is inhibited due to the formation of a catalytically inactive metal silicide, though growth on thick oxide layers is straightforward. We show that metal diffusion through the silicon dioxide limits the minimum thickness of silicon dioxide capable of permitting high-yield growth of carbon nanotubes. Using X-ray photoelectron spectroscopy (XPS), we have probed the interaction between iron and nickel single-walled nanotube catalysts and Si/SiO2 substrates with a range of oxide thickness. At low temperatures on substrates with thin SiO2 layers, the metal oxide particles are reduced through bonding exchange with the silicon substrate. As we heat the substrate further, there is a shift in the atomic core levels of the catalyst on thin oxides due to the formation of a metal silicide. Most importantly, the silicide formation occurs while the oxide layer remains, indicating that metal diffusion through the silicon dioxide layer is responsible for the silicide formation. We show that oxides as thin as 4 nm are effective diffusion barriers and allow high yield nanotube growth.

SESSION Ra21: Nanostructures for Biology and Medicine III
Chair: Amy Blum
Thursday Evening, December 1, 2005
Room 207 (Hynes)

6:15 PM Ra21.1
Surfactant-like peptides: Supramolecular assembly and peptide-membrane interaction to engineer novel drug delivery systems. Salvatore Chessa1, Isabella Miglioli1, Martina Baumann1, Shuangnan Zhang2 and Marcus Tezker2; 1Materials, Swiss Federal Institute of Technology, Zurich, Switzerland; 2Biology, MIT, Boston, Massachusetts.

In the last few years, significant advances have been made in the use of peptides as building blocks to produce biological materials for a wide range of applications [1]. Thus, synthesis and characterization of short peptides that can adopt a stable three-dimensional structure in solution are crucial for the construction of bio-active and bio-inspired de-novo polypeptides. Selected peptides and hybrid peptides (combinations of peptide sequences with organic moieties in a single molecule) self-assemble in a variety of motifs to form pores, channels and tubules. Various physiological functions, such as ion transport through cell membranes, and physical functions such as solubilizing difficult-to-dissolve molecules, are facilitated by the tubes that are formed [2]. Peptide-lipid membrane interactions play a critical role in the regulation of several biological phenomena, including the insertion and folding of membrane proteins, the translocation of polypeptides through membranes and the cytoplasmic action of antimicrobial peptides. However, a systematic study of the interaction of different peptide assemblies with membranes is still missing [3]. The aim of the present study is the systematic design and synthesis of cationic surfactant-like peptides, the structural characterization of supramolecular entities, and the evaluation of their interactions with supported bilayers serving as a model for cell membranes. The development of such biologically inspired delivery vehicles should fulfill several criteria that are important for the envisaged application such as biodegradability, cell-membrane transmembrane membrane disruption and lack of cytotoxicity. To assess the approximate size of the peptide assemblies, transmission electron microscopy (TEM) will be used to study the supramolecular assembly of the samples in solution as a function of concentration and pH, complemented by morphological studies of peptide assemblies at surfaces based on atomic force microscopy. Molecular mechanics calculations are performed to simulate the assembly of selected peptide sequences in aqueous solution and the comparison of such results with those experimentally obtained is also discussed. References 1. Santoso, S., et al. Self-assembly of surfactant-like peptides with variable glycine tails to form nanotubes and nanovesicles. Nano Letters, 2002, 2(7): p. 687-691. 2. von Maltzahn, G., et al. Positively charged surfactant-like peptides self-assemble into nanostuctures. Langmuir, 2003, 19(10): p. 4352-4357. 3. Mosolits, H., et al. The interaction of bioactive peptides with an immobilized phosphatidylcholine monolayer. Biophysical Journal, 1999. 77(3): p. 1428-1444.

Ra21.2
Abstract Withdrawn

6:30 PM Ra21.3
Nano-Confined Polymer Hydrogels For Drug Delivery System Using Radiation Synthesis. Jung Chul An, Lourdes Guadalupe Salamanca-Riba, Joseph Silverman and Mohamad Al-Shikhly; Materials Science and Engineering, University of Maryland, College Park, Maryland.

We have synthesized polymer nanohydrogel for Drug Delivery System (DDS) applications by nano-confined radiation methods. Both high energy electron beam and gamma rays were used as a radiation source. The synthesis conditions (total dose, dose rate, and pulse repetition rate) and the concentration of the solution, control the size and molecular weight of the nanohydrogels. The diameter of the nanohydrogels is in the range of 100 - 200 nm as measured from static light scattering experiments. Irradiation of solutions with dilute concentrations results in intra crosslinking within a single chain rather than inter crosslinking under high dose rate and high repetition rate of electron beam irradiation. Alumina nanoporous templates with 200 nm diameter pores were also used to synthesize polymer nanohydrogels in the low dose rate gamma irradiation for comparison. The alumina template gives spatial isolation of single polymer chain by the confinement within the channels resulting in preferred intra crosslinking. Hydrogels with diameters of 100 - 200 nm were synthesized within the capillary channels of the nanoporous template. Environmental Scanning electron microscopy and atomic force microscopy are used to investigate the morphology of the nanohydrogels after irradiation. Various approaches to produce nano hydrogel with radiation synthesis will be presented in this study. This work was supported by the DOE/Industry Matching Grants Program under contract number DEFG0702ID14556.

6:45 PM Ra21.4
Hydroxyapatite/Collagen Self-Organized Nanocomposite for Bone Tissue Regeneration Scaffold. Mariko Matsuishi, Kenichi Shimomiya, Yuchio Sotome1, Yoshihoro Asou2, Yoshinobu Koyama1, Kazuo Takakuda1, Kenichi Shimomiyas and Junzo Tanaka1; 1Biomaterials Center, National Institute for Materials Science, Tsukuba, Ibaraki, Japan; 2Orthopedic Surgery, Tokyo Medical and Dental University, Bunkyo-ku, Tokyo, Japan; 3Institute for Biomaterials and Bioengineering, Tokyo Medical and Dental University, Chiyoda-ku, Tokyo, Japan.

We have already reported the hydroxyapatite/collagen (HAp/Col)
self-organized nanocomposite in the previous meeting of MRS. The nanocomposite has bone-like nanostructure and ability to incorporate into regenerative medicine. The preparation of bone-like nanocomposite, the authors prepared the HAP/Col sponge-like porous body and paper-like membrane using its long fiber, and carried out the first trial to apply for bone tissue engineering. The HAP/Col long fibers with bone-like nanostructure were synthesized by multistep is crystallization method previously reported under fine control of starting material concentrations. For the sponge-like porous body, the fiber obtained was vacuum dried and mixed with pure water and 1 wt% of sodium carbonate. In sodium carbonate and phosphate buffer saline were added to promote fibrbillogenesis of collagen, mixed well and incubated at 37°C. The HAP/Col gel was lyophilized and crosslinked. For the membrane, the dried HAP/Col fibers dispersed in pure water and flatly flatly freeze dried sheet was vacuum dried. The sponge-like porous body showed viscoelastic property in wet condition. The membrane has paper-like softness at 200 μm in thickness and cardboard-like rigid at 500 μm. The tensile strength at wet condition of the sponge-like porous body and flatly flatly freeze dried cardboard membrane is 80 kPa and 1 kPa, respectively. The strength was enough to handle at both cell culture and material/cell hybrid transplantation. The MG-63 cells, derived from human osteosarcoma, were used for cell culture test. From the preliminary test, the composite adsorb large amounts of Ca and Mg from culture medium and inhibit cell proliferation; therefore, the materials were soaked in the Dulbecco’s modified Eagle’s essential medium (DMEM) supplemented with 10% fetal bovine serum and 1% penicillin and streptomycin to allow ions (and proteins) adsorption onto the material. The cells were seeded onto the material and cell proliferation was assessed. Although the cell proliferation was reduced by the surface roughness in comparison to tissue culture polystyrene (TCP), the growth of cells were similar to that of TCP. The porous body and membrane expected to be useful for bone tissue engineering. Acknowledgment: A part of this research was supported by Research Promotion Bureau, Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan under the contract No.17-83.

7:00 PM Ra21.5 Interpenetrate Nanstructured Composites Mimicking Bone. Sang Soo Joe1, Rajendra K. Kumar1, Matthew J. Olseta2,1 and Laurie B. Gower1,2; 1Materials Science & Engineering, University of Florida, Gainesville, Florida; 2Materials Science & Engineering, Pennsylvania State University, State College, Pennsylvania.

Bone is a hierarchically-structured natural composite material, which at the primary level, consists of an interpenetrating network of hydroxyapatite nanocrystals dispersed within the interstices of self-assembled collagen fibrils. In fact, the structure is so unique and different than synthetic materials, it is difficult for the materials engineer to define: Is it a collagen fiber-reinforced bioceramic-matrix composite? Or is it a nanoscale reinforced collagen-matrix composite? This intrafibrillar mineralization that is achieved during bone formation has eluded scientists who seek to duplicate this nanostructured architecture using conventional synthetic techniques. We have been able to achieve intrafibrillar mineralization of collagen using a polymer-induced liquid-precursor (PILP) process, in which acidic polyepptides transform the solution crystallization process into a precursor process by sequetering ions and generating liquid-liquid phase separation in the matrix. This technique was supported by Research Promotion Bureau, Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan under the contract No.17-83.

7:15 PM Ra21.6 Nanotubes: Ceramic Film Formation on Self-Assembled Monolayers via a Biomimetic Approach. Guangrong Zhang and Junghyun Cho; Mechanical Engineering, State University of New York, Binghamton, New York.

A biomimetic approach is employed to deposit ceramic films on organic self-assembled monolayers (SAMs) coated substrates. Specifically, zirconia (ZrO2) films are grown in a zirconium sulfate precursor solution at near room temperatures (< 80°C). This process, directed by the nanoscale organic template, mimics the controlled nucleation and growth of the biomimetic such as bones and teeth. The phosphate-terminated SAMs are prepared through a two-phased method in which phosphonic precursors are predeposited on the substrate. The p2 PET method previously described offers an alternative method often found in a solution method. The resultant zirconia films consist of nanosized particles (<5-10 nm) that precipitate out in a supersaturated precursor solution. The underlying mechanisms of generating the nanostructured films are systematically studied by tailoring solution chemistry and SAM functionalities. Cross-sectional, high-resolution TEM and STEM works are performed to quantitatively analyze the film structure and chemistry, as well as the interfacial region of the zirconia/SAM films. Further, the film nanoindentation testing is developed to assess the thickness and ‘film-only’ properties for direct comparison among the films processed with different processing parameters and microstructures. This ceramic film growth and mechanism can be sufficiently general that it may be applicable to other oxide systems.

7:30 PM Ra21.7 Colorimetric Sensors Based on Chemically Controlled Disassembly of Nanoparticle Aggregates Linked by Catalytic DNA, Aptamers, and Aptazymes. Juween Liu and Yi Lu; Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois.

DNA-functionalized nanoparticles have been demonstrated to be programmable building blocks for directed nanomaterial assembly. Taking advantage of the distance-dependent optical property of metallic nanoparticles, the resulting novel materials can be used as highly sensitive colorimetric sensors for sequence-selective DNA detection. A DNA can recognize its complementary DNA, which forms the basis for DNA detections. To apply the nanoparticle-based detection method to a broad range of analytes beyond DNA, we employed functional DNA to assemble nanoparticles. Three classes of functional DNA were prepared: metal-specific catalytic DNA, DNA aptamers, and aptamer-regulated catalytic DNA (aptazymes). Catalytic DNA are DNA molecules with catalytic activities. Most catalytic DNA molecules require metal cofactors for their activities. Therefore, they are ideal for metal ion sensing. DNA aptamers are DNA molecules that can bind target analytes with high affinity and specificity. Since its first discovery in the early 1990s, DNA aptamers have been selected to bind a broad range of analytes, ranging from small organic molecules to proteins and even anthrax spores. First, a Pb(II)-specific catalytic DNA and its substrate were employed to assemble gold nanoparticles. The catalytic DNA can cleave its substrate DNA in the presence of Pb(II), and the substrate DNA was physically responsible to assemble nanoparticles. As a result, the nanoparticle aggregates disassembled in the presence of Pb(II) with a blue-to-red color transition observed. We demonstrated that an aggregate containing ~10000 nanoparticles can be disassembled in less than 5 minutes in the presence of Pb(II). To apply the detection method to more analytes beyond metal ions, DNA aptamers and aptazymes were also employed to assemble nanoparticles. The resulting functional materials can detect metal ions, small organic molecules and proteins. While most people are interested in the controlled assembly of nanomaterials, we demonstrate here that chemically controlled disassembly is equally interesting and useful.

7:45 PM Ra21.8 Selective Placement of Templated DNA Nanowires Between Microstructured Electrodes. Joseph Kinsella1 and Alben Ivanisevic1,2; 1Purdue University, West Lafayette, Indiana; 2Biomedical Engineering, Purdue University, West Lafayette, Indiana; Chemistry, Purdue University, West Lafayette, Indiana.

We report the deposition of polyelectrolyte films for DNA nanowires structures. Dip-pen nanolithography (DPN) was first used to fabricate a layer of the positively charged polyelectrolyte, poly(alamine hydrochloride) (PAH), on a spin-on silicon oxide surface between gold electrodes. The PAH films were further modified using the DPN procedure to deposit hard-tissue like polyelectrolyte, poly(styrene sulfonate) (PSS), on top of the PAH film. The functionalized was used as a scaffold to stretch DNA templates coated with positively charged magnetic nanoparticles. To verify the deposition of the polyelectrolyte films between the microfabricated gold electrodes Atomic Force Microscopy, X-ray Photoelectron Spectroscopy, Force Volume Imaging, and Adhesion Microscopy were used. From these experiments we have concluded that the selective deposition of the polyelectrolyte films can be effectively incorporated into microfabricated devices for the guided assembly of DNA templates. Prototype device structures were tested and the formation of nanoscale scale lines in the DNA template wires was explored using restriction enzyme digest. This work can become the basis for novel architectures for (bio)sensors.
SESSION Rb21: Carbon Nanotubes III
Chair: R. Ramesh
Thursday Evening, December 1, 2005
Room 208 (Hynes)

6:00 PM Rb21.1
Effects of Self-Organisation on Charge Carrier Mobility in Poly(3-hexylthiophene) Carbon Nanotube Nanocomposites. Roland Ghim Siong Geh 1, Eric Rolf Wachwicki 2, Nunzio Motta 3 and John Marcus Bell 1; 1Centre for Built Environment and Engineering Research, Queensland University of Technology, Brisbane, Queensland, Australia; 2School of Physical and Chemical Sciences, Queensland University of Technology, Brisbane, Queensland, Australia.

There has been much excitement generated by organic photovoltaic (OPV) devices in recent years, following the demonstrated success of the “bulk heterojunction” concept, in which a composite film of two interpenetrating phases is used as the photovoltaic active layer. We now know that the degree of molecular order of a material can profoundly affect device performance in organic electronic technological applications. In blends of poly(alkyl-thiophene) and fullerene derivatives, increasing the percentage of fullerene derivatives in P3HT has been shown to destroy the self-organized structure in P3HT 1. It has also been demonstrated that the reduced self-organization of P3HT with high amounts of fullerene leads to decreased external quantum efficiencies in organic solar cells made from composites of these materials. Moreover, hole mobilities of poly(p)-type conjugated polymers have been known to decrease with increasing fullerene content 2. In this work, we observe that when nanotubes are substituted for the fullerenes, a high degree of organization of the P3HT is retained even at low nanotube concentrations near the percolation threshold. To achieve a better understanding of this issue we have studied by STM the structural properties and the details of poly(alkylthiophene) self-assembly and organization on single-walled carbon nanotubes surface (SWCN). Monolayers of regioregular poly(3-hexylthiophene) (rrP3HT) on SWNTs have been imaged for the first time using scanning tunneling microscopy (STM). The microscopic images show polymer chains wrapped around individual carbon nanotubes and allow the measurement of interchain spacing. The polymer chain-to-chain distance is approximately 1.08nm, compared to the measured interchain distance for rrP3HT absorbed on highly-ordered pyrolytic graphite (HOPG) of 1.4nm. This disparity in interchain distances (SWCN vs. HOPG) indicates that the assembly of polymer onto SWNT is not as simple as absorption on HOPG; the substrate curvature and electronic effects plays an important role in assembly of ordered domains. UV-visible spectroscopic data are also presented, which provides strong evidence for increased interchain interactions in composites of rrP3HT and SWNTs compared to the pure polymer 3; this shows that adding nanotubes to the polymer results in increased interchain order. The STM local-probe studies of the native polymer as well as the composite confirmed that the polymer interacts with nanotubes to produce a highly ordered material at the molecular level. Finally, current-voltage characterisation of hole-only sandwich-type devices built from these superlattices shows a clear field dependence of the hole current. At low bias, current density increases by an order of magnitude, whereas at high bias, the increase amounts to 3 orders of magnitude. In the latter case the transport regime changes from a space charge limited current (SCLC) to a trap limited model with exponential trap distribution; this shows not only that the nanotubes have the effect of increasing the hole conductivity, but that hole trap density is increased, possibly because of defect sites on the acid-treated nanotubes. We propose that increased hole mobility is due to an increased degree of order induced in the polymer by the presence of nanotubes. This and other issues pertaining to using these composites in devices will be discussed. We propose that increased hole mobility is due to an increased degree of order induced in the polymer by the presence of nanotubes. This and other issues pertaining to using these composites in devices will be discussed. 5


6:30 PM Rb21.2
Crystallization driven, periodical patterning on individual carbon nanotubes. Christopher Y. Li, Lingyu Li, Bing Li and Michael J. Birnkrant; Materials Science and Engineering and A. J. Drexel Nanotechnology Institute, Drexel University, Philadelphia, Pennsylvania.

We report herein a unique means to periodically pattern polymer nanofilms on individual carbon nanotubes (CNTs) using controlled polymer crystallization. One dimensional (1D) CNTs were periodically decorated with polymer lamellar crystals, resulting in nano hybrid shish-kebab (NHSK) structures. The periodicity of the polymer lamellae varies from 3 nm to 100 nm. These CNTs containing hybrid approximately 5 nm thick (along CNT direction) with a lateral size of ~ 20 nm to micrometers, which can be readily controlled by varying the crystallization condition. Both polyethylene and Nylon 6,6 have been successfully decorated on a variety of CNTs containing hybrid CNTs. The detailed mechanism of forming this periodic structure on CNTs will be discussed. Since the polymer kebabs can be easily removed, using 1D lithographic technique, these unique NHSKs can serve the templates to fabricate a variety of CNTs-containing hybrid materials with controlled patterning on the CNT surface. This method thus opens a gateway to periodically patterning on CNTs or similar 1D nanowires in an ordered and controlled manner, an attractive research field that is yet to be explored. It also directly leads to the synthesis of polymer/CNT nanocomposites with controllable tube-to-tube distance. Supported by NSF DMR-0239415, ACS-PRF, 3M and DuPont.

6:45 PM Rb21.3
Preparation of Mesoporous CN, BN, and BCN. Aijun Vinu, International Center for Young Scientists, National Institute for Materials Science, Tsukuba, Ibaraki, Japan.

We report here the preparation of the highly ordered mesoporous carbon nitride material, designated as MCN-1, having uniform pore size distribution through the simple polymerization reaction between ethylenediamine and carbon tetrachloride. The ordered mesoporous carbon nitride MCN-1 structure was investigated by powder X-ray diffraction and nitrogen gas adsorption measurements. The XRD pattern of MCN-1 material shows three, clear peaks that can be assigned to (100), (110), and (200) diffractions of two dimensional hexagonal lattice (space group p6mm) with a lattice constant a100 = 9.42 nm, similar to the XRD pattern of parent mesoporous silica template SBA-15 which consists of the hexagonal arrangement of cylindrical pores and the pores are interlinked by the micropores present in the walls. Such materials with one dimensional mesopores are arranged in a hexagonal net are defined as two dimensional because the diffraction peaks pattern shows two dimensional p6mm symmetry. The powder diffraction pattern of MCN-1 also shows a single broad diffraction peak (inset) near 25.8°, corresponding to an interlayer distance of 3.42 Å, which is similar to the spacing obtained in the nonporous carbon nitride sphere. This indicates the presence of turbostratic ordering of the carbon and nitrogen atoms in the graphene layers of MCN-1. The MCN-1 material exhibits high specific surface area, specific pore volume and uniform mesopores size distribution, could offer great potential for the applications, such as catalytic supports, gas storage, lubricants, biomolecule adsorption and drug delivery. We have also successfully prepared mesoporous boron nitride on boron carbon nitride as a functionalized carbon material as template at a very high temperature. These materials were extensively characterized by TEM, XRD, EELS, and N2 adsorption. Detailed characterization of those materials will also be discussed in the presentation.

7:00 PM Rb21.4
Self-assembled monolayers of carbon nanotubes. Vladimir Samulius 1, 2, Jean Galbert 1, Vitaly Ksenichenk 2, Laazo Foffo 3, Jaseung Koo 4, Jonathan Sokolov 1 and Miriam Rafailovich 1, 1 Materials Science, SUNY@B, Stony Brook, New York; 2 Laboratoire National des Champs Magnetiques Pules, Toulouse, France; 3 Department of Physics, State University of Belarus, Minsk, Belarus; 4 Ecole Polytechnique Federale de Lausanne, Lausanne, Switzerland.

Electronic transport properties of carbon nanotubes are of particular interest to technologists due to their potential applications in electronic and optoelectronic devices. The electronic properties of the small bundles of carbon nanotubes have been found to be different from their individual nanotubes due to strong interactions between the nanotubes. In an attempt to control the electronic properties, we have developed: 1) a controlled method of self-assembly of functionalized carbon nanotubes into 2-D layers with highly regular structure and unique electronic properties. In contrast to the standard morphologies of the samples of arrays of nanotubes involving definition of bundles (ropes) mats, networks, etc., based on non-controlled deposition from an organic solvent dispersion of pristine nanotubes, we use the Langmuir-Blodgett (LB) technique of self-assembly of carbon nanotubes oriented and highly soluble in the organic solvents carbon nanotubes. 2) a method of alignment carbon nanotubes in the self-assembled 2-D arrays. The method we propose offers a radical departure from the existing methodology due to the capability of controlling the surfaces with dense, molecularly ordered ultra-thin films of nanotubes of
controlled thickness and orientation. The electrical and magneto-transport properties of the monolayers (arrays) of multi-wall and single-wall carbon nanotubes in a temperature range 1.8-300K and in magnetic fields up to 35 T have been tested.

7:15 PM Rb21.5
Properties of Chemically Modified Carbon Nanotubes, Ryo(to) Kunishiro1, Hirotaka Ohashi2, Masahiro Yanashita3, Takeshi Akasaki3, Yutaka Maeda4, Shinya Takahashi5, Shigeki Maruyama5, Takeshi Iizuka2, Kikizo Hatakeyama1 and Katsumi Tanigaki1,1; Tohoku University, Sendai, Japan; 2JST, CREST, Kawanaguchi, JAPAN; 3University of Delaware, USA; 4Tokyo Gakugei University, Tokyo, Japan; 5The University of Tokyo, Tokyo, Japan.

From the viewpoint of nano structure materials, fullerences, carbon nanotubes (CNTs), and their related ones are very interesting due to their unique electronic properties. Especially CNTs are expected to be used for applications in the near future. In order to introduce intriguing electronic properties to CNTs, two techniques of chemical and physical doping can be adopted. In the case of chemical doping, various atoms and molecules have been used as dopants. The resulting solids have exhibited various kinds of interesting properties depending on the doping level. Physical doping, in contrast, is a method of using field effect transistors (FETs) for carrier doping. The FET technique is a very useful method not only for studying the fundamental properties but also for device applications in the future. Both techniques are very essential for understanding the electronic properties from the fundamental aspects point of view. As for CNTs, chemical carrier doping has been reported so far for controlling carrier concentration and integralization. However, for chemical doping, the effects are generally possible; One is endohedral doping and the other is the exohedral chemical modifications of CNTs. It has been exemplified that doping with alkali metals can introduce electron carriers into CNTs. Further, endohedral doping of CNTs was reported to be controlled by the endohedral insertion of organic molecules inside the CNTs. A similar carrier doping could exohedrally be possible when the CNTs surface is chemically modified. With such chemical modifications, the charge transfer from the substituent groups to CNTs will be expected and this could modify the electronic properties of CNTs. We have made a chemical modification of CNTs using a Si-containing molecule of SiH3Bu showing relatively strongly electron donating character. We have examined how the FET properties of these chemically modified CNTs will change. In order to investigate the FET properties, the chemically modified CNTs were dispersed on a SiO2/Si FET substrate with Au/Ti electrodes on its surface, and the measurements were carried out at ambient temperature using a conventional method for CNT-FET studies. As a reference, the experiments were also made in the same manner on chemically non-modified CNTs. It will be demonstrated in the conference that p-type pristine CNTs can be converted to n-type ones by this modification and this could be interpreted in terms of the electronic states produced as a result of hole carrier injections generated by the SiH3Bu modifications. These results show the possibility for the accurate control of CNTs by means of chemical modifications, by changing the type as well as the concentration of substituent groups that can be adopted to the surface chemical modifications on CNTs.

7:30 PM Rb21.6

For cooling of future high power chips, the thermal conductivity of the thermal interface material (TIM) lying under the back of the chip and the heatsink or heat spreader is one of the most fundamental limitations in the package stack. As a part of this program we included carbon based materials as the possible candidate thermal solution material. Although many people have been discussing the thermal application of carbon nanotubes (CNT) system to take advantage of their high thermal conductivity, little information is known on the attainable thermal resistance using CNTs. The thermal conductivity of CNTs is itself reported to be as high as 1900 W/mK for single wall CNT by laser probing method but its relationship to the attainable heat resistance as a TIM is still unclear. Therefore, we prepared a 100-micron thick aligned CNT film deposited by CVD method and evaluated the thermal conductivity perpendicular to the substrate using a liquid heat contact method measuring the temperature decay of a laser pulse. The thermal conductivity of the CNT film was 4.4-4.7 W/mK, which can be translated to single molecule CNT value of about 1300 W/mK, roughly consistent with the reported CNT values, when two factors are taken into account. First, the CNTs in the deposited film were not aligned. Second, the cross-sections of polymer-impregnated samples and second, the CNT are approximately three times longer than the nominal 100-micron thickness of the deposit. Based on these results, it is concluded that CNT deposits could give useful TIMs if the volume filling could be increased to 5%. A film of such 5% CNT with 100-micron thickness is expected to have a heat resistance of 0.01-0.04 cm2/W. Although increasing the volume filling factor may require further effort, the results also indicates a use of of CNTs in TIMs. If we can interpret this result as the usefulness of graphene structure, we can utilize other forms of continuous graphene structure for TIM applications. The material system has to be compliant as well as thermally conductive for the TIM applications. Although high packing of nanotubes and maintaining compliance may be a tradeoff relationship, we expect that reasonable compliance can be achieved by adding soft polymer material among the aligned nanotubes.

7:45 PM Rb21.7
Fast and Position-Controlled Growth of Single-Walled Carbon Nanotubes. Zaojin Liu1, David Styers-Barnett1, Alex A. Puretzky2, Christopher M. Rouleau1, Hongtao Cui2 and David B. Geohegan1,2; 1Center for Nanophase Materials Sciences, Oak Ridge National Lab, Oak Ridge, Tennessee; 2Department of Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee; 3Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Fast-heating chemical vapor deposition is a proven efficient approach for the growth of long individual single walled carbon nanotubes (SWCNTs). However, obtaining insights into the growth mechanism of how fast a carbon nanotube can grow is still of both scientific and technical importance for designing future experiments to achieve better control of the nanotube growth. In this paper, we describe a new laser-irradiated CVD technique to synthesize SWCNTs using laser irradiation as a source of heat. A high power industrial Nd:YAG laser (600 W average power, 1-500 Hz repetition rate, 0.5-10nm pulse width) was employed. These properties can be precisely controlled by choosing the proper laser power, repetition rate, pulse width and number of laser pulse. Scanning electron microscopy (SEM), micro-Raman scattering spectroscopy, transmission electron microscopy (TEM) and atomic force microscopy (AFM) were used to characterize the nanomaterials produced at different regions within the laser-irradiated zone. The lengths of the nanotubes produced were compared with the thermal treatment of the catalyst films as measured by in situ by optical microscopy. Growth rates, single wall nanotube yield, and diameter distributions of SWCNTs are estimated for various thermal treatments for different hydrocarbon feedstock gases. Growth rates for carbon nanotubes vary dramatically depending on catalysts and parameters of the heating profile, indicating laser-CVD technique may provide local control over growth conditions and may pave a way for investigating the growth mechanism of fast-heating carbon nanotubes. Research on Functional Nanomaterials at the Center for Nanophase Materials Sciences is supported by the U.S. Department of Energy, Division of Materials Science, Basic Energy Sciences.

SESSION Ra22/Rb22: Poster Session IV
Chair: Zhong Wang Thursday Evening, December 1, 2005
8:00 PM
Exhibition Hall D (Hynes)

Ra22.1/Rb22.1
Template fabrication for the ordered growth of semiconductor nanowires. Bodo Fuhrmann1, Hartmut S. Leipner2, Hans-Reiner Hochoe1, Peter Werner3, Margit Zacharias4 and Ulrich Goesele4; 1Center of Materials Science, Martin-Luther-University Halle, Halle/ Saale, Germany; 2Max-Planck-Institute of Microstructure Physics, Halle/ Saale, Germany.

Due to their importance in fundamental research and possible applications, semiconductor nanowires are of great interest. Different growth techniques are used for the growth of semiconductor nanowires, e.g. pulsed laser deposition, metal-organic chemical vapor deposition or molecular beam epitaxy. While the length of the wires mainly depends on the growth conditions, size and location of the nanowires are strongly related to the deposition of metal particles used as mediators of nanowire growth. Beyond the nanowire growth itself, the control of position and the tuning of the dimensions is a main point of interest in present research. The obvious way to do this is the preparation of ordered metal particle arrays by a suitable lithographic method. Optical lithography on the one hand is not applicable because the desired dimensions lie in the nm range. Electron beam lithography on the other hand is determined by the point of resolution, but is cost intensive and hardly available. We have used in our work nanopatterning lithography to fabricate ordered arrays of metal nanoparticles. In nanopatterning lithography, hexagonal closed...
packed monolayers or bilayers of monodisperse particles are used as a shadow mask for the subsequent processing of the substrate, which is in our case the deposition by thermal evaporation of a subsequent thermal annealing step the triangular shaped metal islands are transferred into semispheres. Size and distance of the metal particles depend mainly on the size of the particles used for the mask. We have used the thermal evaporation of polystyrene particles with diameters in the range 287 nm to 1.32 μm. The spectrum of applicable substrates could be extended to hydrophobic substrates like GaAs and GaN by applying a mask transfer technique. In this technique, first a silicon oxide mask is deposited on a hydrophilic substrate, then stabilized by deposition of a metal layer and finally transferred onto the desired substrate. The advantage of this technique is that the holes between the spheres become smaller by increasing the thickness of the stabilization layer. This option gives the possibility to control the size of the metal particles independently from their distance, which is mainly determined by the diameter of the polystyrene particles. On this basis ordered arrays of gold particles with diameters in the range 250 nm to 500 nm were fabricated for the growth of arrays of nanowires of ZnO on GaN and sapphire, GaAs on GaAs (-11, 1)As, and Si on Si (111). Ra22.4/Rb22.4
Carbon nanotube/V205 nanowire hetero-film actuator. Kang Ho Lee1, Seong Min Yee1, Se Joong Park1, Jung Hwan Huh1, Gyu Tae Kim1, Sung Joon Park2 and Jeong Sook Hg2; 1 Electrical Engineering, Korea University, Seoul, South Korea; 2 Chemical and Biological Engineering, Korea University, Seoul, South Korea.
Hetero-film actuator composed of carbon nanotubes and V205 nanowires were demonstrated in a bimetal configuration. The successive filtration of V205 nanowire solution followed by carbon nanotube dispersed water solution in the same way produced a black-gray colored sheets. A significant actuation was observed in sodium chlorided electrolyte solution with a bending direction to the carbon nanotube side at the positive bias voltage against the copper counter-electrode. As the frequency of the applied voltage increased up to 50 Hz, the amplitudes decreased, indicating a rather slow response of the hetero-film actuator in the electrolyte solution. The hybrid structure enabled an easy fabrication of the film actuator with the enhanced efficiencies.

Ra22.5/Rb22.5
Ferrofluids demonstrate self-organized spins in response to a strong magnetic field. These "spikes" of density give rise as a result of dipole-dipole interactions (both attraction and repulsion) of the nanoparticles comprising the ferrofluid, balanced by the surface tension of the liquid phase. Examples of extensive rod structures have been reported in the literature, in systems where the structures that formed dissipated without the constant application of an organizing magnetic field. In these cases, the organized rods were free in solution, rather than attached to a substrate or platform. These types of systems could show utility in a number of areas, including as polarizers, birefringent filters, and dichroics. For such applications, it may be advantageous to have stable, substrate-bound devices that show response to magnetic fields, but do not dissipate or degrade without a magnetic field present. We present a unique curable ferrofluid that shows self-organization into arrays of rods that may then be cured into stable surface bound arrays. The rods are uniform, as small as 320 nm in diameter, and hexagonally packed with spacings as small as 2.4 microns. The uniform packing extends over hundreds of square microns with very high crystallinity. Spacing and rod diameter are dependent on a number of factors, including field shape and strength, magnetic composition, and spatial confinement. We will present the results of experiments to understand the formation of the rods and their spacing, as well as characterization by multiple techniques. Finally, we will describe possible applications for the rod arrays, and early efforts to study them.

Ra22.6/Rb22.6
Abstract Withdrawn

Ra22.7/Rb22.7
Sub-micrometer patterning of quantum dots and nano-rods. Peter Karageorgiev1, Renata Jarzembskina1, Joel van Embden1,2, Maciej Olej2, Nicolas Pazo Perez1, Thomas Buesgen1, Paul Mulvaney1,2 and Michael Giersig1; 1 Center of advanced European studies and research (c.a.s.e.r.), Bonn, Germany; 2 School of Chemistry, University of Melbourne, Melbourne, Australian Capital Territory, Australia.
We present a method for fabrication of 2D structures consisting of different type nanoparticles ordered in nanometric domains. The confinement and deposition of the nanoparticles in domains is based on the use of cantilevered nano-pipette as an atomic-force-microscopy sensor, which directs a flow of a particle solution to the substrate surface. An advantage of the approach is that it allows a deposition without any chemical modification of the particles. The size of the domains depends on the solvent, the concentration of particles, the flow rate and power level of the sample surface and can be controlled up to dimensions comparable with the aperture of the pipette (100-300 nm). Structural and scanning near-field optical characterization of patterns comprising colloidal particles shows the expected or rotational ordered, which can be attributed to pre-orientation of the particles by the narrow aperture and orientation due to scanning of the pipette.

Ra22.3/Rb22.3
NISi Nanowires and Nanobridges Formed by Metal-Induced Growth. Joomdong Kim, Dongho Lee and Wayne A. Anderson; Electrical Engineering, University at Buffalo, Buffalo, New York.
Nanowires are attractive entities as one-dimensional building blocks to use in nanoelectronics and nanoscale connections. This approach is a breakthrough to overcome the difficulty in scaling down of integrated circuits. We will present a unique method to grow NiSi nanowires (NWs) and form nanobridges (NBs) by metal induced growth (MIG). Additionally, the processing temperature is below 600 °C reducing potential damages on fabricated structures. Ni as a catalyst layer was thermally deposited on SiO2-coated Si wafers. During dc magnetron sputtering of the Si from a 2 inch diameter target, Ni atoms react with sputtered Si nanoparticles. The solid reaction of Si and Ni reduces the processing temperature and produces linearly grown nanowires. The nanowires were 2-8 μm in length and 30-80 nm in diameter. Dry etching and metal lift-off procedures made different sized trenches and revealed that the longest NBs could reach to the NW length. A field emission scanning electron microscope (FESEM, Hitachi S-4000 accelerated by 20 ~ 30 kV) was used to observe the nanowires. X-ray diffraction (XRD) analysis showed the presence of NiSi peaks as a key factor to grow NWs. The MIG method provides advantages of lowering processing temperature as well as self-assembled characteristics of nanowires, which has a potential to alter the conventional lithographic techniques to provide an alternate thermal step, and more reliable contact scheme in nanoelectronic applications.
Metal Nanoparticle Formation Directed by a Radiation-synthesis Copolymer Template. Alia Paige Weaver, Joseph Silverman, Guadalupe Salamanca-Riba and Mohamad Al-Sheikhly; Materials Science and Engineering, University of Maryland, College Park, Maryland.

Metal particle nanostructures are an area of intense research interest due to their possible role as building blocks for next generation electronic and magnetic components, and for sensor applications. In order for these materials to be useful, the particles must be positioned in a strategic manner such that their dispersion is controlled. A variety of synthetic methods have been developed for the formation of these types of structures, and a great deal of effort is currently being focused on the use of organic templates to mediate the nucleation density of these particles. In this presentation, we report a procedure utilizing a radiation-synthesized copolymer as a directing agent for the production of iron nanoparticles. Cobalt-60 gamma irradiation was used to synthesize a 2-ethylhexyl acrylate/acyclic acid copolymer which serves as a molecular template for the fabrication of metal nanoparticles. The morphology of this polymer produces local changes in the energy barrier for nucleation of the iron, thus providing greater control of the distribution of the particles. The particle size produced has been investigated as a function of total dose, dose rate, and concentration of acryl acid. This work was supported by the DOE/Industry Matching Grants Program under contract number DEFG07021D14556.

Simulation of the Assembly of Acene-Functionalized Nano Building Blocks. Feng Qi1, Murad Durandurdu2 and John Kieffer1; 1Materials Science and Engineering, the University of Michigan, Ann Arbor, Michigan; 2Physics, University of Texas - El Paso, El Paso, Texas.

We use multi-scale simulations, including ab initio quantum mechanical calculations, molecular dynamics (MD) simulations, Monte Carlo (MC) and constrained molecular dynamics simulations to study a series of novel acene-functionalized polyhedral oligomeric silsesquioxane (POSS) assemblies as nano building block. The conformations and electronic properties of individual functionalized molecules were first determined using ab initio calculations. Then the equilibrium structures of those molecules that exhibit the most promising electronic properties were determined by simulating their assembly using MC and constrained MD methods, and self-assembled structures, which include both amorphous and crystalline configurations, the most likely to develop were predicted based on energetic considerations. Finally, these assemblies were characterized in terms of their electronic, structural, and mechanical properties. Accordingly, acene functionalized POSS assemblies in crystal form have similar band gaps than pure acene molecules, but have superior thermal and mechanical bulk properties. Moreover, the predicted crystal form shows parallel stacking of acene groups, which provides for increased pi-orbital overlap, and thus, better electronic conductivity. The self-assembled amorphous structures show thermal and mechanical properties superior to those of polymer crystalline phases. The packing of acene molecules can also be affected by the presence of templating surfaces.

Templated Deposition of Polyelectrolyte-Functionalized Colloids. Marianne S. Terro and Paula T. Hammond; Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

The selective adsorption behavior of polyelectrolytes and polyelectrolyte multilayers is of great importance to the production of nano and micro-scale features within organic thin films; such patterns and functionalized devices, proteomic arrays, and sensors based on molecular recognition. In previous work, our group has demonstrated the use of chemical templating of surfaces for in-situ patterning of polyelectrolyte multilayers. This approach has recently been extended to polyelectrolyte-functionalized colloids, making possible the assembly of multi-component colloidal arrays via selective adsorption. Chemical motifs capable of multiple hydrogen bonding are of particular interest for such selective systems as their interactions are both highly specific and readily tunable. In our current word, we explore the use of RNA homopolymers as guides for selective adsorption. Polyadenylene, polyctydidylic, polyguanylic, and polyuridylic acid were layered onto the surfaces of polyelectrolytes as well as printed by soft lithography to create chemically patterned surfaces and the ability of the adena-uracil and cytidine-guanine pairs to direct deposition of the functionalized colloids on the patterned surfaces was studied. We have also expanded our assembly of colloids asymmetrically functionalized with two complementary polybases.


Functionalizing carbon nanotubes (CNTs) is of widespread interest for separating CNTs of different chiralities, assembling and interconnecting CNTs, and tailoring the matrix-CNT interactions in nanocomposites. Derivatization methods used today require multiple steps such as heating and aggressive refluxing with strong acids, often in combination with ultrasonication. These cause problems such as tube shortening due to bond fission, and high impurity concentrations due to prolonged residence of CNTs with nanotubes with other low dimensional structures (e.g., nanoparticles and biomolecules) is also attractive for new CNT-based hybrid device concepts that harness the unique properties of the constituent nanostructures. Many current functionalization methods result in low temporal yields of non-invasive and non-thermal excitations is attractive for obviating such shortcomings, and for enabling the maturation of simpler and more readily scalable functionalization and derivatization methods. Here, we demonstrate the use of microwaves to rapidly functionalize and derivatize CNTs with metallic nanotubes formed by reduction of metal ions, all in a single processing step. Raman and infrared spectroscopy results indicate that the defects generated in the chemical/thermal reaction process of the CNTs and enable its functionalization by reaction with water and oxygen at the defect sites. For example, microwave exposure of CNTs dispersed in a mixture of chloroauric acid and ethylenediamine reduces the nanotubes hydrophilic. Preferential microwave-activated reduction of chloroauric acid by ethylene glycol at the functionalized sites results in the uniform decoration of nanotubes with gold nanoparticles while preserving the overall structural integrity of the CNTs, confirmed by transmission electron microscopy and diffraction. To illustrate the feasibility of our approach, we have also derivatized CNTs with magnetic and electrically functionalized nanoparticles such as CoPt4, Cu and SiO2. This strategy of harnessing microwave-assisted functionalization coupled with in situ nanotube synthesis provides a rapid and efficient method to attach a variety of nanostructures onto CNTs for applications in future devices and composites.

Nanostructure fabrication through template directed multi-layer atomic layer deposition: non-close-packed inverse opals. Elton Graugnard, Jeffrey S. King and Christopher J. Summers; Materials Science & Engineering, Georgia Institute of Technology, Atlanta, Georgia.

We present a powerful, flexible and unique concept for fabricating nanoscale devices based on multi-layer atomic layer deposition (ALD) in patterned template structures. The ultra-conformal nature of ALD allows the nanoscale features of almost any template to be faithfully maintained through nanoscale growth. The proper selection of coating precursors can yield the desired properties of thin films, for example, index, luminescent, or magnetic films. Likewise, the number and sequence of materials can augment the template in varying degrees from a simple tuning of the shape or feature size to complete inversion of the pattern. Thus, multi-layer ALD allows patterned ALD to be tuned to serve as scaffolding for fabricating a device whose structural properties are defined by the template, while the material properties are controlled independently by the choice of films grown by ALD. Although this concept has application to many areas of materials science, we demonstrate the specific application of engineering enhanced photonic crystal structures. The multi-layer ALD technique provides a controllable method for fabrication of high quality non-close-packed inverse opals with the widest possible photonic band gap. Additionally, with this method, the inverse opal pore size can be increased to allow for a high degree of dielectric backfilling. Here we report using multi-layer ALD of ZnO, Al2O3, and TiO2 to fabricate inverse opals, non-close-packed inverse opals, resulting in Bragg reflection of over 600 nm and enhancement of the Bragg peak width by >150%. The optical properties of the non-close-packed inverse opals are discussed and a model is presented for characterizing the controlled fabrication of optimized photonic crystal structures using multi-component conformal film deposition. Using this flexible technique we have extended the inverse opal architecture to create new structures that have enhanced photonic band gaps providing wider photonic band gaps for a given dielectric constant. Thus, it should be possible to fabricate optimized structures (NCP or otherwise) with a lower minimum dielectric contrast requirement, potentially making a full photonic band gap a reality. Beyond photonic crystals, this technique allows materials with different electric, magnetic, and optical properties to be patterned and combined at the nanoscale, creating new composite materials. Taking advantage of the large number of materials that can be conformally
deposited by ALD either individually or in multi-layers, and combining them with the large number of template fabrication techniques allowed a nearly infinite number of new photonic and electronic device structures to be fabricated.

Ra22.13/Rb22.13
Simulated Self-Assembly of Functionalized Silsesquioxane Building Blocks. Jinhua Zhou, Feng Qi and John Kieffer; Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan.

We have developed a computational framework for the simulation of structural assembly in Polyhedral oligomeric silsesquioxane (POSS) nanocomposites, by combining computational techniques ranging from ab initio quantum chemical calculations to molecular dynamics simulations to coarse-grained mesoscopic modeling methods. Using ab initio calculations we predict the inherent properties of molecular building blocks. Using large-scale molecular dynamics simulations we reproduce the microscopic and macroscopic evolution processes that occur during nano-assembly, and thereby generate realistic models that serve to establish structure-property-processing relationships for these materials. In this presentation the general approach taken with our the computational framework will be outlined and results from two representative materials simulation studies will be discussed. One example details the self-assembly behavior of POSS cubes attached to a polymer backbone in pendant fashion. The other one describes the peculiar and spatially controlled surface behavior of mono-tethered POSS that causes nano-phase separation and can be exploited for pattern formation at this scale.

Ra22.14/Rb22.14
Self-assembly of nanoparticles and polymer into "patchy" microspheres. Vinit Murthy1 and Michael Wong2; 1Chemical and Biomolecular Engineering, Rice University, Houston, Texas; 2Chemistry, Rice University, Houston, Texas.

A new mode of assembling charged nanoparticles and polyanimes to give three dimensional fundamental constructs such as microcapsules was reported recently (Rana et al., Adv. Mater. 17 (9), 2005, 1145). Briefly, upon addition of multivalent anions (e.g., citrate−3−) polyanimes (e.g., poly(L-lysine)) form metastable aggregates via charge interactions. Contacting these spherical aggregates with negatively charged nanoparticles (e.g., silica, d ~ 15 nm) leads to the formation of nanoscaled multimeric capsules. The shell comprises the nanoparticles intercalated with the oppositely-charged polymer chains, and the core interior contains polymer (or water, depending on the formulation). For the first time, we report the synthesis of microcapsules that contain smaller, discrete polyanime domains within the shell wall, on the shell wall exterior, and in the polymer-filled core interior. We will provide optical microscopy evidence for such structures, and will discuss their synthesis and formation mechanism. The "patchy" nature of the superstructure controlled surface functionalization, suggesting the possibility of guided formation of three-dimensional microcapsular assemblies.

Ra22.15/Rb22.15
Materials and Processes for High Resolution Nanoscale Fabrication using Thermal Cantilever Array Lithography. Yueming Hua1, Shubham Saxena2, William P. King2 and Clifford L. Hohmann1; 1School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, Georgia; 2Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia.

The long term goal of our work is to develop a revolutionary nanofabrication technology based on the use of arrays of heated atomic force microscope cantilevers for nanoscale thermal manufacturing processes being investigated, patterning of various materials is performed using thermal cantilever arrays in which heated cantilever tips having nanometer-scale sharpness write structures onto a surface. This writing can be performed using various operational modes ranging from thermal dip pen or DPN deposition of materials from the cantilever tip to the direct thermal decomposition and removal of material from a surface. Since this fabrication method requires no mask or template, it is potentially a very low cost alternative to other existing nanopatterning technologies. Also, since the cantilever array can be easily scaled to large numbers of cantilever tips, the throughput of such a multi-tip system can be large using highly parallel writing strategies. This parallel writing capability overcomes the major limitation to the other primary existing maskless nanofabrication technology, namely the single beam serial writing nature of electron beam lithography. Finally, the thermal cantilevers fabricated thus far can already access a wide range of temperatures from ambient to ~500°C. This large temperature range enables the use of a variety of thermally activated processes for the direct patterning, deposition, or removal of materials. In order to design such thermal cantilever array systems and processes, significant research on the fundamental issues which control the performance of these systems and the materials used with them is required. Preliminary work in our labs at Georgia Tech has already shown the feasibility of directly depositing conductive metal patterns using a thermal cantilever tip. We have also shown the basic feasibility of using the local thermal decomposition of polymers to form polymer micro- and nanostructures. This paper will focus on our work directed at designing and optimizing "thermally sacrificial polymers" which can be used as the analog of conventional photoresists for such a thermal cantilever array lithography system. Such sacrificial polymers are designed so that they cleanly decompose to gaseous byproducts when heated to a well defined temperature. Thus local heating of a thin film of such a polymer allows for the clean removal of the heated area to produce polymer physical relief structures. The impact of the polymer structure and physical properties on the thermal imaging process will be discussed and illustrated using results from our polymer synthetic and imaging testing work. Additional imaging modes for polymers will also be presented and compared to the sacrificial polymer imaging approach.

Ra22.16/Rb22.16
Growth of Self Assembled Metal Nano-Particles and Ultra-Thin Films Observed with In-Situ Ellipsometry and Resistance Measurements. Luke Ryves1 and Tom W. H. Oates2; 1School of Physics, University of Sydney, Sydney, New South Wales, Australia; 2Forschungszentrum Rossendorf, Dresden, Germany.

Thin coatings of metal nano-particles have the potential for use in bio-sensor applications, whereas ultra-thin continuous films are required for electronic devices and nano-laminated hard coatings. Coatings were deposited in a high current pulsed vacuum arc. In-situ spectroscopic ellipsometry has been used to calculate the coverage of nano-particles during growth, to find the percolation threshold, and to monitor post deposition changes in the coatings. These results are compared with in-situ measurements of resistance and substrate temperature, and ex-situ electron microscopy.

Ra22.17/Rb22.17
Optical Trapping for Agile Nanosyntesis and Testing. Thomas LeBrun and Arvind Balijepalli; NIST, Gaithersburg, Maryland.

Despite the rapid advance of tools to make and characterize structures at the nanoscale, a key gap remains to a large extent largely unable to manipulate individual nanocomponents to build functional nanodevices and test their performance. Optical trapping can offer a agile tool for nanosynthesis, and we will describe the development of Optical Tweezers (OT) for efficient nanosynthesis and testing. OT presents a number of advantages for manipulating nanocomponents, including full six-degree-of-freedom manipulation, compatibility with a range of materials and shapes, and simultaneous manipulation of multiple particles in real-world environments such as biological media in-vitro and in-vivo. We will outline the physics that determines the capabilities and limitations of optical tweezers for nanosynthesis, and describe the engineering that allows some of the limitations to be overcome. We will also describe the development of an open software interface and an architecture for the instrument control system to transform the tool from a simple trap to an agile tool that allows an inexperienced operator to manipulate nanocomponents in six degrees of freedom, and prototype functional devices in a lab-like environment. These nanosynthesis tools will be demonstrated with examples including nanowire device fabrication and control of biological nanoparticles such as liposomes for detection and treatment of cancer.

Ra22.18/Rb22.18
Capillary Growth of Oriented Composite Mesostructures under Nanoscale Confinement. Rong Kou, Dougall Wong and Yunfeng Lu; Department of Chemical and Biomolecular Engineering, Tulane university, New Orleans, Louisiana.

Cooperative assembly of silicate/copolymer replicates liquid crystalline mesophase of copolymer resulting in highly ordered mesostructures of inorganic/organic composite (e.g. cubic, hexagonal, lamellar structure). The self-assembly process always shows non-preferred orientation within the mesostructured composite. Oriented composite mesostructure will be of great interest due to favorable orientations that may provide enhanced device performance. However, fabrication of such oriented and highly ordered mesostructured composite still remain a challenge. In this presentation, we will show capillary-induced growth of oriented silicate/copolymer composite nanowire within nanoscale cylindrical alumina pores. Morphology of the oriented composite nanowires were studied using XRD, TEM and SEM. The liquid crystalline silicate/copolymer mesophase is driven into cylindrical alumina pores to form wire-like structure by capillary force. Shearing force within
the liquid crystalline mesophase induced by interfacial capillary force aligns the composite mesostructure for both hexagonal and lamellar structures. Landauer nanowires grow along curved substrate wall surface resulting in oriented concentric lamellar mesophase. The corresponding mesoporous silica wires with oriented hexagonal tubular and concentric lamellar pore channels were obtained after removal of organic silica extracting precursors. The mesoporous silica nanowires possess desirable oriented nanopore channels along cylindrical alumina pores. The diameter of the oriented mesoporous silica nanowires are controlled by the diameter of cylindrical alumina pores. Both oriented tubular and mesoporous silica wire is tunable. The novel structured nanowires and corresponding mesoporous silica/alumina composite are expected in membrane based application such as separation, templating synthesis, etc. This work will bring the insight of nanoscale confinement effect on self-assembly process.

Ra22.19/Rb22.19


One-dimensional nanomaterials such as metallic nanowires and carbon nanotubes are suited for nanoscale building blocks in opto-electronic devices and micro/nano-electromechanical systems (MEMS/NEMS). Understanding their mechanical properties is essential for such applications. In this study, we first address the structural dependence and size effect of the Young’s modulus of Au nanowires by using the molecular dynamics (MD) method with the modified embedded atom method (MEAM). Ten kinds of nanowires modelled with help of multi-shell structures and the fcc structures are created. The uniaxial tensile forces are imposed on the atoms at the both ends of the nanowires model. The stress-strain curves yield the Young’s moduli of the nanowires. The dependencies on the structure, size, and temperature are discussed. Next, we investigate the Young’s modulus of carbon nanotubes by using the MD with the reactive empirical bond order(REBO) potential. Six kinds of nanotubes with different chirality are prepared. The stress-strain curves derived from the uniaxial tensile and compressive simulations yield the Young’s moduli of the nanotube models. Their chirality dependences are discussed.

Ra22.20/Rb22.20

Three Dimensional Nanotextured Opal-Like Silica Foams. Florent Carn, Pascal Masse, Serge Ravaie, Hassan Saadaoui and Renal Backov; Centre de Recherche Paul Pascal (UPR-CNRS 8641), Pessac, France.

Designing new porous materials in a monolithic form with framework involving hierarchical pore system and tailored macroscopic form is an emerging area of technological interest toward heterogeneous catalysis, separations, artificial bone structure, thermal and/or acoustic insulation, ion-exchange operation. In addition to the micro- and/or meso-structure organisation, shaping porous solids in the form of monolith with well-defined macropore morphology and tunable surface roughness are also important factor that influence the suitability for potential applications. In this context, such materials with higher order architecture can be obtained by using soft matter macroscopic template such as biliquid[1] or air-liquid foam[2]. We describe here a low-cost and effective way of preparing hierarchically organised porous silica monolith arising from an air-liquid foam structure transcription by colloidal crystallisation. The opal-like skeleton provide a tunable surface roughness by using different size of silica colloidal particles while the macropore morphology (i.e. pore wall thickness, pore wall length) can be tune by a continuous control over the foam's liquid fraction and the gas bubble size during the mineralization process. Moreover open or closed pore structure can be reach upon the foam's liquid fraction and the colloidal particle size involved during the foaming process. This work[3] extends the recently reported study[4] on the preparation of SiO$_2$ foam using molecular precursor. This time by mimicking natural microstructure of super-hydrophobic leaves, the use of colloidal particle allow the surface roughness shaping leading to amplified surface hydrophobic character. Furthermore, predominantly closed cell materials are needed for thermal insulation and open interconnected materials are needed for using involving fluid or gas transport such as filters and catalysts. 1- F. Carn, A. Colin, M-F. Achard, H. Deleuze, E. Sellier, M. Birot, R. Backov J. Mater. Chem., 2004, 14, 1370; 2- F. Carn, A. Colin, M-F. Achard, H. Deleuze, C. Sanchez, R. Backov Adv. Mater., 2005, 17, 62; 3- M. Masse, S. Ravaie, H. Deleuze and R. Backov Langmuir (submitted). 4- F. Carn, A. Colin, M-F. Achard, H. Deleuze, R. Backov Adv. Mater., 2004, 6, 140.

Ra22.21/Rb22.21


While investigating thiole deprotection methods for a polymer with pendant aliphatic thioacetate groups, we successfully explored the use of tetrabutylammonium cyanide (TBACN) as a catalyst on a series of model compounds. Routinely used conventional deprotection thioacetates utilizing several strong bases and acids proved inadequate whereas the initial studies of TBACN catalyst and solvent conditions were promising on three model compounds. Particularly attractive are the mild reaction conditions and the reduced byproduct formation typically seen using literature methods, and yields of greater than 80% for the free thiols. Consequently, a series of compounds were selected to analyze the scope and range of the method using various conditions including primary, secondary and tertiary amine substrates, solvent, and catalyst quantity. Background work, synthesis, yields and limitations of this new method are presented.

Ra22.22/Rb22.22

Abstract Withdrawn

Ra22.23/Rb22.23

Nano Organic-Inorganic Hybrid Materials as Corrosion Protective Layers on Aluminum surface. Young-Ching Sheen, Chih-Kwuang Chen, Chih Kuang Chang and Shi-Min Shao; Union Chemical Laboratories, ITRI, Taich, Taiwan.

Chromates and its salts like hexavalent chromium and chromium oxide (Cr2O3) have been used as effective corrosion inhibitors on steel, aluminum and aluminum alloys for many years. Traditional chromate-based surface treatments for the corrosion resistance purposes, such as chemical conversion and anodizing treatment, are very toxic and offer many waste and environmental problems. The durability, hardness and adhesion power because the dense passivation layer was formed on metal surfaces. Moreover, chromates especially the hexavalent chromium have self-healing ability which makes coatings possess an extra long-term wear time and avoid the fracture of metal. The hexavalent chromium does not been considered as an environmental friendly material because of its toxicity and carcinogenic danger even though it has superior corrosion resistance properties on various metals. The properties of hexavalent chromium have caused European Union will prohibit to import totally from 2007. Thus, searching for a new replacement material or an approach for protective as effective as hexavalent chromium is a momentous topic under these restrictions of law.

In this study, we developed a new approach which without chromium component to enhance the corrosion resistance after the surface coating on metals. In the organic/inorganic (O/I) hybrid systems, the epoxy resins and silica particles were treated as the organic parts and inorganic parts, respectively, and they were considered as barrier layers to prevent the permeation of water, air and electrolyte like chloride ions. Furthermore, the efficient organic and inorganic corrosion inhibitors were incorporated in these O/I hybrid coatings as passivation layers when they had reacted with the metal surface to form a continuous and dense thin film at the interface between coating and metal surface. Besides, the organic corrosion inhibitors were composed of phosphate like phosphate and sulfer like 2-mercaptopenzimidazole(2-MBI), and the nano-sized inorganic corrosion inhibitors were manufactured by grinding processes from zinc phosphate and had been well dispered in our resin solutions. Finally, the hybrid materials were used in a coating manner. The coatings were coated on the aluminum plates, and their anti-corrosion properties had been examined by salt spray testing and potentiodynamic polarization analyses. The O/I hybrid coating films were found to pass the 1000 h salt spray testing and have much lower corrosion currents (0.9 na/cm$^2$) compared with the bare aluminum (2742 na/cm$^2$) based on the polarization curve. Both salt spray testing and electrochemical analyses showed that the coatings with corrosion inhibitors had provided excellent corrosion protection by forming a physical barrier layer and a continuous passivation film on aluminum surface simultaneously and independently.

Ra22.24/Rb22.24

Selective Deposition of Polymer Nano-Particles on Silicon Microfabricated Substrate. Manabu Tanaka 1, Hiro峪ki Nishide 1, Nanobu Shimamoto 2, Takashi Tanii 3 and Iwao Ohdomari 2.

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Recently, there is great interest in arrangements of nano-particles (nanometer-sized homogeneous particles with diameters from a few nanometers to sub-micrometers) on substrates. Several approaches have been studied to arrange nano-particles on substrates, including laser manipulation, ink-jet printing, nanoprobe lithography, and a nano-particle arrangement using the substrate as a template. Among them, the template-assisted procedures are simple and feasible
without any special equipments and techniques. This report describes the selective deposition of polystyrene nano-particles in various nano- or micro-scale patterns on silicon substrates through a simple dipping and pulling-up procedure. A Nano-particle array dot, the zero-dimensional arrangement, was first achieved on the silicon nano-etchpit array substrate which possesses a nanometer-sized recessed cyclic ordering (a pin formed through the etching) at the lattice points with a constant interval on the silicon substrate as an array. "Particle-packing" and "particle chain", the two- and one-dimensional particle arrangement, by using other types of silicon microfabrication techniques were subsequently achieved. In addition, as an example of functional nano-particles, nanometer-sized and monodispersed polymer particles bearing stable radicals (unpaired electrons) was newly synthesized. Magnetic properties of the radical nano-particles and their arrangement on the silicon microfabricated substrate are also described.

Ra22.25/Rb22.25
Selective Chemical Vapor Growth of Carbon Nanotubes for Application of Electronic-Measuring Nano-Probes
Hiroki Okuyama, Nobuyuki Iwata and Hiroshi Yamamoto; College of Science and Technology, Niihon University, Chiba, Japan.

It is necessary to prepare nano-scaled probes and to control accurate approaching toward specimen for measuring electronic properties of nano-structured specimen. Carbon nanotubes (CNTs) have many unique characteristics, for example, high mechanical strength, flexibility and conductivity. Furthermore, CNTs are grown from only fine particles of catalyst by using chemical vapor deposition (CVD). Those characteristics are applied to prepare novel CNT probes and in situ to prepare and to damage the electron beam during TEM. This report will present how to demonstrate the process for selective growth of CNTs on patterned metal layers. A Ni catalyst and a Mo metal layer were deposited on a quartz substrate through a mask. The boundary of the metal pattern was properly prepared to become thin gradually. The Ni / Mo films were prepared by RF magnetron sputtering equipment. The growth conditions (substrate temperature, sputtering power and growth time) were 120 °C, 50 W and 1 min for Mo, 70 °C, 20 W and 1 min for Ni respectively. The CNTs were grown by CVD method. The reactor tube of the CVD equipment was heated up to 600 °C. The flow of H2 / Ar (5 cm / 200 cm cm) was introduced into the reactor tube during heating. The background pressure was 0.1 Pa, the total pressure at the temperature of the furnace was 8 kPa. When the temperature of the furnace reached a growth temperature, the 10 cm of ethylene (C2H4) was fed into the reactor for 30 min for the CNTs growth. From results of SEM observations, CNTs with 15 nm diameters grew up near the boundary where the surface of the Mo film was rough and porous. The amount of CNTs reduced gradually from boundary to inside of the metal pattern. The width of the CNT grown region was about 30 μm. In contrast the smooth Mo surfaces resulted in no growth of CNTs. Particles of the Ni catalyst were not observed in the resolution of SEM. The reason why CNTs grew up near by the boundary is that the Ni catalysts formed fine particle at the grown region. The Ni catalysts didn't become fine particle on the smooth surface of Mo. Rough morphology of Mo was because the Ni catalysts could not become fine particles. The Mo thickness of the rough region was thinner than that of the smooth region. Conclusively it was demonstrated that a selective growth of CNTs was realized by controlling the thickness of the underlaying metal layer, the CNT growth rate, the heating rate and the probes, which are prepared by this method, will be reported.

Ra22.26/Rb22.26
Nanotube Coalescence Inducing Mode: A Novel Vibrational Mode in Carbon Systems. Morinobu Endo1, Mauricio Terrones2, Yoong-ahn Kim1, Takuya Hayashi1, Hiroiki Muramatsu1, Riichiho Saito1, Federico Villalpando1, Shin Grobe1 and Mildred Dresselhaus3; 1Faculty of Engineering, Shinshu University, Nagano, Japan; 2Advanced Materials Department, IBM, San Luis Potosi, Mexico; 3Department of Physics, Tokohu University, Aoba Sendai, Japan; 4Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; 5Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts; 6Department of Physics, and Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts.

We inspected a new resonant Raman mode located at 1855cm-1 which is attributed to vibrations of linear carbon chains located between double-walled carbon nanotubes (DWCNT). This mode has now been termed as a "coalescence induced mode" (CIM) because it occurs just at the onset of the nanotube coalescence process. In order to understand this phenomenon, high purity DWCNT bundles were thermally treated at various temperatures, ranging from 1000°C to 2000°C. For each temperature step, Raman spectra were taken at different excitation energies and compared with HRTEM images. A separate section of the sample was mixed with elemental boron at 0.05% and the same experimental procedure was repeated to understand the effect of boron doping in the coalescence process. It was observed that the CIM feature appears in DWCNTs at 1855cm-1. The intensity of the CIM mode reaches a maximum at a critical temperature and disappears once the adjacent tubes start to merge. The CIM vibration is provoked by 1D carbon chains (3-4 angstrom-long) established directly between adjacent DWCNTs. The adjacent carbon chains induce a zipper action while the tubes coalesce, and the process is enhanced in boron doped samples. Once coalescence is initiated, the CIM disappears and a new Radial Breathing Mode (RBM) appears, which correspond to larger diameter carbon nanotubes. The effects were confirmed using high-resolution transmission electron microscopy (HRTEM). The CIM mode could now be used to identify sp hybridized carbon in various systems such as irradiated graphite, polymerized C60 molecules, functionalized fullerene and nanotubes, carbonyls, etc.

Ra22.27/Rb22.27
Smart™ Defects in Colloidal Photonic Crystals.
Friederike Fleischhacker1,2, Andre C. Arsenault2, Nicolas Tetreault1, Zhao Wang1, Vladimir Kitaev1, Frank C. Poiris1, Agustin Mihi1, Hernan Migues1, Georg von Freymann3, Ian Manners1, Rudolf Zenitl1 and Geoffrey A. Ozin1; 1Department of Chemistry, University of Toronto, Toronto, Ontario, Canada; 2Department of Chemistry and Pharmacy, University of Mainz, Mainz, Germany; 3Centro de Tecnologia Nanofotonica, Universidad Politècnica de Valencia, Spain.

We present a bottom-up approach for the construction of "Smart" active defects in colloidal photonic crystals (CPCs). These structures (light-emitting polyelectrolyte multilayer) (PEM) are defects embedded in silica CPCs through a combination of evaporation induced self-assembly and microcontact printing. We show how the enormous chemical diversity inherent to PEMs can be harnessed to create chemically active defects structures responsive to solvent vapors, light, temperature, enzymes as well as redox cycling. A sharp transition state within the photonic stopband, induced by the PEM defect, can be precisely, reproducibly and in some cases reversibly tuned by these external stimuli. These materials could find numerous applications as optically monitored chemical sensors, adjustable notch filters and CPC-based frequency tunable laser sources.

Ra22.28/Rb22.28
Abstract Withdrawn

Ra22.29/Rb22.29
Fabrication of Arrays of Hollow Metal Pillars Using Nanosphere Lithography. Jang Se Gyul1, Dae-Geun Choi2 and Seung-Man Yang1; 1Biochemical Eng., KAIST, Daejeon, South Korea; 2Intelligent Precision Machine, KIMM, Daejeon, South Korea.

Arrays of nano-pillars and nano-rings of metals have attracted great attention due to their potentially important properties including superconducting and magneto-optical properties, tuning of the localized surface plasmon resonance, enhancement of raman scattering, fast switching effect and heat emission performance. Recently, several fabrication methods by the metalization of the anodic aluminum oxide (AAO) template were reported for the fabrication of nano-ring and nano-pillar array. However, the control of the feature sizes and aspect ratios is not easy because the feature sizes are limited by the employed AAO template. Consequently, AAO templates with controllable dimensions have to be prepared to fabricate the nanoarray structures of various feature sizes. In addition, the thickness of the pillar is limited to some degree because the top pores of an AAO membrane can be blocked by the excessive metal deposition. Here, we report a novel approach for the hexagonally ordered nano-pillar array using reactive ion etching (RIE) through the nanosphere array as an etching mask. First, RIE through the colloidal mask produced polycrystalline nano-cylinder array, and subsequently various metals were sputtered over the nano-cylinder arrays. Then, the colloidal particles on the nano-cylinder arrays were removed, and finally the nano-pillar array was fabricated by removing the polycrystonic layers. The height and diameter were controlled by simply adjusting the polymer film thickness and the RIE conditions during the formation of the nano-cylinders. Moreover, the thickness of the remaining nano-pillars was controlled by the variation of the sputtered thickness of metals. UV-NIL absorption spectra showed that our nano-pillar array was suitable for the detection of biomolecules with red-shift of the absorption peaks.

Ra22.30/Rb22.30
Flexible anti-reflection coatings from layer-by-layer assembled nanoparticles. Zhizhong Wu1, Adam Nolle2, Joe Walsh1, Lei Zhai3, Robert Cohen1 and Michael Rubner1; 1Materials Science and
Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; 3Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

In biological vision systems, lenses are often flexible and fluidic, therefore the focal lengths can be tuned through a change in the refractive index of the liquid (or) lens shape. For example, crystalline fish eye lenses possess a varying index of refraction via an inhomogeneous gradient of protein/water, which, when deformed, allows for a variable field of view. Recently, much attention has been directed to the fabrication of anti-reflection coatings on PDMS flexible substrates using the layer-by-layer assembly of silica nanoparticles and poly(diallyldimethyl ammonium chloride) (PDAC). The coatings showed good anti-reflection properties on the flexible substrates. The maximum transmission of the PDMS substrates was improved to as high as 99%. SEM and TEM images showed that the porous nature of the film, a structural feature that lowers the film’s refractive index, originated from the random packing feature of silica nanoparticles on PDMS substrates. Preliminary results show that the coatings can be used on a deformable PDMS lens.

Ra22.31/Rb22.31 Joining Techniques for Template Synthesised Nano-components, Jordan S. Pech1,2,3, Jonathan J. Mallett4, András E. Vlada2, Jon R. Pratt5, Daniel Josell3 and Gordon A. Shaw2; 1Manufacturing Metrology Division, National Institute of Standards and Technology, Gaithersburg, Maryland; 2Mechanical Engineering, Binghamton University, Binghamton, New York; 3Precision Engineering Division, National Institute of Standards and Technology, Gaithersburg, Maryland; 4Metalurgy Division, National Institute of Standards and Technology, Gaithersburg, Maryland.

Template Synthesised nano-components of various Ni, Co and Pt alloys have been fabricated and characterized. These components are grown in the pores of an aluminum-oxide membrane which is then dissolved leaving free standing high aspect ratio nanowires 200 nm in diameter and up to 50 μm long. The morphology, composition, structure, and chemical properties of these wires were studied using scanning electron microscopy, atomic force microscopy, X-ray diffraction, and refractometry. Electrochemical deposition is utilized to pursue joining the nanowires to macroscopic wires as well as atomic force microscope tips. Once understood, this joining technique can then be used in the creation of functional nanodevices.

Ra22.32/Rb22.32 Synthesis and Characterization of BaZrO3 Perovskite Nanocrystal, Hongjun Zhou1, Yunbing Mao2 and Stanislaus S. Wong1,2; 1Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York; 2Materials and Chemistry Sciences Department, Brookhaven National Laboratory, Upton, New York.

Single-crystalline perovskite nanostructures of reproducible shape have been prepared in large quantities using a simple, readily scaleable solid-state reaction in the presence of salt mixtures such as NaCl, NaOH, and NaClO4/HCl. The mechanism of synthesizing pristine, single-crystalline BaZrO3 nanostructures has been systematically investigated. Different experimental processing parameters such as the type and amount of salt, temperature, and reaction time appear to affect the resulting product characteristics (including morphology) in the molten salt method. We have determined that the type of salt utilized is the most important parameter governing the reaction and growth environment. Extensive characterization of these nanostructures has been performed using scanning electron microscopy (SEM), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED), energy-dispersive X-ray spectroscopy (EDS), and X-ray diffraction (XRD).

Ra22.33/Rb22.33 Patterning of Single-Walled Carbon Nanotubes Using Wet Chemical Self-Assembling and Photolithographic Technique, Myung-Hwa Yoo1,2,3, Yong-Bae Yoon1, Hyeon-Jun Song1, Jong-Ho Park3, Hyeon-Soo Lee1,2,3, Jin-Sung Lee1,2,3, Myung-Sup Yoon4, and Jeong-Ki Lim1; 1Department of Chemistry, Sungkyunkwan University, Suwon, South Korea; 2Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, Daejeon, South Korea; 3Corporate R&D Center, LG Chem Research Park, Daejeon, South Korea.

Single-walled carbon nanotubes (SWNTs) have been chemically attached with high density onto a pre-patterned substrate. In order to form the SWNT pattern, the substrate was treated with acetic acid group protected amine, and an amine pre-pattern was formed using a photolithographic process with a novel polymeric photo acid generator (PAG). The polymeric PAG has triphenylsulfonium salt moieties on its inner backbone and moderate molecular weight. It is applied to photomasks or nonmonomeric PAGs, the polymeric PAG is more useful for simple and efficient selective surface modification due to its improved spin-coating properties. The SWNT monolayer pattern was then formed through the anti-coating reaction between the carboxylic acid groups of carboxylated SWNTs (ca-SWNTs) and the pre-patterned amino groups. High-density multilayer was fabricated via further repeated reaction between the carboxylic acid groups of the ca-SWNTs and the amino groups of the linker with the aid of a condensation agent. The formation of covalent amide bonding was confirmed by X-ray photoelectron spectroscopy (XPS) analysis. SEM and UV-vis-NIR results show that the patterned SWNT films have uniform coverage with high surface density. Unlike previously reported patterned SWNT arrays, this ca-SWNT patterned layer has high surface density and excellent surface adhesion due to its direct chemical bonding to the substrate. Also, the resolution of the SWNT pattern can be tuned to suit those patterns obtained by conventional methods. Further, the high density structure of the ca-SWNT film has good electrical conductivity and electron emission properties, and the strong adhesion of the patterned SWNT layer should improve the reliability of devices using such films. We found that the high-density multilayer SWNT patterns emit electrons under an applied electrical field. The electrical resistivities of the SWNT layer were found to be about 5 × 10−6 Ω, with a turn-on field of about 3 V/μm at an emission current density of 10 mA/cm2. This approach enables the formation of micro-patterned ca-SWNT arrays on solid substrates at mild temperatures. Also, this patterning method provides strong adhesion between the SWNTs and the substrates, resulting in high surface density structure of the transparent substrates, which is critical to their practical applications such as solar cells and batteries, flat panel displays, transistors, chemical and biological sensors, and semiconductor devices.

Ra22.34/Rb22.34 Synthesis and optical properties of manganese-doped ZnS nanoribbons by post-annealing, Yang Li, Juan Antonio Zapata, Yue Xiao, Shao, Ying-Wei Tang and Sang Min Yoon; 1Department of Physics & Materials Science, COSDAS, Hong Kong.

ZnS doped with manganese (Mn) exhibits significant light-emitting properties, and efficient phosphor application in flat panel displays. In this work, we demonstrate a simple method for Mn doping of ZnS nanostuctures by post-annealing treatment. ZnS nanoribbons synthesized by thermal evaporation are doped with manganese (Mn) by simple annealing in MnS powder. The morphology of single-crystal ZnS nanoribbons of a uniform hexagonal wurtzite 2H structure remains unchanged after Mn incorporation at an annealing temperature below 700 oC. The photoluminescent characteristics show the intrinsic ZnS emission is gradually replaced by a Mn2+ induced feature with increasing annealing temperature, which is attributed to increasing incorporation of Mn2+ ions.

Ra22.35/Rb22.35 Self-Organization of Colloidal Particles in Monodisperse Aqueous Emulsions, Shin Hyun Kim1, Gi-Ra Yi2, Jong-Min Lim1 and Seung-Man Yang1; 1Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, Daejeon, South Korea; 2Corporate R&D Center, LG Chem Research Park, Daejeon, South Korea.

Over the years, confined geometries such as emulsions, aerogels, capillaries, and patterned substrates have been introduced to self-organization of colloidal particles by several research groups. Using these confining geometries, we are able to create controlled structures of colloid crystals with specific photonic properties. Especially, emission droplets are of potential interest for confined geometries for the evaporation-induced self-organization of the colloidal particles to produce colloidal clusters or crystals. In particular, colloidal crystals in spherical symmetry (or photonic balls) possess photonic bandgaps for the normal incident light independently of the position all over the spherical surface, unlike usual colloidal crystals. In this paper, we report a fabrication method of monodisperse spherical colloidal crystals using water-in-oil emulsion droplets as confining geometries. For monodisperse photonic balls, we controlled the size of aqueous emission droplets by a drop break-off method in a coflowing stream of oily hexadecane. In this case, we obtained the photonic balls dispersed in hexadecane and subsequently redispersed in other solvents easily. After a heat treatment of the emission droplets at 70°C for several hours, photonic balls began to exhibit an iridescent color, and the reflection spectra were responding readily and precisely to any change in physical properties including the size of the photonic colloidal particles, refractive index mismatch, and angle of the incident beam. For better photonic structures, inverted photonic balls, in which air cages were packed in a dielectric medium,
were also prepared by colloidal templating. In doing this, we first obtained the composite colloidal crystals in which the silica nanoparticles were fabricated to be dispersed inside the interstices between polystyrene microspheres, and then removed the polystyrene microspheres by thermal decomposition leaving behind well-ordered air cages in silica matrix.

**Ra22.36/Rb22.36**

**Fabrication of One-dimensional Colloidal Assemblies via Electrophoresis.** Jong-Min Lim1, Jun Hyuk Moon1,2, Gi-Ra Yi1 and Seung-Man Yang1; 1Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, Daejeon, South Korea; 2Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania; 3Corporate R&D Center, LG Chem Research Park, Daejeon, South Korea.

The self-assembled structure of monodisperse colloidal particles has attracted great interest due to their wide range of applications such as photonic crystals, chemical and biological sensors and catalytic supports. Recently, several methods were suggested to fabricate the one-dimensional (1D) colloidal assemblies including growth of 1D structures in patterned substrates. However, these methods require additional procedures to make the patterned substrates and it is usually difficult to transfer the assembled structures to other substrates. In this work, we developed a simple and highly efficient electrophoresis process to fabricate one-dimensional colloidal assemblies. To do this, we first prepared a mixed solution of colloidal particles and polymeric liquid, and then, the mixture solution was introduced into a capillary needle which was under a high electric field. As the electrosynthetic fiber became thinned due to the formation of the instability region of whipping, the colloidal particles embedded inside of the electrosynthetic fibers began to arrange into pearl-necklace structures by shear-induced self-assembly. A designed collector, which was composed of two copper plates with a constant gap, was used to fabricate aligned colloidal assemblies. Finally, we determined the optimal conditions such as field strength, throughput rate, particle loading and types of polymers for the stable electrophoresis process to produce well-ordered colloidal structures. The self-assembled structures were easily transferred to other substrates required for various applications.

**Ra22.37/Rb22.37**

**Structure of carbon nano-particles by novel template method.** Toshifumi Shiraya1, Hiroyuki Aikyoi1, Masaki Yamamoto1 and Takashi Kytani2, 1Soft Materials Science Laboratory, Mitsubishi Chemical Group Science and Research Center, Yokohama, Japan; 2Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Japan.

Many researches for the synthesis of nano-carbon materials with precisely controlled nano-structures have been carried out. For examples, to control the lengths and diameters of carbon nanotubes (CNTs), the template carbonization method using an anodic oxide film have been proposed (1). In addition, controlling graphene layer orientation is also important for the application of nano-carbon materials. For example, 1-layer CNTs are categorized in which the curved graphene planes lie parallel to the tube axis. Platelet nanofibers, however, have graphene layers which lie perpendicular to the fiber axis (2). As a result, they are suitable for the different applications, such as electrophoresis. Furthermore, the dispersibility of nano-carbon materials into solvents is the important subject for applications of them. We will report the new template method for preparing novel carbon nano-particles using polymer carbon-nanoparticles, which were elongated beforehand, and heat-resistant materials as templates. By using this method, one elongated polymeric nano-particle could be converted to one hollow carbon nano-particle. Therefore, we could easily control the sizes and shapes of carbon nano-particles. Further, we can synthesize different types of carbon nano-particles which had different graphene layer orientations could be prepared by changing the template synthesis condition. In the present work, we will also show the dispersibility of the carbon nano-particles into water.


**Ra22.38/Rb22.38**

**Low-threshold lasing in a dye-doped low molecular cholesteric LC layer sandwiched by polymeric cholesteric LC films.** Myoung Hoon Song1, Natsumi Tomoe1, Yoichi Takanishi1, Ken Ishikawa1, Suzuki Hisimura1, Takehiro Togosaka1, Timothy E. Swager1 and Hideo Takazoe1; 1Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Tokyo, Japan; 2Central Technical Research Laboratory, Nitto Denko Company, Yokohama, Japan; 3Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts.

People have intensively studied organic lasers, since organic materials are easy to be fabricated for devices and to be modified to realize a variety of attractive properties by changing the substituted groups. Particularly, continuous wave lasing is desired for practical devices. However, it has not been realized yet because of the thermal effects and low threshold properties. Moreover, by introducing defects into a periodic structure, additional resonant modes appear inside the PBG. These resonant modes are localized at the defect position, thus low-threshold lasing would be expected to occur. In this work, we will introduce a new type of defect mode structure that exhibits low threshold property. The helical pitch of low molecular weight CLC mixture was controlled by changing the ratio of a chiral dopant (MLC2247 Merck Co.) and a nematic liquid crystal (ZLI2293 Merck Co.). The CLC was doped with a laser dye of 2 wt%. Polymeric CLCs (PCLCs) were mixtures of chiral achiral nematic liquid crystals (Nippon Oil Corporation). The PCLC films were fabricated by spin coating onto glass substrates coated with a polyimide aligning layer (AL1254,JSR). The dye-doped CLC is sandwiched between glass substrates coated with PCLC, and we call it g-layer cells. Low molecular weight CLC has a helical structure with left-handedness, which is opposite to that of PCLCs. Due to the difference between optical pitches and handedness of two kinds of CLCs, a defect mode lasing was observed. For comparison, we prepared three types of cells; a simple DBF type cell using only a low molecular weight CLC (single-layer cell), a glass sandwich cell of low molecular weight CLC in which one of glass substrates is coated with the PCLC (2-layer cell) and the PCLC/glass layer cell. We used the optical parameteric oscillator (Surelite OPO: Continuum) pumped by third-harmonic light of a Nd:YAG laser (Surelite II: Continuum) was used as a light source for lasing experiments. The laser emission from the CLC was detected by a spectrophotometer (HR2000: Ocean Optics). The single and 2-layer cells exhibit almost the same threshold energy (500 nJ/pulse). In contrast, it is found that threshold energy of the 3-layer cell is much lower than the other cells; i.e., 180 nJ/pulse. Moreover, in this case, lasing emission from the 3-layer cell is composed of circularly polarized lights while only circularly polarized light with the same sense as the CLC helix is observed in the single-layer cell. The intensity of a left-circularly-polarized light is stronger than that of a right one. This phenomenon is consistent with the calculation using a 4X4 matrix method, indicating that the lasing emission from the 3-layer cell is caused by the defects.

**Ra22.39/Rb22.39**

**HRTEM and EELS Studies of GdSi2 Nanocrystals Grown by Self-Assembly.** Jianming Zhang2, Martin A. Crimp3 and Jun Nogami1; 1Chemical Engineering and Materials Science, Michigan State University, East Lansing, Michigan; 2Materials Science and Engineering, University of Toronto, Toronto, Ontario, Canada.

Rare-earth metal silicide nanowires are candidates for low resistance interconnects in future nanometer scale electronic devices. Since the formation of self-assembled single-crystal nanowires is a challenge, recent efforts focused on the epitaxial growth of RE silicides on silicon surfaces. In order to expand our understanding of the heteroepitaxial growth mechanisms of gadolinium silicide (GdSi2) on (0 0 1) Si (001) and (111) B Si, transectional cross-sectional high resolution transmission electron microscopy (HRTEM) are used to investigate the crystal and interfacial structures at the atomic scale. Complementary information from electron energy loss spectroscopy (EELS) is used to provide spatially resolved information about the electronic structures of these silicide nanocrystals by analyzing the energy-loss near-edge fine structure (ELNES). Comparisons of the Gd EELS M45 edge of metallic Gd, bulk GdSi2 and Gd-silicide nanocrystals will be presented.

**Ra22.40/Rb22.40**

**Metal Hollow Nanoparticles Derived by Bio-Templating.** Jie-Woo Choi1, Sang H. Choi2, Peter T. Lillehei2, Sang-Hyun Chu1, Gichi Hong1 and Gerald D. Wachter1; 1STC/NSF/CARF, Hampton, Virginia; 2NASA Langley Research Center, Hampton, Virginia; 3National Institute of Aerospace, Hampton, Virginia; 4Chemistry and Biochemistry, Brigham Young University, Provo, Utah.

There has been great interest in the synthesis and characterization of hollow metal nanoparticles due to their surface plasmonic properties and catalytic activities, which are different from their solid counterparts. Most of the previous works utilize large hollow metal nanocrystals of several hundreds of nanometers. Very recently, a couple of research groups demonstrated the preparation of hollow nanocrystals on the scale of tens of nanometers by a replacement reaction with a solid Ag template and a nano scale Kirkpatrick effect, respectively. However, the fabrication process is complicated and requires organic solvents. In this work, ferritin is used as a biotemplate.
to produce hollow nanoparticles and as a separator between the hollow nanoparticles. The protein cage of ferritin is very stable and robust in aqueous and organic solvents. Previous studies using the ferritin cage were focused on demonstrating the fabrication of solid nanoparticles through reconstitution of the ferritin iron core with different metals rather than investigating the mechanism of the metal growth. We propose a mechanism of cobalt-oxide and iron oxide growth in apoHsF (Sigma), which has a protein shell without a core, and the fabrication of hollow nanoparticles by controlling the number of metal atoms in the ferritin. When the ferritin has 2000 Co atoms in the interior nanocavity, several cobalt oxide with mean diameters of 1.8 nm are formed in the interior. Scanning transmission electron microscopy (STEM) and transmission electron microscopy (TEM) imaging allows us to see only the metal cores inside the ferritin cage due to the relatively low density of the protein shell. The metal ions enter through the hydrophilic channels along the three fold symmetric axis of the protein and combine with the carbohydrate groups of glutamic acid residues on the ferritin interior wall, forming discrete nanocavities during the coprecipitation reaction. Once these seeds of metal oxide nanoparticles form inside the ferritin, they grow auto-catalytically along the ferritin interior wall and then merge together upon further addition of CoCl2 and H2O2. When the ferritin contains over 1000 Co atoms, the cobalt oxide forms a hollow nanoparticle. When 2000 Co atoms are contained in the ferritin, a clear circle with a hollow core is observed indicating merging between the nanoparticles. The size of hollow nanoparticle is around 120 nm, which is formed by the coprecipitation reaction inside the ferritin core. We will present the first fabrication of hollow cobalt oxide and iron oxide nanoparticles using a bio-template in aqueous solution and describe the metal oxide growth mechanism in the ferritin interior. This growth mechanism facilitates the construction of hollow metal oxide nanoparticles by controlling the number of metal atoms inserted in the ferritin interior.

Ra22.41/Rb22.41
Process structure and properties of quantum dot nanofiber composite. Hsue Yang1, Hui Li2, Wei-Heng Shih2 and Frank Ko3,4,1; 1School of Biomedical Engineering, Science & Health Systems, Drexel University, Philadelphia, Pennsylvania; 2Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania.

A new type of fluorescent fibrous composite material ranging several hundred nanometers to less than a micrometer consist of quantum dots and polymeric fibers has been fabricated through the electrospraying process. The quantum dots are single crystals that possess unique electrical and optical properties. Especially quantum dots offer several advantages over organic dyes traditionally used for cell labeling. Unlike fluorescent dye, the emission and excitation wavelength of quantum dots do not overlap and the optical properties is controllable by changing the size of quantum dots. The emission light intensity is higher than the dye. Also, it is very stable over a period of time. The electrospinning in the form of fine fibers from solution or melt polymer. When high voltage is applied to polymer solution, the charged polymer solution forms a jet and travels to grounded tip to form the solution into the solvent evaporation and fine fibers are collected on the target. The various concentrations of aqueous Cds quantum dot solutions were prepared. Resulting in quantum dots with 5nm in diameters was found to be well suspended and stable for several months on the shelf. 5wt% of Polyethylene Oxide (PEO, Mw 600,000) were dissolved in prepared Cds solution then magnetically stirred for 24 hours. The prepared Cds-PEO solutions and collected fibers were characterized by optical fluorescent and electron microscopy. The design of this new hybrid quantum dot/nanofiber technology opens the door to many applications including drug delivery, scaffold for tissue engineering and security device.

Ra22.42/Rb22.42
Self Assembled Nanostructure in Metal Thin Films on Single Crystalline Substrates. Zhiqun Tan1,2, Albert Davydov1,2,1, Alexander Shapiro2, Leonid A. Bendersky2, Julia Slutsker2 and Alexander L. Roytburd1,2,1; 1University of Maryland, College Park, Maryland; 2NIST, Gaithersburg, Maryland.

The goal of our study is to engineer a self-assembled two-phase nanostructure as a result of eutectic decomposition of metallic film on a single crystal substrate. As a model system, we studied thin films grown on hydrogen terminated Si(111) using electron beam deposition system under high vacuum. A structure consisting Ag nanoparticles of 200–300 nm and a Cu matrix was obtained during evaporation at 873K with 1:1 composition ratio. The average distance between the particles is about 200nm. X-ray shows a good epitaxial relationship between the two phases and the substrate. Effects of growth temperature on nanostructured formation have been studied. The experimental results were interpreted adequately by the thermodynamic theory and phase field modeling.

Ra22.49/Rb22.49
Synthesis of hierarchically porous materials using colloidal and amphiphilic templates.

Petr Vasiliev1, Zhijian Shen1, Robert Hodgkins1, Erik Sundstrom1, Peter Alberius2 and Lennart Bergstrom3; 1Department of Physical, Inorganic and Structural Chemistry, Stockholm University, Stockholm, Sweden; 2Institute for Surface Chemistry, Stockholm, Sweden.

The possibility to control the pore size and pore structure resulting in a material characterized by a high surface area, accessible mesoporous pores, hydrothermal- and mechanical stability is of interest in various applications, e.g. as membranes, sensors, catalyst support, slow release agents, chromatography and ground water treatment. We will show how hierarchically porous bulk materials can be produced by two different approaches. Mesoporous spherical particles, prepared by a recently developed spray-drying technique, have been fused (initial stage of sintering) together into cylindrical disc shaped materials with the use of the spark plasma sintering (SPS) technique. SPS can simultaneously subject powder bodies to a rapid temperature increase and a compressive stress. By keeping the temperature low (from 600 to 800 °C), and the holding time below 10 minutes, it was possible to form a continuous body where the particles were connected by necks formed at the surface of the particles, while the mesoporous structure was retained within the particles. The particles, porosity, necking and mechanical properties of the fused mesoporous particles are strongly dependent on the applied pressure and temperature. It will be discussed how the removal of holes from the final mesoporous material, and the size of these holes, is mainly determined by the particle size and the inter-granular (mesoporous) structure is controlled by the conditions in the particle synthesis step. Polymeric particles have also been used as templates to produce cellular silica materials that display micro- and mesoporosity. It will be shown how the pore size as well as the thickness of the ceramic walls within the final cellular structure can be varied independently by choosing different templates and reaction conditions.

Ra22.44/Rb22.44
Silated acidic polymers for nanoimprint lithography on flexible substrates. Wenchang Liao and Steve Jhing-Hu; National Cheng Kung University, Tainan, Taiwan.

A series of new silated acidic resist were prepared for nanoimprint lithography on plastic substrates. The resist sint were synthesized by copolymerization of several acrylic monomers including at least one acidic and one silated monomer. For use on flexible plastic substrates, the glass transition temperatures of these resists were adjusted to a range of 20–40 °C. They were easily removed by environmental friendly aqueous base solution during the stripping process without using reactive ion etching (RIE) process or an organic solvent which is used in conventional imprint process. They can enhance the throughput and save cost during the stripping process, and also have good etching resistibility. Replications of high-density line and space patterns with resolution of 100 nm were obtained on a flexible ITO/PEI substrate. The subsequent ITO etching patterns were also achieved.

Ra22.45/Rb22.45
Structural Studies of Inorganic Metal Oxides Encapsulated in Single-Walled Carbon Nanotubes. Pedro M. E. J. Costa1,2, Steffi Friedrichs1,2, Jeremy Sloan1 and Malcolm L. H. Green3; 1Materials Science, University of Cambridge, Cambridge, United Kingdom; 2Inorganic Chemistry Laboratory, University of Oxford, Oxford, United Kingdom.

The seminal report by Sumio Iijima describing the observation of carbon nanotubes has been key to the immense body of research carried out on these structures. Behind the scientific enthusiasm lies the potential of revolutionary nanotechnological applications that span from nanoelectronic computer circuitry to miniaturised and highly-efficient gas sensors. One particular area that has seen interesting advances recently is the encapsulation of substances in the internal tubular structure of carbon nanotubes. Working as test-bed composite materials for electron microscopy techniques development or as 1D templates for the synthesis of nanowires, filled carbon nanotubes offer a new window of opportunities for the study of the physical properties and fundamental aspects of their structure. A model symmetry of confined structures. The first successful and controlled filling of carbon nanotubes was performed using Pb3O4 and Multi Walled Carbon Nanotubes in Ar atmosphere. Other studies soon followed which dealt with oxide systems ranging from first row transition metal oxides (V2O5, NiO) to lanthanide nanoparticles (Sm2O3). Nonetheless, the filling of lower numbered walls carbon nanotubes (Single and Double) with inorganic oxides has been scarce. This may be due to several factors such as the reactivity of the metal oxides and the fact that commonly being reactive, their melting points are too high to enable melt-phase nanotube fillings.
Furthermore, the wide range of chemical and physical properties of these systems renders them more difficult to understand in contrast to other systems containing the same functional groups as the monolayer capped metal oxide nanoparticles reported for SWNTs include SnO2, CrO3. One of the main tools used in the characterisation of nanomaterials is undoubtedly the Transmission Electron Microscope, which allows structure imaging with very high resolution. This, however, is impaired by the inherent limitations of the equipment such as lens aberrations. Recently, this area of structural analysis has seen important progress with the introduction of software-based approaches to aberration correction. The TEM images obtained require that a series of images are taken at different defoci it is now possible, after performing the restoration of the exit surface wavefunction, to obtain super-resolved images of the materials within the carbon nanotubes. We would like to report the successful filling of Wallied Carbon Nanotubes with various inorganic metal oxides. Depending on the oxide used, the filling behaviour differs and structures obtained range from clusters (ReOx) to well-defined wires (PuO6, TeO2). These composites were used as a state-of-the-art phase-rectification technique which results in the synthesis of the high resolution of nanomaterials free of aberrations. Additionally, it is also shown how chemistry can be performed inside the restricted environment represented by the inner tube of SWNTs (partial washing of encapsulated material, reduction of oxides to metal).

**Ra22.46/Rb22.46**

**Mechanical Behavior of Functionalized Multi-Walled Carbon Nanotubes Thin Films**

Shun-ichi Ogasawara, 1 Kenichi Motomiya, 1 Balachandran Jayadevan, 1 Kenichiro Sasano, 2 Hisamichi Kimura, 2 Rizik Hatakeyama, 3 and Kazuyuki Tobii 1

1 Graduate School of Environmental Studies, Tohoku University, Sendai, Japan; 2 Institute for Materials Research, Tohoku University, Sendai, Japan; 3 Graduate School of Engineering, Tohoku University, Sendai, Japan.

Multi-walled carbon nanotubes (MWCNTs) are composed of strong graphene sp2 bonds that hinder their functionalization. Consequently, the preparation of MWCNTs solid bodies have been found to be difficult. However, we believe that the preparation of MWCNTs solid bodies could be realized by making the surfaces of MWCNTs active by forming defects that facilitate the functionalization as well as binding between tubes. In this paper, we report the synthesis of thin films using chemically functionalized MWCNTs, and their mechanical properties. As-grown MWCNTs were air oxidized and treated with N,N-dimethylformamide (DMF) to remove any residual functional groups on the metal particles respectively. Then, the samples thus obtained were treated with nitric acid at 373 K for 10 hours to induce defects on the surface of the tubes. As a consequence, the surface becomes functionalized with carboxyl and hydroxyl groups [1]. Then, these functionalized tubes were polymerized to prepare MWCNT thin films using the following steps. Firstly, the functionalized MWCNTs were ultrasonicated for an hour in N, N-dimethylformamide (DMF), and the solution was stored for 24 hours. Finally, MWCNT thin films with different thickness were prepared by filtering dispersion with varying MWCNT concentrations. However, the mechanical strength of these MWCNT films is significantly lower than as there is no chemical bonding between tubes. Therefore, it is believed that the formation of chemical bonds between tubes is vital to obtain robust films. Here, we attempted to reinforce the films by using the polymerizing effect. The MWCNT films were dried and used in N,N-dimethylformamide (DMF) dissolved DMF solution [2] to facilitate the formation of ester bond between MWCNTs, whose surface is modified with carboxyl and hydroxyl groups. And the above treatment was carried out at 333 K for 10 hours under nitrogen atmosphere. As a result, the mechanical strength of the MWCNT films was reinforced. In this presentation, we will discuss the results of Vickers hardness and tensile test. [1] S. Niyogi, M. A. Hanon, H. Hsu, B. Zhao, P.Bowenriek, R. Sen, M. E. Ito, S. Ogawa, Chem. Mater., 1105, 2002 [2] Sano A. Kamino, J. Okumura, and S. Shinkai, Science, 293, 1299, 2001.

**Ra22.47/Rb22.47**

**The Effect of Electric Field on the Morphology of Poly(styrene-b-ferrocenylmethyilsilane) Langmuir-Blodgett Films.**

Arielle Jonel Galambos, 1 Benjamin Eghbali, 2 G. Julius Vancso 3, Jonathan Sokolov 4 and Miriam Rafalovich 5; 1 Wellesley College, Stony Brook, New York; 2 Mat. Sci. Eng., Stony Brook University, Stony Brook, New York; 3 DRS High School, Czerniewsk, New York; 4 Faculty of Chemical Engineering, University of Twente, A. E. Enschede, Netherlands.

Poly(styrene-b-ferrocenylmethyilsilane) (PS-b-PFS, NPS:NPSF= 54:52) and Poly(styrene-b-2-vinylpyridine) (PS-P2VP, NPS/NPVP= 1k/1k) block copolymer mixtures have previously been shown to produce a high degree of order. [1] Here we explored mixtures of PS-P2VP with poly(n-propylmethacrylate) (PnPMA) (100/MPMMA (165%) copolymer or homopolymers of PS (N=10000) or PMPMA (Mw=120K). Solutions of different ratios of the PS-b-PFS co-polymer with the other components were spread at the air/water interface, lifted onto hydrophile Si wafers and imaged with a DI-3000 Scanning probe microscope. Some of the few encapsulated metal oxides reported for SWNTs include SnO2 and CrO3. One of the main tools used in the characterisation of nanomaterials is undoubtedly the Transmission Electron Microscope, which allows structure imaging with very high resolution. This, however, is impaired by the inherent limitations of the equipment such as lens aberrations. Recently, this area of structural analysis has seen important progress with the introduction of software-based approaches to aberration correction. The TEM images obtained require that a series of images are taken at different defoci it is now possible, after performing the restoration of the exit surface wavefunction, to obtain super-resolved images of the materials within the carbon nanotubes. We would like to report the successful filling of Wallied Carbon Nanotubes with various inorganic metal oxides. Depending on the oxide used, the filling behaviour differs and structures obtained range from clusters (ReOx) to well-defined wires (PuO6, TeO2). These composites were used as a state-of-the-art phase-rectification technique which results in the synthesis of the high resolution of nanomaterials free of aberrations. Additionally, it is also shown how chemistry can be performed inside the restricted environment represented by the inner tube of SWNTs (partial washing of encapsulated material, reduction of oxides to metal).

**Ra22.48/Rb22.48**

**Synthesis of a Novel Nanocomposite Material: Covalent Linking of Carbon Nanotube and Poly(lactic acid).**

Donghui Zhang 1, 2, Madhuvaithi A. Kandadai 1 and Seamus Curran 3.

1 Chemistry and Biochemistry, New Mexico State University, Las Cruces, New Mexico; 2 Physics Department, New Mexico State University, Las Cruces, New Mexico.

Carbon nanotubes (CNT) have exhibited many unique physical properties. Notably, it has unusually high tensile strength and modest to high conductivity. So CNT can be used as filler for strengthening polymer materials as well as enhancing conductivity. However, to maximize effects of CNT filler and enhance overall performance of a CNT / polymer composite, a good interfacial interaction can be required. This can be achieved through covalent linking of CNT with polymer matrix. Poly(l-lactic acid) (PLLA) is a biodegradable polymer derived from ring-opening polymerization of l-lactide or condensation of l-lactide. It has been additionally used as biomedical implant material due to its high production cost until very recently. Cargill Inc. developed a procedure for manufacturing poly(l-lactide) in large scale using corn or sugar beet as raw materials. For the first time, poly(l-lactide) production became competitive with conventional feedstock-based plastics in terms of price and overall performance and is considered as the new generation of green thermoplastic. Despite of its high tensile modulus and tensile strength, it is inherently brittle. Different approaches can be taken to improve polymer toughness, addition of filler being one of the common tactics. In this regard, we describe the preparation of covalently linked CNT and PLLA nanocomposite through ring-opening polymerization of l-lactide directly off the carbon surface. The CNT/ PLLA nanocomposite, characterized by NMR, Raman and fluorescence spectroscopy as well as SEM and AFM. The conductivity of the nanocomposite as well as its chemical properties will also be discussed.

**Ra22.49/Rb22.49**

**Transition metal nanoparticles spontaneously aligned on chemically tuned single walled carbon nanotubes with conjugated molecules.**

Yoonmi Lee and Hee Cheul Choi, Chemistry, Pohang University of Science and Technology, Pohang, South Korea.

Recent observation of spontaneous reduction of noble metal ions on the sidewalls of single-walled carbon nanotubes (SWNTs) has opened a window to understand fundamental knowledge about surface chemical properties of SWNTs as well as to apply for innovative hybrid systems such as hybrid junction nanoelectronics and metal-nanotube composites. The spontaneous formation of metal nanoparticles on SWNTs is guided by thermodynamically favorable electron transfer from SWNTs to noble metal ions. In the case of transition metal ions, however, this would not occur because of the unfavorable energy relation between SWNTs and the standard reduction potentials of transition metal ions. In order to overcome this issue, we have introduced a smart anchoring molecule, 2,2,2-trifluoro-terpyridine (Terpy) to interact with both SWNTs and transition metal ions, resulting in the spontaneous formation of transition nanoparticles on the sidewalls of SWNTs. Terpy has been non-covalently functionalized on SWNTs grown by chemical vapor deposition (CVD) method, and their successful functionalization has been characterized by UV-visible spectroscopy. Transition metal nanoparticles such as Ru, Cu, Zn and Sn are formed spontaneously on Terpy-SWNTs at room temperature in aqueous solution and are confirmed by Atomic Force Microscopy (AFM). Spontaneous electron transfer phenomena occurring after Terpy functionalization and Ru nanoparticle formation are clearly observed by measuring conductance changes and threshold voltage shifts using SWNT field effect transistor (FET) devices. X-ray photoelectron spectroscopy (XPS) also has confirmed the electron transfer during the reaction processes by observing Ru species having lower oxidation states.

**Ra22.50/Rb22.50**

**Novel Tree-shaped Macromolecular Amphiphiles: Self-assembly and Applications.**

Lu Tian and Paula T. Hammond; Department of Chemical Engineering, Massachusetts Institute of
Technology, Cambridge, Massachusetts.

In this work, we report a novel amphiphilic biocompatible linear-dendritic block copolymer rationally designed to serve as a “tree-shaped” self-assembly building block for advanced biomedical applications. Consisting of poly(ω-n-dodecyl-L-glutamate) as a hydrophilic comb-like linear block and polyester dendron modified with poly(ethylene glycol) (PEG) as a hydrophobic dendritic block, these macromolecular amphiphiles incorporate the advantages of properties of traditional spherical dendrimers and diblock copolymers. Utilizing the self-assembly properties of these self-assembling, micellar systems containing hydrophobic dendritic exteriors and hydrophobic comb-like linear chain interiors are created, resulting in colloid nanoparticles with outstanding stability and the unique exterior multivalent functionality of a dendrimer. These polymeric micelles are being studied for hydrophobic drug delivery and stabilization of gold nanoparticles in aqueous solution. Multi-angle dynamic light scattering, UV-VIS spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM) were performed to characterize these micellar aggregations. In addition, some interesting self-assembly behaviors of these macromolecular amphiphiles at high concentrations will be presented.

**Ra22.51/Rb22.51**

Organic-Inorganic Hybrid Nanocomposites Prepared by the Incorporation of Silicon Oxide into Polymers. Il-lin Kim, O-Sung Kwon, Jae-Bum Park and Ho Joo; Research Institute of Chemical & Electronic Materials, Samsung-Cheil Industries Inc., Uiwang, Gyeyonggi, South Korea.

Organic-inorganic nanocomposites have been attracting much attention due to their potential applications, such as colloidal stabilizers, electron-optical devices, and nanocomposite materials. Recently, we developed a new class of organo-inorganic nanocomposites incorporating spherical silica nanoparticles (10−20 nm diameter) into acrylonitrile-butadiene-styrene copolymers (ABS) using a strong acid-base interaction between hydroxyl groups of silica surfaces and carboxyl groups of ABS. Encapsulation of ABS particles with silica nanoparticles was taking place in situ during ABS coagulation process, resulting in the formation of colloidal nanocomposites with a core-shell morphology. Interestingly, the resulting nanocomposites with 1.0−1.8 wt. % silica nanoparticles exhibit the improvement of impact strength by 30−45%, without sacrifice of elastic modulus, hardness, and tensile strength. The interfacial interaction between the silica and the ABS phases plays a major role in controlling the microstructures and the properties of the composite materials. The morphology and properties of nanocomposites were characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), differential scanning calorimeter (DSC), tensile tests, impact strength tests, and thermogravimetry. TEM studies showed good dispersion of silica nanoparticles regardless of particle size and SEM analysis revealed that silica nanoparticles resided both in the SAN matrix and on the surface of g-ABS domain of the polymer.

**Ra22.52/Rb22.52**

Low Temperature Synthesis of FePt Nanoparticles by using Polyol Process. Akira Kodaia, Yoshihiro Sato, Kozo Shinkai, Balachandran Jayadevan and Kazuyuki Tohji; Graduate School of Environmental Studies, Tohoku University, Sendai, Japan.

Structural phase transition in Fe-Pt system from a disordered fcc to ordered fct results in a strong increase in magnetic hardness of the alloy, which make them suitable for magnetic applications. However, the transition temperature (Tc) is high to be used in any industrial applications. The phase transition being a thermally activated process and the transition mainly proceed by growth of the as-prepared nucleation sites, the Tc depends on experimental conditions. As the solution reactions are often controlled kinetically rather than thermodynamically leading to the initial trapping and growth of metastable phases, metals and alloy particles with different crystal structures can be synthesized by controlling the reaction kinetics [1-2]. Though the mechanism for the direct formation of fct-FePt nanoparticles are yet to be understood, the author believe that milder synthesis conditions could promote the formation of the ordered phase. Thus, in this paper, we explored the possibilities of the synthesis of FePt nanoparticles at temperatures less than 400 K. When synthesized in polyol, two types scenarios can be envisaged. In the first case, one type of metal is reduced easily compared to the other and this acts as a catalyst for the reduction of the second type and consequent formation of alloy is realized. This was the case in our previous report [2], where both types metal ions are coreduced to form the alloy. To attempt the synthesis of alloy under the latter case, the synthesis of Fe at low temperature is a prerequisite. We attempted the synthesis of iron by polyol and succeeded in synthesizing Fe nanoparticles by using as the metal precursor in TM EG at temperatures lower than 400 K. Thus, we attempted the synthesis of FePt through coreduction of Fe and Pt. Fe3Pt2 was synthesized. The phases formed during the reaction were a function of platinum salt type, reaction temperature, Fe/Pt ratio, concentration NaOH, and type of polyol. Synthesis of Fe3Pt2 occurred when the FeCl2•2H2O and H2PtCl6•H2O were reduced in TM EG at 393 K under Fe/Pt and hydroxide/metal ratios were 1 and 20 at 393 K. Along with other results obtained under various experimental parameters listed above, the magnetic properties of FePt synthesized at 393 K will also be reported. P. Prášek and T. Yajima; Institute of Physical Chemistry, Czech Academy of Sciences, Prague, Czech Republic.

**Ra22.53/Rb22.53**


Various nanoparticles have attracted growing interests in chemistry, biology and materials science because of enormous potential applications in chemical/biological sensing, catalysis, drug delivery, and medical imaging. One of the important applications involves the exploration of DNA-anchored nanoparticles assembly. The key to such application requires the ability to control the size, shape and interparticle spatial properties at a nanoscale level. This presentation describes our recent results in constructing size-, shape- and composition-controllable nanoparticles (e.g., Au, Ag, Pt, Au, Pt, Fe3O4, Fe3O4 etc.) as core-shell nanoparticles that function as bio-affinitive molecules. While many types of DNA-nanoparticle network structures are known to assemble and disassemble via altering temperatures, other physical, chemical and biological stimuli are exploited for manipulating the nanostructured nanocomposites are used for targeting sequence specific sites, and the reactivities of assembly and disassembly are probed using spectroscopic, TEM, and QCM techniques. Implications of our findings to the potential application of the nanocostruclure in detecting orthogonic or biohazardous organisms will also be discussed.

**Ra22.54/Rb22.54**

Assembly of Nanomaterials using Polymers and Biomaterials: Sensing and Electronic Applications. Jueboon Lee1, Alexander O. Govorov2 and Nicholas A. Kотов3, 1Chemical, Material Science Engineering, and Biomedical Engineering, University of Michigan, Ann Arbor, Michigan; 2Physics and Astronomy, Ohio University, Athens, Ohio.

This paper presents theoretical and experimental demonstration of the enhanced photoluminescence and its blueshift of CdTe nanoparticles (NP) and nanowires (NW) that are polymerically and biologically conjugated with different sizes of metallic nanoparticles such as Au and Ag in aqueous state. This results from the exciton-plasmon resonance interaction collectively like surface enhanced Raman scattering (SERS) effects. With this superstructure, several applications are addressed such as dynamic nano/microfluidic sensing devices for nanothermometer, energy transfer devices for solar cell, and biological applications.

**Ra22.55/Rb22.55**

Preparation of large area nanoparticle thin film: Characterization and mechanistic study. Bratindranath Mukherjee, Shisesta A. Shetty and Bavishkar Narayanan; Materials Research Centre, Indian Institute of Science, Bangalore, India.

Nanoparticle thin films have a wide range of applications such as nanoelectronics, magnetic storage devices, biocompatible, optical grating and anti-refective coating. Present work describes a method to prepare large area nanoparticle thin film of the order of few cm2. XRD, VSM, TEM, SEM, AFM, SERS study has been done to characterize the films produced on wide range of conducting as well as nonconductive substrates such as carbon coated copper grid, silicon, m-plane of alumina, glass, NaCl single crystal. Critical experiment has been done to understand the process of deposition of the colloidal nanoparticle thin film and a mechanism has been proposed.

**Ra22.56/Rb22.56**

Confinement of conducting polymer in the nanoparticle (mesoporous silica and organosilica). Hiroshi Nakata, Shinji Hara, Susumu Inagaki and Ryoji Arai; TOYOTA Central R&D Laboratories, Inc., Aichi, Japan.

Conducting polymers with unidirectionally aligned polymer chain, such as polymers confined in one-dimensional channels of mesoporous
materials, are expected to lead the novel applications for electroactive and optoelectronic devices. Although many approaches have been proposed for the fabrication of reliable nanometer-scale device structures, the fabrication of polymers into the pores of mesoporous materials, only insufficient amount of polymers was confined to realize the above applications. In order to increase the amount of confined polymers, we investigated the adsorption behavior of poly(2-methoxy-5-(2-ethyl-hexoxy)-1,4-phenylene vinylene) (MEH-PPV) to various mesoporous materials, such as mesoporous silica (SFM-16) and mesoporous organosilica, both of which were organically modified. The surface of the pores was modified with various terminal organic groups (e.g., SH, SO3H and C6H5) through grafting the organosilane coupling agents. Adsorption of MHE-PPV was characterized by immersion of the mesoporous silica to a chloroform solution of MHE-PPV. The mesoporous silica adsorbed MHE-PPV was characterized by XRD, N2 adsorption and TG-DTA measurements. It was found that the grafted organic groups significantly influence the adsorption amount of MHE-PPV. We also examined the optical properties of the confined UV-vis spectroscopy. The optical adsorption edge of confined MHE-PPV was clearly blue-shifted when compared to that of a free MHE-PPV. On the other hand, the grafted organic groups showed small influence on the optical adsorption edge of the confined MHE-PPV.

SESSION Ra23: Nano/Molecular Electronics
Chair: Massimiliano Cavallini
Friday Morning, December 2, 2005
Room 207 (Hynes)

8:30 AM Ra23.1

Considerable attention has been devoted to developing molecular-scale devices that function as nonlinear circuit elements and nanowires that interconnect these circuit elements. In this talk, we will discuss the fabrication and characterization of a new nanoscale crossed-wire molecular junction device comprised of lithographically-defined bottom metal contacts and self-assembled metal nanowire top contacts. This structure serves as an active testbed for studying the electrical properties of nanoscale molecular junctions because the flexibility of the fabrication process permits rapid integration of junctions with different molecules and metal contacts. The integrity of the integration process was validated by isolating individual crossed-wire molecular junctions and connecting them to large-area metal probe pads for electrical characterization. Temperature dependent current-voltage (I-T) characteristics and inelastic electron tunneling (IET) spectra were collected on a series of junctions containing alkanethiol self-assembled monolayers (SAMs) of Decane (C10), Dodecane(C12), Tetradecane (C14), Hexadecane (C16), and Octadecane (C18). In these junctions, the bottom contact was formed by self-assembling the alkanethiol molecules directly onto the thermally evaporated Au wires, while the top contact was formed by physically contacting the SAM with a single Au nanowire of diameter less than 200 nm. All of the alkanethiol junctions exhibited temperature independent I-V properties (0.1 - 300 K), which confirms that the dominant transport mechanism is coherence tunneling. The junction conductance increased with decreasing alkanethiol chain length giving rise to a bias-independent decay coefficient of β~1. This is in agreement with previously published data collected using other molecular junction testbeds including conducting probe atomic force microscopy, which has a similar configuration of top and bottom contacts. IET spectra exhibited peaks that are consistent with the vibrational modes expected for these alkanethiol junctions. Additional data that investigates the properties of junctions formed using dithiolate alkane molecules as well as conjugated molecules such as oligo(phenylene-ethylene) will also be presented.

8:45 AM Ra23.2
Combining self-assembly with new lithographic methods for the fabrication of reliable nanometer-scale device structures. Charan Scruian1, Mary Elizabeth Anderson2, Mark W. Horn1 and Paul S. Weiss3; 1Chemistry and Physics, Pennsylvania State University, State College, Pennsylvania; 2Engineering Science and Mechanics, Pennsylvania State University, State College, Pennsylvania.

We create metal electrode structures with precise proximal placement in the 10-40 nm regime by combining the superior qualities of traditional top-down and bottom-up lithography. Selective self-assembly of amercaptoalkanoic acids on patterned gold surfaces is utilized to grow films of metal-organic coordinated multilayers, whose thickness is controlled with nanometer scale resolution tailored by the number of molecular layers and their lengths. These films are employed as lift-off resists to create tailored gaps between lithographically patterned electrodes. The configuration of our process has included a variety of electrode dimensions and tailored nanogaps resulting in an initial yield of ~90% (for electrode lengths less than or equal to 5 μm). To improve the electrical fidelity of our device structures, a new negative-tone lithographic process, which is more compatible with self-assembly techniques, has been developed. Electrode dimensions have been scaled down to the sub-100 nm regime using e-beam lithography. Methods are also underway to direct the materials assembly with our technique to the heights of initial and secondary structures to be identical. We will report on the improved electrical fidelity of electrodes fabricated using these new processes. The optimization of lithographic processes compatible with self-assembly has opened a novel avenue to create nanoscale architectures for reliable device fabrication. We continue to push this technology toward mainstream industrial manufacturing and these techniques will be discussed. 1 A. Hatzis and P.S. Weiss, Science, 307, 1010 (2005), 2 M. E. Anderson et al., Vacuum Science and Technology B 20, 2739 (2002), 3 M. E. Anderson et al., Journal of Vacuum Science and Technology B 21, 3116 (2003), 4 M. E. Anderson et al., MicroElectronic Engineering, 78-79, 248 (2005)

9:00 AM Ra23.3
Electrical Measurements of Parallel, Linear Arrays of 1.5 nm Au-Nanoparticles Assembled on SiO2 Using DNA Scaffold Directed Assembly. Gregory J. Kears and James E. Hutchison; Chemistry, University of Oregon, Eugene, Oregon.

Nanoparticles are of great interest as components in new materials and devices due to their size dependent optical and electronic properties. Two significant challenges in developing nanoparticle-based devices are assembling nanoparticles in a useful way and bridging nanoscale assemblies to microscale electronics. We have developed methods to form arrays of 1.5 nm particles that can be easily integrated with the microscale in order to exploit the properties of the nanoscale components while allowing access to the device back-end. Metascale contacts to these individual arrays of core diameters of less than 2 μm exhibit Coulomb blockade at room temperature, which can be exploited to develop new electronic devices such as single electron transistors (SET). These devices offer several advantages over semiconductor-based transistors: (i) they operate at 1-2 orders of magnitude smaller than current state-of-the-art transistors, (ii) SETs are not hindered by electron tunneling that can lead to device heating and/or failure in semiconductor based transistors, and (iii) it is possible to use a greener, bottom-up assembly approach to develop complex structures. We have developed a convenient synthetic route to monodisperse 1.5 nm gold nanoparticles that can be functionalized with a wide range of ligand shells. Using these particles, we have shown that, in solution, nanoparticles can be organized into linear arrays using electrostatic interactions between the negatively charged backbone of DNA and the positively charged ligand shell of functionalized nanoparticles. These interactions result in extended linear chains of close-packed nanoparticles. Close-packings of the nanoparticles on the DNA scaffold allows precise control over interparticle spacing by the appropriate choice of ligand shell. In order to make useful devices of these arrays, we have been working to align DNA on surfaces prior to condensation with nanoparticles to obtain parallel, linear arrays of nanoparticles. Using specially fabricated TEM grids composed of a silicon grid with thermally grown, electron transparent SiO2 windows, we have shown that we can create long-range (tens of micrometers) parallel arrays of nanoparticles on thermal SiO2 in a three step assembly process involving (i) silanization of the SiO2 surface, which promotes molecular combing of DNA and limits nonspecific adsorption of positively charged nanoparticles, (ii) molecular combing of DNA on the silanized surface, and (iii) nanoparticle assembly on the linear arrays of DNA. TEM analysis of these arrays shows that the arrays are parallel over the entire substrate and that high purity nanoparticles maintain their core size and spacing as determined by the thickness of the ligand shell. With these arrays we are able to develop electronic test structures for measuring Coulomb blockade at room temperature. This is the first step toward developing arrays of single electron transistors that operate at room temperature.

9:15 AM Ra23.4
Exciton Energy Transfer in Supramolecular Systems of Semiconducting Nanoparticles and Free-Basis Porphyrins. Thomas Blau dek1, Edvard Zenkevi ch2, Alexander Shulga3, Frank Cichos3 and Christian von Borczyskowski2; 1Photonics and Optical Materials, TU Chemnitz, Chemnitz, Germany; 2Optical Spectroscopy and Molecular Physics, TU Chemnitz, Chemnitz, Germany; 3Institute of Molecular and Atomic Physics, Belarusian Academy of Sciences, Minsk, Belarus.

One of the core challenges of modern technology is the merging of its oppositional approaches toward the nanometer scale. Whereas the
top-down approaches driven mainly by the physical engineering are facing their limits, bottom-up techniques emerging from chemistry are seen as an alternative approach in both fundamental science and technology. Within the latter, molecular electronics is a field of growing interest, with distinct applications in mind characterized by custom-tailored properties and a low-cost fabrication. Referring to the bottom-up concept, the scientific interest is placed on the elementary interaction processes between inorganic and organic entities in nanoscale systems. During the past decade, we have developed concepts on self-assembly of porphyrin arrays that are tunable with respect to their chemical properties. Recently, we reported on the self-assembly of pyridyl-substituted porphyrin on semiconductor nanocrystals (NPs) [2]. Due to their atomic-like electron structure and tunable emission properties the latter are important building blocks in nanophotonic systems. In this presentation, we report on an efficient exciton energy transfer process directed from the NP to the porphyrin molecules in the assemblies. We present data from both steady-state spectroscopy and time-resolved photoneticsence dispersed in solution. The various experimental approaches are discussed with respect to the transfer efficiency. We elucidate the roles of complexation and ensemble heterogeneity of the NPs and how these influence the photophysical properties, i.e. fluorescence quantum yield and decay rates. The results are extended by estimations on the general validity of the approach in assemblies designed from NPs and other molecules, with the latter either suitable for array formation such as pyrrolenine and dyes or known in biophysical applications such as surfactants with thiol and amino end-groups. References 1 E. Zenkevich, C. von Borczyskowski: #Multiporphyrin Self-Assembled Arrays in Solutions and Films: Thermodynamics, Spectroscopy, and Photophysics, # Tripathy, K. H. Nalwa Eds.; #Handbook of Polyololaxes and Their Applications, Vol. 2, Chapter 11, Stephenson Ranch: Am. Scientific Publishers (2002). 2 E Zenkevich, F. Cichos, A. Shulga, E. Petrov, T. Blaudeck, and C. von Borczyskowski: Nanocrystals Designed from Semiconducting Quantum Dots and Molecular Arrays, J. Phys. Chem. B 109, 8679 (2005).


Metal nanocrystals can behave as artificial atoms due to their diameter-dependent single electron charging energies. Organically passivated nanocrystals with narrow size distributions can self-assemble into ordered arrays, offering the possibility of artificial atomic solids with unique collective electronic properties, derived from both the size-dependent electronic properties of the individual nanocrystal cores and the inter-nanocrystal electronic coupling mechanisms. The electronic properties of artificial atomic solids based on arrays of metal nanocrystals depend on the relative magnitudes of the classical electrostatic array charging energy, the inter-site quantum mechanical site-site energy dispersion, which arises from the non-zero size and geometric disorder in nanocrystal arrays. Control of these energy terms is a prerequisite for manipulating the properties of artificial atomic solids. We present our progress on probing the electronic properties of artificial atomic solids via variable temperature charge transport measurements on arrays of ligand stabilized CoPt3 metal nanocrystals self-assembled between lateral contact electrodes, together with development of combined synthesis and processing routes to manipulate these properties. The electronic properties of these arrays, measured following mild thermal annealing, are found to be characteristic of weakly-coupled artificial atomic solids. In fact, we show that control of the array charging energy can be achieved by varying the nanocrystal core diameter under conditions of controlled inter-nanocrystal separation. Also, mild thermal annealing is used to tune the electronic properties of nanocrystal arrays progressively from insulating through to metallic regimes. This is consistent with a Mott-Hubbard model for artificial atom solids. Finally, we demonstrate a new route for growth of 1D nanocrystal structures based on the use of an external magnetic field to direct the destabilization and anisotropic aggregation of CoPt3 nanocrystal dispersions. The wires comprise ordered dispersions of discrete nanocrystals, separated from each other by protective organic ligand shells. Magnetic fields can also be employed for directed assembly of the wires across electrodes. Electrical data indicates that the activated charge transport properties of the wires are determined by the nanocrystal charging energy, governed by the size and capacitance of the individual nanocrystals. Together, these results highlight just some of the possibilities for development of hybrid top-down and bottom-up assembly methodologies for fabrication of future nanoelectronic devices.

9:45 AM RA23.6 Low-Temperature Synthesis and Thermoelectric Properties of Molecularly Capped Bismuth Telluride Nanoparticles from Microemulsions. Arup Purkayastha,1 Department of Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York; 2Department of Mechanical Aerospace and Nuclear Engineering, Rensselaer Polytechnic Institute, Troy, New York.

We report a new room temperature synthesis method to create bismuth-telluride nanoparticles from microemulsions. By virtue of the unique thermoelectric properties of bismuth telluride, this material has been exploited for cooling and power generation applications1. Nanostructuring allows for further dramatic improvements in thermoelectric efficiency due to phonon and electron confinement effects2. Previous works have reported the synthesis of bismuth telluride nanoparticles by co-precipitation3 solvothermal synthesis4 or using microemulsions. The microemulsion method is very promising in terms of producing very small nanoparticles with control over size and size distribution. In our synthesis, hydrazine monohydrate was added to the microemulsion formed from an aqueous solution of bismuth tribromide, thiourea, tributylamine, isoctanoic acid, and an ionic surfactant AOT at room temperature. Upon nanoparticle formation, the surfactant was removed by washing and centrifuging repeatedly with toluene to get the final black solid. The bismuth telluride nanoparticles are found in the regime of 1-5 nm. The particle size and shape (spherical to rod shaped) could be controlled by tailoring the water to surfactant ratio. Thermoelectric transport measurements in bismuth telluride nanoparticles films and powders show significantly enhanced thermoelectric properties compared to bulk. References 1. Goldsmid, H. J.; Douglas, R. W. Br. J. Appl. Phys. 1954, 5, 458. 2. Shen, G.; Dresselhaus, M. S.; Dresselhaus, G.; Fleury, J. P.; and Caillat, T.: International Materials Reviews, (2003), 48, 45. 3. Ritter, J. L., Inorg. Chem. 1994, 33, 6419. 4. Deng, Y.; Zhou, X.-S.; Wei, G.-D.; Liu, J.; Nan, C.-W.; Zhao, S.-J. J. Phys. Chem. Solids 2002, 63, 2119.

SESSION Rb23: Nanoparticles III
Chair: Joydeep Dutta
Friday Morning, December 2, 2005
Room 208 (Hynes)

8:30 AM Rb23.1 1-D Assemblies of Gold Nanoparticles with Tunable Interparticle Distances. Michel K. Corbiere1,2, Jean Boisseau1, Jacques Beauvais3 and Bruce R. Lennox1,2. 1Chemistry, McGill University, Montreal, Quebec, Canada; 2Electrical and Computer Engineering, Sherbrooke University, Sherbrooke, Quebec, Canada.

We report the preparation and controlled assembly of gold nanoparticles in 1-dimension. Ours is a straightforward approach, where an electron beam is used to write patterns from thin films of gold(1) compounds on various substrates. The negative patterns are then developed in suitable organic solvents, leaving for the substrate only the e-beam-exposed parts. After development, lines of organogold compound with linewidths as small as 15 nm are obtained. Subsequent pyrolysis of the organogold compound removes the organic material from the pattern and leads to the growth of nanogold wires (diameters of 2 to 20 nm depending on the conditions, verified by TEM and SEM). Lines of single particles (1-D) are obtained (Figure 1). Variations in the e-beam exposure conditions allow us to precisely tailor the interparticle distances within the 1-D lines, while variations in the initial organogold film thickness or organogold compound nature allow for controlling the gold nanoparticle diameters. By varying the electron beam dose, we are also able to control nanoparticle densities in 2-D arrays. This method is extremely versatile and can be used to prepare 1-D and 2-D assemblies with desired shapes on large scales and on a wide variety of surfaces.

9:00 AM Rb23.2 Self-Assembly of Polymer-Tethered Nanorods. Mark A. Hersch1, Zhengyi Zhang2 and Sharon C. Glotzer1,2. 1Department of Chemical Engineering, University of Michigan, Ann Arbor, Michigan; 2Department of Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan.

Nanoparticles functionalized by polymer brushes constitute a class of shape amphiphiles that share important attributes with block copolymer surfactants and liquid crystals[1]. Through these attributes, the tethers may be used to assemble nanoparticles into useful and unusual structures. Here we present new results of molecular simulations that predict the phases formed by the self-assembly of rod-like particles functionalized by a polymer tether. For end-tethered rods[2], we predict that microphase separation of the immiscible tethers and rods coupled with the liquid crystal ordering of the rods induces the formation of a smectic C phase, with perforated lamellar phase and a honeycomb phase; the latter two have been observed experimentally for rod-coil block copolymer systems but have not been predicted previously via theory or simulation. We also
predict a new phase - a racemic mixture of hexagonally-ordered chiral cylinders that self-assemble from these achiral building blocks. We compare the phase formed from end-tethered nanorods with those formed from side-tethered nanorods, and present new results that show how the tethered building block topology affects their local and mesoscopic packing. In particular, we predict several new phases for side-tethered nanorods that have not been observed in block copolymer, surfactant or liquid crystal systems and which have potential use as functional nanocable materials. [1] Z.L. Zhang, M.A. Horsch, M.H. Lamm and S.C. Glotzer, Nano Letters, 3, 1341 (2003). [2] M.A. Horsch, Z.L. Zhang and S.C. Glotzer, Physical Review Letters, in press.

9:15 AM Rh29.3
Kinetics of Place-Exchange Reactions of Alkyl Thiol on Gold NPs. Adil Kassam, Gern Brenner and R. Bruce Lennox; Chemistry, McGill, Montreal, Quebec, Canada.

After the initial report of a relatively facile method to synthesize gold nanoparticles (Au-NPs) by Brust et al.[1], the research into these systems has exploded. In order for these Au-NPs to be used in biological and materials applications, their surface ligand composition must be known and readily manipulated. The place-exchange reaction of the surface-bound thiol is one reaction that enables the functionalization of particles for these applications.[2] By developing a methodology to study place exchange reactions of alkyl thiols of different chain length using gas chromatography, we have been able to study the entire course of the place exchange reaction with great accuracy and precision. The kinetics of the place exchange reactions have been fitted to both a Langmuir kinetics and an equilibrium model. In addition, the observed reactions proceed to a thermodynamic equilibrium governed by the ratio of the incoming thiol concentration to the amount of thiol on the starting Au-NPs. These results should enable researchers to tailor the Au-NPs with known composition. Other aspects of the reaction including temperature and chain length dependence of the reaction will be discussed. (1) Brust et al. J. Chem. Soc. Chem. Commun. 1994 801-802. (2) Hostetler, M., Templeton, A., Murray, R.W.; Langmuir 1999, 15, 5782-5789

9:30 AM Rh29.4

The ability to control the size and monodispersity of metal nanoparticle building blocks for use in sensing materials is a challenge of increasing interest. While previous work has shown the viability of obtaining select particle sizes by manipulating the feed ratios of metal precursors, very little work has focused on the controlled modification of core size and shape using pre-synthesized nanoparticles. The main obstacle precluding this work has been an incomplete understanding of the synthetic parameters affecting the particle growth environment. Here we describe an improved isothermal and isopotential synthetic route for the controlled evolution of core size and shape from pre-fabricated nanoparticles. This improved synthesis eliminates many subjective process parameters and allows us to control the size and monolayer protected gold nanoparticles reproducibly with monodisperse core diameters between 3 and 10 nm. These nanoparticles have then been used as size-selectable building blocks for the construction of thin film assemblies in our nanoparticle sensor-array devices, and have allowed us to further investigate and refine sensor-array performance.

9:45 AM Rh29.5
Self Assembly and Nano-Ordering of Zirconia during Sol-Gel Synthesis. Gerald Spjöksma1,2, Margareta Sundberg2, Henny J. M. Bouwmeester1, Vadim G. Kessler1 and Dave H. A. Blank1; 1Inorganic material science, University of Twente, Enschede, Netherlands, 2Department of Nanoscience, Lund University, Sweden. Synthesis of ZrO2 (Zirconia) in chemistry, Arhenius Laboratory, Stockholm University, Stockholm, Sweden.

Zirconia is an important material widely used in ceramics, gas sensors, catalysts and opto-electrics. In the recent years the general focus of materials research has been on the preparation of nano-structured thin films, powders and nanotubes. With the trend of further of miniaturization there has been an increasing interest in zirconia. This high-k material is an attractive candidate for very large scale integrated circuits and as gate dielectric in metal oxide-semiconductor (MOS) devices. Moreover the latter application requires low dimension ordered materials, e.g., wires or rods. The latter can either be produced through preparation of metal wires with subsequent oxidation or via sol-gel process where a template is filled with the desired oxide, which is then crystallized upon heating. This last method has allowed the production of wires with a diameter around 80 nm. Further scaling down in dimension is restricted by the required template. Here we report the direct formation of highly ordered zirconia nanotubes by using an anisotropic molecular precursor. The obtained material contained wire shaped material with a length up to ~400 nm and a diameter of ~8 nm, the latter dimension is an order of magnitude smaller than the state of the art zirconia nanowires. The mechanism presented in this work opened the door to formation of wires and other nano-scale ordered materials. Besides the formation of nanorods we will show the preparation and characterization of hollow spheres with a diameter around 250 nm and a shell thickness of 5 nm. The formation mechanism of these type structures allows in-situ encapsulation of medicine what makes this method an attractive new tool for drug delivery applications.

11:00 AM Rh24.2
Photochemical Metal Organic Deposition of Patterned Nanostructured Oxide Films. Xin Zhang and Ross H. Hill; Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada.

Photochemical metal organic deposition is a method for depositing patterned metal or metal oxide layers that has potential for making microelectronics, optical devices and sensors. This photosensitive patterning method, operating under ambient conditions, uses photosensitive metal complexes as precursors to deposit patterned layers on substrates. In this paper, recent advances in the deposition of patterned nanostructured metal oxide films by photochemical metal
organic deposition will be presented. Different strategies are used to control the nanostructure within the films. The first strategy is to choose metal complexes where the decomposition of two metal complexes can be individually controlled. For example, by allowing decomposition of one metal complex to proceed in the absence of radiation, nanostructuring of the material occurs when the resulted metal complex and the second metal complex tend to form separate phases. Then the second metal complex is photochemically decomposed, resulting in the formation of the nanostructured material. The photochemical step provides the opportunity for lithography. This strategy has already been demonstrated by preparing nanostructured tantalum-manganese oxide films from tantalum (V) tetrathexa- acetylacetonate and manganese (II) 2-ethylhexanoate. In this case, decomposition of the tantalum complex is induced by hydrolysis during a ripening process at room temperature. The manganese(II) acetate-titanate-manganese oxide film is solidified by a photochemical decomposition of the manganese complex. By changing the precursor composition or altering the ripening time, tantalum-manganese oxide films with different microstructures have been obtained. By employing long gas pulse lengths (30 s) it was possible to get homogeneous Ni2O3 films conformally covering the pore-walls of the alumina template. The outer diameter of the nano-tubes was tailored between 30 and 70 nm by using alumina templates with different pore sizes. The wall thickness, and hence the inner diameter of the tubes, could be controlled between a few Angstroms to several nanometers by variation of the number of deposition cycles. Large template membranes with pores not opened in the bottom, nanotubes with one side closed (as a test tube) could be fabricated. Free-standing and still parallel, nanotubes could be obtained by selectively etching away the alumina template using phosphoric acid (5 wt.%). From the above mentioned procedure it was possible to fabricate unsurpassed parallel nickel oxide nano-tubes of equal length and equal wall-thickness ordered in a perfect hexagonal pattern. The samples were analysed using X-ray diffraction, high resolution scanning electron microscopy, transmission electron microscopy and energy dispersive X-ray spectroscopy.

SESSION Rh24: Carbon Nanotubes IV
Chair: Zhong Liu
Friday Morning, December 2, 2005
Room 208 (Hynes)

10:30 AM *Rh24.1

In this paper, we report clear evidence for the growth of carbon nanotubes and nanostructures at low substrate temperatures, using direct-current plasma-enhanced chemical vapour deposition. The catalyst particles are mounted on a titanium layer which acts as a thermal barrier, and allows for a larger temperature gradient between the catalytic surface and the substrate. A simple thermodynamic simulation shows that the amount by which the substrate temperature can be lowered is determined by the thickness of the titanium layer. This facilitates the growth of nanotubes, as opposed to nanofilms with the carbon depositing as an amorphous or graphitic structure. In-situ properties are discussed as a function of the bias voltage and hydrocarbon concentration. The heating during growth provided solely by the plasma is below 400°C and is dependent on the process conditions and the dimensions of the electrodes. These conditions need to be taken into account when comparing processes across different growth methods and instruments. The novel approach based on the use of a thermal barriers ensures the synthesis of carbon nanotubes at lower substrate temperatures, which can be attained with a suitable cooling scheme.

11:00 AM *Rh24.2
Fabrication of Carbon Nanotube Devices with Known Chirality. Xue Ming Henry Huang1, Robert Caldwell2, Mingyuan Huang1, Matthew Sfeir2, Feng Wang2, Limin Huang2, Stephen O’Brien2, Tony Heinz2, Louis Brus2 and James Hong1. 1Department of Mechanical Engineering, Nanoscience and Engineering Center, Columbia University, New York, New York; 2Department of Applied Physics, Nanoscience Science and Engineering Center, Columbia University, New York, New York; 3Department of Chemistry, Nanoscience and Engineering Center, Columbia University, New York, New York; 4Department of Physics, Nanoscience Science and Engineering Center, Columbia University, New York, New York.

Carbon nanotubes hold great promise for a number of applications due to their outstanding electrical, thermal, and mechanical properties. However, nanomanufacturing issues constitute a major area of challenge for successful implementation of nanotubes. In
particular, because subtle changes in physical structure (chirality) can
cause the electronic structure to vary from metallic to
semiconducting, the goal of fully controlled nanotube device
fabrication has proven elusive. Using a mechanical transfer technique
in parallel with efforts to combine optical scattering and structural
characterization, we have achieved the goal of placing ‘the nanotube
we want, where we want it’. Long nanotubes are grown by CVD
across a slit etched through a Si wafer, and then examined by optical
specroscopy techniques, in particular Rayleigh scattering. Rayleigh
scattering can readily distinguish different nanotube species, and by
combining this technique with structural characterization by electron
diffraction, we are able to map each spectrum to a unique (n,m)
structure. After structural characterization, a chosen nanotube can be
transferred to a substrate in the desired location, and devices
fabricated using standard e-beam lithography techniques.

11:30 AM Rb24.3
Carbon Nanotube Growth by CH₄, Plasma-Enhanced
Chemical Vapor Deposition and Estimation of Carbon
Amount. Yoshiyuki Suda¹, Atsushi Okita¹, Akinori Oda², Junji
Nakamura¹, Atsushi Ozeki¹, Hirotake Sugawara¹ and Yusuke Sakai¹;
¹Graduate School of Information Science and Technology, Hokkaido
University, Sapporo, Japan; ²Graduate School of Engineering, Nagoya
Institute of Technology, Nagoya, Japan; ³Graduate School of Pure
and Applied Sciences, Tsukuba University, Tsukuba, Japan.

Carbon nanotubes (CNTs) are attracting great interest in their
excellent physical and electronic properties for LSI. Plasma-enhanced
chemical vapor deposition (PECVD) is an advantageous technique
because this can yield CNTs by low temperature operation, which is
essential for its application. However, it is still unclear how plasmas
contribute to the CNT growth [1,2]. We investigate the effect of plasmas
by experiment and plasma simulation for understanding of the
CNT growth [3]. We performed a CNT growth experiment by CH₄
rf PECVD at pressures 1-10 Torr. We used three-layered catalyst film
(Al₂O₃/Fe/Al₂O₃, 3 nm/3 nm/3 nm) for catalyst on SiO₂/Si
substrate. The CNTs length, diameter, and number density were
characterized by scanning electron microscopy. We investigated the
contributions of radicals and ions to CNT by one-dimensional fluid
modeling. This model assumed the sticking probability of radicals on
substrate: CH₃, 0.025; CH₂, 0.025; CH₃, 0.01; C₂H₅, 0.01; H, 0.01,
respectively [4]. The effect of CH₄ plasma on the CNT growth is
discussed from the viewpoint of estimation of carbon amount. As the
experimental results, the CNTs at 1 Torr continued to grow up to 60
min, while their height leveled off by 20 min at 4 Torr. CNTs hardly
grew at 10 Torr and amorphous carbon was deposited instead.
Simulation result shows that carbon was supplied to the substrate via
the flux of radicals and ions such as CH₃, C₂H₅, and C₂H₅⁺. We
estimated the number of C atoms per unit substrate area and
compared it to the number of C atoms in the grown CNTs. The
deposited carbon amount from the experimental result is less than the
carbon supply estimated from the simulation results. This would be
related to the loss by the production of amorphous carbon and its
coverage on the catalyst particles.

1:45 AM Rb24.4
Strain-induced quantum interference effects on the resonant
Raman cross section of carbon nanotubes.
Antonio Goes Sousa¹, N. Kobayashi⁵, Jie Jiang², Alexander
Gruene¹, Riechiro Saito², Setephen Cronin³, Josue Mendes³, Georgii
G. Samsonidze⁵, Gene Dresselhaus¹ and Mildred S. Dresselhaus¹,⁵;
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²Physics, Tohoku University, Young-In, South Korea; ³Physics,
Harvard, Cambridge, Massachusetts; ⁴Physics, MIT, Cambridge,
Massachusetts; ⁵Electrical Engineering and Computer Science, MIT,
Cambridge, Massachusetts.

In this paper we report the effects of strain on the electronic
properties of single wall carbon nanotubes and its consequence on the
resonant Raman cross section. A quantum interference effect has been
predicted for the radial breathing mode spectra for metallic tubes. For
metallic tubes, the lower and upper components of E₃₃ resulting from
the trigonal warping effect are affected differently and for low chiral
angle they cross for some strain value. Near (at) the crossing point,
the resonant Raman spectra profile exhibits a maximum (minimum)
value due to a quantum interference in the Raman cross section. This
Raman cross section interference effect was observed in Raman
experiments carried out on isolated SWNTs. The Raman experiment
performed on an isolated strained metallic SWNT supports our
modelling predictions.

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