Tuesday Afternoon, October 21, 2008

Nanometer-scale Science and Technology
Room: 311 - Session NS+NC-TuA

Nanowires and Nanosize Effects
Moderator: H. Schift, Paul Scherrer Institut, Switzerland

1:40pm NS+NC-TuA1 Optical Second Harmonic Generation from the Pt/Cu Bimetallic Nanowire Array on the NaCl(1 1 0) Faceted Template, *T. Nguyen*, *G. Mizutani*, Japan Advanced Institute of Science and Technology (JAIST)
We have fabricated bimetallic nanowire arrays as a new type of nano-material. We expect that the anisotropy at the interface in each bimetallic nanowire would raise the second harmonic generation (SHG) performance. In order to form bimetallic nanowire arrays we deposited Cu and Pt nanowires successively on the faceted NaCl(1 1 0) template by a shadow deposition method.[1] The sample preparation was carried out in an ultra-high vacuum chamber of the pressure of 1.3 x 10^{-7} Pa. TEM images of these samples showed the average width of nanowires of 20nm and the average spacing of about 40nm. We have also fabricated a sample with a SiO layer of 5nm thickness sandwiched between the Cu and Pt nanowires, in order to remove the effect of the interface between the two metallic nanowires. We have measured the azimuthal angle dependence of the optical second-harmonic (SH) intensity from these samples at the fundamental photon energy of 2.33 eV. The SH intensity from the sample with the sandwiched SiO layer is significantly lower than that from the bimetallic nanowire sample. The patterns of the SH intensity from both samples showed two-fold symmetry. Especially for the s-in/p-out polarization combination the SH intensity pattern from the Pt/Cu bimetallic sample was quite different from that of the Pt/SiO/Cu sample.

[1] A. Sugawara, G. G. Hembree, and M. R. Scheinfein, J. Appl. Phys. 82, 5662 (1997).

2:00pm NS+NC-TuA2 Microcavity Modulation of Photoluminescence from GaN Nanowires, *J.P. Long*, *A.J. Makinen, B.S. Simpkins, M.A. Mastro, P.E. Pehrsson*, Naval Research Laboratory
Photoluminescence (PL) from single semiconducting nanowires (NWs) can exhibit considerable variability along a NW length and among NWs from the same growth batch. While the cause of the variability remains a subject of research and may be related to structural or chemical heterogeneities, here we report a purely optical source of variability caused by microcavity effects within the NW. Such effects must be considered whenever the transverse dimension of a transparent nanostructure exceeds ~λ/2n, where λ is the free-space wavelength and n is the index of refraction. In our experiments, spatially and spectrally resolved micro-PL excited with 325-nm radiation was recorded at room temperature in a ~20-micron long GaN NW with a triangular cross section. An important feature of the NW was a gradual taper in width, from about 1 micron to less than tens of nanometers, that permitted recording the optical response as the NW width varied. The NW emitted band-gap radiation near 375 nm and a broad defect band beginning at ~475 nm and extending to longer wavelengths. The spectrally resolved PL exhibits periodic intensity modulations along the NW length. The periodicity is consistent with enhanced emission occurring when the PL wavelength satisfies the requirement for a transverse standing wave within the NW. We attribute the PL modulation to either or both of two mechanisms, namely a microcavity modulation of emission probability (the "Purcell effect") or a Fabry-Perot etalon effect that modulates the external radiation of internally generated PL.

2:20pm NS+NC-TuA3 Doping PbSe Nanocrystals and Nanowires, *S.C. Erwin*, Naval Research Laboratory
We recently proposed that impurity doping in colloidally grown semiconductor nanocrystals is controlled primarily by kinetics, rather than by thermodynamics.[1,2] In this "trapped dopant" model, the diffusion of an impurity through a nanocrystal is negligible at colloidal growth temperatures. Therefore, an impurity can only be incorporated into a growing nanocrystal if it first adsorbs on the surface and is then overgrown. But this simple surface adsorption process is complicated by a competing process: the binding of the impurity by surfactant molecules, which are used in the growth solution to passivate the nanocrystal and control its growth. Here we use density-functional theory to study the interplay and outcome of these two processes for the doping of PbSe nanocrystals and nanowires by a number of candidate impurities (Mn, Cl, In, Cd, Tl, etc) in the presence of several widely used growth surfactants (oleic acid, trioctylphosphine, hexadecylamine). The results suggest that succeful doping requires making a trade-off between surface adsorption (which favors small impurities) and interior trapping (which favors large impurities). Moreover, the widely used surfactant oleic acid binds strongly to almost all impurities, suggesting that standard growth procedures may require modification for successful doping to be realized.

[1] S.C. Erwin, L. Zu, M.I. Haftel, Al.L. Efros, T.A. Kennedy, and D.J. Norris. Nature 436, 91 (2005).
[2] D.J. Norris, Al.L. Efros, and S.C. Erwin. Science 319, 1776 (2008).

2:40pm NS+NC-TuA4 Silicon Nanowire Resonators as Mass Sensors for a Specific Detection of Proteins, *S. Evoy*, *M. Belov, V.A. Wright, J.M. Buriak*, University of Alberta, Canada, *N. Quitoriano, T. Kamins*, Hewlett-Packard Laboratories
Silicon nanowire resonators have been proposed as highly-sensitive transducers for the detection of molecular systems. High-quality nanometer scale resonators grown by the chemical vapor deposition (CVD) offer a potent approach for the production of cantilevered nanowires. Nanowire resonators were laterally grown from the sides of silicon posts using a CVD metal-catalyzed process. The diameters and lengths of the structures ranged from 40 to 400 nanometers and from 2 to 20 micrometers, respectively. An optical interferometric method was used to determine the resonant frequencies and quality factors of these resonators. Resonant properties of these devices at various temperatures and pressures are discussed. Nanowire resonators (with diameters 100 nanometers and lengths 3.3 micrometers) were functionalized using a monolayer of mercaptopropyltrimethoxysilane as a linker, followed by a functionalization with biotin. The attached biotin molecules enabled the specific attachment and detection of streptavidin molecules. Shifts of resonant frequencies by hundreds of kHz were observed, corresponding to an added streptavidin mass ranging from 1 to 3 femtograms. This work was supported by Alberta Innovation and Science and by Hewlett-Packard Laboratories.

3:00pm NS+NC-TuA5 Solution Processed ZnO Nanowire and Heterostructure Arrays, *K. Yong, Y. Tak*, POSTECH, Korea
We researched an ammonia aqueous solution method for growing well-aligned ZnO nanowire arrays. Uniform ZnO nanowire arrays were grown on the seed layer coated silicon substrates in aqueous solution containing zinc nitrate and ammonia water by hydrothermal process. Synthesized ZnO nanowires were characterized using SEM, TEM, XPS, XRD and PL spectroscopy. Various parameters of ZnO nanowire growth, such as morphology of seed layer, pH, growth temperature, and concentration of zinc salt in aqueous solution were investigated. We also demonstrated the discrete controlled growth of ZnO nanowire length depending on sequential, tailored growth steps. Combining our solution method and general photolithography, we selectively grew ZnO nanowire arrays on patterned silicon substrate. Our concepts on controlled ZnO nanowire growth using a simple solution method would be applicable for various nano-device fabrications. Another part of this presentation is the fabrication of the ZnO nanowire heterostructure arrays. We prepared two kinds of the ZnO nanowire heterostructure, Co3O4/ZnO nanowire array and CdS/ZnO nanowire arrays using solution based deposition technique. Fabricated ZnO nanowire heterostructure arrays were characterized using SEM, TEM, XRD. Photocatalytic and photoelectrochemical property of the ZnO nanowire heterostructure arrays were tested.

4:00pm NS+NC-TuA8 Asymmetric Functionalization of Gold and Silver Nanoparticles for Controlled Assembly, *J.-W. Park*, *R. Sardar, J.S. Shumaker-Parry*, University of Utah
We have developed a simple, inexpensive, versatile asymmetric surface functionalization approach for controlled assembly of gold and silver nanoparticles. The process is based on spatially localizing ligands on the nanoparticle surface and uses commercially available organic reagents. The localization of the ligands allows for controlled assembly and we are able to control interpaticle spacing using different types of linkers. We have used this approach to prepare dimers using an amide coupling reaction between localized ligands on two asymmetrically functionalized nanoparticles. In addition, we demonstrate the synthesis of dimers consisting of particles with different sizes. Without optimization, the dimer yield varies from ~30% to ~65% depending on the nanoparticle sizes. The dimers demonstrate remarkable stability in ethanol without further processing. We also can combine the asymmetrically functionalized nanoparticles with other materials such as polymers for additional organization. For example, we have covalently linked asymmetrically functionalized gold nanoparticles to polymer pendent groups to form one-dimensional nanoparticle chains. The lengths of the nanoparticle chains vary from 256 to 400 nm with regular interparticle spacing (2.7-5.4 nm) within the chains. The chains display distinct optical properties compared to individual nanoparticles. The dimers and chain assemblies are being investigated as tunable optical platforms for surface-enhanced Raman spectroscopy.

4:20pm NS+NC-TuA9 Temperature Effects on the Formation of Thioether Self-Assembled Monolayers on Au(111), *D.O. Bellisario, E.V. Iski, A.E. Baber, H.L. Tierney, E.C.H. Sykes*, Tufts University

Self-assembled monolayers (SAMs) offer many potential advantages to science and industry in the form of parallel nanostructure fabrication, lubricants for MEMS, corrosion protection and sensing. As such, being able to synthesize stable SAMs from different starting materials in a larger number of configurations will enable greater control over the systems for each of these applications. Due to the stability of metal-sulfur bonds, thiol (H-S-R) SAM formation has been studied extensively. In the case of thioethers (R-S-R), it has been recently shown that at temperatures up to 298 K in both ambient[1] and ultra-high vacuum[2] conditions, that the molecules still self-assemble on metal surfaces and exhibit long-range ordering, despite a weaker binding to the surface than thiols. Due to the presence of the additional hydrocarbon tail, thioethers form SAMs with a dramatically different geometry[2]; additionally, the weaker bonding reduces the stability of these systems relative to that of thiol SAMs. In this study it was found that in the Au(111)-$(C_{18}H_{37})_2S$ system, stability may be increased by elevation of the sample temperature to moderate values (400 K) during the monolayer formation. Furthermore, the gold surface reconstruction associated with increased adsorbate-substrate bond strength changes the ordering of thioether SAMs. This strong temperature dependence on the stablility of the thioether SAM's structure suggests that temperature may be an easily controllable parameter in the design and tuning of self-assembled monolayers for specific applications.

[1] Jaegeun Noh, Tomohide Murase, Ken Nakajima, Haiwon Lee, and Masahiko Hara, Journal of Physical Chemistry B, 2000, 104, 7411 -7416;
[2] Stephen C. Jensen, A. E. Baber, H. L. Tierney and E. Charles H. Sykes ACS Nano, 2007, 1, 1, 22-29.

4:40pm NS+NC-TuA10 Isolated Nanoscale Prochiral Reaction Assemblies on Pt(111), *V. Demers-Carpentier, P.H. McBreen*, Laval University, Canada

Chiral surfaces can be used to achieve catalytic chirality transfer. The mechanism through which this occurs is one of very precise nanoscale assembly. In particular, it involves a constraint in which the substrate, prochiral, molecule is forced into contact with the catalyst surface uniquely via a specific enantioface. One method to achieve this is to chemisorb a chiral-modifier so as to form molecular chiral sites. Co-adsorption of the substrate then leads to 1:1 prochiral modifier-substrate complexes. We report a combined STM, HREELS and computational study of such 1:1 prochiral assemblies on Pt(111). The study reveals the existence of chemisorption induced strong C-H to O=C intermolecular hydrogen bonding between co-adsorbed ketones and aromatics on Pt(111). It also shows how this unforeseen interaction may be used to sensitively modulate both chemical reactivity at surfaces and nanoscale assembly at surfaces.

5:00pm NS+NC-TuA11 Magic-Sized Superlattices in Boron Doped Diamond, *I.B. Altfeder, J. Hu, A.A. Voevodin*, Air Force Research Laboratory, *J. Krim*, North Carolina State University

We report scanning tunneling microscopy and transmission electron microscopy study of boron-doped nanocrystaline diamond. On surfaces of diamond grains our study revealed self-assembled nanoscale superlattices whose period is 12 nm. The analysis of data strongly suggests a structural origin of these superlattices that can be attributed to nanoscale self-organization of twinning boundaries. We found two different types of nanoscale superlattices exhibiting either one-dimensional or two-dimensional order. We speculate that the observed effect manifests ordering of boron impurities inside diamond.

5:20pm NS+NC-TuA12 Tailoring Emission Properties of Nano Rare Earth Doped Oxides, *A. Kumar, S.B. Krishna, S. Seal*, University of Central Florida

Ceria (CeO2) is a rare earth metal oxide known for possessing less toxicity than many other metal oxides. Although the beneficial therapeutic properties of ceria nanoparticles have been explored, poor emission properties limit its application in imaging. The continuing quest to understand the interaction of ceria nanoparticles with cell requires better luminescent property of ceria, for which a nanoscale manipulation by doping has been reported. Europium is known for its strong emission and its atomic radii being close to that of cerium favors extensive solid solubility in ceria lattice. A systematic approach has been used to optimize emission intensity by varying the dopant concentration and annealing temperature. The doped oxide particles were synthesized by room temperature chemical precipitation technique. The size and morphology of the particles were characterized by high-resolution transmission electron microcopy (HRTEM). Strain induced on doping was calculated through X-ray Diffraction (XRD) from Williamson-Hall plot and is found to increase with the amount of dopant and decreases with annealing temperature. The emission property of europium doped ceria nanoparticles were studied by photoluminescence spectra. In order to disseminate the influence of surface chemical species, oxidation state, oxygen vacancy and strain on emission, X-ray photoelectron (XPS), Raman and Infra-red (IR) spectral characterizations were carried out. XPS results indicated that the ratio of Ce3+/Ce4+increases with dopant concentration and decreases with annealing temperature. Raman studies show a progressive shift to the higher energy due to local symmetry ordering with the temperature. Emission intensity varies with the wavelength of excitation and observed transitions indicate the presence of Eu3+ in different symmetry environments. The photoluminescence was found to be optimum at 15mol% Eu doped ceria and gets quenched with further doping concentration. Emission spectrum of the doped cerium oxide reveals peak characteristic to energy transfer from host to Eu3+ and this becomes more efficient on annealing. The present results are likely to have a profound impact not only for simultaneous therapeutic and imaging, but also on using ceria as carrier under physiological conditions. The study indicates that the enhanced photoluminescence is related to the manipulation of ceria lattice at nanoscale achieved through doping of suitable element.

Authors Index
Bold page numbers indicate the presenter

— A —
Altfeder, I.B.: NS+NC-TuA11, **2**

— B —
Baber, A.E.: NS+NC-TuA9, 2
Bellisario, D.O.: NS+NC-TuA9, **2**
Belov, M.: NS+NC-TuA4, 1
Buriak, J.M.: NS+NC-TuA4, 1

— D —
Demers-Carpentier, V.: NS+NC-TuA10, **2**

— E —
Erwin, S.C.: NS+NC-TuA3, **1**
Evoy, S.: NS+NC-TuA4, **1**

— H —
Hu, J.: NS+NC-TuA11, 2

— I —
Iski, E.V.: NS+NC-TuA9, 2

— K —
Kamins, T.: NS+NC-TuA4, 1
Krim, J.: NS+NC-TuA11, 2
Krishna, S.B.: NS+NC-TuA12, 2
Kumar, A.: NS+NC-TuA12, **2**

— L —
Long, J.P.: NS+NC-TuA2, **1**

— M —
Makinen, A.J.: NS+NC-TuA2, 1
Mastro, M.A.: NS+NC-TuA2, 1
McBreen, P.H.: NS+NC-TuA10, 2
Mizutani, G.: NS+NC-TuA1, 1

— N —
Nguyen, T.: NS+NC-TuA1, **1**

— P —
Park, J.-W.: NS+NC-TuA8, **1**
Pehrsson, P.E.: NS+NC-TuA2, 1

— Q —
Quitoriano, N.: NS+NC-TuA4, 1

— S —
Sardar, R.: NS+NC-TuA8, 1
Seal, S.: NS+NC-TuA12, 2
Shumaker-Parry, J.S.: NS+NC-TuA8, 1
Simpkins, B.S.: NS+NC-TuA2, 1
Sykes, E.C.H.: NS+NC-TuA9, 2

— T —
Tak, Y.: NS+NC-TuA5, **1**
Tierney, H.L.: NS+NC-TuA9, 2

— V —
Voevodin, A.A.: NS+NC-TuA11, 2

— W —
Wright, V.A.: NS+NC-TuA4, 1

— Y —
Yong, K.: NS+NC-TuA5, 1