

Thursday Afternoon, October 23, 2008

Nanomanufacturing Focus Topic

Room: 309 - Session NM+MS+NS+NC-ThA

Nanomanufacturing II: Nanostructures

Moderator: J. Murday, University of Southern California

2:00pm **NM+MS+NS+NC-ThA1 Superionic Electrochemical Patterning of Metallic Nanostructures**, *P.M. Ferreira, N.X. Fang, K. Hsu, K. Jacob, A. Kumar, P. Schultz*, University of Illinois, Urbana
INVITED

Nanoscale metallic nanostructures find widespread and critical application in many micro and nanoscale technologies. Processes such as electrochemical and electro-discharge machining lack the fine control to obtain sub-micron resolution. As a result, such structures are generally fabricated using indirect patterning techniques, resulting expensive, lengthy multi-step manufacturing operations. In this presentation, we introduce a new means of directly patterning metal films into metallic nanostructures. The process, Solid-State Superionic Stamping (S4), uses a patterned solid-electrolytic stamp or mold to directly create metallic nano- and microstructures through electrochemical anodic dissolution. As a result, it requires very small mechanical forces and no contaminating liquids, and is capable of producing structures with nanoscale precision over large areas. This presentation will discuss the mechanism that underpins the process; characterize its capabilities in creating silver and copper nanostructures; discuss the fabrication of stamps, and some applications that such a process enables. The presentation will conclude with a description of the process technology under development and directions for future research.¹

¹ This research was supported by NSF through the Center for Chemical-Electrical-Mechanical Manufacturing Systems (Nano-CEMMS) under Grant DMI-0312862, the Office of Naval Research under grant N00173-07-G013 and the University of Illinois through the Grainger Foundation grant. We are grateful that part of this work was carried out in the Center for Microanalysis of Materials, University of Illinois, which is partially supported by the U.S. Department of Energy under grant DEFG02-ER45439.

2:40pm **NM+MS+NS+NC-ThA3 Designing Semiconductor Nanocrystals for Optoelectronic and Biological Applications**, *M. Bawendi*, Massachusetts Institute of Technology
INVITED

Semiconductor nanocrystals, aka quantum dots, have become the prototypical material for the emergence of new properties when dimensions are reduced to the nanometer range. The size dependent properties of excitons and multiexcitons in quantum dots, coupled with a material that can be engineered and processed from solution, has led to potential applications in fields that include emissive displays, solar energy conversion, and biological and biomedical fluorescence imaging. A fundamental understanding of exciton processes is critical for any of these applications to become realized. The design and synthesis of well characterized materials is obviously key, not only of the functional inorganic particle itself, but also the ligand shell that protects it and couples it chemically to molecules and matrices of interest. This talk will review some of the chemistry and photophysics of quantum dots and then explore the fundamental properties and challenges behind broadly applying quantum dots as light emitters and light absorbers in devices and for biological imaging.

3:20pm **NM+MS+NS+NC-ThA5 Controlled Assembly and Nanoscale Doping of Semiconductor Quantum Dots Using Focused Ion Beams**, *J.F. Graham, C.D. Kell*, University of Virginia, *J.L. Gray*, University of Pittsburgh, *J.A. Floro, S.A. Wolf*, University of Virginia, *L. Bischoff*, Research Center Dresden-Rossendorf Inc., Germany, *R. Hull*, University of Virginia and Rensselaer Polytechnic Institute

Self-assembled semiconductor quantum dots are a candidate for use in potential nanoelectronic device architectures such as quantum cellular automata and magnetic spin exchange switches. It is possible to grow quantum dots (QDs) with relatively uniform size-distributions using heteroepitaxial techniques, but in order to apply QDs in such nanoelectronic devices they must also be spatially ordered into patterns of varying complexity. In addition, the QDs must possess the magnetic or electronic properties required for device operation. We have previously demonstrated the use of Ga⁺ focused ion beam (FIB) templating of Si surfaces prior to growth in order to fabricate patterns of Ge(Si) QDs of any desired complexity. Our current work employs a mass-selecting FIB with liquid metal alloy ion sources, enabling the generation of a wide range of separated species in focused beams, to template QD structures and electrically or magnetically dope them at a dot-by-dot level for nanoelectronic device applications. Ions can be selected according to isotope mass and charge state by using a mass-selecting Wien filter.

Suitable alloy sources then provide the ability to template a Si substrate with electrically non-invasive ions (i.e. Si or Ge) and implant dopant ions for electronic or magnetic activation (e.g. with B or Mn), with resolution of < 50nm and doses down to a few ions per dot. Key technical issues we are addressing include i) the attainable limits of spatial resolution and the dot-by-dot implantation dose, ii) comparisons between Ga and Si ion templated growth, iii) physical alignment between a templating ion beam and a dopant implantation ion beam and iv) procedures for eliminating unwanted exposure of adjacent areas of the sample to implantation ions.

4:00pm **NM+MS+NS+NC-ThA7 Semiconductor Nanowires: From Materials Science to Device Physics**, *L. Samuelson*, Lund University, Sweden
INVITED

In the general trend towards the use of self-assembly for realization of ultra-small devices on the 10nm-scale, semiconductor nanowires (NWs) have emerged as one of the most interesting candidates. In this talk I will describe different materials science aspects of NW growth, with a focus on III-V NWs grown epitaxially on a single-crystalline substrate as a top-down guided bottom-up growth of NWs. I will present recent progress in studies of structural properties of such NWs, including the importance and control of the stacking sequence of subsequent layers in NWs. I will then describe the controlled formation of axial and radial heterostructures, which is of great importance for the use of NWs for basic physics studies as well as for applications in electronics and photonics. As examples of recent physics studies of NWs I will describe transport via single and multiple quantum dots and optical studies of excitonic recombination in single quantum dots in NWs. Finally, I will give an update on the progress in realizing electronic as well as photonic devices using NWs, and will here primarily present progress in technology and performance of wrap-gate field-effect transistors. I time allows I will conclude with some visions for where I think NW-based science and technology may be heading in the future.

4:40pm **NM+MS+NS+NC-ThA9 Surface Plasmon Enhanced Photoluminescence from Noble Metal/CdS Hybrid Semiconductor Nanowires**, *W. Luo, S.C. Kung, W.V. Veer, R.M. Penner, J.C. Hemminger*, University of California, Irvine

Surface plasmon enhanced techniques provide promising methods to improve the light emission efficiency of semiconductor materials. In this talk, we present the growth of noble metal/CdS hybrid semiconductor nanowires, and the plasmon-enhanced photoluminescence from these nanowires. In our previous studies, we demonstrated the straightforward fabrication of ordered linear arrays of spherical silver nanoparticles with gaps between the individual nanoparticles of less than 10 nm on highly oriented pyrolytic graphite (HOPG) surfaces using physical vapor deposition (PVD) under controlled experimental conditions. These silver nanoparticle arrays were capable of supporting very strong surface plasmon resonances, which was demonstrated by our polarized surface enhanced Raman scattering experiments. In this presentation, we describe experiments where following the PVD growth of Ag or Au nanoparticle arrays on HOPG surfaces, we electrochemically deposit cadmium around these nanoparticle arrays to form hybrid nanowires as thin as 50-60 nm in width. Further annealing of these hybrid nanowires in H₂S at temperatures of 300-320°C enables the formation of CdS nanowires around the Ag or Au nanoparticle cores. Using this combined PVD/electrochemistry/chemical modification approach we have been able to generate ordered 2-D arrays of hybrid semiconductor nanowires that are as small as 100 nm in diameter and 100s of microns in length. Under light illumination, the surface plasmon supported by the Ag or Au nanoparticle cores enhances the photoluminescence of the outer CdS nanowires.

5:00pm **NM+MS+NS+NC-ThA10 Metal Oxide Nanowires by Near Field Electrospinning**, *M. Rinaldi, F. Ruggieri*, University of L'Aquila, Italy, *L. Lozzi*, CNISM and University of L'Aquila, Italy, *S. Santucci*, CNR-INFN and University of L'Aquila, Italy

The growth of metal oxide nanowire is an important challenge for the realization of nanostructured devices, as for example highly sensitive gas sensors.¹ A very easy method to deposit metal oxides is the electrospinning.² This simple and low cost technique allows the growth of very thin nanofibers, whose diameter can be varied from 50 nm to about 1 μm. It is based on the effect of an electric field on a charged liquid (polymer or solution) ejected from a nozzle. The charged jet is accelerated by the electric field, dries and is deposited onto a grounded substrate, forming nanofibers. Generally the nozzle-substrate distance is about 10-15 cm and the applied voltage is about 10-15 kV. Unfortunately this method does not allow easily the growth of well ordered nanofibers. In the present study TiO₂ nanofibers were electrospun with a novel approach of electrospinning called NFES (Near-Field Electrospinning), in which the tip-substrate

distance is strongly reduced to few millimetres, decreasing also the applied bias voltage to few hundreds of volts.³ Significant advancement in collecting aligned electrospun nanofibers has been made with this improved technique that complements conventional electrospinning by providing the feasibility of controllable deposition for sub-100-nm nanofabrication. Well aligned TiO₂ nanofibers were grown onto a silicon dioxide substrate. These nanofibers were up to several millimetres long with a diameter of about 200-400 nm. The scanning electron microscopy showed the presence of microcrystallites, whose crystalline nature was confirmed by X-ray diffraction measurements after a thermal process, also used for removing the polymer. The chemical composition was investigated by X-ray photoemission spectroscopy showing that the nanofibers are composed by stoichiometric TiO₂ crystallites.

¹ S. Piperno, M. Passacantando, S. Santucci, L. Lozzi, S. La Rosa, *J. Appl. Phys.*, vol. 101, (2007) 124504.

² W.E. Teo and S. Ramakrishna, *Nanotechnology*, vol. 17, (2006) R89.

³ D. Sun, C. Chang, S. Li, and L. Lin, *Nanoletters*, vol 6, (2006), p. 839.

5:20pm NM+MS+NS+NC-ThA11 Luminescent Rare-Earth Doped Metal Oxide Nanostructures, Y. Mao, J. Dorman, J.P. Chang, University of California at Los Angeles

Advanced luminescent materials have practical applications in nearly all devices involving the artificial production of light and considerable research has been carried out to synthesize new luminescent materials. Their luminescent properties have been shown to be dependent on the size and morphology of the crystallites, hence materials with dimensions in the nanometer regime emerges as promising materials. These attributes make them viably applicable in nanoscaled electronics, photonics, display and advanced bioanalysis. In this talk, we present our recent work on the fabrication of rare-earth doped metal oxide nanostructures, including Er:Y₂O₃ nanotubes (NTs) and nanoparticles (NPs) and Er:La₂(Zr_xHf_{1-x})₂O₇ NPs, by hydrothermal and molten-salt syntheses.^{1,2} The formation of nanostructures were probed in-situ by time-resolved synchrotron x-ray diffraction and absorption spectroscopy to delineate the process-structure-property relations. The as-synthesized nanostructures were further characterized by electron microscopy and various spectroscopy³ to be single crystalline, with well controlled size distributions around 100-400 nm in outer diameter and 2-5 μm in length for Er:Y₂O₃ NTs, around 80 nm in diameter for Er:Y₂O₃ NPs, and around 15 nm in diameter for Er: La₂(Zr_xHf_{1-x})₂O₇ NPs. The erbium coordination number and local bonding environment were shown to dictate the measured photoluminescent characteristics, including photoluminescence and cathodoluminescence. Specifically, these 0-100% erbium-doped oxide nanostructures have sharp and well-resolved photoluminescent behavior in the near-infrared region, outstanding green and red upconversion emissions, and excellent cathodoluminescent properties. These properties make these nanostructures promising for applications in display, bioanalysis and telecommunications.

¹Mao, et al. Synthesis and luminescence properties of erbium-doped Y₂O₃ nanotubes, *J. Phys. Chem. C*, 112, 2278 (2008).

² Mao, et al. Molten salt synthesis of highly luminescent erbium-doped yttrium oxide nanoparticles, submitted (2008).

³ Mao, et al. Correlation between luminescent properties and local coordination environment for erbium dopant in yttrium oxide nanotubes, *J. Appl. Phys.* in press (2008).

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