

# SYMPOSIUM N

## N: Quantum Dots, Nanoparticles, and Nanowires

November 30 - December 5, 2003

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## TUTORIAL

### FT N: Luminescent QD-Bioconjugates-Novel and Promising Tools for Biological Tagging Applications.

Sunday, November 30, 2003

1:30 PM - 5:00 PM

Room 208 (Hynes)

The tutorial will focus on several aspects of luminescent bioconjugates made by attaching colloidal semiconductor nanocrystals (quantum dots, QDs) to a variety of biological molecules (proteins, bioreactive receptors, DNAs, etc.), and their use in relevant biotechnological applications. It will begin with a general introduction into the synthesis, characterization, and a summary of the most important and relevant optical and spectroscopic properties of colloidal QDs. Materials made of different compounds will be covered. A description of the various reported approaches to surface-functionalize these materials, and the schemes employed to attach them to various proteins, antibodies, DNA, etc., will follow. The tutorial will also provide an overview of the successful uses of QD-bioconjugates in an array of biological studies, such as fluoro-immunoassays, hybridization assays, and cellular-imaging investigations. Advantages of employing these bio-inorganic complexes in these investigations will be emphasized.

#### Instructors:

**Moungi G. Bawendi**, Massachusetts Institute of Technology

**Warren C. W. Chan**, University of Toronto

**Igor Medintz**, Naval Research Laboratory

#### SESSION N1: Optical and Electronic Properties of Nanoparticles I

Chairs: Christophe Delerue and Ulrike Woggon

Monday Morning, December 1, 2003

Room 302 (Hynes)

#### NOTE EARLY START

#### 8:15 AM INTRODUCTORY REMARKS BY SYMPOSIUM ORGANIZERS

#### 8:30 AM \*N1.1

**Spontaneous Emission and Scattering of Light In Nanostructures: Field Enhancement Factors and Density of States Effects.** Sergey V. Gaponenko, Institute of Molecular and Atomic Physics, National Academy of Sciences of Belarus, Minsk, Belarus.

Nanostructures with characteristic surface relief on the order of 100 nm are known to modify spatial distribution of incident electromagnetic field. Local field enhancement results in enhanced absorption of photons by molecules or nanocrystals adsorbed at the surface. The effect is extremely pronounced in metal dielectric structures because of surface plasmon resonance. A systematic application of the field enhancement in Raman scattering enhancement (Surface Enhanced Raman Scattering, SERS) and in photoluminescence (PL) enhancement with respect to molecular probes is followed nowadays by application of the effect with respect to nanocrystals (quantum dots) adsorbed at metal-dielectric nanotextured surfaces. It is the purpose of the present contribution to review mechanisms of Raman scattering and photoluminescence enhancement factors in the context of their application to enhanced quantum dot luminescence and Raman scattering. We consider not only the local field enhancement in terms of excitation process but also photon density of states in terms of emission processes with Raman and Rayleigh scattering as specific photon emission processes. In this consideration scattering of light experiences enhancement as spontaneous emission does. Therefore field enhancement and density of states effects should manifest themselves in the same manner in photoluminescence and scattering processes. Differences in scattering and luminescence enhancement are due to quenching processes which are crucial for PL and less pronounced for scattering. We consider recent experimental results on single molecule detection by means of SERS, PL enhancement of quantum dots and the approaches to efficient substrates fabrication for the purposes of ultrasensitive spectroscopy.

#### 9:00 AM \*N1.2

**The Effect of Quantum Confinement on the Optical Properties of Semiconductor Nanocrystals.** Christophe Delerue and Guy Allan; ISEN, IEMN, LILLE, France.

The effects of the quantum confinement on the optical properties of semiconductor nanocrystals are reviewed on the basis of tight binding

calculations. In a first part of the talk, we consider intraband transitions of electron injected into spherical nanocrystals. We show that the electronic structure of these charged nanocrystals can be fully interpreted in terms of a shell model which justifies that the nanocrystals are often considered as artificial atoms. In addition, the intraband transitions follow strict selection rules exactly like in atoms. We calculate the oscillator strengths for the allowed transitions and we show that they only weakly depend on internal electric fields. In a second part of the talk, we present calculations of the optical absorption spectra in brick-shaped PbSe quantum dots. In contrast to previous works on quantum confinement effects, we study the evolution with size of the spectra in a wide range of energy, as obtained recently from ellipsometry measurements. Whereas the optical threshold is always blue-shifted when the size is reduced, we calculate that peaks in the spectra corresponding to transitions at some points of the Brillouin zone can be red-shifted. Our theory explains this peculiar behavior in agreement with recent experimental data. We also show that the confinement leads to a strong anisotropy of the dielectric constant for thin nanocrystals.

#### 9:30 AM N1.3

**Prediction of Complex Electronic Phenomena in Simple Semiconductor Quantum Dots.** Alex Zunger, NREL, Golden, Colorado.

Over the past few years we have developed a novel technique for describing the electronic properties of semiconductor nanostructures which overcomes the simplistic, continuum-like few band effective-mass-based technology. The fully atomistic method describes the ONE-ELECTRON physics via a plane-wave pseudopotential approach, and the MANY-BODY physics via a configuration-interaction approach. In this talk, I will describe how this method has revealed recently interesting complex electronic phenomena in simple quantum dots. I will discuss (time permitting) both COLLOIDAL dots and EPITAXIAL dots: (1) Prediction of the way an excited electron in a colloidal CdSe dot will decay to its ground state via Auger thermalization. Comparison of simple and multi-exciton decay. Is Auger decay fast enough? (2) Prediction of Impact Ionization rates in colloidal dots: Can an excited exciton be converted into two ground state electron-hole pairs? (3) Prediction of excitonic fine structure in Self-assembled InGaAs/GaAs dots, showing how even geometrically isotropic dots (e.g. lens shape) can lead to optical anisotropy. (4) Theory of quantum-entanglement in a dot-molecule made of two epitaxial InGaAs/GaAs dots, showing how strain and shape effects disable maximum entanglement due to "symmetry breaking". All results will be compared with experiment, whenever available. Yet unmeasured effects will be outlined as predictions.

#### 9:45 AM N1.4

**Calculated Structural, Optical and Electronic Properties of Silicon and Germanium Nanoclusters.** Andrew Williamson, Aaron Puzder, Fernando Reboredo, Jeffrey Grossman, Christoph Bostedt, Benedict Lorin and Giulia Galli; PAT, LLNL, Livermore, California.

We present the results of first principles, density functional and quantum Monte Carlo calculations of the structural stability and opto-electronic properties of silicon and germanium nanoclusters. First, the relative stability of hydrogen terminated nanoclusters with unreconstructed and reconstructed surfaces is predicted for clusters ranging in size from 30 to 300 atoms. Above 500K, clusters with reconstructed surfaces are found to have lower formation energies. The calculated electronic density of states of these reconstructed clusters is shown to be in close agreement with recent photoemission measurements. The size dependence of the optical absorption and emission of these nanoclusters is also predicted. We find that; (i) highly accurate quantum Monte Carlo calculations are required to make quantitative predictions of the optical gaps of nanoclusters [1], (ii) there is a significant Stokes shift between optical absorption and emission and the magnitude of the Stokes shift depends on the surface structure and chemistry of the nanoclusters [2,3], (iii) the optical absorption gap is dramatically reduced by surface reconstructions and (iv) the optical properties of silicon and germanium are predicted to be similar throughout this size range. This work was performed under the auspices of the U.S. Department of Energy by University of California Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48. [1] A. Williamson et al. Phys. Rev. Lett. 89, 196803 (2002) [2] A. Puzder et al. Phys. Rev. Lett. 88, 097401 (2002) [3] A. Puzder et al. J. Amer. Chem. Soc. 125, 2786 (2003)

#### 10:00 AM N1.5

**Multiparticle Electronic Dynamics in Transition from Zero to One Dimension in Semiconductor Quantum Rods.**

Andrei Piryatinski, Sergei Tretiak, H. Htoon, J. A. Hollingworth, A. V. Malko and V. I. Klimov; Los Alamos National Lab, Los Alamos, New Mexico.

Semiconductor Quantum Rods, i.e. elongated nanocrystals, can be considered as nanostructures whose dimensionality effectively varies between zero (Quantum Dots) and one (Quantum Wires) as their aspect ratio increases. This change of the dimensionality dramatically affects the Quantum Rods electronic structure and excited state dynamics as well as corresponding optical observables. Our experimental study of a series of CdSe elongated nanocrystals (nanorods) has been focused on the scaling of the effective dimensionality of multiparticle, nonradiative Auger recombination. Using high-sensitivity transient absorption techniques, Auger recombination times of two- and three-electron-hole pair states in nanorods with variable aspect ratios have been measured. These measurements reveal that Auger recombination rates change from cubic to quadratic with respect to carrier density as the rod length is increased. We explain this effect by the fact that in sufficiently long rods, the electron hole pairs form 1D excitons and, therefore, Auger recombination can occur as a result of energy transfer from one exciton to another, i.e. via a quadratic process. To model collective multiparticle electronic dynamics we use a many-body approach. The equations of motion which depend on the free carrier and correlated electron-hole (exciton) variables are derived; these equations explain the observed changes in scaling of the Auger process. Correspondent spectroscopic signatures are calculated and compared with the experimental data.

#### 10:45 AM N1.6

**Silver nanoparticle induced modification of spontaneous emission in GaN quantum dots.** Arup Neogi<sup>1</sup>, Brian P. Gorman<sup>1</sup> and Hadis Morkoc<sup>2</sup>; <sup>1</sup>Physics, University of North Texas, Denton, Texas; <sup>2</sup>Physics and Electrical Engineering, Virginia Commonwealth University, Richmond, Virginia.

The ability to control spontaneous emission (SE) by resonant surface-plasmon (SP) interaction can have profound consequences on many optoelectronic devices. Thin metallic films containing nanoscale surface features result in giant enhancement of linear and nonlinear optical responses. These enhancements are associated with excitation of SP, collective electromagnetic modes whose characteristics are strongly dependent on the geometric structure of the metallic component of the medium and can be further enhanced via the directional emission from the semiconductor microcavity. The bulk plasmon energy of silver (3 eV) is modified ( $\sim 2.92$  eV) at the GaN interface, which has a bandgap at  $\sim 3.4$  eV. We have demonstrated the resonant enhancement of SE rate by  $\sim 100$  times in InGaN quantum wells (QWs), which leads to a decrease in emission efficiency. In this work, we report the modification of SP mediated spontaneous recombination of carriers in GaN quantum dots (QD) by using Ag nanolayers and nanoparticles. GaN QDs were grown on GaN/AlN by molecular beam epitaxy and its luminescence spectra can be tuned from the ultraviolet to the visible wavelength region by controlling the size and the induced strain in the QDs. The spontaneous emission in QDs can be engineered by capping the surface with a thin layer of Ag film deposited by thermal vapor deposition. The spontaneous radiative decay rate in the strained QDs is enhanced by 3-5 times as indicated by the decrease in the PL intensity from the silvered side. The reduction in the PL emission can be attributed to the spontaneous energy transfer from the QD electron-hole pairs into the electromagnetic SP modes induced by the Ag layer. This reduction in the PL emission is not due to the change in the absorption and reflection properties of the Ag layer as observed from the unchanged peak PL intensity of the reference layer at 3.42 eV. The change in SE rate is also supported by time-resolved photoluminescence measurements. To enhance the PL efficiency, the QD samples were covered with Ag nanoparticles deposited by spin coating a Ag halide solution over the GaN QDs having a 2 nm AlN cap layer. The QD emission is enhanced and becomes stronger compared to the bulk GaN peak at the lower energy due to the enhanced stimulated absorption and the modification of the radiative recombination channel from the QDs into the SP modes. The enhancement depends on the size and distribution of Ag nanoparticles at the surface of the QDs. Ag nanoparticle acts as radiating dipole sources and the emission from the QD are resonantly coupled into these Ag particles resulting in a relative enhancement of the QD PL emission compared to the off-resonant GaN buffer layer. The change in the PL intensity (both quenching or enhancement) in the QDs is comparable to the GaAs or InP based QWs, but still several factors lower than InGaN QWs. Embedding these QD in a DBR structure or a microcavity can further enhance the emission from these QDs.

#### 11:00 AM N1.7

**Structure and Shape Engineering of Luminescent Semiconductor Nanocrystals.** Dmitri V. Talapin, Ivo Mekis and Horst Weller; Institute of Physical Chemistry, University of Hamburg, Hamburg, Germany.

Size series of nearly monodisperse II-VI and III-V semiconductor nanocrystals were synthesized via the organometallic reactions in

highly boiling solvents. Further engineering the nanocrystal structure and shape leads to precise control of properties and new physical phenomena. Thus, we propose new methods of synthesis of the core-shell particles where an epitaxial shell of a wide bandgap semiconductor (e.g., CdSe/ZnS, CdSe/CdS, InAs/CdSe) results in advanced luminescent properties and high chemical stability. The double shell structures like CdSe/CdS/ZnS and CdSe/ZnSe/ZnS allow gradual switching of the lattice spacing from the emitting CdSe core to the protecting wide bandgap ZnS shell. Growing the asymmetric rod-like CdS shell around spherical CdSe cores yields the colloidal nanoparticles with high PL quantum yields (up to 60%) and linearly polarized luminescence. Highly luminescent InP nanocrystals with the emission color tunable from green to near-IR are the unique environmentally benign luminescent nanomaterial naturally suitable for in vivo luminescent biological labelling. General aspects governing the particle size and size distribution in the colloidal synthesis are discussed and a theoretical description of the experimental results is proposed. A distribution of properties like photoluminescence efficiency, photostability, etc. was observed within ensembles of colloiddally grown II-VI and III-V semiconductor nanocrystals. This phenomenon is attributed to a dynamic distribution of the nanocrystal surface disorder originating from the Ostwald ripening growth mechanism.

#### 11:15 AM N1.8

**Structural and optical properties of CdSe, CdTe and CdSeTe nanoparticles dispersed in SiO2 films.**

Padullaparthy Babu Daya<sup>1,2,3</sup>, Mehta Bodh Raj<sup>1,2,3</sup>, S.M.

Shivaprasad<sup>2,1</sup> and P. D. Paulson<sup>3,1</sup>; <sup>1</sup>Physics, IIT Delhi, New Delhi, Delhi, India; <sup>2</sup>Surface Physics Group, National Physical Laboratory, New Delhi, India; <sup>3</sup>Institute of Energy Conversion, Delaware Newark, Delaware.

Semiconductor nanoparticles dispersed in optically transparent glasses (SDG) have emerged as potential candidates in the field of opto-electronic applications such as optical switching, optical signal processing, and for solar energy conversion devices. One of the advantages of dielectric confinement in these SDG over nanoparticles prepared by usual chemical methods is that inorganic matrix diminishes the crystallite surface activity leading to a chemically stable nanoparticle structures. In the present study, CdTe and CdSe semiconductor nanoparticles have been prepared by magnetron sputtering of high quality elemental Cd, Se and Te along with SiO2 targets. Use of elemental targets allows a better control of the stoichiometry of these films by changing the surface areas of targets. The nanoparticle samples have been characterized using glancing angle x-ray diffraction (GAXRD), optical absorption and x-ray photoelectron spectroscopy (XPS) techniques. GAXRD studies carried out on vacuum annealed CdTe:SiO2 and CdSe:SiO2 samples show the nanoparticle core surrounded by amorphous (CdTeO3 and CdSeO3) interfacial layer and crystalline surface layer in case of air annealed samples. The detailed study carried out on these samples point towards a "surface mediated structural transformation from cubic to hexagonal structural transformation in case of CdTe nanoparticles [1]. In case of CdSe nanoparticles only hexagonal structure is observed. Transmission electron microscopy studies carried out on CdSexTe1-x samples shows the dependence of topography on composition. Almost spherical nanoparticles in case of CdTe [2] and well formed nano rod structures in case of CdSe is observed. Optical properties have been studied using variable angle spectroscopic ellipsometry (VASE) technique. Real and imaginary parts of dielectric constant spectra of nanoparticles have been obtained as a function of composition. VASE studies carried out on CdTe:SiO2 samples show a first time observation of shift of critical point transitions and spin orbit splitting energy from their corresponding bulk values as a function of nanoparticle size leading to modification of electronic band structure of CdTe at reduced dimensions [3]. The above studies clearly indicates that the interfacial layer formed in between the nanoparticle-matrix interface plays a crucial role in determining the structural and optical properties, besides the use of elemental targets being an advantage in achieving stoichiometry of nanoparticles. 1. P. Babu Dayal, B. R. Mehta, S. M. Shivaprasad and Y. Aparna, Appl. Phys. Lett. 81 (2002) 4254 2. P. Babu Dayal and B. R. Mehta (Communicated to Thin Solid Films) 3. P. Babu dayal, B. R. Mehta and P. D. Paulson (communicated to Appl. Phys. Lett.)

#### 11:30 AM N1.9

**CdSe nanorods and nanodots in various structures: a comparative study of optical properties.** Mikhail Artemyev<sup>1</sup>,

Bjoern Moeller<sup>2</sup>, Ulrike Woggon<sup>2</sup> and Gennady Khomutov<sup>3</sup>; <sup>1</sup>Institute for Physico-Chemical Problems, Belarussian State University, Minsk, Belarus; <sup>2</sup>FB Physik, Dortmund University, Dortmund, Germany; <sup>3</sup>Physics department, Moscow State University, Moscow, Russian Federation.

Highly luminescent core-shell (CdSe)ZnS nanodots and nanorods present two classes of structures of different dimensionality. With 3D

and 2D-confined electron-hole pairs respectively, their optical properties are quite different when involved in various micro- and nanostructures. Nanodots with nearly spherical symmetry show extremely sharp emission bands at low temperature in isolated regime and emission is almost unpolarized. Nanodots are isotropic emitters and may be introduced into optical microcavities or utilized alone as stable narrow-band fluorescent markers. On the other hand, highly polarized emission, as well as absorption even at room temperature makes nanorods interesting anisotropic emitters. In this case the nanorods must be organized and oriented in appropriate way. Here, we compare the photoluminescence properties of single nanodots and nanorods, thin films containing both types of nanocrystals, nanorods and nanodots attached to the surface of semiconductor well, stretched macromolecules and polymeric microspheres via the electrostatic attraction and disulfide binding. The electrostatic attachment of nanorods requires their solubilization in hydrophilic solvents (water, methanol) with bifunctional molecules containing both mercapto- and positively charged quaternary ammonium groups. When deposited onto a cleaved semiconductor well or stretched macromolecules their restricted wire-like geometry provokes CdSe nanorods to align unidirectionally along the object length. Unlike nanodots, aligned nanorods possess strongly polarized photoluminescence on a microscopic length scale. We show also, that preferentially tangential alignment of electrostatically attached nanorods on the surface of spherical polymeric microcavities (photonic dots) brings a certain polarization selection rule to allowed photonic modes inside photonic dots. Moreover, the combination of nanodots and tangentially aligned nanorods at the surface of photonic dots may allow a polarization selective cavity controlled energy transfer from smaller nanodots to larger nanorods. This effect may be seen as partial dumping of the one sort of photon modes (TE) in the region of nanodots emission. [1]. M. Artemyev, B. Möller, U. Woggon. Unidirectional alignment of CdSe nanorods. *Nano Lett.* 3(2002), 509-512. [2]. B. Möller, U. Woggon, M. Artemyev, R. Wannemacher. Mode control by nanoengineering of light emitters in spherical microcavities (submitted to *Appl. Phys. Lett.*).

**11:45 AM N1.10**  
**Nonlinear Optical Properties of Silver Nanowires Embedded in Nanoporous Alumina Membranes.** Michael Kroll, Sean O'Flaherty and Werner J. Blau; Physics, Trinity College Dublin, Dublin, Ireland.

Due to their possible application in future nanoelectronics and as magnetic data storage devices metallic nanowires have attracted considerable interest. Using mesoporous alumina membranes as a host material nanowires with controllable diameters and lengths can be prepared. These membranes provide up to  $10^{12}$  pores per  $\text{cm}^2$  that are perpendicular to the membrane surface, parallel to each other and have adjustable uniform pore diameters of 5 to 250 nm. The membrane thickness and thus the length of the pores can be controlled within the range of some hundred nanometers and several hundred microns. One-dimensional nanostructured materials can be prepared by depositing the material into the pores using chemical or electrochemical deposition methods. One-dimensional nanostructures are supposed to show an anisotropy in their physical properties due to the confinement of the charge carriers in two dimensions. Therefore the optical properties of silver nanowires embedded in nanoporous alumina membranes depend on the relative orientation of the sample to the light beam and the polarisation of the light. Moreover the diameter of the wires and the aspect ratio determine their optical properties. The (linear) optical absorption spectra of silver nanowire / alumina composites generally show a broad absorption in the visible range which can be attributed to a collective excitation of the surface plasmons. Using a short-pulsed Nd:YAG laser one can investigate the nonlinear optical properties as a function of the wire diameter. For a certain laser intensity the plasmon resonance is completely excited leading to a constant decrease of the absorption coefficient and therefore an enhanced transmission (saturable absorption). When further increasing the laser intensity the absorption coefficient starts to increase again. This is attributed to an ionisation of the silver wire and a different optical behaviour of the ionised species. The electron is trapped in the dielectric surrounding of the metal wires. Once ionised the optical behaviour of the metal wires even at lower laser intensities remains changed for several hours. The excitation of the plasmon resonance leads to an enhancement of the local electrical field near the silver wire surface. This effect can be used to study Raman spectra of organic molecules attached to the wires making use of the Surface Enhanced Raman Scattering (SERS) effect. This paper summarises the optical properties of silver nanowires in nanoporous alumina as a function of the wire diameter. It describes measurements of the nonlinear optical properties and the (diameter dependent) SERS spectra of 1,3-benzenedithiol attached to the wires.

SESSION N2: Optical and Electronic Properties of Nanoparticles II

Chairs: F. Henneberger and Alex Zunger  
 Monday Afternoon, December 1, 2003  
 Room 302 (Hynes)

**1:30 PM \*N2.1**  
**Nanocrystal Quantum Dot Spectroscopy And Applications.**  
 Mounji G. Bawendi, Department of Chemistry, MIT, Cambridge, Massachusetts.

This talk will review some of the insights that have been obtained from studying both the fundamental aspects of the chemistry of nanocrystal quantum dots and the study of the fluorescence properties of single nanocrystal dots. These insights will be further explored in the context of the incorporation of nanocrystal dots in organic light emitting devices, and in the context of the observation of stimulated emission and lasing from nanocrystal dots under optical pumping. Recent biomedical imaging results using near infrared emitting dots for the purpose of sentinel lymph node mapping will also be highlighted.

**2:00 PM N2.2**  
**Exciton-Exciton and Exciton-Plasmon Interactions in Semiconductor and Hybrid Semiconductor/Metal Nanoassemblies.** Marc Achermann<sup>1</sup>, Melissa A. Petruska<sup>1</sup>, Laurent P. Balet<sup>1</sup>, Mark I. Stockman<sup>2</sup> and Victor I. Klimov<sup>1</sup>; <sup>1</sup>Chemistry Division, Los Alamos National Laboratory, Los Alamos, New Mexico; <sup>2</sup>Department of Physics and Astronomy, Georgia State University, Atlanta, Georgia.

Nonradiative energy transfer (ET) via incoherent Coulomb interactions (exciton-exciton coupling) is an important communication and transport mechanism at the nanoscale. In living plants, for example, this mechanism enables the delivery of energy from strongly absorbing antenna complexes to the reaction center; as a result, the effective absorption cross section of this center can be greatly increased. In nonmetal/metal assemblies, the exciton-plasmon interactions can lead to the efficient transfer of energy from an exciton in the nonmetal to plasmons excited in the metal component, resulting in the efficient quenching of the exciton emission. Both exciton-exciton and exciton-plasmon interactions strongly depend on the spectral properties and the geometrical arrangement of the constituents. In this respect, semiconductor nanocrystal quantum dots (NQDs) are well suited for studies of such interactions due to their size-tunable optical properties and the ease with which NQDs can be assembled into small and large arrays or combined with metal-based structures. In this paper, we investigate spectrally resolved dynamics of exciton recombination and ET in single monolayers and bilayers of NQDs assembled using Langmuir-Blodgett (LB) techniques either on dielectric or on metal substrates. In compressed LB films on glass slides, we observe the ET component with an  $\sim 50$  ps constant, which is close to the theoretical limit for ET rates for two dots in the immediate vicinity of each other interacting in the resonant regime. We show that observed dynamics can be quantitatively modeled assuming that ET is dominated by interactions of a donor NQD with acceptor NQDs from the first three "shells" surrounding the donor. We also observe an ET-induced effective enhancement of the absorption cross section (up to a factor of 4) for larger NQDs on the "red" side of the size distribution. By assembling bilayers of NQDs of two different sizes, we are able to improve the donor-acceptor spectral overlap for transfer in a specific ("vertical") direction. These bilayers show fast, unidirectional ET with a time constant of  $\sim 120$  ps. Using LB techniques, we also fabricate well-defined NQD-metal structures, which we use to study the effect of exciton-plasmon interactions on the rates of radiative and nonradiative decay of NQD excitons. To analyze the observed results, we develop an analytical theory based on the local random-phase approximation. We show that for systems under investigation, the traditional "dielectric-medium" approximation fails both qualitatively and quantitatively.

**2:15 PM N2.3**  
**Tunable Near-Infrared Optical Gain and Amplified Spontaneous Emission in PbSe Nanocrystals.**  
 Richard D. Schaller, Melissa A. Petruska and Victor I. Klimov; Chemistry Division, Los Alamos National Lab, Los Alamos, New Mexico.

PbSe nanocrystals are efficient infra-red (IR) emitters with potential applications ranging from telecommunications to biological labeling. These nanocrystals can be synthesized with narrow size dispersion and high photoluminescence (PL) quantum yields (up to  $\sim 80\%$  at room temperature), providing size-controlled tunability of the energy gap from near- to mid-IR wavelengths. Here, we analyze the fundamental physics of light amplification and lasing in PbSe nanocrystals with emission energies in the near-IR. Our studies indicate that one complication for achieving the optical gain regime is

associated with high degeneracy of the lowest electron and hole states. Specifically, our pump-dependent transient absorption studies indicate that saturation of the lowest optical transition requires 8 electron-hole (e-h) pairs, which reflects the 8-fold degeneracy of the ground state in PbSe. This high degeneracy results in a large optical gain threshold, which is theoretically 4 e-h pairs per nanocrystal and is even higher (~8 e-h pairs) according to our experimental data. An additional complication is associated with ultrafast multiparticle Auger recombination, which leads to very short (~10 ps in high quality samples) optical gain lifetimes. However, we also find that because of large gain cross sections, the critical nanocrystal densities required for achieving the regime of amplified spontaneous emission (ASE) are not very high and correspond to ~1% filling factors. In order to observe ASE, we incorporate PbSe nanocrystals into titania sol-gel matrices with high volume fractions of ~10%. By exciting Ti:sapphire laser we observe the development of the spectrally narrow ASE band, which shows a super linear growth with pump power. We detect ASE at both cryogenic and room temperatures. Further, by changing the nanocrystal size we can tune the ASE band from ~1.3-1.6 microns, which covers the range of several telecommunication windows. Our findings indicate the feasibility of nanocrystal based optical amplifiers and lasers for near-IR spectral energies. In addition to tunability these novel IR-gain materials provide chemical flexibility that can allow their direct incorporation into fiber circuits and photonic structures.

### 2:30 PM N2.4

#### Room Temperature Stimulated Emission from Self-Organized ZnO Nanodots Grown by Metalorganic Chemical Vapor Deposition.

Sang-Woo Kim<sup>1</sup>, Kazunobu Kojima<sup>1</sup>, Shizuo Fujita<sup>2</sup>, Yoichi Kawakami<sup>1</sup> and Shigeo Fujita<sup>1</sup>; <sup>1</sup>Department of Electronic Science and Engineering, Kyoto University, Kyoto, Japan; <sup>2</sup>International Innovation Center, Kyoto University, Kyoto, Japan.

Recently, ZnO with a wide band-gap of 3.3 eV at room temperature (RT) has attracted much attention due to the prominent excitonic properties supported by a large exciton binding energy (60 meV at RT) for possible application to another efficient RT ultraviolet (UV) lasers. In this regard, exciton-based optical properties of ZnO such as UV stimulated emission and lasing have been intensively investigated in ZnO thin films, quantum wells, and nanostructures. Since the various nanostructures are effective to utilize excitonic properties with enhanced confinement of excitons, up to date a number of studies for optically pumped stimulated emission from one-dimensional ZnO nanostructures (such as nanowires) at RT have been reported. However, for ZnO with lower dimensionality, i.e., for zero-dimensional ZnO nanostructures (such as nanodots), RT stimulated emission has scarcely been demonstrated. In this paper, we report a RT stimulated emission phenomenon from self-organized ZnO nanodots on SiO<sub>2</sub>/Si substrates. The ZnO nanodots with 32-nm diameter, 12-nm height, and over  $6 \times 10^{10} \text{ cm}^{-2}$  density were grown by metalorganic chemical vapor deposition. Under continuous wave He-Cd excitation at RT the free exciton emission located at 3.26 eV was dominant without any deep-level emission. On the other hand, when the optical pumping was introduced using the frequency-tripled output (355 nm, 10 ns) from a pulsed mode-locked Nd:YAG laser operating at a repetition rate of 10 Hz, broad spontaneous emission peaking at 3.22 eV below a threshold was observed. With increasing the optical pumping intensity above a threshold value, e.g., 17 mJ/cm<sup>2</sup> per pulse, a sharp single P band emerged at 3.18 eV directly from the broad spontaneous emission band. With further increase of the pumping intensity, the P band emission was superlinearly increased with increasing pumping intensity. This emission is due to an exciton-exciton collision recombination process, indicating a spatial exciton confinement effect. The full width at half maximum of the P band emission was about 0.25 nm. The result that the position of such the ultra-narrow P band emission is constant with the pumping intensity can be another evidence of an excitonic origin. Detailed characterization of the stimulated emission and discussion on the gain mechanism are continued and to be included in the presentation at the meeting.

### 3:00 PM N2.5

#### Lasing from Semiconductor Quantum Rods in a Cylindrical Microcavity.

Miri Kazes<sup>1,2</sup>, David Y Lewis<sup>1,2</sup> and Uri Banin<sup>1,2</sup>; <sup>1</sup>Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem, Israel; <sup>2</sup>The Center for Nanoscience and Nanotechnology, The Hebrew University of Jerusalem, Jerusalem, Israel.

Semiconductor nanocrystals show potential for applications ranging from photonics and resonator on-a-chip devices to biosensing. An obvious advantage of such nano particles is the remarkable spectral coverage for luminescence that is afforded via the quantum confinement effect by merely controlling the size of the nanocrystals. Nanocrystals are interesting new candidates for lasing materials expected to provide low lasing thresholds and lasing that is insensitive to temperature. In spite of these advantages there are also very fast loss mechanisms and mainly the fast Auger recombination process that

prevents efficient lasing. In order to overcome the losses we utilize a high Q cylindrical microcavity, showing Whispering Gallery Mode (WGM) lasing for CdSe/ZnS quantum rods both in solution and in a film. The WGM form of the observed lasing, in contrast to radial mode lasing, was verified by the dependence of peak spacing on the cavity diameter. The peak spacing measured for a 200 micron and a 150 micron cavity diameters gave 0.32nm and 0.5nm spacings respectively, as expected from theory. CdSe/ZnS quantum rods, in comparison to quantum dots, exhibited remarkably reduced lasing thresholds essentially assigned to increased oscillator strength, increased Stokes shift that reduces losses due to reabsorption, and slower Auger rates which are dependent on size. Furthermore, an efficient and reproducible method is employed for preparation of nanocrystal cylindrical films for robust lasing. This was applied to CdSe/ZnS quantum rod samples of varied dimensions and was also demonstrated for quantum dot samples. Thus far, an investigation into the preparation process indicates a possibility of a laser ablation process in which the film is deposited via the ablation of the quantum rod solution inside the capillary. Further irradiation of the film causes annealing which assists in forming a smooth film essential for WGM lasing and the possible annealing of the quantum rods themselves, resulting in a stable lasing over hundreds of pump pulses. Lasing thresholds are low as 0.02mJ and lasing intensities are three orders of magnitude larger than the saturated fluorescence intensity.

### 3:15 PM N2.6

#### Single-Nanocrystal Photoluminescence and Absorption Spectroscopies in Single- and Multiexciton Regimes.

Han Htoon, Paris J Cox, Jennifer A Hollingworth and Victor I Klimov; C-PCS MS J585, Los Alamos National Lab, Los Alamos, New Mexico.

Chemically synthesized semiconductor nanocrystals are promising materials for a variety of applications ranging from bio-labeling and chemo-sensing to solid-state lighting and optical amplification. Recently, proof-of-principle experiments have demonstrated the applicability of individual dots as single photon sources and quantum logic gates. However, this work has exclusively concentrated on individual quantum dots grown by epitaxial techniques. It is highly desirable to extend these novel single-dot technologies into the domain of chemically synthesized nanocrystals that could allow new confinement regimes, wide-range spectral tunability, and scalability. A serious obstacle towards implementations of single nanocrystal technologies is the instability of photoluminescence (PL), known also as PL intermittence or "blinking". The exact nature of this effect is still under debate. However, strong arguments have been made in favor of dynamical PL quenching induced by Auger recombination following the ionization of a nanocrystal. In our efforts to understand, and to ultimately control the blinking behavior, we study single nanocrystal PL in both single- and multi-exciton regimes. We explore the effect of the nanocrystal shape and surface conditions on the PL stability. Finally, we investigate single nanocrystal absorption spectra by applying PL excitation measurements. Specifically, we use series of elongated nanocrystals (quantum rods) to study the evolution of electronic structure during the transition from zero- to one-dimensional confinement regimes.

### 3:30 PM N2.7

#### Does single colloidal quantum dot optical behavior reflect itself in the optical response of a collection of dots?

Inhee Chung and Mounji G. Bawendi; chemistry, MIT, Cambridge, Massachusetts.

Single nanocrystal quantum dot fluorescence intermittency is thought to result from temporal charging and neutralization of individual dots. This intermittency can be phenomenologically described by power-law distributions of on and off-times over experimental time-scales, with characteristic maximum on-times that are condition dependent. We construct a phenomenological model for single dot blinking that includes lower and upper bounds for both on and off-times. These single QD statistics leads to pseudo-reversible photo-darkening of the fluorescence from collections of dots that stabilizes to a steady state value. We show that the variability in the long time fluorescence dynamics from collections of QDs from different samples can be traced to differences in upper bounds of on and off-times observed from single dots within those samples.

### 3:45 PM N2.8

#### Chemistry and Optical Properties of Individual Quantum Dots Determined with EELS in the TEM.

Geoff McCool<sup>1</sup>, Ashley Harvey<sup>1</sup>, Subhash Risbud<sup>1</sup>, Philip Power<sup>2</sup>, Ian Kennedy<sup>3</sup>, Kent Pinkerton<sup>4</sup>, Ilke Arslan<sup>4,5</sup>, Rolf Erni<sup>4,5</sup>, Nigel Browning<sup>4,5</sup>, Anne Mayes<sup>6</sup> and Valerie J. Leppert<sup>1</sup>; <sup>1</sup>Chem Eng and Mat Sci, UC Davis, Davis, California; <sup>2</sup>Chemistry, UC Davis, Davis, California; <sup>3</sup>Mechanical and Aeronautical Engineering, UC Davis, Davis, California; <sup>4</sup>Center for Health and Environment, UC Davis, Davis, California; <sup>5</sup>National Center for Electron Microscopy, Lawrence

Berkeley National Laboratory, Berkeley, California; <sup>6</sup>Materials Science and Engineering, MIT, Cambridge, Massachusetts.

New advances in the energy and spatial resolution of electron energy-loss spectroscopy (EELS) in the transmission electron microscope (TEM) offer the opportunity of measuring the local chemistry of individual nanoparticles, as well as properties such as the band gap. The imaging and diffraction capabilities of the TEM also allow these measurements to be correlated with the structure, size, and morphology of individual nanoparticles. Here, our recent work using EELS to measure the properties of individual semiconductor nanoparticles with nm or better spatial resolution will be presented. Specific examples will be given of EELS experiments to determine the local band gap and chemistry of semiconductor quantum dots and their interfaces with organic media. The unique ability of EELS to distinguish the chemistry and electronic properties of individual nanoparticles, and even differentiate between their surface and interior properties, will be discussed.

#### 4:00 PM N2.9

##### **Quantum-Dot-Based Measurement of Gene Expression.**

Stephan Thiberge<sup>1</sup>, Yoram Gerchman<sup>1</sup>, Kam Jim<sup>4</sup>, Lydia Sohn<sup>2</sup> and Ron Weiss<sup>1,3</sup>; <sup>1</sup>Electrical Engineering, Princeton University, Princeton, New Jersey; <sup>2</sup>Mechanical Engineering, University of California, Berkeley, Berkeley, California; <sup>3</sup>Molecular Biology, Princeton University, Princeton, New Jersey; <sup>4</sup>Computer Science, Princeton University, Princeton, New Jersey.

We propose a new, highly sensitive, high-throughput mechanism for measuring gene expression using gene transcripts barcoded with quantum dots. Accurate, high-throughput measurements of gene expression are crucial for many biomedical, biotechnology, and scientific applications. However, existing mechanisms such as gene chips, Reverse Transcriptase Polymerase Chain Reaction (RT-PCR), and Serial Analysis of Gene Expression (SAGE) do not offer a single satisfying solution. Our novel approach for measuring gene expression utilizes a new computer algorithm to generate a unique barcode for each gene transcript. The algorithm automatically selects a library of 20-mer oligonucleotides complementary to carefully chosen gene regions and assigns each oligonucleotide a specific color. The barcode scheme ensures that any given gene of interest will be hybridized with a unique set of colors. Based on the algorithm's output, we synthesize the different oligonucleotides and tag them with quantum dots of the appropriate fluorescence. We extract messenger RNA (mRNA) from the cells under study, reverse transcribe the mRNA into cDNA, and hybridize the cDNA with the tagged oligonucleotides. The above process results in a set of gene products each labeled with a unique set of colors. An integrated microfluidic device placed under a microscope detects the barcoded DNA using Near Field Optics, a single UV laser, and a set of photo-detectors with appropriate filters. The small size and high intensity of the quantum dots provide an important accuracy advantage over existing approaches by allowing us to quantify single mRNA transcripts, potentially extracted from single cells. As a result, our approach does not require PCR amplification which typically distorts the distribution of the original transcripts. We will present our barcoding algorithm and preliminary experimental results of reading barcoded DNA using the integrated microfluidic device and standard optical detectors.

#### 4:15 PM N2.10

##### **Electronic Energy Transfer from Photoexcited Silicon Nanocrystals to Molecular Oxygen.** Egon Gross<sup>1</sup>, Dmitri

Kovalev<sup>1</sup>, Nicolai Kuenzner<sup>1</sup>, Joachim Diener<sup>1</sup>, Frederick Koch<sup>1</sup>, Victor Timoshenko<sup>2</sup> and Minoru Fujii<sup>3</sup>; <sup>1</sup>Physik Department E16, Technische Universitaet Muenchen, Garching, Germany; <sup>2</sup>Faculty of Physics, Moscow State M. V. Lomonosov University, Moscow, Russian Federation; <sup>3</sup>Department of Electrical and Electronics Engineering, Faculty of Engineering, Kobe University, Kobe, Japan.

The energy transfer of electronic excitation plays an essential role in numerous scientific branches such as photophysics and biochemistry. To elucidate the fundamental physical effects occurring during energy transfer processes semiconductor nanostructures are viewed as a promising approach. The extensive progress achieved in this field stems from the combination of physical concepts with ideas of other research disciplines, like chemistry, biology and engineering. Recently, the photosensitization of molecular oxygen has gained considerable interest. Oxygen molecules in the electronic ground state are chemically inert due to their spin-triplet characteristic. However, excitation of an intermediate substance (photosensitizer) and subsequent transfer of energy to oxygen activates the molecule to an excited spin-singlet state. The high chemical reactivity of singlet oxygen is employed in technical and medical applications, e.g. photodynamic cancer therapy. We report on a spectroscopic study of electronic energy transfer from excitons confined in silicon nanocrystals to oxygen molecules, being either physisorbed on the nanocrystal surface or present in the gas phase. The broad

photoluminescence spectrum of the nanocrystal assembly probes the transfer of excitation and verifies that nonresonant energy transfer proceeds via multi-phonon emission. At low temperatures a small spatial separation of the interacting species and a long lifetime of triplet state excitons result in a high photosensitization efficiency. Time-resolved measurements reveal the characteristic time of energy transfer to be in the range of microseconds. The controlled modification of the surface termination of the nanocrystals indicates that the energy transfer is mediated by short-range direct electron exchange. Magneto-optical experiments confirm the importance of the spin orientation of the exchanged electrons for the transfer rate. The photosensitization of oxygen molecules in the gas phase at elevated temperature is demonstrated. Additionally, the energy transfer to the oxygen dimer is resolved spectroscopically. Room temperature photooxidation of silicon nanocrystals evidences the direct chemical action of photosensitized oxygen molecules. The photoluminescence degradation of silicon nanocrystals in ambients containing molecular oxygen is shown to be directly related to the singlet oxygen generation and subsequent photooxidation. The presented results establish the utilization of silicon nanocrystals as efficient photosensitizers.

#### 4:30 PM N2.11

##### **Optical Spectroscopy Studies of the Metal Oxide Nanowires.**

Bin Chen<sup>1</sup>, Houtee Ng<sup>1</sup>, Meyya Meyyapan<sup>1</sup>, Tao Tang<sup>2</sup>, Song Han<sup>2</sup>, Chao Li<sup>2</sup>, Daihua Zhang<sup>2</sup>, Jin Wu<sup>2</sup>, XiaoLei Liu<sup>2</sup> and Chongwu Zhou<sup>2</sup>; <sup>1</sup>Ames Research Center, Moffett Field, California; <sup>2</sup>Dept. of E.E.-Electrophysics, NASA University of Southern California, Los Angeles, California.

One-dimensional inorganic nanowires are expected to play important roles in optoelectronic device applications. The unique properties such as grain boundary and high surface area of these nanostructures are clearly different from the corresponding bulk material. Highly orientated ZnO nanowires are studied with Raman and photoluminescence spectroscopy. The high efficiency of the phonon and electron coupling enable us to observe up to 4th order of the Raman scattering. The nanowire orientation relative to the substrate correlated to optical characteristics will be discussed. The results are analyzed and compared with other forms of ZnO such as thin film, polycrystalline powder and solid. The Raman bandwidths and shifts were also studied to reveal the difference in the nanowire to investigate phonon confinement. This confinement is further demonstrated with In<sub>2</sub>O<sub>3</sub> nanowires at 5, 10, 20, 30 nm in diameter. Photoluminescence results show the band gap shifts with the different nanowire sizes. Raman spectroscopy also relate the structural changes related to the strain with the unique properties of nanowire. We will discuss that how the sizes, as well as the defects and the strains possibly induced by the synthesis conditions, influence the band structure and optical phonon properties. We demonstrate the changes of the band gap in the concept of the strain associated with the nanometer structure of nanowires with the correlation between the increased band gap and decreased lattice constants of InN nanowire of 20 nm diameter. Preliminary results from the other Ga<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub>, CdO and GaN nanowires will also be discussed in the context.

#### 4:45 PM N2.12

**CU-dots: A Novel Class of Radiative Nanoparticles.** Hooisweng Ow<sup>1</sup>, Daniel Larson<sup>2</sup>, Prabuddha Sengupta<sup>3</sup>, Barbara Baird<sup>3</sup>, Watt Webb<sup>2</sup> and Ulrich Wiesner<sup>1</sup>; <sup>1</sup>Materials Science and Engineering, Cornell University, Ithaca, New York; <sup>2</sup>Applied and Engineering Physics, Cornell University, Ithaca, New York; <sup>3</sup>Chemistry and Chemical Biology, Cornell University, Ithaca, New York.

This contribution describes the development of a novel class of radiative nanoparticles (CU dots) within the framework of a newly formed Interdisciplinary Research Group (IRG) of the Cornell Center for Materials Research (CCMR). The dots consist of a core containing multiple organic fluorophores surrounded by a dense silica shell. Their size can be varied down to 25 nm diameter with excellent control over size distributions. Flexible synthesis protocols enable incorporation of various classes of dyes thus allowing coverage of the whole UV-VIS spectrum in emission and absorption. The design overcomes major disadvantages of other organic dye based photonic building blocks as well as quantum dots: multiple dyes with enhanced quantum efficiencies render the particles very bright; stable fluorophores and a dense silica shell prevent fast bleaching; the synthesis is short and benign; the particles do not blink; silica is fully integrable with semiconductor processing technology and its surface allows versatile chemical functionalization through well established routes, e.g., for directed assembly or placement of the particles in hierarchical structures or devices. Finally, silica is FDA approved which is important for applications in the life sciences which will be demonstrated. Since active nanoparticles with such architectures were not available before, exciting novel linear and nonlinear photophysical phenomena are expected. Integration of these nanometer scale materials into photonic building blocks are studied within the IRG through incorporation into index matched waveguiding structures

prepared by a variety of advanced 2D and 3D lithographic methods pioneered at Cornell – thereby generating new device functionality and providing unprecedented insights into fundamental science on the nanometer scale.

SESSION N3: Poster Session I  
Chairs: Hedi Mattoussi and Ulrike Woggon  
Monday Evening, December 1, 2003  
8:00 PM  
Exhibition Hall D (Hynes)

### **N3.1**

**STM Electrical Characterization of Nanostructures.** David Danzig and Fredy R. Zypman; Physics Department, Yeshiva University, New York, New York.

Recently, it has been possible to prepare quantum dots and plasmon resonant nanoparticles coupled to optical microcavities. Since surface plasmons extend from deci-nanometer to hecta-nanometers, they can be used to study cell membranes and the corresponding osmosis. The amplitude of plasmons is dependent on the morphology and electronic density of states at the interface. This has two implications. Experimentally it is necessary to have models that allow converting measured data into microscopic information as, for example, processing a current-voltage curve to obtain electronic density of states (DOS). From a theoretical standpoint, there is the need of new frameworks to test extant theories and to further develop them. With this in mind, we will present a new theoretical solution to the problem of mapping Scanning Tunneling Microscopy current-voltage curves into DOS-Energy curves for nanoscale structures. Our model is based on a self-consistent solution to the quantum problem of electrons in the presence of a collection of positive centers. The problem, being simpler than its three dimensional counterparts is solved exactly for DOS and for the current-voltage curves. The main result is that the current-voltage peaks at the position of the energies of the electron in the nanostructure and the positions of the peaks are extremely sensitive to its chemical composition.

### **N3.2**

**Preparation of Tungsten Bronze Nanowires.** Hang Qi, Cuiying Wang and Jie Liu; Chemistry, Duke University, Durham, North Carolina.

One-dimensional (1D) nanostructured materials, such as nanotubes and nanowires have attracted much attention due to their unique properties originating from their high surface area and low dimensionality. Over the past decade, many efforts have been made to synthesize various 1D nanoscale materials including metal, oxide, chalcogenide, nitride and carbide nanorods and nanowires, to name a few. Nanostructured transition metal oxides have been shown to possess many interesting properties that make them promising candidates for a vast range of applications including lithium-ion batteries, catalysts, electrochromic devices, nanoscale lasers and sensors. Tungsten bronze, a crystalline, nonstoichiometric ternary tungsten oxide intercalation compound, is a potentially promising candidate for devices because the optical and electrical properties of tungsten bronze vary with the concentration of the inserted ions [1-3]. However, previous reports about tungsten bronze have only focused on the bulk material; no method has been reported for the preparation of tungsten bronze nanowires, despite the fact that tungsten bronze has been studied for more than a century. Herein, we report two simple techniques to prepare tungsten bronze nanowires. Tungsten bronze nanowires with a diameter of less than 100nm and a length of more than 10 micrometers have been successfully prepared. A Vapor-Liquid-Solid (VLS) mechanism has been proposed to explain the growth of these tungsten bronze nanowires. Ref [1] C. G. Granquist, Handbook of Inorganic Electrochromic Materials, Elsevier, Amsterdam 1995 [2] S.-H. Lee, H. M. Cheong, J.-G. Zhang, A. Mascarenhas, D. K. Benson, S. K. Deb, Appl. Phys. Lett.1999, 74, 242 [3] J.-G. Zhang, D. K. Benson, E. C. Tracy, S. K. Deb, A. W. Czanderna, J. Electrochem. Soc. 1997, 144, 2022

### **N3.3**

**Abstract Withdrawn**

### **N3.4**

**Fabrication of High Quality Photoluminescent II-VI Ternary Nanocrystals.** Ying Qin<sup>1</sup> and Mingyong Han<sup>1,2</sup>; <sup>1</sup>Materials Science, National University of Singapore, Singapore, Singapore; <sup>2</sup>, Institute of Materials Research and Engineering, Singapore, Singapore.

Colloidal ternary CdxZn1-xSe and CdxZn1-xTe nanocrystals have been fabricated by pyrolysis of organometallic reagents through either quasi-one-pot or direct-one-pot synthesis procedures. The CdxZn1-xSe or CdxZn1-xTe nanocrystals could be prepared by introducing excess Zn precursor into the small CdSe or CdTe nuclei which could be synthesized using mixtures of either primary amines (HDA) and

trioctylphosphine oxide (TOPO) or primary phosphonic acid (ODPA) and octadecene (ODE) as the coordinating solvents. The ternary alloy could be formed by keeping vigorously stirring at high temperature (300~320 oC) for several hours. The alloying process has been monitored by UV-Vis and PL spectra which showed a continuously blue-shift of both the first excitonic absorption onset and the bandedge emission peak of the nanocrystals. The blue-shift but not red-shift in the spectroscopy, together with the XRD proof indicate that the fabricated nanocrystals are alloy but not core-shell structure. The different color-emission could be simply tuned by changing the constituent stoichiometry of the alloyed nanocrystals. This method could synthesize blue-color (470 nm) PL emitted CdxZn1-xSe quantum dots in particle size as large as 7 nm with high quantum yield (80 %) and narrow FWHM (21-30 nm). The colloidal nanocrystals could be further transferred into aqueous phase by simply exchange the surface ligands to mercapto group. The optical stability of ternary CdxZn1-xSe in both phases was also explored.

### **N3.5**

**New Zinc and Cadmium Chalcogenide Structured Nanoparticles.** Steven Daniels<sup>1</sup>, Nigel Pickett<sup>1</sup>, Jason Smith<sup>2</sup> and Paul O'Brien<sup>1</sup>; <sup>1</sup>Department of Chemistry, University of Manchester, Manchester, United Kingdom; <sup>2</sup>Physics Division, School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh, United Kingdom.

Novel quantum dot-quantum well (QD-QW) structured nanoparticles have been prepared using a combination of various single-source precursors. The QDQW consists of a ZnS or CdS core, a thin shell of active CdSe, and an outer cladding of CdS/ZnS with an organic capping agent. The overall structures of ca 4nm in diameter were characterized by high-resolution transmission electron microscopy (HRTEM), powder X-ray diffraction (PXRD), photo-luminescence (PL) and UV-vis spectroscopy. In attempts to relieve the considerable strain caused by the lattice mismatch between ZnS and CdSe the Zn(Cd)S/CdSe/ZnS structure was developed to relieve interfacial strain. A graded boundary CdS/ZnS shell was incorporated into the structure, hence the overall structure became Zn(Cd)S/CdSe/CdS:ZnS with the final structure containing very small but significant amounts of CdS. The synthetic routes employed and the resulting QD-QWs optical and electronic properties will be presented.

### **N3.6**

**Complex Band Structure Analysis of the Finite Bias Transport in Silicon Nanowires.** Pawel Pomorski<sup>1</sup>, Brian Larade<sup>3</sup>, Hong Guo<sup>2</sup> and Christopher Martin Roland<sup>1</sup>; <sup>1</sup>Physics, NC State University, Raleigh, North Carolina; <sup>2</sup>Physics, McGill University, Montreal, Quebec, Canada; <sup>3</sup>HP Labs, Palo Alto, California.

With a recently developed ab initio nonequilibrium Greens function formalism, we have re-examined the problem of quantum transport through prototypical Silicon nanowires. Metallic behavior is predicted for very short nanowires, which crosses over to semiconducting behavior as the length of the wire is increased. This behavior finds its origins in the evanescent modes that are present in these finite-sized systems, and which cannot be ignored. A complex band structure analysis makes the contributions of these modes particularly transparent. In addition, nanowires doped with Aluminum atoms were also considered, and issues related to the importance of induced impurity bands and charge transfer are also discussed.

### **N3.7**

**UV Emitting SiC Quantum Dots: Optical Gaps and Thermodynamic Stability.** Fernando Agustin Reboredo<sup>1</sup>, Laurent Pizzagalli<sup>2</sup> and Giulia Galli<sup>1</sup>; <sup>1</sup>PAT, Lawrence Livermore National Lab, Livermore, California; <sup>2</sup>Laboratoire de Metallurgie Physique, Universite de Poitiers, Futuroscope Cedex, France.

We present an extensive, ab-initio theoretical study of the quantum dots (QDs) that could be potentially synthesized from compounds containing C, Si and H. The properties of SiC QDs are compared to alkyl and H terminated Si and diamond QDs. Our first principles study of 1 to 3 nm cubic SiC nanoparticles shows that quantum confinement and surface termination effects are equally important in determining their optical gaps. Independent of size, hydrogenated, unreconstructed C terminated surfaces and (2x1)-reconstructed Si terminated surfaces give rise to the most stable SiC QDs (which, for the same diameter, have gaps differing by as much as 1 to 1.5 eV depending on the surface termination). Unreconstructed, C-terminated SiC dots with diameters smaller than 2 nm have gaps larger than those of C, Si and Ge nanoparticles. We therefore predict that SiC nanostructures could be potential candidate materials for semiconductor based UV light sources and that their band gap can be engineered as a function of their size and surface composition to obtain absorption and emission varying from the UV to the green. On the basis of the total energies obtained theoretically, we discuss the experimental conditions under which each type of dot and surface

termination could be obtained near thermodynamic equilibrium.

**N3.8**  
**CuO Nanowires Synthesized by Heating Copper Substrates in Air.** Xuchuan Jiang and Younan Xia; Chemistry, Univ. of Washington, Seattle, Washington.

A vapor-phase approach has been demonstrated to the facile synthesis of uniform cupric oxide (CuO) nanowires supported on the surfaces of various copper substrates including grids, foils, and wires. In a typical procedure, the substrate was oxidized in air and within the temperature range from 400 to 700 C. Electron microscopic studies indicated that these nanowires had a controllable diameter in the range of 30-100 nm, with lengths of up to 15 micrometers by varying the temperature and growth time. Electron diffraction and high-resolution TEM studies implied that each CuO nanowire was a bicrystal with a twin plane in its middle along the longitudinal axis. CuO has been known as a p-type semiconductor that exhibits a narrow band gap (1.2 eV) and a number of other interesting properties, and it has also been widely used in photovoltaics and batteries. In this presentation, we will discuss the preparation procedure, structural characterization, as well as a possible mechanism responsible for the growth of these nanowires.

**N3.9**  
**Quantum Size Confinement Effects of Excitons in AgX Nanocrystals.** Vladimir P. Oleshko, Materials Science and Engineering, University of Virginia, Charlottesville, Virginia.

Nanocrystalline silver halides exhibit quantum size effects due to contributions to the energy-level structure from carrier confinement and surface states. Using cryo-energy-filtering TEM (EFTEM)/EELS and cryo STEM/EDXS, we show that drastic changes of photophysical properties of  $\text{AgBr}_{0.95}\text{I}_{0.05}$  nanocrystals (NCs) are accompanied with morphological transformations, while their size decreases below 100 nm. The shapes of NCs transform from cubic to sphere-like ones and the size and crystal shape uniformity as well as halide composition uniformity are improving within the normal size distribution. Tuning energy loss allowed visualization of excitations related to excitons at  $E=16\pm 5$  eV energy losses: a weak rim around the crystals extended at distances of about 5 nm away from the particle corresponds satisfactorily to the expected Wannier-Mott exciton size for AgBr. The imaginary part of relative dielectric permittivity,  $\epsilon_2$ , calculated using Kramers-Kronig relations showed an enhanced intensity of the band at 4 eV for  $50\pm 4$  nm-sized NCs as compared to those of  $109\pm 7$  nm in size, while the bands at 7 eV and at 10 eV appear to be suppressed. An increase of the intensity of exciton-assisted direct interband transition at 4 eV ( $\Gamma_8^-$ ,  $\Gamma_6^- \rightarrow \Gamma_6$ ) correlates with the size-dependent enhancement of free exciton luminescence. The non-uniform contrast and dark areas inside NCs observed under filtering were referred to predominant excitations at the surfaces and near the edges. When the fields due to surface losses reach throughout the structure, they couple and the probability for their generation becomes periodic in the NC size. Since electronic sum rules must be satisfied, the surface excitations reduce the strength of the bulk excitations. Coupling of surface and volume losses caused oscillations of the image intensities with the NC size. The appearance of such intensity oscillations obviously represents a size confinement effect on excitations of valence 4d ( $\text{Ag}^+$ ) and 4p ( $\text{Br}^-$ ) electrons induced by the electron beam.

**N3.10**  
**Quantum Conductivity of Spatially Inhomogeneous Systems.** Liudmila A. Pozhar, MLBP, Air Force Research Laboratory, Wright-Patterson Air Force Base, Ohio.

A fundamental quantum-theoretical approach to charge transport in spatially inhomogeneous systems, such as semiconductor quantum dots, artificial atoms, etc., is developed and used to derive explicit expression for the tensorial quantum conductivity, dielectric and magnetic susceptibilities of such systems in terms of the equilibrium two-time temperature Green's functions. This theoretical approach and explicit formulae resulted from it are analyzed and used to develop a concept of virtual (i.e., theory-based, computational) fabrication of sub-nanostructured materials with pre-designed electronic properties. This concept is the first tractable and self-consistent attempt to use the fundamental theoretical predictions and computational manipulations of (1) the system structure, composition, chemistry and topology, and (2) processing parameters (such as temperature, pressure, average density, etc.) to ensure the desired charge transport properties of the synthesized sub-nanomaterials.

**N3.11**  
**Synthesis and Optical Properties of Au-filled Silicon Nitride Nanotubes.** Ming Shien Hu<sup>1</sup>, Lu Sheng Hong<sup>1</sup>, Ching Hsing Shen<sup>2</sup>, Kuei Hsien Chen<sup>2</sup> and Li Chyong Chen<sup>3</sup>; <sup>1</sup>Department of Chemical

Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan; <sup>2</sup>Institute of Atomic and Molecular Science, Academia Sinica, Taipei, Taiwan; <sup>3</sup>Center for Condensed Matter Science, National Taiwan University, Taipei, Taiwan.

Amorphous silicon nitride, is a crucial dielectric material which is extensively used in microelectronic devices as the gate dielectric in thin film transistors, as a charge storage medium in nonvolatile metal-nitride-oxide semiconductor (MNOS) memories and is applied in scanning probe microscope including scanning near-field optical microscope (SNOM) and atomic force microscope (AFM). Silicon-based nanomaterials have been the focus of research interest due to the possibility of fabricating Si-based light emitting devices compatible with the integrated Si circuit. Blue light emission from silica nanotubes has been attributed to the Si-OH complex located on the inner and outer surface of nanotubes. Recently, visible luminescence from amorphous silicon nitride films has been demonstrated. White electroluminescence devices based on a-SiN:H thin films has also been presented. Moreover, cathodoluminescence study on amorphous silicon nitride films also shows a sharp peak at 3.16 eV. Nanometer-sized amorphous silicon nitride particles with a number of dangling bonds on the surface has been demonstrated to be the origin of luminescence. However, either the synthesis or the study on optical properties of silicon nitride nanostructures is rather limited. In this present work, Au@SiN:H nanocables composed of amorphous silicon nitride (a-SiN<sub>x</sub>:H) nanotubes filled with metallic Au cores have been prepared by SiH<sub>4</sub>/NH<sub>3</sub>/H<sub>2</sub>-microwave plasma enhanced chemical vapor deposition (MWCVD) using Au as a catalyst. Cathodoluminescence study on the as-prepared Au-filled silicon nitride nanotubes shows a strong blue light emission. Moreover, shape control of the coaxial Au@SiN:H nanostructures is also demonstrated in this present study. The as-synthesized Au-filled silicon nitride nanotubes may open up new applications in scanning probe microscope and optoelectronic nanodevices.

**N3.12**  
**Enhanced Formation of Light-Emitting Si Nanocrystals by Implantation of P Ions.** Gregory A. Kachurin<sup>1</sup>, Svetlana G.

Cherkova<sup>1</sup>, Vladimir A. Volodin<sup>1</sup>, Anton K. Gutakovskiy<sup>1</sup>, Aleksandr G. Cherkov<sup>1</sup> and David I. Tetelbaum<sup>2</sup>; <sup>1</sup>SO RAN, Institute of Semiconductor Physics, Novosibirsk, Russian Federation; <sup>2</sup>NIFTI, Nizhegorodsky State University, N. Novgorod, Russian Federation.

Si nanocrystals have been formed by implantation of 140 keV Si ions in SiO<sub>2</sub> layers to a dose of  $10^{17}$  cm<sup>-2</sup> with subsequent annealing at 1000 oC and 1100 oC for 2 hours. The nanocrystals luminesced in the visible-IR range due to the quantum confinement effects. Then  $10^{13}$ - $10^{16}$  cm<sup>-2</sup> P ions were implanted at energy of 150 keV to provide the similar depth distributions for Si and P ions. The P implantations were followed by 1000 oC anneals for 30 mins. Photoluminescence, Raman scattering and HREM were used for characterizations. Increase in photoluminescence intensity was observed after the lowest and the highest P doses with the peak position (~780 nm) being unchanged. That pointed to an increase in number of the light sources. Raman spectroscopy and HREM study have approved directly the enhanced formation of light-emitting Si nanocrystals. The lowest P ion dose was equal to ~0.05 P atoms and to several displacements per nanocrystal. Thus, the low-dose effect was ascribed to the radiation induced shock crystallization of stressed Si nano-inclusions. After the highest dose P concentration reached about 0.1 at. % (~50 P atoms / nanocrystal), for which in bulk Si well known impurity enhanced crystallization takes place. Therefore, it is concluded heavy P doping facilitates formation of Si nanocrystals. The obtained results have shown the annealing temperature of 1000 oC is critical for Si nanocrystals formation. Very high crystallization temperature and stresses inside the nano-inclusions are believed to be due to the surface tension. Though there were evidences P atoms present inside Si nanocrystals, there were no indications that additional equilibrium electrons influenced the luminescence.

**N3.13**  
**Chemical Vapor Deposition Growth and Characterization of ZnO Thin Films and Nanorods.** Xiang Liu, Xiaohua Wu, Jun Liu, Hui Cao and Robert P.H. Chang; Materials Research Center, Northwestern University, Evanston, Illinois.

ZnO is a wide band gap semiconductor material. It is a promising candidate for short wavelength optoelectronic devices due to its unique properties. High quality ZnO thin films and different nanostructures of ZnO, including nanocrystalline films, nanowires and nanorods are grown by chemical vapor depositions carried out in a chemical vapor deposition system. The structural and optical properties of ZnO are characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM), photoluminescence (PL) etc. The relations between different growth conditions and the film properties are discussed. The transition of ZnO morphology from epitaxial



continuous thin film to nanorods is presented. Based on systematic studies on ZnO nucleation, a novel two-step growth process is developed to grow well-aligned ZnO nanorods. By controlling the oxygen content in the gas mixture during the nucleation and growth steps, formation of self-assembled ZnO nanorods is achieved without any metal catalysts. High-resolution TEM studies show that ZnO nanorods are single crystals growing along *c* axis. Alignment of these nanorods depends on the lattice compatibilities between ZnO and the substrate. Optical properties, especially the random lasing phenomena of ZnO nanostructures are presented. Room temperature photoluminescence measurement of these ZnO nanorods gives an UV peak at 380 nm with full width at half maximum (FWHM) of 106 meV which is comparable to high quality ZnO films grown by molecular beam epitaxy (MBE). Annealing experiments are done in different atmospheres in order to study the origin of deep level defect emissions in photoluminescence.

### N3.14

**Controlled Production of Core/Shell Aerosol Nanoparticles.** Martin N A Karlsson<sup>1</sup>, Knut Deppert<sup>1</sup>, Lisa Karlsson<sup>2</sup>, Jan-Olle Malm<sup>2</sup> and Brent Alan Wacaser<sup>1</sup>; <sup>1</sup>Solid State Physics, Lund University, Lund, Sweden; <sup>2</sup>Materials Chemistry, Lund University, Lund, Sweden.

An aerosol based method has been developed to produce core-shell nanoparticles. The process control achieved in this method allows for production and deposition of size and composition selected nanoparticles. The particles are formed in a three furnace evaporation/condensation generator. In the first furnace ultra-pure nitrogen is flowed through vapor evaporated from a solid source material. As the gas leaves the furnace, it is cooled causing supersaturation, nucleation, and finally agglomeration of the nanoparticles. The particles, now suspended in the gas, are subsequently electrically charged, classified, and size selected online using standard aerosol techniques. In the second furnace the agglomerates are sintered forming crystalline core particles. The third furnace contains vapor evaporated from another solid source and as the aerosol exits this furnace condensation of the shell material onto the cores occurs and results in core/shell nanoparticles. The shell thickness can be varied depending on temperature, pressure, and flow rate and is independent of core size. Prior to deposition further online analysis and size selection of the core/shell particles is implemented. Deposition is performed in an electrostatic precipitator onto any substrate (e.g. transmission electron microscope grid for further characterization). Our method can be applied to any core shell system as long as congruent evaporation of the individual source materials can be accomplished and alloying does not occur. As an example, we will present results of the formation and online characterization of nanoparticles with gold cores and gallium shells. Structural and compositional characterization, performed by high resolution transmission electron microscopy, will also be presented. Nanoparticles have a wide variety of applications, and as an example of one application we will present results using the Au/Ga core/shell nanoparticles as catalysts for epitaxial semiconductor nanowire growth.

### N3.15

**Nano Zirconium Oxide Colloids Formation Through Ion Exchanged Forced Hydrolysis.** Suresh Kumar Govindaswamy<sup>1,2</sup> and Xiangdong Feng<sup>1</sup>; <sup>1</sup>Ferro Corporation, Independence, Ohio; <sup>2</sup>Chemical Engineering, Clarkson University, Chennai, New York.

Nano crystalline ZrO<sub>2</sub> colloids were prepared by an ion exchanged forced hydrolysis method. The driving force for the hydrolysis was enhanced by anion exchanging the zirconyl nitrate solution to higher pH before heating. The effect of the hydrothermal treatment temperature and the duration of treatment on the synthesized particles size and shape were investigated. The synthesized ZrO<sub>2</sub> particles were about 100nm in sizes with monoclinic structure.

### N3.16

**Structure and Photoluminescence of CuInS<sub>2</sub> Nanowires Synthesized by Chemical Treatment.** Kazuki Wakita<sup>1</sup>, Yoshihiro Miyoshi<sup>1</sup>, Masaya Iwai<sup>1</sup>, Hideto Fujibuchi<sup>1</sup> and Atsushi Ashida<sup>2</sup>; <sup>1</sup>Physics and Electronics, Osaka Prefecture University, Sakai, Osaka, Japan; <sup>2</sup>Applied Materials Science, Osaka Prefecture University, Sakai, Osaka, Japan.

Chalcopyrite semiconductor CuInS<sub>2</sub> is one of the most promising candidates for photovoltaic application, whose optical properties and photoluminescence are well-studied and explained earlier within band structure and symmetry properties of this material<sup>1-3</sup>. On the other hand, a recent attempt to synthesize nanowires of CuInS<sub>2</sub> by a chemical treatment method has also been reported to be successful according to X-ray diffraction and transmission electron microscopy structural data by Y. Jiang *et al.*<sup>4</sup>. However, no reports have been

given so far on the optical properties and luminescence of CuInS<sub>2</sub> nanowires. At the same time, optical studies of nanowires are believed to be useful for comprehensive assessment of the functionalities of CuInS<sub>2</sub> at the nanoscale. Using Cu, In, and S powders as source materials and ethylenediamine as solvent, we synthesized CuInS<sub>2</sub> nanowires with a diameter ranging from 20 to 200 nm, and a purpose to disclose a relation between the conditions of chemical synthesis, nanowires structure and spectral peculiarities of the photoluminescence (PL). Although PL spectra of the nanowired samples were broad occupying spectral range between 1.5 and 2.5 eV, we believe we observed edge emission, broad-band appearance of which was related with above size-distribution of the nanowire diameters. Discussion is given to the quantum effects modifying electronic spectrum of CuInS<sub>2</sub> and leading to the already-mentioned broad-band PL spectra of the nanowires. References 1) K. Wakita, H. Hirooka, S. Yasuda and N. Yamamoto, *J. Appl. Phys.* Vol.83, (1998) p.443. 2) K. Wakita, F. Fujita, N. Yamamoto, *J. Appl. Phys.* Vol.90, (2001) p.1292. 3) K. Wakita, K. Nishi, Y. Ohta, N. Nakayama *Appl. Phys. Lett.*, Vol.80, (2002) p. 3316. 4) Y. Jiang *et al.*, *J. Mater. Res.* Vol. 16, 2001 p.2805.

### N3.17

**Spin and Energy Transfer Between Quantum Dots Without Tunneling.** Alexander O Govorov, Department of Physics and Astronomy, Ohio University, Athens, Ohio.

In most cases, transport of charges and spins in solids occurs via tunneling or injection. This would not be the case for colloidal quantum dots because colloidal nanocrystals strongly confine electrons and do not permit efficient tunnel coupling. However, optically-excited excitons can be transferred between nanocrystals via the long-range Coulomb interaction. Such transport has been observed in several recent experiments and is often referred to as Förster energy transfer. Here we describe a mechanism of spin transfer between quantum dots that does not involve tunneling. Incident circularly-polarized photons create inter-band excitons with non-zero electron spin in the first quantum dot. When the quantum-dot pair is properly designed, this excitation can be transferred to the neighboring dot via the Coulomb interaction with either conservation or inversion of the electron spin. The second dot can radiate circularly-polarized photons at lower energy. Selection rules for spin transfer are determined by the resonant conditions and by the strong spin-orbit interaction in the valence band of nanocrystals. In particular, the resonance between heavy-hole states leads to conservation of spin, whereas the heavy hole - light hole resonance results in spin inversion [1]. Coulomb-induced energy and spin transfer in pairs and chains of dots can become very efficient under resonant conditions and at low temperatures. The electron can preserve its spin orientation even in randomly oriented nanocrystals. [1] A.O. Govorov, *Phys. Rev. B*, in press.

### N3.18

**Synthesis and Characterization of Self-Assembled Cu<sub>2</sub>O Nanodots by MOCVD.** Haitao Zhang<sup>1,3</sup>, Duane M. Goodner<sup>1,3</sup>, Guizhong Zhang<sup>2,3</sup>, Gang Wang<sup>2,3</sup>, Lan Luan<sup>2,3</sup>, Michael J. Bedzyk<sup>1,2,3</sup>, John B. Ketterson<sup>2,3</sup> and Robert P. H. Chang<sup>1,3</sup>; <sup>1</sup>Materials Science and Engineering, Northwestern University, Evanston, Illinois; <sup>2</sup>Physics and Astronomy, Northwestern University, Evanston, Illinois; <sup>3</sup>Materials Research Center, Northwestern University, Evanston, Illinois.

Cuprous oxide (Cu<sub>2</sub>O) is a unique semiconductor, which has been widely studied as a candidate material for the observation of Bose-Einstein condensation (BEC) of its excitons due to their exceptionally long lifetimes. We have grown self-assembled Cu<sub>2</sub>O nanodots on LaAlO<sub>3</sub> (LAO) (100) and MgO (110) substrates using metal-organic chemical vapor deposition (MOCVD) at high temperatures (800°C) and low Cu precursor fluxes (~10<sup>-4</sup> Å/sec). X-ray diffraction (XRD) reveals that these dots grow epitaxially on lanthanum aluminate and magnesium oxide substrates with the relationships: Cu<sub>2</sub>O (100) — LAO (100) with Cu<sub>2</sub>O [001] — LAO [001] and Cu<sub>2</sub>O (110) — MgO (110) with Cu<sub>2</sub>O [001] — MgO [001]. Scanning electron microscope (SEM) images indicate that the dots have an ordered alignment along the surface. The dots are found to be hut shaped, and the dot size changes from about 50nm to 150nm with the increasing deposition time. Ostwald ripening takes place with a further increase of the deposition time. The evolution of the nanodot morphology is more complex than conventional semiconductor systems. A strain-relief-assisted, Volmer-Weber (VW) growth mode is proposed as the growth mechanism of these nanodots. Atomic force microscopy (AFM), synchrotron XRD, and low temperature photoluminescence (PL) measurements on these structures will be presented.

### N3.19

**Single Crystalline Nanowires of Lead Synthesized by Thermally Decomposing Lead Acetate in Ethylene Glycol.** Yuliang Wang, Thurston Herricks and Younan Xia; Univ. of

Washington, Seattle, Washington.

In this presentation, we will report a solution-phase route to the facile synthesis of single crystalline lead nanowires with lateral dimensions as thin as 35 nm and lengths up to 250  $\mu\text{m}$ . The preparation of these lead nanowires were realized by thermally decompose lead acetate in ethylene glycol at latter's boiling temperature. SEM, TEM, High-Resolution TEM, SAED and XRD techniques were used to characterize the overall qualities of the morphology, composition and crystallinity of the as-synthesized nanowires. Experimental evidence also suggested that the growth of these wires were initiated at the surface of large crystals (microscale) that were produced during synthesis. The electron transport measurements on individual nanowires (using the four-probe method) indicate a phase transition to the superconducting state around 7.13 K, a temperature similar to the value (7.20 K) reported for bulk lead. Different from polycrystalline samples, no significant variation in the transition temperature was observed for nanowires with diameters down to 50 nm.

### N3.20

**Si-N nanowire formation at low temperature from Silicon microparticles.** Chandana Rath<sup>1</sup>, Jordi Farjas<sup>1</sup>, Pere Roura<sup>1</sup>, Albert Pinyol<sup>2</sup> and Enric Bertran<sup>2</sup>; <sup>1</sup>Física, Universitat de Girona, Girona, Spain; <sup>2</sup>FEMAN, Física Aplicada i Òptica, Universitat de Barcelona, Barcelona, Spain.

Lately, nanowires have attracted greater attention because of their potential applications in nanoelectronics, photonics and mechanical properties enhancement[1,2]. Consequently, several methods for Si<sub>3</sub>N<sub>4</sub> nanowires synthesis have been set up[3-12]. In a previous work[13], we have reported the formation of a-Si<sub>3</sub>N<sub>4</sub> nanowires. These nanowires were obtained from amorphous Si nanoparticles grown at room temperature by plasma-enhanced chemical vapor deposition (PECVD), and annealed under N<sub>2</sub> at 1673 K during one hour. Nanowires are formed from reactions involving Si, SiO<sub>2</sub> and surrounding N<sub>2</sub> molecules[12], followed by further epitaxial growth. Crystal growth takes place at a temperature much lower than that applied to crystallize amorphous Si-N powder[14]. One remarkable feature is their high aspect ratio; nanowires are 40-100 nm wide and several microns long. Besides, we have recently observed the formation of such nanowires from crystalline silicon microparticles annealed under a mixture of N<sub>2</sub> and O<sub>2</sub> at 1373 K during one hour. In the present work we study the reaction kinetics of nanowire formation from Silicon microparticles and nanoparticles by means of thermogravimetry. The on temperature and gas composition is analyzed as well as the effect of reducing the particle size. Particles and nanowires morphology and structure are analyzed through scanning electron microscopy (SEM), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM) and selected area electron-diffraction (SAED). 1. C. M. Lieber, *Sci. Am.* 285, Iss 3, 58 (2001). 2. E.W. Wong, P.E. Sheehan, C.M. Lieber, *Science*, 277, 1971 (1999). 3. M.J. Wang, H. Wada, *J. mater. Sci.*, 25, 1690 (1990). 4. P. D. Ramesh, K.J. Rao, *J. Mater. Res.* 9, 2330 (1994). 5. K. Kijima, N. Setaka, H. Tanaka, *J. Crystal Growth*, 24/25, 183 (1974). 7. S. Motojima, T. Yamana, T. Araki, H. Iwanaga, *J. Electrochem. Soc.*, 142, 3141 (1995). 8. P.S. Gopalakrishnan, P.S. Lakshminarimham, *J. Mater. Sci. Lett.* 12, 1422 (1993). 9. Y. Inomata, T. Yamane, *J. Crystal Growth*, 21, 317 (1974). 10. H. Chen, Y. Cao, X. Xiang, J. Li, C.C. Ge, *J. Alloys and Compounds*, 325, L1 (2001). 11. T. Hashishin, Y. Kaneko, H. Iwanaga, Y. Yamamoto, *J. mater. Sci.*, 34, 2193 (1999). 12. Y. Zhang, N. Wang, R. he, J. Liu, X. Zhang, *J. Crystal Growth*, 233, 803 (2001). 13. G. Viera, E. Bertran, M.C. Polo, J. Farjas, P. Roura, *MRS Symp. Proc.* 609, A24.5.1-6 (2000). 14. P. Ho, R.J. Buss, R.E. Loehman, *J. Mater. Res.*, 4(4), 873 (1989).

### N3.21

**Pulmonary Bioassay Toxicity Study with Single Wall Carbon Nanotubes in Rats.** David Brian Warheit, Kenneth L Reed and Thomas R Webb; Pulmonary Toxicology, DuPont Haskell Laboratory, Newark, Delaware.

The pulmonary toxicity of intratracheally instilled single wall carbon nanotubes (SWCNT) was evaluated in rats. The lungs of rats were instilled with doses of either 1 or 5 mg/kg of 1) SWCNT; 2) quartz particles (positive control), or carbonyl iron particles (CI- negative control). Phosphate-buffered saline (PBS) + Tween 80 served as additional controls. After exposures, the lungs of PBS and particle-exposed rats were assessed using bronchoalveolar lavage (BAL) fluid biomarkers, cell proliferation methods, and by histopathology of lung tissue at 1 day, 1 week, 1 or 3 months postexposure. Exposures to high dose (5 mg/kg) SWCNT produced mortality in ~15% of SWCNT-instilled rats within 24 hrs post-instillation due to mechanical blockage of the airways. The BAL and cell proliferation results showed that lung exposures to quartz particles but not SWCNT or CI produced persistent lung

inflammation, cytotoxicity and lung cell proliferation. Histopathological evaluations of lung tissue demonstrated that quartz exposure produced dose-dependent inflammation along with foamy alveolar macrophage accumulation and tissue thickening at bronchoalveolar sites. SWCNT produced a non dose-dependent series of multifocal granulomas in the airways, evidence of a foreign tissue body reaction. Due to the agglomerative nature of the SWCNT, the absence of pulmonary biomarkers for inflammation and cell proliferation, the lack of a dose response relationship and nonprogressive time course, as well as the low exposure potential measured in exposure assessment studies at the workplace, the physiological relevance of these results remains to be determined.

### N3.22

**A Generalized and Simple Synthesis of Semiconducting Metal Sulfide Nanocrystals.** Jin Joo, Hyon Bin Na, Taekyung Yu, Jung Ho Yu and Taeghwan Hyeon; School of Chemical Engineering, Seoul National University, Seoul, South Korea.

We report on the synthesis of semiconducting sulfide nanocrystals of cadmium, zinc, lead, and manganese through a simple and inexpensive synthetic process. The current synthetic procedure employs the formation of a metal-surfactant complex followed by aging at high temperature. Metal chlorides and elemental sulfur were used as reactants. Under optimized reaction conditions, multi-grams of nanocrystals can be synthesized without any size selection process. Metal chloride was dissolved in oleylamine to form a metal-oleylamine complex. To the resulting solution, elemental sulfur dissolved in oleylamine was injected at an appropriate temperature. The mixture solution was slowly heated to generate metal sulfide nanocrystals. Monodisperse cube-shaped PbS nanocrystals with particle sizes ranging from 6 nm to 13 nm were synthesized. 8 nm sized spherical ZnS nanocrystals were synthesized using zinc chloride and sulfur as reagents. When CdCl<sub>2</sub> and sulfur were reacted in oleylamine, we were able to synthesize CdS nanocrystals with various sizes and shapes including bipods, tripods, and spheres. We synthesized MnS nanocrystals with various sizes and shapes. Uniform-sized and rod-shaped MnS nanocrystals were synthesized. Novel bullet-shaped and hexagon-shaped MnS nanocrystals were also synthesized. The synthetic procedures developed in the present study offer several very important advantageous features for the synthesis of sulfide nanocrystals. First, the synthetic process is environmentally friendly and inexpensive, which employs inexpensive and non-toxic reagents such as metal chlorides and sulfur. Second, the synthetic method is a generalized process that can be applied to synthesize different kinds of sulfide nanocrystals having various particle sizes and shapes. Third, the process allows uniform sized sulfide nanocrystals to be obtained without a further size selection process and the indications are that scale-up can be achieved relatively easily.

### N3.23

**Microstructure and superconductivity of Au/ Sn/Au junction nanowires.** Jinguo Wang<sup>1,2</sup>, Mingliang Tian<sup>1,2,3</sup>, Thomas E. Mallouk<sup>1,2,4</sup> and Moses H-W. Chan<sup>1,2,3</sup>; <sup>1</sup>Materials Research Institute, Pennsylvania State University, University Park, Pennsylvania; <sup>2</sup>The Center for Nanoscale Science (MRSEC), Pennsylvania State University, University Park, Pennsylvania; <sup>3</sup>Department of Physics, Pennsylvania State University, University Park, Pennsylvania; <sup>4</sup>Department of Chemistry, Pennsylvania State University, University Park, Pennsylvania.

Superconductivity in confined system has attracted considerable attention. When the sample size is smaller than the Ginzburg-Landau coherence length, the properties were expected to change remarkably. However, the nature of the superconductivity in 1D was debated so far due to the limitation of the sample quality or nano-contacts with normal metal probes. Here, we studied the relationship between microstructures and superconductivity of Au/ Sn/Au nanowires by X-ray diffraction, HRTEM, STEM, EDS and electrical transport measurement. The results showed that the Au/Sn nano-junctions contain three intermetallic phases AuSn, AuSn<sub>2</sub> and AuSn<sub>4</sub> depending on the length of Sn, and the formation of the intermetallic compounds is dependent on the diffusion of Au+ in Sn under the electric field. These results indicate that the interface of Au/Sn nano-junction must be considered seriously in the transport measurement. Mechanisms of the diffusion of Au in Sn wire and the formation of intermetallics as well as the effect on the superconductivity were discussed briefly.

### N3.24

**Synthesis of Water-Soluble Gold Nanoparticles: A Mechanistic Study.** Andrew B Schoch, Robert G Shimmin and Paul V Braun; Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois.

1 to 5 nm water-soluble gold nanoparticles were synthesized in a modified one-phase Brust synthesis with thiolated, methyl-terminated, poly(ethylene glycol) (Me-PEG-SH). The Me-PEG-SH capping agents

were synthesized from Me-PEG of molecular weights 350, 550, 750 and 2000 in a Mitsunobu reaction followed by acidic solvolysis to achieve the thiol end group functionalization and were realized in over 90% purity. In addition to the study of these four lengths of Me-PEG-SH, the synthesis was conducted at 1:1, 1:2, 1:4 and 1:8 thiol:gold molar ratios. This two variable system has allowed us to conduct a thorough investigation of the mechanism for formation of these particles and the impact on particle size and population distribution. At various molecular weights of the Me-PEG-SH and thiol:gold ratios a bimodal diameter distribution was observed. These results can be rationalized for the first time in terms of the difference in diffusivity between gold atoms complexed and not complexed to the polymeric thiols of varying molecular weight.

### **N3.25**

**A Novel thick film quantum confined  $Y_2O_3:Eu^{3+}$  nanophosphor synthesized by post-dispersion treatment at low temperature.** Sung-Jei Hong, Min-Gi Kwak, Dae-Gyu Moon, Won-Geun Kim and Jeong-In Han; Information Display Research Center, Korea Electronics Technology Institute, PyungTaek-Si, KyungGi-Do, South Korea.

In this work, a novel thick film quantum confined nanophosphor could be synthesized by using post-dispersion treatment at low temperature. The thick film nanophosphor is consistent of sub nano scaled  $Y_2O_3$  particle confining  $Eu^{3+}$  ion in. To synthesize the thick film,  $YO_2:Eu^{3+}$  precursors with concentration of 7wt% Eu were prepared. Then, post-dispersion treatment of the precursors was done under low temperature. The post-dispersion treatment is to prevent the agglomeration between the precursors by mixing the organic dispersing agent with them before heat-treatment. We printed and heat-treated the mixture of the precursor and the organic dispersing agent on silicon wafer. We attempted to optimize the size of the nanophosphor by varying temperature of the post treatment ranging from 500°C to 900°C. The particle size was observed with high resolution transmission electron microscope (HRTEM). As a result, the size was proportional to the temperature. In case of the post treatment at 700°C, the size was about 20nm. As the temperature was raised to 900°C, the size also coarsened to 30nm. However, the quantum confined nanophosphor could be synthesized by suppressing the temperature of the post treatment below 500°C. The mean size of the particle was 4nm, and even maximal size did not exceed 6nm. Also, the confined Eu was uniformly distributed with deviation below 0.4wt%. The phase analysis of the quantum confined nanophosphor with X-ray diffractometer (XRD) indicated that the main phase structure was cubic having preferred orientation of  $\langle 222 \rangle$ ,  $\langle 440 \rangle$ , and  $\langle 400 \rangle$ . Only a small amount of monoclinic structure was detected in the crystallite. The photo-luminescence (PL) properties of the quantum confined nanophosphor was characterized with monochromatic systems of which wavelengths are between 200nm and 800nm. As a result, the main PL peak was detected at 612nm, and the novel thick film quantum confined nanophosphor with red color could be fabricated in this work.

### **N3.26**

**Synthesis of Free-Standing III-V Semiconductor Nanowires.** Juan Carlos Gonzalez<sup>1</sup>, Humberto Rodriguez Gutierrez<sup>2</sup>, J Bettini<sup>1</sup>, D Zanchet<sup>1</sup>, F.M. Matinaga<sup>3</sup>, M.A. Cotta<sup>2</sup> and D. Ugarte<sup>1</sup>; <sup>1</sup>Laboratorio Nacional de Luz Sincrotron, Campinas, SP, Brazil; <sup>2</sup>LPD/DFA, Instituto de Fisica Gleb Wataghin, UNICAMP, Campinas, SP, Brazil; <sup>3</sup>Departamento de Fisica, Universidade Federal de Minas Gerais, Belo Horizonte, MG, Brazil.

The concept of using nanostructures as building blocks for electronic and optoelectronic devices has attracted great interest in recent years. In this work, we describe our recent results on the growth of free-standing III-V nanowires (NW's) by using a Chemical Beam Epitaxy System (CBE). III-V NW's were grown using Au and Ag nanoparticles (NP's) acting as seeds within a vapor-liquid-solid growth process. Nanoparticles were spun on the surface of epitaxial-ready (100) InP substrates. Using this method NW's of approximately 50 nm in diameter and longer than 5000 nm can be obtained. Moreover, nanowire morphology strongly depends on the growth conditions. Size and spatial distribution of the seed particles were characterized by High Resolution Transmission Electron Microscopy (HRTEM) and Atomic Force Microscopy (AFM). The morphology, crystal structure and chemical composition of the wires were studied by Field Emission Scanning Electron Microscopy (FE-SEM), TEM and Energy Dispersive X-ray Spectroscopy (EDS). Photoluminescence spectroscopy (PL) was used to investigate the optical properties of the NW's. Nanowire crystalline quality was verified by electron diffraction and TEM, they were found to be mainly oriented along the [100] and [110] crystallographic directions. InP/InAs/InP one-dimensional heterostructures were also obtained by this method.

### **N3.27**

**Synthesis and Characterization of Colloidal Chalcopyrite**

**Nanoparticles.** Stephanie L. Castro<sup>1</sup>, Sheila G Bailey<sup>2</sup>, Ryne P Raffelle<sup>3</sup>, Kulbinder K Banger<sup>1</sup>, Stephen Fahey<sup>3</sup> and Aloysius F Hepp<sup>2</sup>; <sup>1</sup>Ohio Aerospace Institute, Cleveland, Ohio; <sup>2</sup>NASA Glenn Research Center, Cleveland, Ohio; <sup>3</sup>Physics, Rochester Institute of Technology, Rochester, New York.

We discuss the synthesis of colloidal nanoparticles of  $CuInS_2$  and  $CuInSe_2$  formed by the thermal decomposition of the single-source precursors  $(PPh_3)_2CuIn(SET)_4$  and  $(PPh_3)_2CuIn(SePh)_4$ , respectively, in a non-coordinating solvent in the presence of thiolated ligands. As synthesized, the nanoparticles are dispersible in non-polar organic solvents and exhibit room-temperature fluorescence. Absorption and fluorescence emission spectra show a large shift in the band-gap to higher energy, indicative of quantum confinement. The effects of surface ligand exchange on the optical properties of the nanoparticles will be also be discussed. The nanocrystals can be dispersed in water by altering the surface ligands; electrostatic layer-by-layer assembly of the particles into dense films is investigated by tapping-mode AFM. TEM and AFM are used to investigate the size and morphology of the nanoparticles.

### **N3.28**

**The Effect of Gate Geometry on the Charging Characteristics of Metal Nanocrystal Memories.** Anirudh Gorur-Seetharam, Chungho Lee and Edwin C Kan; School of Electrical and Computer Engineering, Cornell University, Ithaca, New York.

Metal nanocrystal memories are promising candidates for aggressive scaling of conventional nonvolatile floating-gate devices. The discrete storage nodes of metal nanocrystals provide advantages in the design tradeoffs of write/erase voltage and retention time [1]. The effective potential well designed by metal work function engineering enables the use of an oxide in the direct tunneling regime, where the oxide endurance in repeated write/erase cycles dramatically improves. Unlike conventional continuous poly-Si floating gate designs, the charge flux in and out of the nanocrystals can take advantage of the fringing fields from the control gate to minimize the write/erase time. This paper is a study of the influence of fringing fields along the perimeter of the control gate on the charging characteristics of metal nanocrystal memories. We varied the control gate geometry of a metal-oxide-semiconductor (MOS) capacitor with embedded metal nanocrystals. Three types of gate geometries, namely a circle, a square and a quasi-fractal pattern with the same area have been considered. Devices have been fabricated on both p-type and n-type silicon substrates. The nanocrystals are formed by a self-assembly process on an ultra-thin tunnel oxide (2-3 nm). Scanning transmission electron microscopy (STEM) studies were used to verify the thickness of the tunnel oxide and the formation of the nanocrystals. Convergent beam electron diffraction (CBED) studies were used to confirm the crystallinity of the embedded metal dots. Scanning electron micrographs have been used to obtain the nanocrystal size distribution and area density [2]. Electrical characterization has been carried out by capacitance-voltage and current-voltage measurements. We will present the geometry-dependent effect on the electrical write/erase characteristics, which can be explained by the differences in the fringing fields. References: [1] Z. Liu et al, 'Metal nanocrystal memories. I. Device design and fabrication', IEEE Trans. Electron Devices, vol. 49, no: 9, Sept. 2002. [2] C. Lee et al, 'Investigation on process dependence of self-assembled metal nanocrystals', MRS 2002 Fall meeting.

### **N3.29**

**Incorporation of highly luminescent quantum dots in hybrid organic-inorganic sol-gel film.** Alessandro Martucci<sup>1</sup>, Craig Bullen<sup>2</sup> and Paul Mulvaney<sup>2</sup>; <sup>1</sup>Ingegneria Meccanica - S. Materiali, Universita' di Padova, Padova, Italy; <sup>2</sup>School of Chemistry, University of Melbourne, Melbourne, Victoria, Australia.

In the last 20 years different approaches have been developed to synthesize colloidal nanocrystals of controlled composition, size, shape and surface states. The organometallic approach is probably the most studied one and highly luminescent semiconductor nanoparticles can be prepared with controlled size, size distribution and surface states. Such colloids have many potential applications (photovoltaic, display, laser, etc.) but for many of these applications it is necessary to embed the colloids in solid matrix with controlled composition. In this paper we describe a method for transferring semiconductor quantum dots produced in non-polar solvents by organometallic approach in sol-gel film.  $ZrO_2$ -ORMOSIL film have been homogeneously doped with different semiconductor quantum dots (both core CdSe and core-shell CdSe@CdS). Both the absorption and the emission properties of the semiconductor nanocrystals are slightly affected by the incorporation into the sol-gel matrix. The  $ZrO_2$  content of the hybrid organic-inorganic films can be easily adjusted to get film with sufficiently high refractive index for the realization of semiconductor doped waveguides for optical integrated devices.

### **N3.30**

#### **Tunable Optical Absorption of Composites of Nanocrystalline Copper Prepared by *in situ* Chemical Reduction within a Cu<sup>2+</sup>-Polymer Complex.** Cheng Huang<sup>1</sup>, Gang Huang<sup>2</sup> and C.Z.

Yang<sup>3</sup>; <sup>1</sup>Materials Research Institute and Electrical Engineering Department, The Pennsylvania State University, University Park, Pennsylvania; <sup>2</sup>Electronic Materials and Thin Film Devices Division and Physics Department, Suzhou University, Suzhou, Jiangsu, China; <sup>3</sup>Department of Polymer Science and Engineering, Nanjing University, Nanjing, Jiangsu, China.

Research on nanocrystalline materials and the physics behind their properties have attracted considerable attention. A number of physical and chemical techniques have been used to synthesize different nanomaterials and nanocomposites. Optical absorption characteristics of composites containing nanosized metals or semiconductors have been investigated for potential applications in nonlinear optics and photonic crystals and also to understand the effect of particle size on the band gap of the material concerned. These materials show a large third-order nonlinear susceptibility. A polymer-matrix nanocomposite containing copper particles has been prepared by *in situ* chemical reduction within a polymer-metal complex solid film. The copper particle size in the order of 10 nm is controlled by the initial content of the metal ions in the complex. Their fractal pattern and the value of the fractal dimension indicate that there exists a cluster-cluster aggregation process in the present system. Optical absorption spectra of copper-polymer nanocomposites show distinct plasma absorption bands and quantum size effect in the samples. More studies on optical properties of composites containing nanosized metals are within the Drudeframe on the basis of Mie theory, but the electrons behave in a wavelike rather than a particlelike way as the particle size decreases to below 10 nm, and the classical Drude model should be modified considering the quantum confinement effect. In this paper, the calculated blueshift of the resonance peak based on a quantum-sphere model (QSM) proposed by Huang and Lue, gives remarkable agreement with the experimental data as the size of copper particles embedded in the polymer becomes smaller.

### **N3.31**

#### **Proximity Effects in Nanostructures.** Tony Alvarez, Dongbo Li, Xiaojun Li and Dawn Bonnell; University of Pennsylvania, Philadelphia, Pennsylvania.

One of the often unstated goals in reducing the sizes of structures to the nanometer regime is to put more function, i.e. more structures, in a smaller area. However, when closely positioned, a nanostructure will affect the properties of another that is within the range of the relevant interaction parameter. At one limit this is quantum mechanical entanglement and quantum computing. A classical example is the operation of a Scanning Gate Microscope on a molecular wire. This paper will present systematic studies of the effect of local electromagnetic field variations on the response functions of metal and oxide nanoparticles, and organic molecular wires. Nanostructures are arranged and contacted with ferroelectric lithography and/or e-beam lithography. Local properties are determined with first and second harmonic scanning probes, such as scanning surface potentiometry and scanning impedance spectroscopy. These results quantify the effects of cross interactions, or proximity effects, in these nanostructures. Implications in terms of limitations on device configuration and potential for unexpected properties will be discussed.

### **N3.32**

#### **Large Quantity Free-standing ZnO nanowires.**

Debasish Banerjee<sup>1</sup>, J.Y. Lao<sup>1</sup>, D. Z. Wang<sup>1</sup>, J. Y. Huang<sup>1</sup>, B.

Kimball<sup>2</sup>, D. Steeves<sup>2</sup>, M. Sennett<sup>2</sup> and Z.F. Ren<sup>1</sup>; <sup>1</sup>Physics, Boston college, Chestnut Hill, Massachusetts; <sup>2</sup>Natick Soldier Center, Natick, Massachusetts.

Free Standing ZnO nanowires were grown in gram quantity on graphite flakes (used as collector) using vapor transport and condensation approach. Fine graphite flakes were used to promote the growth. The graphite flakes are the key for large quantity yield and were easily removed, evidenced by x-ray diffraction patterns, by oxidation. The percentage yield (weight ratio of graphite flakes before experiment to that of after experiment) of the nanowire has been controlled throughly by controlling the various growth parameters like pressure, temperature inside the tube furnace and also the amount of graphite in the original mixture of the source to study the vapor transport mechanism and growth process. The scanning and transmission electron microscopes studies show that the diameter and length on the nanowires vary from 20 to 100 nm and 0.5 to 15 micrometer, respectively. A very high yield of more than 200% was achieved with 40% of ZnO in original source converted to nanowires. A detailed study of photoluminescence spectra of ZnO nanowires grown on both graphite flakes and substrate has been demonstrated in

contrast to commercial ZnO powder. A reduced band-edge ultraviolet (380nm) and deep-band (520nm) emission have been observed. This study reveals a route to grow several other vapor transport oriented nanostructure synthesis in large quantity and to understand its transport mechanism and growth process.

### **N3.33**

#### **Fabrication of Ordered Array of Colossal Magnetoresistance Oxides by a Novel Sol Gel Template Aided Synthesis.**

Shantha Shankar Kundapura, Sohini Kar and Arup Kumar Raychaudhuri; Physics, Indian Institute of Science, Bangalore, Karnataka, India.

We have fabricated linear array of nanowires of technologically important colossal magnetoresistive oxide lanthanum calcium manganite, La<sub>0.67</sub>Ca<sub>0.33</sub>MnO<sub>3</sub> (LCMO) using anodized alumina (AAO) membranes with pore diameters 20 nm and 100 nm as templates. We will discuss the novel polymeric sol-gel process using metal nitrates in aqueous solution and employing ethylene glycol as the polymerizing agent, developed by us as a general method for the fabrication of nanowires and nano powders of advanced multicomponent oxides. X-ray powder diffraction, energy dispersive x-ray analysis (EDAX) and selected area electron diffraction (SAED) studies indicated that single phase, stoichiometric polycrystalline nanowires could be prepared by heat treating to temperatures as low as 700°C and the wires stabilize in orthorhombic phase. The morphology of the wires is studied by scanning electron microscopy on the array of nanowires embedded in the alumina matrix and also transmission electron microscopy on the nanowires freed from the membranes. We will also present the interesting magnetic properties exhibited by these nanowires. The AC susceptibility data indicated that the nanowires exhibit an enhanced ferromagnetic-paramagnetic transition temperature as compared to single crystal of the same composition and the shift in T<sub>c</sub> is dependent on the nanowire diameter (about 100 K in case of 100 nm wire and 120 K in case of 20 nm wire). The enhancement in T<sub>c</sub> could be attributed to the lattice volume contraction in the nanowires, as seen by X-ray analyses. Our findings demonstrate that nanowires of manganites could be a new medium for studying intricate physics in these fascinating materials.

### **N3.34**

#### **Synthesis of Boron Nitride Nanolayers Encapsulating Fe Fine Particles and Unique Boron Nitride Tubes.** Hisato Tokoro<sup>1</sup>,

Shigeo Fujii<sup>1</sup> and Takeo Oku<sup>2</sup>; <sup>1</sup>Hitachi Metals Co., Ltd., Kumagaya, Japan; <sup>2</sup>Osaka University, Ibaraki, Japan.

Metal nanoparticles such as Fe, Co and some Fe-based alloys have been studied in view of physical or industrial interest. Unfortunately they are easy to be oxidized in the air. A coating technique has been a most promising technique to cope with this problem. We have developed a new technique, which synthesized Boron Nitride (BN) encapsulating Fe fine particles, a few hundreds diameter, as well as BN related tubes. Fe<sub>2</sub>O<sub>3</sub> (Hematite) and B particles are used as starting materials and then mixed well, followed by annealing at around 1473 K under nitrogen atmosphere. Weight ratio of Fe<sub>2</sub>O<sub>3</sub> to B is varied according to desired magnetic properties. X-ray diffraction measurement reveals that Fe<sub>2</sub>O<sub>3</sub> is reduced to Fe and hexagonal BN is produced. Products exhibit a soft magnetic properties showing a low coercivity of about 1.5 kA/m and a Ms of from 83 Am<sup>2</sup>/kg to 32 Am<sup>2</sup>/kg depending on the weight ratio at sample preparation. A high resolution transmission electron microscope (HRTEM) is employed to observe morphology of the products. It makes it clear that a few hundred nanometers size Fe particles are created and their surfaces are coated with BN nanolayers, which have a few nm in thickness and well-oriented (002) plane stacking. It is noted that unique BN tube-like materials are also synthesized as products. They have cylindrical structures of about 100 nm in outer diameter with multi-layers of (002) plane, and some have Fe nanoparticles at the edge. A detailed study and a reaction mechanism will be presented at the conference.

### **N3.35**

#### **Spectroscopic Studies of InP Nanocrystals Synthesized**

**Through a Fast Reaction.** Madalina Furis<sup>1</sup>, David J. MacRae<sup>2</sup>, Yudhisthira Sahoo<sup>2</sup>, Alexander N. Cartwright<sup>1</sup> and Paras N. Prasad<sup>2</sup>; <sup>1</sup>Electrical Engineering, University of Buffalo, Buffalo, New York; <sup>2</sup>Chemistry, University of Buffalo, Buffalo, New York.

The method of preparing semiconductor nanocrystals by hot colloidal route has now been established for well over a decade. The II-VI system has witnessed more success than the III-V because of the subtle difference in the polarity of their surfaces. Synthesis of InP quantum dots in a hot co-ordinating solvent such as triethylphosphine oxide typically has required a long reaction time, upward of 72 hours, which may be followed by size sorting to get fairly monodisperse nanocrystals. However, using different precursors in a non-coordinating solvent cuts down the reaction time to about five

percent of the usual time. In this paper, we show that by starting with carefully chosen precursors, it is possible to use a fast reaction time to obtain quantum dots of InP. Furthermore, we will present detailed structural and spectroscopic characterization of the obtained nanoparticles. Specifically, the photoluminescence (PL) spectra collected from these nanocrystals exhibits a sharp feature associated with the band-edge emission and a broad infrared background associated with deep surface traps emission. The emission efficiency of the as-grown nanocrystals varies between 0.3% to 2% from sample to sample. After undergoing an HF etching process, the emission efficiency increases to 18% and the emission associated with deep surface states is eliminated from the PL spectrum. Time-resolved photoluminescence (TRPL) experiments conducted at room temperature on the as-grown and HF-etched nanocrystals show that before etching the PL intensity decay is multiexponential, with a fast (3ns) component independent of wavelength, associated with the non-radiative recombination processes. The etching process effectively eliminates the non-radiative component and the PL decay can be fitted with a single exponential decay characterized by long (60ns) lifetimes. We tentatively associate these long lifetimes with the recombination of carriers from spin-forbidden states.

### **N3.36**

**Electrical Transport in Disordered Arrays of Molecularly-linked Au Nanoparticles.** Paul Trudeau, Alioska Escorcia and Al-Amin Dhirani; Chemistry, University of Toronto, Toronto, Ontario, Canada.

We explore the electrical characteristics of disordered films of strongly coupled, molecularly-linked gold nanoparticles as a function of particle size and temperature. Films are prepared by successive exposure of functionalized substrates to first gold nanoparticle sol and second an organic bifunctional cross linker. This approach allows film conductivity to be tuned over several orders of magnitude. Differential conductivity ( $dI/dV$ ) measurements vs. voltage and temperature exhibit features which track a number of competing transport mechanisms. Low conductivity films show thermally activated transport, while the temperature dependence of  $dI/dV$  in highly conducting films is characteristic of phonon scattering. A model describing electrical measurements is presented.

SESSION N4: Synthesis, Shape Control and Characterization  
Chairs: Mounji G. Bawendi and Horst Weller  
Tuesday Morning, December 2, 2003  
Room 302 (Hynes)

### **8:30 AM \*N4.1**

**Fluorescence, Magnetism and Self-Assembly of Nanoparticles.** Horst Weller, Institute of Physical Chemistry, University of Hamburg, Hamburg, Germany.

This talk describes recent developments in the synthesis and characterization of semiconductor and metal nanoparticles. Results on the growth kinetics and the control of size, shape and surface chemistry will be addressed. We present Monte Carlo simulations of an ensemble of growing particles showing that optimal conditions for the synthesis of highly luminescent semiconductor nanoparticles are maintained if the exchange rate of monomers at the particles' surface is high during the growth. Energy-dependent XPS studies allow to distinguish surface atoms from bulk atoms within the nanoclusters. It is shown how chemical surface modification yielding highly luminescent particles removes surface states which are obviously responsible for non radiative recombination. Examples for 2D and 3D self assembly of nanoparticles are given. We report on the formation of colloidal crystals from semiconductor and magnetic nanoparticles. In mixtures of differently sized particles complex 3D structures are formed which are analog to inter-metallic phases. Self assembly of ZnO nanoparticles in solution finally leads to the formation of single crystalline nanorods via oriented attachment.

### **9:00 AM N4.2**

**Synthesis and Characterization of Colloidal EuS Nanocrystals.** Margaret A. Hines and Gregory D. Scholes; Chemistry, University of Toronto, Toronto, Ontario, Canada.

Europium sulfide is of interest to researchers for its ferromagnetic properties. Particle size affects the optomagnetic and luminescent properties of the material. Additionally, its optical properties are dominated by a 4f to 5d electronic transition of the Eu(II) ion. Therefore, EuS nanocrystals are a desired material of fundamental interest as well as for their potential use in device applications. We will report the synthetic details for the preparation of nanocrystalline EuS. The synthesis involves injection of a single source precursor, Europium Diethyldithiocarbamate complexed with 1,10-Phenanthroline, into a hot organic coordinating solvent that

induces thermal decomposition and results in EuS colloidal particles. Characterization of the physical, optical, and magnetic properties will be reported.

### **9:15 AM N4.3**

**Synthesis and Characterization of Transition Metal Doped Semiconductor Nanoparticles.** Khalid M. Hanif, Donny Magana and Geoffry Strouse; Chemistry and Biochemistry, UC Santa Barbara, Santa Barbara, California.

Throughout the past decade a considerable effort has been put forth to synthesize high quality quantum dots. This interest has arisen due to the interesting size dependant optical properties that arise from these materials. One of the main challenges facing researchers today is to dope these materials in a controllable manner. In the bulk and in the thin films procedures exist which allow much control over the doping. Most of the efforts put forth in doping nanoparticles have shown that the dopant ion mainly resides on the surface of the quantum dots or only low levels of core doping can be achieved. The main focus of our research has been the doping of CdSe with Co(II), Mn(II) and Cu(I). These materials have been characterized by a variety of techniques including XRD, ICP-AE, TEM, SQUIDS and high field magneto-photoluminescence. Our studies have shown that we are able to attain high levels of core doping >5% in our quantum dots. As a result these materials have exhibited interesting magnetic properties.

### **9:30 AM N4.4**

**Molecular Scale Single Crystal Silicon Nanowires; Synthesis, Reaction, and Structure Characterization.** Yue Wu<sup>1</sup>, Jie Xiang<sup>1</sup>, Carl J. Barrelet<sup>1</sup>, David C. Bell<sup>2</sup> and Charles M. Lieber<sup>1,3</sup>; <sup>1</sup>Dept. Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts; <sup>2</sup>Center for Imaging Mesoscale Structures, Harvard University, Cambridge, Massachusetts; <sup>3</sup>Division of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts.

Silicon nanowires (SiNWs) represent attractive building blocks for diverse applications in nanoelectronics because their composition, size, and electronic properties, can be rationally controlled during synthesis. For example, studies to date have shown that silicon nanowires can be used as building blocks for field-effect transistors (FETs), logic gates, sensors, and memory arrays. In particular, SiNWs FETs have already demonstrated transport characteristics that match or exceed conventional planar devices fabricated by top-down approaches and such performance can be improved further with reduction of silicon nanowire diameter to the molecular scale. Here we report the controlled synthesis of single crystal silicon nanowires with diameters approaching the molecular scale. The importance of surface energies in determining growth direction of the molecular scale silicon nanowires has been addressed through modeling and using cross-sectional transmission electron microscopy studies. Moreover, recent studies of the reactions and transformation of these nanowires will be discussed. The implications of these results for fundamental and applied studies will be discussed.

### **9:45 AM N4.5**

**Aligned Growth of ZnO Nanorods-Nanobelts Structures.** Puxian Gao<sup>1,2</sup> and Zhong Lin Wang<sup>1,2</sup>; <sup>1</sup>School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia; <sup>2</sup>Center for Nanoscience and Nanotechnology, Georgia Institute of Technology, Atlanta, Georgia.

By using thermal evaporation through a vapor-liquid-solid process, several forms of aligned nanowires and nanobelts of ZnO have been synthesized. The Sn particles produced by the reduction of SnO<sub>2</sub> act as catalysts; a string of single crystal nanowire-nanobelt junction array is formed due to a fast growth of ZnO nanowires along [0001] and the subsequent "epitaxial" radial growth of the ZnO nanoribbons along the six <01-10> directions around the nanowire. Uniform orientation aligned ZnO nanorods have been grown epitaxially on the (0001) ZnO substrate via homo-epitaxial growth. The nanorods grow along [0001] with Sn particles at the tips. By controlling the experimental conditions, ZnO nanowires, with lengths from hundreds of nanometer to tens of micrometers and diameter of 50 nanometers, have been grown. Using the (01-10) ZnO single crystal as substrate, the aligned [01-10] nanobelts are formed, which follows the same growth process as the nanowire-nanobelt junction arrays. The "liana" shaped nanostructures and aligned ZnO nanorods/nanobelts could be candidates for fabricating ultrahigh sensitive sensors and opto-electronic devices. [1] Z.W. Pan, Z.R. Dai and Z.L. Wang, Science, 291 (2001) 1947-1949. [2] P. X. Gao and Z. L. Wang, J. Phys. Chem., 49(106) (2002) 12653-12658. \* Corresponding author: zhong.wang@mse.gatech.edu

### **10:30 AM \*N4.6**

**Nanocrystal and Nanowire Synthesis in Supercritical**

**Solvents.** Brian A Korgel, Tobias Hanrath, Lindsay Pell, Forrest Davidson and April Schrick; Chemical Engineering, University of Texas at Austin, Austin, Texas.

We have been developing synthetic methods for semiconductor nanocrystals and nanowires using high temperature supercritical solvents. By pressurizing the solvent, temperatures ranging from 350C to as high as 750C can be explored for nanostructure synthesis. Using this approach, we have synthesized Group IV nanocrystals, silicon and germanium, which due to their strong covalent bonding, require high temperatures to crystallize the nanocrystal cores. Furthermore, the high temperatures promote covalent bonding between various ligands and the nanocrystal surface. These nanocrystals exhibit optical properties, such as visible photoluminescence, due to quantum confinement effects, which will be presented. We have also utilized these reaction conditions to synthesize silicon, germanium, and gallium arsenide nanowires through a supercritical fluid-liquid-solid (SFLS) synthesis that uses sterically-stabilized gold nanocrystals to seed nanowire growth through a mechanism analogous to the vapor-liquid-solid (VLS) growth process in the gas phase. In this process, the reaction temperature must exceed the metal:semiconductor eutectic temperature, which is approximately 360C for Au:Si and Au:Ge, and 460C for Au:GaAs. We have developed a high-throughput continuous reactor capable of producing grams/day of nanowires. The nanowires can be doped and surface-modified in situ and then isolated, processed, and deposited onto substrates to make single nanowire electrical devices. We will present the transport measurements on Si, Ge and GaAs nanowires.

#### 11:00 AM N4.7

**Shape control of III-V semiconductor nanocrystals: Synthesis and properties of InAs quantum rods.** Uri Banin, ShiHai Kan, Assaf Aharoni, Taleb Mokari and Itzhak Shweky; Department of Physical Chemistry and the Center for Nanoscience and Nanotechnology, the Hebrew University of Jerusalem, Jerusalem, Israel.

Dimensionality and size are two governing factors for the properties of semiconductor nanostructures with both basic and applied significance. Here we report on a general method for growth of soluble nanorods. The method is useful in particular for III-V semiconductors with cubic lattice, where the utilization of surfactant-controlled rod-growth is not easily realized. The growth takes place via the solution-liquid-solid mechanism where proper precursors are injected into a coordinating solvent. Centrifugation is used for separation of rod-fractions with different lengths. The reaction is demonstrated for InAs, InP and GaAs. Focusing on InAs rods as a model system, we examined the effects of the type of metal catalyst, and the tuning of reaction conditions with respect to temperature, concentration, catalyst content and reaction time. The structural properties of the rods were characterized by transmission electron microscopy, X-ray diffraction and energy dispersive X-ray spectroscopy. Rods have a cubic lattice and grow mainly along the [111] direction. The relative gold content decreases in shorter rods suggesting metal depletion as a cause for limiting the growth. Room and low temperature optical spectroscopy measurements show that the band-gap shifts to the red upon increasing rod length revealing strong quantum confinement along the long axis in InAs rods. This provides spectral coverage of the near-IR range relevant for telecommunication applications with a useful feature of polarized emission. Emission intensity also decreases with increased rod-length. These length dependent properties manifest the transition from 0D to 1D quantum confined systems.

#### 11:15 AM N4.8

**Colloidal Synthesis and Self-assembly of Magnetic Alloy Nanocrystals.** Elena V. Shevchenko, Dmitri V. Talapin and Horst Weller; Institute of Physical Chemistry, University of Hamburg, Hamburg, Germany.

Colloids of crystalline magnetic alloys (CoPt<sub>3</sub>, FePt, CoPd<sub>2</sub>) with particle size tunable from ~3 nm to ~15 nm were synthesized using a novel stabilizing agent - 1-adamantane carboxylic acid. As-prepared nanocrystals have narrow (std. div. 5-7%) size distributions. The possibility of the nanocrystal shape control, e.g. controllable formation of spherical, cubic CoPt<sub>3</sub> nanocrystals as well as CoPt<sub>3</sub> nanowires was demonstrated. Precise control of the nanocrystal size can be achieved via tuning the balance between the nucleation and growth rates. The experimental results indicate that nucleation of investigated alloy nanocrystals occurs through the formation of the transition metal clusters which play the role of nucleation seeds for further growth of the alloy. Formation of these clusters is the rate-limiting step for the entire nucleation process, whereas the concentration of platinum or palladium precursors does not affect the nucleation rate. The magnetic measurements revealed a strong dependence of the blocking temperature, coercivity and saturation magnetisation on the nanocrystals size and the nature of surface capping ligands. The monodisperse magnetic alloy nanocrystals can

self-assemble into one-, two- and three-dimensional superstructures. Perfectly faceted macroscopic (~20-30 microns) colloidal crystals of magnetic alloy nanocrystals (CoPt<sub>3</sub> and PtFe) have been obtained for the first time. HRSEM investigation showed the long range ordering of the nanocrystals with the coherence over ten microns. Novel self-assembled superstructures of magnetic nanocrystals were observed under external magnetic fields. In relatively weak magnetic fields (~0.01-0.02 Tesla) shape control of growing colloidal crystals can be achieved.

#### 11:30 AM \*N4.9

**Nanowires by Solution-Phase Methods.** Younan Xia, Chemistry, University of Washington, Seattle, Washington.

We have recently developed a number of solution-phase methods for the large-scale synthesis of highly crystalline nanowires with uniform and well-controlled diameters. Typical examples include trigonal-phase selenium, trigonal-phase tellurium, silver, gold, and lead. The morphological control was achieved through the use of an appropriate capping reagent or the intrinsically anisotropic structure of a solid. This talk will explicitly discuss the procedures of these methods, with a focus on the mechanism and potential extension of each approach. I will also discuss the electrical transport, photoelectric, and surface plasmon resonance properties associated with these one-dimensional nanostructures.

#### SESSION N5: QD-Bioconjugates: Design and Use in Biotechnological Applications

Chairs: A. P. Alivisatos and C. J. Murphy  
Tuesday Afternoon, December 2, 2003  
Room 302 (Hynes)

#### 1:30 PM \*N5.1

**Use of Quantum Dot Bioconjugates For Long-Term Imaging of Live Cells.** Sanford M. Simon and Jyoti Jaiswal; Laboratory of Cellular Biophysics, The Rockefeller University, New York, New York.

Semiconductor nanocrystals (quantum dots, QDs) are a promising alternative to organic dyes for fluorescence-based applications. We will cover a variety of approaches that we have developed for using DHLA capped QDs for specific labeling and long-term imaging of proteins in living cells and living cells in organisms. Live cells labeled with QDs using these approaches can be imaged for several days as they grow and develop, allowing harnessing the potentials and promises of QDs for live cell imaging.

#### 2:00 PM N5.2

**Near-Infrared In Vivo Imaging Using Quantum Dots.**

Sungjee Kim<sup>1</sup>, Mounqi G. Bawendi<sup>1</sup>, Yong Taik Lim<sup>2</sup>, Alec M.

DeGrand<sup>2</sup>, Jaihyoung Lee<sup>2</sup>, Akira Nakayama<sup>2</sup>, John V. Frangioni<sup>2</sup>, Edward G. Soltesz<sup>3</sup>, J. Anthony Parker<sup>3</sup>, Tomislav Mihajlic<sup>3</sup>, Rita G. Laurence<sup>3</sup>, Delphine M. Dor<sup>3</sup> and Lawrence H. Cohn<sup>3</sup>;  
<sup>1</sup>Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts; <sup>2</sup>Radiology, Beth Israel Deaconess Medical Center, Boston, Massachusetts; <sup>3</sup>Surgery, Brigham and Women's Hospital, Boston, Massachusetts.

Near-infrared is the most viable optical probe for noninvasive in vivo biomedical imaging, and quantum dots can be ideal nano-emitters for such applications. In order to demonstrate the design flexibilities and unique capabilities of quantum dots for near-infrared in vivo imaging, we report various in vivo imaging including sentinel lymph nodes and coronary vessels. We introduce new type-II band engineering and oligomeric phosphine surface coating for the quantum dot surface. The type-II engineering allows the flexibility to simultaneously optimize the quantum dot size and the emission wavelength, resulting in deep photon penetrations and maximal absorption cross sections. The oligomeric phosphine coating provides excellent colloidal aqueous stabilities while minimizing the hydrodynamic size. Using these quantum dots in small and large animal models, we show how real-time near-infrared in vivo imaging can be performed.

#### 2:15 PM N5.3

**Multiplexed Resonance Energy Transfer Using single Quantum Dot Donors in Multi-Dye Labeled Quantum Dot Protein Conjugates.** Aaron R Clapp<sup>1</sup>, Igor L Medintz<sup>2</sup>, J Matthew Mauro<sup>2</sup> and Hedi Mattoussi<sup>1</sup>; <sup>1</sup>Optical Sciences Division, Naval Research Laboratory, Washington, District of Columbia; <sup>2</sup>Center for Bio/Molecular Science and Engineering, Naval Research Laboratory, Washington, District of Columbia.

We have shown that QDs are excellent Förster resonance energy transfer (FRET) donors due to their size-tunable spectral properties and the ability to accommodate several acceptor molecules in a regular arrangement on the QD surface.<sup>1-3</sup> In the present study, a

single population of water-soluble CdSe-ZnS QDs was coated with several genetically engineered maltose binding proteins (MBP) that were covalently pre-labeled with various fluorescent dyes; a 1:1 dye to protein labeling ratio was used. The distinctly labeled proteins were immobilized on the QD surface using a non-covalent self-assembly scheme to create hybridized QD-protein conjugates. By keeping the total number of proteins per QD-conjugate fixed and varying the fraction of dye-labeled MBP we were able to simulate multiple specific binding events at the QD surface. Due to the close proximity and favorable spectral overlap, energy from the photo-excited QDs was transferred non-radiatively to the surface immobilized dyes, and unique signatures in the composite photoluminescence spectra were measured. The collected spectra were deconvoluted and compared with previously measured individual spectra to extract actual binding ratios for each MBP-dye species. While FRET was efficient between the QD and organic dyes, inter-dye energy transfer was negligible due to low direct excitation. These results build on the advantages offered by QD donors where interactions with multiple energy acceptors provide enhanced FRET signal. It further opens up the possibility of achieving multi-analyte FRET-based sensing assemblies using a single QD population as energy donor. 1. A.R. Clapp et al., submitted. 2. I.L. Medintz et al., submitted. 3. E.R. Goldman et al., J. Am. Chem. Soc. 124, 6378 (2002).

#### 2:30 PM N5.4

**Nanoscale Quantum Dot-Bioconjugate Sensors Based on Förster Resonance Energy Transfer.** Igor L Medintz<sup>1</sup>, Aaron R. Clapp<sup>2</sup>, Hedi Mattoussi<sup>2</sup>, Ellen R Goldman<sup>1</sup> and J Matthew Mauro<sup>1</sup>; <sup>1</sup>Center for Bio/Molecular Science and Engineering, Code 6910, U.S. Naval Research Laboratory, Washington, District of Columbia; <sup>2</sup>Optical Sciences Division, Code 5611, U.S. Naval Research Laboratory, Washington, District of Columbia.

Designing and developing robust recognition-based sensing assemblies that can quantitatively monitor interactions of a target molecule with a biological receptor are the focus of many research groups. We have developed prototype quantum dot (QD)-bioconjugate sensors and employed them to detect soluble analytes. We utilized E. coli maltose binding protein (MBP) and targeted its preferred substrate, maltose. To form the nanosensor assembly, MBP was first coordinated to the QD surface and a displaceable  $\beta$ -cyclodextrin conjugated-QSY9 dark quencher was allowed to bind to the centrally located sugar-binding site of MBP, resulting in quenching of the QD photoluminescence. This result is due to fluorescence resonance energy transfer (FRET) between the QD donor at the center of the conjugate and the proximal QSY9 quencher. Added maltose displaced the  $\beta$ -cyclodextrin-QSY9 conjugate, and increased QD photoluminescence in a systematic and concentration dependent manner. Analysis of the QD PL recovery provided a measure of the dissociation constant for maltose and demonstrated sensor sensitivity and specificity. Derivatives of this sensor were developed that utilize a 2-step FRET mechanism to overcome inherent QD donor-acceptor distance limitations. Insight from this prototype sensor allowed us to derive a structural model of the QD-bioconjugate and propose designs for single QD multi-analyte FRET sensors. This format can be applied to other receptor proteins or bio-recognition units and may facilitate development of a new generation of hybrid QD-based biosensors.

#### 2:45 PM N5.5

**Single gold nanoparticle light scattering used for ultra-sensitive biomolecular recognition.** Thomas A. Klar<sup>1</sup>, Gunnar Raschke<sup>1</sup>, Thomas Franzl<sup>1</sup>, Stefan Kowarik<sup>1</sup>, Carsten Sonnichsen<sup>1</sup>, Jochen Feldmann<sup>1</sup>, Konrad Kurzinger<sup>2</sup> and Alfons Nichtl<sup>2</sup>; <sup>1</sup>Photonics and Optoelectronics Group, Sektion Physik, Ludwig-Maximilians-University Munich, Munich, Bavaria, Germany; <sup>2</sup>Roche Diagnostics GmbH, Penzberg, Bavaria, Germany.

Molecular recognition is a key technology in clinical diagnostics as well as in pharmacology. Here we present a new approach based on spectroscopy of single gold-nanoparticles functionalized with biotin for the detection of streptavidin binding events.[1] Sub wavelength sized noble metal nanoparticles show a pronounced resonance in their scattering spectra for visible light. This particle plasmon resonance is decisively influenced by the dielectric properties of the particles' nanoenvironment. Molecular binding events alter this nanoenvironment and can therefore be deduced from a shifted resonance position in the scattering spectrum. Our molecular sensor is based on changing and measuring the spectrum of an individual nanoparticle. This single nanoparticle assay is sensitive enough to detect spectral shifts of only a few meV and hence is able to detect binding events of molecules with a molecular weight of only 52 000 D (streptavidin) under physiological conditions. Further advantages of single nanoparticle assays compared to ensemble assays are that in principle only a small absolute number of analyte molecules is needed and that they feature the possibility of miniaturization and hence massive parallelization. [1] G. Raschke et al., Nano Letters, in press (2003).

#### 3:00 PM N5.6 Abstract Withdrawn

#### 3:30 PM N5.7

**Control of Biomolecular Activity by Nanoparticle Antennas.** Kimberly Hamad-Schifferli, Mechanical and Biological Engineering, MIT, Cambridge, Massachusetts.

Interfacing to biological molecules has faced many challenges. Traditional methods involve extraction of the biomolecule and placement on a two-dimensional surface, which is difficult to extend to manipulation in complex biological environments such as cells and tissues. In order to address these and other challenges, we have developed a means of controlling biomolecular activity in solution by metal nanocrystals. The nanocrystals are covalently linked to a DNA or protein and inductively heated by a radiofrequency alternating external magnetic field. Heat is transferred from the nanocrystal to the biomolecule, resulting in partial denaturation and thus suppression of activity. Induction heating of nanocrystals linked to DNA oligonucleotides in solution has been shown to dehybridize the DNA in a manner that is both localized and reversible. This technique has potential to control a wide range of biological functions, as well as foreseeable in vivo applications in diagnosis and therapeutics.

#### 3:45 PM N5.8

**Design of Water-Soluble Quantum Dots with Novel Surface Ligands for Biological Applications.** Harry Tetsuo Uyeda<sup>1</sup>, Igor L Medintz<sup>2</sup> and Hedi Mattoussi<sup>1</sup>; <sup>1</sup>Division of Optical Sciences, U.S. Naval Research Laboratory, Washington, District of Columbia; <sup>2</sup>Center for Bio/Molecular Science and Engineering, U.S. Naval Research Laboratory, Washington, District of Columbia.

Recently, the utility of stable water-soluble luminescent colloidal quantum dots (QDs), either pure or conjugated to biomolecular receptors, has been demonstrated in biosensing and cellular imaging applications.<sup>1,2</sup> However, due to the process in which these materials are synthesized and their inorganic QD core, the surface properties limit the ability to manipulate them in aqueous environments and apply simple covalent conjugation techniques to prepare stable versatile QD-bioconjugates. We have designed a series of organic oligo- and poly-ethylene glycol based surface capping ligands that allow for QD manipulation in aqueous media over a wide pH range. We utilized readily available thioctic acid and various oligo- and poly-ethylene glycols in simple esterification schemes, followed by reduction of the dithiolane to produce multi-gram quantities of capping substrates. To form the water-soluble QD assembly, native trioctylphosphine and trioctylphosphine oxide (TOP/TOPO) capped nanocrystals were mixed with an excess of the desired surface ligand and incubated to displace the TOP/TOPO molecules. This readily resulted in aqueous dispersions that were homogeneous and stable in various pH ranges over an extended period of time. Furthermore, the luminescence of such systems was preserved and essentially independent of pH. Mixed surface capping strategies utilizing ratios of dihydrolipoic acid to the pegylated dihydrolipoic acid were also prepared. Such systems allow one to covalently attach amine containing biomolecules to nanoparticle systems bearing carboxylates, employing known coupling agents, such as (dimethylamino)propyl-3-ethyl-carbodiimide (EDC). This design and conjugation strategy may facilitate the development of a new generation of QD-bioconjugate based biosensors which can be directly utilized in cellular imaging and other studies. 1. J. Jaiswal et al. Nature Biotech. 21, 47, 2003. 2. E.R. Goldman et al. J. Am. Chem. Soc. 124, 6378, 2002.

#### 4:00 PM N5.9

**Characterization and biological labeling of QD-micelles.** Byung Ryool Hyun<sup>1</sup>, Stephen Clark<sup>1</sup>, Joel S Tabb<sup>2</sup>, Chris Chase<sup>2</sup> and Frank W Wise<sup>1</sup>; <sup>1</sup>Applied physics, Cornell University, Ithaca, New York; <sup>2</sup>Agave BioSystems, Ithaca, New York.

We characterized the CdSe/ZnS quantum dots (QDs) encapsulated in n-poly(ethylene glycol) phosphatidylethanolamine (PEG-PE) micelles by two-photon fluorescence correlation spectroscopy (FCS). From the measured diffusion coefficient, the hydrodynamic radius was calculated by Stokes-Einstein equation to be 21 nm. This indicates hydrodynamic sizes approximately 2.5 times larger than the physical size of the QD-micelles as determined by electron microscopy. This is similar to values obtained with other water-soluble QDs. For biolabeling applications, biotinylated QD-micelles were prepared by incorporating small percentages of biotinylated PEG-PE into the QD-micelles. Conjugation of biotinylated QD-micelles to streptavidin-coated microspheres was readily achieved. This opens the way for simplified bioconjugation and fluorescent labeling experiments. Images of bacteria and mammalian cells labeled with the QD-micelles will be presented.

4:15 PM N5.10

#### Biofunctional Magnetic Nanoparticles for Pathogen

**Detection.** Hongwei Gu<sup>1</sup>, Chenjie Xu<sup>1</sup>, R. K. Zheng<sup>2</sup>, P. L. Ho<sup>3</sup>, X. X. Zhang<sup>2</sup> and Bing Xu<sup>1</sup>; <sup>1</sup>Chemistry, Hong Kong University of Science & Technology, Kowloon, Hong Kong; <sup>2</sup>Physics, Hong Kong University of Science & Technology, Kowloon, Hong Kong; <sup>3</sup>Microbiology, University of Hong Kong, Pokfulam Road, Hong Kong.

Magnetic nanoparticles have attracted considerable attentions in the past few years because of their importance in both science and technology (e.g., to promise a new media in ultrahigh-density magnetic recording or memories). Comparing to magnetic beads (with the sizes of 1~5  $\mu\text{m}$ ) conventionally used in biological separation, magnetic nanoparticles promise new phenomena and applications because of their high surface/volume ratio and easiness to enter cells. Despite of rapid advances in the research of magnetic nanoparticles aimed at microelectronics, the applications of magnetic nanoparticles in biomedicine just emerge. In order to develop a quick assay for detecting bacteria at ultra-low concentration for environmental monitoring and clinical diagnosis, we designed a system that combines two kinds of interactions: 1) magnetic dipole interaction that allows magnetic nanoparticles to aggregate under magnetic field; and 2) specific ligand-receptor interaction that offers tight binding between magnetic nanoparticles and bacteria when the ligands covalently bond to the surfaces of the magnetic nanoparticles. To prove the concept, we attached vancomycin (Van), an antibiotic, to the surface of FePt nanoparticles (~4 nm in diameter). Vancomycin can bind to the terminal peptide, D-Ala-D-Ala, on the cell wall of a Gram-positive bacterium via hydrogen bonds, and previous studies have demonstrated that multivalent Vans have high affinities toward the multiple D-Ala-D-Ala receptors. Our designed vancomycin and FePt magnetic nanoparticle conjugates (FePt-Van) exhibited high sensitivity to the bacteria, and it can capture bacteria at concentration as low as ~4 cfu/mL within one hour, which is an order of magnitude more sensitive than the current best assay for bacteria detection based on luminescence (detection limit: 180 cfu/mL). We envision that this process may ultimately lead to the instant and sensitive detection of pathogens (e.g., bacteria, viruses) at ultra-low concentrations without time consuming procedures, such as incubation or amplification by polymerase chain reaction.

4:30 PM N5.11

#### Nanoparticles for tumor imaging via targeted delivery.

Hoon Choi<sup>1</sup>, I-Wei Chen<sup>1</sup>, Seok Rye Choi<sup>2</sup> and Hank F. Kung<sup>2</sup>; <sup>1</sup>Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania; <sup>2</sup>Department of Radiology, University of Pennsylvania, Philadelphia, Pennsylvania.

Targeted delivery is a highly desirable strategy for enhancing therapeutic efficacy and reducing drug dosage and toxicity. Folate receptor is a glycosylphosphatidylinositol(GPI)-anchored, high affinity folate binding protein overexpressed in various types of human tumors. It functions by capturing folate to feed rapidly dividing cancer cells. Folate conjugates are delivered into the cell via a process called receptor-mediated endocytosis, in which a folate molecule bound to the receptor is first delivered into the cell as a group, then the folate is released and the receptor recycled back to the surface to capture more folate. In this study, nanometer-sized fluorescent superparamagnetic folate-conjugated iron-oxide (IO) colloids were prepared for targeted delivery to folate receptor-expressing cells. Dextran-coated drug carriers have long circulation time because of their ability to escape capture by macrophage cells. Therefore, we employed nanometer-sized hydrophilic dextran-coated IO particles as bare colloids to ensure long circulation, and we subsequently tethered folic acid and fluorescent imaging agents onto the (coated) iron oxide surface via coupling reactions. KB cells, a human nasopharyngeal epidermal carcinoma cell line expressing surface receptors for folic acid, were used as the delivery target. The FITC on folate-conjugated IO nanoparticle allowed direct visualization of the nanoparticle uptake into tumor cells. Internalization of IO nanoparticles in KB cells only occurs when they are conjugated to folate and when the folate receptors are accessible on the cells. The endocytosis was rapid, as indicated by the short incubation time in our experiments. The results support the notion that the endocytosis of the nanoparticles into tumor cells via folate receptors was sufficiently efficient *in vitro*. A quantitative analysis of cell uptake by FACS as well as *in vivo* tumor imaging was also performed

4:45 PM N5.12

#### Multifunctional Nanomaterials and Nanosystems.

Cengiz Sinan Ozkan<sup>1</sup>, sathyajith Ravindran<sup>2</sup>, Sumit Chaudhary<sup>3</sup>, Mihrimah Ozkan<sup>2,3</sup> and Huajian Gao<sup>4</sup>; <sup>1</sup>Mechanical Engineering, University of California at Riverside, Riverside, California; <sup>2</sup>Chemical Engineering, University of California at Riverside, Riverside, California; <sup>3</sup>Electrical Engineering, University of California at Riverside, Riverside, California; <sup>4</sup>Max Planck Institute, Stuttgart, Germany.

Conventional nanofabrication strategies must be augmented by new techniques including self assembly methods in order to truly take advantage of the quantum nature of novel nanoscale devices and systems and permit the use of these properties for real applications in a larger system (> 10 nm and < 1000 nm). In this paper, a novel technique for the fabrication of nano-assemblies of carbon nanotubes (CNT) and quantum dots (QD)-formation of CNT-QD conjugates will be described. CNTs are primarily functionalized with carboxylic end groups by oxidation in concentrated sulfuric acid. Thiol stabilized QDs in aqueous solution with amino end groups were conjugated to carbon nanotubes using the ethylene carbodiimide coupling reaction. Next, I will discuss the possibilities of using carbon nanotubes for encapsulation and mass transport. Fourier transform infrared spectroscopy data for the chemical modification of carbon nanotubes and scanning and transmission electron microscopy images of the nanobuilding blocks and the nanotube filling process will be presented. Potential applications of our studies include the fabrication of novel electronic and biophotonic devices and biosensors.

SESSION N6: In-Room Poster Session II - QDs and Nanoparticles for Biological Applications

Chairs: A. P. Alivisatos and C. J. Murphy

Tuesday Afternoon, December 2, 2003

4:00 PM

Room 302 (Hynes)

**N6.1**

#### Periodic templated arrays of nanoparticles for optical sensing of chemical and biological analytes.

Joseph Miragliotta and Jennifer L Sample; Johns Hopkins University Applied Physics Laboratory, Laurel, Maryland.

There have been numerous attempts over the past two decades to identify a substrate protocol that provides high enhancement and reproducibility for surface enhanced Raman scattering (SERS). In this paper, we discuss a substrate system that incorporates a crystallization process in the presence of both latex spheres and silver or gold nanoparticles. The resulting periodic array provides a SERS activity that can be utilized for the detection of many low-molecular weight analytes. We find that the choice of latex sphere surface chemistry allows coarse selectivity for analyte detection from complex sample matrices. We report identification of toxins from mixtures, which may be important for quick sensing of small molecular biological warfare agents.

**N6.2**

#### Optimization of Quantum Dot - Nerve Cell Interfaces.

Jessica Winter<sup>1</sup>, Brian Korgel<sup>1</sup> and Christine Schmidt<sup>2</sup>; <sup>1</sup>Chemical Engineering, University of Texas at Austin, Austin, Texas; <sup>2</sup>Biomedical Engineering, University of Texas at Austin, Austin, Texas.

Nerve cells communicate by passing electrical signals through extensions from their cell bodies. Micron-scale devices such as microelectrode arrays and field effect transistors have already been used to externally manipulate these signals. However, these devices are almost as large as the cell body of the neuron. In order to make functional electrical connections to nerve extensions or their component ion channels that propagate signals, it will be necessary to utilize increasingly smaller components. We propose the use of semiconductor quantum dots, which can be optically activated, as a potential means of perturbing the nerve membrane potentials. As a first step, we have created qdot-neuron interfaces with cadmium sulfide quantum dots. The qdots may be attached to cells either non-specifically or through selected interactions exploiting biorecognition molecules attached to the qdot particle surface. We have investigated the effect of altered synthesis conditions including pH, concentration, reactant ratio, ligand length, ligand R group, and ligand concentration on the nature and quality of qdot-cell binding. We discuss the effect of these altered synthesis conditions on particle fluorescence intensity and color. Additionally, we studied the interaction of these particles with cells and determined that larger particles are more likely to bind non-specifically than smaller particles produced with the same amount of passivating ligand. It is possible this results from reduced surface area coverage of passivating chemical. Finally, we have produced particles passivated with the biorecognition peptide CGGGRGDS in the absence of other chemical stabilizers and characterized their surfaces using NMR and IR. We have shown that particle fluorescence and intensity may be controlled with synthesis conditions. However, these changes will also affect non-specific binding of particles to the cell surface. In order to optimize qdots for cell labeling, it is critical to balance these effects to achieve the desired particle fluorescence intensity, fluorescent emission color, and cell binding capability. These findings will not only enable us to optimize particles for the creation of electrical interfaces, but



also demonstrate important concepts for qdot use as fluorescent cell labels. Understanding the effect of reaction conditions on the optical properties of qdots produced as well as their relationship to cell binding, will allow future researchers to optimize qdots for labeling of specific cellular components.

### **N6.3**

**Semiconductor Quantum Dots for Studies of Sphingolipid Metabolism.** Stephen Clark<sup>1</sup>, Byung-Ryool Hyun<sup>1</sup>, Watt W. Webb<sup>1</sup>, David G. Russell<sup>2</sup> and Frank W. Wise<sup>1</sup>; <sup>1</sup>Applied Physics, Cornell University, Ithaca, New York; <sup>2</sup>Microbiology and Immunology, Cornell University, Ithaca, New York.

Semiconductor quantum dots (QDs), particularly CdSe/ZnS dots, are becoming important fluorescent probes for biological applications. In addition to having a large absorption cross-section and high fluorescence quantum yield, QDs have been shown to be sensitive to charge and electric field. The sphingolipids are an important class of lipids involved in the signal transduction pathways that mediate cell growth, differentiation, and death. Sphingosine is the most common backbone of the sphingolipids, and phosphorylation of sphingosine is an important step in sphingolipid metabolism. Using a method similar to the encapsulation of QDs with phospholipids, QDs have been encapsulated with sphingosine. Initial characterization indicates that there is no significant loss in fluorescence quantum yield. Fluorescence correlation spectroscopy indicates that is very little clustering of the encapsulated QDs. Upon phosphorylation, the sphingosine becomes charged. We report on the encapsulation method and the detection of phosphorylation with the QDs.

### **N6.4**

**Photoluminescence properties and zeta potential of water-dispersible CdTe nanocrystals.** Masanori Ando, Chunliang Li and Norio Murase; Photonics Res. Inst., AIST, Ikeda, Japan.

Semiconductor nanocrystals attract much attention due to their size-dependent color in photoluminescence (PL). A promising method for application is to incorporate them into glass matrices because glass has superior transparency, chemical durability and robustness against UV irradiation. For a purpose to incorporate them in glass by a sol-gel method, dispersibility of nanocrystals in water is of principal importance. The PL is strongly dependent on the surface state of the nanocrystals both in solution and solid matrix. This work reports the zeta potential of CdTe nanocrystals dispersed in water as functions of PL intensity, pH, and dissociation ratio of a surfactant used. The knowledge thus obtained is used to prepare highly luminescent glass phosphor. CdTe nanocrystals showing green PL (diameter: 3nm) were synthesized in aqueous solution by a previously reported method in the presence of a surfactant (thioglycolic acid (TGA)). We measured the zeta potential and PL intensity as a function of pH of the colloidal solution. The green PL intensity gradually increased when the pH decreased from 10 and reached the maximum at pH5.1. On the other hand, the relative ratio of the dissociation form of the carboxyl group in TGA decreased dramatically below pH5 accompanied by a significant decrease of the absolute value of zeta potential. This shows that the particles are stable only in a basic region. Therefore, we chose an alkoxide having an amino group for a matrix. The amino group has a good affinity to TGA as well as promotes the sol-gel reaction. As the result, the CdTe nanocrystals have been dispersed finely in the glass matrix without a deterioration of PL intensity. This study is a part of Nanotechnology Glass Project sponsored by NEDO, Japan.

### **N6.5**

**Photoluminescence and Magnetic Properties of Laser Synthesized  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> Nanoparticles for Biological Assay Applications.** Ashley Harvey<sup>1</sup>, Valerie Leppert<sup>1</sup>, Subhash Risbud<sup>1</sup> and Ian Kennedy<sup>2</sup>; <sup>1</sup>Chemical Engineering and Materials Science, University of California, Davis, California; <sup>2</sup>Mechanical and Aeronautical Engineering, University of California, Davis, California.

Iron oxide nanoparticles were synthesized with the goal of creating magnetic nanoparticles with visible luminescence. The laser ablation of an iron metal target in an oxygen environment produced particles with diameters ranging from 10 to 50 nm, as imaged with high-resolution transmission electron microscopy. Selected area electron diffraction showed the particles to be  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, and energy dispersive x-ray spectroscopy showed that the particles were 60 atomic percent oxygen and 40 atomic percent iron, confirming  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>. Fluorescence and absorption spectroscopy were performed and photoluminescence was detected in the wavelength range of 350-450 nm. Magnetic separation experiments demonstrated that the nanoparticles could be separated from solution, allowing them to be used in a combined optical and magnetic bioassay format. The origins of this novel photoluminescent and magnetic material, as well as possible applications in biological assays are discussed.

### **N6.6**

**Stable Aqueous Suspensions of Magnetic Nanoparticles for Biomedical Applications.** Alireza Goodarzi<sup>2,3</sup>, Ruth A. Mistretta<sup>2,3</sup>, Mark T. Swihart<sup>2,1</sup>, Yudhisthira Sahoo<sup>2,3</sup> and Paras N. Prasad<sup>2,3</sup>; <sup>1</sup>Chemical Engineering, University at Buffalo (SUNY), Buffalo, New York; <sup>2</sup>Institute for Lasers, Photonics, and Biophotonics, University at Buffalo (SUNY), Buffalo, New York; <sup>3</sup>Chemistry, University at Buffalo (SUNY), Buffalo, New York.

Magnetic nanoparticles have potential applications in medical diagnostics and therapy. A thermodynamically stable suspension at optimum pH and temperature is vital for both *in vitro* and *in vivo* investigations of these biomedical applications. A facile synthesis route has been developed to prepare well-dispersed and homogeneous aqueous suspensions of Fe<sub>3</sub>O<sub>4</sub> (magnetite) nanoparticles, typically 6 to 12 nm in diameter. To do so, Fe<sub>3</sub>O<sub>4</sub> is precipitated from a mixture of Fe<sup>2+</sup> and Fe<sup>3+</sup> salts, then treated with citric acid to form a stable dispersion in water. This gives a homogeneous suspension of Fe<sub>3</sub>O<sub>4</sub> nanoparticles that can easily withstand a 0.5 T external magnetic field without precipitating. Transmission electron microscopy, magnetization measurement by a superconducting quantum interference device, FTIR spectroscopy, thermogravimetric studies and other tools are employed to characterize the nanoparticles and the binding of the citric acid to them. These particles will ultimately be used to selectively bind to tumor cells for therapeutic purposes. Tumor-specific hormones can be attached to them via the carboxyl groups of the citric acid. Application of a large DC magnetic field (as in an MRI machine) can then cause magnetocytolysis of the tumor cells. This talk will focus on the synthesis and characterization of the aqueous suspensions of magnetic nanoparticles, in the context of the requirements for these biomedical applications.

SESSION N7: Silicon Nanocrystal and Nanowires

Chairs: Philippe Fauchet and Brian Korgel

Tuesday Evening, December 2, 2003

Room 302 (Hynes)

### **8:00 PM N7.1**

**Optical gain and lasing with silicon quantum dots: is it possible?** Philippe M Fauchet, ECE, University of Rochester, Rochester, New York.

Achieving optical gain in silicon has long been thought to be impossible because of the low radiative recombination efficiency due to the indirect gap of silicon and competition from Auger recombination and free carrier absorption. Since 2000, there have been numerous reports of optical gain in waveguide structures containing silicon quantum dots in the 2 to 4 nm range prepared by different techniques. However, there are inconsistencies between the various experimental reports and theoretical studies have not conclusively identified the possible mechanisms for gain. In this presentation, a critical review of the current status of optical gain in silicon quantum dots will first be presented. Experimental results obtained in different laboratories but using the same structures will then be discussed in detail. Note that gain has already been observed in two different laboratories under pulsed (but not cw) optical pumping. Attempts at making a laser will be described and the most recent results presented. The presentation will conclude by a short discussion of the possible applications of a silicon laser, given the present results and anticipated progress.

### **8:15 PM N7.2**

**Non-stationary Blinking of Individual Silicon Nanocrystals.** Frank Cichos, Joerg Martin and Christian von Borczyskowski; Institute of Physics, Chemnitz University of Technology, Chemnitz, Germany.

Silicon nanocrystals (Si-nc) are of potential interest not only for integrated opto-electronics but also for astrophysics. It is supposed that Si-nc are responsible for the so called extended red emission (ERE) a broad emission feature of interstellar matter in the wavelength region of 600 nm to 900 nm. Specially the latter phenomenon requires a detailed knowledge of photophysical processes occurring in such nanocrystals. By studying ensemble emission of Si-nc prepared from porous silicon, we find a continuous intensity decay upon irradiation. Along with this bleaching a spectral red shift of the mean emission wavelength is observed. Both emission intensity and emission wavelength decay non-exponentially and both changes are found to be reversible when switching off the laser for a certain waiting time. To explore this behavior in detail, we have carried out experiments on individual Si-nc. As other semiconductor nanocrystals, the Si-nc show an emission intermittency, where the dark state is most likely formed by an ionized nanocrystal, from which one carrier has been ejected. We characterize the blinking by calculating probability density distributions to find certain on and off time durations. Both distributions fit well to a power law. However, the exponent of the on time distribution is found to be larger than 2

which implies a finite mean on time. The off time distribution obeys an exponent of 1.3, which results in an infinite mean off time. Such a distribution without finite mean is intimately linked with a non-stationary photophysics, since each observation of an off time will drive the mean off time further to infinity. Thus the average off time measured from many individual single particle time traces increases with time. This is the reason for the apparent bleaching effect as mentioned at the beginning, which is due to its statistical nature reversible. We further define a new quantity  $F(t)$  which is intended to characterize the time dependence of the blinking and to extend the limited view the power law exponents provide on the detailed photophysics. For all our experiments  $F(t)$  shows at least two different processes which contribute to the off time statistics. One of them can be understood in terms of the random walk model, where the ejected charge undergoes a random walk through a spatial/energetical distribution of trap states. The average off time increases because the excursion of the carrier gets wider with each ejection as predicted by simple diffusion theory. This results in an increase of  $F(t)$  with a square root of  $t$  which is observed. Further the decay of the ensemble intensity is predicted to be a shifted In addition we find that a fraction of the ejected charges do not return to the valence band but to the conduction band, which gives then rise to a delayed luminescence on a time scale of seconds. This luminescence decays again non-exponentially but with a power law.

#### 8:30 PM N7.3

**Optical Properties of Silicon Nanocrystal Assemblies Mediated by Auger Processes.** Dmitri Kovalev, Joachim Diener and Fred Koch; Technical University of Munich, Garching, Germany.

The Auger process is a predominant nonradiative process in semiconductors at high carriers or doping concentrations. In bulk Si due to an extremely long radiative lifetime Auger recombination is a main recombination channel at high level of optical excitation. One of the most important properties of the nanocrystal assemblies is their strong nonlinear optical response. Recently the importance of the competition between radiative and Auger recombination for the electronic and optical properties of semiconductor quantum dots was recognised. The main feature of light emission from silicon nanocrystals is an extremely long exciton lifetime. Therefore at 1 W/cm<sup>2</sup> of CW optical excitation in average each crystallite is already occupied by at least one electron-hole pair. If a second photon is absorbed in a nanocrystal which is already occupied by a long-lived electron-hole pair, nonradiative Auger recombination will occur. We demonstrate that this results in a variety of optical phenomena: photoluminescence saturation, shortening of exciton lifetime, dynamic and persistent spectral hole burning phenomena and efficient photoluminescence up-conversion already under moderate levels of optical excitation. Therefore the Auger process is an inherent limitation for light emission efficiency from silicon nanocrystal assemblies: the luminosity of a light emitting device based on silicon nanocrystals is limited to one photon per nanocrystal per exciton lifetime.

#### 8:45 PM N7.4

**Development of LPCVD Silicon Nitride (SiN) Dots for Discrete Traps Memory Cells.** Nicolas Buffet<sup>1</sup>, Pierre Mur<sup>1</sup>, Denis Mariolle<sup>1</sup>, Barbara De Salvo<sup>1</sup>, G Njotira<sup>2</sup>, Salvatore Lombardo<sup>2</sup>, Frederic Mazen<sup>3</sup>, Bernard Pelissier<sup>3</sup>, Thierry Baron<sup>3</sup>, Mei Wan<sup>4</sup> and Kees Van der Jeugd<sup>4</sup>; <sup>1</sup>DTS, CEA-LETI, Grenoble, France; <sup>2</sup>IMM, CNR, Catania, Italy; <sup>3</sup>LTM, CNRS, Grenoble, France; <sup>4</sup>ASM, Leuven, Belgium.

To overcome the downscaling limitations of the continuous floating gate Flash memory cells beyond the 80 nm technology node, alternative structures using discrete traps are widely mentioned. Silicon nanocrystal memory are largely widespread in the literature but SiN dots seem to exhibit memory characteristics superior to those of the silicon dots ones. Thus the aim of this study is to develop a silicon nitride dot process in an industrial 200 mm vertical LPCVD furnace. So the influence of the process parameters, temperature deposition, total pressure, deposition time and gas flow ratio (SiH<sub>2</sub>Cl<sub>2</sub>/NH<sub>3</sub>), on the optical and morphological characteristics of the deposits will be shown using Atomic Force Microscopy, Spectroscopic Ellipsometry, Transmission Electron Microscopy and X-ray Photoelectron Spectroscopy. After silicon nitride deposition on 7 nm thick SiO<sub>2</sub> tunnel oxide, the Root Mean Square (RMS) value of the substrates is used to obtain an indirect information on the SiN dots density. To increase the RMS value, we have shown that it is necessary to use higher temperature deposition, lower gas flow ratio and lower total pressure. Memory cells with discrete storage SiN nodes or Si<sub>3</sub>N<sub>4</sub> continuous layer were compared but no clear behavior appeared between the two types of devices. Both could be written by Fowler-Nordheim while the erasing by Fowler-Nordheim is impossible. Thus these devices operate as One Time Programmable (OTP) memory. Our experimental study has shown that with thick tunnel oxide, the SiN dots behavior is dominated by the material properties

(Si<sub>3</sub>N<sub>4</sub> deep energy electrons traps) and not by the particular dot shape. We have also obtained silicon-rich SiN dots (analyzed by X-ray Photoelectron Spectroscopy) from thermal nitridation of LPCVD Si dots. The integration onto memory devices of these nitrided dots is still on going and electrical results will be shown.

#### 9:00 PM N7.5

**Resonant Carrier Tunneling in Coupled Silicon Nanocrystals.** Volodymyr Duzhko, Boris Kamenev and Leonid Tsybeskov; ECE, NJIT, Newark, New Jersey.

We present comprehensive studies of carrier transport in layered structures containing size-selected Si nanocrystals separated by tunnel transparent (~ 18Å thick) layers of silicon dioxide. Low temperature current-voltage characteristics reveal resonances and negative differential conductivity (NDC) associated with hole tunneling. Time-resolved carrier transport data show that the fastest transition time corresponds to the resonant bias [1]. We find that carrier velocity has two components: a fast component, which is temperature independent and a slow, temperature dependent component. The experimental results have been numerically modeled using a system of steady-state and time-dependent balance equations for carriers in coupled nanocrystals [2]. These calculations support our model and explain previously observed current instabilities and self-sustained current oscillations in our samples [3]. 1. Duzhko et al., APL, submitted for publication 2. Kamenev et al., PRL, submitted for publication 3. Tsybeskov et al., Europhys. Lett., 55, 552 (2001)

#### 9:15 PM N7.6

**Size-controlled Si nanocrystals: quantum confinement and Foerster transfer.** Johannes Heitmann, Lixin Yi, Vadim G. Talalae and Margit Zacharias; MPI of Microstructure Physics, Halle, Germany.

Dense packed, size controlled Si quantum dots are prepared by phase separation of SiO<sub>x</sub>/SiO<sub>2</sub> superlattices. The crystal size can be controlled in the range from 2 to 5 nm. The resulting Gaussian shaped size distributions in the samples show a deviation from the average size of ±0.2-0.4 nm. The Si based luminescence at 750-950 nm is clearly related to quantum confinement effects, which is proved by several excitonic properties of the luminescence, like increasing exciton energy, direct recombination probability and increasing exchange energy of electron and hole with decreasing crystal size. The temperature dependence of the luminescence emission energy shows strong deviations compared to the temperature behavior of the band gap of bulk crystalline Si for temperatures below 50 K. This deviation and the size dependence of the different quantum confinement effects can be explained by exciton diffusion between the Si nanocrystals. The energy of optical excited Si nanocrystals can be transferred almost completely to the Er<sup>3+</sup> ions resulting in a strong luminescence at 1.5 μm. This highly efficient energy transfer between Si nanocrystals and Er<sup>3+</sup> ions is mainly characterized by the Foerster mechanism. The efficiency of the energy transfer increases with the energy of the exciting photons, with smaller crystal sizes and with increasing overlap of the exciton energy in the Si nanocrystals and Er<sup>3+</sup> energy levels. The dependence of the energy transfer on the nanocrystal properties and on the exciton diffusion among the nanocrystals will be presented.

#### 9:30 PM N7.7

**Erbium-Doped Group IV Semiconductor Nanowires: Structural and Photophysical Effects of Rare Earth Incorporation.** Jeffery L. Coffey, Zhaoyu Wang, Ji Wu and Robert Senter; Department of Chemistry, Texas Christian University, Fort Worth, Texas.

Crystalline Group IV semiconductor nanowires (NWs) comprised of Si or Ge are attracting extensive attention as a consequence of unique fundamental electronic & structural behavior relevant to device platforms. In the continuing evolution of wire architectures, the incorporation of dopant or impurity centers into a given nanowire is a logical step. The rare earth ion erbium is of particular interest for incorporation into such structures because its luminescent transition at 1540 nm lies at a transmission maximum for silica based waveguides; erbium-rich silicon phases also demonstrate enhanced conductivity, particularly as effective Schottky contacts on n-type Si. In this presentation we describe our approaches to the preparation of nanowires of both Si and Ge and the subsequent introduction of erbium ions along the surface of a given nanowire. For the Si system a traditional VLS approach is utilized (in conjunction with a vapor deposition method for Er ion incorporation) to produce wires whose diameter can be controlled by the origin of the Au catalyst employed. In the Ge NW case, a new vapor transport method was used to tune Ge NW width, followed subsequently by erbium exposure. In addition to direct visualization by electron microscopy, the impact of semiconductor host structure on the near IR photoluminescence associated with the erbium centers will be discussed. The role of size

and surface chemistry on the first order solid/solid phase transformation of these nanowires will also be described.

#### 9:45 PM N7.8

**Surface Terminations of Silicon Nanocrystals.** Julie S. Biteen<sup>1</sup>, Nathan S. Lewis<sup>1</sup>, Albert Polman<sup>2,1</sup> and Harry A. Atwater<sup>1</sup>,  
<sup>1</sup>California Institute of Technology, Pasadena, California; <sup>2</sup>FOM Institute for Atomic and Molecular Physics, Amsterdam, Netherlands.

We have studied silicon nanocrystals with different terminating groups to examine the role of the surface in quantum-confined excitonic emission for Si nanocrystal arrays. Models for optical gain and lasing in Si nanocrystals invoke multi-level systems that include, along with the Si band edges, deep lying radiative Si=O double bond donor- and acceptor-like interface states. Recent theoretical studies of Si nanocrystals<sup>1</sup> propose that double-bonded surface groups should produce deep-lying states within the Si band gap, while single-bonded substrates (such as methyl) should leave the band gap nearly unaltered. This suggests that an appropriate choice of surface passivation group may permit lasing and allow engineering of the emission energy. The surface termination states of Si nanocrystals are intimately related to their optical properties, and most studies of Si nanocrystals for device applications have focused on dense arrays of oxygen-terminated silicon nanocrystals. We study unembedded Si nanocrystal ensembles with narrow size distributions and diameters of 2 to 5 nm. The particles are synthesized by ion implantation into SiO<sub>2</sub> films followed by high-temperature annealing, and then removed from the SiO<sub>2</sub> film and deposited on Si or sapphire substrates by HF etching, leaving hydrogen-terminated samples. Unless further processed, these are subject to ambient oxidation over time, and we discuss the time-evolution of their photoluminescence and oxidation state measured by X-ray photoelectron and photoluminescence spectroscopies, including an observed oxidation-induced emission energy red-shift that we attribute the Si=O donor state. A second set of samples was methyl-passivated with a two-step halogenation/alkylation procedure that begins from completely unoxidized, hydrogen-terminated nanocrystals and has an intermediate chlorine-termination. X-ray photoelectron spectra taken after ambient exposure indicate that methylated nanocrystals show enhanced resistance to oxidation relative to hydrogen-terminated nanocrystals. We will present photoluminescence spectra and decay traces, as well as photoconductive decay lifetime measurements of methyl- and chlorine-passivated Si nanocrystals, and compare them to their hydrogen-terminated and oxygen-terminated precursors. <sup>1</sup>A. Puzder et al., J. Am. Chem. Soc., **125**, 2786 (2003).

#### 10:00 PM N7.9

**Phonon Confinement in Elemental Semiconductor Nanowires - Is it Real?** Kofi W. Adu<sup>1</sup>, Rajeev Gupta<sup>1</sup>, Un J Kim<sup>1</sup>, Qihua Xiong<sup>1</sup>, John J Zengel<sup>1</sup> and Peter C Eklund<sup>1,2</sup>; <sup>1</sup>Physics, Pennsylvania State University, University Park, Pennsylvania; <sup>2</sup>Materials Science, Pennsylvania State University, University Park, Pennsylvania.

We present results on Raman scattering measurements on small diameter (~6-10 nm) Silicon and Germanium nanowires prepared by pulsed laser vaporization. These experiments were carried out in ambient conditions at different excitation wavelengths - 514.5, 488, 457.9 and 647.1 nm. At each excitation, we varied the laser power to examine the influence of laser power density on the 1st order Raman active TO (LO) phonon peak. We observe, for all excitation wavelengths at low powers, a symmetric band is observed at ~ 300 (Ge) and 520 cm<sup>-1</sup> (Si), similar to that observed in the bulk. No evidence is found for an asymmetric lineshape predicted by Richter, or Fauchet and Campbell, for phonon confinement in wire with our diameter. However, as the laser power density is increased, in each case (Si or Ge), the Raman band becomes asymmetric. We find that this asymmetry is dependent on the excitation laser frequency and the power density. We analyze these results in terms of the Fano resonance between a discrete phonon band and a laser-induced electronic continuum scattering. By carefully doing the experiments with wires on different substrates we are able to separate laser induced heating and electronic continuum contributions. Our results suggest that the electronic continuum scattering in these nanowires is photo-induced and not thermally generated. We also estimate the phonon confinement effects for our nanowires based on the phenomenological model proposed by Fauchet and Campbell. The most probable diameter for the Si and Ge nanowires core was ~ 7 nm. Transmission electron microscopy and atomic force microscopy were used to characterize the samples and determine the diameter distribution.

SESSION N8: Joint Session with T6 and Z6: Quantum Dots and Wires: Structure, Spectroscopy, and Transport  
Chairs: Hedi Mattoussi and Andrew Norman  
Wednesday Morning, December 3, 2003  
Room 302 (Hynes)

#### 8:30 AM \*N8.1

**Nanowire Semiconductor Materials for Low-dimensional Physics and Applications.** Lars Samuelson, Solid State Physics, Lund University, Lund, Sweden.

Self-assembly of quantum structures into zero-dimensional (quantum dot) and one-dimensional (nanowire) structures is becoming a very hot item in materials science as well as for what it may offer for basic physics and for nanoelectronic/photonic applications. In this talk I will first discuss the formation of quantum dots via the Stranski-Krastanow (SK) self-assembling growth mode which has allowed the study of highly ideal quantum dot structures for basic investigations of the physics of few-particle configurations and exciton phenomena in single quantum dots, as well as for their use in different quantum optics applications. By assembly of SK quantum dots for electrical addressing, it has been possible to fabricate tunneling devices in which electrons tunnel via the zero-dimensional states of the quantum dot as the active element or for electrons tunneling via double-dot artificial molecule structures. Very recently this more traditional approach to optical and electrical applications of quantum dots has been rivaled by the alternative approach to form quantum dots arranged inside one-dimensional nanowires. I will present optical properties of quantum dots inside nanowires as well as resonant tunneling via single quantum dots placed in-between tunnel barriers inside such nanowire structures. Direct comparison between SK-grown quantum dots and quantum dots formed inside nanowires will be made. This research is supported from the Swedish Research Council (VR) and the Swedish Foundation for Strategic Research (SSF). The presentation will be based on contributions from Werner Seifert and Magnus Borgstrom in MOVPE-growth, Soren Jeppesen, Jonas Ohlsson and Ann Persson in CBE-growth, Reine Wallenberg et al. in TEM-imaging, Anders Mikkelsen et al. in STM-imaging, Claes Thelander, Mikael Bjork, Tomas Bryllert and Thomas Martensson in transport device studies, Valery Zwiller, Jonas Persson, Lars Landin, Nicolay Panev and Niklas Skold in PL-studies and Mats-Erik Pistol, Craig Pryor, Magnus Holm, Martin Persson and Hongqi Xu in theory/modelling.

#### 9:00 AM N8.2

**Observation of Quasi-Periodic Twinning Superlattice in GaAs Nanowires.** K W Adu<sup>1</sup>, U J Kim<sup>1</sup>, B K Pradhan<sup>4</sup>, D Tham<sup>3</sup>, D Yates<sup>3</sup>, J E Fischer<sup>3</sup>, U D Venkateswaran<sup>5</sup> and P C Eklund<sup>1,2</sup>;  
<sup>1</sup>Physics, Pennsylvania State University, University Park, Pennsylvania; <sup>2</sup>Materials Science & Engineering, The Pennsylvania State University, University Park, Pennsylvania; <sup>3</sup>Material Science and Engineering and LRSM, University of Pennsylvania, Philadelphia, Pennsylvania; <sup>4</sup>Commercial Technology, Columbia Chemical Company, Marietta, Georgia; <sup>5</sup>Physics, Oakland University, Oakland, Michigan.

A single material superlattice or "twinning superlattice" can have significantly different properties from the bulk. The structure does not suffer from interface degradation due to mismatch or incoherent electron scattering from defects that occur in a conventional superlattice. Theoretical investigations of the electronic band structure of such periodically twinned materials reveal a red shift in the band gap. For example, the twinning superlattice of Si exhibits a bandgap of 0.6eV, while the bandgap for the bulk is 1.1eV. We have used a simple thermal batch process to grow GaAs nanowires with an almost periodic twinning superlattice. As the wire diameter (d) ranges from 5nm to 100nm, the superlattice period decreases, e.g., at d=10nm diameter, a typical period would be ~5 unit cells along the (111) growth direction. The photoluminescence (PL) spectrum exhibits 3 peaks at 300 K: a doublet (1072nm, 915nm) and weak peak at 580nm (bulk GaAs has bandgap PL at 850nm). The doublet is identified with a redshift in the bandgap; the origin of the peak at 580 nm is not currently understood, and it becomes intense at T=30K. We observe an ~ 11cm<sup>-1</sup> downshift and a broadening of the LO and TO phonon modes relative to bulk GaAs via Raman scattering that is identified with a thermal broadening and phonon confinement effects. Also results of SEM, HRTEM and optical absorption will be presented. We believe that this simple synthesis route, if properly understood, might be used to fabricate perfectly periodic nanowire: GaAs twinning superlattice, and other twinned superlattice nanowires as well.

#### 9:15 AM N8.3

**Optical Studies of Charged Single Self-Assembled Quantum Dots.** Morgan E. Ware<sup>1</sup>, Allan Bracker<sup>1</sup>, Daniel Gammon<sup>1</sup> and David Gershoni<sup>2</sup>; <sup>1</sup>Naval Research Laboratory, Washington, District of Columbia; <sup>2</sup>Physics Department, Technion-Israel Institute of Technology, Haifa, Israel.

Semiconductor quantum dots have been viewed in recent years as attractive components for implementing quantum computation schemes [1]. In particular, the unpaired spin of an electronically charged semiconductor quantum dot is especially exciting, not only because of its relatively long spin dephasing time, but also because a

single spin in a single dot can be controlled and measured optically [2]. Knowledge of the discrete energy spectrum of these dots is vital for any future progress in this field. We have grown InAs/GaAs self-assembled quantum dot samples by molecular beam epitaxy using an indium flush technique [3]. Submicron aluminum apertures created by electron beam lithography have been used as a shadow mask such that single quantum dots can be selectively excited and measured. In addition, we have employed this shadow mask as the metal contact of a Schottky diode structure, providing us the capability to control the charge state of the isolated quantum dot. By varying the bias across the diode and at the same time measuring the photoluminescence from the dot, we precisely control and identify the charge states of the dot [4,5]. By analyzing the magnetic field dependence of the photoluminescence we can fully characterize the degeneracy of these charge states [6] and their polarization selection rules. The basic understanding of this system will be discussed as it provides the groundwork for further studies of more complex systems. [1] D. Loss, D. P. DiVincenzo, Phys. Rev. A 57, 120 (1998). [2] D. Gammon et al., Phys. Rev. Lett., 86, 5176 (2001). [3] Z. R. Wasilewski, S. Fafard, and J. P. McCaffrey, J. Cryst. Growth 201/202, 1131 (1999). [4] R. J. Warburton, et al., Nature, 405, 926, (2000) [5] D.V. Regelman, E. Dekel, D. Gershoni, et al., Phys. Rev. B 64, 165301, (2001) [6] J.G. Tischler, A. S. Bracker, D. Gammon, Phys. Rev. B 66, 081310(R) (2002).

#### 9:30 AM \*N8.4

##### Engineering Quantum Structures and their Behavior.

Gregory J. Salamo, Physics, Univ of Arkansas, Fayetteville, Arkansas.

Recent clever techniques for fabricating nanosize materials, one-atomic-layer-at-a-time, have simultaneously opened the door to new physics, chemistry, biology, and engineering. Nanosize materials simply do not behave as the bulk. Indeed, the rules that govern the behavior of these tiny structures are not known and must be uncovered. Going smaller is a fantastic adventure opening a new frontier in science and engineering. So many of our ideas have come from a better understanding of nature, that the trend is sure to continue as we examine and view nature on a nanoscale. In this talk we will discuss our recent efforts to engineer shape, size, density, and position of nanostructures and of the interactions between them, and to develop a clear understanding of their optical and electrical behavior. While self-assembly is providing exciting quantum dot structures to explore, it is equally exciting to try to use the rules we uncover to encourage dot formation to take a desired path. Can we understand the formation of faceted nanostructures? Can we encourage or seed dot structures to form specific arrays? Is it possible to engineer greater homogeneity of dot shape and size? Can we design both the optical and electrical behavior of either individual or arrays of nanostructures? In this talk we will review our progress to answer these questions and discuss the possibilities and challenges ahead. For example, we will discuss the formation of individual faceted nanostructures as well as the fabrication of a vertically and laterally ordered QD stacks forming three-dimensional QD arrays. We will present results from the photoluminescence (PL) spectra from individual dots and discuss the role of such phenomena as the phonon bath. We will also discuss an investigation of the PL spectra from ordered arrays of QDs, both as a function of temperature and optical excitation intensity, which reveal both a lateral and vertical transfer of excitation. Moreover, we will present results that explore the tunneling law between quantum dots. As another example, we will discuss the importance of surfaces with high Miller indices, as a template to the formation of nanostructures as well as their potential role in determining the shape and increased size uniformity of the confined structures. Importantly, these observations lead to an even more basic question of when and why high index surfaces are stable. Indeed, we have found that in order to understand the origin of high index surfaces that bound nanostructures we have to study them directly. Yet in another example we will discuss the manipulation of surface reconstruction and a critical role that it can play in the selection of dot or wire nanostructures. Finally, we will discuss the many exciting opportunities that may be ahead although we expect and look forward to many surprises.

#### 10:30 AM \*N8.5

**Growth, Structure, and Optical Properties Of III-Nitride Quantum Dots.** Hadis Morkoc<sup>1</sup>, Arup Neogi<sup>2</sup> and Martin Kuball<sup>3</sup>; <sup>1</sup>EE and Physics, Virginia Commonwealth University, Richmond, Virginia; <sup>2</sup>North Texas University, Denton, Texas; <sup>3</sup>University of Bristol, Bristol, United Kingdom.

Quantum dots in conventional semiconductors have been explored for their many degrees of confinement resulting in unique density of states which are thought to lead to low laser threshold current, among other applications. In the case of GaN, an additional advantage is that the layer or layers of quantum dots will decouple the active layers to be studied from the substrate or buffer layer and, thus reduce number of extended and point defects, because they would

nucleate on dislocated regions. In this vein, GaN dots have been grown on c-plane sapphire and (111) Si substrates by reactive molecular beam epitaxy. A method involving two-dimensional growth followed by a controlled annealing during which dots are formed was employed. Due to the dot nature and large dot density, relatively high luminescence efficiencies were obtained on both substrates. Single layer dots were used for AFM analysis whereas 30 layer dots were used for photoluminescence experiments. AlN barrier layers, some too thick for mechanical interaction, some thin enough for vertical coupling were used. Strong polarization effects lead to a sizeable red shift, which depends on the size of the dots. Optical processes in these quantum dots will be discussed in detail.

#### 11:00 AM N8.6

##### Diffuse X-Ray Scattering of InGaAs/GaAs Quantum Dots.

Rolf Koehler<sup>1</sup>, Michael Hanke<sup>1</sup>, Daniil Grigoriev<sup>1</sup>, Martin Schmidbauer<sup>1</sup>, Peter Schaefer<sup>1</sup>, Udo Pohl<sup>2</sup>, Roman Sellin<sup>2</sup>, Dieter Bimberg<sup>2</sup>, Nikolai Zakharov<sup>3</sup> and Peter Werner<sup>3</sup>; <sup>1</sup>Institute of Physics, Humboldt-University Berlin, Berlin, Germany; <sup>2</sup>Institute of Solid State Physics, Technical University Berlin, Berlin, Germany; <sup>3</sup>Max-Planck-Institute of Microstructure Physics, Halle, Germany.

Strained self-organised InGaAs/GaAs(001) quantum dots (QDs) are presently subject of intense research efforts due to their promising potential for optoelectronic device applications. We will report about structural investigations on five-fold stacks of In<sub>0.6</sub>Ga<sub>0.4</sub>As QDs within a GaAs matrix grown by means of metalorganic chemical vapor deposition. The GaAs spacer thickness between the subsequent QD layers amounts to 20 nm, a thickness at which vertical QD correlation is believed to vanish, however, cross-sectional transmission electron micrographs (TEM) reveal a pronounced vertical correlation, whereas no lateral ordering could be observed in plan-view images. Applying highly strain sensitive high resolution x-ray diffraction in vicinity of different reciprocal lattice points we provide a non-destructive access to the detailed QD shape and local strain status within the QDs and the surrounding matrix material. Since the expected diffuse signal will be extremely weak all measurements were carried out at synchrotron beamlines. Scattering simulations are based on a dynamical treatment within the framework of Distorted Wave Born Approximation. The strain field which enters the simulation procedure has been calculated by finite element method. Grazing incidence diffraction (GID) near the (200) and (020) reciprocal lattice points did not show any significant difference between the [100] and [010] directions. A similar shape isotropy was found with respect to [110] and [110], proving an at least four-fold lateral QD symmetry. Moreover, scattering simulations regarding various dot shapes clearly indicate prismatic QDs with a flat top rather than pyramids. The mean lateral QD distance significantly influences the diffuse scattered intensity in GID geometry. Thus, we could deduce a value of approximately 80 nm, which corresponds well to the QD density of about 2E10 cm<sup>-2</sup> estimated from plan-view TEM.

#### 11:15 AM N8.7

##### THz Manipulation of Excitonic Levels in Single InAs Quantum Dots.

Frederik F. Schrey, Thomas Mueller, Gottfried Strasser and Karl Unterrainer; FKE, Vienna Univ. of Technology, Vienna, Austria.

The energy spacing of electronic states in self-assembled quantum dots (QDs) coupled with efficient electron capture capabilities into these discrete states predestine dots to be used as MIR photodetectors, emitters and turns them into candidates for q-bit operations. In contrast to subband transitions in two-dimensional structures the density of states is sharply peaked at the transition energy, which reduces the phase space for scattering. Therefore we expect longer relaxation and dephasing rates in QDs compared to quantum wells. A strong requirement for q-bit applications is the knowledge about a possible radiative coupling between the electronic levels. In our experiments we superimpose a pulsed NIR excitation laser field with a low intensity cw THz field on a single quantum dot. The dot is separated from other dots by etching a micropillar structure into the GaAs matrix. Furthermore the pillar structure allows a more efficient coupling to the THz radiation. The exciton recombination is recorded with a micro luminescence (PL) setup for NIR excitation as well as for combined NIR/THz excitation. First results show an electron transfer from the lower excitonic levels into higher levels, which changes the count rates for the emission lines. The efficiency of this process seems to depend on the NIR pump intensity and is object of further studies. Furthermore ultrabroadband MIR time-domain spectroscopy allows us to study the dynamical properties within the electronic dot levels. In a first approach we study the electron capture respectively injection into the electronic levels of dot ensembles. Combined with the micro-PL system we want to investigate the dynamics of electrons in single dots. We hope to gain knowledge of the relaxation and dephasing processes and to achieve coherent excitations within the electronic dot levels, which would allow very fast control of QD based devices.

**11:30 AM N8.8****Near-Field Magneto-Photoluminescence of Single Self-Organized Quantum Dots.** Alexander Mintairov<sup>1</sup>, JamesMerz<sup>1</sup>, Alexei Vlasov<sup>1</sup> and Alexander Govorov<sup>2</sup>; <sup>1</sup>University of Notre Dame, Notre Dame, Indiana; <sup>2</sup>Physics and Astronomy, Ohio University, Athens, Ohio.

We present measurements of Zeeman splitting and diamagnetic shifts of single self-organized InAs/AlAs, InAs/GaAs and InP/GaInP quantum dots using low temperature (10K) near-field scanning optical microscopy with spatial resolution <200 nm, operating at magnetic field strengths up to 10 T. The measurements allow us distinguish dots of different sizes, atomic content and homogeneity and attribute their specific structural properties, with their magneto-optical properties. For InAs/GaAs and InAs/GaAs QDs we found an increase of the diamagnetic coefficient from 0.4 to 15 meV/T<sup>2</sup> with increasing emission energy. This corresponds to an increase of the QD size from 5 to 10 nm. This observation is quite unexpected and implies lower In content for larger dots, compensating the usual quantum confinement effects. We estimated the difference in In composition between small and large dots to be quite large, approximately 40%. For InP/GaInP QDs we observed an anomalous behavior of the Zeeman splitting dependence on the initial value of magnetic field. When the magnetic field is swept from 10 to 0T, the spin splitting shows oscillatory behavior and it does not vanish at zero magnetic field. We interpret this observation to involve an internal effective magnetic field induced by polarized nuclear spins via the hyperfine interaction. Interestingly, the single InP dots with non-zero splitting typically have broad line widths. This fact suggests that the broadening can come from the interaction between the exciton and nuclear spins.

**11:45 AM N8.9****Evidence of Aharonov-Bohm effect on neutral excitons in type-II quantum dots.** Evaldo Ribeiro<sup>1</sup>, Alexander O Govorov<sup>2</sup>, Wilson de Carvalho Jr.<sup>1</sup> and Gilberto Medeiros-Ribeiro<sup>1</sup>; <sup>1</sup>LNLS, Campinas, SP, Brazil; <sup>2</sup>Department of Physics and Astronomy, Clippinger Research Labs, Ohio University, Athens, Ohio.

By allowing a charged particle to circulate a confined magnetic field flux region, Aharonov and Bohm showed in 1959 that, surprisingly, there exist effects of the vector potential on the charged particles moving outside the magnetic field region. After following the circular path the particle wavefunction acquires a phase that is proportional to the magnetic flux contained within the closed path. For these effects to exist, phase coherence is mandatory. All observable phenomena depend only upon the magnetic flux  $\Phi$  through the excluded region, and are shown to be periodic with period  $\Phi_0 = hc/e$ . This oscillatory characteristic is the signature of the Aharonov-Bohm (AB) effect. It is commonly believed that the AB effect is a typical feature of the motion of a charged particle interacting with the electromagnetic vector potential. Here we present a magnetophotoluminescence study of type-II InP/GaAs self-assembled quantum dots, unambiguously revealing the AB type oscillations for neutral excitons when the hole ground state changes its angular momentum from  $l_h = 0$  to  $l_h = 1, 2,$  and  $3$ . Although forbidden, the transitions from the electron ground state to higher angular momenta hole states reflect a broken symmetry for this island system. This can be understood in terms of the anisotropy of the islands revealed in both Atomic Force Microscopy experiments on uncapped islands as well as polarization dependent photoluminescence spectra. In addition to that, due to the fact one does not have a hard wall confining potential, a spillage of the electron and hole wavefunctions out and into the islands can be anticipated. The wavefunction overlap can be inferred from the photoluminescence intensity, and revealed a complex behavior which could be understood by the successive adjustments of the wave function lobes to the non-uniform edges of the island, being more sensitive at higher magnetic fields. The hole ring parameters derived from a simple model are in excellent agreement with the structural parameters determined for this system.

SESSION N9: Self-Assembled QDs, Nanoparticles and Nanowires

Chairs: U. Banin and S. V. Gaponenko  
Wednesday Afternoon, December 3, 2003  
Room 302 (Hynes)**1:30 PM \*N9.1****Stranski-Krastanov CdSe Quantum Dot Heterostructures: Self-Organized Growth, Quantum Interference, Spin Control, and Magnetic Properties.** F. Henneberger, Physics Department, Humboldt-Universitat Berlin, Berlin, Germany.

We report on the MBE growth of CdSe/ZnSe quantum dot heterostructures. A specific growth procedure allows to suppress strongly interdiffusion and to establish a distinct Stranski-Krastanov

morphology. As revealed by AFM and HRTEM, the dots consist of a massive core of pure CdSe of about 2 nm x 5 nm size dimension. The single-dot optical line width is on the 10- $\mu$ eV energy scale. No spectral jitter is observed. We study quantum interferences within the exciton fine structure doublet. The decoherence times are longer than the radiative life-time. We investigate the potential of charged dots for optical spin control. Heavy-light coupling as well as the trion triplet state are crucial factors. The low-temperature spin relaxation times exceed 10 ns. Diluted magnetic quantum dots are formed under incorporation of Mn. We find g-factors as large as 300 and 90 % spin polarization at magnetic fields of only 0.8 Tesla. The single-dot line width is more than two orders of magnitude larger for pure CdSe structures. This dramatic increase is a consequence of magnetic fluctuations inherent in these dots.

**2:00 PM N9.2****Trion and Exciton Dynamics in Single CdSe/ZnSe Quantum Dots.** Brian Robert Patton, Wolfgang Langbein and Ulrike Woggon; Experimental Physics IIb, University of Dortmund, Dortmund, Germany.

By using recent advances in the patterning and etching of epitaxially grown semiconductor structures it has become possible to address individual quantum dots. We present an analysis of the decay dynamics of excitons and charged excitons (trions) in single CdSe quantum dots embedded in a ZnSe matrix. In particular, we are interested in the temperature dependence of the radiative recombination of the quasi-particles. We show a good agreement to a model of exciton recombination which takes into account the phonon-mediated spin-flip both to and from the optically dark state. The sample we investigated was patterned with varying sized mesa structures. The smaller mesas contained less than five optically active quantum dots. Charge carriers were photo-excited in the barrier and we studied the emission from the single dots identified by spectral jitter due to the trapping of charge carriers in the nanoenvirons of each dot. A streak camera with a 4ps resolution allows the examination of the temperature-dependent, time-resolved recombination of the trion and exciton transitions. In reference to the above model, the transition between dark and bright states for the exciton was found to have an associated rate of  $\gamma_0 = (13\text{ns})^{-1}$  and a bright-dark splitting energy of  $\delta_0 = 1.5\text{meV}$ . The lack of such a dark state prevents such refilling dynamics in the trion emission. Furthermore, we allow for a thermally-activated escape from the dot with constants  $\delta_e = 30\text{meV}$  and  $\gamma_e = 30\text{ns}^{-1}$ . The trion does show, however, a spin-flip process in the initial relaxation at low T whereby a charge carrier which is Pauli-blocked from relaxing to the ground state reverses its spin with a time-constant of 30 - 50ps. From the polarization-resolved emission we find exchange splitting energies of 0.2 to 1.2meV, trion binding energies of 15 to 22meV and biexciton binding energies of 19 to 26meV.

**2:15 PM N9.3****Intraband Relaxation in Colloid Quantum Dots.**

Philippe Guyot-Sionnest, Congjun Wang and Brian L. Wehrenberg; Chemistry and Physics, University of Chicago, Chicago, Illinois.

Picosecond infrared pump-probe spectroscopy is used to monitor relaxation rates of electrons from the P-states to S-state of colloid quantum dots. The currently accepted mechanism for breaking the phonon bottleneck invokes an Auger coupling between electrons and holes. This conventional view is directly tested by placing the electron in the S-state either by interband photoexcitation or by electrochemical reduction. The latter allows for no hole present. The electron is then excited to the P-state with an infrared pump pulse and its relaxation to the S-state is followed with the infrared probe pulse. Similarities and differences in relaxation dynamics for several systems with and without holes will be presented.

**2:30 PM N9.4****Intraband energy relaxation in colloidal PbSe quantum dots,** Jeffrey Matthew Harbold<sup>1</sup>, Frank Wise<sup>1</sup>, Hui Du<sup>2</sup> and Todd Krauss<sup>2</sup>;<sup>1</sup>Applied Physics, Cornell University, Ithaca, New York; <sup>2</sup>Department of Chemistry, University of Rochester, Rochester, New York.

Nanocrystals of the IV-VI semiconductors PbS, PbSe, and PbTe provide unique opportunities to investigate the effects of strong confinement on charge carriers. Additionally, these materials have size-quantized optical transitions in the infrared, making them candidate materials for photonics applications such as infrared imaging and broadband optical amplification. The competition between radiative and non-radiative relaxation determines the viability of such an amplifier and thus motivates the study of carrier dynamics in strongly-confined quantum dots. For example, carriers injected into the higher excited states of an ideal quantum dot should only experience relaxation through phonon emission in the rare case that the phonon energies match the energy-level spacing. We studied the intraband energy relaxation in colloidal PbSe nanocrystal

samples, ranging from 3 to 5 nm in size. Using two-color transient absorption spectroscopy, we observe a 1P to 1S relaxation over approximately 10 optical phonon energies with time constant between 300 and 500 femtoseconds for excitation levels ranging from 1 to 10 electron-hole pairs per nanocrystal. Understanding the alternate pathways which bypass the phonon bottleneck in IV-VI quantum dots could additionally provide insight to the carrier dynamics in II-VI and III-V semiconductors nanocrystals.

#### 2:45 PM N9.5

**Dark exciton signatures in time-resolved photoluminescence of single quantum dots.** Jason M. Smith<sup>1</sup>, Paul A. Dalgarno<sup>1</sup>, Richard J. Warburton<sup>1</sup>, Brian D. Gerardot<sup>2</sup> and Pierre M. Petroff<sup>2</sup>; <sup>1</sup>School of Engineering & Physical Sciences, Heriot-Watt University, Edinburgh, United Kingdom; <sup>2</sup>Materials Department and QUEST, University of California at Santa Barbara, Santa Barbara, California.

Dark excitons are important in determining the optoelectronic behaviour of semiconductor quantum dots, as in many highly confined structures the lowest energy exciton state is dark, with angular momentum  $J = 2$ . Since they do not couple to an optical field, the properties of dark excitons are very difficult to probe. We present here new information regarding dark excitons in InAs self assembled quantum dots, obtained by measuring the decay lifetimes of luminescence from single nanostructures. By performing time-resolved photoluminescence on a single dot in a charge tuneable heterostructure we can probe the differences in recombination dynamics between neutral and negatively charged excitons. We find that the luminescence decay from neutral excitons contains a second lifetime component of several nanoseconds that is not present in the luminescence from singly or doubly charged excitons. We attribute the slowly decaying component to excitation cycles in which the initial exciton formed in the dot is dark, and which slowly scatters into the neighboring bright state ( $J = 1$ ) before recombining radiatively. The nature of the scattering mechanism is revealed by the dependence of the lifetime on the electrical bias applied across the charge-tuneable device. That the lifetime changes by an order of magnitude within a short bias range implies that the dark-to-bright transmutation does not occur through a simple spin flip. Rather it appears to come about by the dot briefly entering a higher energy charging state which allows exchange of the existing electron with another from the n-type contact region. These measurements provide valuable insight into the carrier dynamics of quantum dots, and in particular provide a novel probe of dark exciton states.

#### 3:00 PM N9.6

**Anomalous linewidth of Surface Phonon modes in GaP Nanowires.** Rajeev Gupta<sup>1</sup>, Benjamin Buller<sup>3</sup>, Uma D Venkateswaran<sup>3</sup>, Qihua Xiong<sup>1</sup>, Gerald D Mahan<sup>1</sup> and Peter C Eklund<sup>1,2</sup>; <sup>1</sup>Physics, Pennsylvania State University, University Park, Pennsylvania; <sup>2</sup>Materials Science, Pennsylvania State University, University Park, Pennsylvania; <sup>3</sup>Physics, Oakland University, Rochester, Michigan.

We present a detailed Raman study of GaP nanowires. The nanowires used for the Raman measurements were prepared by pulsed laser deposition technique and characterized for stoichiometry and crystallinity by energy dispersive x-ray spectroscopy and transmission electron microscopy. We observe two Raman-active modes at 367 and 401  $\text{cm}^{-1}$  identified as the transverse and longitudinal optical phonon bands, respectively. In addition to these bands we observe another broad band at  $\sim 397 \text{ cm}^{-1}$  in air. Measurements carried out as a function of the dielectric constant of the medium surrounding the nanowires unambiguously identify this intermediate frequency band as a surface phonon mode. The surface mode frequency decreases as the dielectric constant of the media increases, as expected theoretically from continuum models. The Raman measurements as a function of temperature (10-300 K) reveal that the Raman phonon frequency of the longitudinal and transverse optical Raman bands decrease and the linewidth broadens with increasing temperature, as expected for bulk GaP. Interestingly, the surface phonon frequency remains nearly constant at all temperatures. Furthermore, the surface phonon linewidth shows a very anomalous temperature dependence, i.e., it decreases as the temperature increases, suggesting decay channels are being lost at elevated temperatures.

#### 3:30 PM N9.7

**Zn/ZnO core/shell hetero-nanobelts and nanotubes.** Xiang yang Kong, Yong Ding and Zhong Lin Wang; School of materials science and Engineering, Georgia Institute of Technology, Atlanta, GA, Georgia.

Since the discovery of oxide nanobelts [1], one dimensional (1-D) facet controlled nanomaterials have attracted much attention. In this paper, we present a novel facet-controlled hetero-nanobelts of Zn/ZnO, which are of rectangular cross-section and composed of metallic zinc core and semiconducting ZnO shell. The structure-controlled nanobelts

were synthesized by a solid-vapor decomposition process. X-ray diffraction indicates that the as-received products are mainly zinc with minor ZnO. Transmission electron microscopy (TEM) and electron diffraction analysis show that the hetero-nanobelt grow along either [2-1-10] or [01-10]. The top facet is (0001) plane. The interface between the Zn core and the ZnO shell is epitaxial and uniform although the lattice mismatch between the two is 17%. High-resolution TEM imaging indicates that the thin ZnO shell and zinc core are both single crystalline. By examining the nanobelts parallel to its top surface, edge-type mismatch dislocations were found at the interface between Zn and ZnO, but these dislocations do not affect the overall epitaxial growth of the ZnO shell. ZnO nanotubes with rectangular cross-section have also been synthesized, which are composed of textured polycrystalline ZnO nanocrystals. The formation of the Zn/ZnO core-shell nanobelts is proposed to be a surface oxidation process during the growth, while the ZnO nanotube is the result of evaporating the Zn core. The textured nanotube wall is suggested to be formed by releasing mismatch strain energy. Heterostructured nanobelts composed of different materials can be tailored to exhibit superior functionality for various applications in nanotechnology, such as nanotransducers and nanosensors utilizing the unique facet controlled heterostructures. [1] Pan, Z.W., Dai, Z.R., Wang, Z.L., Nanobelts of semiconducting oxides, Science 291, 1947-1949 (2001)

#### 3:45 PM N9.8

**Bulk Magnetic and Thermodynamic Characterization of CoFe<sub>2</sub>O<sub>4</sub> Nanoparticles.** Gavin Lawes<sup>1</sup>, Brian Naughton<sup>2</sup>, Ram Seshadri<sup>2</sup> and Arthur Ramirez<sup>1</sup>; <sup>1</sup>Los Alamos National Laboratory, Los Alamos, New Mexico; <sup>2</sup>Materials Department, University of California, Santa Barbara, California.

Magnetic nanoparticles are an integral component of a variety of products, and their commercial importance is expected to increase in the future. In order to better understand the materials properties of magnetic nanoparticles, and specifically their properties as a function of particle size, we have investigated samples of CoFe<sub>2</sub>O<sub>4</sub> nanoparticles with characteristic lengths from 1 nm to 15 nm. These nanoparticles were fabricated using a novel technique capable of producing the gram quantities necessary for bulk measurements. We investigated the magnetic and thermodynamic properties of these samples using a high sensitivity SQUID magnetometer and a commercial calorimeter in order to characterize their suitability for industrial applications. Furthermore, by measuring the low temperature magnetization and specific heat of the samples with different length scales, we obtained information about the importance of size effects, such as surface contributions, to the materials characteristics of the nanoparticles.

#### 4:00 PM N9.9

**Atomic Organization In Magnetic Bimetallic Nanoparticles: An Experimental and Theoretical Approach.** Marie-Jose Casanove<sup>1</sup>, Marie-Claire Fromen<sup>1</sup>, Pierre Lecante<sup>1</sup>, Joseph Morillo<sup>1</sup> and Pascale Bayle-Guillemaud<sup>2</sup>; <sup>1</sup>CEMES, CNRS, TOULOUSE, France; <sup>2</sup>DRFMC, CEA, Grenoble, France.

Nanometer-sized metallic particles are well-known to exhibit unique strong size-related magnetic effects. Moreover, alloying 3d and 4d elements is an effective way to induce spin polarization in 4d metals. Magnetic 3d-4d bimetallic nanoparticles are then particularly interesting as they may combine a large magnetic moment with a high anisotropy. Indeed, a strong enhancement of the saturation magnetization in ultrafine CoRh particles (in the 1.6 to 2 nm range) compared to the predicted value of the bulk alloy was recently demonstrated [1] and later confirmed by density functional theory calculations on much smaller particles [2]. This motivates a systematic study of the atomic organization in these alloyed particles, both from a structural and chemical point of view, using appropriate experimental and theoretical methods. Ultrafine bimetallic CoRh nanoparticles (1.5 to 3 nm of diameter) synthesized by a soft chemical route with compositions ranging from pure cobalt to pure rhodium have been investigated using high-resolution and energy filtered transmission electron microscopy, wide angle x-ray scattering and extended x-ray absorption fine structure techniques. Besides, they have been studied with the use of an n-body semi-empirical interaction model: quenched molecular dynamics and Monte-Carlo simulated annealing have been used in order to find the most stable isomers as a function of the composition and size of the nanoparticles. The smaller particles in the Co rich side exhibit a progressive loss of crystallinity with increasing Co content leading to an original polytetrahedral structure whereas on the rhodium rich side, they are always well crystallized. Moreover, there is a general tendency to Co surface segregation which is more pronounced for the Rh rich smaller particles leading to a Rh-core/Co-shell structure highly favourable for magnetic moment exaltation. These general tendencies have been confirmed by the simulations. [1] D. Zitoun et al. Phys. Rev. Lett. 89, 37203 (2002). [2] S. Denler et al., Surf. Sci. 532-535 (2003); Eur. J. Phys. D (2003, in press)

4:15 PM **N9.10**

**IC Compatible Nanoparticles for Metal-Catalyzed Nanowire Growth.** T. I. Kamins, X. Li, S. Sharma and R. Stanley Williams; Quantum Science Research, Hewlett-Packard Laboratories, Palo Alto, California.

Metal-catalyzed Si nanowires have been proposed as the active elements of nanoelectronic devices and as interconnections between microelectronics and nanoelectronics. For the former application, especially, the effect of a small quantity of catalyst being included in the nanowire must be considered. For the latter application, the possibility of metal migrating into the underlying conventional electronics is critical. Therefore, a metal compatible with Si IC technology is favored. Ti has been previously shown to be an effective catalyst that is compatible with Si ICs. To explore other possible, IC-compatible catalysts, several silicide-forming metals, including Pt, Pd and Ni, were investigated. The characteristics of the resulting nanoparticles and the nanowires grown on these nanoparticles will be reported in this paper. Thin layers of metals were deposited by electron-beam evaporation on Si substrates and annealed at several different temperatures to control the size of the catalyzing nanoparticle. Forming the desired nanoparticle involves a balance between surface diffusion of the metal to a nucleus (so that the majority of the substrate is free of metal) and agglomeration (which can increase the size of the nanoparticles unacceptably). These trends are especially evident with Pt, for which elongated islands form under some annealing conditions because of anisotropic lattice mismatch. Si nanowires were grown on samples with selected combinations of metals and annealing. The strong correlation between the nanoparticles and the nanowires will be shown for these silicide-forming metals; for example, a bimodal size distribution of Pt/Si nanoparticles leads to a bimodal distribution of nanowire diameters.

4:30 PM **N9.11**

**Nanodevices, Nanosensors, Nanocantilevers and Nanoresonators Based on Semiconducting Oxide Nanobelts.** Zhong L Wang, School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia.

This presentation addresses four novel applications of the semiconducting oxide nanobelts [1]: nano-size field-effect transistors (FETs), nano sensors and nanocantilevers. We have fabricated FETs based on single SnO<sub>2</sub> and ZnO nanobelts of thicknesses between 10 nm and 30 nm [2]. Switching ratios as large as six orders of magnitude and conductivities as high as 15 (Ohm-cm)<sup>-1</sup> are observed. Annealing SnO<sub>2</sub> nanobelt FETs in an oxygen-deficient atmosphere produces a negative shift in gate threshold voltage, indicating doping by the generation of surface oxygen vacancies. This treatment provides an effective way of tuning the electrical performance of the nanobelt devices. ZnO nanobelt FETs are sensitive to ultraviolet light. Gas sensors have been fabricated using the single crystalline SnO<sub>2</sub> nanobelts [3]. Electrical characterization showed that the contacts were ohmic and the nanobelts were sensitive to environmental polluting species like CO and NO<sub>2</sub> as well as ethanol for breath analyzers and food control applications. The results demonstrate the potential of fabricating nano-size sensors using the integrity of a single nanobelt with a sensitivity at the level of a few ppb. Nanobelts have been demonstrated as ultra-sensitive cantilever. Semiconducting oxide nanobelts of ZnO have been sectioned and manipulated, for micro-electromechanical systems (MEMS), using an atomic force microscopy probe. Structurally modified nanobelts demonstrate potential for nanocantilever based technologies. With dimensions ~35 - 1,800 times smaller than conventional cantilevers, the nanocantilevers are expected to have improved physical, chemical, and biological sensitivity for scanning probe microscopy and sensor applications [4]. Finally, nanobelt as nanoresonator will be illustrated [5]. [1] Z.W. Pan, Z.R. Dai and Z.L. Wang, Science, 291 (2001) 1947. [2] E. Comini, G. Faglia, G. Sberveglieri, Z. W. Pan, Z.L. Wang Applied Physics Letters, 81 (2002) 1869. [3] M. Arnold, P. Avouris, Z.L. Wang, J. Phys. Chem. B107 (2002) 659. [4] W. Hughes and Z.L. Wang, Appl. Phys. Letts., 82 (2003) 2886-2888 [highlighted as Research News by Nature]. [5] X.D. Bai, P.X. Gao, E.G. Wang and Z.L. Wang, Appl. Phys. Letts., in press. [6] Thanks go to Michael S. Arnold, Phaedon Avouris, E. Comini, G. Faglia, G. Sberveglieri, Will Hughes, Xuedong Bai, Enge Wang, Puxian Gao, Xiangyang Kong and Zhengwei Pan for their contribution in this work.

4:45 PM **N9.12**

**Deposition of Functionalized Gold Nanoparticles by the Layer-by-Layer Electrostatic Technique.** Shashi Paul<sup>1</sup>, M Palumbo<sup>1</sup>, M C Petty<sup>1</sup>, N Cant<sup>2</sup> and S D Evans<sup>2</sup>; <sup>1</sup>School of Engineering, Durham University, Durham, United Kingdom; <sup>2</sup>Physics and Astronomy, University of Leeds, Leeds, United Kingdom.

Intensive research is currently underway to exploit the intriguing optical or electronic behaviour of nano-sized particles. The basis of

the unique properties of these particles is their smallness of size; dimensions on the nanometre scale can result in interesting quantum mechanical phenomena, such as Coulomb blockade. There are currently a number of ways by which the nanoparticles can be deposited onto solid substrates. Here, we report on the use of the layer-by-layer electrostatic method, which has shown much promise for the deposition of thin films of certain organic materials. In this technique, layers of oppositely charged materials are built-up by dipping an appropriate substrate into solutions of polyelectrolytes. For example, the high cationic charge density of poly(ethyleneimine) (PEI) charges a surface positively. In this work, we have deposited carboxylic acid (-COOH) derivatized gold nanoparticles onto a PEI-coated silicon substrate (p-type, 1-2 Ω cm, (100) orientation, with a thermally grown oxide layer). The PEI-coated substrate was left in water containing the nanoparticles and adjusted to an alkaline pH. The silicon surface, thereby coated with PEI and the gold nanoparticles, was studied using atomic force microscopy. Particles with a size of around 30 nm were clearly evident. The surface distribution of these is compared to that obtained when the nanoparticles were assembled onto an amine functionalized SiO<sub>2</sub> surface. The effect the PEI solution pH on the deposition of the gold particles is also discussed. This work opens up a novel way to attach nanoparticles to a substrate. The application of such a thin film architecture to molecular memory devices is described.

SESSION N10: Metallic, Magnetic and Semiconductor Nanoparticles: Growth and Characterization  
Chairs: C. J. Murphy and Z. L. Wang  
Wednesday Evening, December 3, 2003  
Room 302 (Hynes)

8:00 PM **\*N10.1**

**Seeded and Non-seeded Methods to Make Metallic Nanorods and Nanowires in Aqueous Solution.** Catherine J. Murphy, Dept. of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina.

Gold and silver nanorods of controlled aspect ratio and constant width (30 nm) are made via a seed-mediated growth approach in water in the presence of a directing surfactant. Both the headgroup of the surfactant, and the length of its hydrocarbon tail, are critical for producing nanorods instead of nanospheres. A seedless approach to making silver nanowires, in boiling water, gives a high yield of wires but with less control over the aspect ratio.

8:30 PM **\*N10.2**

**Synthesis and Magnetic Properties of Monodisperse Magnetic Nanoparticles and Uniform-Sized Magnetic Nanowires.** Taeghwan Hyeon, Jongnam Park, Eunae Kang and Youjin Lee; School of Chemical Engineering, Seoul National University, Seoul, South Korea.

We report on the synthesis of monodisperse magnetic nanoparticles and magnetic nanowires with uniform diameters. We developed a new synthetic procedure to produce monodisperse magnetic nanoparticles of iron, cobalt, iron-cobalt alloys, nickel, manganese oxide, iron oxide and cobalt ferrite without any size selection process. High temperature aging of metal-surfactant complexes, which were synthesized from the reaction of metal precursors and appropriate surfactant, produced monodisperse metal nanoparticles. The resulting metallic nanoparticles were transformed to monodisperse ferrite nanocrystals by mild and controlled oxidation. Particle size can be varied from 2 nm to 20 nm by controlling the experimental parameters. We synthesized nanorods of iron and Fe-Pt from the oriented attachment of the corresponding monodisperse nanoparticles. Thermal decomposition of metal-surfactant complexes in the presence of appropriate surfactant and oxidant produced uniform-sized magnetic nanowires of iron oxide and manganese oxide. We also developed a new large-scale and simple procedure to synthesize uniform-sized ferrite nanoparticles, which employs the reaction of metal precursors in reverse micelles. Synthesis and magnetic properties of these magnetic nanostructured materials will be presented.

9:00 PM **N10.3**

**Design and Control of Branched Inorganic Nanocrystals.** Delia J Milliron, Steven Hughes, Yi Cui and A. Paul Alivisatos; Dept of Chemistry, University of California, Berkeley, California.

Building on well established syntheses of colloidal inorganic nanorods, high yield synthesis of tetrapod shaped nanocrystals has been achieved by controlling the phase during nucleation and growth. Four coordinate semiconductors commonly occur in two crystal structures, fairly close in energy. Reaction conditions, including temperature and surfactants, can be manipulated to control the phase of the growing nanocrystals. In the formation of CdTe tetrapods, nucleation occurs

in the zinc blende phase, followed by growth of anisotropic wurtzite arms. Four equivalent faces of the zinc blende nuclei are chemically identical to the fast growing face of the wurtzite structure, effectively initiating growth along the wurtzite *c*-axis. Independent control of the length and diameter of the four symmetric arms was accomplished by varying ratios of the precursors with each other and with the coordinating surfactant. The optical bandgap of the tetrapods depends strongly on the arm diameters, but very weakly on arm length. This independent tunability of overall size and bandgap is ideal for optoelectronic applications such as photovoltaic cells. Novel nanocrystal heterostructures were synthesized which incorporate multiple semiconducting materials in controlled linear and branched geometries. The synthesis of these new nanocrystals utilizes phase control to introduce branched or linear junctions at any point during the synthesis, not only at nucleation. This important extension of the techniques developed for tetrapod growth results in nanocrystals with truly controlled branching and the possibility of multiple materials in specific geometric arrangements. For example, a rod of CdSe can be grown to a specified length after which CdTe branches, again of specified length, can be grown from one end, yielding an asymmetric tetrapod with arms of different length and different composition. The resulting nanoscale heterostructures can exhibit complex optoelectronic properties such as spatially directed energy transfer and charge separation similar to those of organic dendrimers, but in a rigid, well-defined structure. Their multiple semiconducting arms could serve as contact points for complex nanoscale electronic circuits. Because the component segments exhibit properties of nanorods and they can be combined in a systematic fashion, we anticipate broadly ranging applications.

#### 9:15 PM N10.4

**Gold Alloy Nanoparticle Catalysts.** Mathew M. Maye<sup>1</sup>, Jin Luo<sup>1</sup>, Li Han<sup>1</sup>, Nancy N. Kariuki<sup>1</sup>, Sandy Chen<sup>1</sup>, Wai-Ben Chan<sup>1</sup>, Jennifer Mitchell<sup>1</sup>, Yuehe Lin<sup>2</sup>, Mark H. Engelhard<sup>2</sup>, Chongmin Wang<sup>2</sup> and Chuan-Jian Zhong<sup>1</sup>; <sup>1</sup>Chemistry, SUNY-Binghamton, Binghamton, New York; <sup>2</sup>Environmental and Molecular Science Laboratory, Pacific Northwest National Laboratory, Richland, Washington.

Gold-based nanoparticles (1-5 nm) are recently emerging as highly active catalysts. A major factor of the catalytic activity is related to the unique size- and composition-dependant structural properties. This presentation focuses on the investigation of the catalytic properties of gold-based alloy nanoparticles supported on carbon materials. The size and alloy composition of the alloy nanoparticles are systematically manipulated by different synthetic and processing protocols. The catalytic activity towards the electrooxidation of methanol and carbon monoxide and the electroreduction of oxygen are characterized. To delineate the size and composition correlation of the catalytic properties, we employed an array of surface analytical techniques to probe the structural and morphological evolution and reconstitution of the nanoparticles upon catalytic activation, including atomic force microscopy, transmission electron microscopy, surface infrared reflection spectroscopy, X-ray photoelectron spectroscopy, thermal analysis, and electrochemical quartz crystal nanobalance. The combined results of these characterizations have demonstrated the viability of tailoring the nanostructured catalysts in terms of size and composition. The potential applications in fuel cell catalysis will also be discussed.

#### 9:30 PM N10.5

**Self-Assembly of Ethylene Oxide Encapsulated Gold Nanoclusters in Aqueous Medium.** Edward Foos<sup>1</sup>, Jason Congdon<sup>1,2</sup>, Arthur Snow<sup>1</sup> and Mario Ancona<sup>2</sup>; <sup>1</sup>Chemistry Division, Code 6123, Naval Research Laboratory, Washington, District of Columbia; <sup>2</sup>Electronics Division, Naval Research Laboratory, Washington, District of Columbia.

The study of gold nanoclusters and their intriguing electronic properties has received much attention recently, yet a real challenge remains in exploiting these properties and coupling nanoscale structures to macroscale electronics. Here we report the successful self-assembly of ethylene oxide stabilized gold nanoclusters on interdigital electrodes in an all aqueous system. We have been pursuing the use of these hybrid nano/microscale architectures in the areas of chemical sensors and nanocluster based electron transport, and thus far have focused primarily on the use of alkanethiol encapsulated gold nanoclusters due to their ease of preparation and manipulation. Recently we have synthesized an ethylene oxide encapsulated cluster which retains many of the desirable properties of its alkane counterpart, yet is soluble in water. Study of the self-assembly of these water-soluble clusters in an aqueous environment will help shed light on the role of both solvent and cluster shell polarity in the ligand exchange chemistry and in electron transport. We find that the thiol exchange reaction utilized for the nanocluster/substrate coupling occurs more completely in the aqueous solvent system when compared to a polar organic solvent system. Overall, we believe that this aqueous self-assembly process can be

used to produce films of interest for applications where biocompatibility is important.

#### 9:45 PM N10.6

**Alloyed Nanocrystals: an Inspiring Nanocrystal Material.** Xinhua Zhong<sup>1</sup>, Mingyong Han<sup>2,1</sup> and Wolfgang Knoll<sup>1</sup>; <sup>1</sup>National University of Singapore, Singapore, Singapore; <sup>2</sup>Institute of Materials Research and Engineering, Singapore, Singapore.

In the last two decades, the main focus has been on the preparation of different color-emitting quantum dots (QDs) with different particle sizes due to the size-tunable properties. However, the tuning of physical and chemical properties by changing the particle size could cause problems in many applications, in particular, when unstable small particles (less than ~2 nm) are used. Little attention has been paid to the fact that different color-emitting QDs can also be made through the control of constituent stoichiometries in alloyed nanoparticles. Recently, we prepared a series of ternary alloyed nanocrystals (Zn<sub>x</sub>Cd<sub>1-x</sub>Se, Zn<sub>x</sub>Cd<sub>1-x</sub>S) via different synthetic approaches at high temperature. For example, Zn<sub>x</sub>Cd<sub>1-x</sub>Se QDs can be prepared by the incorporation of stoichiometric amounts of Zn/Se into the pre-prepared CdSe nanocrystals at high temperature; or it can also be synthesized by alloying ZnSe with the existing small sized CdSe seeds if Zn precursor was added directly into the high-temperature reaction mixture containing initially formed embryonic CdSe QDs and a large excess of Se precursor at the beginning of the CdSe nuclei growth stage. The photoluminescence (PL) properties for the obtained Zn<sub>x</sub>Cd<sub>1-x</sub>Se nanocrystals (PL efficiency of 70-85%, fwhm = 22-30 nm) are comparable to those for the best reported CdSe-based QDs. In particular, they also have good PL properties in the blue spectral range. Moreover, the alloy nanocrystals can retain their high luminescence (PL efficiency of over 40%) when dispersed in aqueous solutions and maintain a symmetric peak shape and spectral position under rigorous experimental conditions. Zn<sub>x</sub>Cd<sub>1-x</sub>S alloyed nanocrystals can be fabricated by the reaction of ZnO, CdO mixture in octadecene/oleic acid solvent system at high temperature with sulfur stock solution in octadecene, or Zn<sub>x</sub>Cd<sub>1-x</sub>S QDs are formed by the reaction of Zn, Cd precursors (zinc stearate and cadmium stearate) in alkylamine (such as hexadecylamine) solvent system at high temperature with the injected sulfur stock solution in amine. The obtained ternary wide band-gap Zn<sub>x</sub>Cd<sub>1-x</sub>S nanocrystals possess superior optical properties, especially the narrowest room-temperature emission spectral width (fwhm) of 14 nm in an ensemble measurement, which is comparable to the homogenous linewidth of single CdSe quantum dots at room temperature. These highly luminescent, stable alloy nanocrystals are potential ideal nano-emitters for light emitting devices or semiconductor lasers in optoelectronic applications. They are also very promising biological labels.

SESSION N11: Poster Session III  
Chairs: S. V. Gaponenko and Z. L. Wang  
Wednesday Evening, December 3, 2003  
8:00 PM  
Exhibition Hall D (Hynes)

#### N11.1

**Multi-color Luminescence from Surface Oxidized Silicon Nanoparticles.** Keisuke Sato<sup>1</sup>, Kenji Hirakuri<sup>1</sup>, Mitsuo Iwase<sup>2</sup>, Tomio Izumi<sup>3</sup> and Hiroshi Morisaki<sup>4</sup>; <sup>1</sup>Dept. of Electronic and Computer Engineering, Tokyo Denki University, Ishizaka, Hatoyama, Hikigun, Saitama, Japan; <sup>2</sup>Dept. of Materials Science, Tokai University, 1117 Kitakaname, Hiratsuka, Kanagawa, Japan; <sup>3</sup>Dept. of Electronics, Tokai University, 1117 Kitakaname, Hiratsuka, Kanagawa, Japan; <sup>4</sup>Dept. of Electronic Engineering, The University of Electro-Communications, 1-5-1 Chofugaoka, Chofu, Tokyo, Japan.

Silicon (Si) nanoparticles are useful candidate materials for development of new flat panel displays including electroluminescent (EL) display and field emission display. Previously, we obtained red light emission with good stability and high brightness from the Si nanoparticles based EL device under relatively low operating voltage. In this paper, we fabricate the EL device using surface oxidized Si nanoparticles to realize the Si-based EL display, which has high brightness, good stability and full color. Moreover, we report luminescence and electrical properties from the EL device. The Si nanoparticles were formed in the silicon dioxide (SiO<sub>2</sub>) layer by co-sputtering of Si/SiO<sub>2</sub> targets and subsequently annealing at high temperature. The Si nanoparticles, then, were appeared on the sample surface by treating in hydrofluoric (HF) acid solution. The particle size of Si nanoparticles, which appeared on the surface, was varied by the oxidation in air and/or high temperature to obtain the multi-color luminescence from the Si nanoparticles. Moreover, the oxidized Si nanoparticles were used for the luminous layer of EL devices. The oxidized Si nanoparticles based EL devices showed continuous



luminescent color from red light to blue light, because of reduction of particle size due to oxidation on the Si nanoparticle surface. The RGB lights could be seen with naked eye under room illumination below the forward bias of 9.5 V. Furthermore, its devices had good stability for aging of a long period of time by the existence of thin SiO<sub>2</sub> layer on the Si nanoparticle surface. This work was supported by the Research and Education Grant-in-Aid of the Illuminating Engineering Institute of Japan. 1) Also with: Department of Electronics, Tokai University, 1117 Kitakaname, Hiratsuka, Kanagawa, 259-1292, JAPAN.

### **N11.2**

#### **Excitonic photoluminescence and energy transfer in nanocrystalline Si/ Si dioxide superlattice structures.**

Victor Yurevich Timoshenko<sup>1</sup>, Olga A. Slalygina<sup>1</sup>, Maxim G. Lisachenko<sup>1</sup>, Pavel K. Kashkarov<sup>1</sup>, Dmitri Kovalev<sup>2</sup>, Johannes Heitmann<sup>3</sup>, Margit Zacharias<sup>3</sup>, Boris V. Kamenev<sup>4</sup> and Leonid Tsybeskov<sup>4</sup>; <sup>1</sup>Physics Department, Moscow State M.V.Lomonosov University, Moscow, Russian Federation; <sup>2</sup>Physics Department E16, Munich Technical University, Garching, Germany; <sup>3</sup>Max-Planck-Institute of Microstructure Physics, Halle, Germany; <sup>4</sup>Electrical and Computer Engineering Department, New Jersey Institute of Technology, Newark, New Jersey.

Photoluminescence (PL) of Si nanocrystal (nc-Si) assemblies formed by thermal crystallization of amorphous Si/SiO<sub>2</sub> and SiO/SiO<sub>2</sub> superlattices (SLs) has been investigated at different temperatures and excitation conditions. The low temperature resonant PL spectroscopy reveals phonon-assisted excitonic recombination for all structures studied. The ratio between TO-phonon-assisted and zero-phonon PL features is smaller for nc-Si formed from a-SiO/SiO<sub>2</sub> SLs and it decreases with decreasing nanocrystal size. The non-resonantly excited PL of nc-Si/SiO<sub>2</sub> structures produced from a-Si/SiO<sub>2</sub> SLs exhibits rather low (even at low temperatures) yield of PL. This implies a fast energy transfer from the large fraction of excitons to nonradiative recombination defects. The samples formed from a-SiO/SiO<sub>2</sub> SLs possess higher quantum yield (upto 1% at room temperature) of PL and the PL band maximum varies from 1.2 to 1.8 eV with decreasing nc-Si size from 6 to 2 nm. The time-resolved measurements show nearly monoexponential decay of the PL in the structures from a-Si/SiO<sub>2</sub> SLs. The temperature dependent PL lifetimes are well described by a model of the singlet-triplet exciton splitting. The excitonic PL of nc-Si from a-SiO/SiO<sub>2</sub> SLs are characterized by a strongly non-exponential and excitation-dependent decay. This is indicative of the excitation energy transfer between neighboring Si nanocrystals. We demonstrate that in Er-doped SLs the energy of optical excitation of nc-Si is almost completely transferred to the Er ions, what results in an emission at 1540 nm. This highly efficient sensitizing of the erbium PL is explained by a strong coupling between excitons in nc-Si and Er ions in surrounding SiO<sub>2</sub>. Our temperature and excitation dependent experiments show that the energy transfer from the excitons to the rare earth ions competes successfully with nonradiative recombination processes in nc-Si/SiO<sub>2</sub> structures.

### **N11.3**

**Manipulation of Non-Magnetic Nanowires Using Magnetic Ends.** Anne K Bentley<sup>2</sup>, Jeremy S Trethewey<sup>1</sup>, Arthur B Ellis<sup>2,3</sup> and Wendy C. Crone<sup>1</sup>; <sup>1</sup>Engineering Physics, Univ. of Wisconsin-Madison, Madison, Wisconsin; <sup>2</sup>Chemistry Department, University of Wisconsin-Madison, Madison, Wisconsin; <sup>3</sup>Chemistry Division, National Science Foundation, Arlington, Virginia.

We have prepared metallic alloy nanowires with Ni ends using sequential electrodeposition into porous alumina templates. The alloy system explored in this work is CuSn. The alloy phase of the nanowires has been controlled by varying the electrodeposition conditions and characterized using X-ray diffraction and electron dispersive spectroscopy. After the alumina template is dissolved, the nanowires (200 nm in diameter and up to 50  $\mu$ m long) have been suspended in viscous solvents. Their behavior was monitored using optical methods as their orientation and position were controlled using magnetic fields. The magnetic ends on the non-magnetic nanowires have enabled us to position the nanowires for mechanical testing.

### **N11.4**

#### **Composites of Colloidal Semiconductor and Magnetic Nanoparticles with Gold.** Andrey L. Rogach<sup>1</sup>, Dmitry S.

Koktysh<sup>1</sup>, Yury Rakovich<sup>2</sup> and Jochen Feldmann<sup>1</sup>; <sup>1</sup>Physics Department, University of Munich, Munich, Germany; <sup>2</sup>Physics Department, Trinity College, Dublin, Ireland.

Composite colloidal nanoparticles combine useful properties of their components. We present core-shell structures and co-colloids consisting of either luminescent II-VI semiconductor nanocrystals or magnetic nanoparticles and gold, and demonstrate the possibility of tuning the properties of the resulting composites. Core-shell nanoparticles were prepared by adapting the seed-mediated growth

approach. The fabrication of co-colloids was based on interactions between colloidal components in an aqueous medium. For the synthesized composite nanocrystals, the optical properties of both semiconductor and magnetic particles were strongly influenced by the surface plasmon resonance of gold, as shown by temporally integrated and time resolved photoluminescence measurements. The final goal of our studies is to create functional nanocomposite colloids combining useful luminescent and magnetic properties of the correspondent counterparts with a possibility to utilize well-understood surface chemistry of gold for the realm of biological detection.

### **N11.5**

#### **Interface Effect on Optical Phonons in CdSe/ZnS**

**Nanocrystals: Resonant Raman Spectroscopy.** Alexandre V. Baranov<sup>2</sup>, Dmitry V. Talapin<sup>3</sup>, Tania Perova<sup>4</sup>, Alan Moore<sup>4</sup>, Yury P. Rakovich<sup>5</sup>, John Donegan<sup>5</sup> and Andrey L. Rogach<sup>1</sup>; <sup>1</sup>Physics Department, University of Munich, Munich, Germany; <sup>2</sup>S.I.Vavilov State Optical Institute, St.-Petersburg, Russian Federation; <sup>3</sup>Institute of Physical Chemistry, University of Hamburg, Hamburg, Germany; <sup>4</sup>Department of Electronic and Electrical Engineering, Trinity College, Dublin, Ireland; <sup>5</sup>Physics Department, Trinity College, Dublin, Ireland.

The evolution of optical phonon spectra of colloidal core/shell CdSe/ZnS nanocrystals of 4 nm core size with an increase of the shell thickness from 0.5 to 3.4 monolayers has been studied by resonant Raman spectroscopy at room temperature. We have investigated in detail the shape of longitudinal optical (1LO and 2LO) and surface optical phonon lines of CdSe core. The red shift due to confinement of the LO phonons was observed. Only SO phonons with angular momentum of  $l=2$  were found to be active in resonant Raman scattering with lineshape and phonon frequencies depending on ZnS shell thickness. An increase in Raman scattering by surface (core/shell interface) phonons and the red shift of the corresponding phonon band have been observed and assigned to variations in the shell structure. We have also observed the line of the LO phonons of the ZnS shell at about 350  $\text{cm}^{-1}$  with intensity comparable to that of 2LO CdSe peak. The dependencies of the ZnS LO phonon energy, the lineshape, and its integral intensity on the ZnS shell thickness were studied. The results obtained suggest that a morphological transition from semi-disordered coherent (at very low coverage) to the incoherent epitaxial (at shell thickness more than 2 monolayers) takes place in the growth mechanism of the ZnS shell on the CdSe core. The shell-induced disorder is supposed to provide a major contribution to lineshape of the Raman spectra at higher ZnS coverage. As a result, defect-free core/shell interface is supposed to be more important for producing strongly luminescent nanocrystals than the increase of the shell thickness. This conclusion is supported by results of X-ray diffraction studies, and by photoluminescence and absorption spectroscopy.

### **N11.6**

#### **Photocurrent mechanism in a hybrid system of 1-thioglycerol and HgTe quantum dots.** Hyunsuk Kim, Kyoungah Cho,

Byungdon Min, Jong Soo Lee and Sangsig Kim; Electrical Department, Korea University, Seoul, South Korea.

Photocurrent mechanism in a hybrid system of 1-thioglycerol and HgTe quantum dots (QDs) was studied for the first time in the infrared (IR) range. 1-thioglycerol-capped HgTe QDs were prepared using colloidal method in aqueous solution; the synthesis and size of the HgTe QDs were examined by x-ray diffraction, Raman scattering, and high-resolution transmission electron microscopy. Absorption and photoluminescence spectra of the capped HgTe QDs revealed the strong excitonic peaks in the wavelength range from 900 to 1100nm, because of their widened band gap due to the shrinkage of their sizes to about 3 nm. The wavelength dependence of the photocurrent for the hybrid system of the 1-thioglycerol and HgTe QDs was very close to that of the absorption spectrum, indicating that charge carriers photo-excited in the HgTe QDs give direct contribution to the photocurrent in the media of 1-thioglycerol. In this hybrid system, the photo-excited electrons in the HgTe QDs are strongly confined, but the photo-excited holes act as free carriers. Hence, in the photocurrent mechanism of the this hybrid system, only holes among electron-hole pairs created by incident photons in the HgTe QDs are transferred to 1-thioglycerol surrounding HgTe QDs and contribute photocurrent flowing in the media of 1-thioglycerol.

### **N11.7**

#### **PL Spectroscopy of Si Nanowires Grown by MWCVD.**

Nikolay Suetin, Vladimir Dvorkin, Nikolay Dzbanovskiy and Vladimir Pirogov; Institute of Nuclear Physics, Moscow State University, Moscow, Russian Federation.

Silicon nanowires (SiNWs) are the promising candidate for nanoelectronics and Si-based photoelectronic devices. Laser ablation, thermal evaporation and CVD from silanes have been successfully used to synthesize SiNWs. New modification of MW Plasma Enhanced

CVD process was developed using solid state Si target (Si wafer). The Si whiskers were grown by MWCVD method in H<sub>2</sub> plasma at pressure of about 150 Torr and substrate temperature 1100-1200 C, measured by Williamson Pro-S pyrometer. The Si(111) wafer covered by 20 nm Au layer was used as a substrate. The Si growing material was produced by etching of solid Si plate of 0.4 mm thick placed above the wafer at a distance of about 1 mm and heated over 1000 C by MW plasma. Deposited SiNWs were studied by SEM, Raman and PL spectroscopy. Diameter of deposited wires can vary from few nanometers to microns by changing of Au layer thickness and deposition parameters (MW power, hydrogen pressure). PL spectra were measured both from just grown samples and after oxidation. PL bands with peaks in the range of 541-726 nm were observed. Correlation between PL emission spectrum and SiNW properties are studied. This research was supported by ISTC grant #2559.

#### **N11.8**

**Visible Light Emission from Erbium Doped Yttria Stabilized Zirconia.** Michael Cross and Walter Varhue; Materials Science Program, University of Vermont, Burlington, Vermont.

One of the major shortcomings of silicon (Si) as a semiconductor material is its inability to yield efficient light emission. There has been a continued interest in adding rare earth ion impurities such as erbium (Er) to the Si lattice to act as light emitting centers. The low band gap of Si however has complicated this practice by quenching and absorbing this possible emission. Increasing the band gap of the host has been successfully tried in the case of GaN<sup>1</sup> and Si rich SiO<sub>x</sub><sup>2</sup> alloys. A similar approach has been tried here, where ErO<sub>x</sub> nanocrystals have been formed in a yttria stabilized zirconia (YSZ) host deposited on a Si(100) substrate. The YSZ is deposited as a heteroepitaxial, insulating layer on the Si substrate by a reactive sputtering technique. The Er is also incorporated by a sputtering process and its placement in the YSZ host can be easily controlled. The device structure formed is a simple metal/insulator/phosphor sandwich. Since YSZ is a crystalline material, there is the potential for improved performance of this device. The device has been found to emit visible green light at low bias voltages. Current work involves measuring the IR emission spectrum from these devices. 1. M. Garter, R. Birkhahn, A.J. Steckl, and J. Scofield, "Visible and Infrared Rare-Earth Activated Electroluminescence from Erbium Doped GaN", MRS Internet J, Nitride Semiconductor, Res 4S1, G11.3 (1999). 2. T. Whitaker, "Silicon-Based Infrared LEDs Challenge GaAs", Compound Semiconductors, Vol 8, No. 11 (Dec.2002).

#### **N11.9**

**Fabrication of Single-Crystal Tin Nanowires and Their Physical Properties.** Mingliang Tian<sup>1,2</sup>, Jinguo Wang<sup>2,1</sup>, James Kurtz<sup>1,2</sup>, Ying Liu<sup>1,2</sup>, Thomas Mallouk<sup>3,2</sup> and Moses Chan<sup>1,2</sup>; <sup>1</sup>Department of Physics, Penn State University, University Park, Pennsylvania; <sup>2</sup>Materials Research Institute, Penn State University, University Park, Pennsylvania; <sup>3</sup>Department of Chemistry, Penn State University, University Park, Pennsylvania.

The nature of dissipation in ultra-thin one-dimensional (1D) superconducting wires below T<sub>c</sub> has attracted considerable attention. The early understanding of the dissipation in 1D is based on the work of LAMH, i.e., thermally activated phase slip (TAPS). Typically, the TAPS region is of the order of 0.01 K near the T<sub>c</sub>. For samples with sufficient small diameters and for temperatures sufficient low, a non-zero resistive region far below T<sub>c</sub> was observed, which was suggested as due to the so-called quantum phase slips (QPS), but this idea is extensively debated so far. The most previous experimental work in 1D superconducting system was carried out in granular or amorphous wires so that our understanding for the nature of dissipation in 1D is often limited by the sample's morphology, like disorder or grainularity. Here we report our detailed experimental work on single-crystal tin nanowires. The wires were fabricated by electrochemical depositing Sn into porous membranes, and the diameters are in the range of 20-160 nm, with length up to 40 microns. Temperature and magnetic field dependent resistance, V-I characteristics and magnetization measurements showed that the residual resistance in ultra-thin wires far below T<sub>c</sub> might have an origin of quasi-particles excitation, not QPS of cooper pairs.

#### **N11.10**

**Sulfobetaine Stabilized Cobalt-Gold Core-Shell Nanoparticles.** Zhanhu Guo<sup>3,1</sup>, Challa Kumar<sup>1</sup>, Elizabeth Podlaha<sup>3</sup>, Edward Doomes<sup>1</sup>, Larry L Henry<sup>2</sup> and Josef Hornes<sup>1</sup>; <sup>1</sup>Center for Advanced Microstructures and Devices, Louisiana State University, Baton Rouge, Louisiana; <sup>2</sup>Department of Physics, Southern University A&M college, Baton Rouge, Louisiana; <sup>3</sup>Department of Chemical Engineering, Louisiana State University, Baton Rouge, Louisiana.

A wet chemical synthetic approach was developed for synthesis of cobalt core gold shell nanoparticles using hydrophilic surfactant sulfobetaine [3-(N,N-dimethyldodecylammonium)propane sulfonate] as

a stabilizing agent. Sulfobetaine ensured compatibility of nanoparticles in a variety of polar solvents and the gold protective shell offers the possibility of utilizing cobalt nanoparticles in applications requiring harsh environment and bio-molecular functionalization. The core-shell nanoparticles were characterized using UV-Vis spectroscopy, HRTEM, EDAX, SAED and XRD. X-ray Absorption Spectroscopy (XAS) techniques were also used to confirm the presence of cobalt core and gold shell. A detailed examination of the magnetic properties of core-shell nanoparticles with cobalt nanoparticles using SQUID magnetometry revealed the ferromagnetic nature of cobalt core in the core shell particles. Oxidative stability of core shell nanoparticles under atmospheric conditions was monitored using X-ray Absorption Near Edge Structure (XANES) spectroscopy and magnetic properties.

#### **N11.11**

**Elucidation of the Electronic Properties of Alkanethiolate-Stabilized Gold Clusters and Nanoparticles Using Scanning Tunneling Microscopy.** Rachel Smith<sup>1</sup>, Sanjini Nanayakkara<sup>1</sup>, Brent Mantooth<sup>1</sup>, Thomas Pearl<sup>2,1</sup>, Paul Weiss<sup>1</sup>, Gerd Woehle<sup>3</sup> and James Hutchison<sup>3</sup>; <sup>1</sup>Chemistry, The Pennsylvania State University, University Park, Pennsylvania; <sup>2</sup>Physics, North Carolina State University, Raleigh, North Carolina; <sup>3</sup>Chemistry, University of Oregon, Eugene, Oregon.

The single electron transport properties of metal nanoparticles have led to great interest in their potential integration into nanoscale electronics. Here, we discuss and compare the electronic (I(V)) characteristics of isolated, solution-derived octanethiolate-stabilized gold clusters [Au<sub>11</sub>(S(CH<sub>2</sub>)<sub>7</sub>CH<sub>3</sub>)<sub>10</sub>] and nanoparticles [Au<sub>101</sub>(S(CH<sub>2</sub>)<sub>7</sub>CH<sub>3</sub>)<sub>43</sub>], taken in both cryogenic (4K, UHV) and ambient conditions using scanning tunneling microscopy (STM) and spectroscopy (STS). The clusters and particles (d<sub>CORE</sub> = 0.8 ± 0.2 nm and 1.5 ± 0.5 nm, respectively) are synthesized in solution by ligand exchange of their phosphine-stabilized analogues with octanethiol and are subsequently immobilized on alkanethiolate self-assembled monolayers with inserted dithiol molecules. At low and room temperatures, the Au<sub>11</sub> clusters demonstrate clear Coulomb blockade behavior, with zero-conductance gaps resulting from quantum size effects; the Au<sub>101</sub> nanoparticles also show blockade behavior at room temperature.

#### **N11.12**

**Nanoscale Mechanical and Electromechanical Behavior of Individual Semiconducting Nanowire.** Scott X. Mao<sup>1</sup>, Zongling Wang<sup>2</sup> and Minhua Zhao<sup>3</sup>; <sup>1</sup>Institute of Nanoscience and Technology and Dept. of Mechanical Eng., University of Pittsburgh, Pittsburgh, Pennsylvania; <sup>2</sup>Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia; <sup>3</sup>Mechanical Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania.

Nanobelts are a group of materials that have a rectangle-like cross section with typical widths of several hundred nanometers, width-to-thickness ratios of 5 to 10, and lengths of hundreds of micron meters. Nanoindentations were made on individual ZnO and SnO<sub>2</sub> nanobelts by using atomic force microscope (AFM) and Hysitron Triboscope indenters. Hardness and Young's modulus of the nanobelts have been measured and compared with its bulk crystal. It was shown that the indentation size effect was still obvious for the indentation depth under 50 nm. It is also demonstrated that nanomachining is possible on nanobelt using AFM tip. Electromechanical behavior of the nanobelts has been measured by electric force microscope.

#### **N11.13**

**Optical Properties of CdSe Nanoparticle Assemblies.** Rafael Leon<sup>1,2</sup>, Thomas Huser<sup>2</sup>, Denise M Krol<sup>1,2</sup>, Daniele Gerion<sup>2</sup> and Natalia Zaitseva<sup>2</sup>; <sup>1</sup>Applied Science, UC Davis, Livermore, California; <sup>2</sup>Lawrence Livermore National Laboratory, Livermore, California.

We report on three-dimensional fluorescence imaging of micron-size faceted crystals precipitated from solutions of CdSe nanocrystals. Such crystals have previously been suggested to be superlattices of CdSe quantum dots. Possible applications for these materials include their use in non-linear optical devices or as optical gain media. Because the optical properties of the CdSe semiconductor nanoparticles strongly depend on their size, surface structure, and interactions with their environment, it is important to assess how they behave when closely-packed into micrometer-scale assemblies. The micron-size crystals were grown by slow evaporation from toluene solutions of mono-disperse (in the range of 3-6 nm) CdSe nanocrystals, produced by traditional wet-chemistry techniques. By using a confocal microscope with laser illumination, three-dimensional raster-scanning and synchronized hyper-spectral detection, we have generated spatial profiles of the fluorescence emission intensity and spectrum. We will report on the degree of spatial homogeneity of this luminescence, and the fluorescence decay lifetime of the luminescence

of these samples. The fluorescence data will be compared with results from x-ray diffraction and electron microscopy.

#### **N11.14**

**Enhanced spontaneous emission from colloidal quantum dots embedded in a monolithic microcavity.** Carl Poitras<sup>1</sup>, Michal Lipson<sup>1</sup>, Megan H Hahn<sup>2</sup>, Hui Du<sup>2</sup> and Todd D Krauss<sup>2</sup>;  
<sup>1</sup>Department of Electrical and Computer Engineering, Cornell University, Ithaca, New York; <sup>2</sup>Department of Chemistry, University of Rochester, Rochester, New York.

The embedment of colloidal quantum dots (QD) in photonic structures opens the possibility of endowing optoelectronic properties to a wide variety of intrinsically optically inactive materials. By embedding the QDs resonant structures, the emission of the dots can be controlled. To date, several attempts to incorporate colloidal dots in photonic structures have been made. However, enhancement of the spontaneous emission has not yet been shown, mainly because of the large size of the structures compared to the emission wavelength of the QDs. Here, we demonstrate the enhancement of the spontaneous emission of colloidal QDs embedded in a 1D cavity. Colloidal CdSe QDs were embedded in a microcavity formed between two distributed Bragg reflectors (DBRs). The microcavity consists of a 95 nm film (spin coated) of the QDs sandwiched between two SiO<sub>2</sub> layers. Each DBR consists of twelve sputtered quarter-wavelength thick alternating layers of TiO<sub>2</sub> and SiO<sub>2</sub>. The entire structure was deposited in a wedged manner to obtain a continuum of Fabry-Perot resonances that are position determined (approximately 4nm/mm) across the cavity sample. We measured a Q of 135 of the cavity. A reference sample was prepared by spin-coating QDs with the same thickness on a glass slide and sputtering a 75 nm thick layer of SiO<sub>2</sub> as a cap layer. The QD absorption at the emission wavelength is enhanced by an order of magnitude due to the cavity effect. This absorption enhancement is dominant due to the significant free space absorption at the emission wavelength. The enhancement of the absorption limits the effective Q that can be achieved since the electric field build-up in the cavity is decreased. Photoluminescence measurements were performed using 1.4 mW/mm<sup>2</sup> of the 457.9 nm line of an argon laser as an optical pump, at room temperature. The spectrally integrated photoluminescence from the cavity structure in resonance with the QDs' free space emission line is enhanced by a factor of 2.7 +/- 0.6 compared to the photoluminescence from the reference structure. The results are in good agreement with the theoretical integrated emission enhancement of 4.5. The enhancement indicates coupling of the QDs to the cavity mode opening the possibility of controlling externally the intensity and lifetime of the QDs. The embedment of colloidal QDs in photonic structures holds great promise for enabling new active technological breakthroughs in the area of photonics, such as the integration of monolithic light emission and modulation devices on-chip.

#### **N11.15**

**Synthesis of Erbium doped SiO<sub>x</sub> Nanorods using Hot-Wire CVD method.** TeChi Wong, Chi-Chung Yu and Jih-Jen Wu; Chemical engineering, Cheng Kung University, Tainan, Taiwan.

Erbium doped SiO<sub>x</sub> nanorods have been synthesized with hot-wire CVD. Energy-dispersive X-ray (EDX) measurement indicates that the presence of erbium in these nanorods. Scanning electron microscopy (SEM) images reveal that the Er doped nanorods have different morphology in comparison with the undoped SiO<sub>x</sub> nanorods. The near infrared luminescence from the intra-4f transition of Er ion and structural characteristic of the Er doped SiO<sub>x</sub> nanorods will be discussed in this paper.

#### **N11.16**

**Direct Synthesis Of Monodisperse Nanoparticles Of Transition Metals And Their Oxides Without A Size Selection Process.** Jongnam Park, Jin Joo and Taeghwan Hyeon; School of Chemical Engineering, Seoul National University, Seoul, South Korea.

We report on the synthesis of monodisperse nanoparticles of transition metals and their oxides without any size selection process. The size uniformity is the most important issue in the synthesis of nanoparticles. Monodisperse nanoparticles possess a very narrow particle size distribution with standard deviation of less than 5 %, and they are usually obtained after very difficult size selection process. Recently, our research group developed a new synthetic procedure to produce monodisperse nanoparticles of iron, iron oxide and cobalt ferrite. Highly crystalline and monodisperse maghemite and cobalt ferrite nanocrystals were synthesized directly without any size selection process. High temperature aging of metal-oleic acid metal complex was found to generate monodisperse metal nanoparticles. The resulting metallic nanoparticles were transformed to monodisperse ferrite nanocrystals by mild oxidation. Particle size can be varied from 2 nm to 20 nm by controlling the experimental parameters. Using a similar synthetic procedure, we synthesized spherical and monodisperse nanoparticles of palladium, gold, iron,

cobalt, manganese, nickel, and iron-cobalt alloys. Monodisperse manganese oxide nanoparticles with variable sizes were synthesized and their magnetic properties were investigated. Non-hydrolytic sol-gel reaction of zirconium halides (chloride and bromide) and zirconium tetra-isopropoxide generated highly crystalline and monodisperse zirconia nanocrystals with particle sizes of 3 nm and 4 nm. Thermal decomposition of metal-surfactant complexes in the presence of appropriate surfactant and oxidant produced uniform-sized magnetic nanowires of iron oxide and manganese oxide.

#### **N11.17**

**Optical Interactions in Ensembles of GaN Nanoparticles.**

Leah Bergman<sup>1</sup>, Andrew P. Purdy<sup>2</sup>, Xiang-Bai Chen<sup>1</sup>, Heather Hoock<sup>1</sup> and Althea Walker<sup>1</sup>; <sup>1</sup>Physics, University of Idaho, Moscow, Idaho; <sup>2</sup>Chemistry Division, Naval Research Laboratory, Washington, District of Columbia.

We present optical analysis concerning the redshift of the photoluminescence (PL) of ensembles of GaN nanocrystals. We found that the extent of the redshift depends on the laser power as well as on the ensemble size. For ensembles of size  $\sim 30 \mu\text{m}$ , the laser power in our experimental specification impacted the PL energy and caused a redshift of up to 120 meV. This phenomena was not observed for a small ensemble of  $\sim 1 \mu\text{m}$  or less. For a small ensemble the PL redshift was negligible and depended weakly on the laser power; similar behavior was found in GaN thin film. The above findings were observed in the PL of GaN nanocrystalline of Wurtzite as well as cubic structure and of different morphologies. Our results point to a laser heating event occurring in the large ensemble; the emitted PL and scattered light is confined among the nanocrystallites thus causing the heating. For a small ensemble the light has a higher probability of diffusing outside the enclosure, and thus no laser heating occurs. Moreover, no damage to the nanocrystallites due to heating was observed; the tuning of the PL energy position via the laser power was found to be a reversible process, i.e., we obtained the same energy versus power dependence going up in power and then going down in power. The actual temperature of an ensemble may be determined via Raman analysis, a study that will be presented as well.

#### **N11.18**

**Formation and Properties of Silicon/Silicide/Oxide Nanochains.** Hideo Kohno<sup>1</sup>, Yutaka Ohno<sup>1</sup>, Satoshi Ichikawa<sup>2</sup>, Tomoki Akita<sup>2</sup>, Koji Tanaka<sup>2</sup> and Seiji Takeda<sup>1</sup>; <sup>1</sup>Osaka Univ., Toyonaka, Osaka, Japan; <sup>2</sup>AIST Kansai, Ikeda, Osaka, Japan.

Heterostructured nanowires have attracted intense interest for potential use as building blocks of nanostructure-based devices. Especially, nanowires with semiconductor/metal junctions are expected to provide useful functions such as a Schottky diode. In this study, we report the fabrication of silicon/silicide/oxide heterostructured nanowires (silicon/silicide/oxide nanochains) [Appl. Phys. Lett., accepted] using basic silicon/oxide nanochains [H. Kohno and S. Takeda, Appl. Phys. Lett. 73, 3144 (1998)] as templates. In silicon/silicide/oxide nanochains, composite nanoparticles of silicon and copper silicide were connected by amorphous silicon oxide neck forming a chain-like structure. For fabricating silicon/silicide/oxide nanochains, silicon/oxide nanochains were heated with a small piece of copper to 700 degree C for 10 min in an evacuated silica container. Infused copper reacted with crystalline-silicon particle resulting in the formation of hemispherical silicide leaving the rest hemispherical silicon. The diameter of silicon/silicide composite nanoparticles was roughly 10 - 30 nm. The silicon/silicide/oxide nanochains were examined by TEM, EDX and PL. In addition, inner potential was probed by electron holography.

#### **N11.19**

**Preparation of Metal Oxide Nanowires by Hydrothermal Synthesis in Supercritical Water.** Yukiya Hakuta and Hiromichi Hayashi; Supercritical Fluid Research Center, National Institute of Advanced Industrial Science and Technology, Sendai, Japan.

We report a fabrication of photocatalyst potassium titanate nanowires by hydrothermal synthesis under supercritical conditions with a rapid heating. A mixed solution of titanium hydroxide sols and aqueous potassium hydroxide solution was used as starting solutions. Reaction temperature was in the range of 350 C to 420 C and pressure was in the range of 20 to 30 MPa. Titanium ion concentration set to be 0.02M. The K/Ti molar ratio was varied to be 2 to 20 by changing potassium hydroxide concentration. Products were characterized by X-ray diffraction, transmission electron microscopy (TEM) and BET analysis. In the case of 20 of K/Ti molar ratio, pure potassium titanate (K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub>) was obtained. According to TEM observations, K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> particles obtained were nanowires with diameters of 12 nm and lengths ranging from 500 to 1,000nm. These particles applied to photodecomposition of methanol. Photocatalytic reactivity of the KTO nanowires were some orders of magnitude better than that of KTO particles with lengths of micron orders. In addition, we

demonstrate preparation of other metal oxide nanowires that are AlOOH and MnO<sub>2</sub> by this supercritical water method.

#### **N11.20**

**Size-Reduction of Silicon Nanowires in a Micro-Electrochemical Cell.** Robert Juhász, Jakob Wistrom and Jan Linnros; Microelectronics and Information Technology, Royal Institute of Technology, Kista-Stockholm, Sweden.

Silicon nanowires of diameters down to 40 nm has been fabricated on p-type Silicon-on-Insulator material by electron beam lithography and reactive ion etching followed by photo-electrochemical size-reduction in an hydrofluoric acid solution. Our previous results on nanopillar size-reduction indicate that controlled reduction down to 10 nm diameter or smaller is possible. Typical nanowire dimensions before size-reduction are 100 nm diameter and 1 μm length. Connection leads also defined in the silicon layer of typically 50 μm widths connects the wire to square metal pads. To enable accurate control of the size-reduction process, a micro-electrochemical cell has been developed, enabling only a single nanowire to be exposed to the etching solution (through a 1 mm diameter opening) while being illuminated by a laser or a lamp. This allows contact leads to be extended to contact pads located outside the cell (defined by optical lithography) which can be connected by probes during the etching. A Pt wire connects to the etching solution and a fourth contact is made to the sample backside. During etching, this arrangement allows for in-situ electrical characterization of the wire and back gating to control the conductance of the wire. Electrical characterization of both initially fabricated nanowires as well as size-reduced nanowires has been performed at room temperature demonstrating a scaling of the conductance with cross-sectional size. Finally, we believe the micro-electrochemical cell to be an appealing approach, not only for electrochemical etching of isolated nano-devices, but also for (bio-) detector applications, since the nanowire can be selectively subjected to different biological or chemical solutions, while being electrically characterized.

#### **N11.21**

**Superparamagnetic Iron Oxide Nanoarticles for Biomedical Applications.** Mathieu Chastellain, Alke Petri and Heinrich Hofmann; Material Sciences Institute, Swiss Federal Institute of Technology (EPFL), Lausanne, Switzerland.

Nanoscaled particles have been intensively studied in these past years for biomedical purpose. A wide range of in vivo as well as in vitro applications have been or are currently developed. In this field, particles showing a superparamagnetic behaviour are of particular interest as they are sensitive to magnetic fields without retaining magnetisation after removal of the latter. Not only superparamagnetic particles can be guided but they also exhibit heating properties when submitted to appropriate alternating magnetic fields. These characteristics make them promising for targeted applications where they could act as carriers as well as activators. The local temperature increase can be used for confined control release of linked entities or to modify specific cells activities in a well defined area. From a practical point of view, such a versatile tool presents the advantages of enhanced yields for in-vitro processes and do not require invasive operations like classical in-vivo therapies. As biocompatibility is required, iron oxide nanoparticles are usually selected. To ensure colloidal stability and allow a further functionalisation of the surface the particles are either coated or embedded in a matrix to form beads with one or more iron oxide cores. The composite magnetic properties might then differ from the ones primary particles show and great care should be paid to interparticle interactions. The present work is focused on application in hyperthermia (controlled heating in a well defined area), separation (in vitro) and drug delivery (targeted drug release). The synthesis and characterisation of nanoscaled iron oxide particles embedded or coated with different compounds is presented. The composites as well as primary iron oxide particles composition, size distribution and magnetic properties are described. Biocompatibility aspects are also considered.

#### **N11.22**

**Quantum Confinement Effect of Si Nanowires.** Kui Yu, Y.H. Tang and J.A. Ripmeester; Steacie Institute for Molecular Sciences, National Research Council Canada, Ottawa, Ontario, Canada.

Silicon nanowires are promising candidates to target nano-electronic applications. Recently, various fabrication methods have been reported, but they are short of a fundamental investigation to bring insights into the micro-structure and electronic structure of the nanowires to facilitate future design aiming at nano-electronic devices. We report here a thorough characterization of quantum confinement of the Si nanowires, which were prepared by a CVD (chemical vapor deposition) method. The instrument consists of a quartz tube that is mounted inside a high-temperature tube furnace. The Si nanowires prepared consist of two parts: crystalline Si (inner part) and

amorphous silica (outer layer). After preparation, oxidation (ca. 1000 °C) was performed on the Si nanowires in order to reduce the wire diameter (Si core). High-Resolution Transmission Electron Microscopy (HRTEM) was carried out to image the nanowires before and after oxidation. Raman experiments showed blue shifts of the Si feature peak with the increase of the oxidation time during the post treatment. Also, solid state NMR experiments provided information on the quantum confinement effect.

#### **N11.23**

**ZnS Nanoparticles Synthesis and Characterization.** Yvonne Axmann, Alke Petri and Heinrich Hofmann; Materials Science and Engineering Department, Swiss Institute of Technology, Lausanne, Vaud, Switzerland.

The optical properties of nanocrystalline semiconductors have been studied extensively in recent years and a wide range of synthetic methods have been developed [1]. Many approaches involve non-aqueous methods and the classical techniques of colloidal chemistry. However, biological and medical applications require water-dispersible nanocrystals that can be covalently coupled to biomolecules for use in e.g. ultra sensitive biological detection. In our work we characterize L-cysteine coated ZnS:Mn nanoparticles by a variety of methods. The particles are prepared in a colloidal synthesis using L-cysteine as surfactant and show an orange fluorescence at 585 nm characteristic for the <sup>4</sup>T<sub>1</sub> → <sup>6</sup>A<sub>1</sub> transition of Mn<sup>2+</sup> ions in a crystalline ZnS-matrix [2]. The absorption spectrum exhibits a shoulder at 285 nm, which is blue-shifted compared with the absorption of bulk ZnS (342 nm) [3] indicating a quantum size effect. For the determination of the particle size distribution different techniques were applied, for example TEM picture analysis, photon correlation spectroscopy, or analytical ultra centrifugation. The doping of the particles with Mn<sup>2+</sup> was investigated by means of atomic absorption spectroscopy. The luminescence intensity shows a maximum at a Mn<sup>2+</sup> content of 0.2 mol% related to Zinc under the chosen experimental conditions. The most limiting factor for the luminescence intensity of nanoparticles is the radiatively recombination of the electron and the hole at the particle surface. Unsaturated valences at the surface act as recombination centres and so their saturation leads to an increase in luminescence intensity [1]. To saturate these "dangling bonds" the particles are coated with silica. This coating has many advantages, it is chemically inert, optically transparent [4], the shell has a sufficient lattice match with the ZnS and its refractive index is smaller than the one of ZnS so that the excitation light is diffracted into the particle core. The thus coated particles show luminescence intensity, which is 3.5 times higher than the intensity obtained without the silica coating. [1] A. P. Alivisatos, J. Phys. Chem., 100 (1996) 13226. [2] H.-E. Gumlich, J. Lumin., 23 (1981) 73. [3] N. Murase, J. Phys. Chem. B, 103 (1999) 754. [4] K. P. Velikov, Langmuir, 17 (2001) 4779.

#### **N11.24**

**Systematic Investigation of the Factors Governing Photoluminescence (PL) of CdSe From CdO and Corresponding Core-Shell Quantum Dots.** Kui Yu, Steacie Institute for Molecular Sciences, National Research Council Canada, Ottawa, Ontario, Canada.

A comprehensive study was performed on the factors affecting the PL properties of CdSe quantum dots synthesized with CdO as the Cd precursor. The factors investigated include (1) nucleation and growth temperature, (2) CdO concentrations and Cd-to-Se ratios, (3) additives, (4) the nature and composition of the reaction media. We developed a novel approach to evaluate semi-quantitatively the surface quality of quantum dots, based on our thorough investigation addressing the various factors affecting the PL properties of CdSe quantum dots during their growth. Post-treatments for the surface passivation were performed, involving the modification by organic species (e.g. amines) and growing an inorganic shell hetero-epitaxially. The increase of irradiative recombination of light-generated charge carriers was monitored during the post-treatment. In addition to the surface of quantum dots, this new evaluation method seems to be powerful also to estimate the efficiency of the post-treatment for surface passivation. The issue of high-quality quantum dots is addressed in detailed, based on the new evaluation method.

#### **N11.25**

**Early Stages of Platinum Nanoparticles Growth by Means of Pulsed Laser Ablation Technique.** Richard Dolbec, Eric Irissou, Federico Rosei, Daniel Guay, Mohammed Chaker and My Ali El Khakani; U. of Quebec, INRS EMT, Varennes, Quebec, Canada.

Platinum nanoparticles were deposited onto Highly Oriented Pyrolytic Graphite (HOPG) substrate by laser ablating a Pt target at room temperature into a vacuum chamber. By varying the helium background pressure (10<sup>-5</sup> - 0.5 Torr) and the target-to-substrate

distance (30 - 60mm), we were able to explore a large range of kinetic energies (i.e., from  $\sim 5$  to  $\sim 130$  eV/atom) of the Pt ablated species impinging the surface of the HOPG substrates. The effect of the kinetic energy on the size and the surface density of Pt nanoparticles has been systematically ex-situ investigated by means of scanning tunneling microscopy (STM). Interestingly, it is shown that, the size of the PLD Pt nanoparticles is mainly influenced by the nominal deposited Pt thickness (tn), regardless of the incident kinetic energy of the ablated species. Indeed, below a critical coverage of about 0.5 ML, the nucleation of Pt nanoparticles presenting a nearly constant mean diameter (dm) of  $1.25 \pm 0.25$  nm is observed. However, as the coverage is increased above 0.5 ML, dm increases according to a power law of the type  $dm \sim \ln(1/Z)$ , with  $Z = 4.7 \pm 0.1$ . Finally, the growth of spatially separated Pt nanoparticles seems to be limited by a critical tn value which was found to be related to the kinetic energy of the ablated species.

#### N11.26

**GaP Nanostructures : Nanowires, Nanobelts, Nanocables, and Nanocapsules.** Hee Won Seo, Seung Yong Bae and Jeunghee Park; Material Chemistry, Korea University, Seoul, South Korea.

Various GaP nanostructures such as nanowires, nanobelts, nanocables, and nanocapsules were synthesized by sublimation of ball-milled powders. They have a single-crystalline zinc blende structure with [111] growth direction. The morphology and structure were controlled by reactant gas, growth time, flow rate, and growth temperature. The size, morphology and properties of the nanostructures were examined by scanning electron microscopy, transmission electron microscopy, electron energy-loss spectroscopy (EELS), electron diffraction, energy dispersive x-ray spectroscopy, powder x-ray diffraction, and Raman spectroscopy using a 514.5 nm argon ion laser. The photoluminescence was carried out using the 458 nm line of an argon ion laser as the excitation source. The GaP nanowires are straight, cylindrical, and smooth in surface, with mean diameter of 40 nm and length up to 300 nm. The nitrogen-doped nanobelts and nanowires were synthesized by ammonia ambient gas. EELS data reveals that the nitrogen doping occurs mainly in the surface region. The PL spectrum shows the typical isoelectronic bound exciton peaks in the range of  $2.11 \sim 2.25$  eV, suggesting a concentration of  $\sim 10^{18}$  cm<sup>-3</sup> nitrogen atoms. We also synthesized two types of GaP nanocables; GaP nanowire sheathed with the amorphous silicon oxide layers and with the graphite layers. The core-shell diameter is under 30 nm and the outerlayer can be removed by acid treatment to produce the 10 nm diameter GaP nanowires. The GaP encapsulated with BCN nanotubes were synthesized under the ammonia flow using the ball-milled carbon-containing boron oxide powders. The number of BCN layers is typically 10~20.

#### N11.27

**Controlled Structure of Gallium Oxide and Indium Oxide Nanowires.** Chun Hye Jin, Bae Seung Yong and Park Jeunghee; Chemistry, Korea University, Seoul, South Korea.

Gallium oxide (Ga<sub>2</sub>O<sub>3</sub>) and indium oxide (In<sub>2</sub>O<sub>3</sub>) nanostructures were synthesized by chemical vapor deposition. Ga<sub>2</sub>O<sub>3</sub> nanowires were synthesized using gallium/gallium oxide mixture and oxygen. The diameter of the nanowires is 30-80 nm with an average value of 50 nm. They are consisted of single-crystalline monoclinic crystal. While the nanowires grown without catalyst exhibit a significant planar defect, the nanowires grown with nickel catalytic nanoparticles are almost defect-free. The growth direction of the nanowires grown without the catalyst is uniformly [010]. In contrast, the nanowires grown with the catalyst have random growth direction. X-ray diffraction, Raman spectroscopy, and photoluminescence are well correlated with the structural characteristics of the nanowires. The result provides an evidence for the catalyst effect in controlling the structure of nanowires. In<sub>2</sub>O<sub>3</sub> nanostructures were also synthesized in a controlled manner by selecting the catalyst. The reactants were indium and indium/indium oxide mixture. The nanowires were produced using catalytic gold nanoparticle and gallium metal. But the unique bifurcated-structure nanobelts were instead grown without gallium metal. The nanowires have uniform [100] growth direction with rectangular cross-section. We converted the In<sub>2</sub>O<sub>3</sub> nanowires to Ga<sub>2</sub>O<sub>3</sub> nanowires.

#### N11.28

**Red-ox transmetalation synthesis of CoPt core shell structure and its phase transition to fct CoPt nanoparticle with enhanced magnetism.** Jinwoo Cheon, Chemistry, Yonsei Univ, Seoul, South Korea.

We present systematic studies of nanoscale phase transitions of magnetic nanocrystals. We first synthesized  $\sim 6$  nm Co(core)-Pt(shell) nanoparticles by red-ox transmetalation process and then thermally induced their structural transformation to ferromagnetic Co<sub>1</sub>Pt<sub>1</sub> solid solution. These novel structures were

characterized by x-ray absorption, SQUID and TEM. Both core-shell and phase changed CoPt solid solution structures were carefully probed by Co K-edge and Pt LIII-edge XANES and EXAFS refinements. Resulting solid solution type fct (face-centered tetragonal) CoPt nanoparticles show site ordering of Co and Pt atoms in the face-centered tetragonal phase and enhanced magnetic properties with high coercivity at room temperature.

#### N11.29

**Vapor-Liquid-Solid Growth of Silicon-Germanium Nanowires.** Kok-Keong Lew<sup>1,2</sup>, Ling Pan<sup>1,2</sup>, Elizabeth C. Dickey<sup>1,2</sup> and Joan M. Redwing<sup>1,2</sup>; <sup>1</sup>Materials Research Institute, The Pennsylvania State University, University Park, Pennsylvania; <sup>2</sup>Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania.

The fabrication of SiGe/Si nanowires with built-in heterostructures along the radial or axial direction of the wire is of significant interest for nanoscale device applications. Vapor-liquid-solid (VLS) growth is a promising approach to SiGe nanowire synthesis since both Si and Ge form a eutectic liquid alloy phase with gold at approximately 360°C. The use of silane (SiH<sub>4</sub>) and germane (GeH<sub>4</sub>) as gaseous sources for VLS growth is challenging, however, due to the large difference in the thermal stability of these sources. In this study, we have investigated the effect of growth conditions on the composition, microstructure and growth rate of SiGe nanowires. Anodized alumina membranes with a nominal pore diameter of 200 nm were used as templates for electrodeposition of gold metal catalyst plugs and subsequent VLS growth. Mixtures of 10% SiH<sub>4</sub> in H<sub>2</sub> and 1% GeH<sub>4</sub> in H<sub>2</sub> were used, and the inlet GeH<sub>4</sub>/SiH<sub>4</sub> ratio was varied from 0.01 to 0.04. The reactor pressure was held constant at 12 Torr and the growth temperature was varied from 350 to 500°C. At 500°C, GeH<sub>4</sub> was found to readily decompose to form a thin film of Ge on the membrane surface and outer surface of the nanowires, resulting in a suppression of nanowire growth. A reduction in the growth temperature to 400°C resulted in SiGe nanowire growth with negligible Ge coating. Electron diffraction patterns and high resolution electron microscopy observations revealed that the SiGe nanowires grown under these conditions were single crystal with a thin (2-3 nm) native oxide coating. Z-contrast scanning transmission electron microscopy imaging and quantitative energy dispersive x-ray spectroscopy were used to confirm the presence of Si and Ge in the nanowires and to profile the elemental composition throughout the wire.

#### N11.30

**Control of Morphology and Growth Direction of Gallium Nitride Nanostructures.** Seung Yong Bae, Hee Won Seo and Jeunghee Park; Korea Univ., Jochiwon, South Korea.

Various shaped single-crystalline gallium nitride (GaN) nanostructures were produced by chemical vapor deposition method in the temperature range of 900-1200 °C. Scanning electron microscopy, transmission electron microscopy, electron diffraction, x-ray diffraction, electron energy loss spectroscopy, Raman spectroscopy, and photoluminescence were used to investigate the structural and optical properties of the GaN nanostructures. We controlled the GaN nanostructures by the catalyst and temperature. Cylindrical and triangular shaped nanorods were synthesized using iron and gold nanoparticles as catalysts, respectively, in the temperature range of 900-1000 °C. We synthesized the nanobelts, nanosaws, and porous nanowires using gallium source/ boron oxide mixture. When the temperature of source was 1100 °C, the nanobelts having a triangle tip were grown. At the temperature higher up to 1200 °C the nanosaws and porous nanowires were formed with a large scale. The cylindrical nanowires have random growth direction, while the trigonal nanorods have uniform growth direction [010]. Growth direction of the nanobelts is perpendicular to the [010]. Interestingly, the nanosaws and porous nanowires exhibit the same growth direction [011]. The shift of Raman, XRD, and PL bands from those of bulk were correlated with the strains of the GaN nanostructures.

SESSION N12: Electrical, Electronic Properties and Devices I

Chairs: Philippe Guyot-Sionnest and Todd D. Krauss  
Thursday Morning, December 4, 2003  
Room 302 (Hynes)

#### 8:30 AM \*N12.1

**Electron Conduction in Quantum Dot Solids.**

Daniel Vanmaekelbergh<sup>1</sup>, John J. Kelly<sup>1</sup>, Aarnoud L. Roest<sup>1</sup>, Arjan J. Houtepen<sup>1</sup> and Eric Meulenkaamp<sup>2</sup>; <sup>1</sup>Condensed Matter, Utrecht University, Utrecht, Netherlands; <sup>2</sup>Philips Research Lab., Eindhoven, Netherlands.

The optical and electrical properties of quantum dot solids will be

determined by the atom-like orbitals of the nanocrystal building blocks and their electronic coupling, Coulomb repulsion and disorder effects. Although these effects have been considered in some detail in theoretical work(1), experimental research in this field has just started. An essential requirement in the research on quantum dot solids or assemblies is the control of the number of electrons per quantum dot i.e. the electron number  $N$ . We have studied storage and transport of electrons in an assembly of ZnO nanocrystals (3-5 nm) using a transistor-type set-up with an electrochemical gate(2,3). The average electron number  $\langle N \rangle$  is controlled by the electrochemical potential of the assembly. Depending on the size of the ZnO nanocrystals and the electrolyte solution we could reversibly store between one and ten electrons in the atom-like S and P conduction orbitals of the ZnO quantum dots. With optical experiments we showed that charge storage in surface band gap states is not important. Long-range transport in the ZnO assembly was studied by measuring the linear conductance between a source and drain electrode for varying  $\langle N \rangle$ . With an aqueous electrolyte, the mobility shows a staircase as a function of  $\langle N \rangle$ , indicative of a regime of tunneling between the S orbitals, for  $0 < \langle N \rangle < 2$  followed by a regime where transport occurs by tunneling through P-orbitals  $2 < \langle N \rangle < 8$ . The mobility is T-independent. In contrast, with non-aqueous electrolytes permeated in the pores, electron-electron repulsion is important in the storage and transport. Our results will be compared with recent work obtained with CdSe and PbSe QD Solids(4). 1. Quantum dots as chemical building blocks: elementary theoretical considerations. Remacle, F. & Levine, R. D. *ChemPhysChem* 2, 20-36 (2001). 2. Staircase in the Electron Mobility of a ZnO Quantum Dot Assembly due to Shell Filling. Roest, A. L., Kelly, J. J., Vanmaekelbergh, D. & Meulenkaamp, E. A. *Phys. Rev. Lett.* 89, 036801 (2002). 3. Optical Transitions in Artificial Few-Electron Atoms Strongly Confined inside ZnO Nanocrystals. Germeau, A. et al. *Physical Review Letters* 90, 097401/1-097401/4 (2003). 4. n-Type conducting CdSe nanocrystal solids. Yu, D., Wang, C. & Guyot-Sionnest, P. *Science* 300, 1277-80 (2003).

#### 9:00 AM N12.2

**Temperature-Dependent Electronic Transport of n-type CdSe Nanocrystal Solids.** Dong Yu, Congjun Wang and Philippe Guyot-Sionnest; Physics, University of Chicago, Chicago, IL, Illinois.

Chemically synthesized CdSe nanocrystal thin films are n-doped by potassium evaporation or by electrochemistry, which leads to an increase in conductivity of many orders of magnitude. UV-visible and infrared measurements confirm conduction band electron injection. At cryogenic temperatures, the n-type artificial solids show voltage thresholds above which current-voltage curves deviate from Ohmic behavior to a power law behavior with a temperature-dependent exponent.

#### 9:15 AM N12.3

**n-Type Semiconductor Nanocrystals.** Congjun Wang, Dong Yu and Philippe Guyot-Sionnest; James Franck Institute, University of Chicago, Chicago, Illinois.

Charges are shown to have decisive impact on the properties of semiconductor nanocrystal quantum dots. With improvement in thin film processing, reversible electrochemical charge injection in S and P states of monodispersed CdSe quantum dot films has been achieved. This leads to extraordinary optical and electrical properties: Strong and fast electrochromic responses are observed in both mid-infrared and visible spectral ranges, while the electrical conduction increases by more than 10 orders of magnitude. The exquisite control of electronic states of monodispersed semiconductor nanocrystals along with the discovery of conductivity arising from charging provides a novel paradigm for engineering a whole new class of conducting nanomaterials. [*Science* 291, 2390 (2001); *J. Phys. Chem. B, ASAP*, 10.1021/jp0275084 (2003); *Science* 300, 1277 (2003).]

#### 9:30 AM N12.4

**Low-Temperature Electron Transport in InP Nanowires.** Jorden van Dam<sup>1</sup>, Silvano De Franceschi<sup>1</sup>, Yong-Joo Doh<sup>1</sup>, Erik Bakkers<sup>2</sup> and Leo Kouwenhoven<sup>1</sup>; <sup>1</sup>NanoScience, Delft University of Technology, Delft, Netherlands; <sup>2</sup>Philips Research Laboratories, Eindhoven, Netherlands.

We report on the transport properties of nanofabricated field-effect devices based on individual InP nanowires grown by the vapor-liquid-solid technique. The nanowires are n-type doped, have a diameter in the 10-100 nm range, and a length of several microns. Source and drain leads are provided by Ti/Al electrodes defined by electron-beam lithography with separations down to 100 nm. The electrical contacts exhibit Ohmic behavior, with resistances as low as a few kOhm and small temperature dependence down to 0.3 K. At low temperature, several fingerprints of phase-coherent mesoscopic transport are observed. In devices with relatively high contact resistances, Coulomb blockade becomes prominent below a few Kelvin

leading to single-electron tunneling transport. We measure charging energies of  $\sim 1$  meV. Energy-level spectroscopy is performed via differential-conductance measurements in the non-linear regime. We find evidence of energy quantization resulting from the confinement in the wire. Devices with low contact resistances show no Coulomb blockade effect. In this case, it is possible to study the intrinsic transport properties of a single nanowire. To this aim, we have fabricated single-wire devices with multiple electrodes having low contact resistance. Preliminary measurements show that transport is diffusive down to 0.3 K, and for wire lengths of  $\sim 1$  micron. The nanowire conductance exhibits reproducible oscillations as a function of a gate voltage whose amplitude increases at low temperatures. These conductance fluctuations represent a signature of phase-coherent transport.

#### 9:45 AM N12.5

**Monocrystalline InP Nanotubes.** Erik Bakkers<sup>1</sup>, Marcel Verheijen<sup>1</sup>, Lou-Fei Feiner<sup>1</sup>, Jorden van Dam<sup>2</sup>, Silvano De Franceschi<sup>2</sup> and Leo Kouwenhoven<sup>2</sup>; <sup>1</sup>Inorganic Materials, Philips Research Laboratories, Eindhoven, Netherlands; <sup>2</sup>Department of Nanoscience, Delft University of Technology, Delft, Netherlands.

It is well established that the electronic structure of semiconducting nanowires is determined by both the chemical composition and the radial quantum confinement, the latter being governed by the diameter. We demonstrate that the confinement effect in such one-dimensional structures can be enhanced substantially in nanotubes as compared to nanowires. We report the synthesis of optically active Indium Phosphide (InP) nanotubes via the same vapor-liquid-solid (VLS) growth mechanism by which crystalline nanowires, showing excellent electrical properties, are fabricated. The nanotubes are formed at higher temperatures than at which nanowires grow, and a simple model explaining their formation is presented. The nanotubes are monocrystalline and have the (bulk) zinc blende structure and therefore represent a new class of tube materials[1]. The wall thickness can be controlled by the synthesis temperature and is in the range of 2-20 nm. The tubes show photoluminescence, which is considerably (by up to 0.7 eV) blue-shifted with respect to bulk emission, indicating that the optical properties are not dominated by defect states. Using a simple effective mass model, we show that the blue-shift is controlled by the wall-thickness, explaining why the shift is substantially larger than achievable in nanowires. Reference [1] E.P.A.M. Bakkers, and M.A. Verheijen, *J. Am. Chem. Soc.* 2003, 125, 3440

#### 10:30 AM \*N12.6

**Nanocrystalline Junctions, from Lithium-Ion Batteries to Electrochromic Displays and Solar Cells.** Michael Graetzel, Faculty of Basic Science, Swiss Federal Institute of Technology, Lausanne, Vaud, Switzerland.

Nanocrystalline films are made up of a network of mesoscopic oxide particles such as TiO<sub>2</sub>, ZnO and WO<sub>3</sub>, which are interconnected to allow for electronic conduction to take place. The pores between the particles are filled with a semiconducting or a conducting medium, such as a p-type semiconductor, a polymer, a hole transmitter or an electrolyte, constituting a junction of extremely large contact area. In this way interpenetrating bicontinuous network composites are formed which are phase-separated by a heterojunction. The unique optoelectronic features of such films will be discussed. In particular, the factors that govern interfacial charge transfer reactions and lateral electron transfer along surface attached redox relays will be analyzed. Such mesoporous films find applications in a number of devices, including dye-sensitized solar cells, electrochromic displays, biosensors and intercalation batteries. The operation of these nanocrystalline systems will be analyzed and several new examples presented. Of particular importance is the engineering of the interface on the molecular scale to obtain optimal and stable performance. Thus, the use of self-assembly assisting agents in conjunction with amphiphilic sensitizers has led to a recent breakthrough in the achievement of long term stability of the dye sensitized nanocrystalline solar cells under both long term heat stress and light soaking. This has fostered the first practical applications of these cells. Literature: M. Graetzel, *Nature*, London 414, 338-348 (2001). Work supported by the Swiss National Science Foundation, the Swiss Commission for Technology and Innovation, the Swiss Energy Office, the European Joule program, the United States Airforce and INAP Gelsenkirchen.

#### 11:00 AM N12.7

**Nanoscale Selective, Highly Efficient Formation of Doped and Metal Atom Seeded Visible Light Tunable TiO<sub>2</sub>-xNx Nanoparticles: Application to Sensors, Microreactors, and Solar Cells.** James L Gole<sup>1</sup>, John Stout<sup>1</sup> and Clemens Burda<sup>2</sup>; <sup>1</sup>School of Physics, Georgia Institute of Technology, Atlanta, Georgia; <sup>2</sup>Department of Chemistry, Case Western Reserve, Cleveland, Ohio.

Using a nanoscale exclusive synthesis route, in seconds, at room

temperature, we produce nitrogen doped, stable, and environmentally benign TiO<sub>2</sub>-xNx photocatalysts whose optical response can be tuned across the entire visible region. This synthesis, which can be simultaneously accompanied by metal atom seeding, can be accomplished through the direct nitration of anatase TiO<sub>2</sub> nanostructures with alkyl ammonium salts. Tunability throughout the visible depends on the degree of TiO<sub>2</sub> nanoparticle agglomeration and the influence of metal seeding. The introduction of a small quantity of palladium in the form of the acetate, chloride, or nitrate catalyzes further nitrogen uptake, appears to lead to a partial phase transformation, displays a counterion effect, and produces a material absorbing well into the near infrared. Silver introduced as the nitrate into a TiO<sub>2</sub> or TiO<sub>2</sub>-xNx nanostructure framework, forms seeded Ag<sub>x</sub>O - TiO<sub>2</sub> or TiO<sub>2</sub>-xNx nanostructure mixtures which can be induced to self-assemble to agglomerate nano-needle and planar arrays using select metals. Surprisingly, no organics are incorporated into the final TiO<sub>2</sub>-xNx products. These visible light absorbing photocatalysts readily photodegrade methylene blue and gaseous acetaldehyde. They can be transformed from liquids to gels and placed on the surfaces of sensor and microreactor based configurations to 1) produce an improved photocatalytically induced solar based sensor response, and 2) facilitate catalytically induced disinfection of airborne pathogens. In contrast to a nitration process which is facile at the nanoscale, we find little or no direct nitration of micrometer sized anatase or rutile TiO<sub>2</sub> powders at room temperature. Thus, we demonstrate an example of how a traversal to the nanoscale can vastly improve the efficiency for producing important submicron particles.

#### 11:15 AM N12.8

**Electronic structure of piezoelectric InAs-InP nanowires.**  
Matthew Zervos and Lou-Fe Feiner; Philips Research, Eindhoven, Netherlands.

We study in the effective mass approximation the electronic structure of an InAs quantum wire with built-in InAs/InP heterojunctions via self consistent Poisson-Schrödinger calculations in cylindrical coordinates. Rapid convergence and efficiency are achieved by (i) a suitable transformation of the radial part of the Hamiltonian matrix thereby maintaining symmetry (ii) using quantum mechanical perturbation theory to derive an expression for the change in electron density with electrostatic potential. We calculate the energy levels in a 150Å long InAs quantum dot surrounded by 50Å strained InP barriers within an InAs nanowire of radius 200Å having a doping level of  $1 \times 10^{16}$  (cm<sup>-3</sup>) and conduction band discontinuities of 0.6eV. In equilibrium the lowest InAs quantum dot state is 15 meV above the Fermi level and upon variation of the source-drain voltage  $V_{sd}$  the structure gets into resonance at  $V_{sd}=88$  mV. This is in good agreement with an experimental study of resonant tunneling in a nominally undoped InAs-InP nanowire of similar dimensions where resonance was detected at 80 mV and a small shift (5mV) was detected upon inverting the voltage polarity. We rule out barrier asymmetry, band-bending due to impurities or defects and contact effects as being the origin of the current asymmetry and attribute it to the strain induced piezoelectric charges at the InP/InAs interfaces.

#### 11:30 AM N12.9

**Large-scale Hierarchical Organization of Nanowires for Integrated Arrays of High Performance Semiconductor Nanowire Devices.** Song Jin, Dongmok Whang and Charles M. Lieber; Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts.

Semiconductor nanowires and carbon nanotubes are promising building blocks for the bottom-up assembly of integrated electronic and photonic systems since these materials can exhibit diverse device behavior and simultaneously function as the wires that access and interconnect devices. Efforts to date have focused primarily on the demonstration of individual nanodevices. Yet to move forward and possibly go beyond existing technologies will require the development of approaches that enable controlled assembly and integration of these building blocks on a scale far beyond that of individual or small numbers of devices produced by fluidic and electric-field directed assembly. We developed a solution-based approach for hierarchically organizing nanowire building blocks en masse into integrated arrays tiled over large areas and a parallel and scalable general strategy for the fabrication of large-scale arrays of nanowire devices. Nanowires were aligned with controlled nanometer to micrometer scale pitch using the Langmuir-Blodgett technique, transferred to planar substrates in a layer-by-layer process to form parallel and crossed nanowire structures over centimeter length scales, and then efficiently patterned into repeating arrays of controlled dimensions and pitch using photolithography. From these arrays, high performance field-effect transistors in centimeter scale arrays can be fabricated in high yields without individual nanowire alignment through careful design of the electrode layouts. Furthermore, the good reproducibility allows for a scaling up of the performance and on current of the nanodevices when individual nanowire devices are intentionally

summed together to meet the requirements for macroelectronic applications and display technologies. The generality of this solution-based bottom-up assembly approach enables facile integration of diverse nanoscale building blocks on various substrates with flexible electrode designs, potentially enabling a broad range of applications.

#### 11:45 AM N12.10

**Ferroelectricity in Individual Barium Titanate Nanowires.**  
Jonathan E. Spanier, Jeffrey J. Urban, Wan Soo Yun, Lian Ouyang and Hongkun Park; Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts.

Determination of the effects of reduced crystal dimension and size on ferroelectricity has been elusive due to difficulties of preparing high-quality nanocrystalline samples with uniform sizes. Here, we present an investigation that directly addresses this issue without ensemble averaging. Ferroelectric polarizations are selectively and reproducibly induced, manipulated, and imaged within individual, single-crystalline barium titanate (BaTiO<sub>3</sub>) nanowires using scanning probe microscopy (SPM). Ferroelectric phase transition temperatures ( $T_C$ ) of these nanowires are individually measured as a function of nanowire diameter using variable-temperature SPM, and the results are analyzed using a theoretical model based on the Landau-Ginzburg-Devonshire theory. The measurements show that  $T_C$  is depressed as the nanowire diameter gets smaller, approaching room temperature as the diameter reaches 3 nm. The theoretical analysis reproduces the scaling relation between  $T_C$  and nanowire diameter and provides an estimate of the length scale over which the surface affects the interior polarization. This work is supported by NSF.

#### SESSION N13: Electrical, Electronic Properties and Devices II

Chairs: Michael Gratzel and Daniel Vanmaekelbergh  
Thursday Afternoon, December 4, 2003  
Room 302 (Hynes)

#### 1:30 PM \*N13.1

**Electrostatic Force Microscopy Study of Nanocrystal Photoionization on Silicon Surfaces.** Oksana Cherniavskaya<sup>1</sup>, Louis E Brus<sup>1</sup>, Liwei Chen<sup>1</sup> and Chaya H Ben-Porat<sup>1</sup>; <sup>1</sup>Chemistry, Columbia University, New York, New York; <sup>2</sup>Chemistry, Columbia University, New York, New York.

Quantitative analysis of electrostatic force microscopy (EFM) images was used to study the photoionization of CdSe/CdS core-shell and PbSe nanocrystals on N and P-doped silicon substrates with 12 and 21 Å thick, thermally grown, oxide layers. The EFM signal from PbSe was less than expected from a single charge and was shown to be due to these high dielectric constant particles being polarized by the charges trapped in the silicon oxide. By contrast, CdSe nanocrystals showed a rich variety of charging kinetics that are highly dependent on the type of substrate and the excitation wavelength used.

#### 2:00 PM N13.2

**Surface States in Passivated, Unpassivated and Core/Shell Nanocrystals: Electronic Structure and Optical Properties.** Garnett W Bryant<sup>1</sup> and W Jaskolski<sup>2</sup>; <sup>1</sup>Atomic Physics Division, National Institute of Standards and Technology, Gaithersburg, Maryland; <sup>2</sup>Instytut Fizyki, UMK, Torun, Poland.

Surface effects significantly influence the functionality of semiconductor nanocrystals. Passivation with ligands or high band-gap semiconductor shells is necessary to reduce trap densities, enhance quantum yield and increase photostability. A full theoretical understanding of these surface effects requires atomistic models capable of describing surface faceting and relaxation; site-dependent, partial and random passivation; the molecular structure of passivants; and few-monolayer shells. We present an atomistic tight-binding theory of the electronic structure and optical properties of passivated, unpassivated and core/shell nanocrystals to study these surface effects. We consider spherical CdS nanocrystals with unrelaxed, unrelaxed surfaces that are passivated at all sites, only at cations, only at anions, or unpassivated at all sites. Different behavior is obtained for each case. Fully passivated dots with all dangling bonds saturated have no surface states in the fundamental band gap and all near-band-edge states are quantum-confined internal states. When only surface cations are passivated, an anion-derived surface state band and a band of backbonded surface states exists near the valence band edge. When only surface anions are passivated, a broad band of mixed surface/internal states exists between the conduction band edge and the onset of internal states. The energy of the lowest strong optical transition is determined mostly by the energy of the lowest internal conduction state. Incomplete passivation of dangling bonds can push this level well above the energy for fully passivated dots or down to the conduction band edge. Because of this strong sensitivity

to passivation, explicit models for surface effects are necessary for precise modeling of the lowest internal states. Capping the CdS dot with more than two monolayers of ZnS significantly reduces the influence of the surface on the internal electronic structure and optical properties. Dependence on dot size and on random site passivation will be discussed.

### 2:15 PM N13.3

**Single Electron Force Effects of Nanoparticle Charge States observed by Hybrid Scanning Tunneling - Atomic Force Microscopy.** Yoshinori Suganuma, Paul-Emile Trudeau and Al-Amin Dhirani; Chemistry, University of Toronto, Toronto, Ontario, Canada.

According to the "orthodox" model for single electron tunneling, sudden changes in current-voltage characteristics of nanoparticle (NP) - tunnel junction systems ("Coulomb blockade" (CB) and "Coulomb staircase" (CS) phenomena) arise fundamentally due to charge quantization. We have embedded a NP in the tunnel junction of a hybrid scanning tunneling - atomic force microscope (STM-AFM) and have simultaneously measured current and forces generated as a function of voltage. We observe that CB and CS phenomena are in fact associated with quantized changes in force, directly confirming the discrete charge nature of the phenomena. Threshold voltages for single electron events were found to be tunable with nanoparticle size as predicted by theory. The combined STM-AFM can provide novel insights into current flow at nanoscale. These include a detection of time averaged forces generated by single electrons hopping on/off an NP, as well as forces generated by fluctuations in NP background charge distributions. An intriguing application of the system to mechanical switching of current by single electrons is also discussed.

### 2:30 PM N13.4

**Self Assembly of Chemical Nanostructures for Functional Electronics.** Yi Cui<sup>1,2</sup>, J. Alexander Little<sup>2</sup>, Mikael Bjork<sup>1</sup> and A. Paul Alivisatos<sup>1,2</sup>; <sup>1</sup>Chemistry, University of California, Berkeley, Berkeley, California; <sup>2</sup>Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California.

Chemically synthesized nanocrystals such as metallic and semiconductor nanoparticles, nanorods and tetrapods are the most important building units for nano science and technology because they have uniform size, controlled shape, defined chemical composition, and tunable surface chemical functionality. However, the investigation of their electrical properties and the applications in functional electronics have been largely limited by the lack of a strategy to produce reliable electrical wiring to individual nanocrystals or well-defined ensembles. Herein, we present our recent experimental results in controllably assembling nanocrystals onto desired positions by capillary force interaction. The sub 100nm diameter nanoparticles were assembled into hole and trench template arrays defined by lithography. The capillary force is demonstrated to be the most critical interaction to position nanoparticles selectively into the holes and trenches versus other flat places. The number and geometry of nanoparticles under equilibrium assembly are determined by the size of nanoparticles and templates. Most significantly, this approach was successfully applied to extremely small particle sizes - down to 2 nm diameter. Functional electronic devices based on these controlled nanoparticle assembly will be discussed. We will also demonstrate that this assembly method could be done as a wafer scale process, opening up the opportunity for integrated electronics applications.

### 2:45 PM N13.5

**Influence of the Network Geometry on Electron Transport in Nanoparticle Networks.** Kurt Benkstein, Nikos Kopidakis, Jao van de Lagemaat and Arthur Frank; NREL, Golden, Colorado.

Computer simulations are applied to understand the influence of network geometry on the electron transport dynamics in random nanoparticle networks, and the predicted results are compared with those measured in one class of random nanoparticle networks: dye-sensitized nanocrystalline TiO<sub>2</sub> solar cells. The model is applicable to all classes of random nanoparticle networks, such as highly disordered quantum dot arrays. The random nanoparticle networks are simulated by the step-wise condensation of a diffusion-limited aggregate. The fractal dimension of the nanoparticle films was estimated from the simulations to be 2.28, which is in quantitative agreement with gas-sorption measurements of TiO<sub>2</sub> nanoparticle films. Electron transport on the computer-generated networks is simulated by random walk. The experimental measurements and random-walk simulations are found to be in quantitative agreement. For both a power-law dependence of the electron diffusion coefficient D on the film porosity P is found as described by the relation:  $D \propto P - P_c - \mu$ . This power-law relation can also be derived from percolation theory, although only qualitatively. The critical porosity P<sub>c</sub> (percolation threshold) and the conductivity exponent  $\mu$  are found to be  $0.76 \pm 0.01$  and  $0.82 \pm 0.05$ , respectively. It is estimated that during their respective transit

through 50 and 75% porous 10- $\mu$ m thick films as employed in the dye-cell, the average number of particles visited by electrons increases by 10-fold, from 10<sup>6</sup> to 10<sup>7</sup>.

### 3:00 PM N13.6

**Reading and Programming a Silicon Nanocrystal Optical Memory.** Robert J Walters<sup>1</sup>, Julie D Casperson<sup>1</sup>, Pieter G Kik<sup>1</sup>, Harry A Atwater<sup>1</sup>, Robert Lindstedt<sup>2</sup> and George I Bourianoff<sup>2</sup>; <sup>1</sup>Thomas J. Watson Laboratory of Applied Physics, California Institute of Technology, Pasadena, California; <sup>2</sup>Intel Corporation, Portland, Oregon.

Silicon nanocrystal floating gate devices are promising candidates for CMOS integration of optically addressable non-volatile memory elements. Such devices have been previously shown to exhibit a spectrally uniform modulation of photoluminescence intensity proportional to their programmed memory state. The observed attenuation of photoluminescence in the charged device state is attributed to a nonradiative Auger recombination process in the presence of the additional charge carrier. We have fabricated silicon nanocrystal optical memory devices on 300mm wafers with silicon nanocrystals formed by high temperature annealing of silicon implanted into thermally grown gate oxides. A semitransparent polysilicon gate contact allows simultaneous optical and electronic access to the nanocrystals that form the floating gate of the transistor. Retention times have previously been limited to time scales of order 1 minute by gate oxide leakage induced by the implantation process. We will discuss progress in the redesign of our devices for improved retention times. It is inferred from the symmetry of the quenching of photoluminescence at both positive and negative gate biases that both electron and hole Auger recombination processes occur. Measurements of the radiative decay lifetime in various device states can be used to test the validity of this model and clarify the physical processes underlying the optical addressing of these devices. We will present the details of our work addressing this issue. Optical programming of silicon nanocrystal optical memories can be achieved through internal photoemission of stored charge under UV illumination. This process has long been used commercially in the erasure of EPROM memory chips. We will additionally discuss the efficiency and dynamics of erasure via internal photoemission in our memory devices.

### 3:30 PM N13.7

**Electric Force Microscopy of Individually Charged Semiconductor Nanoparticles.** Thierry Melin, Heinrich Diesinger, Dominique Deresmes and Didier Stievenard; ISEN, IEMN-CNRS, Villeneuve d, France.

We perform Electric Force Microscopy (EFM) experiments[1] on individually charged silicon nanoparticles deposited on conductive substrates. Due to the conductive character of the host substrate, an AFM/EFM injection technique[2] can be used to store up to 200 electrons or holes in nanoparticles [3], leading to surface dipoles of moments up to 3.104\$ Debye. Experimentally, the EFM detection is performed with a static tip-substrate polarization so as to distinguish between force gradients associated with : - i) the nanoparticle topography (capacitive interaction); - ii) stored charges interacting with the biased EFM tip apex (dipole-charge interaction); - iii) image forces (dipole-dipole interaction), of weak amplitude, and identified in the limit of highly charged (150 e) nanoparticles. Theoretically, we provide a fully analytical model - valid for arbitrary tip and nanoparticle geometries - to quantitatively measure stored charges from the ratio between the capacitive and dipole-charge interactions. The model is extensively compared with numerical calculations where the tip shape (EFM/AFM cantilever tip, carbon nanotube tip) and nanoparticle geometry (size in the 20-50nm range, shape, aspect ratio) can be varied. Analytical predictions are shown to fall in agreement with numerical calculations within 10\$ the case of time-dependent EFM measurements. Finally, we will address the issue of the nanoparticle charging mechanisms. Surface versus bulk charge injection will be discussed based on experimental charging/discharging dynamics, charge storage efficiency and current-voltage characteristics. Quantum-size effects and electrostatic interactions will be discussed. [1] T.D. Krauss and L.E. Brus, Phys. Rev. Lett. 83 4840 (1999). [2] E. Boer et al., Appl. Phys. Lett. 78 3133 (2001). [3] T. Melin, D. Deresmes and D. Stievenard, Appl. Phys. Lett. 81 5054 (2002). [4] T. Melin, H. Diesinger, D. Deresmes and D. Stievenard, submitted.

### 3:45 PM N13.8

**Energy Transfer Within and In-between Layers of Spectrally and Spatially Separated Semiconductor Nanocrystals.** Andrey L. Rogach<sup>1</sup>, Thomas Franzl<sup>1</sup>, Dmitry S. Koktysh<sup>1</sup>, Nikolai Gaponik<sup>2</sup>, Thomas A. Klar<sup>1</sup> and Jochen Feldmann<sup>1</sup>; <sup>1</sup>Physics Department, University of Munich, Munich, Germany; <sup>2</sup>Institute of Physical Chemistry, University of Hamburg, Hamburg, Germany.

We report on Foerster resonant energy transfer (FRET) in thin films



of CdTe nanocrystals. The alternating layers of nanocrystals of two different sizes were formed by the layer-by-layer assembly. Temporally and spectrally resolved fluorescence spectroscopy reveals spectral diffusion of the fluorescence signal for quantum dots within one layer as well as energy transfer from layers of small dots to layers of larger dots. We assign these two effects to resonant energy transfer within each layer of nominally equal-sized quantum dots and energy transfer in-between adjacent layers of differently sized quantum dots. The demonstrated double layer sample shows an interlayer FRET efficiency of almost 50%. The concept of layer-by-layer energy transfer can be extended to the creation of graded thin film devices.

#### 4:00 PM N13.9

**Controlled Electrophoretic Deposition of Smooth and Robust Patterned Films of CdSe Nanocrystals.** Mohammad A Islam<sup>1,2</sup>, Yuqi Xia<sup>2</sup>, Donald A. Telesca<sup>1,2</sup>, Michael L. Steigerwald<sup>2</sup> and Irving P. Herman<sup>1,2</sup>; <sup>1</sup>Applied Physics and Applied Mathematics, Columbia University, New York, New York; <sup>2</sup>Materials Research Science and Engineering Center, Columbia University, New York, New York.

Electrophoretic deposition is an alternative to the conventional dry casting and spin casting methods of forming films or arrays of nanocrystals. We have shown that locally smooth patterned and unpatterned CdSe nanocrystal films of controlled thickness can be fabricated by electrophoretic deposition from CdSe/TOPO nanocrystal/hexane solutions by using high dc voltage. Uniform, apparently identical films formed on both electrodes. Visible microscopy, scanning electron microscopy (SEM), profilometry, and atomic force microscopy (AFM) showed that both films had very few defects and were very smooth, with < 2.5 nm rms roughness for ~0.5 micron thick films. The morphology of the films was found to be extremely sensitive to a multi-step post synthesis reprecipitation treatment of the nanocrystals. Using this treatment, deposition on patterned electrodes produced locally selective films with minimal particulate formation. The chemical, and presumably mechanical, robustness of the films was improved by treating the electrode surfaces with an adhesion promoter before the deposition and treating the electrophoretic films afterwards with a linker reagent. These linked electrophoretic films do not dissolve or flake off in a variety of solvents like hexane, octane, methanol, chloroform, acetone, and chlorobenzene. These high quality dense arrays of the CdSe nanocrystals could be useful in fabricating devices such as LEDs. This work was supported by the MRSEC program of the National Science Foundation, Award No. 0213574.

#### 4:15 PM N13.10

**Nanowire nanoLEDs as integrated light sources for microfluidic devices.** Oliver Hayden and Charles M Lieber; Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts.

Light emitting diodes (LEDs) formed by the assembly of p- and n-type nanowires in crossed wire architecture represent a unique approach for creating highly integrated light sources spanning a broad range of wavelengths. Here, we describe the assembly of cadmium sulphide (CdS) nanoLEDs with high spectral purity, and the integration of light sources in microfluidic devices. The nanowire LEDs were prepared by fluid-directed assembly of n-type CdS and p-type silicon nanowires on oxidized silicon substrates. The n-CdS/p-Si crossed nanowire devices exhibit strong electroluminescence with a peak maximum at 510 nm and a full-width at half maximum of ca. 15 nm. These crossed nanowire devices were used to excite the fluorescence of fluorescently-labelled microspheres flowing in a microfluidic channel, and the resulting microsphere emission was recorded using standard CCD detector. The implications of these results for highly integrated lab-on-a-chip devices will be discussed.

#### 4:30 PM N13.11

**Electrochromic Properties of Colloidal PbSe Nanocrystals.** Brian L. Wehrenberg and Philippe Guyot-Sionnest; James Franck Institute, The University of Chicago, Chicago, Illinois.

Colloidal PbSe nanocrystals exhibit a size-tunable first exciton in the 0.5 to 1 eV range. Charges can be electrochemically injected into films of PbSe nanocrystals, allowing further control of their optical properties. For the first time holes, as well as electrons, have been selectively injected into the quantum-confined states of nanocrystals. Specifically, electrons have been sequentially injected into both the 1S<sub>e</sub> and 1P<sub>e</sub> states and holes have been injected into the 1S<sub>h</sub> state. The occupation of these states by the injected charge carriers bleaches interband transitions involving those states while simultaneously inducing intraband transitions from the newly occupied states. This ability to dope the nanocrystals both n- and p-type offers promise for the fabrication of several novel optoelectronic devices.

#### 4:45 PM N13.12

**Ohmic and Schottky Contacts on ZnO Nanorods.**

Won Il Park<sup>1</sup>, Gyu-Chul Yi<sup>1</sup>, Jae-Woo Kim<sup>2</sup> and Su-Moon Park<sup>2</sup>; <sup>1</sup>Materials Science and Engineering, POSTECH, Kyungbuk, South Korea; <sup>2</sup>Chemistry, POSTECH, Pohang, South Korea.

There has recently been great interest in the preparation and characterizations of one-dimensional (1-D) semiconductor nanostructures for nanoscale electronic and optoelectronic device applications. Both homogeneous, p-n junction, and heteroepitaxial nanowires and nanorods have already been employed in several prototypes of nanodevices. Despite significant progress in the fabrication of nanodevices based on the 1-D nanomaterials, reliable nanoscale metal-semiconductor (M/SC) contacts are still required for miniaturization of device scale and increase in the nanodevice density. A M/SC rectifying junction, called a Schottky diode, is useful in electronic and optoelectronic device applications since the Schottky diode generally shows faster switching and smaller turn-on voltage than a p-n junction diode does. In addition, a good ohmic contact showing high thermal stability and a low contact resistance is also required for nano-device applications. Nevertheless, only little research has been performed for nano-contacts on semiconductor nanorods. Here, we report on fabrications and characterizations of both ohmic and Schottky contacts for ZnO nanorod arrays. For the fabrication of metal-ZnO nanorod heterostructures, diverse metal layers including Au(100Å) and Ti(100Å)/Au(50Å) were evaporated on vertically aligned ZnO nanorod arrays grown by non-catalytic vapor phase epitaxy. Since metal is selectively deposited on ZnO nanorod top surfaces, the interface between the metal layer and ZnO nanorod was atomically abrupt as determined by transmission electron microscopy (TEM). To understand electrical characteristics at the M/SC junction interfaces, the current-voltage (I-V) measurements of metal-ZnO nanorods were performed using current-sensing atomic force microscopy. Depending on the metals deposited on ZnO nanorod tips, either rectifying or linear I-V relationships were observed, indicating that our method can be used for fabrications of Schottky and/or ohmic contacts on the nanorod tips. Our controlled fabrication of nano-contacts on ZnO nanorod arrays opens up significant opportunities for the fabrication of nanodevice structures on a single nanorod.

SESSION N14: In-Room Poster Session IV  
Chairs: Michael Gratzel and Daniel Vanmaekelbergh  
Thursday Afternoon, December 4, 2003  
4:00 PM  
Room 302 (Hynes)

#### N14.1

**Modified Spontaneous Emission of CdTe Quantum Dots Inside a Photonic Crystal.** Jiayu Zhang and Min Xiao; Department of Physics, University of Arkansas, Fayetteville, Arkansas.

Angular dependence of spontaneous emission of CdTe quantum dots (QDs) inside a photonic crystal with a pseudogap is reported. The sensitive dependences of the radiative lifetime and the photoluminescence spectrum of CdTe QDs on the observation angle demonstrate the effect of the photonic band gap on spontaneous emission of the QDs.

#### N14.2

**Role of Self-assembled Au nanodots in improving the electrical and optical characteristics of ZnO films.**

Ashutosh Tiwari, c jin, A Chugh and J. Narayan; Materials Science & Engineering, north carolina state university, raleigh, North Carolina.

We have studied the effect of embedding nano-crystalline Au particles on the electrical and optical characteristics of ZnO films. Au embedded epitaxial ZnO films were deposited on (0001) Sapphire substrates using a pulsed laser deposition technique. The crystalline quality of both the ZnO matrix and Au nanoparticles were investigated by x-ray diffraction and transmission electron microscopy. These films were characterized by Photoluminescence, optical absorption and low temperature electrical resistivity measurements. Photoluminescence spectra of these films show a sharp excitonic peak at 3.3 eV without any signature of green band emission. Electrical resistivity measurements showed these films to be highly conducting with room temperature resistivity of ~3.5 mΩ-cm. Growth of highly conducting ZnO-Au composite films with improved optical characteristics is an important step in the fast emerging optoelectronics industry.

#### N14.3

**Nanowires As Anode Materials For Lithium Ion Batteries.**

Heon-Jin Choi, Han-Kyu Sung, Jae-Hwan Park, Jae-Gwan Park, Byung-Won Cho and Won-Il Cho; Korea Institute of Science and Technology, Seoul, South Korea.

Nanowires have great potential for use as building blocks in the fabrication of electronic-, optoelectronic-, and sensor devices on a nano meter scale. It evolves novel properties intrinsically associated with low dimensionality and size confinement as well as makes it possible to //bottom-up// construction of nano devices using them as building blocks. The dimensionality and size would also make the nanowires as novel electrode materials as well as important building blocks for lithium ion batteries. This talk will focus on the synthesis and characterization of nanowires for the fabrication of nanowire-based lithium ion batteries. Following a brief introduction on a figure of merits of nanowires as cathode/anode materials for lithium ion batteries, a method to prepare SnO<sub>2</sub>, ZnO and Si nanowires will be presented. Fabrication of lithium ion batteries consisted of nanowires as anode and lithium as counter electrode, and their characteristics will be followed with an emphasis on the nano-size effects on the electrochemical properties involving intercalation of lithium. A trial to fabricate new battery structures by growing nanowires directly on a conductive collector and their electrochemical properties will also be illustrated. Lastly, the feasibility of nanowires as building blocks for lithium ion batteries will be discussed.

#### **N14.4**

**Synthesis of Colloidal InSb Nanocrystals.** Congjun Wang and Philippe Guyot-Sionnest; James Franck Institute, University of Chicago, Chicago, Illinois.

Tremendous effort has been dedicated to synthesizing high quality semiconductor nanocrystals of different materials with different properties, which is of great interest for both theoretical studies and practical applications. Bulk InSb has a narrow band gap (0.17 eV at room temperature) and extremely high electron mobility, which makes it desirable for infrared technology and high speed electronic devices. Because of its small effective electron mass and large exciton Bohr radius (~ 54 nm), nanometer-sized InSb crystals are expected to demonstrate strong quantum confinement effect. We have prepared for the first time, to the best of our knowledge, colloidal InSb nanocrystal quantum dots with relatively narrow size distribution and high crystallinity.

#### **N14.5**

**Synthesis and Functionalization of II-VI Semiconductor Nanocrystals.** Peter Reiss, Claudia Querner, Sophie Carayon, Joel Bleuse, Frederic Chandezon and Adam Pron; Departement de Recherche Fondamentale sur la Matiere Condensee, CEA Grenoble, Grenoble, France.

We present new synthetic routes for the fabrication of fluorescent CdSe/ZnSe and CdSe/ZnSe/ZnS core/shell nanocrystals of low polydispersity. The principal advantage of the proposed methods relies on the fact that at no reaction step pyrophoric, organometallic reagents are used. In particular, dimethylcadmium and diethylzinc, which are typically applied as sources of Cd and Zn in the organometallic nanocrystal synthesis, are replaced by cadmium oxide and zinc stearate, respectively. The CdSe/ZnSe system exhibits quantum yields exceeding 60% at RT due to an efficient removal of structural defects in the shell and at the core/shell interface.<sup>1</sup> Furthermore, the presence of the same anion both in the core and shell materials permits a facile conversion of the core/shell nanocrystals into Cd<sub>1-x</sub>Zn<sub>x</sub>Se alloy nanocrystals by annealing. The alloying process results in a larger bandgap and facilitates the preparation of blue-emitting nanocrystals. Results from photoluminescence experiments carried out for the colloidal solutions and for single particles immobilized in solid polymer matrices are presented for both types of nanocrystals. The new double shell system CdSe/ZnSe/ZnS has an intermediate shell of ZnSe between the CdSe core and the outer ZnS shell. Thereby the lattice mismatch parameter is significantly reduced and a "smooth" passage between the two crystallographically different components (CdSe and ZnS) is assured. At the same time the outer ZnS shell improves the charge carrier confinement in the core due to its larger band gap as compared to ZnSe. Photoluminescence spectroscopy of the CdSe/ZnSe/ZnS nanocrystals corroborates these arguments, as an increase in the fluorescence intensity is observed relatively to CdSe/ZnSe and CdSe/ZnS systems.<sup>2</sup> Finally a new type of ligands for the functionalization of II-VI semiconductor nanocrystals is presented. They are characterized by their high affinity for the metal atoms at the nanocrystal surface, thus providing rapid exchange with ligands originating from the synthesis medium and high stability against photo-degradation. Furthermore, the new ligands can be prepared in a facile manner, which allows for a high flexibility in the choice of additional functional groups. The latter enable tuning of the "solubility" of the nanocrystals, which then can be dispersed in solvents of different polarity (hydrocarbons, alcohols, water) or be grafted to other molecules of physical or biological interest. <sup>1</sup>P. Reiss, J. Bleuse, A. Pron, Nano Lett. 2002, 2(7), 781. <sup>2</sup>P. Reiss, S. Carayon, J. Bleuse, A. Pron, Synt. Met. in press.

#### **N14.6**

**Branched Semiconductor Nanowires for Nanoelectronics.** Deli Wang<sup>1</sup>, Fang Qian<sup>1</sup>, Zhaohui Zhong<sup>1</sup> and Charles M. Lieber<sup>1,2</sup>; <sup>1</sup>Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts; <sup>2</sup>Division of Engineering and Applied Science, Harvard University, Cambridge, Massachusetts.

Semiconductor nanowires represent a key class of building blocks used in the bottom-up approach nanotechnology to assemble a broad range of functional electronic and photonic devices. The building blocks are central to the success of this approach, and moreover, the increasing synthetic control over the structural complexity of the blocks, such as growth of nanowire heterostructures, can provide enhanced or entirely new function. Here, we report the syntheses of branched silicon nanowires via metal-catalyzed chemical vapor deposition. Multiple generations of nanowire branches were grown epitaxially from nanowire backbones with well-controlled density, composition, and doping. Individual n-type/p-type branched structures were shown to function as well-defined p-n diodes and junction field-effect transistors. The implications of these results and ongoing studies of other branched nanowire systems for electronic and photonic applications will be discussed.

#### **N14.7**

**P-Type Gallium Nitride Nanowires for Electronic and Photonic Nanodevices.** Fang Qian<sup>1</sup>, Zhaohui Zhong<sup>1</sup>, Deli Wang<sup>1</sup> and Charles M. Lieber<sup>1,2</sup>; <sup>1</sup>Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts; <sup>2</sup>Division of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts.

Semiconductor nanowires (NWs) have demonstrated significant potential as fundamental building blocks for nanoelectronic and nanophotonic devices. A key feature of semiconductor NWs that has enabled much of their success has been the growth of materials with reproducible electronic properties, including the controlled incorporation of both n- and p-type dopants. In the case of gallium nitride (GaN), the NWs are intrinsically n-type, and this has made difficult the exploration of a wide-range of nanodevices, such as UV-blue light emitting diodes (LEDs) and lasers. Here, we report the synthesis of magnesium-doped GaN NWs via metal-catalyzed chemical vapor deposition. Nanowires prepared on c-plane sapphire substrates were found to grow normal to the substrate, and transmission electron microscopy studies demonstrated that the nanowires had single-crystal structures with a <0001> growth axis that is consistent with substrate epitaxy. Individual magnesium-doped GaN NWs configured as field-effect transistors demonstrate that optimally doped nanowires were p-type with hole mobilities of ca. 12 cm<sup>2</sup>/V-s. In addition, transport studies of crossed GaN NW structures assembled from p- and n-type materials show that these junctions function as well-defined p-n diodes with UV-blue emission in forward bias. The implications of these results and ongoing hierarchical growth studies will be discussed.

SESSION N15: Poster Session V  
Chairs: Philippe Guyot-Sionnest and Moonsub Shim  
Thursday Evening, December 4, 2003  
8:00 PM  
Exhibition Hall D (Hynes)

#### **N15.1**

**Room Temperature Synthesis of Highly Fluorescent Zinc Blende CdSe Nanocrystals.** Rongfu Li<sup>1</sup>, Jeunghoon Lee<sup>1</sup> and Fotios Papadimitrakopoulos<sup>2,1</sup>; <sup>1</sup>Institute of Materials Science, Polymer Program, Univ. of Conn., Storrs, Storrs, Connecticut; <sup>2</sup>Department of Chemistry, Univ. of Conn., Storrs, Connecticut.

The ability of tuning the PL emission color of CdSe nanocrystals (NCs) by changing the size has prompted the biological application of CdSe NCs. However, making the TOPO/TOP capped CdSe NCs soluble and stable in water, compatible with biosystems is not trivial. In this paper, we report a method to synthesize highly photoluminescent zinc blende CdSe NCs, with relatively narrow size distributions and soluble in ethanol. For this we employ a water phase synthesis of CdSe NCs that utilizes CdCl<sub>2</sub>, Se, and NaOH as reagents. X-ray diffraction results show that the CdSe NCs are of zinc blende crystal structure. This is then followed by a low-temperature (25- 85 deg C) chemical etching in a water-soluble amine-based etching solution. That gave rise to a strong photoluminescence due to etching away surface traps that mainly contribute to non-radiative recombination. Upon etching at such low temperature conditions, it was confirmed with XRD that the CdSe zinc blende crystal structure is maintained. Furthermore, after precipitation from the etching solution, the CdSe NCs shows the same band edge PL as that of CdSe

NCs obtained in high temperature synthesis and no trap state emission was observed. Zinc blende CdSe NCs with narrow size distribution manifested by the narrow and strong PL emission (FWHM 25 - 35 nm) was obtained by adjusting the temperature and the concentration of CdSe NCs in the etchant. Under certain conditions, very narrow emission from very small CdSe NCs (439 nm with FWHM 15 nm, 465 nm with FWHM 30 nm) was also observed in this etching process. Further efforts were exerted on transforming the ethanol soluble CdSe NCs to water soluble CdSe NCs, which will finally satisfy the requirement of biological application of CdSe NC.

#### **N15.2**

##### **Degree of Asymmetry of CdSe Quantum Dots Grown in Glass Probed by Four Wave Mixing.** Aleksey Filin<sup>1</sup>, K. Babocsi<sup>2</sup>,

M. Schmitt<sup>2</sup>, P. D. Persans<sup>1</sup>, W. Kiefer<sup>2</sup> and V. D. Kulakovskii<sup>3</sup>;

<sup>1</sup>Physics, Rensselaer Polytechnic Institute, Troy, New York;

<sup>2</sup>University of Wuerzburg, Wuerzburg, Germany; <sup>3</sup>Institute of Solid State Physics, RAS, Chernogolovka, Russian Federation.

Information about quantum dot (QD) asymmetry is derived by analyzing polarization properties of the time-integrated four wave mixing (FWM) signal. The lowering of QD symmetry results in the splitting of bright  $J = \pm 1$  exciton states. That causes the polarization oscillation of circularly excited excitons between these two split states. In a QD ensemble with a random distribution in the exciton level splitting, this results in the decay of the difference in FWM signals observed in scattering of  $\sigma^-$  and  $\sigma^+$  polarized light on the population grating created by two  $\sigma^+$  pulses, the decay time reflecting the degree of QD asymmetry. We have investigated the decay time of the difference in two polarized signals for quantum dots of equal size grown in a glass matrix under different conditions. Increasing growth temperature and decreasing growth time lead to lowering of QD symmetry. We discuss this experimental result in terms of thermophysics of nanoparticle growth in glass. Partial funding by DOE BES grant DE-FG 0297ER45662 is acknowledged.

#### **N15.3**

##### **Structural Dynamics Characterization of Poly(Allyl Amine)-Encapsulated CdSe Nanocrystals.** Jeunghoon Lee<sup>1,2</sup>,

Baocheng Yang<sup>3,2</sup>, Rongfu Li<sup>1,2</sup>, Thomas A. P. Seery<sup>3,2,1</sup> and Fotios

Papadimitrakopoulos<sup>2,3,1</sup>, <sup>1</sup>Polymer Program, University of

Connecticut, Storrs, Connecticut; <sup>2</sup>Institute of Material Science,

University of Connecticut, Storrs, Connecticut; <sup>3</sup>Department of

Chemistry, University of Connecticut, Storrs, Connecticut.

CdSe nanocrystals (NC) have attracted a great deal of interest during the past decade. Their broad absorption and sharp emission characteristics along with high photoluminescence quantum yield make an ideal candidate for biological tagging. There have been a number of strategies to make water soluble CdSe NCs. Among the more prominent ones include surface exchange with hydrophilic thiols and/or building hydrophilic silica shell. Our group has been developing alternative solubilization methods based on a simple procedure to encapsulate CdSe NC in hydrophilic polymers that readily disperses in water. By utilizing the combination of dynamic and static light scattering, hydrodynamic radius ( $R_h$ ), radius of gyration ( $R_g$ ) and their ratio (the  $\rho$  parameter ( $R_g/R_h$ ), which is indicative of the density of the nanoscopic polymer/NC composite structure), were obtained. These structural information were then compared with photoluminescence (PL) quantum yields (QY) to shed more light into the encapsulation mechanism. Our results indicate that tighter structures are obtained at higher polymer concentration and ionic strength that lead to an increase in the PL QY by effectively excluding quencher moieties from the NC surface. Upon closer examination, we have found that both  $R_h$  and  $R_g$ , along with the corresponding PL QY exhibit a complex evolution behavior with time. The maximum PL QY in water recorded with these polymer encapsulated CdSe nanocrystals systems is in the order of 10%.

#### **N15.4**

##### **Quantum Dots for Solid State Lighting Applications: Effects of Photoluminescent Thermal Quenching.** Billie L. Abrams,

Lauren E. S. Rohwer, Jess P. Wilcoxon, Stephen M. Woessner and Steven G. Thoma; Sandia National Labs, Albuquerque, New Mexico.

Quantum dots (QDs) are promising alternatives to conventional phosphors for use in light emitting diodes (LEDs) for the Solid State Lighting Initiative. In this work the thermal quenching behavior of a series of CdS and CdSe quantum dots embedded in polymer matrices was studied and compared to conventional phosphors such as ZnS:Ag,Cl, BaMgAl10O17:Eu and SrGa2S4:Eu. Due to the fact that any light emitting material in close proximity to an LED die will experience a temperature rise on the order of 100-150°C, it is important to understand the effects of temperature on light emission. It is important that the quantum efficiency of the quantum dots be maintained at these elevated operating temperatures. The photoluminescent (PL) emission of CdS and CdSe quantum dots can

be tuned by controlling the surface properties. A series of CdS and CdSe quantum dots (~2-3 nm in size) with different surface properties were embedded in polymers, e.g., epoxy, silicone, and subjected to temperature cycling from room temperature to 100°C. Thermal quenching temperatures (defined as the temperature at which the PL is 50% of the original PL) ranging from 75°C to 100°C were measured. These thermal quenching temperatures were lower than those for the conventional phosphors (>150°C). Accompanying the decrease in PL emission was a blue spectral shift. Upon cooling back to room temperature the PL intensity and position was fully recovered for both the quantum dots and the conventional phosphors. PL and PLE (PL excitation) were taken during the heating and cooling cycles in a SPEX Fluorolog II spectrometer using a Xe arc lamp as a light source. Theoretically, QDs should not exhibit thermal quenching since the vibrational lattice modes are not present. However, since the emission of the quantum dots depends upon the surrounding surface chemistry, a new path of thermal degradation becomes apparent. The bonds between the quantum dots and the surrounding organic ligands may be adversely affected by increased temperature leading to thermal quenching of PL. This may also explain the shift in emission as a function of temperature. Thus, a different thermal quenching mechanism may exist for the quantum dots as compared to conventional phosphors. One possible way to decrease thermal effects on the PL of these quantum dots is by anchoring the QDs to an embedding epoxy. Acknowledgments: Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

#### **N15.5**

##### **Synthesis of ZnO Nano Particles Using Block-Copolymer**

**Route.** Anthony Diaz<sup>1</sup>, Lisa Munoz<sup>2</sup>, Vinay Gupta<sup>3,1</sup>, Rasmi R Das<sup>1</sup>, Pijush Bhattacharya<sup>1</sup>, Ana R. Guadalupe<sup>2</sup> and

Ram S Katiyar<sup>1</sup>; <sup>1</sup>Department of Physics, University of Puerto Rico,

San Juan, Puerto Rico; <sup>2</sup>Department of Chemistry, University of

Puerto Rico, San Juan, Puerto Rico; <sup>3</sup>Department of Physics and

Astrophysics, University of Delhi, Delhi.

Zinc oxide (ZnO) is a promising materials for optoelectronic applications due to its wide bandgap (~3.3 eV) and higher excitonic energy (~60 meV). The quantum confinement of the excitons in zinc oxide nanoparticles leads to enhance the optical properties in excitonic transition. In this study, we have synthesized zinc oxide nanoparticles (np-ZnO) using Poly(styrene-b-poly-4-vinylpyridine) block copolymer (BC) route. The above BC was dissolved in appropriate solvent as to form micelles within nanoscale size. ZnCl<sub>2</sub> salt was mixed with the micelles in 1:1 (wt/v) ratio to form a sol. The spin-coating technique was used to deposit thin films of zinc embedded in the polymer matrix on silicon and glass substrates. The coated film was oxidized in the oxygen plasma ambient to form different size (20-50 nm) of zinc oxide nanoparticles. X-ray photoelectron spectroscopy (XPS) was used to identify the presence of zinc oxide nanoparticles. The size and shape of the particles were estimated using transmission electron microscopy (TEM). The UV-visible, FT-IR and micro-Raman spectroscopy were used for the optical and vibrational characteristics. Detailed results of optical properties of np-ZnO will be correlated with the particle size.

#### **N15.6**

##### **Electronic Structure and Surface Effects of Semiconductor**

**Nanocrystals.** Christoph Bostedt<sup>1</sup>, Tony van Buuren<sup>1</sup>, Trevor

Wiley<sup>1</sup>, Thomas Moeller<sup>2</sup> and Louis J Terminello<sup>1</sup>; <sup>1</sup>CMS - MSTD,

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With nanostructured materials one can manipulate and control the properties of a material through the fabrication of nanometer scale structures. Tailoring the electronic properties of nanostructures is often achieved by confining electrons to dimensions comparable to their wavelength, which leads to quantum well states that modify the density of states. Until recently the effect of the surface layer on the electronic and structural properties of the quantum dots has been neglected due to the inherent difficulty in both measuring and modeling this region. X ray absorption (XAS) and photoemission (PES) spectroscopy have been performed on Silicon, and Germanium nanocrystals. Clean Ge nanocrystal films are found to exhibit much stronger quantum confinement effects at the band edges than similar sized Si and Diamond particles. This effect leads to a critical particle size of 2.0 nm below which the band gap of Ge becomes larger than that of Si. Additionally our experimental results show how the surface of bare nanocrystals is disordered and specific reconstruction mechanisms are suggested. The impact of the surface reconstruction on the particle electronic structure is discussed and compared to state of the art electronic structure calculations. 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.

### **N15.7**

#### **Abstract Withdrawn**

### **N15.8**

#### **Investigation of Particle-Size Dependent Phase Transitions in $Zr_{1-x}Ce_xO_2$ Nanoparticles Through Micro-Raman Scattering.**

**Richard D Robinson<sup>1</sup>**, Feng Zhang<sup>1</sup>, Jonathan Hanson<sup>2</sup>, Siu-Wai Chan<sup>1</sup> and Irving P Herman<sup>1</sup>; <sup>1</sup>Department of Applied Physics and Applied Mathematics, Columbia University, New York, New York; <sup>2</sup>Chemistry Department, Brookhaven National Lab, Upton, New York.

The size-dependent crystal structure of cerium-zirconium oxide ( $Zr_{1-x}Ce_xO_2$ ) nanometer scale particles made by a hydrothermal method were studied by micro-Raman scattering and x-ray diffraction. Transitions between the stable cubic and tetragonal phases were identified by the existence of two low frequency Raman modes ( $140\text{ cm}^{-1}$  and  $265\text{ cm}^{-1}$ ) that appear only in the tetragonal structure. As the particle size decreased the phase boundary between the cubic and tetragonal phases shifted from that seen in bulk, increasing the extent of the stable cubic phase. The Raman peak positions and linewidths were also tracked between particle size and composition. X-ray diffraction was used to determine phase boundaries and supports the findings. This work was supported by the MRSEC Program of the National Science Foundation under Award Number DMR-0213574.

### **N15.9**

#### **Novel Surface and Bulk Electronic Structure in Diamond Nanoparticles.**

**Anthony van Buuren**, Christoph Bostedt, Jean-Yves Raty, Kevin Moore, Trevor Willey, Giulia Galli and Lou Terminello; LLNL, Livermore, California.

Nanometer sized diamond produced in detonations may have much in common with nanodiamonds found in meteorites. This new family of detonation-synthesized carbon nanoclusters has a core of diamond with a coating of fullerene like carbon. X-ray diffraction and TEM show that the detonation-synthesized carbon nanoclusters have the diamond crystal structure and are approximately  $4.0 \pm 1.0$  nm in diameter. The electronic structure of diamond nanoparticles has been measured with x-ray absorption and x-ray emission spectroscopies and high-resolution spatial resolution TEM electron energy loss spectroscopy (EELS). These nano-sized diamonds do not display the characteristic properties of other group IV nanoparticles: such as a widening of the energy gap between the conduction and valence bands owing to quantum-confinement effects. For the 4nm nanodiamond, there is no shift of the band energies relative to bulk diamond. A pre-edge feature in the X-ray absorption spectra that is not present in the bulk samples is consistent with a fullerene surface. The electronic structure of the surface and interior of individual diamond nanoparticles was measured from the EELS spectra acquired with a field emission TEM. This measurement shows the nanoparticles have a diamond core surrounded by a fullerene like surface structure. Standard density-functional theory calculations on diamond clusters hold the key to understanding what is happening on the surface of these nano-diamonds. In this calculation changes in the optical band gap occur only when the particle is less than 2 nm in size and have a hydrogen-terminated surface. Moreover, calculations show that when the surface is cleared of terminating hydrogen, the remaining surface carbon atoms rearrange to a fullerene-like surface. This discovery sheds light on the synthesis of novel optical and extraterrestrial materials. The work is supported by the US-DOE, BES Material Sciences under contract W-7405-ENG-48, LLNL.

### **N15.10**

#### **Microstructure of ZnO and In2O3 Nanowire/Nanorod,**

**Nanobelt/Nanowall, and Nanocircuit.** **J.Y. Huang**, J.Y. Lao, D.Z. Wang, D. Banerjee and Z.F. Ren; Physics, Boston College, Chestnut Hill, Massachusetts.

The microstructure of ZnO and In2O3 nanowire/nanorod, nanobelt/nanowall, and nanocircuit synthesized by thermal evaporation and condensation method were studied by high resolution transmission electron microscopy (HRTEM) and scanning electron microscopy (SEM). HRTEM revealed that a number of basal plane dislocations, i.e.  $1/3[1120]$  type, exist in the ZnO nanobelt and nanowall. HRTEM also indicates that the surface structure of the ZnO nanowires differs considerably, namely, it can be either flat, or saw-tooth like, or faceted on different atomic planes, or it can be coated with or without amorphous layers, depending on the process condition. The effect of the defect structure and the different surface structure on the physical properties is discussed. The In2O3 nanowires and nanocrystals self-assemble to form complicated micrometer or nanoscale networks similar to that of integrated electronic circuits. These nanowire and/or nanocrystal networks may provide key clues to the fabrication of nanoelectronic circuits or nanodevices.

### **N15.11**

#### **Fabrication of Highly-Ordered Nanopores and Metallic**

#### **Nanowire Arrays on Silicon for Nanoscale Electronic Device Applications.**

**Ramkumar Krishnan<sup>1</sup>**, Kornelius Nielsch<sup>1</sup>, Henry I Smith<sup>2</sup>, Caroline A Ross<sup>1</sup> and Carl V Thompson<sup>1</sup>; <sup>1</sup>Department of Materials Science & Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; <sup>2</sup>Department of Electrical Engineering & Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Metallic nano-wires, rods, and dots can be used in a number of applications relevant to hyper-integration technology, including nanowire-interconnects (wires), on-chip magnetic storage devices (rods), on-chip Peltier cooling devices (wires and rods), and plasmonic wave guides (dots). In this paper, we will describe a new template-directed self-assembly technique to produce metallic nanowires with controlled diameter and spacing on a silicon wafer. Anodic porous alumina is an example of self-ordered nano-structured material that is well-suited as templates for growing metallic nanowires for applications in magnetic, electronic and opto-electronic devices. The pores form a hexagonally ordered structure with short-range order and vertical orientation. Pore size can be varied from 4nm-300nm by controlling the conditions for electrochemical oxidation of aluminum. Although, there has been extensive work done to obtain porous alumina with well-defined pore diameters and distances, little has been done to integrate this process into wafer-level processes or to improve the long range ordering of pores. In the current study, highly ordered alumina nanopores with controlled symmetry have been grown by electrochemical etching of aluminum evaporated on nanoscale-corrugated silicon surfaces. The silicon surface was patterned using interference lithography and periodic inverted pyramid structures were obtained via chemical wet etching of silicon. Thin aluminum films were then evaporated and electrochemically etched to obtain nano-porous alumina. The effect of the anodization potential and electrolyte composition on pore formation and ordering processes will be discussed and examples of both ordering of pores at lithographic length and sub-lithographic length scales will be demonstrated. Nanowire arrays grown by electrodeposition using ordered alumina templates and the effect of electrochemical conditions on the nanowire growth process will also be addressed. Applications of ordered nanowire arrays in the area of nanoscale electronic devices will be discussed.

### **N15.12**

#### **Diffusion-Limited Recombination In Dye-Sensitized**

#### **Nanocrystalline TiO<sub>2</sub> Solar Cells.**

**Nikos Kopidakis**, Kurt Benkstein, Jao van de Lagemaat and Arthur Frank; NREL, Golden, Colorado.

A simple method for doping TiO<sub>2</sub> nanoparticle films is presented. Doping causes a dramatic decrease of the electron diffusion coefficient in the nanoparticle network. A multiple electron-trapping model involving native traps as well as doping-induced ones is invoked to explain the dependence of the electron diffusion coefficient on photoinduced charge density at various doping densities. It is also observed that the recombination lifetime of photocarriers increases in unison with the diffusion time, which provides the first direct evidence that trap-limited electron diffusion limits recombination with the redox electrolyte in a working solar cell. A model is presented that accounts for diffusion-limited recombination in dye-sensitized nanocrystalline TiO<sub>2</sub> solar cells.

### **N15.13**

#### **Quantum Simulations of the Effect of Synthesis Conditions on the Structural and Optical Properties of Passivated Silicon Nanoclusters.**

**Erik W. Draeger**, Jeffrey C Grossman, Andrew J Williamson and Giulia Galli; Physics and Advanced Technologies, Lawrence Livermore National Laboratory, Livermore, California.

We studied the effect of synthesis conditions on the structural and optical properties of silicon nanoparticles, using first-principles molecular dynamics and quantum Monte Carlo<sup>1</sup>. Depending on the synthesis environment and passivation mechanism, clusters of a given size can form with dramatically different core structures. Starting from a high temperature silicon vapor and then rapidly passivating and cooling, our quantum simulations yielded metastable non-crystalline structures which consistently have large optical gaps in good agreement with experimental measurements. Other techniques, such as colloidal synthesis or etching of porous silicon, are expected to produce crystalline nanostructures. When the curved surface is taken into account, there exist multiple reconstructions of crystalline silicon nanoclusters which are unique to highly curved nanostructures and which have no bulk analogue. These reconstructions have very different optical gaps even for clusters of the same size and stoichiometry. We show that for both reconstructed crystalline clusters and non-crystalline clusters, the impact of oxygen atoms attached to the surface on the optical gap is small but may provide a signature for nanocluster structure at the 1 nm size range, where direct measurement techniques are inconclusive. With a combined total

simulation time of 1 ns, this study represents a systematic comparison of structures produced by different synthesis techniques and can be applied to other nanoscale systems. This work was performed under the auspices of the U.S. Department of Energy by University of California Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48. [1] E. W. Draeger, J. C. Grossman, A. J. Williamson, and G. Galli, Phys. Rev. Lett. 90, 167402 (2003).

**N15.14**  
**Structural, Electronic, and Optical Properties of CdSe Nanocrystals: First-Principles Computations.** Aaron Puzder, Andrew J. Williamson and Giulia Galli; Lawrence Livermore National Laboratory, Livermore, California.

We report on a series of complete *ab initio* calculations of CdSe nanocrystals with diameters up to 1.5 nm. For each nanocluster, the relaxed atomic structure, electronic states, and optical properties are calculated using the most thorough treatment to date. We predict a substantial structural relaxation of each cluster, especially at the surface, while still maintaining a wurtzite core. In contrast to Type IV and III/V nanoparticles, the predicted CdSe atomic structures are found to be insensitive to the presence of surface passivation. We find that CdSe nanocrystals with ideal wurtzite structures are quasi-metallic and that surface relaxations, not passivation with organic ligands, are responsible for opening up a gap in the clusters. We predict the existence of a single midgap state, which is responsible for sub-bandgap emission often observed in CdSe nanoclusters. Finally, we report on calculated dipole moments for ideal and relaxed clusters, both in the presence of passivating ligands and without. This work was performed under the auspices of the U.S. Department of Energy at the University of California/Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

**N15.15**  
**High-Sensitivity Nanoparticle Surface Plasmon Sensor Based on Ultraflat Nanosphere Lithography.** Bongsu Jung<sup>1</sup> and Wolfgang Frey<sup>1,2</sup>; <sup>1</sup>Biomedical Engineering, The University of Texas at Austin, Austin, Texas; <sup>2</sup>Center for Nano- and Molecular Science and Technology, The University of Texas at Austin, Austin, Texas.

Sensor arrays have proven to be a major tool for genomic analysis, gene expression assays, and the detection of nucleotide polymorphisms. It is to be expected that proteomic chips will play a similar role in the near future for the analysis of proteins coded by newly discovered genes, the determination of signaling cascades, and the determination of protein expression levels, which take post-translational modifications into account. While it is easy to fluorescently label cDNA, and GFP fusion proteins are a powerful tool to detect the expression of proteins, most identification procedures still involve the binding of an immunolabel for fluorescence. Secondary labeling, however, involves extensive washing and increased background due to non-specific interactions. Additionally, labels are impossible to develop for large screening of candidate libraries of drugs, where labeling steps could also interfere with binding. Also, fluorescence is often not easily quantifiable, which makes binding kinetics studies difficult. Label-free detection methods are therefore needed in many applications, and surface plasmon resonance in thin metal films has become a standard method for measuring binding kinetics. High-density array formats, however, require a less technically involved and more parallel detection technique than existing label-free methods. Such high-density array formats are possible based on nanoparticle surface plasmon resonance, in which the electronic resonance changes with a change in mass at the surface, and can be detected by simple absorption measurement in a UV-Vis spectrometer. In principle, a single particle can be used as a sensor. The size and shape of these metal nanoparticles determine the position of the resonance and the sensitivity to change in the environment, and larger and non-spherical particles achieve higher sensitivity. These parameters are, however, not easily controlled by bulk synthesis methods, and sharp features are often not stable under changing chemical environments such as during bioconjugation procedures. We have used a self-assembly shadow-masking lithography technique combined with a dry lift-off, which we earlier termed ultraflat nanosphere lithography, to create an array of nanoparticles of controlled size and of non-spherical shape that is partially embedded in a second material of choice. The resulting array of silver or gold nanoparticles is capable of detecting thiol surface modification and protein binding kinetics. We present data on the shift of the absorption maximum upon binding, kinetic data for fixed wavelength absorption, and the dependence of the sensitivity of the sensor on the lateral size and height of the particles, and on the substrate material. Each sensing element can be miniaturized without loss of sensitivity for real-time protein binding kinetics measurements in an array format.

**N15.16**  
**Diameter Control of Ti-Catalyzed Silicon Nanowires.**

**Shashank Sharma**, Theodore I Kamins and R Stanley Williams; Hewlett-Packard Laboratories, Palo Alto, California.

Semiconductor nanowires are expected to be of interest for a variety of electronic, optical, and optoelectronic device applications. However, in order to integrate semiconductor nanowires in conventional microelectronic technology, it is imperative to control the nanowire characteristics such as diameter and the uniformity of the diameter along the nanowire length. In this paper, we address these key issues in the nanowire growth using nanometer scale Ti-silicide catalyzed chemical vapor deposition technique. Nanometer scale Ti-silicide islands have been previously used to catalyze the growth of silicon in one dimension into nanowires. Silicide nanoparticles catalyze the decomposition of a silicon-containing gas at rates orders of magnitudes higher than the uncatalyzed, normal silicon deposition rates. The resulting silicon diffuses through or around the solid silicide nanoparticle, and attaches at the silicide-silicon interface. Further growth takes place in one dimension due to rapid diffusion rates of silicon through or around the silicide nanoparticle. Due to the catalytic activity of the silicide, the nanowire diameter is limited by the size of the silicide nanoparticle. Moreover, the nanowire diameter distribution strongly depends on the starting silicide island distribution. Thus, in order to control the nanowire diameter and diameter distribution, it is imperative to control the silicide nucleation. In this paper, we will show the dependence of the Ti-silicide formation on different substrate materials commonly used in Si IC technology and the annealing conditions. We will discuss the resulting nanowire characteristics such as nanowire morphology, diameter, and diameter distribution. In addition to controlling the nanowire diameter and diameter distribution, it is necessary to control the nanowire diameter along the length. Under a specific set of process parameters, the Ti-catalyzed growth resulted in tapered silicon nanowires. The tapered nanowires were typically several microns long with diameters of tens of nanometers near the base and less than 5 nanometers at the tip. In this paper, we will also present results of our detailed investigation describing the mechanism leading to the tapered nanowire growth.

**N15.17**  
**Monolayer Formation of CdSe/ZnS Quantum Dots by Multiple Dip-Coating Process for Electroluminescent Device.** Viena Kim, Changwoo Kwon, Jung-Sub Wi, Tae-Sik Yoon and Ki-Bum Kim; School of Materials Science and Engineering, Research Institute of Advanced Materials, Seoul National University, Seoul, South Korea.

Quantum dot-light emitting diode (QD-LED) with a hybrid structure of inorganic/organic LED is of interest for its high electroluminescent efficiency of semiconductor quantum dots. In order to fabricate the electroluminescent device out of quantum dots, it is required to place quantum dots with a high spatial density within a device structure. In this study, we employed the multiple dip-coating process by repeating the adsorption of colloidal quantum dots in solution and drying the solvent after pulling out the substrate which results in the formation of assembled quantum dots structure. With this process, we formed a monolayer of 4-nm-size CdSe/ZnS core-shell quantum dots on a hole-transfer layer (poly(3,4-ethylenedioxythiophene), called as PEDOT). The coverage of CdSe/ZnS quantum dots increases up to > 70 % corresponding to the density of quantum dots about  $3 \times 10^{12}/\text{cm}^2$ . The photoluminescence intensity of quantum dots was shown to increase with increasing coverage on PEDOT substrate. In addition, we have studied the assembly of quantum dots on patterned substrate by combining the conventional lithography process and multiple dip-coating process in order to demonstrate the feasibility of full-color electroluminescence device fabrication by using these colloidal quantum dots.

**N15.18**  
**Light Induced Conversion of Silver Nanospheres to Nanoprisms.** Rongchao Jin, Yunwei Charles Cao, Gabriella Metraux, Encai Hao, George Schatz and Chad Mirkin; Department of Chemistry, Northwestern University, Evanston, Illinois.

A light-induced method for converting spherical Ag nanoparticles into triangular nanoprisms has been developed. The photo-process has been characterized by time-dependent UV-Vis spectroscopy and transmission electron microscopy (TEM). Interestingly, two different types of particle growth modes, unimodal and bimodal growth processes, were discovered for the photoinduced conversion process. When visible light (white) from a conventional fluorescent light tube was used as the excitation source, we found that Ag nanospheres were converted into nanoprisms via a unimodal growth process. In contrast, when a narrow band light source (e.g. 550+-20 nm) was used to photolyse the Ag colloid, bimodal growth process was observed, which lead to two different size distributions of the nanoprisms. Importantly, we find that the growth process can be selectively switched between bimodal and unimodal distributions using dual beam illumination of

the spherical nanoparticles. This type of photo-control over nanostructure growth allows one to synthesize relatively monodisperse Ag nanoprisms with a preselected edge length in the 30-120 nm range simply by using one beam to turn off bimodal growth and the other (wavelength varied over the 450-700 nm range) for controlling particle size. The light wavelength control over particle size is distinct from most traditional methods that rely on the choice of surfactants, precursors, or solution temperature. In addition, Ag nanoprisms show distinctive optical properties that directly relate to the nanoprism shape of the particles, which could be useful in developing multicolor diagnostic labels based not only on nanoparticle composition and size but also on shape. Theoretical calculations coupled with experimental observations allow for the assignment of the nanoprism plasmon bands and the first identification of two distinct quadrupole plasmon resonances for a nanoparticle.

#### **N15.19**

**Influence of the organic ligands of the electronic and optical properties of metal nanoparticles.** Francesco Stellacci, Robert J Barsotti, Gretchen A DeVries, Alicia M Jackson and Arum A Yu; Materials Science and Engineering, MIT, Cambridge, Massachusetts.

Ligand coated metal nanoparticles are supramolecular assemblies of a metallic crystal coated with a relatively large number of organic ligands. Their main strength is in the fact that they combine the advantages of small metals, such as single electron transistor (SET) behavior or surface plasmon resonance, together with most of the advantages of the organic ligands that are used to coat them, such as solubility in organic solvents and processability via self-assembly methods. Moreover, even complex nanoparticles coated with multiple types of ligands can be synthesized in just one step. The role of the ligand in determining and modulating the properties of the nanoparticles will be discussed by comparing the optical and electronic properties of nanoparticles with the same core but with different ligand shell composition. For example, a new family of mixed-ligand nanoparticles will be presented, in such nanoparticles sub-nanometer ( $\sim 3 \text{ \AA}$  in depth) ridges form. When the peaks and the valleys of these ridges have different hydrophobicity the solubility, wettability and electronic properties of the nanoparticles show unique behaviors. The synthesis and the unique self-assembly properties of such particles will be presented. The supramolecular mechanism that leads to the formation of such ordered structures on the shell of the particles will be discussed. Additionally, as the ligand nature changes the SET behavior of these particles and the optical properties vary accordingly. Preliminary results comparing the properties of metal nanoparticles with the same ligand composition but with different supramolecular arrangement in the ligand shell will be presented. Finally, a method for the in situ replacement of ligands on the shell of nanoparticles bound to a surface will be presented. With this method, an extension of Replacement Lithography, it is possible to fabricate a 13 nm wide nanowire composed of fluorescent nanoparticles within a monolayer of alkane-thiol coated nanoparticles.

#### **N15.20**

**Band Gap Tailoring of Nd<sup>3+</sup> Doped TiO<sub>2</sub> Nanoparticles.** S. Ismat Shah<sup>1,2</sup>, Weidong Li<sup>1</sup>, Y Wang<sup>2</sup>, S Rykov<sup>3</sup>, H Lin<sup>3</sup>, C-P. Huang<sup>3</sup>, D. Doren<sup>4</sup>, J Chen<sup>5</sup> and M Barteau<sup>5</sup>; <sup>1</sup>Materials Science and Engineering, University of Delaware, Newark, Delaware; <sup>2</sup>Physics and Astronomy, University of Delaware, Newark, Delaware; <sup>3</sup>Civil and Environmental Engineering, University of Delaware, Newark, Delaware; <sup>4</sup>Chemistry and Biology, University of Delaware, Newark, Delaware; <sup>5</sup>Chemical Engineering, University of Delaware, Newark, Delaware.

Undoped and Nd<sub>3+</sub> (0.6, 1, 1.5%) doped TiO<sub>2</sub> nanoparticles were synthesized by metalloorganic chemical vapor deposition (MOCVD) in order to tailor the band gap of TiO<sub>2</sub>. TiO<sub>2</sub> stoichiometry and Nd concentration were determined by x-ray photoelectron spectroscopy (XPS) and energy dispersive x-ray spectroscopy (EDS). The structure and particle size of the samples were determined by X-ray diffraction (XRD) and transmission electron microscopy (TEM) which showed that all samples had anatase structure with an average particle size of 20-23 nm. The doping successfully reduced the band gap. The band gap was measured by ultraviolet-visible (UV-VIS) light absorption experiments and by near edge X-ray absorption fine structure (NEXAFS). The maximum band gap reduction was 0.55 eV for 1.5 at% Nd-doped TiO<sub>2</sub> nanoparticles. Density functional theory calculations using the generalized gradient approximation with the linearized augmented plane wave method were used to interpret the band gap narrowing. The band gap narrowing was primarily attributed to the substitutional Nd<sup>3+</sup> ions which introduced electron states into the band gap of TiO<sub>2</sub> to form the new lowest unoccupied molecular orbital. The TiO<sub>2</sub> nanoparticles with reduced band gap are much desired for photo-driven applications such as photocatalysis and photovoltaics. The experiments of visible light degradation of 2-chlorophenol solutions showed that Nd doped TiO<sub>2</sub> nanoparticles had enhanced photoreactivity.

#### **N15.21**

**Optical Gain in Si-Based Quantum Dots.** Susumu Fukatsu<sup>1,2</sup>, Masafumi Jo<sup>1</sup>, Nozomu Yasuhara<sup>1</sup> and Kiyoshi Kawamoto<sup>1</sup>; <sup>1</sup>Graduate School of Arts and Sciences, University of Tokyo, Meguro, Tokyo, Japan; <sup>2</sup>PRESTO, Japan Science and Technology Corporation, Kawaguchi, Saitama, Japan.

We report on the observation of optical gain of interband radiative recombination in a new class of Si-based quantum dots (QDs) created by embedding III-V compound semiconductors in Si. Samples were self-assembled QDs (SAQDs) grown by evaporating column III-V species (III=In,Ga; V=As,Sb) onto Si(001) in Si molecular beam epitaxy. Electron diffraction and surface scans on uncapped samples confirmed SAQDs with physical dimensions of the order of 10nm for a few monolayers equivalent of III-V supply. SAQDs exhibited an intense luminescence band over the 1- $\mu$ m region that survived up to room temperature. Optical gain experiment was performed on SAQDs by monitoring amplified spontaneous emission (ASE) coupled out from the pump section under intense, Q-switched laser pulses. Edge-emitting luminescence from the signal source under weak excitation was chopped and butt-coupled to a cleaved facet of the pump section. For comparative purposes, strained SiGe quantum well was also used. The ASE was observed for GaSb SAQDs alone whereas it was totally absent and only absorption loss was observed for the rest of III-V SAQDs and SiGe as well. In view of the predicted type-II band line-up which will drive the SAQDs into an indirect-gap system, the gain establishment in III-V SAQDs in Si should be accounted for by considering admixed wavefunctions of direct-gap GaSb and indirect-gap Si. Strong localization of electrons at the III-V/Si interface due to the built-in electric dipole is what that counts. In fact, the electron localization allows intense luminescence as a result of an enhanced immunity against dissipation. At low temperature, a very fast decay indicative of stimulated emission was found to develop whenever the optical gain was observed. Such fast decays are characterized by unusual wavelength dependence of decay rates, demonstrating the significance of interface-localized electron-hole pairs in providing population inversion in a new class of Si-based QDs.

#### **N15.22**

**Nanocrystal Quantum Dot-Titania Nanocomposites: From Fabrication to Photonic Structures.** Melissa A. Petruska, Richard D. Schaller, Anton V. Malko, Andrew P. Bartko and Victor I. Klimov; Chemistry Division, Los Alamos National Laboratory, Los Alamos, New Mexico.

Nanocrystal quantum dots (NQDs) are of considerable interest because of their size-controlled spectral tunability and their chemical flexibility, factors that make NQDs ideal building blocks in materials fabrication. The synthesis of NQDs and their manipulation as artificial atoms into two- and three-dimensional assemblies can be exploited to fabricate networks in which the interactions between the NQDs and their surrounding media are explored. As an example, a significant challenge for achieving optical applications of NQDs is the incorporation of nanoparticles into transparent host matrices while preserving high photoluminescence (PL) quantum yields (QYs) and achieving large NQD filling factors, which are essential for obtaining optimum NQD performance in optical applications. We have recently developed a new, generalized method for preparing such nanocomposite materials in which NQDs are incorporated into titania and silica matrices, in many cases without a significant decrease in their PL QY [1]. In contrast to our earlier procedure [2], our new approach avoids the ligand exchange step that is often necessary to render the NQDs hydrophilic and suitable for sol-gel processing. By exploiting this universal procedure, we can readily manipulate a wide variety of NQD shapes and compositions into such assemblies. These NQD-titania nanocomposites also have excellent optical quality and are ideally suited for use in photonic devices such as microresonators, photonic crystals, and fiber circuits. We have previously demonstrated microring lasing action from a CdSe NQD nanocomposite gain medium contained in a microcapillary tube [2]. More recently, we have investigated combining our nanocomposites with isolated and coupled microsphere resonators and photonic crystals. We use these structures to study the effect of the "restricted" density of photonic states on the linear and nonlinear optical performance of NQD-based nanocomposites. [1] M. A. Petruska, A. P. Bartko, and V. I. Klimov, submitted. [2] M. A. Petruska, A. V. Malko, P. M. Voyles, and V. I. Klimov, Adv. Mater. 2003, 15, 610.

#### **N15.23**

**The magnetic behavior of triangular shape permalloy nanoparticle arrays.** Jau-ye Shiu, Inst. Appl. Sci. & Eng. Res., Academia Sinica, Taipei, Taiwan.

During the past few decades, the density of magnetic storage has been improved considerably. To increase the storage capacity, it is necessary to reduce the size of magnetic grains. However, as the domain size decreases, their thermal stability will also decrease, which

results in the loss of magnetization. To overcome the limit imposed by such superparamagnetic behavior, lots of recent research attentions have been focused on the patterned magnetic media. To maximize the storage density, it is preferable to create periodical magnetic patterns, in which single-domain magnetic dots are well-separated from each other. In this experiment, we have utilized nanosphere lithography to create large-area well-ordered two dimension arrays of permalloy (Ni80Fe20) nanoparticles. Nanosphere lithography is an inexpensive, simple, parallel, and high throughput fabrication technique. We have employed monodisperse polystyrene beads with diameter of 650, 560, 440, 350, 280 nm to fabricate triangle-shape permalloy (Ni80Fe20) nano-arrays with lateral dimension in the region of 160~90 nm, and thickness in the region of 10~50 nm. The magnetic behavior of these triangle-shape nano-arrays has been investigated by longitudinal magnetic optic Kerr effect (LMOKE) and magnetic force microscopy (MFM). It was found that the coercivity of the permalloy nanoparticle arrays increases with decreasing the thickness of the nanoparticle. This can be attributed to the interface effect between the arrays and the substrate.

#### **N15.24**

**Lasing in Single CdS Nanowires.** Ritesh Agarwal, Carl Barrelet and Charles M Lieber; Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts.

Single CdS nanowires were recently reported to function as optical cavities and were configured as injection lasers. Here we describe temperature dependent spectroscopy studies that address the mechanism of lasing in these novel nanostructures. At 4.2K, the photoluminescence spectrum reveals rich spectral features, including well resolved peaks corresponding to bound excitons. Investigations of the excitation intensity dependence of the P-band, which corresponds to exciton-exciton interaction, exhibit a non-linear behavior with an exponent of ca. 1.8. As the pump power is increased further, the P band shows a highly non-linear increase in emission intensity and eventually collapses to single mode lasing. The linewidth of this peak above the lasing threshold is 1.2 meV. Further increase in the intensity of the pump source by more than an order of magnitude did not cause any red shift in this lasing line, and thus suggests that lasing is excitonic in nature and not due to the formation of an electron-hole plasma. Similar behavior was observed from 4.2K to 70K indicating that the mechanism of lasing is due to exciton-exciton interaction, while at higher temperatures data suggests that lasing is due to exciton-electron or exciton-LO phonon interactions. The implications of these and other results for the design of low threshold nanowires lasers will be discussed.

#### **N15.25**

**Four-Point Resistivity Measurements of Boron Doped Silicon Nanowires.** Yanfeng Wang<sup>1</sup>, Marco Cabassi<sup>1</sup>, Kok-Keong Lew<sup>2</sup>, Joan M. Redwing<sup>2</sup> and Theresa S. Mayer<sup>1</sup>; <sup>1</sup>Electrical Engineering, The Pennsylvania State University, State College, Pennsylvania; <sup>2</sup>Material Science and Engineering, The Pennsylvania State University, State College, Pennsylvania.

There has been considerable interest in bottom-up integration of semiconductor nanowires for their application in future logic, optoelectronic, and sensing circuits. To achieve these goals, robust synthetic approaches must be developed for incorporating p- and n-type dopants and to characterize the electrical transport properties of the resulting structures. In this talk, we present results showing the dependence of nanowire resistivity on intentional p-type doping of single crystal silicon nanowires. The silicon nanowires used in these studies were synthesized by template-directed vapor-liquid-solid (VLS) growth using 10% silane in H<sub>2</sub> as the Si source gas and diborane as the p-type dopant source. Au metal plugs were deposited within the 80-nm diameter pores of anodized alumina membranes to catalyze the growth of the nanowires at a growth temperature of 500C. The boron concentration was varied by changing the ratio of diborane to SiH<sub>4</sub> while maintaining a constant total flow rate in the reactor. Following synthesis, silicon nanowires with an average diameter of 80-nm and length of 10-um were removed from the membrane and suspended in an isopropanol solution. Nanowires were integrated for resistivity measurements by electrofluidically assembling individual nanowires between pairs of metal electrodes used to force a constant current through the nanowire. Electron-beam lithography was then used to add two additional 100-nm wide voltage leads to complete the test structures. Nanowire resistivity was determined by measuring the voltage drop induced between the voltage leads as a function of the current forced through the nanowire using a lock-in amplifier operated in differential input modes. Initial 4-point data suggest that the background concentration of nominally undoped wires is greater than 10<sup>16</sup> Ohm-cm, and that the p-type doping concentration can be increased with increasing diborane partial pressure. Additional temperature dependent measurements are being done between 13K and 370K to obtain information about the activation energy of the impurities incorporated during growth.

#### **N15.26**

##### **Radiation Tolerance of Si Nanocrystal Non-volatile**

**Memories.** Mihail P Petkov<sup>1</sup>, L. Douglas Bell<sup>1</sup> and Harry A Atwater<sup>2</sup>; <sup>1</sup>Jet Propulsion Laboratory, Pasadena, California; <sup>2</sup>Applied Physics, Caltech, Pasadena, California.

We report results from radiation exposure measurements on prototype nanocrystalline Si (nc-Si) non-volatile memory (NVM) devices. nc-Si is formed in a thin SiO<sub>2</sub> blanket layer on a Si wafer by Si implantation and subsequent high-temperature annealing. This structure is patterned into ring-gate field-effect transistors (FETs) with different width-to-length ratios of the gate. The active area of the gate contains large number of nc-Si domains, on each of which charge can be stored via tunneling at suitable electric fields. The novelty of this technology is in the statistical approach to assessing bit status (open/closed FET). It is believed that the radiation-induced loss of charge on a large fraction of the crystals may not necessarily lead to information loss (bit flip). Resistance to radiation-induced bit loss is of great interest to NASA for missions into extreme environments such as that of the Jovian system where radiation levels are high. However, the radiation tolerance of nc-Si NVM has not been evaluated to date. We monitored the hysteresis memory effect by measuring drain-source current versus gate voltage, to assess the memory performance in radiation environments. In addition, complementary gate-substrate C-V measurements were conducted on areas outside the FET active region, as well as using metal dots deposited on non-patterned wafers. The devices were irradiated to doses of 1 Mrad (Si) by a <sup>60</sup>Co source with a dose rate of 25 Mrad/s. I-V and C-V characteristics were measured ex-situ. During the irradiation, a square-wave write/erase potential was applied to the gates of all transistors in order to enhance the degradation effect due to trapping of charge carriers. The preliminary results show no significant changes in the memory-related hysteresis in both the I-V and C-V characteristics. Photoluminescence measurements have also confirmed that the nc-Si domains remain unaffected up to at least 1 Mrad cumulative dose. This work continues with device evaluation to higher doses and with irradiation by high-energy particles.

#### **N15.27**

**Development of Nanoparticles with Tunable UV Absorption Characteristics.** Daniel Morel, Syed Imad-Uddin Ahmed and Henry Haefke; Micro and Nanomaterials, CSEM Swiss Center for Electronics and Microtechnology, Neuchatel, Switzerland.

Abstract Engineering of nanoparticles to detect UV light within a specified range and its feasibility to make a device has been demonstrated. It is shown that the absorption edge of a material can be shifted to significantly lower wavelengths in the UV range by using nanoparticles and that this feature can be incorporated within a device. All experimental work was focused on ZnO based on its already established use in products involving UV applications. Both commercially obtained ZnO nanoparticles as well as in-house synthesized ZnO nanoparticles were examined. For the in-house developed particles it was shown that varying the diameter of the ZnO nanoparticles could vary the absorption wavelength from 315 to 365 nm. Commercially available nanoparticles did not show this shift due to their relatively larger sizes ( diameter  $\approx$  20 nm) as well as their broad size distributions. A photocurrent effect of UV light on thin films prepared with nanoparticles has been demonstrated. For the commercial ZnO with particle size of 22 nm, the main increase of the photocurrent appears when UV light at a wavelength of 366 nm strikes the sample. Photocurrent effect on a thin film prepared from nanoparticles (diameter = 5 nm) is different depending on the wavelength of the radiation. No photocurrent is generated when the sample is exposed to a radiation of  $\lambda = 366$  nm, ( $E_g = 3.39$  eV), but at a higher energy ( $\lambda = 254$  nm,  $E_g = 4.88$  eV), a photoelectronic effect was observed. The obtained results reveal that not only the optical band-gap value depends on the size of the nanoparticles but also the electronic band gap of the material.

#### **N15.28**

##### **Synthesis of Nanowires and Heterostructures for Photonic**

**Devices.** Carl Julien Barrelet<sup>1</sup>, Yue Wu<sup>1</sup>, David C Bell<sup>2</sup> and Charles M Lieber<sup>1,3</sup>; <sup>1</sup>Chemistry Department, Harvard University, Cambridge, Massachusetts; <sup>2</sup>Center for Imaging and Mesoscale Structures, Harvard University, Cambridge, Massachusetts; <sup>3</sup>Division of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts.

Compound semiconductor nanowires have been successfully used as light emitting diodes, photodetectors and electrically driven lasers. Critical to the properties and behavior of these and other potential devices are the crystallinity, stoichiometry and size of the nanowire building blocks. These key properties can in principle be varied during growth, and thus the development of synthetic methods that enable their control is expected to have significant impact on future progress.

We report the first use of single-source molecular precursors for the growth of CdS, CdSe and ZnS nanowires by nanocluster-crystal nanowires with controlled diameters and high-quality optical properties. High resolution transmission electron microscopy studies show that the nanowires are single-crystal wurtzite structures with stoichiometric compositions. The optical properties of individual nanowires were studied by photoluminescence (PL) and exhibit narrow band-edge emission. The high-quality optical properties make these nanowire powerful candidates for applications in photonic devices. Finally, recent studies of CdS, CdSe and ZnS heterostructures will also be presented.

#### **N15.29**

##### **Site-selective anchoring of nanocluster heteroassemblies.**

Raghuvveer S Makala<sup>1</sup>, Trupti Maddanimath<sup>1</sup>, P G Ganesan<sup>1</sup>, G Ramanath<sup>1</sup>, M Marshall<sup>2</sup>, J Mabon<sup>2</sup> and I Petrov<sup>2</sup>; <sup>1</sup>Materials Science & Engineering, Rensselaer Polytechnic Institute, Troy, New York; <sup>2</sup>Center for Microanalysis of Materials, University of Illinois, Urbana-Champaign, Illinois.

Creating organized assemblies of heterogeneous nanoscale units in ordered and/or site selective configurations is an attractive strategy for building a new class of skeletal templates and scaffolds for nano- and bio-composites. By using strings consisting of alternating nanoclusters of different kinds organized in linear or 2 D configurations would enable the realization of multifunctional nanocomposites by harnessing their novel electronic, magnetic and optical properties arising from quantum confinement, order and periodic heterogeneities in such nanoassemblies. In this study, we investigate the effect of Ga<sup>+</sup> ion beam irradiation to effect site selective molecular tethering of nanoclusters through local defect creation on multiwalled carbon nanotubes (MWNTs). We also report the usage of self-assembled molecular layers (SAMs) of different lengths and terminal functionalities to interlink and/or anchor nanoclusters to ordered arrays of MWNTs. We have synthesized 1 - 50 nm sized nanoclusters of different kinds and size/ distributions by variants of the Brust synthesis route and explored the covalent and hydrophobic linkage through the use of different kinds of SAMs for capping and interlinking, or using bifunctional molecules with appropriate terminal groups to achieve both functions. The nanocluster heteroassemblies thus synthesized have been characterized using SEM, TEM and EDS for studying structure, shape, coverage and composition.

#### **N15.30**

##### **Impact of Surface Chemistry on the Optical Properties of Polymer-Embedded Silicon Nanoparticles.** William D. Kirkey<sup>1</sup>,

Michael Pan<sup>1</sup>, Alexander N. Cartwright<sup>1</sup>, Yudhisthira Sahoo<sup>2</sup>, Paras N. Prasad<sup>2</sup>, Xuegeng Li<sup>3</sup>, Yuanqing He<sup>3</sup> and Mark T. Swihart<sup>3</sup>; <sup>1</sup>Electrical Engineering, State University of New York at Buffalo, Buffalo, New York; <sup>2</sup>Chemistry, State University of New York at Buffalo, Buffalo, New York; <sup>3</sup>Chemical Engineering, State University of New York at Buffalo, Buffalo, New York.

Nanocrystalline silicon has received a great deal of attention in recent years as a material that might be easily integrated into silicon wafer processing and utilized for biological and chemical sensing or for light-emitting devices. The well-established effects of the surface termination and the surrounding environment on the silicon luminescence are advantageous for sensing applications, but present a problem when stable light emission is the goal. Polymers such as polymethylmethacrylate (PMMA) have been used effectively to shield luminescent silicon nanostructures and nanoparticles. We seek to use electrically conducting polymers, such as those commonly utilized in polymeric LEDs, as protective hosts for silicon nanoparticles. The proper design of multilayered devices based on these materials will yield efficient light-emitters in which charge carriers localize and recombine within the nanoparticles. Furthermore, these may combine the flexibility and processability of polymeric LEDs with the reliability of inorganic materials. We have synthesized luminescent silicon nanoparticles and have characterized their photoluminescence (PL) using continuous-wave and time-resolved spectroscopy. These particles have been incorporated into a variety of transparent solid hosts. As expected, the photoluminescence obtained from particle-containing PMMA matrices and xerogels is very similar to that of the particles in solution, both in spectral content and PL decay characteristics. However, when incorporated into a variety of conducting polymers, such as poly(N-vinylcarbazole) (PVK), the nanoparticles do not retain their photoluminescent properties. A variety of Lewis bases have been reported as effective PL quenchers for porous silicon. We believe that these polymers quench the luminescence through similar mechanisms. Strategies for overcoming this quenching, including protective passivation of the nanoparticle surface and modification of the polymeric host, are presented.

#### **N15.31**

##### **Multicolour photochromism in silver nanoparticles in a TiO<sub>2</sub>**

**matrix.** Matthias Wuttig and John Okumu; I. Institute of Physics, RWTH Aachen, Aachen, Germany.

Recently it has been shown that silver nanoparticles in a TiO<sub>2</sub> matrix prepared by sol-gel and spin coating techniques show multicolour photochromism [Okho et al. 2003]. In this study we report on an alternative route, namely DC magnetron sputtering of a TiO<sub>2</sub> / Ag / TiO<sub>2</sub> trilayer system and subsequent annealing, to prepare Ag nanoparticles embedded in a TiO<sub>2</sub> matrix. This technique would be the desired method for applications that require large area coatings like displays. In the process of sputtering the second layer of TiO<sub>2</sub>, the silver layer is destroyed, but on annealing, due to the high surface free energy of silver atoms, Ag clusters are formed. TEM and optical spectroscopy show that the silver nanoparticles range in size from approximately 15nm to over 120nm with varying shapes. This leads to a broad absorption spectrum of the films with the characteristic surface plasmon resonances of silver nanoparticles. The broad absorption spectrum is a prerequisite to colour the samples under monochromatic visible light to the same colour as that of the illuminating light. Decoloration is obtained by illuminating with UV irradiation. At higher illuminating powers we also observe a behaviour similar to spectral hole burning. The colouration/de-colouration mechanism is explained in terms of the energy levels involved.

#### **N15.32**

##### **Laser Ablation Synthesis of Oxide Nanowires and Their**

**Properties.** zuqin liu, Daihua Zhang, Chao Li and Chongwu Zhou; Department of Electrical Engineering - Electrophysics, University of Southern California, Los Angeles, California.

Synthesis of one-dimensional functional metal oxide nanowires has attracted a lot of attention because of their unique properties for applications ranging from nanoelectronic devices to gas sensors. In this paper, we report an efficient and reliable laser-ablation approach for large-scale synthesis of SnO<sub>2</sub> and ZnO nanowires. The nanowire growth followed the vapor-liquid-solid model. Precise control over the nanowire diameters has been achieved by using monodispersed gold clusters as the catalyst. Detailed material analysis such as transmission electron microscopy (TEM) and x-ray diffraction (XRD) were used to confirm the crystal structure of the nanowires. In addition, field effect transistors have been constructed based on individual SnO<sub>2</sub> nanowires, and excellent n-type transistor characteristics were observed. Detailed analysis revealed threshold voltages ~ -50V with on/off ratios as high as 10<sup>3</sup> at room temperature. These nanowire transistors were further demonstrated to work as sensitive UV detectors.

#### **N15.33**

##### **Preparation of SiO<sub>2</sub> Gels Containing Small -Size CdS**

**Particles.** Vilma C Costa<sup>1</sup>, Fernando S Lameiras<sup>1</sup> and Maria T C Sansiviero<sup>2</sup>; <sup>1</sup>CT1, CNEN/CDTN, Belo Horizonte, MG, Brazil; <sup>2</sup>Chemistry, Universidade Federal de Minas Gerais, Belo Horizonte, MG, Brazil.

In the present work, small-particle-size CdS-doped silica glasses have been synthesized by the sol-gel process. Gels were prepared through the hydrolysis of silicon tetraethoxide, cadmium acetate and thiourea, SC(NH<sub>2</sub>)<sub>2</sub>. TEOS was hydrolysed in a mixed solution of H<sub>2</sub>O and ethanol (TEOS/H<sub>2</sub>O/EtOH = 1:4:5). Cadmium acetate and thiourea were dissolved in methanol (TEOS/MeOH = 1:4 and Cd/SC(NH<sub>2</sub>)<sub>2</sub> = 1:2), and added to the TEOS solution. Molar ratio Cd/Si was 0.01 and 0.03. Silica gels containing cadmium-thiourea complexes were heat-treated at 330 °C in air for decomposition of the complexes to CdS. In another heating procedure the gels were heated in H<sub>2</sub>S at 150 °C for 12 h. We have investigated the preparation process and the optical properties of CdS-doped SiO<sub>2</sub> through IR spectroscopy, X-ray diffraction, atomic force microscopy and optical absorption. The size of the doped crystallites was evaluated. The absorption edges of these glasses were blue-shifted depending on the concentration of the initial salt and heat-treatment conditions.

#### **N15.34**

##### **PEDOT/Co Nanowire Synthesis Using AAO Template.**

Wansoo Huh<sup>1</sup>, Barry Farmer<sup>2</sup>, Richard Vaia<sup>2</sup>, Don Shiffler<sup>3</sup>, Loon-Seng Tan<sup>2</sup> and Bala Sankaran<sup>2</sup>; <sup>1</sup>Chemical & Environmental Engineering, Soongsil University, Seoul, South Korea; <sup>2</sup>AFRL/MLBP, Air Force Research Laboratory, WPAFB, Ohio; <sup>3</sup>AFRL/DE, Air Force Research Laboratory, Kirtland, New Mexico.

Aluminum oxide(AAO) template can be prepared by anodization process in oxalic acid solution and it can be used for the various application of nano-structured materials. Depending upon the electrolyte, anodization temperature, and anodization time, the diameter and length of the pore can be controlled and the different type of nano-materials can be deposited inside the pore. In this study, Co is deposited inside the pore at first and different length of Co nanowire can be obtained. After preparing Co nanowire, ether dioxy



thiophene(EDOT) was polymerized inside the pore by applying AC voltage. Poly(ether dioxy thiophene)(PEDOT) was synthesized to form the conducting nanowire which is connected to Co nanowire. The prepared PEDOT/Co nanowire was isolated from the AAO template and the physical and conducting properties were characterized.

#### **N15.35**

**Growth of InGaN Nanorods as the Blue Light Source for White Light Devices.** Hwa-Mok Kim<sup>1</sup>, Tae Won Kang<sup>1</sup> and Kwan Soo Chung<sup>2</sup>; <sup>1</sup>QSRC, Dongguk University, Seoul, South Korea; <sup>2</sup>Department of Electronic Engineering, Kyunghee University, Yongin, South Korea.

The ternary InGaN alloys are capable of emitting photons from 0.9 eV (~1380 nm infrared) to 3.4 eV (~365 nm ultra violet) by varying indium mole fraction from 0 to 1. Unfortunately, many threading dislocations (TDs) are produced in bulk GaN and InGaN due to lattice mismatch with the substrate, and thus they affect significantly the device performance as non-radiative recombination centers. On the other hand, the growth mechanism for nanorods is completely different, and threading dislocations can be all but non-existent in InGaN nanorods. Therefore, the InGaN nanorods have the potential for negligible non-radiative recombination loss, and thus the efficiency of down-conversion is much higher than in bulk InGaN/GaN. In spite of this great advantage, no one has successfully grown InGaN nanorods to date. Here, we reported the growth of the defect-free InGaN nanorods by hydride vapor phase epitaxy (HVPE) using In metal. InGaN nanorods were grown directly on the (111) silicon substrate without catalysts or template layers. Indium and gallium (Ga) metal were used as In and Ga precursor (group III), respectively. NH<sub>3</sub> was used as nitrogen precursor (group V). p- and n-type nanorods were doped with Cp<sub>2</sub>Mg or Mg metal and SiH<sub>4</sub>, respectively. This work was supported by KOSEF through the QSRC at Dongguk Univ. in 2003.

#### **N15.36**

**CdSe Quantum Dots Synthesized From CdO: (2) Systematic Investigation on Surface Passivation with Organic Amine and Inorganic Shell.** Kui Yu, B. Zaman, V. Chu, J. Cornelis, N. Patriito, T. Wagle and J.A. Ripmeester; Steacie Institute for Molecular Sciences, National Research Council Canada, Ottawa, Ontario, Canada.

A comprehensive investigation was carried out on the surface passivation of CdSe quantum dots, synthesized with CdO as the Cd precursor in the traditional coordinating solvent system, consisting of mixtures of tri-n-octylphosphine (TOP) and tri-n-octylphosphine oxide (TOPO). The surface passivation was performed on the CdSe dots with efficient photoluminescence, and was achieved by post treatment with both organic species (such as amines) and inorganic species (such as ZnS). The change in the PL properties during the surface passivation was monitored. Further post-treatment on the CdS/ZnS core-shell dots was also carried out with amines, and the change in the PL properties was monitored. The efficiency of the post treatment was evaluated by our newly developed approach (presented in Part 1), regarding the PL properties. The insight gained helps us to design new strategies for the surface passivation to generate quantum dots with improved PL properties. Based on our systematic studies (Part 1) performed on the CdSe cores, namely (1) nucleation and growth temperature effect, (2) Cd-to-Se ratio effect, (3) acid additive effect, and (4) reaction medium effect, a two-step approach was carried out in the synthesis of the core-shell dots with the exactly same core but with the shell of the different thicknesses and different materials (ZnS, ZnSe, and CdS). A comprehensive investigation on the PL properties of the core-shell dots was performed. Particularly, the PL behaviors in culture media were studied in detail. A thorough comparison of the PL properties of the various core-shell dots was addressed. The insight gained helps us to design superior approaches in the fabrication of core-shell quantum dots for their bio-applications in imaging and labeling.

#### **N15.37**

**Trap Effects in PbS Quantum Dots.** Peter D. Persans, Aleksey Filin, Feiran Huang, Andrew Vitek, Pratima G. N. Rao and Robert Doremus; Physics, Rensselaer Polytechnic Institute, Troy, New York.

In PbS quantum dots with diameter of ~3 nm, the lowest excited state falls at 1550 nm (0.8 eV). Such particles are therefore potentially important as saturable absorbers, optical switching elements, or emitters for telecommunications. The speed and magnitude of nonlinear optical and luminescence responses determine the utility of this system. We have found that traps dominate important relaxation processes in particles prepared by precipitation in borosilicate glass. The primary photoluminescence peak energy falls about 50 meV below the lowest absorption peak energy and has a long decay time of ~4 $\mu$ s. Photoinduced bleaching of the lowest absorption peak has a long lifetime of ~2 $\mu$ s. Photoinduced bleaching also exhibits a surprisingly

long rise time of hundreds of nanoseconds. Such long-lifetime effects must be attributed to multiple traps. We will discuss the nature of these traps and contrast our observations with previous ultrafast studies. This work is supported in part by the Department of Energy, Office of Basic Energy Sciences, grant number DE-FG02-97ER45662.

#### **N15.38**

**Low Temperature Synthesis of Nanowires by CVD of Metal-Organic Precursors.** Sanjay Mathur and Hao Shen; CVD, Institute of New Materials, Saarbruecken, Germany.

Semiconductor materials in confined (nano)geometries display interesting electronic, optical and mechanical properties due to the quantization of electronic states. A controlled synthesis of one-dimensional structures can be achieved by the combination of eutectic formation and decomposition of molecular precursors on the substrate surface. Single crystal Ge nanowires in high yield were obtained by the decomposition of germanium di-cyclopentadienylide ([Ge(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>]), on iron substrates, in a CVD process at 325 degree. High-resolution electron microscopy (SEM/TEM) showed Ge 1D structures to be uniform in terms of diameter (20 nm) and length (> 25 micrometer). The wire growth is selective and appears to be governed by a Ge-Fe alloy epilayer formed by reactions between germanium clusters and iron substrates, during the initial stages of the CVD process. Increasing Ge content induces a phase separation in the Ge-Fe solid-solution resulting in the spontaneous formation of single crystalline germanium nuclei that act as templates for nanowire growth. X-ray and electron diffraction revealed the NWs to be single crystals of cubic germanium with a preferred growth direction [11-2]. The interplay between precursor flux and deposition temperature has been used for controlling the structure (crystalline and/or amorphous) and morphology (wires or whiskers) of the CVD deposits. Low-temperature formation of high purity nanowires is attributed to the clean decomposition pattern of the molecular precursor. This strategy has been extended to other systems such as ZnO, SnO<sub>2</sub>, etc. using molecular precursors in the CVD process.

#### **N15.39**

**Solution-phase, Large-scale Synthesis of Single-crystalline ZnO Nanorods and Nanowires.** Bin Cheng and Edward T. Samulski; Chemistry, University of North Carolina, Chapel Hill, North Carolina.

Bin Cheng, and Edward T. Samulski\* Department of Chemistry University of North Carolina, Chapel Hill, NC 27599-3290 \*To whom correspondence should be addressed, et@unc.edu One-dimensional (1-D) ZnO nanostructures were prepared in solution at low temperature. The aspect ratio of the 1-D ZnO nanostructures was tunable. Nanorods or nanowires were obtained via different carefully controlled experimental conditions. The crystallinities, structure, and morphologies of the as-prepared ZnO nanorods and nanowires were characterized by XRD, TEM, SAED, HRTEM and SEM. The results show that these 1-D ZnO nanostructures are single-crystals, which grow along (0001) direction. The photoluminescence of the 1-D ZnO nanostructures was also measured.

#### **N15.40**

**Optical Properties of Ordered Arrays of Silver Nanoparticles.** Matthew David McMahon<sup>1</sup>, Rene Lopez<sup>1</sup>, Kenneth E. Schriver<sup>1</sup>, Anthony B. Hmelo<sup>1</sup>, Robert H. Magruder<sup>2,3</sup>, Leonard C. Feldman<sup>1</sup>, Robert A. Weller<sup>3,4</sup> and Richard F. Haglund<sup>1</sup>; <sup>1</sup>Physics and Astronomy, Vanderbilt University, Nashville, Tennessee; <sup>2</sup>Physics, Belmont University, Nashville, Tennessee; <sup>3</sup>Electrical Engineering and Computer Science, Vanderbilt University, Nashville, Tennessee.

Ordered arrays of metal nanocrystals have potential applications as elements of photonic circuits, as sensitizers for fluorescence emitters and photodetectors, and as anchor points for biological molecules. Here we report optical measurements of two-dimensional ordered arrays of metal nanoparticles fabricated using a focused ion beam (FIB) as a lithography tool. The FIB is programmed to pattern a 70 nm PMMA resist layer, which is subsequently developed to produce a mask with holes at the patterned locations. The resist is removed following pulsed laser deposition (PLD) of a thin Ag film, leaving behind an ordered array of disk-shaped Ag nanoparticles averaging 60 nm in diameter and 15 nm high on the chosen substrate (silicon or ITO). We present results based on the SEM, AFM and SNOM characterization of arrays having various basis geometries, including single particles, two particles, and three particles arranged as vertices of an equilateral triangle. For single-particle arrays, the lattice distance was varied from 70 nm to 1  $\mu$ m. For arrays with a multi-particle basis, the lattice distance was set to 1  $\mu$ m and the intra-basis distance was varied from 70 nm to 500 nm. In each case, the lateral extent of the arrays was ~50  $\mu$ m. A SNOM microscope was used in confocal mode to measure the spectrum of the nanoparticle arrays and demonstrate the redshift associated with the change in the interparticle distance, and the geometry dependence of the spectrum.

#### **N15.41**

**Diameter-Controlled Synthesis of Silicon Nanowires Using Nanoporous Anodized Aluminum Membranes.** Timothy Bogart, Kok-Keong Lew, Soham Dey, Suzanne E Mohny and Joan M Redwing; Material Science and Engineering, Materials Research Institute, Penn State University, University Park, Pennsylvania.

The fabrication of single crystal silicon nanowires with well-defined and monodisperse diameters is important both for fundamental studies of size effects as well as for the development of nanoscale devices. We previously demonstrated the use of commercial nanoporous alumina membranes with a nominal pore diameter of 200 nm as templates for vapor-liquid-solid (VLS) growth of silicon nanowires. In this study, we have prepared anodized aluminum membranes with average pore diameters ranging from 45 nm to 150 nm, and investigated VLS growth conditions required to synthesize silicon nanowires with well-controlled diameters using these membranes. The membranes were produced by anodization of aluminum in oxalic acid. A thin layer of gold was electrodeposited into the membrane pores to serve as a catalyst for VLS growth. The nanowires were grown at 500°C using a 5% mixture of SiH<sub>4</sub> in H<sub>2</sub> at reactor pressures ranging from 3 to 13 Torr depending on the pore diameter. Samples were prepared in which the Si nanowires were grown either entirely within the membrane or protruded out of the top surface of the membrane. Scanning electron microscopy was used to measure the diameter of approximately 50 nanowires for each sample studied. For nanowires grown within the membrane pores, the average nanowire diameter closely corresponded to the average pore diameter of the membrane. The average nanowire diameter increased by approximately 20 nm for all of the samples studied when the nanowires grew out of the top surface of the membrane. Transmission electron microscopy characterization revealed a change in the shape of the gold tip when the nanowires emerged from the membrane pores, which is believed to be responsible for the change in nanowire diameter. The results of this study demonstrate that nanoporous alumina membranes can be used to control the diameter of silicon nanowires synthesized by VLS growth.

#### **N15.42**

**Quantum Simulations of Hydrophobic Hydration.**

Jeffrey Curtis Grossman, Eric Schwegler and Giulia Galli; Lawrence Livermore National Laboratory, Livermore, California.

The accelerated development of nano-miniaturization and the merging of semiconductor and biological technologies is already leading to atomic scale "nano-bio" devices that contain hydrophobic elements, and a detailed description of the structure of water at these interfaces will play an important role in understanding how such novel technologies should be designed and applied. Our work\*, using quantum molecular dynamics simulations, demonstrates the need for a new description of water behavior at the interface of a hydrophobic solute. Our simulations for methane and silane in water reveal two new attributes of hydrophobic hydration that have not been observed previously: (1) the dipole tilt angles are different than the symmetric distribution expected from classical calculations; (2) while the tilt angles are the same from one solute to another, the spatial and radial distribution functions are dramatically different. These observations challenge traditional assumptions about hydrophobicity and require new postulations which will be discussed. \* J.C. Grossman, E. Schwegler, G. Galli, submitted to Phys. Rev. Lett.

#### **N15.43**

**Synthesis of milligram quantity of crystalline Ge nanodots: a step towards nanocrystalline silicon?** Daniele Gerion<sup>1</sup>, Natalia Zaitseva<sup>1</sup>, Cheng Saw<sup>1</sup>, Maria Francesca Casula<sup>2</sup>, Jennifer Harper<sup>1</sup> and Giulia Galli<sup>1</sup>; <sup>1</sup>Lawrence Livermore National Laboratory, Livermore, California; <sup>2</sup>University of California, Berkeley, California.

Nanocrystalline silicon and germanium play a key role in the field of semiconductors from the standpoint of both fundamental properties and technological impact. Up to date the study and applications of nanocrystalline Ge and Si have been limited by the availability of an appropriate synthetic procedure leading to monodisperse nanoparticles with tunable size and high crystallinity in high yield. We use commercially available precursors to synthesize large quantities of pure Ge nanocrystals by a one-pot, autoclave-based high temperature procedure. The choice of adequate precursors, solvents, surfactants and temperature of reaction are key parameters for the success of the synthesis. Nanocrystalline germanium was isolated as a black powder (> 100 mg) and characterized by XRD, HRTEM, EDX and XANES. All results are in agreement, indicating the formation of nanocrystalline cubic germanium with average size of about 8 nm and size distribution of about 5 nm. The concentration of the precursors has a strong effect on the particle size, and is still under investigation. The synthesis of smaller nanocrystals is of particular interest in order to make the particles dispersible in liquid media. The procedure for

the synthesis of Ge can be extended to the preparation of nanocrystalline Si. Preliminary results indicate that higher temperatures will be required in this case. It is important to point out that, at the temperatures required for the reaction, most of the organics present in the reaction mixture are thermally decomposed and the byproducts exhibit strong fluorescence in the range from 400 to 550 nm that shifts with the excitation wavelength. As a result, fluorescence measurements alone cannot be used to ascertain the presence of nanocrystals with different sizes in high-temperature solution synthesis of Ge and Si nanocrystals due to the interference from organics.

#### **N15.44**

**Cathodoluminescence of single-crystalline ZnO nanopencils.**

Manuel J Romero, Yanfa Yan, Ping Liu and Mowafak Al-Jassim; National Renewable Energy Laboratory, Golden, Colorado.

Zinc oxide nanostructures are attracting great attention for their potential in a variety of optoelectronic applications such as lasers, field electron emitters and field-effect transistors. However, improvements in self-organization during the synthesis will be required to fabricate practical devices. Quantum-related effects have been demonstrated for ZnO nanostructures, which open possibilities for tunable emission and tailoring of electronic properties. In this contribution, cathodoluminescence spectroscopy and imaging are employed to investigate optical properties of ZnO nanopencils, where nanorods with sharp tips develop at the end of hexagonal-faced nanorods. Such structures represent a unique opportunity to investigate the evolution of the optical properties from the micron to the nanoscale. For this measurements, we have developed a system for the detection of cathodoluminescence capable of high-sensitivity, ultrafast spectrum acquisition in synchronization with the electron-beam. A spatial resolution better than 30 nm has been proven under the excitation conditions used in these experiments. Although the evolution of the emission spectrum from micro- to nanorods can be basically explained by differences in stoichiometry and point-defect physics, we have observed a shift of the excitonic emission at the tip, which can be associated to quantum effects. The presence of a strong depletion region at the tip seems to be responsible for the observed effect and suggests that the nanopencils may exhibit enhanced field electron emission.

#### **N15.45**

**Quantum Dot Synthesis In A Microfluidic Reactor:**

**Nucleation And Growth.** Thomas A. Sounart<sup>2</sup>, Jessica E. Bickel<sup>2</sup>, Michael B. Sinclair<sup>2</sup>, James A. Voigt<sup>2</sup>, Terry A. Michalske<sup>2</sup> and Terry A. Michalske<sup>2</sup>; <sup>1</sup>Chemical Syntheses and Nanomaterials, Sandia National Lab, Albuquerque, New Mexico; <sup>2</sup>Sandia National Lab, Albuquerque, New Mexico.

A continuous microfluidic reactor system has been used to synthesize CdS quantum dots and to characterize their nucleation and growth processes. Using a two-feed stream system, an aqueous solution containing CdSO<sub>4</sub> was continuously fed into one side of a rectangular microchannel while a solution containing Na<sub>2</sub>S was fed into the other. The laminar flow of the impinging streams allowed for controlled diffusional mixing of the reacting cadmium and sulfide ions at the interface between the two solutions. Using spatially resolved fluorescence imaging of the solution-solution interface coupled with varying reactant concentrations and flow rates, information on CdS particle nucleation and growth kinetics has been obtained from spectral analysis. The large effect different capping agents, such as cysteine and polyphosphate, have on particle nucleation and growth kinetics will be discussed. This data is being incorporated into microreactor models to learn how to better control quantum dot size and morphology. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-ACO4-94AL85000.

#### **N15.46**

**Oriented Titania-Based Nanotubes: Synthesis and Application.** Z. Ryan Tian<sup>1</sup>, Jun Liu<sup>1</sup>, James A. Voigt<sup>1</sup>, Huifang

Xu<sup>2</sup>, Hongting Zhao<sup>1</sup> and Bonnie Mckenzie<sup>1</sup>; <sup>1</sup>Sandia National Lab, Albuquerque, New Mexico; <sup>2</sup>Dept. of Earth and Planetary Science, University of New Mexico, Albuquerque, New Mexico.

Highly oriented nanostructures in the form of large, uniform arrays have many important technological applications. Here we report for the first time a one-step, templateless method to directly prepare large arrays of oriented titania nanotubes and continuous films. The growth process and structural evolution were studied by high-resolution transmission electron microscopy and by X-ray diffractometry. Extended crystalline sheets were observed in the early stage of reaction. These sheets folded to form long extended nanotubes. The new TiO<sub>2</sub> nanostructure is an exciting addition to a fast growing family of oriented nanowire and nanorod structures, such as carbon nanotubes, ZnO columnar arrays, and conductive polymer

arrays. Due to the unique electronic and optical properties of TiO<sub>2</sub>, the oriented arrays of TiO<sub>2</sub> nanotubes, continuous films and coatings are expected to have many novel potential applications in catalysis, filtration, sensing, and photovoltaics. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-ACO4-94AL85000.

#### **N15.47**

**Template-less assembly of nanowire networks from nanoparticles.** T. Maddanmath<sup>1</sup>, J. D'Arcy Gall<sup>1</sup>, A. V. Ellis<sup>1</sup>, P. G. Ganesan<sup>1</sup>, K. Vijayamohan<sup>2</sup> and G. Ramanath<sup>1</sup>; <sup>1</sup>Materials Science and Eng., RPI, Troy, New York; <sup>2</sup>National Chemical Laboratories, Pune, India.

Typically, 1-D nanostructures and their assemblies are synthesized, fabricated or assembled via lithographic templating and high-temperature vapor-phase methods, or surfactant-mediated techniques. Here, we demonstrate a completely new template-less, room-temperature approach of assembling networks of gold nanowires from 5 nm nanoparticles using biphasic organic-aqueous liquid mixtures and mechanical agitation. Key aspects of this assembly process are revealed by a combination of scanning and transmission electron microscopy, electron and light spectroscopy measurements. We show that fcc Au nanoparticles impinge and coalesce at high-mobility liquid-liquid interfaces, giving rise to polycrystalline nanowires with diameters identical to that of the nanoparticles. In addition to nanocrystal coalescence, molecules of the organic phase displace weakly bound anionic species that solvate the nanoparticles, and bind to the Au surface. This renders the nanowire surface hydrophobic, and expels the networks into the organic layer. We can adjust the balance between the rates of coalescence and passivation, and tune the morphology of the coalesced nanoparticle assemblies by altering the solvent chemistry. The nanowire yield is a strong function of the ionic strength and solution pH, indicating that the surface chemistry of the nanoparticles is a crucial factor that controls nanowire formation. Based upon our results, we will present a phenomenological model of nanowire formation, and demonstrate the adaptation of the process to form nanowires of other materials systems such as Pt and Ag. Such templateless approaches of building meso-structures from nanoscale building blocks could open up new flexible assembly strategies to create architectures for applications in catalysis, sensing, molecular entrapment and delivery.

#### **N15.48**

**Synthesis and Applications of Macroscopically Hierarchical Metallic, Semiconductor, and Polymeric Nanowire and Nanomesh Thin Films.** Yunfeng Lu, Donghai Wang, Maria Gil, Yun Zhuang, Xiangling Ji and Eric Hampsey; Chemical Engineering Department, Tulane University, New Orleans, Louisiana.

The research on nanostructured materials has been one of the most active areas due to their unique magnetic, optical, electronic, mechanic, and other properties. Physical properties and potential applications associated with one-dimensional nanoscaled materials such as nanowires, nanoarrays, and nanomeshes are of particular interest. However, current synthesis approaches usually leads to the formation of nanowires that are lack of control in their macroscopic morphology, which may limit their applications in sensors, nano-devices, membranes, microelectronics, aerospace, and other applications. Our research attempts to bridge the nanoscale metallic, semiconductor, and polymeric architectures with the macroscopic device fabrications. One example is the synthesis of macroscopic metallic, semiconductor, or polymeric nanowires or nanomeshes in the form of thin films via electrodeposition techniques using mesoporous silica as templates. This method continually grows metal, semiconductor, or polymer within the pore channels of the templates from the bottom conductive substrate upward till the mesoporous channels are filled. Removal of the templates results in various macroscopic hierarchical nanowires or nanomeshes. The structures of the nanostructured thin films have been characterized by X-ray diffraction (XRD), transmission electron microscope (TEM), and electron energy-loss spectroscopy (EELS), and other techniques. We have also explored their applications in fuel cells, electrodes, magnetic materials, photovoltaics, sensors, and other applications.

#### **N15.49**

**Crosslinked Micelle-Encapsulated Nanostructures: Improved Stability and Functionality for the Nanotoolbox.** T. Andrew Taton, Youngjong Kang, Aimee R. Erickson and Castro S. Laicer; Chemistry, University of Minnesota, Minneapolis, Minnesota.

Chemists and materials scientists have become increasingly adept at fabricating complex nanostructures from exotic inorganic materials. However, the stability and functionality of these nanomaterials is sometimes limited by their poor surface chemistry. We have developed a general strategy for creating artificial 'surfaces' for colloidal

nanostructures, by trapping them within the cores of amphiphilic block-copolymer micelles. Crosslinking one of the two blocks of the copolymer fixes the amphiphilic micellar shell, and leads to permanent stabilization of the composite inorganic-organic nanostructure. We find that encapsulated nanoparticles, nanorods and nanotubes can be dispersed in a wide variety of solvents and materials without flocculation or fusion. We have used microscopy and spectroscopy to characterize both the structure of the polymer shells and their response to their environment. The broad stability of these structures appears to be caused by the fact that either the hydrophobic or hydrophilic block of the copolymer, or sometimes both blocks, appear to be solvated in nearly all matrices. Nevertheless, the crosslinked polymer micelles remain stably linked to their inorganic nanostructures during materials processing conditions. We anticipate that the shell-crosslinking approach will enable many of the less tractable nanomaterials now being synthesized to be readily composited with bulk polymer materials and used as tracers in biological media.

#### **N15.50**

**Linear and nonlinear properties of semiconductor nanocrystals in polymer based planar waveguides.** Vikram Sundar<sup>1</sup>, ylva olsson<sup>1</sup>, ronen rapaport<sup>1</sup>, gang chen<sup>1</sup>, dan fuchs<sup>1</sup>, jonathan steckel<sup>2</sup> and moungi bawendi<sup>2</sup>; <sup>1</sup>bell laboratories, lucent.technologies, murray hill, New Jersey; <sup>2</sup>chemistry and material science and engineering, massachusetts institute of technology, cambridge, Massachusetts.

We report on first optical measurements of semiconductor nanocrystals incorporated into fluorinated polymer based waveguides. Nanocrystals of different compositions and sizes were successfully used, with a spectral span both in the visible and IR. Photoluminescence measurements show that these nanocrystals preserve their optical activity inside the polymer host. Results of nonlinear, time-resolved optical measurements are presented and indicate a picosecond response time for the embedded nanocrystals. The measurements were performed on both thin films and planar waveguides defined using optical lithography. These results are a step toward integrating semiconductor nanocrystals into planar lightwave circuits as active components in applications such as light emitters and amplifiers, as well as in nonlinear optical devices.

#### **N15.51**

**How do confinement and disorder affect phonons in metal nanograins?** Gustavo Arnaldo Narvaez<sup>1</sup>, Jeongnim Kim<sup>2</sup> and John W. Wilkins<sup>1</sup>; <sup>1</sup>Physics, The Ohio State University, Columbus, Ohio; <sup>2</sup>NCSA/MCC, University of Illinois Urbana-Champaign, Urbana-Champaign, Illinois.

Confinement and disorder become more relevant as the size of electronic devices decreases. While the effect of size and disorder on electronic transport in nanoscopic devices such as ultra-small metal grains recently has been the target of intense research, their role on phonons has yet to be understood. We present results of atomistic simulations of the phonon and electronic spectra of Ag metallic nanograins. We address the role of geometry and disorder by studying the energetics of different grain shapes – surface facets and geometry – and the subsequent changes in the phonon density of states, electronic energy levels, and electron-phonon coupling. Furthermore, we discuss the electronic relaxation process via phonons by combining arguments derived from random matrix theory and simulations.

#### **N15.52**

**Preparation and Photoluminescent Properties of Nanosized Yttrium Aluminum Garnet Phosphors.** Chung-Hsin Lu, We-Tse Hsu and Chien-Hao Huang; Chem. Eng., National Taiwan Univ., Taipei, Taiwan.

Development of new nanophotonic materials has become a great challenge to the people working in materials research in view of their ever increasing scope for novel applications and interesting optoelectronic properties. With the advent of these new class of materials, creation of new technologies such as quantum well lasers and UV radiation blockers have become possible. Luminescent Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>:Ce<sup>3+</sup> (YAG:Ce<sup>3+</sup>) ceramics nanometer-sized particles were prepared by a new sol-gel pyrolysis method. The fuel system yielded nanoparticles exhibiting single-crystal features. The developed sol-gel process can significantly reduce the required temperatures for synthesizing YAG:Ce<sup>3+</sup> phosphors. In addition, the partial aliovalent substitution of Y<sup>3+</sup> in YAG results in new defect complexes serving as precursors for the generation of excitons. Under band-edge photoexcitation, the excitons thus generated can resonate with excited levels of Ce<sup>3+</sup> which have a profound dependence on the particle-size.

#### **N15.53**

**Synthesis and Characterization of Nanosized Titania Photocatalysts.** Chung-Hsin Lu, Wei-Hong Wu and Jen-Hsien

Huang; Chem. Eng., National Taiwan Univ., Taipei, Taiwan.

Titania has been widely investigated owing to its potential in the application of degrading pollutants and wasted. The photocatalytic activity of anatase type titania is higher than the other types due to its wide band gap energy. In this study, a new hydrothermal process has been developed for synthesizing anatase type titania. Titania nanoparticles with a pure phase were successfully produced by this developed process. The particle size and crystallite size of titania significantly depended on the synthesis conditions. The band gap energy calculated from UV-visible spectra markedly varied with the particle size of titania powders. The properties of titania used as the photocatalyst have been also elevated. It was demonstrated that the synthesized titania effectively decomposed methylene blue under UV explosion during short reaction time. In addition, the decomposition ability of titania was determined by their particle size and surface area. For improving the photocatalyst properties of titania, the synthesis conditions should be well controlled for tailoring the particulate properties of titania nanoparticles.

#### **N15.54**

##### **Vapor-Phase Synthesis and Surface Functionalization of ZnSe Nanoparticles in a Counterflow Jet Reactor.**

Christos Sarigiannidis<sup>1</sup>, Maria Koutsona<sup>4</sup>, Athos Petrou<sup>2</sup> and T J Mountziaris<sup>1,3</sup>; <sup>1</sup>Chemical Engineering, SUNY at Buffalo, Buffalo, New York; <sup>2</sup>Physics, SUNY at Buffalo, Buffalo, New York; <sup>3</sup>National Science Foundation, Arlington, Virginia; <sup>4</sup>ExxonMobil Research, Fairfax, Virginia.

We report experimental results on the synthesis and surface modification of crystalline ZnSe nanoparticles in a counterflow jet reactor. The focus of our work is on controlling particle size and on surface functionalization that enables the use of the particles in applications. Crystalline ZnSe nanoparticles were synthesized by reacting vapors of dimethylzinc:triethylamine adduct with hydrogen selenide gas (diluted in hydrogen) at room temperature and low pressures. In a typical experiment the two reactants are fed continuously into a vertical cylindrical chamber, each one from a separate inlet of an opposed flow configuration. Nuclei (clusters) form near the stagnation point where the two reactants mix and subsequently flow radially towards the reactor exit. The particles grow by surface reactions and particle-particle coalescence. The latter is the primary growth mechanism, because particle nucleation is fast under typical operating conditions and reactants are rapidly consumed. The synthesis of optically-active nanocrystals with sizes below the 9nm confinement threshold of ZnSe has been demonstrated by using this technique. To control the particle size and to functionalize the surface of the particles, vapors of thiol-conjugated molecules are introduced into the reactor. Experiments conducted using vapors of 1-pentanethiol demonstrated the effectiveness of using this compound as coalescence inhibitor for controlling nanocrystal size. The use of bi-functional molecules, such as mercapto-ethanol, is being studied for producing functionalized nanocrystals containing polar groups on their surface. The nanoparticles have been collected by diffusion onto Si wafers, fused silica glass substrates, and TEM grids that are placed downstream from the particle formation region. They have also been deposited on substrates that are functionalized with self-assembled monolayers of thiols. Deposition on patterned substrates is being investigated to develop techniques for selective deposition of the particles into regular arrays. The optical properties of the nanocrystals are being studied using absorption, photoluminescence, and Raman spectroscopy. High resolution TEM is being used to study the structural properties of the particles. By connecting particle-level characterization with macroscopic (reactor-level) operating conditions, we are elucidating the physicochemical mechanisms that control the growth rate, size distribution, and structure of the particles. Detailed process models that describe flow, mass transfer and particle growth dynamics in the reactor have been developed and are being used to optimize the experimental system. We are also working to extend this technique to other II-VI systems, such as CdSe, and to diluted magnetic semiconductors, such as (Zn,Mn)Se.

#### **N15.55**

##### **Synthesis and Size Control of Luminescent II-VI Semiconductor Nanocrystals by a Novel Microemulsion-Gas Contacting Technique.** Georgios Karanikolos<sup>1</sup>, Paschalis Alexandridis<sup>1</sup>, Athos Petrou<sup>2</sup> and T J Mountziaris<sup>1,3</sup>;

<sup>1</sup>Chemical Engineering, SUNY at Buffalo, Buffalo, New York; <sup>2</sup>Physics, SUNY at Buffalo, Buffalo, New York; <sup>3</sup>National Science Foundation, Arlington, Virginia.

We report the development of a new method for synthesis of luminescent compound semiconductor nanocrystals that utilizes stable, well-characterized microemulsions as templates for precise control of particle size. The technique exploits the dispersed phase of the microemulsion to form numerous identical "nanoreactors". A single nanocrystal with desirable size is grown in each nanodroplet by

dissolving a precise amount of the group II reactant in the dispersed phase, forming the microemulsion, and bubbling the group VI reactant through the microemulsion to convert the group II reactant to particles. ZnSe quantum dots were synthesized by reacting hydrogen selenide gas with diethylzinc dissolved in heptane nanodroplets of a microemulsion formed by self-assembly of a poly (ethylene oxide)-poly (propylene oxide)-poly (ethylene oxide) amphiphilic block copolymer in formamide. By adjusting the surfactant to dispersed phase ratio, stable microemulsions were obtained with heptane droplets of ~40nm in diameter. Hydrogen selenide diluted in hydrogen was bubbled through the microemulsion, dissolved in formamide, diffused through the interface into the nanodroplets and reacted with diethylzinc to yield ZnSe nuclei (clusters). The initial ZnSe clusters grew by surface reactions with unreacted precursors and by cluster-cluster coalescence to form a single nanocrystal per nanodroplet. The energy release during cluster-cluster coalescence was apparently sufficient to anneal the particles into nanocrystals. The "as-prepared" ZnSe nanocrystals exhibit size-dependent luminescence and excellent photostability, when kept in the microemulsion. The nanocrystal populations were characterized by using HRTEM, XRD, photoluminescence, Raman, and absorption spectroscopy. The technique appears to offer "dial-a-size" capability by simple manipulation of the initial concentration of diethylzinc in the heptane. We have recently obtained promising preliminary results on CdSe nanocrystal synthesis from Cd-alkyls and hydrogen selenide. We are also working on extending the technique to "water-in-oil" microemulsion templates, with appropriate modifications to the nanocrystal growth chemistry. The incorporation of functional capping agents directly into the dispersed phase and techniques for extracting the functionalized nanocrystals from the microemulsion are under development and will be discussed.

#### **SESSION N16: Carbon Nanotubes (CNT) and Related Properties**

Chairs: Todd D. Krauss and Pehr Pehrsson  
Friday Morning, December 5, 2003  
Room 302 (Hynes)

#### **8:30 AM N16.1**

##### **Photoluminescence of Individual Single-Walled carbon**

**Nanotubes.** Todd D. Krauss<sup>1</sup>, Achim Hartschuh<sup>2,3</sup>, Lukas Novotny<sup>2</sup> and Hermenegildo Pedrosa<sup>1</sup>; <sup>1</sup>Department of Chemistry, University of Rochester, Rochester, New York; <sup>2</sup>Institute of Optics, University of Rochester, Rochester, New York; <sup>3</sup>Physikalisches Chemie I, Universität Siegen, Siegen, Germany.

Single-walled carbon nanotubes (SWNTs) are highly elongated, tubular graphitic molecules that are currently the subject of intense investigations arising from their unique physical properties and the potential for revolutionary applications. Due to the effects of quantum mechanical confinement, SWNT electronic properties exhibit a strong structural dependence, which is in part what makes these materials so attractive and potentially useful. However, current synthetic methods suffer from the inability to produce nanotubes with a single structure. Thus, in optical spectroscopic studies of macroscopic samples, large inhomogeneities in the ensemble have led to an averaged overall behavior that has obscured crucial electronic characteristics of the individual nanotube. The unavoidable ensemble averaging that arises when working with macroscopic samples has significantly impeded insight into SWNT optical properties and has slowed development of novel SWNT photonic applications. We will present measurements of the electronic structure of individual SWNTs using single molecule photoluminescence spectroscopy. Spectra from individual SWNTs with identical diameters while similar, exhibit a distribution of peak positions and line widths not observed in ensemble studies of isolated SWNTs. Because of the strong correlation between SWNT electronic configuration (and hence optical emission) and structure or local environment, we attribute the non-uniform emission properties to localized defects and localized electrostatic perturbations. Unlike for single molecules or semiconductor nanoparticles, for SWNTs the photoluminescence unexpectedly does not show any intensity or spectral fluctuations. The fact that SWNTs show no emission intensity blinking or bleaching demonstrates that SWNTs have the potential to provide a stable, single molecule infrared photon source, which would have a significant impact for future nanometer scale integrated photonic devices and single nanotube biological sensors.

#### **8:45 AM N16.2**

**Photo-induced Processes in Carbon Nanotubes.** Moonsub Shim, Materials Science & Engineering, Univ of Illinois, Urbana, Illinois.

Adsorption of molecules, whether intentionally or unavoidably adsorbed, can cause significant changes in the electronic properties of carbon nanotubes. The extreme sensitivity of carbon nanotubes to oxygen is currently a debated issue that has important implications on our understanding of (and therefore on the exploitation of) unique

electrical conductivity of carbon nanotubes. Photo-induced processes including photodesorption and photochemical effects are discussed especially with respect to variations in electrical conductivity of individual nanotube transistors and films.

#### 9:00 AM N16.3

**Interface and oxide contamination monitoring in integration of fullerenes and carbon nanotubes with aggressively scaled CMOS gate stacks.** Udayan Ganguly<sup>1</sup>, Chungho Lee<sup>2</sup> and Edwin C Kan<sup>2</sup>; <sup>1</sup>Materials Science and Engineering, Cornell University, Ithaca, New York; <sup>2</sup>School of Electrical and Computer Engineering, Cornell University, Ithaca, New York.

The integration of fullerenes and carbon nanotubes in the gate stack of CMOS technology is a promising hybrid approach of top-down and bottom-up fabrication process. As an enabling technology with rich chemistry of carbon, such integration can enrich CMOS applications such as nonvolatile nanocrystal memory (with monodisperse storage) [1-3] and C<sub>v</sub>MOS (with nanoscale tip resolution) [4]. Fullerenes and carbon nanotubes can be incorporated onto the gate oxide by a solution spin-coat method. 1,2 dichlorobenzene (DCB) provides high solubility for both materials [5,6]. DCB also dissolves readily in isopropyl alcohol (IPA), which can be used to rinse its residue. The solution for both fullerenes and nanotubes can be prepared by mild sonication. Centrifugation is then performed to precipitate out the larger particles, such as clusters, ropes and bundles. The supernatant solution containing individual nanoparticles or nanotubes is extracted with a pipette. The solution is now diluted to produce appropriate surface density of nanostructures on spin coating. An ultra thin oxide, of thickness 2 - 5 nm, is grown on silicon wafers. The prepared solutions of carbon nanotubes and fullerene and pure solvents are spun onto wafers with various oxide thicknesses. A control-gate oxide of thickness 20-40nm is then deposited by a method compatible with the carbon nanostructures. Top metal is deposited and patterned to produce MOS capacitors. CV measurements are used for the extraction of Si-SiO<sub>2</sub> interface states, minority lifetime and fixed oxide charge. IV measurements are used to extract oxide trap concentration and effective thickness through quantum oscillation. Surface states, generated by different solvents with and without solute, are compared with reference capacitors, fabricated without any solvent treatment. Thus, a quantitative measure of the contamination level due to individual solvents and solution treatments on ultra thin gate oxide is obtained as process monitors for integration of fullerenes and carbon nanotubes in CMOS gate stack. References: [1] Z. Liu, C. Lee, G. Pei, V. Narayanan and E. C. Kan, (MRS) Material Research Symposium, Boston, MA, Nov. 26-30, 2001, Proc. Vol. 686, A5.3. [2] Z. Liu, C. Lee, V. Narayanan, G. Pei and E. C. Kan, IEEE Trans. Electron Devices, vol. 49, no. 9, p.1606-1613, Sept. 2002. [3] C. Lee, Z. Liu and E. C. Kan, (MRS) Material Research Symposium, Boston, MA, Dec. 2002, Proc. Vol. 737, F8.18. [4] Y. N. Shen, Z. Liu, B. A. Minch, and E. C. Kan, Transducers'03: The 12th International Conference on Solid-State Sensors, Actuators and Microsystems, June 8-12, 2003, Boston, MA. [5] R.S. Ruoff, D.S. Tse, R. Malhotra, D.C. Lorents., J. Physical Chemistry, no. 97, p.3379, 1993 [6] J. L. Bahr, E. T. Mickelson, M. J. Bronikowski, R. E. Smalley, J. M. Tour, Chemical Communications, p.193, 2001

#### 9:15 AM N16.4

**Ultrafast ground state recovery of isolated single-walled carbon nanotubes.** Libai Huang, Hermenegildo N Pedrosa and Todd D Krauss; Department of Chemistry, University of Rochester, Rochester, New York.

The electronic properties of single-walled carbon nanotubes (SWNTs) are of significant fundamental and technical interest. However, many crucial parameters of electronic structure, such as the radiative and nonradiative lifetime of the first excited state, are yet to be determined. These lifetimes fundamentally determine the photoluminescence quantum efficiency and also the relative strength of resonant linear and nonlinear optical processes. Thus, these parameters are important not only for a complete fundamental understanding of SWNTs, but also for potential optoelectronic applications. We will present studies of the ultrafast relaxation of photoexcited electrons in isolated SWNTs using transient absorption spectroscopy. Excitation wavelengths were tuned between 1300 and 1550 nm, corresponding to resonant excitation of the lowest electronic transition in SWNTs with diameters between 0.84 and 1.00 nm. As expected for a quasi two-level system, all SWNTs samples showed a saturation of absorption at the pump wavelength. Quite surprisingly, however, the loss of excited state population was extremely fast, with more than 90% of the initial optical bleach signal recovering in a few hundred fs and the remaining 10% recovering in a few ps. For isolated SWNTs the recovery time was 100-200 fs longer than corresponding SWNT bundles due to the absence of nanotube-nanotube coupling. For a typical optical transition the fluorescence quantum yield is determined by the ratio of the radiative to the nonradiative lifetime. Fluorescence quantum yield

measurements yield values  $\sim 7 \times 10^{-4}$ , thus providing for the first time a measure of the SWNT radiative lifetime of  $\sim 0.5$  ns.

#### 9:30 AM N16.5

**Stimulated Emission of Infrared Radiation in Isolated Single-Walled Carbon Nanotubes.** Michael Scott Arnold<sup>1</sup>, Jay E. Sharping<sup>2</sup>, Prem Kumar<sup>2,5</sup>, Samuel I. Stupp<sup>1,3,4</sup> and Mark C. Hersam<sup>1</sup>; <sup>1</sup>Materials Science and Engineering, Northwestern University, Evanston, Illinois; <sup>2</sup>Electrical and Computer Engineering, Northwestern University, Evanston, Illinois; <sup>3</sup>Feinberg School of Medicine, Northwestern University, Chicago, Illinois; <sup>4</sup>Chemistry, Northwestern University, Evanston, Illinois; <sup>5</sup>Physics and Astronomy, Northwestern University, Evanston, Illinois.

We report here on the observation of "stimulated" as opposed to "spontaneous" emission from semiconducting single-walled carbon nanotubes (SWNTs) isolated in aqueous suspensions. These observations suggest the possibility of creating tunable infrared lasers using SWNTs, and the near-infrared range is important because of applications in fiber optic communications and medical imaging. This contribution will describe the characterization of the spectral and polarization dependencies of stimulated emission by an optical pump-probe technique, which offers new insight into the one-dimensional nature of SWNTs. Also, pump and probe intensity dependencies illuminate both carrier dynamics and saturation effects in these nanomaterials. Stimulated emission intensity in SWNTs is maximized at the E11 transition, for excitation at corresponding E22 transitions, and for co-linear polarization of pump and probe beams - reflecting anisotropic absorption and emission optical cross-sections. Generation of stimulated emission is twice as efficient for co-linear polarizations of the pump and probe as for cross-linear polarizations. At large pump intensities greater than 1 kW/cm<sup>2</sup>, saturation effects are observed - this is consistent with an excited semiconductor near critical inversion and enhanced non-radiative Auger recombination. At large probe intensities greater than 500W/cm<sup>2</sup>, saturation of stimulated emission is also observed due to an increase in the effective interband recombination rate due to stimulated recombination. The observed stimulated emission suggests that isolated SWNTs can be incorporated into future infrared optical amplification materials. Currently, efforts are underway to more precisely quantify the interband relaxation time of isolated SWNTs by pulsed pump-probe delay spectroscopy.

#### 9:45 AM N16.6

**Measurement of Decay Lengths of Carriers in Nanotubes and Nanotube Networks.** Michael Stadermann<sup>1</sup>, Michael Falvo<sup>2</sup>, John Boland<sup>1</sup>, Richard Superfine<sup>2,3,4</sup> and Sean Washburn<sup>2,3,4</sup>; <sup>1</sup>Chemistry, UNC Chapel Hill, Chapel Hill, North Carolina; <sup>2</sup>Physics and Astronomy, UNC Chapel Hill, Chapel Hill, North Carolina; <sup>3</sup>Computer Science, UNC Chapel Hill, Chapel Hill, North Carolina; <sup>4</sup>Curriculum in Material Science, UNC Chapel Hill, Chapel Hill, North Carolina.

Since their discovery, carbon nanotubes have held promise for use as nanoscale wires or electrical devices. The transport properties of carbon nanotubes and their contacts to metal have been the focus of many research efforts. In this work, we directly measure the transport properties of individual carbon nanotubes and nanotube networks using an AFM imaging method that allows simultaneous measurement of topography and local conductance. This method allows high resolution images of changes in conductance along the nanotubes and at nanotube/nanotube junctions. In networks, the method allows us to tell which nanotubes are connected electrically, and to map the location of abrupt changes in conductance.

#### 10:30 AM \*N16.7

**Dielectrophoretic Sorting of Metallic and Semiconducting Single-Walled Carbon Nanotubes.** Pehr Pehrsson and Jeffrey W Baldwin; Chemistry Division, Naval Research Lab, Washington, D.C., District of Columbia.

An asymmetric, alternating field is used to position and align single-walled carbon nanotubes (SWNTs) across metal contacts on silicon oxide surfaces by dielectrophoresis (DEP). The selection of appropriate DEP conditions reduces the proportion of metallic to semiconducting SWNTs tubes compared to that in the starting material. This sorting of tube types is confirmed by Raman spectroscopy. Likewise, current-voltage measurements on the as-received tubes are more Ohmic than on the material deposited by DEP. Dielectrophoresis thus offers a potentially valuable method for the separation of the two tube types, which is very important for the large-scale fabrication of nanotube-based electronics and other devices. Functionalization of the nanotubes with differently charged chemical groups permits separation of the tubes by both dielectrophoresis and electrophoresis. Results will be presented for nanotubes functionalized by oxidation, fluorination and polymer wrapping.

#### 11:00 AM N16.8

**Tailoring the Optical Excitation Energies of Single-walled Carbon Nanotubes.** A. Cao<sup>1</sup>, A. Filin<sup>2</sup>, S. Talapatra<sup>1</sup>, Y. Y. Choi<sup>1</sup>, R. Vajtai<sup>1</sup>, P. Persans<sup>2</sup> and P. M. Ajayan<sup>1</sup>; <sup>1</sup>Materials Science & Engineering, Rensselaer Polytechnic Institute, TROY, New York; <sup>2</sup>Physics, Rensselaer Polytechnic Institute, TROY, New York.

Single-walled carbon nanotubes (SWNTs) are fascinating one-dimensional electronic structures, with their band gaps uniquely determined by the tube diameter and helicity of carbon hexagons. For semiconducting SWNTs, the band gap is inversely proportional to the tube diameter (0.4 to 2 nm). Theoretically, SWNTs should have a lowest optical absorption and luminescence peak ranging from hundreds of nm up to 2000 nm. SWNTs with absorption or emission wavelengths of 1300 and 1550 nm are of particular interest in optical communication applications. Recently, there has been much interest in studying the optical absorption and photoluminescence of SWNTs and their possible applications in electronic-optical devices. Synthesis of SWNTs by arc-discharge using a metal mixture of nickel and yttrium as the catalyst, is a well-known method for large-scale production of SWNT strands. However, the diameters of as-produced SWNTs by this method show a wide distribution, ranging from 1.1 to 1.7 nm, resulting in a broad absorption peak centered at 0.68 eV (1820 nm). In order to obtain a strong absorption at 1550 nm for SWNTs, the tube diameter must be decreased (e.g. a 1.1 nm SWNT has the energy gap of 0.8 eV, corresponding to the wavelength of 1550 nm). Here we show that by changing the parameters of arc-discharge (including Ni/Y content, helium pressure), SWNTs with a smaller average diameter and a narrower distribution can be produced. The SWNT diameter distribution was determined by Raman and transmission electron microscopy (TEM). We have thus been able to tune the optical absorption of arc-SWNTs from 1820 down to 1667 nm. Furthermore, by heating the samples in air at 400 C for 0.5 to 2 hours, we can selectively burn SWNTs with larger diameters. SWNT samples after burning shows an absorption centered at 1600 nm, very close to the standard wavelength (1550 nm) of optical communication. Photoluminescence of the SWNT samples is under investigation.

#### 11:15 AM N16.9

**Probing the Long Range Distance Dependence on Noble Metal Nanoparticles.** Amanda J Haes, Shengli Zou, George C. Schatz and Richard P. Van Duyne; Chemistry, Northwestern University, Evanston, Illinois.

The localized surface plasmon resonance (LSPR) of noble metal nanoparticles has recently been the subject of extensive studies. Previously, it has been demonstrated that Ag nanotriangles that have been synthesized using nanosphere lithography (NSL) behave as extremely sensitive and selective chemical and biological sensors. The present work reveals information regarding the long range distance dependence of the LSPR of silver and gold nanoparticles. Multilayer adsorbates based on the interaction of 11-mercaptoundecanoic acid and copper ions were assembled onto surface confined nanoparticles. Measurement of the LSPR extinction peak shift versus number of layers and adsorbate thickness is non-linear and has a sensing range that is dependent on the composition, shape, in-plane width, and out-of-plane height of the nanoparticles. Theoretical modeling confirms and offers a mathematical interpretation of these results. These experiments indicate that the LSPR sensing capabilities of noble metal nanoparticles can be tuned to match the size of biological and chemical analytes by adjusting the aforementioned properties. The optimization of the LSPR nanosensor for a specific analyte will improve an already sensitive nanoparticle-based sensor.

#### 11:30 AM N16.10

**Field Emission Study of Self-Assembled, Density Varying Multi-Walled Carbon Nanotubes.** Harish M. Manohara, Michael J Bronikowski, Peter H Siegel and Brian D Hunt; Jet Propulsion Laboratory, Pasadena, California.

Field emission tests of multi-walled carbon nanotube (CNT) samples with a distribution density gradient were conducted. The goal of this work is to identify an optimum catalyst thickness to achieve a growth density that gives the most efficient field emission for high-current density applications without resorting to patterning methods. The nanotubes were grown on isolated 100-nm-wide islands of catalytic metals that were assembled on substrates using block-copolymer self-assembly techniques. The "arrays" of metal islands were created by sputter-depositing a 5 to 10-nm thick metal film onto a liftoff mask consisting of a 25-nm thick layer of polystyrene, which had stochastically distributed 100-nm-diameter holes to the substrate with an average separation of about 1  $\mu\text{m}$ . The catalysts used were iron and nickel on SiO<sub>2</sub>/Si substrates. A density gradient in the sputtered metal thickness was created such that the thickness of the metal in the metal islands gradually ranged from a maximum of 5 - 10 nm, down to zero within a "transition region" of  $\sim 1$  to 2 mm in length.

The CNTs grew only from the metal islands with the length and the cluster thickness decreasing as the metal thickness decreased. In field emission tests a preferential emission was observed from the transition region in SiO<sub>2</sub>/Si substrates and the emission from the iron grown CNTs was significantly higher than that from the nickel grown. Aside from these, the emission was found to be significantly higher in the SiO<sub>2</sub>/Si substrates than that from plain Si substrates for the same catalysts. The iron on SiO<sub>2</sub>/Si sample showed an emission threshold at  $\sim 1.5$  V/ $\mu\text{m}$  and a current of 200  $\mu\text{A}$  at  $\sim 4.5$  V/ $\mu\text{m}$ . The preferential emission from the transition region points to an optimal tube density, which can be obtained from catalyst metal thickness < 5- 10 nm, tending to  $\sim 2$  nm.

#### SESSION N17: In-Room Poster Session VI - Carbon Nanotubes

Chairs: Todd D. Krauss and Pehr Pehrsson  
Friday Morning, December 5, 2003  
11:00 AM  
Room 302 (Hynes)

#### N17.1

**Micelle-Encapsulated Carbon Nanotubes: Towards a General Method for Dispersing Nanomaterials.** Youngjong Kang and T. Andrew Taton; Chemistry, University of Minnesota, Minneapolis, Minnesota.

Many applications of nanostructures require that they be dispersed in solvents or composited in material matrices. However, the poor surface chemistry and solubility of some nanomaterials makes forming suspensions and nanocomposites difficult. We have created a general solution toward dispersing nanomaterials in various media by encapsulating nanomaterials within crosslinked polymer micelles. The crosslinked shell serves as a topological barrier to the thermodynamically driven aggregation of nanomaterials. In particular, we have applied this approach to dispersing single-walled carbon nanotubes (SWNTs) in water, organic solvents, and polymer matrices with high stability. In contrast to ordinary SWNTs, encapsulated SWNTs do not form bundles or mats even at high concentrations (> 0.1 wt%). We anticipate that micelle encapsulation will improve the compositing of SWNTs in a wide variety of polymer materials for structural, electronic and thermal applications, and could likewise be applied to a variety of other nanostructures.

#### N17.2

**In Situ studies of Alkali Metal doping of Carbon Nanotube Bundles in Real Time.** Gugang Chen<sup>1</sup>, Clascidia A Furtado<sup>1</sup> and Peter C Eklund<sup>1,2</sup>; <sup>1</sup>Physics, Pennsylvania State University, University Park, Pennsylvania; <sup>2</sup>Materials Science, Pennsylvania State University, University Park, Pennsylvania.

We present new results regarding the details of the time evolution of alkali metal (M=K and Cs) doping in purified bundles of single-walled carbon nanotubes (SWNTs). The doping process was followed using resonant Raman scattering spectroscopy. We used very slow vapor phase doping, and collected over one hundred Raman spectra during each doping experiment. New, doping-induced asymmetric Raman bands in the intermediate frequency range are also observed. We find that, in general, the alkali doping process can be clearly divided into four distinct stages (or periods) leading to the saturation doped compound. We report for the first time that a long "induction period" exists before any signs of doping appear in the Raman spectra. Some interesting differences in the Cs and K doping are observed: For Cs, the induction period is very much longer than K, and the R-band vanishes before the T-band is observed to shift or broaden. For K, both the R- and T-bands evolve simultaneously. In both cases (K and Cs), we find that the vapor phase doping first induces an anomalous upshift of  $\sim 5$  cm<sup>-1</sup> in the Lorentzian T-band components (as does acceptor doping), followed by a subsequent downshift of 34 cm<sup>-1</sup> to a strongly asymmetrically broadened Fano lineshape in the saturation compound. Interestingly, we did not observe the coexistence of various phases, as reported before by other groups. In our slow-doping experiments, the M-SWNT system appears homogeneous at all stages of intercalation. Our results will be interpreted via consideration of intra- and inter-tube interactions and compared to recent electromechanical theory of SWNTs.

#### N17.3

**High-Resolution Near-field Raman Microscopy of Carbon Nanotubes.** Achim Hartschuh<sup>1</sup> and Lukas Novotny<sup>2</sup>; <sup>1</sup>Physikalische Chemie I, Universitaet Siegen, Siegen, Germany; <sup>2</sup>The Institute of Optics, University of Rochester, Rochester, New York.

Combined with near-field optical techniques, Raman spectroscopy is a promising tool for identifying and analyzing the molecular composition of complex materials, providing chemical maps with

nanoscale resolution. We demonstrate imaging of specific vibrational modes in individual single-walled carbon nanotubes with a spatial resolution of less than 15 nm combined with a signal enhancement of more than 2000. The high-resolution capability of the presented method is used to study local variations in the Raman spectra caused by structural defects which would be hidden in farfield measurements.

#### **N17.4**

##### **Scanned Probe Electrical Characterization of Carbon**

**Nanotube and Metal Contacts.** Sujit Kumar Biswas<sup>1</sup>, Robert Vajtai<sup>2</sup>, Leo J Schowalter<sup>1</sup> and Pulickel M Ajayan<sup>2</sup>; <sup>1</sup>Dept. of Physics, Applied Physics and Astronomy, Rensselaer Polytechnic Institute, Troy, New York; <sup>2</sup>Dept. of Material Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York.

Carbon nanotubes have shown promise as self-assembled, electrical interconnects for extremely high density electronics. Nanotubes are contacted to metal electrodes as an interface to the macroscopic world, and so these junctions need to be studied. We have studied single and multi-walled nanotubes on silicon oxide, connected to different metal electrodes, including chromium, aluminium and platinum. We use conductive tip scanning nano-probe techniques, which allow us to study the junctions individually. Scanned surface potential measurements revealed a presence of a 0.3V potential difference between single walled nanotubes and chromium. Current measurement was done using conductive tip atomic force microscopy at a point on the nanotube lying on the oxide. The nanotube was found to be electrically contacted to the metal electrode, and the measured current voltage characteristics were found to be non-linear. This suggests that the contact properties directly influence electrical conduction in such nanotube circuits.

#### **N17.5**

##### **The Role of the Casimir Effect to Change Some Properties of a Single-Wall Carbon Nanotube in Microelectromechanical System.**

Pier Giuseppe Gabrielli<sup>1</sup> and Simone Gabrielli<sup>2</sup>; <sup>1</sup>mat, enea, rome, Italy; <sup>2</sup>dipartimento di fisica, univ. di Roma La Sapienza, rome, Italy.

The sizes of and the separation between the components in some Micro-electromechanical System (MEMS) are in a domain where some quantum mechanical effects will need to be taken into account. When separations between objects are small enough, certain quantum effects become manifestly significant: the Casimir effect, for example, is the force between two solid objects that arises from quantum fluctuations in the ground state energy of the electromagnetic field. Fixing the ends of a slightly stretched carbon nanotube on a microdevice in proximity of and parallel to a rigid flat plate, due to Casimir forces, nanotube deflects, deflection strongly depending on the separation of nanotube and surface and on the geometry. Since single-wall carbon nanotubes (SWNT) are predicted to be metallic or semiconducting depending on their diameter and the helicity, Casimir effect could change diameter and/or the helicity and would be possible to modulate their electronic properties. The strength of Casimir forces and the changes of some properties of SWNT in MEMS due to Casimir effect is discussed.

#### **N17.6**

##### **Pinch-off in a C<sub>60</sub> filled peapod Schottky junction.**

Gyu-Tae Kim<sup>1</sup>, Gang Gu<sup>3</sup>, Po-Wen Chiu<sup>2</sup> and Siegmund Roth<sup>2</sup>;

<sup>1</sup>Electrical Engineering, Korea University, Seoul, South Korea;

<sup>2</sup>Max-Planck Institut fuer Festkoerperforschung, Stuttgart, Germany;

<sup>3</sup>Molecular Nanosystems Inc., Palo Alto, California.

Current-voltage characteristics of C<sub>60</sub> filled peapod heterojunction were recorded, showing a rectification behavior. At the forward bias, a monotonous increase of the current were observed with a saturation tendency, followed by an abrupt increase of the current. The turn-on voltage of the abrupt increase of the current at the forward bias was smaller than that of the reverse bias, indicating the enhanced tunneling behavior at the reverse bias. A saturational behavior at the low forward bias could be understood by considering the pinch-off phenomena as in a field effect transistor. Temperature dependence of the ideality factor of C<sub>60</sub> peapod heterojunction increased as the temperature decreased, indicating the enhanced contribution of the tunneling and the serial resistance of the tube. In this presentation, the origin of the saturation behavior in current-voltage characteristics and the large ideality factor as a diode will be discussed.

#### **N17.7**

##### **Quantum Dots From Carbon Nanotube Junctions.**

Fabrizio Cleri<sup>1</sup>, Pawel Koblinski<sup>2</sup>, Inkyoung Jang<sup>3</sup> and Susan B.

Sinnott<sup>3</sup>; <sup>1</sup>Unita' Materiali e Nuove Tecnologie, ENEA, Roma, Italy;

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Polytechnic Institute, Troy, New York; <sup>3</sup>Department of Materials

Science and Engineering, University of Florida, Gainesville, Florida.

We investigate the electronic properties of covalently-bonded, crossed carbon nanotubes with increasing degree of disorder in the junction region. A tight-binding hamiltonian is coupled to classical molecular dynamics simulations with the Tersoff-Brenner potential, to derive the atomic and electronic structure of the junctions. At one extreme, ideal junctions between coplanar nanotubes with a minimal number of topological defects show a good ohmic behavior. Upon increasing disorder, ohmic conduction is suppressed in favor of hopping conductivity. At the opposite extreme, strongly disordered junctions as could be obtained after electron-beam irradiation of overlaid nanotubes, display weak localization and energy quantization, indicating the formation of a quantum dot contacted to nanowires by tunnel barriers. We report recent results on QD arrays obtained from either semiconducting or metallic carbon nanotubes.