

SYMPOSIUM P

Quantum Confined Semiconductor Nanostructures—Fabrication, Physical Properties, and Applications

November 27 - December 2, 2005

Chairs

Philippe Guyot-Sionnest

James Franck Institute
University of Chicago
5640 Ellis Ave.
Chicago, IL 60637
773-702-7461

Margaret A. Hines

Evident Technologies, Inc.
Ste. 200
216 River St.
Troy, NY 12180
518-276-3444

Victor I. Klimov

Los Alamos National Laboratory
MS J585
Los Alamos, NM 87545
505-665-8284

Hedi Mattoussi

Optical Sciences Division
Naval Research Laboratory
4555 Overlook Ave. SW
Washington, DC 20375
202-767-9473

Symposium Support

Defense Advanced Research Projects Agency
†Evident Technologies, Inc.
Office of Naval Research

†2005 Fall Exhibitor

* Invited paper

TUTORIAL

FTP: Quantum-Confined Semiconductor Nanostructures – Fabrication, Characterization, and Spectroscopic Properties
Sunday, November 27, 2005
1:00 PM - 4:30 PM
Room 210 (Hynes)

The tutorial will provide an overview of quantum-confined semiconductor nanostructures, including fabrication, characterization, and spectroscopic properties, along with a highlight of the most relevant and promising applications.

Nanoscale structures made of semiconductors, such as colloidal nanocrystals/nanorods and epitaxial quantum dots/quantum wires, show unique properties that arise both from effects of quantum confinement and strong influences of surfaces. Recent progress in the design, preparation, and characterization of semiconductor quantum dots and nanorods has significantly advanced our fundamental knowledge of electronic structures, carrier dynamics, and multi-exciton interactions in strongly confined nanoscale materials. Our understanding of interactions between individual nanoscale building blocks in complex assemblies has also significantly advanced over the past several years. This has led several groups to carry out demonstrations of efficient charge and exciton transport in engineered nanocrystal assemblies, control of charge injection into nanoscale particles, and energy and electron transfer phenomena in hybrid nanostructures based on luminescent QDs. It has also led to designing applications involving these materials in areas that might otherwise seem unrelated, including lasing, photovoltaic and light-emitting devices as well as fluorescence-based biological applications.

The tutorial will also provide an overview of the various routes for successful preparation of quantum dots, quantum rods, and the characterization of such materials. There will be an emphasis placed on their structure, as well as optical, spectroscopic, and electronic properties. The tutorial will look closely at the most relevant applications in areas such as light-emitting and photovoltaic devices and other energy-transfer-based devices.

Instructors:
Moungi G. Bawendi
Massachusetts Institute of Technology

Victor I. Klimov
Los Alamos National Laboratory

Xiaogang Peng
University of Arkansas

SESSION P1: Theoretical Concepts of Semiconductor Nanocrystals

Chairs: Steve Erwin and Alex Zunger
Monday Morning, November 28, 2005
Room 210 (Hynes)

8:15 AM INTRODUCTORY REMARKS

8:30 AM *P1.1

Doping Semiconductor Nanocrystals: Impurity Binding, Surface Morphology, and Shape Control. Steven Erwin¹, Lijun Zu², Michael Haftel¹, Alexander Efros¹, Thomas Kennedy¹ and David Norris²; ¹Naval Research Laboratory, Washington, District of Columbia; ²Department of Chemical Engineering & Materials Science, University of Minnesota, Minneapolis, Minnesota.

Doping – the intentional introduction of impurities into a material – is fundamental to controlling the properties of bulk semiconductors. The prospect of new technologies has motivated similar efforts to dope semiconductor nanocrystals since their discovery two decades ago. Despite some successes [1-5], many of these efforts have failed, for reasons that remain mysterious. For example, individual Mn atoms can be incorporated into nanocrystals of CdS and ZnSe [3-5], but not into CdSe [6] – despite comparable solubility limits near 50 percent in the bulk crystals. Such failures have often been attributed to “self-purification,” an allegedly intrinsic mechanism in nanocrystals whereby impurities are expelled to the nearby surface. Here we propose a very different view: that doping is controlled instead by the initial adsorption of impurities on the nanocrystal surface during growth [7]. We show that impurity adsorption – and therefore doping efficiency – is determined by three main factors: the surface morphology of the nanocrystal, its overall shape, and the tendency of surfactants in the growth solution to bind the impurity. Calculated Mn adsorption energies and equilibrium shapes for several cubic and hexagonal nanocrystals lead to specific doping predictions. These are

confirmed by measuring how the Mn concentration in ZnSe varies with nanocrystal size and shape. Our results show that earlier difficulties with doping are not intrinsic, and suggest that a variety of doped nanocrystals – for applications from solar cells to spintronics – can be anticipated. [1] Y. Wang, N. Herron, K. Moller and T. Bein, *Solid State Comm.* 77, 33 (1991). [2] R.N. Bhargava, D. Gallagher, X. Hong and A. Nurmikko, *Phys. Rev. Lett.* 72, 416 (1994). [3] L. Levy, J.F. Hochepeid and M.P. Pileni, *J. Phys. Chem.* 100, 18322 (1996). [4] D.J. Norris, N. Yao, F.T. Charnock and T.A. Kennedy, *Nano Lett.* 1, 3 (2001). [5] J.F. Suyver et al., *Phys. Chem. Chem. Phys.* 2, 5445 (2000). [6] F.V. Mikulec et al., *J. Am. Chem. Soc.* 122, 2532 (2000). [7] S.C. Erwin, L. Zu, M.I. Haftel, A.L. Efros, T.A. Kennedy, and D.J. Norris, *Nature* (in press).

9:00 AM P1.2

Moments-method tight-binding analysis of InAs quantum dots with realistic disorder. Harley T. Johnson¹, Jun-Qiang Lu¹, V. Dasika² and R. S. Goldman²; ¹Mechanical & Industrial Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois; ²Materials Science & Engineering, University of Michigan, Ann Arbor, Michigan.

A novel order(N) tight-binding method is used to study electronic properties of realistic InAs quantum dots embedded in GaAs. The approach is based on the method of moments, which is used to construct the local density of states approximately from a statistical sampling of the local atomistic structure around a particular point in the material. Moments of the density of states are built from products of tight-binding hopping integrals connecting neighboring atoms and orbitals; the parameterization used here is an sp3d5s* model. A combined maximum entropy method and kernel polynomial method is used to infer the density of states from moments obtained in this way. The method is ideally suited for comparison to high resolution local electronic structure measurements done using cross-sectional scanning tunneling microscopy (STM). Calculations show the effects of free surfaces and strain relaxation on electronic structure. Quantum confinement in InAs quantum dots is shown directly by probing local densities of states at various atoms in and around the quantum dots. Using this computational probe method, the relationship between bandgap and quantum dot size is reduced to a simple equation. Finally, the method is directly applied to quantum dot configurations with atomic positions obtained experimentally using STM. The effects of disorder and atomistic features of the quantum dot matrix interface are studied directly using the moments-based tight-binding method.

9:15 AM P1.3

Surface Trap States in Bare and Core/Shell Nanocrystals. Garnett W. Bryant and Jose Diaz Garcia; Atomic Physics Division, National Institute of Standards and Technology, Gaithersburg, Maryland.

Surface effects significantly impact the functionality of semiconductor nanocrystals. Trap states at surfaces affect the blinking of nanocrystals [R. Verberk, A. M. van Oijen, and M. Orrit, *Phys. Rev. B* 66, 233202 (2002)] and greatly influence the utility of nanocrystals as light emitters for nano and biosensing. Passivation with ligands or high band-gap semiconductor shells can control these trap densities, enhance quantum yield and increase photostability. A full theoretical understanding of these surface traps requires atomistic models capable of describing surface faceting and relaxation, few-monolayer shells, unpassivated dangling bonds, coupling between dangling bonds, and clusters of these bonds. We present an atomistic tight-binding theory of the trap states in bare and core/shell CdS and CdSe nanocrystals. We investigate three cases due to incomplete surface passivation: trap states due to isolated unpassivated dangling bonds; trap states due to closely spaced, coupled unpassivated dangling-bond pairs; and trap states due to clusters of unpassivated dangling bonds. We study the site-dependence of isolated traps to identify the character of the trap states and to determine how strongly they couple to the internally confined states. We consider coupled dangling bond pairs and clusters of dangling bonds to determine how the density of trap states is modified by banding among the dangling bond states. Results are presented as a function of trap separation to determine the effective range for coupling between trap states. Results are presented for both bare and core/shell nanocrystals to determine how effectively the trap states can be isolated from the confined internal states by the shell and to better understand how the trap states can contribute to blinking dynamics.

9:30 AM P1.4

Semiconductor Nanorod Optical Properties. Alexander L. Efros, Naval Research Laboratory, Washington, D.C., District of Columbia.

There is growing interest in nanometer-scale crystalline semiconductor structures of various shapes, such as nanocrystals (NCs), nanorods (NRs), and nanowires, created using the “from-the-bottom-up” technological approach. The optical properties of NRs, however, differ

significantly from those of NCs. Compared to NCs, NRs show higher photoluminescence (PL) quantum efficiency, strongly linearly polarized PL, an increase in the global Stokes shift, and significantly faster carrier relaxation. The size and shape dependence of optical and tunneling gaps measured in CdSe NRs shows an unexpectedly large difference that cannot be explained by the electron-hole Coulomb correction to the optical gap used for NCs. We have shown theoretically that this difference in optical properties is caused by one-dimensional excitons formed in elongated nanorods. This theory, which takes into account the anisotropy of spatial and dielectric confinement, describes size dependence of interband optical transitions, exciton binding energies, and the fine structure of the ground exciton state. Our results agree well with the size dependence of the energy gap and the photoluminescence polarization degree measured in CdSe nanorods.

9:45 AM P1.5
CdSe Quantum Dot and Rod Fine Structure at Room Temperature: Exchange Interactions and Exciton Spin Flips.
Gregory Scholes, Jeongho Kim, Vanessa Huxter, Cathy Wong, Karolina Fritz and Nair Sreekumari; Chemistry, University of Toronto, Toronto, Ontario, Canada.

Optical pumping of quantum dots (QDs) transfers photon angular momentum to excitons through its projection onto the wavevector direction in the crystal lattice. Thus, in oriented QDs, circularly polarized light can be used to select exciton total angular momentum. That means that exciton spin states can be established and followed spectroscopically in semiconductor quantum dots. This turns out to be interesting because the dynamics following excitation of the fine structure of a QD exciton state have not been previously observed because of inhomogeneous line broadening and degeneracy of levels in the absence of an applied magnetic field. We will describe how the fine structure of exciton states can be probed in isotropic QD ensembles using nonlinear optical spectroscopies. Thus we show that a variant on the transient grating method can be used to measure directly the dynamics of interconversion between the degenerate exciton states of QDs. The signal is insensitive to inhomogeneous line broadening because its decay is determined by a sign change related to rotational averaging, rather than a frequency shift or bleach recovery. We have found the dynamics of exciton spin flips to be strongly dependent on quantum size effects; with spin flip times varying from <100 fs to greater than 2 ps. These experimental results, for CdSe dots and rods, will be reported together with a discussion of the mechanism that promotes the spin flips. We show that the exchange interaction provides the relevant coupling matrix element, and therefore show how the exchange interaction varies with shape.

10:15 AM *P1.6
New Theoretical Insight on Semiconductor Quantum Dots.
Alex Zunger, National Renewable Energy Laboratory, Golden, Colorado.

An atomistic theory of semiconductor quantum dot is made possible by combining a pseudopotential description of the single-particle physics (inter-band coupling; inter-valley coupling; spin-orbit coupling; strain-induced effects) with a configuration-interaction description of many-body physics (inter electronic Coulomb, exchange, and correlation). Recent insights include: (a) The Story of PbSe: traditional K dot P approaches fail to predict the structure of the absorption spectra. An atomistic theory reveals an unexpected explanation of the origin of these transitions. (b) Dot Molecules: We show how the exciton in a single dot is modified when a second dot is brought in to form a dot molecule. (c) Effects of electric field: we show how the Stark effect changes the spectra, and how the degree of exciton entanglement is surprisingly altered by electric fields. (d) Violation of Hund's rule and the Aufbau principle: calculation of the energy required to add to a dot few electrons or few holes shows how the rules of atomic physics are broken in quantum dots. (e) Systems of dots plus wires: future nanoelectronics could be based on 3D connecting dots plus wires. We show how many electron effects could control the localization of the wavefunction on certain sub systems, and how this could impede transport. In collaboration with: J. An, G. Bester, L. He, A. Franceschetti and G. Narvaez.

10:45 AM P1.7
Electronic Coupling in Two-Dimensional Arrays of PbSe Nanocrystals. Peter Liljeroth¹, Karin Overgaard¹, Bruno Grandidier², Stephen G. Hickey³ and Daniel Vanmaekelbergh¹;
¹Condensed Matter and Interfaces, Debye Institute, University of Utrecht, Utrecht, Netherlands; ²Departement ISEN, Institut d'Electronique, de Microelectronique et de Nanotechnologie, Lille, France; ³Institute of Physical Chemistry, University of Hamburg, Hamburg, Germany.

Two-dimensional arrays of semiconductor nanocrystals can be fabricated by simple drop-casting; if the quantum dots are sufficiently

monodisperse, arrays with local translational order extending over hundreds of nanometres can be obtained.[1] While electronic coupling in metallic nanocrystal superlattices has been demonstrated[2], it remains elusive in arrays of semiconductor quantum dots[3]. The low density of states, with discrete energy levels and disorder effects could be important for this. For instance, the overlap between neighbouring quantum dot orbitals depends also on the rotational ordering of the crystals, i.e. relative orientation of the facets. It is thus possible that, even in nanocrystal superlattices possessing long-range translational order, strong electronic coupling between the particles can only prevail within limited regions of the array. Scanning tunnelling microscopy and spectroscopy can be used to simultaneously probe the topography and the local density of states.[4] Furthermore, tunnelling spectroscopy is carried out in the absence of selection rules, which can hamper the interpretation of optical absorbance spectra. We have carried out measurements on two-dimensional arrays of PbSe nanocrystals deposited on Au and HOPG substrates with UHV STM at low temperatures. The tunnelling spectroscopy experiments show evidence of strong electronic coupling between the nanocrystals on local scale. This coupling modifies the density of states completely; the discrete levels of individual nanocrystals hybridize and the resulting density of states exhibits the step-like structure of a two-dimensional semiconductor. Finally, we observe that the conduction levels couple more strongly than the valence levels. This can be rationalized in terms of the tunnelling barrier height between the nanocrystals: higher lying conduction levels experience a lower effective barrier height. Quantum dot superlattices, with a controlled quantum mechanical coupling between the nanocrystal building blocks form new materials of interest for novel types of LEDs, lasers and solar cells.[5] References [1] Murray, C. B.; Kagan, C. R.; Bawendi, M. G. *Annu. Rev. Mater. Sci.* 2000, 30, 545; Redl, F. X.; Cho, K. S.; Murray, C. B.; O'Brien, S. *Nature* 2003, 423, 968. [2] Markovich, G.; Collier, C. P.; Henrichs, S. E.; Remacle, F.; Levine, R. D.; Heath, J. R. *Acc. Chem. Res.* 1999, 32, 415; Medeiros-Ribeiro, G.; Ohlberg, D. A. A.; Williams, R. S.; Heath, J. R. *Phys. Rev. B* 1999, 59, 1633. [3] Yu, D.; Wang, C.; Wehrenberg, B. L.; Guyot-Sionnest, P. *Phys. Rev. Lett.* 2004, 92, 216802/1; [4] Banin, U.; Millo, O. *Annu. Rev. Phys. Chem.* 2003, 54, 465; Liljeroth, P.; Zeijlmans van Emmichoven, P. A.; Hickey, S. G.; Weller, H.; Grandidier, B.; Allan, G.; Vanmaekelbergh, D. *Phys. Rev. Lett.* 2005, submitted. [5] Wang, C.; Wehrenberg, B. L.; Woo, C. Y.; Guyot-Sionnest, P. *J. Phys. Chem. B* 2004, 108, 9027; Schaller, R. D.; Klimov, V. I. *Phys. Rev. Lett.* 2004, 92, 186601/1.

11:00 AM P1.8
Random telegraph signal and hopping transport in InAs/InP semiconductor nanostructures ensembles. Klaus Orian Vicaro¹, Humberto Rodriguez Gutierrez^{1,3}, Jose Roberto Ribeiro Bortoleto^{1,4}, Luis Nieto Gonzalez¹, Antonio Augusto de Godoy von Zuben¹, Antonio Carlos Seabra², Peter Alexander Schulz¹ and Monica Alonso Cotta¹;
¹DFA-IFGW, UNICAMP, Campinas, Sao Paulo, Brazil; ²PSI-EPUSP, Univ. Sao Paulo, Sao Paulo, Sao Paulo, Brazil; ³Dept. of Physics, Pennsylvania State University, Pennsylvania, Pennsylvania; ⁴LaPTec, GPM-UNESP, Sorocaba, Sao Paulo, Brazil.

Conductive atomic force microscopy (C-AFM) has been widely used to investigate vertical electrical transport across various systems such as semiconductor nanostructures, insulating films and biological samples. This technique provides topographical information simultaneously with electrical current image. On the other hand, devices processed with electron-beam lithograph allow access to the in-plane conductance at low temperatures of small assemblies of semiconductor nanostructures. We report here the study of electrical and electronic properties of small ensembles of semiconductor nanostructures with these two techniques. In this work, we used C-AFM to obtain spatially resolved current images and localized I-V curves under InAs/InP wires, dots and wetting layer in a controlled atmosphere. The InAs nanostructures show different conductances and threshold voltages for current onset. Wires and wetting layer have larger threshold voltages and small conductances, while larger conductance values and smaller threshold voltages were observed for larger dots. These results were thus used to estimate the energy differences between electron states in the different nanostructures. In the processed devices we observed fluctuations on I-V curves at low temperatures for mesa orientations both parallel and perpendicular to the wires long axis direction. Three main behaviors can be identified in the current vs $T^{-1/2}$ plot for various constant applied bias: 1) a semiconductor-like behavior for low temperatures and applied bias; 2) a metallic-like behavior in the same temperature range but for higher applied bias; 3) for temperatures above 60K, an activated behavior was observed with dependence on $T^{-1/2}$ that is usually attributed to constant range hopping transport and suggests an important contribution of carriers trapped in localized states of the nanostructures. The signature of random telegraph signals (RTS) in the current behavior with time at constant applied bias was observed for a suitable range of temperatures and applied bias for a dot ensemble. The observed levels for electrical current in RTS data can

be associated to electrons transferred from the wetting layer to the dots and/or wires and vice-versa. In general, the up and down times for RTS processes are temperature and applied bias dependent: for a dot ensemble both times increase with applied bias, while only the down time increases with temperature. Statistical analysis of the experimental data and comparison with a simulated pure RTS process indicate that a single RTS process is involved in the dot ensemble in the device for a given set of temperature and applied bias values. Fitting the power spectra density of the current vs time curve provides the sum of the two times, while counting the transitions between the plateaus allows to estimate these values separately. The dependence of the up and down times can be associated to intrinsic characteristics of the InAs nanostructures in the ensemble.

11:15 AM **P1.9**

Impurity states in silicon nanocrystals: a theoretical study. Giovanni Cantele¹, Federico Iori³, Elena Degoli², Fabio Trani¹, Eleonora Luppi³, Rita Magri³, Domenico Ninno¹ and Stefano Ossicini²; ¹Dipartimento di Scienze Fisiche, Coherentia-INFM and Università di Napoli "Federico II", Napoli, Italy; ²Dipartimento di Scienze e Metodi dell'Ingegneria, S3-INFM and Università di Modena e Reggio Emilia, Reggio Emilia, Italy; ³Dipartimento di Fisica, S3-INFM and Università di Modena e Reggio Emilia, Modena, Italy.

It is known that doping semiconductor nanocrystals results in a much less efficient increasing of the carriers density than for the bulk crystal. In fact, impurity states can be far apart from the band edges, due to confinement effects, so leading to ionisation thresholds much higher than for the bulk system [1]. Nevertheless, there are experimental evidences that doping control at nanoscale can add optical properties which cannot be achieved in pure systems. This is the case of Silicon nanocrystals (Si-nc), for which it has been shown that the photoluminescence peak can be tuned also below the bulk Si band gap by properly controlling the impurities, for example by B and P co-doping [2]. In this work we report on an ab-initio study of impurity states in Si-nc. Atomistic theoretical studies on doped semiconductor nanocrystals are relatively rare [3]. Here we consider B and P substitutional impurities for a number of Si-nc with radius ranging from 0.5 nm (Si29H36) to 1.1 nm (Si293H172). Formation energies are calculated within plane-wave pseudopotential density functional theory in the GGA approximation. Full relaxation with respect to the atomic positions is taken into account. The structural properties, that is, reconstruction around the impurity, bond lengths and angles have been determined as a function of the cluster dimension. It is shown that the starting bulk silicon Td symmetry is broken, giving rise to a new atomic arrangement with a C3v symmetry. For both B and P single-doped Si-nc [4] the formation energy does increase on decreasing the dimension, showing that the substitutional doping gets progressively more difficult for the smaller nanocrystals. Moreover subsurface impurity positions result to be the most stable ones. The codoping reduces the formation energy [5] favouring this process with respect to the single doping. Such an effect can be attributed to charge compensation between the donor and the acceptor atoms. Also, small structural deformations localised only around the impurity sites are observed (an almost Td configuration is preserved (in this case), and the band gap is reduced with respect to both the undoped and single-doped nanocrystals. [1] M. Lannoo, C. Delerue and G. Allan, Phys. Rev. Lett. 74, 3415 (1995) [2] M. Fujii, Y. Yamaguchi et al., Appl. Phys. Lett. 85, 1158 (2004). [3] D. V. Melnikov and J.R. Chelikowsky, Phys. Rev. Lett. 92, 046802 (2004) [4] G. Cantele, Elena Degoli, Eleonora Luppi, Rita Magri, D. Ninno, G. Iadonisi, and Stefano Ossicini, Phys. Rev. B, submitted. [5] S. Ossicini, F. Iori, E. Degoli, E. Luppi, R. Magri, G. Cantele, F. Trani, and D. Ninno, Appl. Phys. Lett., submitted.

11:30 AM ***P1.10**

Nanoptics with II-VI nanocrystals. Ulrike Woggon, University Dortmund, Dortmund, Germany.

Colloidal CdSe nanorods (NR) and nanodots (QD) are nanoemitters that received much attention in recent years. NRs, for example, emit highly polarized light and can be used as active optical material in laser devices and photonic structures. For these nanocrystals, the exact knowledge of wave function symmetries, energies and optical transition dipole moments is a crucial problem for future applications in quantum optics, laser devices or as polarization sensitive marker or detector. In this work we present low-temperature, polarization-sensitive photoluminescence spectroscopy of single CdSe(ZnS) nanocrystals. We explore a fine structure in the single nanorod emission spectra which we assign to exchange splitting of a 1D-exciton confined in a cylindrical CdSe nanorod. Using an effective-mass model, the observed degree of polarization as well as the temperature-dependent photoluminescence dynamics can be explained based on the revealed ground state exciton symmetry. We find a radius-dependent change in the symmetry of the 1D-exciton ground state which transforms from a dark state for radii R above a critical nanorod radius of $R_{crit} \sim 3.7$ nm into optically allowed states

for radii $R < R_{crit}$ [1]. The engineering of the NC shape increases the dipole oscillator strength for a CdSe NR exciton which opened the way for the experimental observation of the strong coupling regime with semiconductor nanocrystals. We demonstrate a strongly coupled cavity QED system with a CdSe nanocrystal coupled to a single photon mode of a polymer microsphere. The strong exciton-photon coupling is manifested by the observation of a cavity mode splitting of 40 micro eV and lifetime measurements of the coupled exciton-photon state. We demonstrate a possible nanorod application and study CdSe-doped microspheres of radii $R \sim 2\lambda$ as building blocks for coupled resonator optical waveguides [2] and present an epitaxial growth technique which allows to integrate colloidal II-VI nanocrystals into monolithic photonic devices [3]. [1] Exciton fine structure in single CdSe nanorods N. LeThomas, E. Herz, O. Schoeps, U. Woggon, M.V. Artemyev Phys. Rev. Lett 94, 016803 (2005). [2] Coupled resonator optical waveguide (CROW) doped with nanocrystals B. Moeller, U. Woggon, M.V. Artemyev Optics Lett., in press [3] Hybrid epitaxial-colloidal semiconductor nanostructures U. Woggon, E. Herz, O. Schoeps, M.V. Artemyev, C. Arens, N. Rousseau, D. Schikora, K. Lischka, D. Litvinov, D. Gerthsen, Nano Letters 5, 483 (2005).

SESSION P2: Optical and Electronic Properties

Chairs: Maxime Dahan and Frank Wise
Monday Afternoon, November 28, 2005
Room 210 (Hynes)

1:30 PM ***P2.1**

Single Quantum Dot Detection: From Photophysics to Live Cell Imaging. Maxime Dahan, Laboratoire Kastler Brossel, Ecole Normale Supérieure, Paris, France.

Semiconductor CdSe quantum dots are inorganic fluorophores with a wide range of applications. Their large absorption cross-section and their photostability have in particular enabled new experiments at the single molecule level, in both a physical and a biological context. I will first present measurements on the effect of a dielectric interface on the emission properties of individual QDs. By placing a single molecule successively close and far from a dielectric interface and simultaneously measuring its photoluminescence decay and its orientation, both its radiative and non-radiative recombination rates can be determined. Using this simple method, we deduced for CdSe nanocrystals, that the fluorescence quantum efficiency, determined at the single molecule level, is 98 % in average, far above the value expected from conventional ensemble experiments. The bi-dimensionnal nature of the transition dipole was also directly evidenced from a single particle measurement. In a second part, I will describe the current status and future challenges in the application of single QDs detection to the study of live cell dynamics. I will in particular discuss how information deduced from single QD spectroscopy can be used to devise new imaging methods.

2:00 PM **P2.2**

Photoinduced Charge Transfer Between CdSe Nanocrystalline Quantum Dots and Polypyridine Complexes of Ru(II). Milan Sykora¹, Melissa Petruska¹, James

Alstrum-Acevedo² and Victor Klimov¹; ¹C-PCS, LANL, Los Alamos, New Mexico; ²Chemistry, University of North Carolina, Chapel Hill, North Carolina.

Ru-polypyridine complexes have been studied extensively because of their potential applicability in various solar energy conversion schemes as both light sensitizers and molecular catalysts. In the development of practical devices, the complexes are often coupled with semiconductor materials, which provide a means for spatial organization and enhancement of functionality. For example, the use of Ru-polypyridine complexes coupled to large surface area nanocrystalline titanium dioxide (TiO₂) has led to the development of a new class of solar cells. In these devices, the Ru-polypyridine complexes function as sensitizers, while the semiconductor serves as both an electron acceptor and a charge transporter. More recently, Meyer and coworkers have shown that materials with more complex photocatalytic functionalities can be constructed by coupling Ru-polypyridine based catalysts to nanocrystalline TiO₂. In these materials, the oxidizing equivalents stored in the complex following the electron injection into the semiconductor are used to carry out oxidation of various organic species, while the electrons injected into TiO₂ are used to generate hydrogen at a counter electrode. Here, we explore a novel approach for enhancing the photocatalytic activity of Ru complexes by coupling them to semiconductor nanocrystals [nanocrystal quantum dots (NQDs)] that serve as both broad-band sensitizers and "charge multipliers". Semiconductor NQDs have properties that are very appealing for photovoltaic and photocatalytic applications. Their absorption cross sections are two to four orders of magnitude greater than those of organic or inorganic dyes, and their absorption spectra can easily be tuned by varying the size of the nanocrystals. Additionally, as we reported recently, NQDs can convert light quanta to charge carriers with quantum efficiencies greater than

100% via the effect of carrier multiplication. The combination of the superior light harvesting properties of NQDs with the high functionality of Ru-polypyridine complexes can produce high-efficiency photovoltaic and photocatalytic materials. We present our studies of interactions of photoexcited CdSe NQDs with Ru-polypyridine complexes that are tethered to NQD surfaces. By changing the dot size and the type of the metal complex, we vary the free energy of the charge transfer reaction. We also modify the linker to control the strength of the coupling between the metal complex and the NQD. We find direct correlation between the dot size and the charge transfer efficiency, as inferred from both steady-state and time-resolved emission studies. Specifically, by using dots of small sizes tethered to Ru-complexes via carboxylate linkers, we detect a nearly complete quenching of NQD emission, which is indicative of high efficiency charge transfer. From time-resolved measurements, we estimate a charge transfer rate constant of $\sim 10^{10}$ - 10^{11} s⁻¹.

2:15 PM P2.3

Time-Resolved and Antibunching Measurements on Single Photons at 1300nm from InAs Quantum Dots. Carl Zinoni¹, B. Allong¹, V. Zwiller³, L. Li¹, C. Monat¹, L. Lunghi², A. Gerardino² and A. Fiore^{1,2}; ¹Institute of Photonics and Quantum Electronics, EPFL, Lausanne, Switzerland; ²Institute of Photonics and Nanotechnology, CNR, Roma, Italy; ³Institute of Quantum Electronics, ETHZ, Zurich, Switzerland.

Efficient generation of single photons at telecom wavelength (1310nm and 1550nm) on request is crucial for quantum key distribution (QKD). The optical properties of single quantum dots (QDs) have the potential for satisfying the requirements of a convenient single photon source: QDs can be grown in conventional semiconductor epitaxial systems and the nature of the 3D confinement of the wavefunction generates atomic-like spectral features. A single QD can be populated by several electron-hole pairs (excitons), each recombining to emit a photon. Due to Coulomb interactions originating from the strong charge confinement the energy levels are shifted and each transition can be spectrally isolated to produce a single photon source. We have grown self assembled InAs/GaAs quantum dots embedded in a planar microcavity with an average spatial density of $1\mu\text{m}^{-2}$. By means of metallic apertures or etched mesas with $1\mu\text{m}$ -diameter it was possible to isolate a single QD. Photoluminescence measurements on single QDs reveal spectral lines at 1300nm characterized by a FWHM of $40\mu\text{eV}$, which are attributed to exciton, biexciton and charged exciton transitions in the ground state. The identification of the spectral lines is further supported by lifetime measurements, to our knowledge, the first ever to have been made at these wavelength. We demonstrate that our single QDs are efficient sources of triggered single photons coupled to O-band of single mode fibers. The experimental value of second-order correlation function, $g^{(2)}(0)=0.38$, demonstrates strong suppression of multi-photon pulses per excitation cycle and was obtained for a photon count rate of 300 counts/sec per detector at a repetition rate of 4MHz. Assuming that at least one exciton is created in the QD for each laser pulse, we estimate that the coupling efficiency of single photons in the single-mode fiber is 0.5%. Progress in the development and characterization of single photon sources at telecom wavelength has been slowed down by the high noise levels and low quantum efficiencies of single photon detectors at telecom wavelength. To optimise the signal to noise ratio (SNR) we operate our APDs in geiger mode and set an optical active window of 300ps. Although this value is significantly shorter than the measured lifetime of the exciton (1.2ns) we achieve an overall gain in the SNR due to a drastic reduction of a dark events for very short gates. We are therefore able to measure the second order correlation function with integration times comparable to those made in the region of the spectrum where silicon technology is used. Emission wavelength, narrow spectral width, low multi-photon probability and high efficiency make our quantum dots particularly suited for quantum cryptography applications in telecom fibers over long distances.

3:30 PM *P2.4

Electron Relaxation and Energy Transfer in PbSe Quantum Dots. Frank W. Wise, Applied and Engineering Physics, Cornell University, Ithaca, New York.

Recent studies of the relaxation of photoexcited electrons in PbSe quantum dots will be presented. The relaxation of electrons from the 1P state to the 1S state occurs on the picosecond time scale even when the states are more than 10 phonon energies apart. This ultrafast relaxation cannot be explained by mechanisms invoked to explain the absence of a phonon bottleneck in other quantum-dot materials. Linear spectroscopy reveals splitting of the lowest-energy states of PbSe quantum dots, but the splitting is inadequate to account for the ultrafast 1P-to-1S relaxation. We tentatively attribute the splitting to coupling of the equivalent L-valleys from which the quantum-dot states are derived. Finally, we observe microsecond-time-scale radiative recombination and resonant energy transfer between quantum dots. The time scale of these processes is consistent with

dielectric screening of the electric field in the nanocrystals.

4:00 PM P2.5

Intraband relaxation in CdSe nanocrystals and the strong influence of the surface ligands. Philippe Guyot-Sionnest, Brian Wehrenberg and Dong Yu; University of Chicago, Chicago, Illinois.

The intraband relaxation between the 1Pe and 1Se state of CdSe colloidal quantum dots is studied by pump-probe time resolved spectroscopy. Infrared pump-probe measurements with ~ 6 ps pulses show identical relaxation whether the electron has been placed in the 1Se state by above bandgap photoexcitation or by electrochemical charging. This indicates that the intraband relaxation of the electrons is not affected by the photogenerated holes which have been trapped. However, the surface ligands are found to strongly affect the rate of relaxation in colloid solutions. Faster relaxation (< 8 ps) is obtained with phosphonic acid and oleic acid ligands. Alkylamines lead to longer relaxation times of ~ 10 ps and the slowest relaxation is observed for dodecanethiol ligands with relaxation times ~ 30 ps. It is concluded that, in the absence of holes or when the holes are trapped, the intraband relaxation is dominated by the surface and faster relaxation correlates with larger interfacial polarity. Energy transfer to the ligand vibrations may be sufficiently effective to account for the intraband relaxation rate.

4:15 PM P2.6

Impact ionization quantum yield in PbSe nanocrystals.

Guy Allan and Christophe Delerue; ISEN, IEMN, Villeneuve d'Ascq Cedex, France.

It has been demonstrated that impact ionization occurs with very high efficiency in PbSe nanocrystals [1-2]. We obtained the electronic structure of these nanocrystals using the tight-binding sp³d⁵* approximation. A large number of levels are necessary as the impact ionization becomes efficient for photo-excitation energy larger than three times the cluster gap. By comparison to the bulk semiconductor absorption, we show that the electron or hole electronic states photo-created are in an effective mass picture made from bulk states lying near Van Hove singularities along the (100) direction in the bulk Brillouin zone whereas the HOMO and the LUMO are made from states near the L point along the (111) direction. We study how the exciton created by photo-excitation is transferred to biexciton states resonant in energy. The density of these biexciton states increases rapidly with the incident energy. Assuming a constant Coulomb coupling between single and biexciton states, we calculate the quantum yield and find it increases for excitation energies larger than three times the cluster energy gap in agreement with experiments. Comparison is made with InAs nanocrystals. 1. R. D. Schaller and V. Klimov, Phys. Rev. Lett. 92, 186601 (2004) 2. R. J. Ellingson et al., Nano Lett. 5, 865 (2005)

4:30 PM P2.7

Bright, Stable High-Energy PbSe Nanocrystal Quantum Dots.

Jeffrey M. Pietryga, Joanna L. Casson, Jagjit Nanda, Richard D. Schaller, Victor I. Klimov and Jennifer A. Hollingsworth; Chemistry Division, Los Alamos National Laboratory, Los Alamos, New Mexico.

Semiconductor nanocrystal quantum dots (NQDs) have demonstrated tremendous utility as bright, stable emitters suitable for most applications previously filled by organic dyes. With superior photostability, broad absorbance and narrow emission, NQDs show great potential for new applications, especially in energy ranges such as the near-infrared (NIR) in which there are no viable organic options. Lead selenide (PbSe) NQDs can be colloiddally synthesized to exhibit narrow, size-tunable photoluminescence (PL) over a large range of energies from ~ 1.0 eV (1200 nm) to nearly 0.31 eV (4000 nm; Pietryga, et al., JACS 2004), with particularly high emission efficiencies ($>90\%$ quantum yield) in the NIR. However, as synthesized, colloidal PbSe NQDs suffer from poor long-term stability in air, demonstrating a shift to lower PL energies within days, and eventual loss of PL intensity. Our stability studies under controlled environmental conditions, as well as XPS analyses suggest that surface oxidation leads to both effects. We report here post-synthetic treatment of colloidal PbSe NQDs designed to enhance stability by controlling the surface chemistry. We demonstrate retention of high quantum yields in the NIR over several months under ambient conditions. Beyond enhanced stability, the surface-treated PbSe compositions are unique compared to the starting PbSe. First, they are blue-shifted in energy, with the degree of shift controlled by the time of exposure to the surface treatment, allowing access to very "blue" energies: higher than 1.3 eV. Such energies correspond to very small (< 2 nm) untreated PbSe NQDs; whereas, literature reports of band-edge emitting PbSe NQDs have been limited to 3 nm-sized PbSe NQDs, or larger. Second, these high-energy PbSe NQDs are stable against further blue shifting, and they possess high quantum yields up to 100%. Alternatively, we have prepared very-small, high-energy PbSe NQDs by way of a low-temperature growth process. These

NQDs are compared and contrasted with the surface-treated and traditionally prepared NQDs using NIR absorbance, PL, TEM, EDS and XRD.

4:45 PM P2.8

Wavefunction engineering in elongated semiconductor nanocrystals. Josef Muller¹, John Mark Lupton¹, Robert Koeppe¹, Pavlos Lagoudakis¹, Andrey Rogach¹, Jochen Feldmann¹, Dmitri Talapin² and Horst Weller²; ¹Department of Physics, Ludwig-Maximilians-Universitaet, Munich, Germany; ²Institute of Physical Chemistry, University of Hamburg, Hamburg, Germany.

Semiconductor nanocrystals offer a particularly appealing route to wavefunction engineering by means of shape control during particle synthesis. We explore the effect of the transition from three dimensional to two dimensional wavefunction confinement in CdSe nanocrystals capped with an elongated CdS shell of variable length [1]. Whereas holes remain trapped in the CdSe core for all aspect ratios, electrons can delocalise into the shell of the nanoparticle. This is seen both in the shift of the fluorescence and absorption with aspect ratio, but becomes particularly apparent in the decrease of the radiative decay rate with increasing particle length. These effects due to shape dependent wavefunction confinement are accurately reproduced by a numerical model accounting for the electron-hole correlation interaction. Our elongated nanocrystals are particularly well suited for single particle investigations. Breaking the particle symmetry by elongation provides a preferential axis for surface charge migration, which is monitored directly in the spectral fluctuations of the single particle with time [2]. An alternative route to wavefunction engineering is pursued by the application of static electric fields, which give rise to a substantial Stark shift of the exciton in the quantum confined structure [3]. Such electric fields may be either internal (due to surface charges) or external in nature. Placing the nanocrystals in between interdigitated finger electrodes allows the application of lateral electric fields of up to 0.5 MV/cm in strength. Depending on the particle orientation relative to the field, the electron wavefunction can be displaced into the shell of the particle, which reduces both the radiative decay rate as well as the exciton energy. Both effects are accurately reproduced by the numerical model accounting for the correlation energy. As expected, the magnitude of the quantum confined Stark shift of up to 100 meV scales directly with the particle size, as does the overall field-induced modulation in emission intensity of the single particle. Shape control therefore provides a means of tuning the magnitude of the Stark effect. In turn, electric field assisted single particle spectroscopy enables detailed insight into nanoscale charge distributions within colloidal nanocrystals. [1] D. V. Talapin et al., Nano Lett. 3, 1677 (2003) [2] J. Muller, J. M. Lupton, et al., Phys. Rev. Lett. 93, 167402 (2004) [3] S. A. Empedocles et al., Science 278, 2114 (1997)

SESSION P3: Poster Session I

Chairs: Philippe Guyot-Sionnest, Margaret Hines and

Hedi Mattoussi

Monday Evening, November 28, 2005

8:00 PM

Exhibition Hall D (Hynes)

P3.1

Synthesis of photoluminescent Silicon and Germanium nanoparticles by laser ablation. Daria Riabinina, Federico Rosei and Mohamed Chaker; INRS-EMT, University of Quebec, Varennes, Quebec, Canada.

Light emitting semiconductor nanostructures have attracted considerable interest since they have potential applications in future quantum and photonic devices. Ge and Si nanostructures are key elements for the integration and development of optoelectronic devices into existing silicon-based technology [1]. Pulsed laser deposition (PLD) has established itself as a very versatile method for thin film growth of almost any kind of material. Recent studies have shown that photoluminescent Si nanoparticles can be synthesized by PLD under moderate inert gas pressures [2-4]. PLD is recognized as one of the most flexible and promising techniques due to its ability to control the size and distribution of nanoparticles. To the other hand, the reactive laser ablation is a powerful method to control the stoichiometry of deposited films. Optical properties of Si deposited under oxygen pressure were a subject of recent research for optoelectronic applications such as waveguides [5,6]. Some research was performed on formation of Si nanoparticles by PLD under partial argon and oxygen pressure [7] and on fabrication of doped Si nanoparticles [8,9]. In this work, we developed a novel approach for synthesizing Ge and Si nanoparticles by laser ablation. Partial oxidation of ablated species during reactive PLD leads to Ge and Si nanoparticles enclosed in a Ge oxide or Si oxide matrix, respectively. The optical and structural properties of Ge and Si nanoparticles embedded in Ge and Si oxide matrix were studied by Photoluminescence spectroscopy, X-Ray Photoelectron Spectroscopy and X-Ray Diffraction.

Photoluminescence due to the quantum confinement effect was found to be dependent on the oxidation degree of the material. References [1] F. Rosei, J. Phys.: Cond. Matt. 14 (2004) S1373. [2] D.H. Loendes, D.B. Geohegan, A.A. Puresky, D.P. Norton, C.M. Rouleau, Science 273 (1996) 898. [3] A.V. Kabashin, J.-P. Sylvestre, S. Patskovsky, M. Meunier, J. Appl. Phys. 91 (2002) 3248. [4] L. Patrone, D. Nelson, V.I. Safarov, M. Sentis, W. Marine, J. Appl. Phys. 87 (2000) 3829. [5] A. P. Cariacto, M. De Sario, M. Fernandez, G. Leggieri, A. Luches, M. Martino, F. Prudeniano, Appl. Surf. Sci. 197, 458 (2002). [6] A. Masuda, S. Usui, Y. Yamanaka, Y. Yonezawa, T. Minamikawa, M. Suzuki, A. Morimoto, M. Kumeda, T. Shimizu, Thin Solid Films 416, 106 (2002). [7] T. Mazuta, D. Takeuchi, Y. Kawaguchi, T. Makimura, K. Murakami, Appl. Surf. Sci. 197, 574 (2002). [8] C. Li, K. Kondo, T. Makimura, K. Murakami, Appl. Surf. Sci. 197, 607 (2002). [9] T. Makimura, Y. Yamamoto, S. Mitani, T. Mizuta, C. Q. Li, D. Takeuchi, K. Murakami, Appl. Surf. Sci. 197, 670 (2002).

P3.2

Self Assembly of Eu₂O₃ Nanocrystals and Nanoneedles.

Marcela L. Redigolo^{1,4}, Sameer V. Mahajan^{2,4}, Dmitry S. Koktysh^{3,4} and James H. Dickerson^{1,4}; ¹Physics and Astronomy, Vanderbilt University, Nashville, Tennessee; ²Interdisciplinary Program in Materials Science, Vanderbilt University, Nashville, Tennessee; ³Department of Chemistry, Vanderbilt University, Nashville, Tennessee; ⁴Vanderbilt Institute for Nanoscale Science and Engineering, Vanderbilt University, Nashville, Tennessee.

We have prepared europium oxide (Eu₂O₃) nanoneedles and nanospindles through the self assembly of colloidal europium oxide nanocrystals from their highly concentrated solutions. This process involved the stepwise thermal growth of nanocrystals into ordered, high aspect ratio, one dimensional nanoneedles and the subsequent assembly of said nanoneedles into larger, oriented bundles (nanospindles). The Eu₂O₃ nanocrystals were synthesized following a room temperature, colloidal chemistry procedure, adapted from the synthesis of G. Wakefield *et al.*¹ We present the results of this self-assembly phenomenon using nanocrystals from 2.0nm to 20.0nm in diameter. The overall dimension of the nanoneedles and the nanospindles can be tailored, depending both on subtle changes of the alkalinity and temperature of the solution and on the surface passivation of the nanocrystals. Under optimum conditions, anisotropic growth of these structures can be extended up to lengths greater than 1.0 micron. The optical properties of these structures were characterized by UV-vis spectroscopy, to observe the absorption profile of the nanocrystals and nanospindles, and photoluminescence spectroscopy, to determine the size-dependent fluorescence of these nanomaterials. In addition, high resolution transmission electron microscopy was employed to characterize the approximate shape, size distribution, and crystallinity of the structures as they evolved from nanocrystals into nanospindles. Anomalous blue-shifts in the room temperature photoluminescence spectra, from the nanocrystals to the nanoneedles, may reveal a new coupling mechanism between europium chalcogenide nanoparticles, materials whose optical properties generally are derived from atomic transitions of the Eu³⁺ ion. 1) G. Wakefield, H. A. Keron, P. J. Dobson, and J. L. Hutchison, J. of Coll. Interf. Sci. 215, 179, 1999.

P3.3

Multiscale Theory of Low-Temperature Epitaxy of Group-IV Materials: Self-organization and Epitaxial Breakdown.

Christoph A. Haselwandter and Dimitri D. Vvedensky; Physics, Imperial College, London, United Kingdom.

A methodology for the multiscale analysis of lattice models is developed and applied to the low-temperature growth of group-IV semiconductors through molecular beam epitaxy. All intermediate and asymptotic scaling regimes of the lattice model known from computer simulations are correctly reproduced. In addition, it is found that in the physically relevant case of a two-dimensional substrate the asymptotic behavior is controlled by a hitherto unknown fixed point. This provides a fundamental explanation of recent experiments on Ge(001) with the intriguing conclusion that the relaxation mechanism responsible for ordered structures during the early stages of growth produces an instability at longer times that leads to epitaxial breakdown.

P3.4

Formation of Epitaxial Pb And Sn Islands at SiO₂/Si(001)

Interfaces. Felipe Kremer¹, Joao M. J. Lopes¹, Paulo F. P. Fichtner² and Fernando Claudio Zawislak¹; ¹Departamento de Fisica, Universidade Federal do Rio Grande do Sul, Porto Alegre, RS, Brazil; ²Escola de Engenharia, Universidade Federal do Rio Grande do Sul, Porto Alegre, RS, Brazil.

The formation of a dense and uniform system containing Pb or Sn nanoparticles epitaxially oriented to the Si(001) layer at the SiO₂/Si film interface is studied. The nanoparticle systems were obtained by

implanting the atomic species into the SiO₂ film and annealing the implanted samples in the 1173 to 1373 K temperature range for times from 0.5 to 3 h in N₂ atmosphere. The accumulation of Pb or Sn atoms at the interface region as a function of temperature and time is characterized by RBS. This accumulation process leads to the formation of metallic nanoparticles presenting rectangular basis with typical dimensions of 2 to 6 nm and rather steep edges with a typical high of 3 to 4 nm. HRTEM observations and selected area diffraction (SAD) measurements show that the islands are of the metallic phase. Upon prolonged thermal treatments the atoms forming the islands are incorporated into the Si matrix leading to the formation of imbedded metal-rich epitaxial nanocrystals. We demonstrate an original process leading to the formation of a high concentration (around $7 \times 10^{11} \text{ cm}^{-2}$) of epitaxial Pb or Sn islands at the interface of SiO₂/Si(100) systems, having a small size dispersion and a self-organizing tendency. The extension of the method for bi-component systems such as PbS or GaMn opens the possibility for the formation of luminescent or magnetic islands, thus justifying the interest for further investigations of the phenomenon.

P3.5

Determination of GaN Nanowires Growth Directions through Homoepitaxial Studies. Hongwei Li and Mahendra K. Sunkara; Department of Chemical Engineering, Univ. of Louisville, Louisville, Kentucky.

Directed and controlled growth of nanowires is the ultimate goal for the practical application of nanowires. Determining the growth directions and understanding the mechanisms that control growth facets are the important factors towards that goal. Wurtzite GaN has been widely known as an anisotropic crystal which has different physical and electronic properties along different crystallographic directions. GaN nanowires less than 30nm in diameter with three growth directions ($\langle 0001 \rangle$, $\langle 10\text{-}10 \rangle$ and $\langle 10\text{-}11 \rangle$) without using single crystal templates have been synthesized. Homo-epi experiments onto these pre-synthesized GaN nanowires with three distinct growth directions ($\langle 0001 \rangle$, $\langle 10\text{-}10 \rangle$ and $\langle 10\text{-}11 \rangle$) were performed using vapor transport of Ga in dissociated ammonia. The results illustrate distinct morphological growth features, e.g. micro hexagonal prisms for $\langle 0001 \rangle$ nanowires, micro belts for nanowires with $\langle 10\text{-}10 \rangle$ growth direction and micro saws for nanowires with $\langle 10\text{-}11 \rangle$ growth direction. The results with homo-epitaxial growth onto these pre-synthesized sub 30 nm size nanowires also exhibited an interesting phenomenon, i.e., the surface transport of adatoms on the nanowires seems to be enhanced specifically on those $\langle 0001 \rangle$ nanowires. The development of these facets was explained by kinetics growth processes. This homo-epitaxial growth procedure is shown as a simple technique for determining the growth directions of sub-30 nm size wires which otherwise appear as rounded without tedious TEM analysis.

P3.6

TEM Tomography of Semiconductor and Metal Nanoparticles and Bio-Nanoparticle Composites. Scott Phillip Ahrenkiel, Pingrong Yu, James Murphy, Jovan Nedeljkovic, Olga Micić, Qi Xu, Bryon Donohoe and Mike Himmel; National Renewable Energy Laboratory, Golden, Colorado.

The three-dimensional (3D) shapes of semiconductor and metal nanoparticles and configurations of ensembles of bio-nanoparticle composites are imaged using transmission electron microscopy (TEM) tomography. Computed tomography was developed in the medical imaging field, but the concept extends quite naturally to TEM analysis, primarily requiring microscope automation, a relatively large sample tilt angle, and sufficient computational power. The acquired tilt series is used to construct a 3D stack of cross-sectional images, where the image contrast can be related to the variations in attenuation coefficient within the sample. TEM tomography of thin sections prepared by ultramicrotomy has become an important tool for biological applications. Fortunately, sophisticated software tools have become available to align the collections of two-dimensional images and generate the tomographic representations. A dual tilt series from orthogonal axes of a single region of the sample provides an extensive data set for structural analysis. Gold nanoparticle fiducials are typically spread on the sample for precise tracking of the sample coordinates and correspondence of the two tilt series. The reconstructed volumes facilitate viewing and manipulation of the samples in a virtual TEM stage. An ensemble of 57-nm PbSe nanoparticles having a six-pointed star shape has provided an especially interesting application of TEM tomography. Combining the tomographic data with conventional lattice images, we show that each of the six points is aligned with a $\langle 100 \rangle$ axis of the underlying cubic structure. Whereas the shapes are difficult to extract from individual TEM images, the tomographic reconstructions can be freely manipulated, providing direct shape analysis. Correspondence is then clearly drawn between the projected profile of a particular particle in a single TEM image and the geometrical orientation of the particle on

the TEM grid. A related application is the 3D reconstruction of ordered arrays of spherical, 18-nm In nanoparticles. Using tomography, stacking arrangements that would remain difficult to discern from individual TEM images are clearly revealed. Although the tilt series are acquired about only a single axis, the 3D tomogram can be rotated to nearly any desired viewing axis for analysis. We are currently exploring other related applications of TEM tomography, such as determination of the cross-sectional shapes of InP nanorods and the visualization of CdSe nanoparticles bonded to cellulose fibers.

P3.7

Fabrication, Characterization and Superconductivity of Granular Bi Nanowires. Mingliang Tian^{1,2}, Jinguo Wang^{1,3}, Nitesh Kumar^{1,2}, Ying Liu², Thomas Mallouk^{4,1} and Moses Chan^{2,1}; ¹Center for Nanoscale Science, Penn State University, University Park, Pennsylvania; ²Department of Physics, Penn State University, University Park, Pennsylvania; ³Materials Research Institute, Penn State University, University Park, Pennsylvania; ⁴Department of Chemistry, Penn State University, University Park, Pennsylvania.

Rhombohedral Bi is a semimetal which is never superconducting down to low temperature at atmosphere condition. Bulk Bi can be superconducting only at higher pressure condition or in amorphous state. However, individual Bi cluster of size of 2-10 nm in diameter can be superconducting with a T_c of 1.5-5.5 K, closely depending on the cluster size. The superconductivity in Bi cluster may be related to a strongly increased density of states at the cluster surface, not related to the quantum-size effect. In this work we first report fabrication and characterization of granular Bi nanowires showing superconducting properties by electrochemical deposition at room temperature. The wire diameters of Bi is ranged from 20 -100 nm. The superconducting transition temperature T_c and critical field H_c of 70 nm granular Bi wires is respectively 8.2 K and 3.5 Tesla. Superconducting properties of these granular Bi nanowires were found to closely depend on their sample morphology. Our samples were made at room temperature instead of previous low temperature condensation technique for superconducting Bi clusters or amorphous film. All of granular superconducting Bi nanowires are metallic, in contrast to crystalline Bi nanowires showing semiconducting behavior. The relations between sample morphology and superconductivity are investigated.

P3.8

Surface Termination and Doping Effects on the Band Edges in Nanoparticles as Studied by Soft X-Ray Absorption, Fluorescence, and Photoemission Spectroscopy. Robert W. Meulenberg, Tony van Buuren, Trevor Willey and Louis Terminello; Lawrence Livermore National Laboratory, Livermore, California.

For a thorough understanding of nanocrystalline material systems, knowledge of band gap widening and band alignment as a function of particle size, chemical doping, and surface termination is critical to rational design and utilization of these novel materials. We use soft x-ray probes such as x-ray absorption Spectroscopy (XAS), photoelectron spectroscopy (PES), and soft x-ray fluorescence (SXF) experiments to determine the band edge shifts and doping effects on a variety of nanostructured materials in order to better understand the electronic properties. Using XAS, we investigate the local structure and composition of dopant ions dispersed in II-VI and group IV nanocrystals. In the II-VI system, CdSe, we report that dopants can be used as a local probe for identifying changes in the bulk versus surface crystal field energy. In addition, we have probed the chemical environment of Er in Ge nanoparticles and are able to monitor band edge shifts as a function of both particle size and Er concentration. We find that there is a critical amount of Er that can be added to the nanoparticle before an ErGe alloy forms. These results are intriguing as they can be correlated to the observed infrared luminescence that occurs in Er(III) systems. Finally, we study the electronic structure of both Si and Ge nanoparticles ranging in size from 1-5 nm. We report on how the change in surface passivation affects the ratio of VB shift to CB shift in nanoparticle systems and compare to recent theory. This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

P3.9

Elucidating the Importance of Growth Parameters and Fabrication Methods by Electrical Characterization of Individual GaN and In₂O₃ Nanowires. Eric David Stern¹, Elizabeth Broomfield⁴, Daniel Turner-Evans¹, Guosheng Cheng², Elena Cimpoiasu², Stan Guthrie³, Chao Li⁵, James Klemic², Aric Sanders³, Ryan Munden², Chongwu Zhou⁵ and Mark Reed²; ¹Biomedical Engineering, Yale University, New Haven, Connecticut; ²Electrical Engineering and Applied Physics, Yale University, New Haven, Connecticut; ³Physics, Yale University, New Haven, Connecticut; ⁴Yale College, Yale University, New Haven, Connecticut; ⁵Electrical Engineering-Electrophysics, University of Southern

California, Los Angeles, California.

We have performed a statistically significant electrical study of In₂O₃ nanowires (NWs) fabricated by laser ablation and hot-wall-CVD (HW-CVD) fabricated In₂O₃ and GaN NWs by studying over 1200 single NW devices. We have extracted the growth parameters responsible for GaN wire quality and compared the HW-CVD and laser ablation growth methods for In₂O₃ NWs. Nanowires fabricated by both methods grow by the vapor-liquid-solid mechanism and the crystallinity of the NWs has been shown previously^{1,2}. We have developed and implemented a high yield characterization platform that provides a high throughput method for electrical characterization of individual NWs using multiple metal electrodes as well as a gating electrode. After all patterned electrode pairs are electrically screened with an automated probestation, NWs with Ohmic contacts are revisited are thoroughly electrically characterized by taking IDS-VDS sweeps while varying VG. Mobility and carrier concentration values are calculated and devices are then imaged with an SEM to determine NW length and diameter and to screen for multiple crossings. All NW devices measured have shown FET-like behavior. The GaN NWs are near-degenerately doped, $\sim 5 \times 10^{20} \text{ cm}^{-3}$, which is due either to nitrogen vacancies or oxygen impurities. To address this high doping and ascertain which dopant dominates we correlated the effects of varying growth conditions on the carrier concentration of NW devices. In one representative study, for example, we annealed NWs at 900°C in forming gas or ammonia. The forming gas anneal serves as a typical high-temperature anneal and decreased the mean doping to $\sim 10^{20} \text{ cm}^{-3}$, whereas the elemental nitrogen produced by the cracking of ammonia during this anneal should diffuse into the GaN and fill the nitrogen vacancies. T-test results show that the carrier concentration of the unannealed and ammonia-annealed populations, which is $\sim 5 \times 10^{20} \text{ cm}^{-3}$ is significantly different at the 99.9% confidence level. Combined with results from other statistically significant studies showing the effects of catalysts, substrates, and other growth parameters suggest, these data suggest that nitrogen vacancies are the dominant dopant. Comparing our GaN NW data with the literature suggests that laser ablation may be superior to HW-CVD as a fabrication method for NWs³. To investigate the effect of different growth methods on sample quality, statistically significant studies comparing In₂O₃ NWs grown by laser ablation with others grown by HW-CVD will be presented. This work is partially supported by DARPA under SPAWAR contract number N66001-04-1-8902 and by the DHS and NSF (Cheng, et al. Appl Phys Lett. 2003; 83: 1578. 2Li, et al. Adv Mater. 2003; 15: 143. 3Huang, et al. Nano Lett. 2002; 2 (2): 101.

P3.10

Coherent Control of Strain and the Observation of the Quantum Hall Effect in Fully Released Silicon/Silicon-Germanium Nanomembranes. Levente Klein¹, Michelle M. Roberts², Don Savage², Max G. Lagally² and Mark A. Eriksson¹; ¹Physics, University of Wisconsin, Madison, Wisconsin; ²Material Science, University of Wisconsin, Madison, Wisconsin.

Energy band alignment in silicon/silicon-germanium heterostructures is a sensitive function of strain. Conventionally strain is induced through the growth, between two fully relaxed layers, of a thin layer with a different lattice constant. The difference in lattice constant strains the Si layer. We present an alternative, superior, method based on coherent strain sharing in silicon/silicon-germanium nanomembranes. In this approach, thin ($\sim 200 \text{ nm}$) silicon/silicon-germanium heterostructures are grown on silicon-on-insulator (SOI), with all layers below their critical thicknesses for dislocation formation, and released from their underlying substrate (by etching the oxide), allowing the entire structure to expand or contract. This coherent elastic strain sharing modifies the strain in critical layers (such as quantum wells in modulation-doped FETs) and results in desired electronic properties. Hall measurements on the un-released nanomembrane show clear evidence of undesired three-dimensional transport. Upon release from the substrate, the nanomembrane expands and a deep quantum well develops in the Si layer, which is tensilely strained. Measurements of the released nanomembrane (deposited on a solid support) reveal excellent two-dimensional conduction, including the development of the quantum Hall effect at low temperatures. X ray measurements show an increase in the tensile strain of the silicon quantum well upon release, in agreement with both theoretical predictions and electrical transport measurements. We discuss the possibility of integrating high-mobility silicon-germanium nanomembranes upon release with various substrates for hybrid electronic circuits. Research supported by NSF-MERSEC, DOE, and AFOSR

P3.11

Syntheses and Characterization of Novel Semiconductor Nanowires. Song Jin, Matt Bierman and Andrew Schmitt; Chemistry, University of Wisconsin-Madison, Madison, Wisconsin.

Semiconductor nanowires 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. Using vapor-liquid-solid growth mechanism and chemical vapor deposition, the atomic structures of nanowires can be rationally and precisely controlled. We will present our new results for the syntheses and characterization of novel rare earth sulfide nanowires and transition metal silicide nanowires using chemical vapor deposition of single source organometallic precursors or chemical vapor transport method. We will also discuss our preliminary investigation of physical properties. The diverse physical properties displayed by these nanowires make them potentially suitable for nanophotonic, nanoelectronic, and spintronic applications.

P3.12

Approaches towards high gain in self-assembled InAs quantum dot structures. Jobert van Eijsden, Vadim Tokranov, Michael Yakimov and Serge Oktyabrsky; College of Nanoscale Science and Engineering, University at Albany - SUNY, Albany, New York.

Recently, research efforts on self-assembled In(Ga)As quantum dots (QDs) have led to significant advancements in various device applications including lasers, amplifiers and IR photodetectors. In order to develop laser medium with high gain and fast carrier dynamics we have explored various approaches including: increase of QD surface density and number of QD sheets, shape-management of QDs to increase overlap of electron and hole wavefunctions, tunnel QW-QD structures to accelerate capture of carriers into QDs. The QD design and fabrication trade-offs are detailed to emphasize the potentialities and constraints of the stress-driven self-assembly. InAs self-assembled QDs embedded into GaAs/AlAs short-period superlattice were grown by molecular beam epitaxy. In-situ reflection high energy electron diffraction, atomic force microscopy, photoluminescence (PL) and transmission electron microscopy were used to analyze structure and optical properties of QDs. Edge-emitting and Vertical Cavity Surface Emitting Laser (VCSEL) diodes were fabricated using the developed QD medium. To control surface mobility, lateral redistribution of In and shape of QDs we engineered both underlayer and overlayer of a QD sheet and were able to obtain QD density of $5 \times 10^{10} \text{ cm}^{-2}$ per sheet with the volume uniformity corresponding to a PL band FWHM of 30 meV at room temperature (RT). A shape-engineered QD ensemble was responsible for unsurpassed thermal stability of laser diodes with RT characteristic temperature of 380 K. Tunnel QW-QD structures with different separation of ground state (GS) energies were grown by variation of In concentration in QWs. We have developed a tunnel QW-on-QDs structure with a resonance transition which is $\sim 35 \text{ meV}$ red-shifted to QW GS. This peak likely indicates an efficient resonant tunneling of carriers from QW into QD ensemble states. The highest gain was achieved with QW-on-QDs active medium with GS relative separation close to 35-40 meV. Optimized triple-pair tunnel QW-on-QDs laser diode emitting at 1145 nm (corresponding to QD GS) exhibited a saturated modal gain exceeding 80 cm^{-1} with minimum cavity length of 0.14 mm. These lasers demonstrated QD GS emission with a threshold current density J_{th} from 225 A/cm^2 to 1.5 kA/cm^2 (depending on cavity length) with switching to QW GS lasing at 1105 nm at higher J_{th} . RF small signal modulation characteristics of these lasers with QD-based emission wavelength were measured. From the damping factor and resonance frequency dependences on driving current, damping-limited cut-off frequency for this QW-on-QD medium can be estimated above 30 GHz. This medium has also shown lasing in all-epitaxial VCSEL with $J_{th} = 3 \text{ kA/cm}^2$.

P3.13

Atomic-Scale Characterization of GaAsSbN/GaAs Quantum Well Interfaces Grown by Molecular Beam Epitaxy.

Trinity Biggerstaff¹, Gerd Duscher^{1,2}, Stephen J. Pennycook², Sergei Lopatin¹, Nathan Stoddard¹ and Shanthi Iyer³; ¹Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina; ²Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; ³Electrical Engineering, North Carolina A & T State University, Greensboro, North Carolina.

Low dimensional structures are used for a wide range of high efficiency optical devices including light emitting diodes (LEDs) and laser diodes (LDs). In this paper GaAsSbN quantum wells grown by molecular beam epitaxy (MBE) at different temperatures were investigated. Scanning transmission electron microscopy (STEM) with spherical aberration correction was used to determine thickness and interface roughness of these QW structures. Z-contrast imaging allows for the analysis of interface composition in high resolution images. Additionally, microwave photoconductance decay enabled us to measure carrier lifetime. The thickness of the single quantum well in both samples was measured to be 12.5 nm. The interface thickness was measured as the region where Sb decreases from the quantum well concentration to zero in GaAs. This Sb profile was measured with

atomic resolution in Z-contrast imaging. The average interface thicknesses in the QW grown at a higher growth temperature of 470°C and annealed were determined to be 0.9 nm and 0.78 nm closer to the surface and substrate, respectively. The corresponding thicknesses for QWs grown at a lower growth temperature of 450°C were found to be 4.5 nm and 3.9 nm, respectively. Our study indicates improved optical properties are achieved in samples that exhibit sharp QW interfaces.

P3.14

Lasing Characteristics of InAs/GaAs Quantum Dot Laser Diode Grown by Atomic Layer Molecular Beam Epitaxy.

Kwang Woong Kim^{1,2}, Nam Ki Cho¹, S. P. Ryu¹, Jin Dong Song¹, Won Jun Choi¹, Yong Ju Park¹, Jung Il Lee¹ and J. H. Park²; ¹Nano Device Research Center, Korea Institute of Science and Technology, Seoul, South Korea; ²Dept. of Electronics & Computer Engineering, Korea University, Seoul, South Korea.

It has been well known that InAs dot-in-a-well (DWELL) structure exhibits better lasing performance as the active medium of quantum dot laser diode (QDL). In this presentation, we report the lasing characteristics of a QDL with an active medium of 3-stacked InAs DWELL structure, which is sandwiched by 1.5- μm -thick n-type and p-type $\text{Al}_{0.7}\text{Ga}_{0.3}\text{As}$ cladding layer. The InAs DWELL structure was grown by atomic layer molecular beam epitaxy (ALMBE). The laser structure was processed to ridge waveguide type LD with a stripe width of 15 μm . A 2-mm long QDL showed lasing at the wavelength of 1.32 μm at room temperature, which is slightly longer than the ground state of InAs QD due to the heating effect. The threshold current density was 289 A/cm^2 without any facet coating at pulsed mode operation (0.1%). As the device length became shorter, the lasing wavelength was shifted from 1.32 μm of the ground state to 1.24 μm of the first excited state due to the lack of modal gain.

P3.15

Synthesis and Characterization of Diamond-Hexagonal Si and Ge Nanocones. Linyou Cao¹, Lee Laim¹, Chaoying Ni², Bahram

Nabet^{3,1,4} and Jonathan Spanier^{1,3,4}; ¹Materials Science & Engineering, Drexel University, Philadelphia, Pennsylvania; ²W. M. Keck Electron Microscopy Facility, University of Delaware, Newark, Delaware; ³Electrical and Computer Engineering, Drexel University, Philadelphia, Pennsylvania; ⁴A. J. Drexel Nanotechnology Institute, Drexel University, Philadelphia, Pennsylvania.

Control of the size, topology and structure of crystalline nanostructures is an important feature for enabling investigation of the shape- and structure-dependence of many properties and in identifying new materials and device applications of nanostructures. Here we report the synthesis of arrays of nanostructured, crystalline tapered Si and Ge polyhedra. These Si and Ge nanocones (SiNCs, GeNCs) possess tips with near-atomic sharpness, micron-scaled bases, hexagonal cross-sections, and adjustable apex angles via metal nanocluster-catalyzed chemical vapor deposition. High-resolution transmission electron microscopy, selected-area electron diffraction and Raman-scattering spectroscopy and analysis indicate that the SiNCs are of the diamond-hexagonal phase (Si-IV). SiNC- and GeNC-enabled surfaces and probes having NC of adjustable shape, electronic doping and composition may find a range of applications, including field emission, scanning and stationary probes, and investigations of optical and electronic properties in tapered nanostructures. Work supported in part by NSF-DMR-0425780, by the Commonwealth of Pennsylvania, and by the U. S. Army Research Office under Award No. W911NF-04-1-0308.

P3.16

Electrical and Optical Properties of Silicon-Rich Silicon Nitride Nanostructures. Jae Hyung Yi, Luca Dal Negro, Jurgen Michel and Lionel C. Kimerling; MIT, Cambridge, Massachusetts.

Silicon (Si) is a widely used material in microelectronics and in the last decade many attempts have been done to combine optical functions with microelectronics on Si chips. Quantum confinement and surface chemistry effects allowed us to improve light emission from Si-nanocrystals (Si-nc) in SiO_x matrices under optical pumping. However, electrical injection of carriers into the insulating SiO_x matrices is not easily achieved due to large insulating electrical barriers, and both injection current levels and device reliability are severely limited in SiO_x-based light emitting structures. Therefore we need alternative CMOS-compatible approach, based on dielectric matrices where charge injection can be more easily achieved and efficiently emitting Si nanocrystals can be successfully embedded [1]. In this study, the electrical and optical properties of Si-rich SiNx (SRN) light-emitting nanostructures are investigated. Plasma Enhanced Chemical Vapor Deposition (PECVD) was used for film deposition and thermal annealing was followed to nucleate Si nano-clusters. This material system shows efficient room temperature photoluminescence at lower annealing temperatures with respect to SiO_x-based systems and much higher injection current density levels

compared to SiO_x matrices can be obtained. Here we report on a detailed study of photoluminescence and I-V characteristics of differently prepared SRN films that can facilitate the current understanding of Si nanostructures in Si nitride. [1] L. Dal Negro, J. H. Yi, V. Nguyen, Y. Yi, J. Michel, L. C. Kimerling, Spectrally enhanced light emission from aperiodic photonic structures, Appl. Phys. Lett., in press (2005).

P3.17

Light Emission in Silicon-rich Silicon nitride Nanostructures. Luca Dal Negro¹, JaeHyung Yi¹, Jurgen Michel¹, Lionel Kimerling¹, Sebastien Hamel², Andrew Williamson² and Giulia Galli²; ¹Materials Science, MIT, Cambridge, Massachusetts; ²Lawrence Livermore National Laboratory, Livermore, California.

The traditional approach to turn silicon (Si) into a light emitting material is to reduce its dimensionality to the nanometer scale, where both quantum confinement and surface chemistry effects improve the efficiency of light generation. The widely investigated material system, Si-nanocrystals (Si-nc) dispersed in SiO₂ glass matrices, shows efficient room temperature light emission under optical pumping and the possibility of achieving sizable optical gain. Light amplification has recently been demonstrated by several groups. However, the presence of an insulating SiO₂ matrix prevents the fabrication of stable and efficient electrically-driven devices due to a huge injection barrier mismatch. In addition, the achievement of high emission efficiency is severely impeded by the slow radiative lifetime of Si-nc in SiO₂ (approx. 10 to 100 μs) which competes with faster non-radiative channels (Auger recombination in particular). Therefore, there is a strong need to investigate alternative CMOS-compatible approaches that can yield efficient and fast light emission from Si-nc nucleated in a different dielectric environment. In this talk we present results of light-emitting Si-rich silicon nitride films (SRN) obtained by PE-CVD deposition followed by low temperature (500-900 °C) thermal annealing. The optical properties of SRN films are studied with micro-Raman and photoluminescence spectroscopy and demonstrate the presence of small Si-clusters with nanosecond recombination times and negligible photoluminescence thermal quenching. First-principles Density Functional Theory simulations indicate that nitrogen atoms bonded to the surface of small ($\sim 1\text{nm}$) Si-nc play a crucial role in the light emission mechanism of SRN films.

P3.18

Electron-Beam-Induced Nano-Twinning and Hexagonal Phase Formation in Doped Silicon Nanowires. Dan Zhi¹, Paul A.

Midgley¹, Colin J. Humpherys¹, Chen Yang² and Charles M. Lieber²; ¹Materials Science and Metallurgy, University of Cambridge, Cambridge, United Kingdom; ²Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts.

Single crystalline Si nanowires, as one-dimensional structures for nano-devices, have attracted increasing attention in recent years. A variety of methods has been employed during these recent years for the manufacturing of Si nanowires. Controlling the nanowire one-dimensional growth and dopant profile is very challenging but offer unique opportunities for combining materials, manipulating properties, and designing novel devices. In order to have simultaneous control over dimensions, morphology, shape and uniformity on a nanometer scale, ways are needed to not only grow nanowires at a desired position, with a specific length and diameter, but also control material composition and defects. In this paper, we examined a series of doped Si nanowires with their size ranging from 5 to 40 nm using high resolution transmission electron microscopy (HRTEM). As previously reported for Si nanocrystals [1,2], we observed the formation of nano-twinning within some of the doped Si nanowires. Other planar defects, such as stacking faults, are also observed associated with these twin structures after electron beam radiation. Most of the stacking faults have a localized intrinsic transformation from a layer sequence ABCABC to ABCABABABC, where a layer with a local hexagonal-closed-packed structure, ABAB, is formed. In the defect region, usually near the edge of the nanowires, such a localized cubic-to-hexagonal phase transformation after electron beam radiation can be determined. The hexagonal phase in a silicon cone was previously reported [3], in which the hexagonal phase was formed due to a bending moment generated in an asymmetrical region during heavy oxidation. The possible mechanism of defect formation and phase transformation in doped Si nanowires after electron beam radiation is also discussed in this paper. [1] Y. Q. Wang, R. Smirani, and G. G. Ross, Nano Lett. 2004, 4, 2041. [2] Y. Q. Wang, R. Smirani, and G. G. Ross, Appl. Phys. Lett. 2005, 86, 221920. [3] C. J. Morgan, A. K. Kirkland, and C. J. Humphreys, Inst. Phys. Conf. Ser. 1993, 138, 267.

P3.19

Ge Nanodots in TiO₂ Matrix: Synthesis and Characterization. Amita Goyal¹, Sukti Hazra³ and S. Ismat

Shah^{1,2,3}; ¹Physics and Astronomy, University of Delaware, Newark,

Delaware; ²Materials Science and Engineering, University of Delaware, Newark, Delaware; ³Center for Composite Materials, University of Delaware, Newark, Delaware.

There has been increasing realization of the importance of non-conventional sources of energy like solar energy. Researchers have already developed various forms of solar cells based on silicon, CdTe, Cu-In-Ga-Se, TiO₂, etc. Solar cells made with some of these materials have been confronted with one or more of the problems of high costs, low sensitivity or low efficiencies, thereby making them unpopular for mass production. Therefore, research to make them more efficient and to create new ways to harness solar energy has continued. We have deposited nanocomposite thin films of TiO₂/Ge by rf magnetron sputtering from a TiO₂/Ge composite target. Titania has a band gap of 3.2 eV and hence can use only 5-7% UV component of the whole solar spectrum. With the addition of Ge nanodots in the TiO₂ matrix, the new system can absorb light in visible region. The thin films were deposited at different values of power ranging from 100 to 200 Watts and temperature ranging from 500^{deg}C to 700^{deg}C in an attempt to incorporate Ge nanodots in the TiO₂ matrix. The first step was to obtain Ge in elemental form in the thin films as expected from thermodynamic arguments based on relative free energies of formation of GeOx and TiO₂. Results of the characterization by using XRD (X-ray Diffraction), XPS (X-ray photoelectron Spectroscopy), TEM (Transmission Electron microscopy), HAADF (High angle annular dark field imaging) and EDAX (Energy Dispersive X-Ray Microanalysis) will be presented. While depositing these films it was observed that the films showed an increasing Ge incorporation with increasing rf power and temperature. In this paper we present the supporting data and the possible reasons for the same. A model to systematically vary the band gap of the nanocomposite by the controlling the size of the Ge nanodots will be presented.

P3.20

Growth and Characterization of Silicon Nanowires by Catalyst Assisted LPCVD. Pierre Ferret¹, Florian Dhalluin^{1,2}, Thierry Baron², Pascal Gentile³, Karim Aissou² and Michael Gordon²; ¹LETI DOPT, CEA, Grenoble, France; ²LTM, CNRS, Grenoble, France; ³DRFCM, CEA, Grenoble, France.

Over the past few years there has been considerable effort toward the synthesis of nanowires using the Vapour-Liquid-Solid (VLS) growth technique and metal catalyst. Even though significant advances have been made on the synthesis of nanowires, fundamental questions remain relating to growth control as well as details about the structural and electrical properties of single wires. Silicon nanowires (SiNWs) were grown on silicon (111) and (100) substrates in a Low Pressure Chemical Vapour Deposition (LPCVD) reactor with base pressure of 22 mbar. Silane (diluted in hydrogen) was used as the precursor gas and could be mixed with HCl for selective control of the growth process. Gold was used as a catalyst. We have studied the initial stages of Si nanowires growth by looking at how the condition of the Au/Si eutectic used for nanowire nucleation affects the nanowire growth process (i.e., nanowire density and length dispersion). It was also observed that not all gold catalyst sites acted as seeds for nanowire growth. More specifically, the nanowire to catalyst ratio can be increased significantly using silane partial pressure. The temperature dependence of the growth rate was measured in the 450 C - 700 C range, showing an activation energy of 71 kJ/mole for nanowire diameters between 20-500 nm. TEM and SEM were used to probe crystalline quality and shape of the SiNWs. Nanowires were generally 6-fold faceted with terraces appearing along the faceted sides and different families of crystalline orientations could be correlated to the nanowire diameter. We show that by monitoring the substrate orientation or patterning the substrate, vertical and horizontal growth can be controlled. Using such a technique, we have grown SiNWs that are directly connected to external electrodes. IV tests of individual SiNWs were also made with an AFM tip in contact mode for a vertically-grown (nanowires perpendicular to substrate) wire configuration. Currents up to 20-30 nA at +/- 1.5V and near-linear IV characteristics were obtained for wires ~100 nm long and ~20 nm diameter.

P3.21

Photoluminescence and Transmission Electron Microscopic Analysis of Self-Assembled InGaAs/GaAs Quantum Dots Grown by Atomic Layer Epitaxy. Dong-Ning Wang¹, Hery Susanto Djie¹, Boon-Siew Ooi¹, James C. M. Hwang¹, Xiao-Ming Fang², Ying Wu², Joel M. Fastenau², Amy W. K. Liu² and George S. N. Chu³; ¹Center of Optical Technologies, Lehigh University, Bethlehem, PA, Pennsylvania; ²IQE Inc., Bethlehem, Pennsylvania; ³Multiplex Inc., South Plainfield, New Jersey.

Recently, there has been a growing interest in self-assembled semiconductor quantum dots (QDs) grown by atomic layer epitaxy (ALE). Using ALE, InAs and GaAs sub-monolayers are alternately grown resulting in enhanced surface migration and larger dots of

better uniformity than those grown by the Stranski-Krastanow (SK) method. The ALE method can also be used to grow multiple layers of QDs to improve the gain of lasers, the responsivity of photodetectors, and the signal-to-noise ratio of hole-burning memory. However, strain buildup in the multi-layer stack may lead to the formation of misfit dislocations that is detrimental to device performance. To date, there has been no comprehensive analysis of ALE QD stacks. Here, we analyze the structural and optical properties of InGaAs/GaAs ALE QD stacks using photoluminescence (PL) and cross-sectional transmission electron microscopy (TEM). Two different device structures were analyzed: (i) an edge-emitting laser with five layers of QDs and 40-nm-thick GaAs spacers, and (ii) an inter-subband photodetector with 20 layers of QDs and 50-nm-thick GaAs spacers. At 77K, both structures gave single-peak PL at 1.19 eV and 1.15 eV, respectively. The difference in PL peak energy can be attributed to the vertical coupling of wave functions in spite of the relatively thick GaAs spacers [1]. The PL linewidth of 58 meV corresponds to a 10% variation of QD size as observed by TEM. The estimated dot density of 1011 dots/cm²/layer is higher than that of typical SK QDs. Due to the relatively thick GaAs spacer, there is no correlation between the position and distribution of QDs in adjacent layers. Consistent with single-peak PL, no wetting layer was observed by TEM. However, while no dislocation was observed from the laser structure, V-shaped dislocations were observed from the photodetector structure that contains more QD layers hence higher strain buildup. The formation of dislocations may limit the number of QD layers that can be used to improve device performance and, therefore, the signal-to-noise ratio of hole-burning memory, should be investigated further. [1] O. Gunawan, H. S. Djie, and B. S. Ooi, Phys. Rev. B 71, 205319 (2005).

P3.22

Fundamental processes involved in silicon nanocrystal growth by chemical vapor deposition. Rajesh A. Rao¹, Ramachandran Muralidhar¹, Tushar Merchant¹, Matt Stoker¹, Sherry Straub¹, Salvatore Lombardo², Rosaria Puglisi² and Giuseppe Nicotra²; ¹APRDL, Freescale Semiconductor, Inc, Austin, Texas; ²Consiglio Nazionale delle Ricerche (CNR) - Istituto per la Microelettronica e Microsistemi (IMM); Catania, Italy.

Silicon nanocrystal based devices require nanocrystal density and size distribution to be tightly controlled for optimum performance. For example, in silicon nanocrystal based memory devices, the memory window arises from a balance between Coulomb blockade and number density of nanocrystals at a fixed average separation between nanocrystals. Further, the area fraction needs to be controlled to minimize lateral charge transport in the nanocrystal layer. Chemical vapor deposition processes show promise in achieving these size, density, and coverage objectives. Hitherto, it was believed that nanocrystal formation by CVD proceeds solely by island growth. This growth tends to be inherently self organized because adatom depletion around growing nuclei suppresses additional nucleation in their immediate vicinity, thereby ensuring that nanocrystals are well separated. In this paper we show that such self organized growth by CVD is observed only at higher temperatures or very low pressures such as in UHVCVD where diffusion processes are fast compared to deposition rates. Plan view SEM and EFTEM images are used to accurately assess the deposition characteristics down to a size of 1nm. At lower temperatures and higher deposition rates such as seen in low pressure CVD processes, clearly defined islands are not observed, instead an incoherent network is observed on the surface, which on subsequent annealing at higher temperatures, forms well spaced and organized nanocrystals. Thus, the self organization is observed to take place during this annealing phase. However, the final nanocrystal characteristics subsequent to annealing seem to evolve from the template of the initially deposited layer. Thus, the two processes of initial deposition and subsequent high temperature inert annealing may be employed to engineer nanocrystals of the desired characteristics and we demonstrate tight distributions for nanocrystal size and spacing obtained by nucleation and subsequent annealing. The characteristics of nanocrystals are superior to those obtained by recrystallization of an amorphous silicon layer.

P3.23

Properties of ZnO nanostructures obtained by magnetron sputtering and low energy ion implantation. Iulia C. Muntele, Sergey Sarkisov, Claudiu I. Muntele, Paul Thevenard and Daryush Ila; Physics, Alabama A&M University, Normal, Alabama.

Zinc oxide is one of the most interesting wide band-gap semiconductors, due to its 3.3eV direct band-gap and the large exciton energy of 60 meV at 300 K. It is easily n-type doped while p-type doping is much more difficult, as in equivalent large band-gap semiconductors like GaN. This is due to the low dielectric constant and very contracted impurity orbitals. Because of its optical, electrical, and piezoelectric properties, ZnO is involved in many applications such as: UV light emitters, UV lasers, non linear optics, transparent electronics, solar cells, MEMS devices, gas sensors, field

emission, spintronics. Due to quantum confinement effects, the ability to fabricate ZnO at controlled nanocluster sizes enhanced the potential for new applications. Variable size ZnO nanostructures embedded in silica substrate were obtained by magnetron sputtering as well as by low energy ion implantation. The samples obtained by both methods were subject to either post annealing or post bombardment treatment. The size, distribution and optical properties of the nanostructures were obtained by atomic force microscopy and optical spectroscopy measurements. Preliminary results show that zinc oxide is stoichiometric. High-energy irradiations led to ZnO nanoneedle synthesis on SiO₂. A strong ultra-violet near band-edge emission is observed at 3.12 and 3.23 eV generally attributed to exciton levels in bulk ZnO. The optical band gap of ZnO nanostructures shifts towards higher energy as the cluster size decreases. Quantum confinement effects in ZnO quantum dots (QDs) of few nanometers can lead to new applications in ultraviolet luminescent devices particularly when QDs are localized in very high electric field. The confinement of exciton wave functions increases the energy of the band gap compared with that in the bulk and divides it into a set of discrete levels. Quantum confinement has to be observed when the size of the nanoclusters approaches the Bohr radius of the exciton.

P3.24

Room Temperature Synthesis of Highly Fluorescent Zinc Blende CdSe Nanocrystals. Kushan Biswas², Rongfu Li¹,

Jeunghoon Lee¹ and Fotios Papadimitrakopoulos^{1,2}; ¹Institute of Materials Science, Polymer Program, Univ. of Conn., Storrs, Storrs, Connecticut; ²Department of Chemistry, University of Connecticut, Storrs, Connecticut.

Size-dependent optical and electronic properties of semiconductor nanostructures have recently attracted considerable attention. Control over size and shape has been successfully demonstrated in the high temperature synthesis of CdSe nanocrystals (NCs). The need however, to employ high boiling-point organic solvents and inert atmospheric conditions for synthesis of these NCs can negatively affect both price and their potential environmental impact. For this we employed a water phase synthesis of CdSe NCs that utilizes CdCl₂, Se, and NaOH as reagents. X-ray diffraction results show that the CdSe NCs are of zinc blende crystal structure. These non-luminescent NCs were subjected to a low-temperature (< 85 Celsius degree) chemical etching in a water-soluble amine-based etching solution, which gives rise to a strong photoluminescence due to de-aggregation and etching away of surface imperfections that contribute to non-radiative recombination. During such low temperature etching conditions, the CdSe zinc blende crystal structure was maintained. These CdSe NCs exhibit the same band edge photoluminescence (PL) and lack of deep-trap emission, similar to those obtained from the high temperature synthesis of wurtzite CdSe NCs. Zinc blende CdSe NCs with narrow size distribution and strong PL emission (FWHM 25-35 nm and quantum efficiency up to 50%) were obtained by adjusting the etching conditions. Under certain conditions, very narrow blue emission from small CdSe NCs (439 nm with FWHM 15 nm) was also obtained.

P3.25

Simulations of the Optical Properties of Silicon Nanoparticles Embedded in Silicon Nitride. Sebastien Hamel¹, Andrew Williamson¹, Giulia Galli¹, Luca Dal Negro², J. H. Yi², J. Michel² and Lionel Kimerling²; ¹PAT/H-div, Lawrence Livermore National Laboratory, Livermore, California; ²MIT, Cambridge, Massachusetts.

There is currently strong interest in the material science community in the optical properties of silicon nanoparticles embedded in silicon nitride. These nanostructures are CMOS-compatible materials which exhibit efficient and fast light emission. The optical properties of these embedded silicon nanoparticles are studied using first-principles Density Functional Theory simulations. We present simulations of the structural, electronic and optical properties of nitrogen-doped silicon nanoparticles both in the gas phase and embedded in a silicon nitride environment. These simulations point to the crucial role played by nitrogen atoms bonded to the surface of small (~1nm) silicon nanoparticles in the light emission mechanism of SiN_x films. We compare the calculated optical gaps and radiative lifetimes of the nanoparticles with recent experimental measurements of light-emitting silicon-rich silicon nitride films obtained by PE-CVD deposition followed by low temperature (500-900 C) thermal annealing.

P3.26

Artificial Molecules of Ga and In with As and P: Correlations Between Structure, Composition and Optoelectronic Properties. Liudmila A. Pozhar¹, Alan T. Yeates², Frank Szmulowicz² and William C. Mitchel²; ¹Chemistry, Western Kentucky University, Bowling Green, Kentucky; ²Materials and Manufacturing Directorate, Air Force Research Lab, Wright-Patterson AFB, Ohio.

Virtual (i.e., fundamental theory-based, computational) synthesis of

small stable atomic clusters (or artificial molecules) allows development of atomic clusters with pre-designed physical, and in particular, optoelectronic properties. In this work, manipulations with the spatial constraints, cluster size, form and composition in the process of virtual synthesis have been used to study possible quantum confinement effects on optoelectronic properties of artificial molecules so synthesized, with an ultimate goal to identify the molecules with desirable optoelectronic properties for various applications. Thus, a range of artificial pyramidal molecules composed of Ga or In atoms with atoms of As and P have been synthesized virtually using restricted Hartree-Fock (RHF) - open shell Hartree Fock (ROHF) and multi configuration self-consistent field (MCSCF) methods. In agreement with previous studies and recent experimental data, such pyramidal clusters have been identified as promising templates for units of sub-nanoscale heterostructures for development of novel tunable sensors and sources. The electronic energy spectra (EES) and direct optical transition energies (OTEs) of these clusters have been investigated and correlated with their structure and composition. Comparison of the EES and OTEs of smaller clusters (such as the smallest stable pre-designed pyramidal molecules containing 3 Ga or In atoms and one atom of As or P, and their vacuum counterparts synthesized in absence of any spatial constraints) with those of larger clusters has made possible elucidation of the effects of spatial constraints and cluster size on the OTEs and electronic band formation. The smallest 4-atomic pyramidal molecules of Ga/In with an atom of As or P can also be used as building blocks to construct computationally large stable clusters (up to micron-size ones) of Ga or In with As in the process of virtual synthesis, thus providing a convenient tool to tackle a problem of across-the-scale modeling of materials.

P3.27

Light transport through semiconductor nanowires.

Pavel S. Dorozhkin^{1,2}, Sergei A. Saunin¹, Vasily V. Gavriluyk¹, Igor Dushkin¹, Yoshio Bando² and Dmitrii Golberg²; ¹NT-MDT Co., Zelenograd, Moscow, Russian Federation; ²National Institute for Materials Science, Tsukuba, Ibaraki, Japan.

While having their electrical transport properties thoroughly investigated, submicron-sized wires (or nanowires) have only recently acquired attention from the point of view of transporting light through them [1]. Semiconductor nanowires uniquely combine optical properties of constituting material and light guiding properties of a sub-wavelength waveguide. Nanowires do not only transfer light along their length but also affect the light wavelength through absorption and re-emission processes. In this report we study light waveguiding properties of semiconductor nanowires of different sizes and materials (CdSe, GaN, InP etc.). We use the NTEGRA Spectra system by NT-MDT that combines SNOM, AFM, confocal microscope and Raman spectroscopy in a single setup. Light of different wavelengths is injected into an individual nanowire either by a SNOM fiber tip or by a diffraction limited (~400 nm) spot of a high aperture objective. The point of light injection is chosen to be either nanowire end, body or defect. A portion of light transmitted through nanowire is collected from its end by a high aperture objective, and analyzed by a spectrometer. We study spectra of transmitted light with respect to the injected light wavelength. We also estimate light transmission efficiency for nanowires of different diameters and materials paying attention on the role of defects on the transmission coefficient. [1] C.J. Barrelet, A.B. Greytak, C.M. Lieber, Nano Lett. 4, 1981 (2004)

P3.28

The Formation of Tungsten Oxide Nanowires Using Thermal Oxidation with Acetylene. Guan Yow Chen, Cristina Guisca, David C. Cox, Vlad Stolojan and S. R. P. Silva; Nano-Electronic Centre, Advanced Technology Institute, University of Surrey, Guildford, Surrey, United Kingdom.

Tungsten oxide nanowires are grown using thermal oxidation with acetylene on tungsten wire. By heating a tungsten wire in a nitrogen ambient, tungsten oxide nanowires, with diameters between 5 to 15nm and lengths of hundreds of nanometers long can be synthesized. We found however that the yield can be significantly increased with the addition of acetylene. The growth is investigated as a function of temperature, acetylene concentration and time. The nanowires are characterized using scanning and transmission electron microscopy and electron energy loss spectroscopy. A possible synthesis mechanism taking into account of the effect of hydrocarbon addition is proposed.

P3.29

Nanometer Scale Noble Metal Structures in Parallel Arrays with Molecular Interparticle Spacing on Si(001).

Jiun-Pyng You¹, Regina Ragan¹, Sehun Kim², Yong Chen², Xuema Li² and R. Stanley Williams²; ¹UC-Irvine, Irvine, California; ²Hewlett-Packard Laboratories, Palo Alto, California.

Noble metal nanocrystals (NC) and nanowires (NW) have

demonstrated the ability for detection of biological molecules such as DNA and proteins in femtomolar quantities and the strong near field coupling between closely spaced particles may lead to a surface enhanced Raman signal that enables single molecule detection. Substantial progress has been made; however, major challenges still exist in fabricating large-area, high-density, and uniformly-sized ensembles of single crystal metallic NC/NW. Hexagonal rare earth silicide (RESi_{2-x}) nanowires have been demonstrated to self-assemble into one dimensional nanostructure during epitaxial growth on Si(001) substrates. The evolution of one dimensional structures of RESi_{2-x} has been attributed to an anisotropic lattice mismatch with Si[110]. Using rare earth disilicide nanowires that self-assemble in unidirectional dense arrays (10^{11} cm^{-2}) as a template, we have fabricated parallel arrays of Pt nanocrystals and Pt and Au nanowires with the average size in diameter of 5 nm and a size distribution of 8 nm (FWHM) over large area ($> 1 \mu\text{m}^2$) calculated by Soft Imaging System (analySIS). The diameters (width) and interparticle spacings of NC (NW) are approximately 3-10 nm. Scanning electron microscopy images taken after reactive ion etching demonstrate the ability to select nanowires or nanocrystals as a function of Pt coverage. The Pt clusters on the nanowires form planar structures, shown in scanning tunneling microscopy images. According to density function theory, the planar configuration of Pt clusters has low strain energy with the NW. So, Pt atoms may energetically assemble into particular cluster size on NW surface in order to reduce the strain energy coming from the lattice mismatch and thus can be used to fabricate NC with a narrow size distribution.

P3.30

Structure of Zn-Te-Se System with Submonolayer Insertion of ZnTe Grown by Migration Enhanced Epitaxy. Yinyan Gong¹, H. F. Yan¹, I. L. Kuskovsky², I. C. Noyan¹, G. F. Neumark¹ and M. C. Tamargo³; ¹Columbia University, New York, New York; ²Queens College of CUNY, New York, New York; ³City College of CUNY, New York, New York.

We have studied, via high resolution x-ray diffraction (HRXRD) as well as optical absorption (OA) and reflection measurements, of ZnSe samples grown by molecular beam epitaxy with insertion of planar- (δ -) regions of both N as acceptor dopant and Te as a "co-dopant" to facilitate the p-type doping; the structures of interest contained three contiguous δ -layers, and are referred to as δ^3 -ZnSe:(Te,N). To study the effect of N on the structure, samples grown under a similar condition without N have also been investigated, are referred to as δ^3 -ZnSe:Te. In practice, the deposition is carried out by molecular beam epitaxy with the δ -regions deposited on top of nominally pure ZnSe layers ("spacers"), and where the δ -layers are deposited on Zn terminated surfaces. We note that to enhance surface diffusion of Te, migration enhanced epitaxy was adopted in the growth of the δ -regions, i.e. Te is deposited in the absence of Zn flux. Moreover, the deposition times of the δ -regions (5s) resulted in depositions of submonolayer amounts. Note the δ -regions, of three δ -layers, will hence be referred to as " δ -layers". Details of the growth procedure of our samples have been described elsewhere. Structural parameters, i.e. the period, thicknesses and alloy compositions of the spacers and the " δ -layers", were extracted by simulating the experimental diffraction curves of the x-ray measurements. For our samples, the substrate is a thick GaAs single crystal so the reflection is dynamical. The epitaxial film has an overall thickness about $0.6\mu\text{m}$, close to the extinction depth. To obtain the best result we simulate (004) ω -2 θ diffraction curves of all our samples (adopting a dynamical diffraction model). The results show that for both type of samples only the " δ -layers" are rich in ZnTe while the "spacers" have only a low Te concentration. The thickness of " δ -layers" is about 0.25ML (1ML = half unit cell) for all the samples. Finally, no noticeable differences in structural parameters are observed between samples with and without N. The HRXRD results are in good agreement with those of optical absorption and reflection measurements. Moreover, the absorption and reflection results show that our samples largely preserve the optical properties of the host material (ZnSe).

P3.31

Dopant Activation of Boron-implanted Silicon Nanowires by Non-melt Excimer Laser Annealing Technique. Li Xu¹, Yaoling Pan³, Nathan Cheung² and Costas P. Grigoropoulos¹; ¹Mechanical Engineering Department, University of California, Berkeley, Berkeley, California; ²Electrical Engineering Department, University of California, Berkeley, California; ³Nanosys Inc., Palo Alto, California.

The field effect transistor (FET) on silicon nanowires is promising to further scale down the size of modern CMOS devices. This work will emphasize on the laser annealing technique for dopant activation of silicon nanowires. BF₂ ions were implanted into nanowires on quartz substrate with the dose of 2×10^{15} at 16keV. XeCl excimer laser with the wavelength of 248nm and FWHM of 38ns was used to anneal the nanowires. Simulation was done to model the optical absorption of the nanowires and heat transfer in the wires and between the wires and

the surrounding. SEM images were taken to inspect the annealed nanowires structure. Resistors were made to examine the dopant activation by measuring the voltage-current performance, and the result was also compared with that annealed by rapid thermal annealing technique (RTA)

P3.32

Photoinduced Fluorescence Enhancement in Mono- and Multilayer Films of CdSe/ZnS Quantum Dots.

Takafumi Uematsu, Shinya Maenosono and Yukio Yamaguchi; Chemical System Engineering, University of Tokyo, Tokyo, Japan.

Reversible photoinduced fluorescence enhancement (PFE) has been investigated as one of the interesting properties of ensembles of CdSe/ZnS core/shell quantum dots (QDs). The fluorescence quantum yields (QY) of the QD film increased by continuous irradiation. In our previous work, it was found that the rate of increase of the QY increased with increasing proximity of QDs when a QD submonolayer with a SiO_x protective layer was irradiated. The result suggests that photoionization of QDs and the ejected electrons, producing suppression of the ionization probability of the remaining neutral QDs. However, the mechanism has not been clarified yet. Here we report about PFE behavior in mono- and multilayer films of CdSe/ZnS core/shell quantum dots (QDs) on glass substrates using various intensities and wavelengths of excitation light. CdSe/ZnS QDs capped with tri-n-octylphosphine oxide (TOPO) were produced using colloidal chemical synthesis and mono- and multilayer QD films were fabricated on glass substrates by spin-coating. The QY of the QD films were observed in a dry nitrogen atmosphere by confocal laser scanning microscopy. The QY of the QD monolayer was largely enhanced by continuous irradiation, while the QD multilayer showed a small enhancement of the QY. In addition, the shorter the excitation wavelength, the more pronounced the PFE. The rate of increase of the QY increased with decreasing excitation intensities at any wavelength. These dependences were observed in both mono- and multilayer films. A comparison of the results for mono- and multilayer films suggests that the photoejection of electrons to the substrate is the origin of PFE. The electrons lead to suppression of the ionization probability of the remaining neutral QDs and then the total QY of the QD monolayer increases. On the other hand, the electrons trapped on the substrate do not affect the QY of the upper layer of QD multilayer because the upper layer is far enough from the substrate. Assuming the charging effect of electrons trapped in the substrate, a phenomenological model is proposed to explain all the experimental results; that is, the dependence on the intensity and wavelength of excitation light, and the qualitative difference in PFE behavior between mono- and multilayer films.

P3.33

Novel inorganic-organic hybrid semiconductors, II-VI(en)0.5, with unusual electronic and optical properties*. Yong Zhang¹,

Gustavo M. Dalpian¹, Brian Fluegel¹, Su-Huai Wei¹, Angelo Mascarenhas¹, Xiaoying Huang² and Jing Li²; ¹National Renewable Energy Lab, Golden, Colorado; ²Rutgers University, Piscataway, New Jersey.

A new family of inorganic-organic hybrid nanostructures based on II-VI semiconductors has recently been synthesized.[1] These are fully ordered crystals without the structural fluctuation typically found in other hybrid materials and nanostructures. We have performed a systematic experimental and theoretical study on a subset of these hybrid materials, namely, α - and β -MQ(en)0.5 (M = Zn, Cd; Q = S, Se, Te; en = ethylenediamine; α and β indicating two phases). Experimentally, we have shown (1) a giant band gap shift as large as ~ 1.5 eV from that of the II-VI parent [1,2]; (2) a strong free-exciton absorption on the order of 10^6 cm^{-1} [3]; (3) exciton-polariton emission at low and room temperature [3]; (4) sharp Raman lines with linewidth as small as that typically observed in a binary semiconductors[1]. Theoretically, we have shown that (1) the quantum confinement effect of the organic molecule to the inorganic slab manifests itself in a unusual manner that is not exhibited in other quantum confined structures, and thus provides a novel approach to tuning the physical properties of the hybrid material[3]; (2) the exciton binding energy is greatly increased and the dielectric constants are significantly decreased, compared to that in the II-VI semiconductor[3]; (3) the total energy of the β phase is usually lower than that of the α phase with one exception for ZnTe(en)0.5, which explains why so far the β phase has only been synthesized for ZnTe(en)0.5[4]; (4) certain hybrid structures might be suitable for making transparent p-type conductors based on the band-alignment consideration.[3]. References: [1] X.-Y. Huang, J. Li, Y. Zhang, and A. Mascarenhas, JACS 125, 7049 (2003). [2] B. Fluegel, Y. Zhang, A. Mascarenhas, X.-Y. Huang, and J. Li, PRB 70, 205308 (2004). [3] Y. Zhang, G. M. Dalpian, B. Fluegel, Su-Huai Wei, A. Mascarenhas, X.-Y. Huang, J. Li, and W.-L. Wang (unpublished). [4] G. M. Dalpian et al. (unpublished). *Work supported by DOE, NREL DDRD, and NSF.

P3.34

Oxygen-adsorption effect on magnetoresistance in disordered nanographite network. Katsunori Takahara, Kazuyuki Takai and Toshiaki Enoki; Chemistry, Tokyo Institute of Technology, Tokyo, Japan.

Activated Carbon Fibers (ACFs), which consist of a 3D disordered network of nanographite metallic domains, have huge specific surface areas of nanopores, which can accommodate a large volume of guest species. Around the edges of the nanographene sheets, there are localized spins for which non-bonding π -electronic state of edge origin are responsible, in spite of diamagnetic features of bulk graphite. The adsorption of guest species, such as water, bromine, oxygen, etc. into the nanopores has been reported to affect the magnetic features of the edge-state spins. In the present work, we investigate the magnetotransport of ACFs in relation to the adsorption of magnetic oxygen molecules, which is compared with that of nonmagnetic guest species, helium, nitrogen, and argon. Heat-treatment of the ACFs samples (specific surface areas of 2000 m²/g) in pristine state was carried out in vacuum with a vacuum rate well below 1×10^{-6} Torr at 473 K for 30 h, in order to eliminate adsorbed molecules. The temperature dependence of resistivity ρ obeys the relation of $\rho = \rho_0 \exp\{-(T_0/T)^{1/2}\}$ indicating that the inter-nanographite-domain electron transport is subjected to the Coulomb-gap-type variable range hopping in the Anderson insulator. A large positive magnetoresistance with its value being a semi-quadratic function of the field applied is observed, which indeed goes up to ca. 400 % at 3 K under the field of 15 T in pristine state and also under the presence of nonmagnetic guest molecules, helium, nitrogen, and argon. The large positive magnetoresistance can be explained in terms of the spin polarization effect, in which the electron in a domain is allowed to hop to the state of the adjacent domain only in case that it has the spin state with its spin orientation being opposite to that of the electron which has been already accommodated. Uptake of magnetic oxygen molecules reduces the magnitude of the magnetoresistance by ca. 50 % with its field dependent feature remaining unchanged. This suggests that the antiferromagnetic internal field of oxygen molecules affects the magnetotransport of graphitic π -electrons, resulting in the degradation of the spin polarization effect, as the oxygen molecules condensed in the nanopores are antiferromagnetically ordered with disordered features. From the change in the magnetoresistance upon oxygen adsorption, the strength of the internal field acting on the π -electrons is estimated as ca. 20 K, which is two orders of magnitude larger than that expected from the contribution of the dipole-dipole interaction. This finding, which demonstrates an important role of exchange interaction in the interaction between the graphitic π -electrons and the oxygen spins, suggests that the adsorbed oxygen molecules are weakly bonded to graphitic planes through charge transfer.

P3.35

Telecommunication Band Photoluminescence of Site-Controlled InAs/InP Quantum Dots. Hai-Zhi Song¹, Tatsuya Usuki¹, Shinichi Hirose¹, Kazuya Takemoto¹, Yoshiaki Nakata¹, Naoki Yokoyama¹ and Yoshiki Sakuma²; ¹Nanotechnology Research Center, Fujitsu Lab. Ltd., Atsugi, Kanagawa 243-0197, Japan; ²National Institute for Materials Science (NIMS), Tsukuba, Ibaraki 305-0044, Japan.

Site-control of self-assembled quantum dots (QDs) is crucially required in the applications to quantum computation and quantum information. To precisely control the site of QDs, we developed a technique consisting of atomic-force microscopic lithography to form oxide dots, wet chemical etching to remove oxides and form holes, and epitaxial regrowth to form QDs on the site of holes. By this method together with a double-cap process in regrowing QDs using metalorganic chemical vapor deposition, we fabricated ordered InAs/InP QD arrays in which there is exactly one dot on one expected site. These InAs/InP QDs can emit photons with wavelength in the range of optical fiber telecommunication bands, i.e. 1300-1550 nm. The observed single dot photoluminescence (PL) from these QDs provides possibility of using them as a candidate of site-controlled single photon sources for quantum communication in telecommunication bands. In order to realize single photon emission from our site-controlled InAs/InP QDs, we need to investigate their detailed single dot PL properties. Firstly, the single dot PL distributes in a range varying with the average effective height of QDs, which is controlled by the capping process in metalorganic chemical vapor deposition. This dependence is in agreement with the theoretical calculation using a quantum disk model. At 10K, the excitation density dependence of the single dot PL intensity varies from linear to quadratic for different QDs. It is suggested that nonradiative recombination plays an important role. Different QDs may have different number of nonradiative centers. With increasing temperature, the excitation density dependence of single dot PL intensity becomes more and more quadratic. In the mean time, the PL

intensity under the same excitation density keeps nearly constant at low temperatures but is thermally quenched at higher temperatures. These results can be well explained by the above-mentioned nonradiative recombination, which is considered temperature independent, and a thermally activated nonradiative process. The former arises from some impurities/defects in the vicinity of QDs and the latter is the result of surface effect and/or phonon scattering as in normal QDs [1]. In contrast, the strong and site-independent PL from the wetting layer does not show detectable effect of impurities/defects, indicating that the impurity/defects exist mainly at the site of QDs. It is thus not difficult to further improve the quality of single dot luminescence for efficient single photon emission by optimizing the fabrication process, e.g. removing oxides without chemical etching. [1] Ignatiev et al.. Phys. Rev. B 61, 15633 (2000).

P3.36

Epitaxial growth of GaN nanowires on the GaN/AlN double buffer layers. Yun-Mo Sung¹, Jung-Chul Lee¹ and Dae-Hee Kim²; ¹Materials Sci. & Eng., Korea University, Seoul, South Korea; ²Mater. Sci. & Eng., Daejin Univ., Pochun-si, South Korea.

GaN, a III-V semiconductor, showing a wide energy band gap and direct transition, has been well known for the effective blue light emission. The GaN in thin film forms has been widely used for light emitting diode (LED) and laser diode (LD) applications. GaN in nanowire forms shows reduced defect density and size confinement effect, and thus showing superior light emitting properties compared to that in thin film forms. In this study Si wafers were used for vapor-liquid-solid (VLS) growth of GaN nanowires and GaN/AlN double buffer layer was employed to minimize the lattice mismatch between GaN nanowires and Si substrates and to induce epitaxial growth of GaN nanowires. The GaN/AlN double buffer layers were formed using reactive RF-sputtering and they showed strong c-axis oriented crystal growth. Scanning electron microscopy (SEM) analyses on the GaN nanowires grown on GaN/AlN/Si substrates showed formation of straight nanowires with ~ 20 -80 nm diameter, while those on the GaN nanowires on bare Si wafers showed formation of tangled nanowires with non-uniform diameters. Transmission electron microscopy (TEM) analyses on the GaN nanowires grown on GaN/AlN/Si showed high crystallinity with negligible defect concentration. Furthermore, GaN nanowires grown on GaN/AlN/Si showed a short wavelength (367.2 nm) and high intensity photoluminescence (PL) emission compared to those grown on bare Si substrates. By introducing GaN/AlN double buffer layers the crystallinity and the PL properties of GaN nanowires were successfully improved.

P3.37

Alloying kinetics of CdSe/ZnSe core/shell nanocrystal quantum dots. Yun-Mo Sung, Yong-Ji Lee and Kyung-Soo Park; Materials Sci. & Eng., Korea University, Seoul, South Korea.

Semiconductor nanocrystals have been intensively studied for their unique photo absorption and emission characteristics. They show specific quantum confinement effects and thus reveal visible range emission depending upon each particle size. To improve quantum efficiency a semiconductor nanocrystal core is often covered with another semiconductor shell with a high-energy band gap. Some research results show that alloyed semiconductors possess superior optical properties compared to core/shell structures. Also, it is easy to control the wave length of light emission simply by controlling the alloy composition. However, sometimes alloying of semiconductors with different atomic size is incomplete and alloying effect is not fully achieved. In this study CdSe/ZnSe core/shell nanocrystals were synthesized and further heated at different temperatures for different time periods. The kinetics of alloying was investigated using X-ray diffraction (XRD). The intensities of XRD peaks from CdSe and ZnSe decreased with alloying temperature and time. The XRD quantitative analyses were performed to obtain the volume fraction of alloying and these values analyses. The Johnson-Mehl-Avrami (JMA) plots were created and Arrhenius plots were also produced using the y-intercepts of JMA plots. The activation energy for alloying was obtained and discussed based upon diffusion of Cd²⁺ ions in the CdSe-ZnSe system. Also, a kinetics equation for Cd²⁺ ion diffusion was derived based upon a diffusion couple model. The diffusion rate of Cd²⁺ ions in ZnSe was estimated and the activation energy value for diffusion was determined. The activation energy value was compared with those from Arrhenius plots.

P3.38

The Luminescence of Single ZnO Microrod. Yichun Lu², Dongxu Zhao³ and Richard Mu¹; ¹Physics, Fisk University, Nashville, TN, Tennessee; ²Northeast Normal University, Changchun, China; ³The Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun, China.

Room-temperature P-band emission induced by an exciton-exciton collision process was observed in single ZnO microrod. Excitation-intensity-dependent photoluminescence (PL) measurements were performed. The excitation intensity-dependent measurement illustrated that the P-band emission could occur at much lower excitation intensity than that reported in literature. When the excitation intensity exceeded 4.0 kW/cm² the intensity of the P band dominated the PL spectra. The regularly spaced sharp lines can be seen clearly in the spectra, which results from the Fabry-Perot cavity that was consist of three pairs of parallel faces of hexagonal ZnO microrods.

P3.39

Abstract Withdrawn

P3.40

Density Functional Theory Study of Nucleation and Crystal Growth of the CdSe Nanocrystals. Jane Rempel¹, Bernhardt L.

Trout¹, Mounji G. Bawendi² and Klavs F. Jensen¹; ¹Chemical Engineering, MIT, Cambridge, Massachusetts; ²Chemistry, MIT, Cambridge, Massachusetts.

Over the past decade, colloidal semiconductor nanocrystals have sparked tremendous interest and considerable efforts have been directed towards the development of synthetic routes. However, the exact reaction mechanisms leading to crystal growth in these systems are still poorly understood. In the present work, we utilize first principles calculations within the framework of density functional theory (DFT-GGA) to quantitatively study the nucleation and growth mechanisms of the CdSe nanocrystals formed via Cd salt and Se phosphineoxide precursor routes. First, we investigate the elementary reaction steps that occur in the organic medium during early stages of nucleation: mechanisms for the reduction of the Cd precursor, formation of the active growth species, and formation of the small CdSe clusters. Second, we examine the fundamental reactions that occur at the nanocrystal surfaces at later stages of crystal growth. We consider the homoepitaxy reactions on several bulk terminated relaxed and reconstructed wurtzite CdSe surfaces that are important during crystal growth. We also explore competitive ligand binding on the same surfaces and the influence ligand binding has on crystal growth. Finally, we relate our findings to the experimental observations, in particular, shape anisotropy.

P3.41

Quantum Dot Targeting to Surface Proteins using Biotin Ligase. Mark R. Howarth¹, Jonathan Zimmer¹, Daniel J.-F.

Chinnapan¹, Pieter C. Dorrestein², Kimberley Gerrow³, Melanie R. Grandy¹, Neil L. Kelleher², Alaa El-Husseini³, Keizo Takao⁴, Yasunori Hayashi⁴, Mounji Bawendi¹ and Alice Y. Ting¹; ¹Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts; ²Department of Chemistry, University of Illinois Urbana-Champaign, Urbana, Illinois; ³Department of Psychiatry, the Brain Research Center, University of British Columbia, Vancouver, British Columbia, Canada; ⁴RIKEN-MIT Neuroscience Research Center, The Picower Center for Learning and Memory, Department of Brain and Cognitive Sciences, Massachusetts Institute of Technology, Cambridge, Massachusetts.

E. coli biotin ligase site-specifically biotinylates a lysine sidechain within a 15-amino acid acceptor peptide (AP) sequence. Mammalian cell surface proteins tagged with AP can be biotinylated by biotin ligase added to the medium, while endogenous proteins remain unmodified. The biotin group then serves as a handle for targeting streptavidin-conjugated quantum dots (QDs). This helps to address two deficiencies of antibody-based labeling: the size of the QD-conjugate after antibody attachment and the instability of many antibody-antigen interactions. Labeling with biotin ligase requires only 2 minutes, is specific for the AP-tagged protein, and is highly sensitive. We used biotin ligase labeling to perform time-lapse imaging of single QDs bound to AP-tagged AMPA receptors in neurons. One problem with the use of streptavidin-conjugated QDs, is that each streptavidin can bind 4 biotinylated surface proteins and so cause cross-linking. To combat this, we have engineered a chimeric streptavidin tetramer with a single functional biotin binding site. This "monovalent" streptavidin has the same affinity and off-rate for biotin as wild-type streptavidin. Labeling of biotinylated cell surface proteins with dye-conjugated monovalent streptavidin produced stable binding but did not cause clustering. Conjugation of monovalent streptavidin to QDs should produce QDs that are small, do not cross-link, and show binding that is stable over hours.

P3.42

Quantum Dots as Energy Acceptors: Studies and Implications Using Long Lifetime Metal Chelate Donor Fluorophores.

Aaron Clapp¹, Igor Medintz² and Hedi Mattoussi¹; ¹Optical Sciences Division, Naval Research Laboratory, Washington, District of Columbia; ²Center for Bio/Molecular Science and Engineering, Naval

Research Laboratory, Washington, District of Columbia.

We have previously shown that water-soluble CdSe-ZnS core-shell QDs function as efficient energy donors in fluorescence resonance energy transfer (FRET) systems, including a prototype biosensor for the explosive TNT.^{1,2} These previous studies have exploited the inherent benefits of using QDs over conventional organic fluorophores for FRET including the flexibility to adjust the emission properties of QDs to better overlap with an acceptor's absorption profile and the ability to position multiple acceptors around a QD surface thereby increasing the effective FRET efficiency. In this study we further investigate the potential utility of QDs as energy acceptors. Distinct dye donors were used in conjunction with different emission QD acceptors where we varied the proportion of dye-labeled proteins in the QD-conjugate to increase the number of dye donors interacting with each QD acceptor. Steady-state fluorescence measurements showed no apparent non-radiative energy transfer from dye to QD in all systems investigated. These findings were corroborated by time-resolved fluorescence measurements where no apparent change in donor or acceptor lifetimes was measured compared to isolated fluorophores. These results suggested that relatively short lifetime organic fluorophores are not ideal energy donors to QDs having a longer exciton lifetime.³ To test the validity of these observations, long lifetime metal chelates (e.g., Lanthanides, Ru, etc.) having triplet state decays on the order of micro- to milliseconds were used as potential energy donors. These dyes were attached to proteins appended with a C-terminal oligohistidine tail and self-assembled on hydrophilic CdSe-ZnS QDs. We evaluate potential non-radiative energy transfer from a metal chelate dye to a QD in this configuration, including effects of the dye lifetime (in comparison to the QD) and dye-to-QD ratios using both steady-state and time resolved spectroscopy. 1. A.R. Clapp et al., J. Am. Chem. Soc. 126, 301 (2004). 2. E.R. Goldman et al. J. Am. Chem. Soc. 127, 6744-6751 (2005). 3. A.R. Clapp et al. J. Am. Chem. Soc. 127, 1242-1250 (2005).

SESSION P4: Synthesis Shape Control and Application in Biology

Chairs: Uri Banin and Jinwoo Cheon
Tuesday Morning, November 29, 2005
Room 210 (Hynes)

8:30 AM *P4.1

Metal-Semiconductor Nano-Dumbbells; Synthesis and Properties. Uri Banin, Physical Chemistry and the Center for Nanoscience and Nanotechnology, Hebrew University of Jerusalem, Jerusalem, Israel.

An important frontier in nanocrystal research is the growth of composites of different materials in the same nanostructure as means of increasing functionality. One particularly interesting combination of materials is that of a metal and semiconductor in the same nanocrystal where metal tips can provide anchor points for electrical connections and for self assembly. We shall present the growth of metal tips on the apexes of semiconductor rods, forming 'nano-dumbbells' (NDB's). From the viewpoint of self-assembly they are equivalent to bi-functional molecules such as the di-thiols manifesting two sided chemical connectivity. The formation of rods with a metal tip on one side will also be described. The mechanism for growth occurring through a unique ripening process leading to a transition from two to one sided growth will be discussed. Such systems manifest a unique model for a metal-semiconductor nanojunction. A fundamental and intriguing problem associated with such systems is the mechanical and electronic properties of the metal-SC nanojunctions. The electronic properties of metal-semiconductor nanojunctions were investigated by scanning tunneling spectroscopy of the gold-tipped CdSe rods and the unique electronic properties of the system will be described.

9:00 AM P4.2

A Microfabricated Gas-Liquid Segmented Flow Reactor for High Temperature Synthesis: The Case of CdSe Quantum Dots. Brian K. Yen¹, Axel Guenther², Martin A. Schmidt³, Klavs F. Jensen² and Mounji G. Bawendi¹; ¹Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts; ²Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; ³Microsystems Technology Laboratories, Massachusetts Institute of Technology, Cambridge, Massachusetts.

We present a silicon-based microreactor that incorporates both gas-liquid segmented flow and multiple temperature zones. In contrast to single-phase flow designs, which are limited by slow diffusive mixing of reactants and broad residence time distributions (RTDs), recirculation within slugs in gas-liquid segmented flow results in both rapid mixing and narrow RTDs. As a model system, monodisperse CdSe quantum dots (QDs) with excellent optical properties are prepared using our reactor. With our design, it is possible to localize multiple temperature zones for QD growth (>260°C) and reaction

quenching (<700C) on the chip. The QD size distributions and reaction yields are superior to those attainable in single-phase flow, with the improvement significantly more pronounced at short times. Since the improvement is a direct consequence of the mixing and RTD features of segmented flow, the reactor design provides a means of greatly reducing the time required to produce high-quality particles compared to existing single-phase approaches. Furthermore, the reactor is applicable to a variety of nanoparticle chemistries because it offers access to a wide range of reaction timescales without sacrificing acceptable size distributions.

9:15 AM P4.3

Bifunctional Magnetic–Optical Nanocomposites From Cobalt–Cadmium Selenide Core–Shell Nanocrystals.

Thomas M Cameron, Hyungrak Kim, Marc Achermann, Laurent P. Balet, Joe D. Thompson, Donald J. Werder, Jennifer A. Hollingsworth and Victor I. Klimov; Los Alamos National Laboratory, Los Alamos, New Mexico.

The successful integration of different nanocrystalline materials into a nanocomposite structure provides the possibility of attaining one multifunctional material displaying properties of the parent materials. Here we report on the synthesis and characterization of magnetic–optical, core–shell, cobalt–cadmium selenide nanocrystals (Co–CdSe), an inorganic bifunctional nanomaterial. Cobalt nanocrystals of sizes spanning the superparamagnetic to ferromagnetic regime are prepared by conventional routes involving the thermal decomposition of $\text{Co}_2(\text{CO})_8$. Once prepared, the cores are overcoated with a variable thickness of CdSe by a facile one–pot reaction, using organometallic precursors. The structures of the hybrid particles are probed by powder X–ray diffraction (pXRD) and transmission electron microscopy (TEM). The cobalt core remains spherical and the CdSe shell is uniform. The bifunctional characteristics of the nanocrystals are borne out through magnetic measurements and optical spectroscopy. The cobalt core retains the general magnetic properties of the original cobalt nanoparticles, and the CdSe shell emits in a fashion similar to nanocrystal quantum dots. However, the respective properties are altered because of the unique core–shell structure. Specifically, while the coercivity was found to be unchanged by shell formation, the blocking temperature for the composite structure was observed to be substantially lower. The former is mainly a function of the magnetocrystalline anisotropy and the domain size of the particles, both of which are essentially unchanged by the shell growth process. On the other hand, blocking temperature is intimately related to surface anisotropy, and should, therefore, be tunable by modifying the surface structure. In addition, we observe that at low temperatures (20 K) shell CdSe photoluminescence (PL) decay was very rapid (<1 ns). In contrast, nanocrystalline CdSe PL decay is typically much slower at such temperatures (>50 ns), indicating that the presence of the magnetic core significantly affects the effective strength of the “emitting” optical transition of the semiconductor shell. We propose a mechanism whereby the magnetic core likely modifies the spin structure of the lowest excitonic state. Finally, we discuss trends associated with controlling both shell thickness and core size.

9:30 AM P4.4

Fluorescence of localized excitons in chemically grown CdSe nanowires. Vladimir Protasenko and Masaru Kuno; Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana.

Thin CdSe nanowires (NWs) with diameter between 7–10 nm have been synthesized using Au/Bi core/shell nanoparticle catalysts. High resolution TEM micrographs reveal that the NWs are crystalline and also show the existence of 2 to 5 nm long wurtzite/zincblende segments along their length. Single NW optical measurements show the following: a) 1D absorption and emission dipoles; b) fluorescence lifetime of ~800 ps; c) spectral heterogeneity along the NW length; and d) time dependent fluctuations of the fluorescence intensity. A qualitative model which explains these effects is proposed. It includes the effect of exciton localization in Type II disordered potentials, variations in the exciton binding energy caused by fluctuations of the dielectric constant of the NW organic ligand shell, and the interaction of localized excitons with trapped and free electrons/holes.

9:45 AM P4.5

Shape Control of CdSe Nanocrystals by Noble Metal

Nanoparticles. Ken-Tye Yong^{1,3}, Yudhisthira Sahoo^{2,3}, Mark T. Swihart^{1,3} and Paras N. Prasad^{2,3}; ¹Department of Chemical and Biological Engineering, The University at Buffalo (SUNY), Buffalo, New York; ²Department of Chemistry, The University at Buffalo (SUNY), Buffalo, New York; ³The Institute for Lasers, Photonics, and Biophotonics, The University at Buffalo (SUNY), Buffalo, New York.

Noble metal nanoparticles of gold (Au), silver (Ag), palladium (Pd) and platinum (Pt) can act as both catalytic and seeding materials for tailoring the shape of CdSe nanocrystals. The Au, Ag and Pd

nanoparticles were synthesized using a two-phase method and the Pt nanoparticles were prepared by a hot colloidal synthesis. When cadmium and selenium precursors were reacted in the presence of one of these types of metallic nanoparticles, anisotropic growth of CdSe nanocrystals resulted. This gave rise to a variety of shapes: rods, obloids, bipods, tripods and tetrapods under different conditions or after different reaction times. The semiconductor nanocrystals were characterized using transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), X-ray Diffraction (XRD), photoluminescence (PL) and UV-vis spectroscopy. Different anisotropic shapes of CdSe nanocrystals were obtained at different reaction times under the same conditions. In all cases, the CdSe nanocrystals grew along the c-axis of the hexagonal wurtzite structure. The aspect ratio of the CdSe quantum rods ranged from ~5 to 12 depending on the metallic nanoparticles used. Under the same reaction conditions, but in the absence of the metal nanoparticles, only spherical CdSe nanocrystals were formed.

10:30 AM *P4.6

Tailored Fabrication of Smart Nano-materials for Bio-Medical Diagnosis. Jinwoo Cheon^{1,2}, Jae-Hyun Lee^{1,2} and Jin-Sil Choi^{1,2};

¹Chemistry, Yonsei University, Seoul, South Korea; ²Nano-Medical National Core Research Center, Yonsei University, Seoul, South Korea.

Inorganic nanocrystals are of current interest due to their novel properties and significant advantages in nano-electronics and bio-medical technology. Here, as a model studying strategy for architectural control toward multi-dimensional structures, in specific, we examine the shape evolution of various semiconductor and magnetic nanocrystals (e.g. wires, cubes, diamonds, and stars) and systematically elucidate the key growth parameters for shape determination of materials. The resulting size and shape dependent novel properties under quantum mechanical regime are uniquely observed. We demonstrate how to assemble these nanocrystals into desired places needed for the fabrication of nanodevices to generate nice Coulomb blockade effect for a single electron transistor. Also, these nanomaterials show exceptional medical diagnostic properties for detecting cancers and other targeted bio-molecules through our nano-MRI (magnetic resonance imaging) technique. This technique can be extended to detecting other harmful viruses and pathogens otherwise impossible previously.

11:00 AM P4.7

Quantum Dot–Peptide–MHC Conjugates as a Tool to Study

Mechanisms of Antigen Recognition by T Cells. Nadia Anikeeva¹, Aaron R. Clapp², Ellen R. Goldman³, Yuri Sykulev¹ and Hedi Mattoussi²; ¹Department of Microbiology and Immunology and Kimmel Cancer Institute, Thomas Jefferson University, Philadelphia, Pennsylvania; ²Optical Sciences Division, Code 5611, US Naval Research Laboratory, Washington, District of Columbia; ³Center for Bio/Molecular Science and Engineering, Code 6900, US Naval Research Laboratory, Washington, District of Columbia.

Luminescent quantum dots (QDs) have unique spectroscopic properties that made them appealing for use in developing a variety of bio-inspired applications, ranging from immunoassay development to in vivo cellular imaging. Such properties include broad absorption and size-tunable photoluminescence (PL) spectra ranging from the UV to IR and exceptional resistance to chemical and photo-degradation. We have developed approaches based on non-covalent self-assembly to conjugate biomolecules to CdSe–ZnS core-shell QDs that were rendered water-soluble using surface cap exchange with dihydrolipoic acid (DHLLA) ligands. Self-assembled QD–protein conjugates were used to develop an array of fluoroimmuno- and Fluorescence resonance energy transfer (FRET)–assays.^{1,2} In this report, we extend our self-assembly approach to conjugate DHLLA-capped nanocrystals to the major histocompatibility complex (MHC) proteins preloaded with antigenic peptides (peptide–MHC complex or pMHC) and appended with oligohistidine attachments. Recognition of an antigenic peptide bound to MHC on the membrane of an infected cell by antigen specific T cell receptor (TCR) initiates T cell response towards that cell. In the QD–pMHC conjugates the number and orientation of soluble pMHC complexes immobilized on each QD can be controlled. In addition, the orientation of pMHC proteins mimics closely the positioning of these molecules on the cell surfaces. We show that in these conjugates pMHCs maintain their specificity to T cell receptor (TCR) of live T cells. Furthermore, due to their multivalency the QD–pMHC assemblies showed increased avidity towards T cell membranes. When used in conjunction with CD8 T cells that are marked by CD8 membrane proteins, manipulations of the MHC protein or/and the type of peptide used have revealed a strong avidity of the CD8 protein to the non-polymorphic domain of MHC class I protein (MHC-I). These interactions appear to be much stronger than expected, suggesting that CD8–MHC-I association precedes recognition of pMHC by TCR and emerges as an essential prerequisite for a rapid and sensitive response of cytotoxic T lymphocytes (CTL)

towards target cells. We will discuss the conjugate design, characterization and some of the salient features of the TCR/pMHC/CD8 complex formation on CTL revealed from this investigation. 1. E.R. Goldman et al., Analytical chemistry 76, 684-688 (2004). 2. I.L. Medintz et al., Nature Materials, 4, 435-446 (2005).

11:15 AM P4.8

Nanoscale Size Effects of Magnetic Nanocrystals and Their Utilization for In Vivo Cancer Diagnosis through Dynamic Targeting and Imaging. Jae-Hyun Lee^{1,2}, Young-wook Jun^{1,2},

Jin-sil Choi^{1,2} and Jinwoo Cheon^{1,2}, ¹Chemistry, Yonsei University, Seoul, South Korea; ²Nano-Medical National Core Research Center, Yonsei University, Seoul, South Korea.

The unique properties of magnetic nanocrystals arising from superparamagnetism provide them high potential as key probes in the next generation biomedical imaging and sensing applications. The understanding of their nanoscale properties under in vitro conditions, however, is limited and the current strategies for their utilization for in vivo systems are unsatisfactory. Here we present the development of a synthetically controlled magnetic nanocrystal model system that correlates the nanoscale tunabilities in terms of the size, composition, magnetism, induced nuclear spin relaxation processes, hydrodynamic size, and the bio-conjugation. Our model system further leads to the development of high performance magnetic nanocrystal probe systems for magnetic resonance imaging (MRI). Upon conjugation to targeting antibody, Herceptin, these nanocrystal conjugates are utilized as MRI probes not only for in vitro diagnosis of cancer cell lines but also for the monitoring of in vivo dynamic targeting events of human cancer cells implanted in live mice by taking advantage of their exceptional properties (e.g. strong MRI enhancement, high colloidal stability, and high binding selectivity).

11:30 AM P4.9

Two-Photon Excitation of Quantum Dot Based Nonradiative Energy Transfer. Aaron Clapp¹, Thomas Pons¹, Igor L. Medintz², Joe Melinger³, James Delahanty² and Hedi Mattoussi¹, ¹Optical Sciences Division, Naval Research Laboratory, Washington, District of Columbia; ²Center for Bio/Molecular Science and Engineering, U.S. Naval Research Laboratory, Washington, District of Columbia; ³Electronics Science and Technology Division, U.S. Naval Research Laboratory, Washington, District of Columbia.

Luminescent quantum dots (QDs) have been proposed as excellent alternatives to traditional organic dyes for fluorescence labeling and emerging nanosensing applications.^{1,2} A related report by Larson et al. recently showed that water-soluble QDs are superior probes for multiphoton fluorescence imaging where typical QD two-photon action cross-sections (a product of the fluorescence quantum yield and two-photon absorption cross-section) are an order of magnitude larger than those of organic molecules that are designed specifically for such applications.³ Multiphoton microscopy is ideal for high-resolution imaging within thick tissue samples, because of its intrinsic optical sectioning ability and limited out-of-focus photodamage.

Near-infrared irradiation used in two-photon excitation can penetrate deep into a sample due to reduced absorption by the surrounding tissue. Combining these two techniques, we used two-photon excitation to realize nonradiative energy transfer between a central CdSe-ZnS QD donor and proximal dyes. The two were brought in close proximity in a biological context using dye-labeled protein self-assembled on the QD surface. We explored effects of varying the emission of the nanocrystal as well as the ratio of dye to QD in each conjugate on the energy transfer efficiency. Data show that the process is consistent with Förster formalism, as in the case of one photon excitation. Further analysis of the FRET data provided information on the QD-protein conjugate configuration as well as the dimensions of the QD and protein used. Because the acceptor dyes have a very low two-photon cross section compared to QDs, two-photon direct excitation of the acceptor is virtually absent and signal from the acceptor originated only from FRET in QD-dye-labeled protein conjugates. The above findings were further demonstrated inside cells. These results could be very beneficial for sensing in live cells and in deep tissue. 1. A.R. Clapp et al., <i>J. Am. Chem. Soc.</i> 2004, 126, 301-310. 2. E.R. Goldman et al., <i>J. Am. Chem. Soc.</i> 2005, 127, 6744-6751. 3. D.R. Larson, et al., <i>Science</i> 2003, 300, 1434-1437.

11:45 AM P4.10

The Growth Mechanism of Freestanding III-V Nanowires.

Ann I. Persson, Linus Jensen, Soren Jeppesen, Mikael Bjork and Lars Samuelson; Physics Department, Solid State Physics, Lund, Sweden.

Freestanding nanowires have a promising future as one-dimensional (1D) building blocks for numerous applications and is an example of self-assembled nanostructures. They can be used for probing the physics of one-dimensional transport, as well as creating new devices based on quantum physics[1]. As we will present in this work they can

also be useful for studying fundamental growth aspects, such as defining the diffusion length on different crystal surfaces. To fully exploit the potential of nanowires it is important to get a thorough understanding of the growth mechanism. Growth of epitaxially nucleated wires is usually described by the vapor-liquid-solid (VLS) growth mechanism, where metallic seed particles, most often of Au, are used to form a eutectic system with the growth material. Recent studies have shown that the seed particle, often described as being in liquid phase, is in solid phase[2]. Despite the solid phase of the seed particle, we believe that it maintains its catalytic property by locally changing the surface reconstruction below the seed particle, at the wire-particle interface. The growth rate at this interface will increase in comparison with the growth rate on surrounding facets and result in anisotropic 1D-growth, i.e. wire growth. Chemical Beam Epitaxy (CBE) is used as growth technique. Earlier results from our investigations all indicate that Au-catalyzed growth of both GaAs and InAs nanowires on the (1 1 1) B surface is strongly dependent on diffusion of group-III material (Ga and In precursors) from the surrounding facets to the growth point. Ideally, the group-III species that lands within one diffusion length away from the Au particle will contribute to wire growth and the group-III species that lands further away will either be desorbed or contribute to two-dimensional (2D) surface growth. The diffusion length of the group-III species will therefore determine the amount of material that optimally can be transferred to the wire-particle interface. However, the diffusion length will be affected by surface conditions, such as surface temperature and surface reconstructions. We propose a method to measure the diffusion length based upon growing positioned wires on a (111)B surface[3]. The wires are placed in a hexagonal pattern that leaves each wire with a specific surface area from which diffusing material may be collected. By varying the specific surface area from which each wire can collect material the diffusion length can be determined as a function of temperature and source pressure. We have with this method also studied how wire growth is affected by growth of heterostructures in the wires. Based on these and earlier results, we propose a model for freestanding nanowire growth in CBE. 1. Samuelson, L. Mater. Today October, 22 (2003) 2. Persson, A. I., et al. Nature Materials 3, 677 (2004) 3. Jensen, L., et al. Nanoletters 4, 1961 (2004)

SESSION P5: Synthesis, Characterization and Applications in Biology

Chairs: Mingyong Han and Shimon Weiss
Tuesday Afternoon, November 29, 2005
Room 210 (Hynes)

1:30 PM *P5.1

Composition-tunable Quantum Dots and Their Novel

Applications. Mingyong Han, ¹Institute of Materials Research and Engineering, A-Star, Singapore, Singapore; ²Bioengineering Division, National University of Singapore, Singapore, Singapore.

Colloidal semiconductor nanocrystals (quantum dots) have attracted great attention for their distinguished roles in fundamental studies and technical applications such as biological labeling and optoelectronic devices. In the last two decades, the main efforts have been focused on the preparation of size-tunable binary or core-shell nanocrystals with different emission colors. Recent advances in our research have led to the exploration of composition-tunable emission of high-quality quantum dots by changing their constituent stoichiometries. In our research, we focus on the development of composition-tunable emission of highly luminescent alloyed quantum dots ZnxCd1-xS/Se across the whole visible spectrum and further applying the multicolor quantum dots to make optoelectronic devices or ultrasensitive nanoprobe for multiplexed analysis of biomolecules (J. Am. Chem. Soc. 2003 125, 8589, and 2003, 125, 13559). We have successfully prepared composition-tunable alloyed nanomaterials with high luminescence and stability tunable across the entire visible spectrum, especially blue emitting ones. High quality quantum dots with predetermined emission color can be synthesized reproducibly by changing synthetic recipes. The narrowest emission spectral width of ~14 nm on ensemble measurement (on the same order of single quantum dots) at room temperature has been demonstrated in our ternary alloyed quantum dots. The successful preparation of high-quality composition-tunable quantum dots makes the new class of nanomaterials very promising as multicolor nanoprobe and novel optoelectronic devices such as light-emitting devices, white lighting, quantum dot lasers, and photovoltaic cells. On the other hand, we will also present our recent research for developing new synthetic methodologies of various semiconductor nanostructures for promising new applications (Angew. Chem. Int. Ed. 2005, 44, 3466; J. Am. Chem. Soc. 2005, 127, 2378).

2:00 PM P5.2

Mechanisms of Nucleation and Growth of Nanowires in Self-Catalysis Schemes: III-V Compound Semiconductors.

Sreeram Vaddiraju¹, Cun-Zheng Ning², Meyya Meyyappan² and Mahendra K. Sunkara¹; ¹Chemical Engineering, University of

Louisville, Louisville, Kentucky; ²Center for Nanotechnology, NASA Ames Research Center, Mountain View, California.

The formation of III-V compound semiconductor nanowires during vapor transport of group III metals in a reactive environment (reactive vapor transport) was studied in detail to understand the nucleation and growth mechanisms involved with the so-called 'self-catalysis' schemes. Specifically, InN and GaSb were the two materials chosen for this study. For the first case, indium nitride (InN) nanowire synthesis using indium vapor transport in dissociated ammonia environment (reactive vapor transport) is studied in detail to understand the nucleation and growth mechanisms involved in the formation of these 1-D nanostructures. Two distinct nucleation and growth mechanisms were observed in the formation of InN nanowires. Under limited indium supply conditions, the results showed that the nucleation of InN crystal occurs first on the substrate. This is followed by selective wetting and formation of indium droplets on top of these InN crystals. The 1-D nanowire growth takes place through liquid phase epitaxy with underlying InN crystals. These details about the nucleation and growth aspects within these self-catalysis schemes were further rationalized by demonstrating the growth of heteroepitaxially-oriented nanowire arrays and 'tree-like' structures. Under excess indium supply conditions, the formation of indium droplets occurred on the substrate in the initial stages. As expected, direct nitridation of these droplets led to the spontaneous nucleation of multiple InN nuclei on the surface of these droplets. In this case, the growth of these nuclei into nanowires occurred by basal attachment in the initial stages, followed by tip-led growth in a self-catalysis mode in the later stages. Similar nucleation and growth mechanisms were observed, for the second case involving the vapor transport of gallium in the presence of antimony (in the gas phase), for GaSb nanowires synthesis.

2:15 PM P5.3

The Preparation and Properties of Luminescent CdS Nanoparticles Doped with Lanthanides. Paul Christian, Simon Pope, Stephen Faulkner and Paul O'Brien; Chemistry, Manchester University, Manchester, United Kingdom.

There has been much interest in the preparation of cadmium chalcogenide nanoparticles within the quantum confinement regime. The luminescence of the pure CdS particles is usually short lived with lifetimes on the scale of nano to femto seconds. There is particular interest in developing materials with longer lifetimes which allow time gated luminescent applications to be developed. Whilst this may be achieved through lanthanide systems sensitized with organic chromophores a semiconductor system may offer more flexibility and increased stability. The preparation of type II semiconducting system has allowed the preparation of core shell nanoparticles which exhibit longer lifetimes, however the synthesis of such materials is not trivial. In this paper we report the facile synthesis of cadmium sulfide nanoparticles doped with lanthanides. These are easily prepared from carboxylate salts in hot amines and result in nanoparticles which have quantum yields in the range of 4-6% and are readily resuspendable in organic media. The photoluminescent lifetimes have been measured on a nanosecond timescale. The emissive properties of the dot, the lanthanide dopant and their interaction will be discussed.

3:30 PM *P5.4

Peptide-Coated Quantum Dots and Their Use in Studying Lipid Rafts. Shimon Weiss, Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, California.

The development and characterization of peptide-coated qdots (pc-qdots) will be reviewed, with an emphasis on live cell imaging applications. In particular, pc-qdots were utilized to study of lipid rafts by labeling GPI-anchored receptors and following their motions within the membrane.

4:00 PM P5.5

Development of FRET-Based QD-Bioconjugate Sensors for Detecting Enzymatic Activity. Igor Langier Medintz¹, Ellen R. Goldman¹, Aaron R. Clapp², Harry Tetsuo Uyeda² and Hedi Mattoussi²; ¹Center for Bio/Molecular Science and Engineering, U.S. Naval Research Laboratory, Washington, District of Columbia; ²Division of Optical Sciences, U.S. Naval Research Laboratory, Washington, District of Columbia.

We have previously demonstrated Forster resonance energy transfer - (FRET) based QD-protein bioconjugates nanosensors for the specific detection of the nutrient maltose and the explosive TNT.1,2 The sensor design exploited a few inherent benefits of using QDs over conventional organic fluorophores for FRET including; 1-the ability to size-tune fluorescent emission as a function of QD core size to better match overlap with a particular acceptor and 2-the option of arraying multiple acceptors around a QD which increases the overall FRET efficiency. In the present investigation, we apply these QD-bioreceptor

assemblies to detect the activity of a variety of enzymatic proteases in vitro. We first explored the use of generic dye-labeled protein substrates immobilized on the QDs as 'proof of concept'. These QD-protein bioconjugates were exposed to increasing concentrations of the endopeptidases proteinase K or papain. The enzymes digestion of the dye-labeled protein substrate frees the dye from close proximity to the QD surface and disrupts FRET. Measurement of the changes in the FRET signal allowed monitoring of the specific protease activity. A calibration curve derived from an increasing number of acceptors per donor allowed transformation of the FRET changes into units of enzymatic activity. The second set of assemblies employed dye-labeled peptides which we used as specific substrates for two different peptidases, caspase-1 and thrombin. These peptidases are involved in inflammation and blood coagulation, respectively. Changes in FRET signal were also monitored when inhibitors were added to the peptide containing assay solutions. Analysis of the data was carried out within the framework of the Michaelis-Menten treatment using different mechanisms of inhibition. Quantitative monitoring of enzymatic activity was demonstrated, and Michaelis-Menten descriptors such as Vmax (maximum reaction rate or enzymatic velocity) and Ki (inhibitor dissociation constant) were derived from the data analysis. These investigations further demonstrate that hybrid inorganic-biological materials such as these QD-peptide/protein conjugates can be integrated into bioassays. The data, subsequent analyses and some practical applications for this technology will also be discussed. 1. I.L. Medintz et al., Nature Materials 2, 630 (2003). 2. E.R. Goldman et al., J. Am. Chem. Soc., 127, 6744 (2005).

4:15 PM P5.6

New Quantum Dot Based Supramolecular Structures for Photochemical Drug Delivery. Daniel Neuman¹, Peter C. Ford¹ and Geoffrey F. Strouse²; ¹Chemistry and Biochemistry, University of California, Santa Barbara, California; ²Chemistry and Biochemistry, Florida State University, Tallahassee, Florida.

We have synthesized supramolecular structures that are composed of chromium (III) complexes of cyclam (cyclam = 1,4,8,11-tetraazacyclotetradecane) covalently bound to the surface of CdSe quantum dots (qdots). Solid-state FT-infrared and CP-MAS ¹³C NMR spectroscopies indicate the coupling of the carboxylic acid passivated qdots with the alcohol appendage of both metalated and un-metalated cyclam type ligands. Previous studies on the nitrito (ONO) derivatives of the chromium cyclam complexes indicated that they are photo-labile towards release of the biological messenger molecule nitric oxide (NO), with quantum yields exceeding 25%. In recent studies of related nitrito derivatives, DeRosa *et al.* have shown that fluorescence resonance energy transfer (FRET) from a covalently attached pyrene chromophore to the Cr(III) center leads to efficient release of NO following irradiation into the strong absorbance bands of the organic chromophore. However, these complexes do not absorb at long wavelengths (>600nm) where biological tissue penetration is enhanced, a key factor in evaluating new potential photodynamic therapy (PDT) agents. The new qdot/chromium cyclam structures described here should have enhanced light absorbing properties due to the CdSe donors having high one and two photon absorption cross-sections. Photoluminescence and NO detection methods are being used to probe the FRET efficiency in the new materials. The photophysical properties of these qdot/chromium cyclam structures, especially with respect to their potential as PDT agents, will be discussed.

4:30 PM P5.7

A Novel Synthetic Route to Biofunctionalized CdTe Nanowires and Quantum Dots. Amiya Priyam¹, Anindita Chatterjee¹, Abhijit Saha¹ and Subhash C. Bhattacharya²; ¹Chemistry, UGC-DAE Consortium for Scientific Research, Kolkata Centre, Kolkata, West Bengal, India; ²Chemistry, Jadavpur University, Kolkata, West Bengal, India.

Exploring novel materials based on semiconductor nanoparticles has become one of the most attractive areas of current research. For the past few years, surface modification of fluorescent semiconductor nanoparticles by biomolecules like peptides & nucleic acids have added a new dimension to the nanoparticle research with respect to their biological applications. Among II-VI semiconductor nanoparticles, our interest in CdTe nanoparticles stems from the fact that it has one of the largest Bohr exciton diameters (15 nm) and therefore it offers a possibility of studying the quantum confinement effects in larger sized nanoclusters. Thiol stabilized cadmium chalcogenide nanoparticles have been known to be of high quality. "Quality" in this respect is expressed in terms of monodispersity, surface control, photochemical stability and high photoluminescence quantum efficiency. Here, we report the synthesis of highly biocompatible and luminescent L-cysteine capped CdTe nanowires and quantum dots with narrow size distribution. The thiol group of cysteine (2-amino,3-mercaptopropanoic acid) binds to the surface of CdTe nanoparticles and carboxyl and amino groups remain free which can be further utilized

for conjugation with other important biomolecules. In the method developed by us, telluric acid ($\text{H}_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$) has been used as a source of telluride ions. To an aqueous solution of telluric acid, appropriate amount of sodium borohydride was added and refluxed for few minutes with constant bubbling with Argon. The colour of solution changed from colourless \rightarrow black \rightarrow purple \rightarrow colourless. The colourless solution, thus obtained, contains NaHTe. To this solution, Argon purged solution of L-cysteine and Cd^{2+} ions was added at pH 11. An intense orange colouration developed indicating formation of CdTe. The precursor solution so obtained was refluxed to promote growth of nanoparticles. Surprisingly, the TEM analysis revealed that nanoparticles so obtained were cylindrically shaped having diameters of 6 nm and length of 50 nm. On the other hand, if NaHTe solution is added to the solution containing Cd^{2+} and cysteine, spherical CdTe particles are obtained with diameter of about 5 nm. It is quite intriguing to obtain nanowires and quantum dots by just by varying the order of addition of the two reagent solutions. Lattice fringes can be seen in TEM images suggesting good crystallinity. The mechanism of growth and factors controlling the shape of nanoparticles are being investigated thoroughly.

4:45 PM **P5.8**

III-V semiconductor core-heteroshell nanocrystals.

Assaf Aharoni and Uri Banin; Institute of Chemistry and the Center for Nanoscience and Nanotechnology, Hebrew University of Jerusalem, Jerusalem, Israel.

The need for nanocrystals with bright and stable fluorescence for various applications covering biology to electrooptics is increasingly growing. This is particularly true for III-V semiconductor nanocrystals that can cover the technologically important near infrared (NIR) spectral range. We report the synthesis and characterization of high quantum efficiency and high stability QD's covering the NIR region consisting of an InAs core protected by a CdSe/ZnSe heteroshell. The ZnSe outer shell provides efficient confinement of electron and hole wave functions and thus diminishes their presence in the vicinity of dark traps located mostly at the surface area. The CdSe buffer which lattice parameters is intermediate between that of InAs and ZnSe, enables a smoother transition from InAs to ZnSe crystal and therefore reduces strain and the formation of defects. The shell formation is based on a layer by layer growth of the shell material at 260°C. The cations and anions of the shell material are introduced into the hot reaction vessel in a variable manner. As the reaction of one ion type is complete its counter ion is inserted to complete the layer. This growth technique enables improved crystalline structure of the formed shells, prevents homogenous nucleation of the shell material and inhomogeneous shell growth on core nanocrystals in solution. Using this technique's we succeeded to synthesize CSS (Core/Shell/Shell) QD's covering the NIR region with Quantum Yields up to more than 50% which are stable in air for months. In addition, the CSS produced are homogenous in size and does not require any size selective separation procedures. These properties make this high performance QD's suitable for biological and telecommunication applications.

SESSION P6: Semiconductor Nanostructures: Growth and Optical Properties
Chair: Michael Barnes
Tuesday Evening, November 29, 2005
Room 210 (Hynes)

8:00 PM ***P6.1**

Two-Photon Resonant Excitation of Confined Biexcitons In CuCl Quantum Dots and Their Subsequent Ultrafast Radiative Decay Capable of Efficient Lasing. **Tadashi Itoh**¹, Y. Kagotani¹, K. Miyajima¹, S. Saito² and M. Ashida¹; ¹Department of Materials Engineering Science, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka, Japan; ²Kansai Advanced Research Center, National Institute of Information and Communications Technology, Kobe, Japan.

Semiconductor quantum dots (QDs) are expected to be an ideal gain medium of lasing since their confined electronic levels possess high density of states with narrow spectral width, giant oscillator strength, weak interaction with phonons, etc. Until now, laser emission of exciton system (biexcitons) confined in II-VI and I-VII semiconductor QDs has been reported. However, in all the previous cases, the lasing was achieved with intense one-photon excitation above the exciton absorption band and, therefore, on account of the collision between two isolated excitons, one cannot avoid the influence of Auger ionization of QDs on the degradation of laser action. In this paper, we report the first successful achievement of stable and efficient lasing of biexcitons confined in CuCl QDs embedded in NaCl single crystalline matrix by utilizing the novel method of two-photon resonant excitation of confined biexcitons. The peak power of excitation for lasing threshold is almost the same regardless of the pulse width of excitation laser between 2 ps to 0.2 ps, that implies the existence of ultrafast radiative relaxation process. Temporal behavior of non-lasing

luminescence spectra of biexcitons under two-photon resonant excitation shows that the decay profile becomes non-exponential at high excitation power and the fast decay component becomes faster for higher excitation power. This characteristic feature of the biexcitonic luminescence is observable only for the two-photon resonant excitation where the population inversion in biexciton-exciton system is realized at the initial stage and indicates the possibility of Dicke's superradiance, which is brought about by the coherent interaction of dipoles among many quantum dots.

8:30 PM **P6.2**

Polymer Nanennae: Oriented Luminescent Nanostructures from Single Molecules of Conducting Polymers.

Michael Barnes, Chemistry, University of Massachusetts-Amherst, Amherst, Massachusetts.

We have recently discovered a surprisingly simple method of preparing uniformly z-oriented nanostructures from single-molecules of semiconducting polymers in solution. These oriented polymer species have a number of extraordinary photophysical properties, resembling in many regards an inorganic quantum dot.[1,2] We have found that oriented polymer nanostructures act as high-purity single-photon sources, with virtually no 2-photon contamination from bi- or multi-exciton states.[3,4] Perhaps most interestingly, however, has been the observation of coupled antennae effects between pairs of oriented particles both in the time and frequency domains.[5] Similar to super- and sub-radiance effects observed for trapped ion pairs,[6] our observations suggest the possibility of generating entangled states in a scalable table-top format. [1] P. Kumar, A. Mehta, M. D. Dadmun, et al., J. of Phys. Chem. B 107, 6252 (2003). [2] A. Mehta, P. Kumar, M. D. Dadmun, et al., Nano Letters 3, 603 (2003). [3] P. Kumar, T. H. Lee, A. Mehta, et al., J. Am. Chem. Soc. 126, 3376 (2004). [4] T. H. Lee, P. Kumar, A. Mehta, et al., Appl. Phys. Lett. 85, 100 (2004). [5] M. D. Barnes, P. Krstic, P. Kumar, A. Mehta, J. C. Wells, Phys Rev B 71, 241303R, (2005) [6] R. G. DeVoe and R. G. Brewer, Phys. Rev. Lett. 76, 2049 (1996).

8:45 PM **P6.3**

Single-crystal Silicon Nanotubes, Hollow Nanocones, and Branched Nanotube Networks. **Brian P. Timko**¹, Alexander D.

Wissner-Gross², Wei Lu¹, Andrew B. Greytak¹ and Charles M. Lieber^{1,3}; ¹Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts; ²Department of Physics, Harvard University, Cambridge, Massachusetts; ³Division of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts.

We report a general approach to single-crystal silicon nanotube synthesis involving epitaxial deposition of silicon on germanium nanowire templates followed by wet etching of the template. This approach enables rational control of the diameter, wall thickness and electronic properties of silicon nanotubes. In addition, the controlled growth of conical and branched germanium cores was used to prepare variable-taper hollow nanocones and nanotube networks. Electrical data show that these devices are conductive and gateable, while fluid transport experiments demonstrate that small molecules can be electrophoretically driven through the tubes.

9:00 PM **P6.4**

Effect of an Injecting Contact on the Conductivity of Close-Packed CdTe Quantum Dots Films. **Venda J. Porter**^{1,2},

Marc A. Kastner^{3,2} and Mounji G. Bawendi^{1,2}; ¹Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts; ²Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; ³Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts.

We present a study of the conductivity of closed packed films of CdTe quantum dots (QDs) in the dark and in the presence of light. The dark conductivity in films of CdTe QDs differs from the conductivity in films of CdSe QDs in that holes are the majority carrier and they can be injected into the film from gold electrodes. Measurements performed on an inverted field effect transistor structure confirm the p-type behavior of the conduction and allow for gate modulation of the current. The injecting contact also results in a photoconduction that is different than that observed in CdSe QD films, namely a photoconductive gain greater than unity and photocurrents larger in magnitude at room temperature than at 77K.

9:15 PM **P6.5**

Quantum Dot/Organic Semiconductor Composites for Radiation Detection. **Ian H. Campbell**, **Brian K. Crone** and **Darryl L. Smith**; Los Alamos National Lab, Los Alamos, New Mexico.

We demonstrate a potential new class of radiation detection material - a composite of inorganic semiconductor quantum dots and conjugated organic semiconductors. The addition of quantum dots to an organic

semiconductor increases the efficiency of photon and charge generation, and improves the radiation stopping power. The quantum dot/organic semiconductor composite is designed so that ionizing radiation produces excitations predominantly in the inorganic semiconductor quantum dots and these excitations are subsequently Forster transferred to the organic material. Depending upon the application, the Forster excited organic material(s) are chosen either to emit a Stokes shifted photon or to dissociate the excitation and produce mobile charges. Simple estimates suggest that an order of magnitude improvement in the radiation detection performance of organic materials is possible in optimized composites, corresponding to an ionization energy of about 3 eV/photon (333,000 photons/MeV). Here, we present initial electron induced scintillation results on CdSe/semiconducting polymer composites demonstrating more than a factor of two increase in photon generation efficiency. These composites are particularly attractive since chemically synthesized quantum dots are routinely surface passivated with organic molecules giving them processing characteristics similar to organic materials.

9:30 PM P6.6

High-yield plasma synthesis of luminescent group IV quantum dots. Uwe R. Kortshagen, Lorenzo Mangolini, Elijah Thimsen and Ryan Gresback; Mechanical Engineering, University of Minnesota, Minneapolis, Minnesota.

Crystalline group IV quantum dots (silicon, germanium) are of interest for a variety of applications from solid state lighting, to opto-electronic devices, to use of fluorescent tagging agents. Compared to other quantum dot materials, group IV materials are appealing due to their low toxicity and small environmental hazard, and their compatibility with silicon technology used for microelectronics. A variety of liquid and gas phase synthesis approaches for group IV materials has been demonstrated in the past. While liquid phase approaches usually offer excellent control over the size of quantum dots, they are often limited with respect to the usable process temperatures by the thermal degradation of solvents. Gas phase approaches can provide high yield and a wide range of temperatures; however, they are often afflicted with problems of particle agglomeration which can annihilate the desired quantum dot behavior. The use of nonthermal plasmas discussed in this presentation can overcome these two main problems of other synthesis approaches: Plasma synthesis strongly reduces or completely eliminates agglomeration since the particles in a plasma are unipolarly negatively charged. In addition, low pressure plasmas provide a unique non-equilibrium environment in which the particle temperature can exceed the temperature of the surrounding gas by several hundreds of Kelvin due to strongly exothermic processes at the particle surface; this enables achieving a high yield of crystalline material in a low temperature environment. We present a method for the production of group IV nanocrystals using a low-pressure continuous flow nonthermal plasma reactor. The reactor consists of a quartz tube with a ring electrode as RF powered electrode. Various precursor gases (SiH₄, SiCl₄, GeCl₄,) are injected with inert gases (Ar, He) as background. The precursor gases are dissociated in the plasma and nanocrystals form in a few ms. The particle size can be adjusted through the plasma residence time in a range from ~2 to 8 nm. Transmission electron microscopy confirms crystallinity. Nanocrystals show photoluminescence after surface passivation with inorganic shell materials such as silicon nitride or silicon oxide. Mass spectroscopic measurements indicate an almost complete utilization of the precursor gas. In the case of silicon, a production rate of photoluminescent nanocrystals of ~ 50 mg per hour has been achieved. The comparatively large yield combined with the fact that very small particles are produced in a single step gas phase process makes this approach very promising for the large scale production of group IV quantum dots. This work is supported in part by NSF under MRSEC Award Number DMR-0212302 and by Innovalight, Inc.

SESSION P7: Electronic and Transport Properties
Chairs: Dimitri Talapin and Artur Zrenner
Wednesday Morning, November 30, 2005
Room 210 (Hynes)

8:30 AM *P7.1

N- and p-Channel Field-Effect Devices Made from Conductive PbSe Nanocrystal Solids. Dimitri V. Talapin, Charles T. Black, Cherie R. Kagan, Ali Afzali, Elena V. Shevchenko and Christopher B. Murray; IBM T.J. Watson Research Center, Yorktown Heights, New York.

We demonstrate the applicability of semiconductor nanocrystal arrays in solution-processed field-effect devices fabricated at room temperature. To improve the conductivity of as-deposited nanocrystal solids, we treated films of close-packed PbSe nanocrystals with hydrazine. Hydrazine-treated PbSe nanocrystal solids show n-type conductivity ~0.8 siemens per centimeter, i.e., about ten orders of magnitude higher than native nanocrystal films. The conductivity of

hydrazine-treated PbSe nanocrystal solids can be switched between n- and p-type transports by controlling the saturation of electronic states at nanocrystal surfaces. Nanocrystal arrays form the n- and p-channels of field-effect transistors with electron and hole mobilities of 0.9 and 0.2 square centimeters per volt-second, respectively, and current modulation $I_{on}/I_{off} \sim 10^3-10^4$. The field-effect mobility in PbSe nanocrystal arrays is comparable to the mobility of pentacene transistors while the easy switch between n- and p-transport allows simple realization of complimentary metal oxide semiconductor (CMOS) circuits. In addition to electronics applications, highly conductive nanocrystal solids offer a promising fabrication approach for efficient and inexpensive thermoelectric and photovoltaic devices.

9:00 AM P7.2

Photoconductivity in arrays of semiconductor nanoparticles. James Edward Murphy^{2,1}, Matthew Beard¹, Randy Ellingson¹ and Arthur Nozik^{1,2}; ¹National Renewable Energy Laboratory, Golden, Colorado; ²Chemistry and Biochemistry, University of Colorado at Boulder, Boulder, Colorado.

Time-Resolved Terahertz Spectroscopy is a new optical method for determining photoconductivity without the need for electrical contacts. It is an ideal method for measuring transport properties in materials where contact resistance presents problems and/or electrical contact is difficult. In addition, the time-dependent photoconductivity is measured with sub-picosecond resolution. We report results on the time-resolved photoconductivity in highly ordered PbSe nanoparticle arrays. The photoconductivity in nanoparticle arrays as a function of both nanoparticle shape and average inter-particle separation will be presented. Preliminary results on PbTe arrays may also be presented. These results have important implications for greatly improved optoelectronic devices, including solar cells for photon conversion to electricity.

9:15 AM P7.3

Polarized X-ray absorption spectroscopy of oriented CdSe nanorod assemblies. Deborah Michiko Aruguete¹, Matthew A.

Marcus², Liang-shi Li³, Andrew Williamson⁴, Sirine C. Fakra², Giulia Galli⁴ and A. Paul Alivisatos^{1,5}; ¹Chemistry, University of California, Berkeley, Berkeley, California; ²Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California; ³Chemistry, Northwestern University, Evanston, Illinois; ⁴Quantum Simulations Group, Lawrence Livermore National Laboratory, Livermore, California; ⁵Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California.

We present a structural study by polarized X-ray spectroscopy of CdSe nanorods (3 × 60 nm) having the wurzite structure. The suspension of rods formed a nematic liquid crystal in which an aligned area could be selected by the use of an X-ray microprobe. We used X-ray dichroism to measure the interatomic distances parallel and perpendicular to the long axis (c-axis) of the rods. We find that the equatorial Se-Se second nearest-neighbor distances expand by 0.014 (+0.008, -0.006) Å relative to those in the bulk, while the axial Cd-Se bonds contract by 0.005 (± 0.001) Å. In contrast to many other nanomaterials of similar size, the average Cd-Se bond distance is the same as that in bulk CdSe within 0.002 Å. We also present evidence concerning the surface termination of the rods.

9:30 AM P7.4

Efficient Energy Transfer from Phosphorescent Organic Thin Film to Colloidal Quantum Dot Monolayer. Polina Anikeeva^{3,1}, Seth Coe-Sullivan¹, Conor Madigan¹, Jonathan Steckel², Mounsi G. Bawendi² and Vladimir Bulovic¹; ¹Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts; ²Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts; ³Material Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

We demonstrate resonant exciton energy transfer between a thin film of phosphorescent dye fac tris(2-phenylpyridine) iridium (Ir(ppy)₃) and a monolayer of colloidal CdSe QDs. We use time resolved photoluminescence (PL) measurements to show an increase of QD luminescence efficiency due to the elongation of the QD PL relaxation time from 50 ns to 400 ns. Assuming a Förster model of Ir(ppy)₃ triplet excitons transfer to a mixed spin state of QDs we calculate the Förster radius of an exciton transfer between Ir(ppy)₃ and QDs. We show that the experimental value of the Förster radius is in a good agreement with the value obtained from the donor emission and the acceptor absorption spectra. In addition, data obtained from the time-resolved energy transfer experiment allow us to estimate PL efficiency of a single monolayer of QDs. Our work demonstrates that QDs can efficiently harvest triplet excitons of organic thin films, in a layered structure typical of QD-LED technology.

9:45 AM **P7.5**

Scanning Tunneling Microscope-Induced Light Emission from a Metal-Quantum Dot-Metal Double Tunnel Junction.

Antti J. Mäkinen, John Wilkinson, Edward E. Foos, Neil J. Watkins and James P. Long; Naval Research Laboratory, Washington, District of Columbia.

Electroluminescence from individual colloidal quantum dots (QDs) may serve as light sources in future nanophotonic applications if the challenges of fabrication can be met and if design principles can be developed. To this end, we have implemented an architecture where core-shell QDs (CdSe/ZnS) are tethered to Au(111) surfaces via self-assembled monolayers of alkane dithiols and characterized by STM-induced light emission (STM-LE). Key to the performance of this scheme are the details of electron and hole injection across the double tunnel junction (DTJ) represented by the triad of STM tip, QD, and substrate. Here, we have used the STM to advantage by controlling the DTJ through the adjustment of the tip height and the bias voltage while simultaneously monitoring STM-LE. In addition, we have characterized the electronic properties of the DTJ through scanning tunneling spectroscopy, which reveals the QD energy levels relative to the substrate Fermi level as well as the coulomb-blockade charging energy of the coupled QD (typically ~ 0.2 V). We will report results for several monodispersed QD samples with center wavelengths ranging from about 525 nm to 570 nm, a wavelength range overlapping with the Au surface plasmon resonances which are found to contribute to the redder end of the STM-LE spectrum.

10:00 AM **P7.6**

Influence of Linker Molecules on Charge Transport through Self-Assembled Single-Nanoparticle Devices.

Amir Zabet-Khosousi, Yoshinori Suganuma and Al-Amin Dhirani; Chemistry, University of Toronto, Toronto, Ontario, Canada.

We investigate electrical characteristics of single-electron electrode/nanoisland/electrode devices formed by alkanedithiol assisted self-assembly. Contrary to predictions of the orthodox model for double tunnel junction devices, we find a significant (\sim fivefold) discrepancy in single-electron charging energies determined by Coulomb blockade (CB) voltage thresholds in current-voltage measurements versus those determined by an Arrhenius analysis of conductance in the CB region. The energies do, however, scale with particle sizes, consistent with single-electron charging phenomena. We propose that the discrepancy is caused by a multibarrier junction potential that leads to a voltage divider effect. Temperature and voltage dependent conductance measurements performed outside the blockade region are consistent with this picture. We simulated our data using a suitably modified orthodox model.

10:30 AM ***P7.7**

Manipulations of a Qubit in a Semiconductor Quantum Dot.

Artur Zrenner, Universitaet Paderborn, Paderborn, Germany.

Semiconductor quantum dots are zero-dimensional model systems with excellent optic and electric properties. In optical experiments on single self-assembled InGaAs quantum dots the exciton ground state transition appears as an extremely narrow resonance of only a few μ eV width. The resonant interaction with cw laser fields can be studied in detail by photocurrent spectroscopy, revealing the effects of nonlinear absorption and power broadening of the line width, as expected for a basically ideal two-level system. For the case of pulsed laser fields and in the absence of decoherence, the two-level system represents a qubit. Excitations with ps laser pulses result in multiple qubit rotations, which can be evidenced in a quantitative way as Rabi oscillations in photocurrent experiments. Double pulse experiments further allow us to infer important system parameters like the excitonic fine structure, the decoherence time, and off-resonance Ramsey fringes of the underlying two level system.

11:00 AM **P7.8**

InGaAs multi-quantum-wire channel MSM photodectors.

Iiho Ahn¹, G. Hugh Song¹ and Jhang Woo Lee²; ¹Information and Communications, GIST, Buk-gu, Gwangju, South Korea; ²R&D Laboratory, Kowon Technology, Yongin, Gyeonggi-do, South Korea.

We demonstrated, for the first time, the metal-semiconductor-metal (MSM) photodetectors with InGaAs multiple-quantum-wire (MQWR) channels. These devices were fabricated in the MBE grown AlGaAs/InGaAs pseudomorphic high electron mobility transistor (p-HEMT) structures and the trapezoid-shaped AlGaAs/InGaAs MQWR channels achieved using a holographic lithography and an anisotropic wet etching techniques. Successive low temperature photoluminescence (PL) measurements supported the depth control during the etching processes. In these devices photo-generated electron-hole pairs would be modulated in the undoped one-dimensional (1-D) InGaAs channels in which electron mobility should be relatively high and bandwidth improvement are expected.

Also the photo-responsivity would be improved due to the side wall light absorption to the MQWRs. The actual device has six finger shaped Ti/Au Schottky contacts with 3μ m gaps in between. The trapezoid-shaped AlGaAs/InGaAs wire cross sections were well delineated by SEM images. The thickness of the remaining AlGaAs barriers on the top of the InGaAs channels was ~ 30 nm. The estimated dimension of InGaAs wire cross sections was typically ~ 35 nm x 15nm. The 10K PL data showed well-defined peaks demonstrating the successful formation of high quality MQWR channels. The effective channel dimension, which is actually reduced by side wall depletion, was determined by PL data as (15 \sim 25)nm x 15nm. The best DC responsivity of 40μ x 40μ m devices is 4.5A/W, which is one order higher than that of the devices without QWR channels fabricated on the same wafer. The dark currents are in the range of ~ 10 nA. Impulse measurements using a 850nm 40ps pulsed laser show the rising time of 22ps and bandwidth of 16GHz. These results are record high in 3μ m long channel MSM photodetectors. The primary S-parameter analysis showed the maximum bandwidth of 160GHz. We will describe detailed wire formation processed and propose an 1-D transport model based on our mobility measurement data and R-F analysis.

11:15 AM **P7.9**

Host Matrix Effects on Photo- and Electroluminescence from CdSe Quantum Dots.

Andrea M. Munro, Marsha S. Ng, Jialong Zhao and David S. Ginger; Chemistry, University of Washington, Seattle, Washington.

We study the photoluminescence and electroluminescence from CdSe quantum dots in LED-like structures. In order to better understand the correlations between charging, blinking, photoluminescence and electroluminescence we combine single molecule spectroscopy with electrical scanning-probe microscopy techniques. We find that photoluminescence, electroluminescence, and blinking dynamics are each very sensitive to the choice of surface-ligand and polymer host and differentiate between the ratios of dark/bright dots and on/off times by contrasting single-molecule and ensemble measurements.

11:30 AM **P7.10**

Ultraviolet electroluminescence from p-GaN/i-ZnO/n-ZnO heterojunction light-emitting diodes.

Yichun Liu², H. Y. Xu², C. L. Shao² and Richard Mu¹; ¹Physics, Fisk University, Nashville, TN, Tennessee; ²Center for Advanced Opto-electronic Functional Material Research, Northeast Normal University, Changchun, China.

In this work, we reported the fabrication and characteristics of light-emitting diodes based on p-GaN/i-ZnO/n-ZnO heterojunction. A 30 nm i-ZnO layer was grown on p-GaN by rf reactive magnetron sputtering, then a n-ZnO was deposited by electron beam evaporation technique. The current-voltage characteristic of the obtained p-i-n heterojunction exhibited a diode-like rectifying behavior. Because the electrons from n-ZnO and the holes from p-GaN could be injected into i-ZnO layer with relatively low carrier concentration and mobility, the radiative recombination was mainly confined in i-ZnO region. As a result, an ultraviolet electro-emission at 3.21 eV, related to ZnO exciton recombination, was observed in room-temperature electroluminescence spectrum of p-i-n heterojunction under forward bias.

11:45 AM **P7.11**

Nanowire Arrays for Solar Cells.

Lori E. Greene^{1,2}, Matt Law^{1,2} and Peidong Yang^{1,2}; ¹Chemistry, University California, Berkeley, Berkeley, California; ²Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California.

Nanowire arrays show great promise as materials for an assortment of technologies ranging from optoelectronics to solar cells. For nanowire arrays to have a technological advantage in these applications, they must have a low production cost, be scalable and have tunable dimensions. Presented here is a method for producing homogenous arrays of ZnO nanowires with a tunable aspect ratio and alignment control using a mild, environmentally benign aqueous solution process at 90°C. This synthesis yields complete and conformal nanowire coverage on a wide range of substrates of any size. The nanowires are grown in two steps: first, ZnO nanocrystals are either deposited on or formed in situ on a substrate to act as seeds for the second step of nanowire growth. The alignment of the final nanowire array is determined in the first step of nanocrystal deposition. A dip-coated layer of preformed ZnO seeds results in quasi-aligned arrays while vertical arrays nucleate from textured ZnO nanocrystals produced by thermally decomposing zinc acetate on a substrate.¹ The wire diameter, length and aspect ratio are tunable by controlling the reactant concentration and growth time. A large range of sizes can be grown: wire diameters range from 10 nm to 300 nm, with lengths of 50 nm to 25 μ m and aspect ratios from 5 to 150. The latest results on TiO₂ nanowire arrays will also be discussed. Functioning dye-sensitized solar cells and polymer-inorganic solar cells have been made based on these ZnO nanowire arrays. The dye-sensitized cells

show a full sun efficiency of 1.5% for nanowire films with one-fifth the surface area of a traditional cell.² (1) Greene, L. E.; Law, M.; Tan, D. H.; Montano, M.; Goldberger, J.; Somorjai, G.; Yang, P. *Nano Lett.* 2005, published online June 18, 2005. (2) Law, M.; Greene, L. E.; Johnson, J. C.; Saykally, R. J.; Yang, P. *Nature Mater.* 2005, 4, 455 - 459

SESSION P8: Quantum Dots in Photonic Structures:
Hybrid Semiconductor/Plasmonic Nanostructures
Chairs: Hedi Mattoussi and Ulrike Woggon
Wednesday Afternoon, November 30, 2005
Room 210 (Hynes)

1:30 PM *P8.1

QDs in Optical Microcavities: Novel Basic Effects and Application Prospects. Jean-Michel Gerard, Nanophysics and Semiconductors Laboratory, CEA-Grenoble/DRFMC/SP2M, Grenoble, France.

Since ~1994 [1,2], numerous experiments on isolated QDs have shown that these nanostructures can be considered to some extent as "artificial atoms." As such, QDs can be used to reproduce in solid-state systems quantum optics experiments originally performed on single atoms in the 80's [3]. Besides their fundamental interest, these experiments open also the way to the development of a novel class of optoelectronic devices using a single or few QDs as active medium, as highlighted by the recent development of single-mode single photon sources [4,5]. On the fundamental side, remarkable progress has been achieved in 2004-2005, including noticeably the observation of the strong coupling regime for a single quantum dot by three different groups [6-8]. After reviewing the present status of CQED experiments with QDs, I will discuss their application prospects, with an emphasis on very high efficiency single photon sources and single quantum dot lasers. [1] J.Y. Marzin et al, *Phys. Rev. Lett.* 73, 716 (1994) [2] K Brunner et al, *Phys. Rev. Lett.* 73, 1138 (1994) [3] for a review, see J.M. Gérard in "Single Quantum Dots: Physics and Applications," P. Michler editor, Topics of Applied Physics, Springer, Heidelberg 2003 [4] E. Moreau et al, *Appl. Phys. Lett.* 79, 2865 (2001) [5] C. Santori et al, *Nature* 419, 594 (2002) [6] J.P. Reithmaier et al, *Nature* 432, 197 (2004) [7] T Yoshie et al, *Nature* 432, 200 (2004) [8] E Peter et al, to appear in *Phys. Rev. Lett.* (2005)

2:00 PM P8.2

Fabrication of Very High-Finesse Microcavity Pillars by Electron Beam Lithography and Deep Inductively Coupled Plasma Etching. Abbas Tahaoui¹, Paul W. Fry¹, Ahmad Daraei², Daniele Sanvitto², Jane A. Timpon², Paulo S. S. Guimaraes², Wai Ng¹, Mark Hopkinson¹, David M. Whittaker² and Maurice S. Skolnick²; ¹Department of Electronic and Electrical Engineering, University of Sheffield, Sheffield, United Kingdom; ²Department of Physics and Astronomy, University of Sheffield, Sheffield, United Kingdom.

Semiconductor micro-resonators¹ have been the subject of significant interest over recent years due to their ability to confine light in up to three spatial dimensions and for their possible applications as single photon sources² and vertical cavity surface emitting lasers. Particular attention has been focused on developing micro-resonators that have small cavity volumes (V) and high quality (Q) factors (defined as the ratio of the mode linewidth to the mode wavelength). Such micro-resonators can allow the observation of strong coupling between single excitons (X) and single photons (P)³. In addition, they can exhibit strong enhancement of the spontaneous emission rates through the Purcell effect. We report the fabrication of GaAs/AlGaAs microcavity pillars with record high Q -values grown by molecular beam epitaxy and processed by electron beam lithography and inductively coupled plasma etching. The cavity contains a single layer of InGaAs self-assembled quantum dots that act as light emitters. The planar cavity itself exhibits record Q values of 30,000, achieved by the use of real time optical feedback during growth. The steps that need to be taken in the experiments to measure the true cavity Q will be described, to eliminate the effects of in-plane dispersion and lateral inhomogeneities. To obtain high quality (Q) factor with small cavity volumes, we have processed circular micropillars of various diameter (from 0.8 to 5 μm). By studying the emission of the fundamental cavity modes, record Q factors of 12,000, 4,000 and 2,000 are obtained for pillars with 1.5, 1.0 and 0.8 μm diameter respectively. Using the Q factor measured for the 1.5 μm diameter pillar, together with the expression for the Purcell factor ($FP = 3Q(\lambda n)^3 / 4\pi^2 V$), gives an estimated 75 times enhancement of the spontaneous emission rate for dots positioned optimally within the cavity at the maximum of the optical field. Our high cavity finesse are possible due to high quality growth and careful optimisation of the etching process used to define the pillars. We have reduced the roughness of the sidewalls of the pillars, leading to significant improvement in the Q value through reduced scattering losses of the cavity. Further enhancement of the Q

factor is shown to be achieved by using an intermediate SiO₂ etch mask, which enables the pillar to be fully etched through the bottom Bragg mirror. We have also fabricated strongly asymmetric elliptical pillars (with major axis of 2 and 0.8 μm). Such pillars exhibit ~90% preferential enhancement of the emission from single dots into horizontal polarisation, a significant result for the production of polarised single photon sources. Selective enhancement by oppositely polarised photonic modes of single dot emission, as a function of temperature will also be presented. 1 K.J. Vahala, *Nature* 424, 839 (2003) 2 M. Pelton et al, *Phys. Rev. Lett.* 89, 233602 (2002) 3 J.P. Reithmaier et al, *Nature* 432, 197 (2004)

2:15 PM P8.3

Size Dependent Exciton Decay Kinetics of Quantum Dots on 'Free Space' and in Photonic Crystals. Daniel Vanmaekelbergh¹, Floris van Driel¹, Willem Vos² and Peter Lodahl²; ¹Utrecht University, Debye Institute, Utrecht, Netherlands; ²University of Twente, Department of Science and Technology and MESA+ Research Institute, Enschede, Netherlands.

The possibility of tailoring the photoluminescence energy by the crystal size has led to a world-wide interest in light-emitting semiconductor nanocrystals or quantum dots (QDs). An open question is how the dynamics of the transitions vary with crystal size. Good quality nanocrystal suspensions with a high luminescence efficiency (>80%), and a good control over the size can be prepared via wet-chemical synthesis routes. The availability of such suspensions allowed us to study the dynamics of radiative exciton decay as a function of the emission frequency. We report on the exciton decay rate as a function of crystal size for CdTe and CdSe QDs in diluted suspensions (i.e. free space) and in photonic crystals[1]. In suspensions we observed nearly single-exponential decay over a broad frequency range. The decay rate increases strongly with the frequency of the emitted light and is 2-5 times smaller than that expected for a simple two-level exciton. This is explained by thermal population of dark excitons, located close to the ground-state exciton. The excellent agreement between the observed decay rates and the rate constants calculated with tight-binding theory indicates that the kinetics reflect radiative processes only and highlights the importance of dark excitonic states. It has been theoretically predicted that the rate of spontaneous emission of light can be controlled by a photonic crystal[2]. A photonic crystal is an ordered structure composed of high refractive index material and air. The refractive index varies with a length scale comparable to the wavelength of visible light. We infiltrated photonic crystals with CdSe QDs and measured the luminescence decay rate. We find that photonic crystals can both enhance and inhibit the rate of spontaneous emission, depending on the lattice parameter of the photonic structure. The difference between the minimum and maximum emission rate was a factor two. With this, the prediction of E. Yablonovitch was confirmed[1]. *email address:d.a.m.vanmaekelbergh@phys.uu.nl 1. P. Lodahl, A. F. van Driel, I. S. Nikolaev, A. Irman, K. Overgaag, D. Vanmaekelbergh, and W. L. Vos, Controlling the dynamics of spontaneous emission from quantum dots by photonic crystals, *Nature* 430, 654 (2004). 2. E. Yablonovitch, Inhibited spontaneous emission in solid-state physics and electronics, *Phys. Rev. Lett.* 58, 2059 (1987).

3:30 PM P8.4

Do Exciton-Polaritons Determine the Optical Properties of ZnO Nanowires? Lambert Karel van Vugt¹, P. Ravindran², S.

Ruhle¹, L. Kuipers³, H. C. Gerritsen² and D. A. M. Vanmaekelbergh¹; ¹Condensed Matter and Interfaces, Debye Institute, Utrecht University, Utrecht, Netherlands; ²Molecular Biophysics, Debye Institute, Utrecht University, Utrecht, Netherlands; ³Nano Photonics Group, FOM Institute for Atomic and Molecular Physics (AMOLF), Amsterdam, Netherlands.

ZnO with its bandgap of 3.37 eV shows an extraordinary large exciton binding energy of around 60 meV. Strong exciton-photon coupling in macroscopic ZnO crystals results in the formation of exciton-polaritons, which have simultaneous excitonic and photonic character.¹ This coupling can be enhanced when polaritons are generated within a microcavity.² ZnO nanowires with their subwavelength diameter are a realization of such microcavities. They show remarkable optical properties: The wires can act as a Fabry-Perot cavity and stimulated emission can be obtained.³ In addition, the wires can act as a low-loss waveguide for wavelengths close to electronic transitions.⁴ We have grown high quality ZnO nanowires epitaxially on sapphire. The wires are highly faceted, have hexagonal cross-sections and grow along the c-axis of the wurtzite ZnO crystal structure. The optical properties of single wires suspended on a glass substrate were studied with two-photon laser scanning microscopy. The setup allowed us to acquire emission spectra at different positions along the wire, to change the E-field polarization with respect to the c-axis and to scan the excitation energy $2h\omega_i$ in the region of the of the exciton (polariton) transitions. Under illumination with intense femto second pulsed NIR laser light ($h\omega_i$), the wires show Second

Harmonic Generation (SHG) for $2\hbar\omega_i < E_g$. For illumination frequencies $\hbar\omega_i < E_g$ and $2\hbar\omega_i > E_g$ we observed SHG as well as excitonic and defect-related luminescence. The spatial images of the spectra show a strong enhancement (up to 8 times) of the emission at the wire ends. Generally this enhancement was stronger on one end of the wire. TEM images show that this enhancement is not due to inhomogeneous thickness of the wire but is related to the end-face roughness. By taking the ratio of the emission intensity at the wire end and in the middle for each wavelength, we obtain an enhancement spectrum. We observe that this enhancement factor depends sensitively on the energy of the emitted light: Enhancement peaks appear at notably different positions than that of the luminescence and SH. The enhancement spectrum also shows remarkable variation with the incoming beam polarization, while the overall luminescence remains unaffected. We discuss our findings in terms of exciton-polaritons standing inside the nanowire. 1) Hopfield, J. J.; Thomas, D. G. *Phys. Rev. Lett.* 1965, 15, 22-25. 2) Weisbuch, C.; Nishioka, M.; Ishikawa, A.; Arakawa, Y. *Phys. Rev. Lett.* 1992, 23, 3314-3317. 3) Johnson, J. C.; Yan, H.; Yang, P.; Saykally, R. J. *J. Phys. Chem. B* 2003, 107, 8816-8828. 4) Law, M.; Sirbully, D. J.; Johnson, J. C.; Goldberger, J.; Saykally, R.J.; Yang, P. *Science* 2004, 305, 1269-1273.

3:45 PM P8.5

Modulation-Doped Nanowires for Nanoelectronics and Nanophotonics. Chen Yang¹, Zhaohui Zhong¹, Carl J. Barrelet¹ and Charles M. Lieber^{1,2}; ¹Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts; ²Division of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts.

Controlled modulation of the composition of nanoscale structures during synthesis offers a means for encoding information or function that is independent of conventional lithography methods. We describe controlled synthesis of modulation-doped silicon nanowires in which key properties, including the size, period and number of differentially doped regions, are defined during growth. These new nanoscale building blocks open up exciting opportunities in several areas. First, an approach for lithography-free addressing based on modulation doped silicon nanowire field-effect transistor arrays has been developed, and the assembly and demonstration of address decoder circuits will be discussed. Second, modulation doping has been used to create controllable barriers within nanowires, which provides a general bottom-up approach to form quantum structures with well-defined size. Single quantum dots as well as coupled quantum dots with controllable inter-dot coupling will be discussed. Third, spatial photocurrent measurements made on p-i-n modulation doped nanowires exhibit large amplification in the intrinsic region due to an avalanche mechanism. Studies of the impact ionization coefficients of electrons and holes in silicon nanowires will also be discussed. These results demonstrate the great potential of modulated silicon nanowires building blocks for both nanoelectronics and nanophotonics.

4:00 PM P8.6

Enhanced Optical Gain through Photonic Crystal/Nanocrystal Composites. Garry R. Maskaly, Melissa A. Petruska, Jagjit Nanda, Ilya V. Bezel, Nanguo Liu, Richard D. Schaller, Han Htoon, Jeffrey M. Pietryga and Victor I. Klimov; C-PCS, Los Alamos National Laboratory, Los Alamos, New Mexico.

Due to their unique optical properties, photonic crystals (PCs) offer the potential to enhance the optical gain of light-emitting materials matched to the photonic bands. In our work, we do not focus on defect state emission, but instead utilize photonic band edge effects. At points in the photonic band structure where the slope of the band is zero, the group velocity of light approaches zero. This occurs at both complete photonic band gap edges and directional gap edges. Utilizing directional gap band edges increases the directionality of high gain modes, decreasing the number of competing gain modes. Furthermore, in FCC-based photonic crystals, using the L-gap edge between the 2nd and 3rd bands gives more tolerance to structural defects than using a complete gap (between the 8th and 9th bands). The tunable light-emission of nanocrystals (NCs) makes them a natural complement to the tunable optical properties of PCs. We incorporate the NC materials into a sol-gel to improve the longevity of NC emission while still allowing a volume fraction of NCs near 20% and a relatively large refractive index of 2.1. [*Adv. Mat.* 14, 739 (2002) & *Adv. Mat.* 15, 610 (2003)] We incorporate the NC/sol-gel composites into a variety of photonic crystal devices. In one system, we embed a titania sol-gel/CdSe composite into a polystyrene opal. This system exhibits both modified spontaneous and stimulated emission relative to control sol-gel/NC films as evidenced by shifts of the photoluminescence and amplified spontaneous emission (ASE) emissions. The gain threshold is reduced by over a factor of two and the optical gain is enhanced several-fold despite a near order-of-magnitude decrease in the NC volume fraction versus the control films. In the NC/PC samples, ASE is still obtained with a

30-micron excitation spot; this is nearly one order-of-magnitude smaller than the spot size required for ASE in control samples. The enhancements produced by these structures brings the optical gain threshold within the range of unamplified Ti:sapphire lasers. We propose means to further decrease the gain threshold to potentially allow for continuous wave pumping of NC lasers. The techniques we present are easily applied to a wide range of NC systems, allowing the enhancement of optical gain across the visible and near-infrared spectra.

4:15 PM P8.7

Coupling Si quantum dots to surface plasmon polaritons. Jeroen Kalkman and Albert Polman; Center for Nanophotonics, FOM-Institute AMOLF, Amsterdam, Netherlands.

Surface plasmon polaritons (SPPs) are electromagnetic modes that propagate at the interface between a metal and a dielectric. When an excited Si quantum dot, embedded in the dielectric, is placed close to such an interface, a near-field interaction between the oscillating dipole and the metal occurs, leading to the generation of a SPP at the dipole frequency. We describe this interaction in terms of a semi-classical model, also taking into account distance-dependent variations in the local density of states and coupling to lossy surface modes. The SPP, propagating along the metal-dielectric interface, can subsequently be coupled out into the far field using a properly engineered grating that relaxes the momentum mismatch between the SPP and a far-field photon. We show that in well-engineered structures the SPP propagation losses are small and the efficiency of converting the SPP to light can be close to unity. We provide direct experimental evidence of enhanced decay rates of Si quantum dots by energy transfer to SPPs at a Ag/SiO₂ interface. Quantum dots are made in SiO₂ at different depths using ion implantation, whereupon the sample was covered with an optically thick silver film. For quantum dots placed 40 nm away from the SiO₂-Ag interface, a two-fold increase in decay rate is observed at 750 nm, while no effect is observed at 100 nm, both in agreement with our calculations. Strong stretched exponential decay characteristics are observed for quantum dots very close to the metal, also in agreement with our model that takes into account the quantum dot depth distribution and convoluted homogeneous broadening effects. By fitting our data to the theoretical calculations, we determine, for the first time, the internal luminescence quantum efficiency of Si quantum dots made by ion implantation: it is close to unity. With our model supported by experiments, we performed calculations on systems that will show much larger enhancements. For example, using a metal with a smaller plasma frequency such as Au, the coupling rate can be further enhanced. Very large effects, however, are expected for coupling to metal films with finite thickness, where complex SPP coupling behavior between the two metallo-dielectric interfaces causes a 1000-fold enhanced coupling rate from Si quantum dots to the SPPs. By using this SPP coupling concept, the saturation output power of LEDs based on Si quantum dots can be enhanced by orders of magnitude. Efficient coupling to SPPs also circumvents non-radiative quench processes that occur in Si quantum dots made by certain methods, thus leading to an enhanced effective emission quantum efficiency.

4:30 PM P8.8

Hybrid Semiconductor-Metal Nanocrystal Superstructures: Photonic Properties and Exciton-Plasmon Interactions. Alexander O. Govorov¹, Garnett W. Bryant², Timur Skeini¹, Jaebeom Lee³ and Nicholas A. Kotov³; ¹Physics and Astronomy, Ohio University, Athens, Ohio; ²Atomic Physics Division, NIST, Gaithersburg, Maryland; ³Department of Chemical Engineering, University of Michigan, Ann Arbor, Michigan.

We describe optical and thermal properties of a novel class of hybrid nanoscale structures composed of metal and semiconductor nanoparticles (NPs), and bio-linkers/polymers. Our study is inspired by recent experiments on bio-conjugated semiconductor-metal NP complexes [1,2,3,4] and their potential applications as sensors. These experiments demonstrate that a different organization (architecture) of a hybrid nano-complex results in qualitatively different optical properties. In many studies, metal (Au) NPs result in quenching the photoluminescence [2,3]. However, certain architecture can be found to achieve a strong PL enhancement [3,4]. For example, the plasmon enhancement effect can be achieved utilizing a collective resonance of many Au-NPs organized in spherical or cylindrical shells [3,4]. Our theory describes and explains the above observations. With a computer code based on the multipole expansion, we can compute optical properties of complexes made of tens and hundreds of NPs of different material. In these complexes, Au NPs act as a photonic amplifier/damper and a CdTe NP as an emitter. Our results incorporate the photon field enhancement effect, dipole-dipole inter-NP interactions, and energy transfer from semiconductor to metal NPs. Using specific polymer linkers, we can make our photonic structures sensitive to temperature since a dimension of polymer can

be temperature-dependent; this suggests applications of NP complexes as sensors of temperature and actuators. [1] E. Dulkeith et al., Phys. Rev. Lett. 89, 203002 (2002); [2] Z. Gueroui and A. Libchaber, Phys. Rev. Lett. 93, 166108 (2004); [3] J. Lee, A. O. Govorov, J. Dulka, and N. A. Kotov, Nano Letters, 4, 2323 (2004); [4] J. Lee, A. O. Govorov, and N. A. Kotov, Angewandte Chemie, recommended for publication.

4:45 PM P8.9

Imaging Single Quantum Dots in a 3D Photonic Crystal.

Michael Barth, Roman Schuster, Achim Gruber and Frank Cichos; Institute of Physics, Chemnitz University of Technology, Chemnitz, Germany.

Photonic crystals are materials with a periodically varying dielectric constant, which introduce a photonic band structure and photonic band gaps by multiple scattering of light on this spatially modulated refractive index. The spatial variation of the refractive index immediately implies that the optical density of states inside a photonic crystal has to be a local property too. Thus a detailed examination and especially the efficient use of even weak photonic systems requires a local probe for the study local optical properties. So far this has only been achieved for 2D photonic structures by means of near field scanning microscopy. Within this presentation we demonstrate for the first time the application of single quantum dots to evaluate the optical properties of a 3D photonic crystal. For this purpose, we have prepared photonic crystals from a colloidal suspension of polystyrene beads. The crystals are doped with a low concentration of core-shell CdSe/ZnS quantum dots, which emit in the region of the photonic band gap. Due to their narrow emission spectrum these quantum dots provide an almost ideal, spectrally selective probe for the optical properties of photonic crystals. With the help of fluorescence microscopy we demonstrate, that individual quantum dots can be imaged with high quality even though they are more than 30 lattice planes inside the photonic crystal. Based on a detailed comparison of the obtained fluorescence images with numerical calculations, we show that the angular radiation characteristics of single quantum dots is modified by the photonic band gap. The variation of the photonic band gap position with the orientation of the crystal prevents light emission from the quantum dot in certain directions. This is to our knowledge the first measurement of photonic band gap effects and anisotropic light propagation based on a single emitter inside a photonic crystal and, as we strongly believe, opens up a new class of experiments studying the local optical properties of 3D photonic crystals.

SESSION P9: Poster Session II

Chairs: Philippe Guyot-Sionnest, Hedi Mattoussi and Ulrike Woggon

Wednesday Evening, November 30, 2005
8:00 PM

Exhibition Hall D (Hynes)

P9.1

Blue Luminescent Semiconductor Nanocrystals and Their Application to Light Emitting Diode. Eunjoo Jang, SAIT, YongIn, South Korea.

The applications of the high quality nanocrystals to bio imaging, multi colour light emitting diode, and photovoltaic devices have become important technological issues at present. The CdSe/ZnS quantum dots are well-defined, outstanding materials for various applications because of their high photoluminescent quantum efficiency. However, it is still difficult to produce pure blue light emitting materials with high efficiency because of the limit in size control and materials selection. We introduce new synthetic method to prepare nanocrystals which emit strong blue light with more than 60% of QE from 420nm, and the performance of electroluminescent device with the prepared nanocrystals as blue light emitters showing good efficiency and nice colour purity. Also, we demonstrate the ability to use photolithographic method to make patterned nanocrystal film for electroluminescent device application. Exposing a nanocrystal film to strong UV light allowed the nanocrystals to form insoluble cross-linked network while the unexposed areas were still soluble to toluene solvent. Therefore, the UV light exposure using a shadow mask followed by solvent rinsing could produce small feature sizes on the order of 2 micrometers of nanocrystal patterns.

P9.2

Synthesis of II-VI semiconductor nanocrystals and luminescent properties. Daocheng Pan, Wei Nie, Qiang Wang, Xiaobo Liu, Yanming Chen, Yuhang Lin, Shichun Jiang, Lijia An, Xiangling Ji and Bingzheng Jiang; State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, Jilin Province, China.

II-VI semiconductor nanocrystals, such as CdS, CdSe, CdTe were synthesized from different approaches, such as organometallic

approach, metal oxide and two-phase routes. The particle size and shape can be tuned through chemical sources and reaction conditions. Firstly, we developed two-phase or two-phase thermal approach to synthesize CdS, extremely small CdSe and CdSe/CdS core-shell quantum dots with a narrow size distribution and a high photoluminescence (PL) quantum yield (QY). In the two-phase system, toluene and water were used as separate solvents. The reaction can be performed under relatively low temperature less than 180°C without any stirring and hot-injection technique required. Secondly, a simple, productive, low-cost route has been developed to synthesize the high-quality one-dimensional and multi-armed nanorods of CdE (E=Se, Te) using CdO as a cadmium source and myristic acid (MA) as a complexing agent. Thirdly, High-quality CdSe quantum dots have been synthesized through an organometallic method with methoxide cadmium as a cadmium precursor. Without any size sorting, the FWHM (full width at half maximum) in PL spectra almost for all CdSe samples is less than 30 nm and only 22 nm from the best sample. The emission peaks with different particle size in toluene can be tuned from 478 nm to 654 nm corresponding to a color change from blue-green to red.

P9.3

Solution based synthesis of confined straight and branched semiconductor nanowires. Masaru K. Kuno and Vladimir Protasenko; Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana.

This presentation will describe the synthesis and characterization of both straight and branched semiconductor nanowires. Particular emphasis will be placed on both CdSe and PbSe systems. A solution based approach is used to make the nanowires employing low melting catalyst particles. Resulting nanowires have diameters (< 10 nm) within the confinement regimes of their respective materials (Bulk exciton Bohr radii: CdSe 5.6 nm, PbSe 46 nm). Branched nanowires also exhibit confinement effects due to their narrow diameters. Branched nanowire morphologies have characteristic tripod, v-shape, t-shape and y-shape morphologies. Preliminary optical properties both at the ensemble and single wire limit are discussed.

P9.4

Synthesis of Core/Shell Quantum Dots via Core-Seeding. Sung Jun Lim, Yongwook Kim, Wonjung Kim and Seung Koo Shin; Chemistry, Pohang University of Science and Technology, Pohang, Kyungbuk, South Korea.

A core-seeding method is employed in the synthesis of CdSe/ZnE (E=S,Se) and CdSe/ZnSe/ZnS core/shell quantum dots (QDs). In the core-seeding method, fine powders of purified core QDs were injected into a hot shell-precursor solution in high concentrations to initiate the shell growth over the injected core seeds. Our methods yielded core/shell nanocrystals without any cross contamination from unwanted nanoparticles of shell material itself. The controlled growth of core/shell QDs now becomes highly reproducible with photoluminescence (PL) yields comparable to those made under the conventional procedure. Both CdSe/ZnS and CdSe/ZnSe/ZnS core/shell QDs were made water-soluble by incorporating either mercaptoalkanoic acid, mercaptoalcohol, or mercaptoalkylamine with differing alkyl chain lengths. We studied the variation of PL of water-soluble QDs in aqueous solution as a function of pH and that on a PMMA thin film as a function of reducing additives, such as β -mercaptoethanol and dithiothreitol.

P9.5

Foerster-Type Resonance Energy Transfer in Polymer-Stabilized Colloidal CdS Quantum Dots Coupled to Dye-Labeled Proteins. Akira Sugimura¹, Yusuke Tokuhira¹, Ikuro Umezumi¹ and Yukio Nagasaki²; ¹Department of Physics, Konan University, Kobe, Japan; ²Tsukuba University, Tsukuba, Japan.

Recently, we reported that functionally PEGylated CdS quantum dots (QDs), which are prepared by a coprecipitation method, show good dispersion stability in aqueous media, and that fluorescent resonance energy transfer from the QDs to the dye molecules is observed when the QDs are coupled with dye-labeled proteins in the solution [1,2]. This result suggests a possibility of applying it to novel molecular recognition system, although more understanding about the mechanism of the resonance energy transfer is necessary in order to design and realize a sensitive bio-analytical system. In the present paper, we study spectrally resolved dynamics of the photo-luminescence (PL) from the above mentioned CdS QDs coupled to dye-labeled proteins by using Q-switched YAG laser. The PL intensity from the independent CdS QDs decreases exponentially, indicating two decay lifetimes. The longer lifetime is several ns, while the shorter one is of the order of tens of ns, corresponding to different surface trapping states. When the CdS QDs are coupled to dye-labeled proteins, both of the lifetimes decrease significantly. This fact indicates that the present resonance energy transfer is

Foerster-type and rules out indirect energy transfer via photon re-absorption process. We now adopt rate equation approach in order to analyze the energy transfer dynamics quantitatively. Fitting the experimental results to the rate equation solution, the energy transfer times from a QD to a dye molecule are obtained to be about 10ns and 200ns for the shorter and longer lifetime states, respectively. Using these values we can estimate the quantum efficiency of the resonance energy transfer rate to be about 40 %. Theoretical value for the Foerster-type resonance energy transfer time can be estimated by using homogenous width for the QD emission line as well as the distance between a QD and the connected dye molecule. Assuming the experimentally obtained emission width to be homogenous one, we obtain fairly good agreements between the experimental and theoretical values for the QD-dye distance and the energy transfer time. This indicates that the observed emission band width in CdS QD is effectively homogenous and that the Foerster-type resonance energy transfer is easier to take place. In conclusion, the spectrally resolved PL dynamics is studied for polymer-stabilized colloidal CdS quantum dots coupled to dye-labeled proteins. It is found that the resonance energy transfer in this system is Foerster type. The emission line width in CdS QD is found to be effectively homogenous, which suggests that the present system is one of the prospective candidates to realize sensitive molecular recognition system. [1] Y. Nagasaki et. al., *Langmuir* 2004, 20, 6396-6400. [2] I. Umezu et. al., *Microelectronic Engineering* 66 (2003) 53-58.

P9.6

Surface Modulation of Magnetic Nanocrystal Probes for Highly Efficient Intracellular Labeling and In Vivo MR Tracking. Jin-sil Choi^{1,2}, Young-wook Jun^{1,2} and Jinwoo Cheon^{1,2}; ¹Chemistry, Yonsei University, Seoul, South Korea; ²Nano-Medical National Core Research Center, Yonsei University, Seoul, South Korea.

High-quality magnetic iron oxide (Fe₃O₄) nanocrystals are developed for use in in vivo cellular magnetic resonance (MR) tracking. The surface properties of nanocrystals are modulated by incorporating surface bound cationic and anionic ligand. The surface-charge-dependent intracellular labeling capacities of surface modified iron oxide was examined by using various types of cells, which reveals that cationic iron oxide nanocrystals are successfully transported into cells. Such cell transport capability of cationic iron oxide nanocrystals leads to significant MR contrasting effects of labeled cells. The cytotoxicity of the nanocrystals is investigated and the results show that the cationic nanocrystals are not toxic at dose levels that employed in intracellular labeling. Finally, the magnetic nanocrystals are successfully utilized MRI imaging probes for monitoring neural stem cell migration in rat spinal cord.

P9.7

Hydrodynamic Dimensions of Hydrophilic Functional QDs. Thomas Pons^{1,2}, Harry Tetsuo Uyeda¹ and Hedi Mattoussi¹; ¹Optical Sciences Division, Naval Research Laboratory, Washington, District of Columbia; ²Chemical and Biomolecular Engineering, Johns Hopkins University, Baltimore, Maryland.

Due to their unique optical and spectroscopic properties luminescent quantum dots (QDs) have attracted a tremendous interest for use in bio-motivated applications. In order to carry out any biological studies these inorganic nanocrystals are coated with ligands that provide them with both hydrophilicity and functionalization. Reported surface functionalization schemes include cap exchange with bifunctional ligands, polymer coating and encapsulation with phospholipid micelles. These schemes along with conjugation to bioreceptors strongly influence the nanoparticle hydrodynamic radius. This parameter is particularly important as it influences properties such as assay design, delivery of QDs and QD-conjugates through cellular membranes and migration inside live cells. Techniques such as transmission electron microscopy probe only the inorganic core size. We use dynamic light scattering (DLS) to measure the diffusion coefficients (D) and derive the hydrodynamic radius (Rh) of CdSe-ZnS core-shell QDs capped with various types of hydrophilic surface coatings. In addition to the hydrodynamic radius, DLS also provides information on the polydispersity of the samples. Furthermore, contrarily to fluorescence correlation spectroscopy, DLS is not subject to artifacts due to blinking or probe volume saturation. We characterize the hydrodynamic radius of nanocrystals of various core size and surface coatings. Ligands explored include dihydroliipoic acid (DHLA), poly(ethylene glycols)-terminated dihydroliipoic acid (DHLA-PEG), polymeric coating, and the native trioctylphosphine/trioctylphosphine oxide (TOP/TOPO) used for solubilization in organic solvents (for comparison). We observe a consistent dependence of the hydrodynamic radius on the size of the inorganic core, and more importantly, on the type and lateral extension of the hydrophilic coating materials. A substantial increase in the hydrodynamic dimensions is measured for polymeric overcoating, for example. We complement our studies with a

derivation of the surface charge of QDs capped with charged end groups (e.g., DHLA either pure or mixed with neutral caps) using Laser Doppler Velocimetry. These properties are extremely relevant for designing assay and sensing schemes based on fluorescence resonance energy transfer (FRET) as well as diffusion in live cells, for instance.

P9.8

Aqueous Synthesis and Surface Modification of Quantum Dots for Biomedical Applications. Hui Li, Wan Y. Shih and Wei-Heng Shih; Department of Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania.

Quantum dots (QDs) are semiconductor nanocrystals that exhibit distinctive photoluminescence properties due to quantum confinement effect. Through an environmentally friendly aqueous method, cadmium sulfide (CdS) and zinc sulfide (ZnS) QDs capped with different molecules were synthesized with size as small as 2-3 nm. The fluorescence emission varies from blue to red depending on the size and/or composition of QDs. The capping molecules, including carboxyl and amino functional groups which were ready for bioconjugation, helped stabilize QDs in aqueous suspension against aggregation and photobleaching. Higher amount and longer chain of capping molecules improved the stability of QDs. Meanwhile, processing temperature has a significant effect on the emission spectrum of QDs. As a fluorescence imaging and tracking tool, the application of aqueous QDs in biomedical systems was also investigated.

P9.9

Biocompatible manganese doped Zinc sulphide nanocrystals. Hemant C. Warad¹, Joydeep Dutta^{1,3}, Chanchana Thanachayanont², Gamolwan Tumcharern³ and Jons Hilborn⁴; ¹Microelectronics FOS, Asian Institute of Technology, Pathumthani, Thailand; ²National Metal and Materials Technology Center, Pathumthani, Thailand; ³National Nanotechnology Center, Pathumthani, Thailand; ⁴Polymer Chemistry, Materials Chemistry, Uppsala University, Uppsala, Sweden.

We will introduce a novel biocompatible (Chitosan) passivation layer for manganese doped zinc sulphide nanophosphors that show interesting enhancement in the luminescence efficiency, which could have applications in biolabeling (markers). Chitosan capped quantum dots of zinc sulphide doped with manganese has been synthesized in the aqueous medium which showed improved luminescence compared to other passivation agents that are generally reported in this literature. Chitosan is a biodegradable, biocompatible polymer with polycationic properties that is extracted from chitin and is one of the most abundant natural organic polymers that form the exoskeleton of crustaceans, like shrimps, crabs, lobsters etc. Chitosan is extracted by alkaline deacetylation of chitin, wherein the amide groups in the chitin monomer is deacetylated to amine (NH₂) groups. Nanoparticles capped with chitosan thus have a surface containing free amino groups to react with other suitable active group. Different chemical receptors can be attached to the amine moiety of chitosan via several reactions; for example, the nucleophilic substitution of bromine by the primary amine or the condensation reaction between aldehyde and the active amine. On the contrary, in case of biomolecule such as antibody, the amino groups will react with esters found in the peptide back bone through aminolysis resulting in the grafting of the amino acid to the nanoparticle surface. This functional group could have interesting possibilities for innovative chemistry. The Manganese doped ZnS nanoparticles show a photoluminescence peak at 590nm which can be correlated to the presence of the manganese centers in the crystallites. The crystallite size determined from X-Ray diffraction was found to be about 2nm which agglomerate to form primary particles of 30 to 40 nm sizes. High-resolution transmission electron microscopy further confirmed this observation where dense crystallites of 3 to 4 nm sizes were observed. Fourier Transform Infrared Spectroscopy is performed to determine the presence of the capping agent on particles that were dried from the colloidal solutions after washing off the unreacted solutes and it was confirmed that NH type of bonds are indeed available on the surface. It is highly probable that the Chitosan passivates electronic defects on the surface of the nanoparticles reducing the non radiative recombination sites and hence improving the luminescence efficiency. This capping agent can be very interesting for solid state device applications as chitosan is very stable at temperatures up to 200 degree C.

P9.10

Tunable multichannel DNA-PbS quantum dot microcavity. Yasha Yi, Rong Sun, E. H. Sargent and L. C. Kimerling; DMSE, MIT, Cambridge, Massachusetts.

Biological imaging is the key technology to study bio-molecules. Recent studies focused on visible wavelength range, which has limitations like photon bleaching and short penetration depth. Here

we successfully fabricated a solution based PbS quantum dots directly attached to single stranded DNA, the PbS quantum dots has light emission at second biological window from 1100-1700nm, which has large penetration depth. We have demonstrated a microcavity structure, which has the tunable and multichannel light emission from this PbS quantum dots attached directly on single stranded DNA (ss-DNA). The SEM image of the microcavity structure shows smooth interface between the PbS quantum dot attached DNA layer and the e-beam deposited dielectric Si/SiO₂ layers. By engineering the microcavity layer thickness, we can selectively confine certain wavelength inside the cavity and the information at this wavelength can be significantly amplified. The combination of nanophotonic structures and quantum dot tagged DNA is very promising to study the single molecule behavior.

P9.11

MRI and NMR investigations of Gd³⁺ Quantum Dot contrast agent. Julie Lynn Herberg¹, Erica Gjersing¹, Robert S. Maxwell¹, Daniele Gerion¹ and Fanqing Frank Chen²; ¹Chemistry and Material Science, Lawrence Livermore National Laboratory, Livermore, California; ²Life Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California.

Primary breast tumors less than about 2 mm in diameter are below the detection limit of most clinical imaging techniques. The clinical impact of this inability to detect small tumors is that cancer is frequently not detected until it has progressed to a stage when the probability of curative treatment is significantly reduced. Rapid, sensitive, specific and noninvasive imaging techniques are urgently needed to detect cancer in its earliest stages to improve clinical outcomes, and to reduce the use of expensive biopsies. In addition, targeted, molecular image-guided intervention has not been evaluated adequately in breast cancer to allow highly localized, non-invasive therapeutic treatments. Magnetic resonance imaging is an ideal tool to study anatomical images, providing information about the physico-chemical state of tissues, and flow diffusion and motion. Contrast agents are often required to enhance the contrast between different types of tissue and increase the chance of detection. Since most soft tissue is comprised of water, MRI actually images the ¹H longitudinal (T₁) and transverse relaxation processes (T₂) in water, which are dependent on tissue type. The main goal of contrast agents in MRI is to accelerate these relaxation processes of water protons in surrounding tissues. This is achieved through adding small amounts of paramagnetic impurities, such as Gd³⁺. By attaching quantum dots, which has been shown to be water-soluble, to the Gd³⁺ contrast agent; the quantum dots coated with nuclear localization peptides can transfect the cells and can be used as a therapeutic agent and a diagnostic agent for MRI. To achieve the most effective response, it is important to understand the concentrations dependences of these paramagnetic impurities on the (T₁) and (T₂) relaxation times in both water and soft tissue. In the present study, (T₁) and (T₂) relaxation times are measured in both NMR and MRI system to determine the properties of a Gd³⁺ quantum dot contrast agent in order to optimize the concentration and desired effects on water and soft tissue. 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 # W-7405-ENG-48.

P9.12

Imaging and Spectrally Discriminated Time-Resolved Photoluminescence of Single Aggregates of Semiconductor Nanoparticles. Thomas Blaudeck and Frank Cichos; Photonics and Optical Materials, TU Chemnitz, Chemnitz, Germany.

Following the bottom-up approach of modern nanotechnology, the understanding of elementary interaction processes between the building blocks is a necessity on the roadmap towards large-scale assemblies and their reaction dynamics. Narrow-band photoluminescence emission and color tunability by size make semiconductor nanoparticles (NPs) or quantum dots appropriate candidates for many future applications. Although there have been intense scientific efforts since at least the 1980s, little is known about the elementary interaction processes of the NPs with their environment. In particular, communication, coupling and coherence between the individual dots account for central topics in numerous scientific efforts. In the regime of strong coupling between individual NPs in an assembly, delocalization of the electronic states across multiple NPs leads to new states and thus yields a change of optical and electronic properties. These processes are thus the key knowledge for the design of materials with custom-tailored optoelectronic properties such as binary optical memories, switches and light-emitting devices. In this report, we present results of single-particle spectroscopy and time-resolved photoluminescence on single NP aggregates. They are formed by coupling two species of NPs to one another, with one species being immobilized on a silica surface by techniques of microcontact printing. The sample preparation is monitored by spectrally resolved wide-field microscopy. In the

correlation experiments we make use of a home-built confocal microscope and time-resolved single-photon counting equipment based on avalanche photodiodes. The optical detection is done in two channels allowing spectral discrimination of the NPs. We look at the intensity fluctuations in each of the channels and interpret the results with respect to their temporal and spectral correlation.

P9.13

Influence of Surface Electrode on Luminescent Properties of Nanocrystalline Silicon Electroluminescent Device. Keisuke Sato and Kenji Hirakuri; Dept. of Electronic and Computer Engineering, Tokyo Denki University, Saitama, Japan.

Nanocrystalline silicon (nc-Si) is useful candidate materials for development of new flat panel displays including electroluminescent (EL) display, flexible display and field emission display. The nc-Si based EL device is mainly composed of surface electrode/luminous layer (nc-Si)/substrate/ohmic back contact structure. The visible luminescence of the EL device is observed by the transmission of photon through the surface electrode from the luminous layer. Therefore, the luminescence intensity is influenced by the type, transmittance, resistivity of surface electrode. In this paper, we have studied the luminescence and electrical properties of EL device using indium tin oxide (ITO) film as the surface electrode, and compare them with those from the EL device using gold (Au) electrode. The silicon dioxide (SiO₂) layer containing nc-Si, which used for the luminous layer, was formed on a p-type Si wafer by cosputtering of Si/SiO₂ targets and subsequently annealing at high temperature. The nc-Si, then, were dispersed uniformly onto the wafer by treating it in hydrofluoric (HF) acid solution in order to remove the SiO₂ layer. After that, the electrode was formed to a surface of luminous layer and a back of wafer. The surface and back electrodes were used the ITO, Au and aluminum (Al), respectively. The EL device using Au electrode exhibited a red luminescence with a peak at 670 nm by applying the direct current (DC) voltage above 4.0 V. On the other hand, the EL device using ITO electrode emitted the red light at the low DC voltage of 3.0 V. Moreover, the red luminescence intensity of the EL device strengthened more than one order of magnitude in comparison with that of EL device using Au electrode. The good performance of the EL device is due to the high transmittance (90 %) and the low contact resistance of ITO electrode.

P9.14

Measurement of photoluminescent quantum yields of thin-films and powders dispersing semiconductor nanocrystals. Chunliang Li¹, Masanori Ando¹, Kazuhiro Nishikawa^{1,2}, Hiroyuki Enomoto² and Norio Murase¹; ¹Photonics Research Institute, National Institute of Advanced Industrial Science and Technology, Ikeda-city, Osaka, Japan; ²Division of Electronics and Applied Physics, Graduate School of Engineering, Osaka Electro-Communication University, Neyagawa-city, Osaka, Japan.

Accompanied by the recent development of lighting devices and displays, the appearance of innovative phosphors is always anticipated. Photoluminescent (PL) quantum yields are the most important factor of these phosphors. Generally, the quantum yield is defined by a probability of photon emission after absorption of irradiated photons in ultra-violet region. So far, two types of experiments have been done for the measurement of the quantum yields. One is for dilute solutions in 1-cm cuvette by using a conventional fluorometer. The other is for powder by using an integral sphere. The measurement by an integral sphere is believed to be precise. However, the configuration is rather complicated and the sensitivity is lower than the cuvette method. Further the relationship between the cuvette method and the integral sphere method has ever been not investigated. Semiconductor nanocrystals prepared by colloidal methods exhibit unique size-dependent strong PL and are of great importance for fundamental research and industrial applications. We incorporated these nanocrystals in transparent glass films having the thickness of 0.1-0.2 mm by using a sol-gel method. We have systematically measured the quantum yield of these films. The measurements are of two kinds. One is a method using only a conventional fluorometer. The other is a method using an integral sphere equipped with a conventional fluorometer. First, we have measured the PL intensity of standard aqueous 0.05 M H₂SO₄ solution of quinine kept in home-made cells having various optical path lengths. The relationships between PL intensities, optical path lengths, and absorbance of the standard dye were obtained. A theoretical consideration gives a general relationship between film thickness, absorbance and PL quantum yields. That relationship was used for the determination of quantum yields by using a conventional method. The same film was used for the measurement of using an integral sphere. It was found out the efficiencies derived by the two method is similar. This means that the correction due to a difference of refractive indices is not so obvious compared with a previous theory based on the point emission source. We have measured the powder samples prepared by grinding the glass film. It was found out that the

quantum yields of the powder measured by the integral sphere go down ca. 15% in average. We attribute this to the scattering loss in the inside of the glass powder because an excitation light goes inside the powder by absorption. On the other hand, the excitation light irradiated on the reference white light scatter (MgO) does not go inside because of negligible absorbance. The error generates because we take the scattered light intensity of the reference in the integral sphere as the level of zero-absorbance.

P9.15

I-V Characterizations of Single ZnO Nanowire using the Three different Gate Types. Dong-Young Jeong^{1,2}, Kihyun

Keem², Kyung-hwan Kim², Jeongmin Kang², Changjoon Yoon², Byungdon Min², Kyungah Cho² and Sangsig Kim²; ¹Institute for Nano Science, Korea University, Seoul, South Korea; ²Department of Electrical Engineering, Korea University, Seoul, South Korea.

In recent years, many researchers studied nanodevices applying the nanowires. But, many devices showed the I-V characteristics controlled by top and back gates only. These nanodevices showed poor electron mobility because of the electron surface scattering. And most nanodevices were making out using e-beam lithography process. It is not suitable for mass production. So, solve the problems, we have developed the nanodevice with cylindrical gate using the ZnO nanowire and the photolithography process. Cylindrical gate structure consists of the ZnO nanowire was floated on the Au/Ti source-drain electrodes and cylindrically surrounds the center of nanowire with 20 ~ 40 nm Al₂O₃ was deposited by atomic layer deposition (ALD). Next process, Au/Ti gate metal was cylindrically deposited on the Al₂O₃ insulator. This cylindrical gated ZnO nanowire device I-V curves show that higher mobility than the back and top gate ZnO nanodevice. And the gate control is possible for 1~2 volts. This is lower than 10 ~ 40 V back gate control voltage. In addition, top gate and cylindrical gate I-V results will be presented.

P9.16

Abstract Withdrawn

P9.17

Nanostructures Based on Porous Anodic Alumina for Solar Cells and Harmful Impurity Detection Application.

Ludmila Anatolievna Nosova¹, Sh U. Yuldashev¹, Thomas Dittrich² and P. K. Khabibullaev¹; ¹Heat Physics Department, Academy of Sciences of Uzbekistan, Tashkent, Uzbekistan; ²Hahn-Mietner Institute, Abt. SE 2, Berlin, Germany.

On this study synthesis of CdS and CuxS nanowires grown into porous anodic alumina (PAA) matrix using different deposition techniques, such as electrochemical deposition and SILAR (successive ion layer adsorption and reaction) technique is presented. Semiconductor nanowires with different pore diameters from 10 to 100 nm are obtained. Design of CdS/CuxS nanostructure for solar cell and harmful impurity detection application is proposed and discussed. The suggested procedure of nanostructure fabrication is relatively cheap, efficient, well-controlled, and easy for realization.

P9.18

Photoluminescent properties of Terbium doped silicon rich oxide. Wei Gao, Tingkai Li, Yoshi Ono and Victor Hsu; 5, Sharp labs of America, Camas, Washington.

Due to the opportunities offered by silicon based optoelectronic devices, silicon nano particles embedded in a silicon oxide matrix has become a candidate for future electroluminescent (EL) devices that would be possible to incorporate with CMOS integrated circuits. It has been reported that undoped silicon nano particle EL exhibits broad emission bands with low efficiency. Rare earth doped silicon nano particles on the other hand, has demonstrated more efficient emission, and narrow bandwidth discrete emissions. It is possible to alter the emission wavelength by using different rare earth dopants to provide better optical communications capability [1]. In this paper, the PL characteristics of Tb doped silicon rich oxide (SRO) films deposited by DC-sputtering followed by post-annealing processes are reported. Tb doped SRO films with Tb concentrations from 0 to 2%, and refractive indices from 1.5 to 1.8 (corresponding to the level of Si richness) have been deposited. PL measurements show that for as-deposited condition, there are two types of emissions. One is the narrow bandwidth emission associated with the Tb intra 4f transitions and the other is a broad bandwidth emission associated with wide size distribution of silicon nano particles. Once the samples were annealed at 950C for 10min, the Tb related discrete emission was significantly enhanced while the silicon nano particle related emission was suppressed to an undetectable level. Before anneal, the PL intensity showed poor correlation with the Tb concentration, while after anneal, the intensity for the Tb peaks show good linear correlation with Tb concentration. Strong PL intensities were obtained from SRO films with Tb concentration of 2% and refractive index of 1.7 after

post-annealing at 950C for 10min. The possible light emitting mechanism is also discussed. [1]. Maria E. Castagna et al. High efficiency light emission devices in silicon. MRS fall meeting, 2002.

P9.19

Porous Silicon Formation Under Open Circuit Potential Conditions: Optical and Structural Characterization.

Vassilios Kapaklis¹, Panagiotis Pouloupoulos², Peter Schweiss³ and Constantin Politis^{1,4}; ¹Engineering Science Department, University of Patras, Patras, Greece; ²Materials Science Department, University of Patras, Patras, Greece; ³Institut fuer Festkoerperphysik, Forschungszentrum Karlsruhe, Karlsruhe, Germany; ⁴Institut fuer Nanotechnologie, Forschungszentrum Karlsruhe, Karlsruhe, Germany.

Porous silicon (PS) can either be formed by anodization in HF-containing solutions under anodic bias or chemically without the application of an external current, by simple immersion of a silicon sample in a HF solution containing some oxidation agent. In the present work we have studied the formation of PS on (100) p-type B doped Si wafers (1 Ω cm), in HF:Ethanol:H₂O₂ aqueous solutions, where the concentration of H₂O₂ is varied. The back surface of the silicon substrates was covered by a sputtered thin film of Pt with a thickness of 7.5-10 nm. Pt was sputtered in order to form a galvanic cell. As a result, homogenous and high quality PS films were obtained and investigated for their optical and structural properties, by photoluminescence (PL) emission spectra, total absorbance spectra, atomic force microscopy (AFM), transmission electron microscopy (TEM) and conventional X-ray diffraction. It has been found that the process of PS formation can be controlled by the concentration of H₂O₂ which can also affect the photoluminescence emission spectra. AFM reveals that the samples surface is relatively flat (rms roughness 4.2 nm) and consists of vertical column like rectangular remnants of the etching process. X-ray diffraction indicates the presence of small Si nanocrystals which have the same crystallographic orientation as the etched wafer. All samples exhibited strong photoluminescence in the well know yellow-red spectral region as well as in the near infrared depending on preparation conditions. Cooling the samples to 100 K and recording of PL spectra shows additional emission bands at lower energies. This process can be effective for the batch production of porous silicon with stable characteristics.

P9.20

Optical Characterization of a 3-Stacked InGaAs Quantum Dot Infrared Photodetector Treated with Hydrogen-Plasma.

Ju Young Lim^{1,2}, S. H. Hwang¹, Jin Dong Song¹, Won Jun Choi¹, Jung Il Lee¹, Yong Ju Park¹ and H. S. Yang²; ¹Nano Device Research Center, Korea Institute of Science and Technology, Seoul, South Korea; ²Physics Dept., Chungang University, Seoul, South Korea.

We have carried out hydrogen-plasma (H-plasma) treatments on a 3-stacked In_{0.5}Ga_{0.5}As quantum dot infrared photodetector (QDIP) structure. The QDIP structure used in this study consists of 3-stacked Si doped (Si ~ 2x10¹⁸/cm³) In_{0.5}Ga_{0.5}As QD layer separated by 18 nm-thick GaAs layer which was grown by molecular beam epitaxy. By using standard device process, the structure was processed to QDIP, which had an active area of 2x2 mm². H-plasma treatment on the QDIP has been carried out at 200 oC for 15 min under 40 sccm of H₂ gas flow rate with a RF plasma power density of 60mW/cm². After H-plasma treatment, photoluminescence (PL) peak was split into two peaks, the energy of one peak is smaller than that of as-grown sample, and the energy of the other peak is larger than that of as-grown sample. The photo-response spectra measured at 10 K showed a blue-shift in its peak by a 109 meV for H-plasma treated sample compared to the as-grown sample. This means that the only QDs showing its PL peak at lower energy contributed the photo-current. Furthermore, the maximum operation temperature was increased from 50 K for the as-grown sample to 130 K for H-plasma treated sample, even though the peak responsivity was reduced by 10 times, which may be due to the introduction of defects during H-plasma treatment.

P9.21

Orbital Occupation in Electron-Charged CdSe Quantum-Dot Solids. Arjan J. Houtepen and Daniel Vanmaekelbergh; Debye Institute, Utrecht, Netherlands.

Assemblies of semiconductor nanocrystals, so-called quantum dot solids, form an interesting class of new materials[1]. The opto-electronic properties of such systems can be tuned by choice of the semiconductor nanocrystals (the building blocks) and the electronic interactions between them. The properties of the building blocks are determined by confinement of the electron and/or hole inside the nanocrystal host. Quantum confinement leads to a set of discrete conduction and valence orbitals and a "band" gap that increases in energy with decreasing crystal size. Electron-charged quantum dot solids may become important in the opto-electronic industry, e.g. for LED's[2], low-threshold lasers[3] and solar cells. Their properties will, for a large part, depend on the exact

distribution of electrons over different states[4-6]; the orbital occupation is, thus, of great fundamental interest. We have prepared high-quality assemblies of monodisperse CdSe quantum dots and employed a combination of electrochemical gating and electrical and optical techniques to study orbital occupation in these quantum-dot solids. Electron occupation in localized states is important in some cases and can be unambiguously distinguished from occupation of the nanocrystal eigenstates. In addition, all excitonic transitions show a red-shift in the transition energy, due to the presence of electron charge. We infer that the energy of the S-electrons is determined by the quantum-confinement energy and by Coulomb repulsions of the S-electron with all other electrons in the assembly. By using a simple electron-repulsion model we explain observed differences in the electron addition energy for different samples, the broadening of the electron occupation as a function of electrochemical potential, and the strong dependence of the electron-addition energy on nanocrystal diameter. In general we show that the charge located in electron traps plays an important role in the properties of the assembly. We believe that the electron traps are related to chemical impurities such as O₂ and H⁺ that absorb on the nanocrystal surface in the assembly. It is clear that such effects must be avoided in future opto-electronic applications based on quantum dot assemblies. *email address: Daniel@phys.uu.nl 1 C. B. Murray, C. R. Kagan, and M. G. Bawendi, Annual Review of Materials Science 30, 545 (2000). 2 V. L. Colvin, M. C. Schlamp, and A. P. Alivisatos, Nature (London) 370, 354 (1994). 3 C. J. Wang, B. L. Wehrenberg, C. Y. Woo, et al., Journal of Physical Chemistry B 108, 9027 (2004). 4 A. L. Roest, J. J. Kelly, D. Vanmaekelbergh, et al., Physical Review Letters 89 (2002). 5 A. Germeau, A. L. Roest, D. Vanmaekelbergh, et al., Physical Review Letters 90 (2003). 6 D. Yu, C. J. Wang, and P. Guyot-Sionnest, Science 300, 1277 (2003).

P9.22

Ultrafast relaxation dynamics of charge carriers in CdSe quantum wires. Istvan Robel^{1,2}, Prashant V. Kamat² and M. Kuno³, ¹Department of Physics, University of Notre Dame, Notre Dame, Indiana; ²Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana; ³Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana.

Ultrafast transient absorption spectroscopy is used to study the relaxation dynamics of excited charge carriers in CdSe nanowires. Samples with diameters of 7-10 nm and length greater than 1 μm were studied in the high-excitation regime to determine the multi-exciton depopulation dynamics in a truly one-dimensional confinement geometry. Femtosecond white light continuum is used to probe the different excitonic bands arising from transverse quantum confinement. Results for inter- and intraband relaxation are discussed as a function of the density of the excited charge carriers.

P9.23

Enhancement of Radiative Recombination Rate of Excitons in Si Nanocrystals on Au Thin Films. Minoru Fujii, Kenji Imakita, Toshihiro Nakamura, Satoshi Miura, Eiji Takeda and Shinji Hayashi; Department of Electrical & Electronics Engineering, Faculty of Engineering, Kobe University, Kobe, Japan.

Silicon nanocrystals (Si-nc's) show strong photoluminescence (PL) at room temperature due to the recombination of excitons confined in the zero-dimensional quantum confined system. Two mechanisms are responsible for the efficient luminescence. The first one is the restriction of carrier transport in nanometer scale regions, and resultant suppression of non-radiative recombination processes via defects or impurities. The second one is the enhancement of the radiative recombination rate due to the better overlap of electron and hole wavefunctions, because of the confinement of excitons in a space smaller than the exciton Bohr radius of bulk Si crystals. However, even for Si-nc's as small as a few nanometers in diameter, indirect bandgap nature of bulk Si crystals is strongly inherited, and thus the radiative recombination rate is still very small. Therefore, further improvement of the radiative rate is desired to realize Si based optoelectronic devices. The radiative rate of an emitter can be modified by controlling the local photonic environments by placing it in a microcavity or in the vicinity of metal surface. The simplest explanation of the phenomena is that the emitter is defined to be an electromagnetic dipole oscillator, interacting with reflected field of the emitter's dipole radiation. If reflected field interacts with the emitter in phase, the radiative decay rate is enhanced, while out of phase, it decreases. As a result, the radiative rate oscillates with the distance between the emitter and the surface. The other expression of the phenomena is that the local photonic mode density (PMD) is changed in the vicinity of metal surface, and this results in the modification of the radiative rate, because it is proportional to PMD. The modification of radiative rate by controlling photonic environment has been demonstrated for dye molecules, rare-earth ions, and semiconductor nanocrystals. However, to our knowledge, no experimental evidence of the radiative rate enhancement of indirect

bandgap semiconductors has been shown. The purposes of this work is to control the radiative recombination rate of Si-nc's by Au thin films. The advantage of Si-nc's to study the effect of PMD on the radiative rates is that the PL band is very broad due to size and shape distributions, and the lifetime at low temperatures is very slow (~5 ms) and almost independent of the PL energy, i.e., the size, because at low temperatures almost all excitons stay in spin-forbidden triplet states. The broad PL band allows us to study the emission energy dependence of the effects in one measurement. We show that the radiative rate can be enhanced by the presence of Au thin films by measuring the time resolved PL spectra of Si-nc's at low temperatures. We demonstrate that the photon energy dependence of the enhancement factor can be well explained by the model which takes into account the modification of PMD by Au thin films.

P9.24

Infrared Electroluminescent Device based on Energy Transfer from Si Nanocrystals to PbSe Nanocrystals. Robert J. Walters, Sungjee Kim, Domenico Pacifici, Darci Taylor and Harry A. Atwater; Applied Physics, California Institute of Technology, Pasadena, California.

We have fabricated infrared light emitting devices in which PbSe nanocrystals are pumped via energy transfer from nearby silicon nanocrystals. Electrical excitation of the silicon nanocrystals is accomplished by sequential charge injection in a field effect light emitting device (FELED) structure. The device consists of an MOS transistor structure with an embedded floating gate comprised of ~5E12 silicon nanocrystals/cm² (2-4nm diameter) isolated from the channel by an ~4nm tunnel oxide and isolated from the gate contact by an ~8nm thick control oxide layer. Organically synthesized colloidal PbSe nanocrystals are drop cast on top of the n polysilicon gate contact. The gate contact thickness has been systematically varied from 5 to 40 nm in an effort to optimize the transfer of energy to the PbSe nanocrystals. In contrast to traditional LEDs in which charges are driven into an active region by a constant current, the charges in this device are injected sequentially into the silicon nanocrystal array from the channel of the transistor by an alternating gate potential. Excitons are thus formed only at bias transitions allowing excitation frequency response measurements to be used to probe characteristic time constants. The subsequent energy transfer to the PbSe nanocrystals can occur via radiation and absorption of near infrared photons or via non-radiative short range processes. Radiative energy transfer is limited by the slow recombination of excitons in silicon nanocrystals (~10-100kHz), while the short range non-radiative processes can be orders of magnitude faster. Non-radiative transfer processes can also be identified through the gate contact thickness dependence of the infrared EL response because the interaction strength for such processes is a function of the separation distance between the Si nanocrystals and the PbSe nanocrystals. We will discuss such observations of infrared electroluminescence in our device and comment on the role of radiative and non-radiative energy transfer processes.

P9.25

Time-resolved Studies of Colloidal ZnCdSe Nanorods. Lindsay Hardison¹, Hyeokjin Lee², Paul H. Holloway² and Valeria D. Kleiman¹, ¹Chemistry, University of Florida, Gainesville, Florida; ²Material Science and Engineering, University of Florida, Gainesville, Florida.

Recently, investigations have focused on the role of size and shape on the quantum confinement observed in CdSe, CdSe(ZnSe) and ZnCdSe nanoparticles. Alloying can be used to prepare colloidal composite nanoparticles, though there is no detailed comparison of the photophysical properties of ZnCdSe particles with different relative amounts of Zn. Research continues to elucidate the energy relaxation and recombination dynamics in nanoparticles. We present here a characterization of the lifetimes and dynamics of colloidal CdSe(ZnSe) and ZnCdSe nanorods using time-resolved photoluminescence (PL) and femtosecond transient absorption (TA). Preparation of a ZnCdSe rod is obtained by alloying a ZnSe shell with CdSe rod-like cores. Increasing alloying time results in more Zn integrated into the core. Since CdSe has a smaller band gap than ZnSe, as Zn diffuses into the core a blue shift in the composite band gap results. The diffusion process is not uniform and leads to broad PL spectra. Time resolved emission can provide information regarding the role of diffused Zn. Emission of an inhomogeneous population distribution (different sizes, shapes or composition) leads to the simultaneous probing of particles with different decaying rates. A stretched exponential function, $I(t) = A \exp[-(t/\tau)^\beta]$, can be used to describe these systems, where $\beta < 1$ corresponds to disperse populations. In the experiments presented here, the PL data yields small β values, independent of the emitted photon energy. At early times the PL probes particles with fast decaying times while at latter times it probes those with longer rates. Comparing CdSe rods encapsulated in ZnSe shells to composite rods (ZnCdSe) we find a significant decrease in the β value (from ~0.53 to

0.425 -0.44). Additional insight can be gained by investigating the ultrafast changes observed in the absorption spectra. Femtosecond TA has been utilized to study the evolution of the absorption bleaching in the nanorods. After excitation at 450 nm, two transitions are observed (1P(e)-1P_{3/2}(h) and 1S(e)-1S_{3/2}(h) denoted as 1P and 1S respectively): the former appearing instantaneously, while the latter reaching its maximum after 2 ps. In all samples, the 1S transition shows a narrowing of its spectrum as time increases. Comparing core (shell) and alloyed samples we observe: a) a more inhomogeneous population is created with the alloying of Zn, b) an increase in the band gap with added Zn (reaching a plateau after 2 hrs of alloying), c) a sharp increase in the 1S bandwidth after the initial diffusion of Zn into the core, d) a narrowing of the 1S band after additional diffusion of Zn, and e) a blue shift of both, 1S and 1P, transitions while the energy spacing between them remains unchanged (~ 25% of band gap). In conclusion, a description of the photophysics and dynamics of colloidal CdSe(ZnSe) and ZnCdSe nanorods has been presented.

P9.26

Dark Exciton State of PbS Nanocrystals in a Silicate Glass. R. Espiau de Lamaestre^{1,2}, Harry Bernas¹, D. Pacifici³, G. Franzo³ and F. Priolo³; ¹CSNSM-CNRS, Université Paris XI, 91405-Orsay, France; ²Fontainebleau Research Center, Corning SAS, 77210 Avon, France; ³MATIS-INFM and Dipartimento di Fisica e Astronomia, 95123 Catania, Italy.

We have synthesized 2.5-3.5 nm diameter PbS nanocrystals by sulfur ion implantation in Pb-based glasses and post-annealing. These nanocrystals display strong optical emission at wavelengths around 1.5 microns due to quantum confinement, and a photoluminescence (PL) excitation cross section that is two orders of magnitude higher than that of Si nanocrystal-activated Er. The PL intensity and decay rate temperature dependences provide evidence for a very large energy splitting (ca. 30 meV) of the emitting exciton ground state fine structure, presumably due to the complex PbS electronic band structure.

P9.27

Electroluminescence Properties of Si MOS Structures Containing Implanted FeSi₂ Nanocrystals. C. F. Chow¹, S. P. Wong^{1,3}, Quan Li^{2,3}, M. A. Lourenco⁴ and K. P. Homewood⁴;

¹Electronic Engineering, Chinese University of Hong Kong, Shatin, Hong Kong; ²Physics, Chinese University of Hong Kong, Shatin, Hong Kong; ³Materials Science and Technology Research Center, Chinese University of Hong Kong, Shatin, Hong Kong; ⁴School of Electronics Engineering, Computer and Mathematics, University of Surrey, Guildford, United Kingdom.

There has been a considerable amount of effort in the study of Si-based light emitting materials and devices in the past decade. Recently, electroluminescence (EL) at room temperature from Si metal-oxide-semiconductor (MOS) structures was reported [1] and room-temperature emission from β -FeSi₂ LED was demonstrated [2]. In this work, FeSi₂ nanocrystals were first formed in p-Si by Fe implantation with various processing conditions. Then MOS structures were fabricated with a thin oxide layer of several nanometer thick grown by rapid thermal oxidation (RTO). The EL properties from these Si MOS structures containing implanted FeSi₂ nanocrystals were measured as a function of temperature from 80 to 300 K. Clear EL signals were obtained even at room temperature for some of the devices fabricated at appropriate processing conditions. While in some samples, only a broad emission peak around 1.6 μ m attributed to the implanted FeSi₂ nanocrystals was observed, in some other samples, both the FeSi₂ peak and the Si band edge emission at around 1.1 μ m were observed. The temperature dependence of the EL intensity from the two peaks showed energy transfer between the two emission peaks. It was also found that there was significant enhancement in the intensity of the Si band edge emission in these structures. The dependence of the EL properties on the processing parameters will be presented and discussed. This work is partially supported by the Research Grants Council of Hong Kong SAR (ref. no. CUHK4231/03E), and C. N. Yang Optical Science Fund. [1] M.-J. Chen et al, J. Appl. Phys. 93 (2003) 4253. [2] M.A. Lourenco et al, Nucl. Instru. Meth. B206 (2003) 436.

P9.28

Improvement of electroluminescence intensity from nanocrystalline silicon. Hiroshi Kunii, Hiroaki Fujibuchi, Keisuke Sato and Kenji Hirakuri; Electronic and Computer Engineering, Tokyo Denki University, Hatoyama, Saitama, Japan.

Nanocrystalline silicon (nc-Si) has been accepted for attractive applications to Si-based display device because it exhibits injection-type electroluminescence (EL) at room temperature. However, the visible luminescence of the nc-Si based EL device has very weak brightness for display applications. In this work, we have developed the EL device to obtain the luminescence with the high

brightness at low direct current (DC) voltage. Moreover the luminescence and electrical properties of the EL devices have been investigated by luminescence spectroscopy and electrical measurements. The nc-Si was formed on the p-type Si (100) substrates by co-sputtering of Si/SiO₂ targets and subsequently annealing in a furnace at the temperature of 1000 °C. Then the nc-Si was dispersed from SiO₂ layer by using hydrofluoric acid steam and supersonic vibration treatments. After treatment the nc-Si adhered to the Si substrates. The top and bottom electrodes were utilized an indium tin oxide (ITO) and aluminum (Al), respectively. The EL devices showed the rectification characteristics on a voltage-current curve. Red luminescence from the EL device could be observed with the naked eye at a DC voltage of 4.5 V. This was caused by the realization of efficient carrier injection into the nc-Si region of luminous layer from the top cathode electrode.

P9.29

A Technique for Synthesizing Sub-10nm Europium Sulfide Nanocrystals. Marcela L. Redigolo^{1,3}, Dmitry S. Koktysh^{2,3},

Sandra J. Rosenthal^{2,3} and James Henry Dickerson^{1,3}; ¹Physics and Astronomy, Vanderbilt University, Nashville, Tennessee; ²Department of Chemistry, Vanderbilt University, Nashville, Tennessee; ³Vanderbilt Institute for Nanoscale Science and Engineering, Vanderbilt University, Nashville, Tennessee.

Recently, the synthesis and characterization of rare-earth chalcogenide nanostructured materials have garnered significant research attention due to their attractive optical, magnetic, and magneto-optical properties. Candidate applications for these materials include nanoscale light-emitting devices, magneto-optical isolators, high-density magnetic thin films, and others. Our contribution to this pursuit is the synthesis and characterization of sub-10nm europium sulfide (EuS) nanocrystals, produced via a novel two-step procedure that involves the preparation and thermolysis of a single precursor source, Eu(II) diethyldithiocarbamate complex with 1,10-phenanthroline. Such a technique provides controlled, selective synthesis of these nanocrystals, whose dimensions approach the quantum confinement regime of EuS, which is recognized to be less than 2.0nm. We believe that this simple thermolysis procedure can be adapted easily to accommodate additional lanthanide-based precursors to yield other rare-earth nanomaterials. Accompanying calculations of the excitonic and Bohr radii of electrons and holes within the nanocrystals establish the upper limit on the size of the materials to observe size-dependent blue shifts in the fluorescence and, likely, enhancements on the material's magnetic moment (μ_{eff}). In support of these statements, we provide structural characterization of EuS nanocrystals, via transmission electron microscopy (TEM), selected area electron diffraction (SAED), and x-ray diffraction spectroscopy (XRD). As well, we present stoichiometry characterization of the materials via Rutherford backscattering spectrometry (RBS). Absorption and photoluminescence spectroscopy measurements also are presented to describe the optical properties of the nanocrystals.

P9.30

LP-MOCVD growth of InAs quantum dot on InxGa1-xAs/InP material system for extending emission wavelength. Zongyou Yin, Xiaohong Tang, Jinghua Zhao and Sentosa Deny; Nanyang Technology University, Singapore, Singapore.

InAs quantum dots (QDs) formed on InP (001) substrate by low-pressure metal-organic chemical vapor deposition (LP-MOCVD) using tertiarybutylarsine (TBA) as arsenic source in nitrogen ambient has been studied. To extend the emission wavelength of the QDs, a strained InxGa1-xAs layer was grown on the InP buffer layer before starting growing the InAs QDs. The indium composition of the inserted InxGa1-xAs layer was varied from 0.53 to 0.72. Samples were characterized by using atomic force microscopy (AFM) and photoluminescence (PL). With the optimized growth conditions, uniform QDs with the surface density of 1.3 \times 10¹⁰/cm² have been achieved. The PL emission wavelength of this QD structure reached 2.27 μ m when measured at 150K. This is believed the longest emission wavelength from the InAs QD structure reported so far. The full width at half maximum (FWHM) of the PL emission spectrum of the QD structure is ~42 meV.

P9.31

Abstract Withdrawn

P9.32

Conversion of ZnSe and CdSe nanowires into Ag₂Se nanowires by ion-exchange. L. Hong, Zhuang Liu, C. X. Shan and S. K. Hark; Physics, The Chinese University of Hong Kong, Hong Kong, Hong Kong.

Ag₂Se in thin film and in bulk form have recently attracted considerable attention, because of its superionic conductivity and colossal magneto-resistivity. In comparison, few studies of Ag₂Se

nanowires have been reported so far. We show that single crystalline orthorhombic Ag₂Se nanowires can be easily and quickly converted from ZnSe and CdSe precursor nanowires through ion exchange reactions. The conversions, when carried out at 90 °C, are essentially completed in 20 minutes. The morphology of the precursors is faithfully retained in the process, despite the fact that a zincblende or wurtzite to orthorhombic structural transformation and a large unit cell volume change are involved. The structure, composition and morphology of the Ag₂Se nanowires were studied by X-ray and electron diffractions, energy dispersive X-ray nano-analysis and electron microscopy. We have studied the temperature and solvent dependence of the ion exchange reactions. Results suggest that the rates of conversions are limited by the outward moving rates of Zn ions in ZnSe or Cd ions in CdSe. The structural phase transition of the Ag₂Se nanowires from semiconducting to the superionic phase will be also discussed. Acknowledgement: The work described in this abstract was partially supported by a grant from the Research Grants Council of the Hong Kong Special Administrative Region, China (Project No. 401003) and a CUHK direct grant (Project code 2060277).

P9.33

Engineering the Natural Quantum Wires in ETS-4.

Bilge Yilmaz, Juliusz Warzywoda and Albert Sacco; Chemical Engineering Department, Northeastern University, Boston, Massachusetts.

In the field of quantum-confined nanostructures, fabrication of quantum wires presents a problem of considerable technical complexity and thus cost. All conventional manufacturing techniques have severe limitations due to both size and geometry. ETS-4 is a synthetic nano-porous crystalline titanasilicate material. Its framework contains linear monatomic titania chains, which are effectively isolated by a siliceous matrix. These chains exhibit quantum confinement effects, and consequently are natural quantum wires. The quantum wires in ETS-4 are the thinnest wires that can be hypothesized, since they are only one atom thick. It is expected that randomly located defects, inherent in the ETS-4 crystal structure, could produce unwanted discontinuities in the quantum wires. Additionally, since the titania chains run along the b-axis, there is a need to control the morphology and size of ETS-4 crystals (in the b direction), as well as their lattice defect concentration. Methods for controlling morphology, crystal quality, relative amount of defects and degree of intergrowth of ETS-4 were developed. A progressive change of ETS-4 morphology from polycrystalline spherulites to monolithic crystals with rectangular prism morphology was achieved by systematically adjusting the synthesis mixture pH between 11.50 and 12.90. The X-ray powder diffraction and energy dispersive X-ray spectroscopy suggested a smaller number of Ti vacancies (defects) in monolithic crystals compared to spherulites. The largest dimension of these monolithic crystals (~20 μm) was determined to coincide with the titania chains running in the b-direction. Variation of cation type and concentration allowed the effective control of the size of monolithic ETS-4 crystals. This novel strategy resulted in large ETS-4 crystals with an average length of ~200 μm. These are the largest ETS-4 crystals reported to date. Single crystal X-ray diffraction analysis demonstrated that these are single crystals with no detected intergrowth. Diffuse reflectance UV-vis (dr-UV-vis) spectroscopy investigation demonstrated the blue shift of the optical band gap for ETS-4, which can be considered as the most straightforward verification of quantum confinement in these systems. The dr-UV-vis and Raman spectra acquired for diverse ETS-4 samples exhibited varied characteristics. This was ascribed to variations in the quantum wire quality. Highly oriented (b-out-of-plane) ETS-4 films were fabricated in situ on various substrates. Since the quantum wires in ETS-4 crystals run in the b-direction only, in principle these films are oriented quantum wire arrays. These films can be utilized to test the potential of ETS-4 crystals as quantum wire components of thermoelectric, optoelectronic and photovoltaic devices.

P9.34

Mapping Strain in Electrophoretically Deposited CdSe Nanocrystal Films by Raman Microprobe Scattering.

Sarbjit Banerjee, Shengguo Jia, Dae-Im Kim, Richard Robinson, Jeffrey Kysar, Joze Bevk and Irving P. Herman; Materials Research Science and Engineering Center, Columbia University, New York, New York.

Mechanical stability and understanding of the elastic behavior of thin films comprised of nanocrystals is an essential requirement for use of these films in practical applications. In this study, we report the first measurements of the magnitude of the elastic strain, resulting from the residual solvent evaporation, in electrophoretically deposited CdSe nanocrystal films. Thin, electrophoretically deposited CdSe nanocrystal films are structurally sound but develop channel cracks and delaminate above a threshold thickness (0.8 microns for 3.2 nm diameter particles) due to the loss of residual solvent. This study

demonstrates the usefulness of Raman microprobe analysis to map elastic strain in different areas of thick, fractured CdSe nanocrystal films by exploiting the strain sensitivity of the Raman longitudinal optic phonon peak. A quantitative evaluation of the tensile strain in the nanocrystal cores can be extracted from the Raman data. The maximum in-plane tensile strain in the CdSe cores before film fracture is as high as ~2.5%, as determined by the 6 cm⁻¹ spatial variation in Raman shift, whereas the overall in-plane film strain is estimated to be ~11.7% from the dimensions of the cracks. From this we infer an overall elastic biaxial modulus of the film of ~13.8 GPa. Micromechanics models suggest that the TOPO matrix in these films has a biaxial modulus of ~5.1 GPa. Detailed examination of cracked and partially delaminated films by SEM and EDX, as well as Raman scattering, also reveals that in delaminated regions bond breaking occurs predominantly between the nanocrystals close to the film/substrate interface, rather than at the interface itself. The results of this study are applicable to other nanocrystal thin films and have important implications for the strain-dependent physical properties of their nanocrystal components. This work was supported primarily by the MRSEC Program of the National Science Foundation under Award No. DMR-0213574 and by the New York State Office of Science, Technology and Academic Research (NYSTAR).

P9.35

Structure and Dynamics of Structured II-VI-Semiconductor Nanoparticles in Selected Environments. [Christina Maria Graf¹](#),

Sofia Dembski¹, Rene Lewinski¹, Burkhard Langer¹, Eckart Ruehl¹ and Reinhard B. Neder²; ¹Institut fuer Physikalische Chemie, Universitaet Wuerzburg, Wuerzburg, Bavaria, Germany; ²Institut fuer Mineralogie und Kristallstrukturlehre, Universitaet Wuerzburg, Wuerzburg, Bavaria, Germany.

Structured semiconductor nanoparticles have unique size-dependent optical and electronic properties. Especially, small nanoparticles have a large surface-to-bulk ratio. Therefore, it is expected that the particle surface dominates their properties, so that the local environment near the surface strongly influences their properties. We present a systematic study on the optical, electronic, and structural properties of structured II-VI-semiconductor nanoparticles. CdSe-ZnS core-shell nanoparticles, which are stabilized by organic ligands, with adjustable size of both the core and the shell, are obtained from the high temperature thermolysis of organometallic precursors in coordinative solvents. These particles are subsequently functionalized either by an exchange of the apolar ligands by more polar ones, such as cysteine or cysteamine, or by the reversible adsorption of the amphiphilic polymer polyvinylpyrrolidone (PVP). As a result, the particles can be studied in various solvents. Alternatively, they are adsorbed on the surface of metal colloids, or they are investigated without any contact to a substrate in a particle trap. Furthermore, the adsorption of PVP allows us to embed the nanoparticles in silica colloids, where the interparticle distances of the quantum dots (QD) in the matrix is accurately controlled. The local structure of the nanoparticle samples is investigated by different spectroscopic approaches. The crystal structure of the QD is characterized by high-resolution electron microscopy (HRTEM) and X-ray diffraction (XRD). The influence of the local environment on the optical properties of the QD is studied by optical absorption and photoluminescence spectroscopy. Experiments on the influence of the particle environment with respect to the particle charge are carried out in an electrodynamic particle trap, where single particles are stored over long time periods. The local electronic structure of the QD is studied by element-specific excitation using soft X-rays near inner-shell absorption edges, where monochromatic synchrotron radiation is used. These results on free nanoparticles are compared to those on the deposited samples.

SESSION P10: Electrical, Electronic Properties and Devices I

Chairs: Khaled Karrai and Richard Schaller

Thursday Morning, December 1, 2005

Room 210 (Hynes)

8:30 AM *P10.1

Resonant Rayleigh Scattering Interferometry of a Single Quantum Dot. [Khaled Karrai](#), A. Hoegle, B. Alen, M. Kroner, S. Seidl, A. Badoleto, R. J. Warburton and P. M. Petroff; Department fuer Physik, Ludwig Maximilians Universitaet, Muenchen, Germany.

Resonant Rayleigh scattering at photon frequency near resonance with the ground state exciton confined in single self-assembled InAs/GaAs quantum dots is investigated at cryogenic temperatures in optical transmission and reflectivity experiments. The Rayleigh scattered photons have the coherence of the laser source and for this reason they lend themselves to very-high resolution spectroscopy. The scattered light field is coherently superimposed on the laser source field allowing this way to perform interferometric measurements. We show that using Rayleigh scattering interferometry on a single quantum dot, the real and imaginary part the exciton resonant

scattering cross section can be obtained independently.

9:00 AM P10.2

High Resolution and High Collection Efficiency Spectroscopy of Single Quantum Dots. Anthony Vamivakas¹, Zhiheng Liu², Stephen Ippolito¹, Bennett Goldberg^{2,1}, Selim Unlu^{1,2} and Richard Mirin³; ¹Electrical and Computer Engineering, Boston University, Boston, Massachusetts; ²Physics, Boston University, Boston, Massachusetts; ³National Institute of Standards and Technology, Boulder, Colorado.

We apply the subsurface Numerical Aperture Increasing Lens (NAIL) technique to microscopy and spectroscopy of single InGaAs quantum dots (QDs) grown by Stranski-Krastanow self-assembly on GaAs substrates [1]. In self-assembled QD samples, a typically >100nm capping layer of the substrate material is grown over the QDs to protect them from any potential environment induced damage. Optically, the capping layer introduces a planar boundary between the object space and the far-field microscope. The dielectric interface acts as a barrier limiting both the resolving and light gathering power of the microscope. Incorporation of the index matched plano-convex NAIL mitigates the difficulties introduced by the planar boundary improving both the resolution and collection efficiency of our optical microscopy system. In contrast to conventional Solid Immersion Lens (SIL) techniques, the NAIL configuration (with the plano-convex lens attached to the substrate side of the sample) moves the interface between sample and SIL away from the focal plane of the confocal microscope thus minimizing interface imperfections on image quality. Treating the QD as an ideal point source and applying the Houston Criterion, we are able to measure an optical resolution for our NAIL-assisted confocal microscope of 350 nm with an emission wavelength of 960nm. The $\sim\lambda/3$ resolution of our system allows us to perform both PL and PLE measurements on single QDs. Potentially, more exciting than the enhanced optical resolution, is the improvement in our ability to collect QD light emission afforded by a NAIL. With our 1.61 mm radius GaAs NAIL, we have measured a 6-fold increase in the collection efficiency of our system. We are now trying to take advantage of the collection efficiency increase in applications where high signal-to-noise ratio is beneficial. Specifically, we are building a Hanbury-Brown Twiss (HBT) photon counting apparatus to do both auto-correlation and cross-correlation measurements on lines in the QD spectra. [1] Z. Liu, B. B. Goldberg, S. B. Ippolito, A. N. Vamivakas, M. S. Unlu, and R. Mirin, "High resolution, high collection efficiency in numerical aperture increasing lens microscopy of individual quantum dots," Appl Phys Lett, accepted for publication.

9:15 AM P10.3

Photodetectors Based on Colloidal Quantum Dot Films. David C. Oertel¹, Alexi C. Arango², Vladimir Bulovic² and Mouni G. Bawendi¹; ¹Chemistry, MIT, Cambridge, Massachusetts; ²Electrical Engineering and Computer Science, MIT, Cambridge, Massachusetts.

Colloidal quantum dots (QDs) are attractive candidates for use in photodetectors, both in the visible and in the near IR, because of their solution processibility and tunability of band gap with size, potentially enabling an inexpensive pathway to large-area, spectrally selective arrays. However, organic capping ligands of high band gap typically hinder charge transport to the extent that geminate exciton recombination dominates charge separation and extraction. Recently, solution-phase, after-casting chemical treatments of films have been shown to significantly improve photoconductivity of close-packed films of CdSe by increasing exciton ionization efficiency. We have produced a device of sandwich geometry, sensitive in the visible, in which the active layer is a 200-nm thick film of treated QDs. The device area is greater than 1 mm², and these devices operate at room temperature. Photocurrent excitation spectra closely resemble the CdSe core absorbance spectrum, and external quantum efficiency is typically 0.05% to 0.1% at 0 V and 10 to 17% at -5 V applied bias. At zero bias, under 110 mW/cm² at 514 nm, the I_{photo}/I_{dark} ratio is on the order of 10⁴, with a measured detection limit of $\sim 10 \mu\text{W}/\text{cm}^2$. The device bandwidth, likely limited by carrier lifetime, is 50 kHz.

9:30 AM P10.4

Single Crystal Nanoparticle Vertical Surround-Gate Field-Effect Transistor. Yongping Ding¹, Ameya Bapat², Ying Dong¹, Uwe R. Kortshagen² and Stephen A. Campbell¹; ¹Dept. of Electrical Engineering, University of Minnesota, Minnesota, Minnesota; ²Dept. of Mechanical Engineering, University of Minnesota, Minneapolis, Minnesota.

The previously reported successful synthesis of large faceted single-crystal Si nanoparticles has motivated the fabrication of Si semiconductor transistors using discrete Si nanoparticles instead of the conventional Si wafers. Here we demonstrate the use of 33 nm

cubic Si nanoparticles to obtain vertical flow, surround gate Schottky barrier field-effect transistors. Ultra-thin PtSi layers are employed as source/drain contact to the bottom and upper faces of the cubic nanoparticles to form Schottky barriers. As to the surround gate, a $\sim 12\text{nm}$ metal layer is sandwiched between the source/drain electrodes but insulated from them by two thin films of SiO₂. Repeated SiO₂ deposition, polishing, and etchback steps are used to achieve self-aligned features and no nanoptical lithography is required. Reasonable turn on/off characteristics and very high current drive are observed in field-effect transistors when properly constructed.

9:45 AM P10.5

Transport Properties of Solution-Grown Single and Multiple CdSe nanowire FETs. Anubhav Khandelwal¹, Debdeep Jena¹, Vladimir Protasenko², Masaru Ken Kuno², April Shricke³ and Brian A. Korgel³; ¹Electrical Engineering, University of Notre Dame, Notre Dame, Indiana; ²Chemistry, University of Notre Dame, Notre Dame, Indiana; ³Chemical Engineering, University of Texas at Austin, Austin, Texas.

We report temperature-dependent transport properties of Solution-Liquid-Solid (SLS) grown single 5-10nm diameter and 5-10 microns long CdSe nanowires. These measurements are then compared with the transport properties of a random network of multiple nanowires of similar diameters. A focussed-ion beam (FIB) technique was used to write metal source-drain contacts to single nanowires; for the multiple nanowires, ordinary optical lithography followed by metal evaporation and lift-off was employed. Different concentrations of nanowires in solution were drop-casted on Si/SiO₂ substrates with a back gate, making it possible to measure, and compare the electrical characteristics of single and multiple nanowire FETs. For single nanowires, dark currents in the pA regime were measured for ~ 1 volt drain-source bias at room temperature. Resistance of a single nanowire is observed to decrease by a factor of 10 when the temperature is increased from 300K to 523K. Photoconductivity is observed with visible light with a typical current increment factor of ~ 10 . Back gated measurements show modulation of the channel current with a low "on" to "off" current ratio of ~ 1 order of magnitude for a single wire. A negative gate voltage is needed to deplete the channel indicating unintentional n-type doping. Gate modulation is observed to weaken considerably in the presence of optical illumination as well as at high temperatures, possibly due to the generation of a large number of intrinsic carriers. The source-drain current is observed to increase from $\sim \text{pA}$ in single wires to $\sim \text{nA}$ in a network of multiple nanowires at room temperature. We observe a higher photoconductivity (than for single wire) and it appears to scale with the total number of nanowires forming the conductive channel. FET characterization gives an "on" to "off" ratio between 3 to 5 orders of magnitude which surprisingly also scales with number of wires. This is interesting and contrary to expected behavior - since the on-off ratio is an intrinsic property of the semiconducting material, it should be independent of the number of nanowires.

10:30 AM *P10.6

Ultra-Efficient Carrier Multiplication in Semiconductor Nanocrystals. Richard D. Schaller, Melissa A. Petruska, Jeffrey M. Pietryga and Victor I. Klimov; Chemistry Division, Los Alamos National Lab, Los Alamos, New Mexico.

The efficiency with which photons are converted into charge carriers determines the ultimate efficiencies of various photo-induced physical and chemical processes including photo-generation of electricity (photovoltaics) and solar fuels, optically pumped lasing, generation of nonlinear-optical responses, etc. Normally it is assumed that the absorption of a single light quantum (a photon) by a semiconductor produces a single electron-hole pair (an exciton), meaning that the quantum efficiency (QE) in generating charge carriers is 100%. However, as we demonstrated recently [Phys. Rev. Lett. 92, 186601 (2004)], quantum-confined semiconductor nanocrystals of PbSe can produce two or even three excitons (QE > 200%) in response to a single absorbed photon via the process known as carrier multiplication (CM). To address the issues of generality of CM and the mechanism for this phenomenon, we perform a comparative study of CM in nanocrystals of PbSe and CdSe that are characterized by a significant difference in both electronic structures and carrier relaxation behaviors. Despite these differences, both compositions exhibit CM with comparable efficiencies (defined in terms of the slope of the QE dependence on photon energy above the CM threshold), which is indicative of the generality of this phenomenon to quantum-confined, semiconductor nanoparticles. We demonstrate that CdSe nanocrystals show a lower activation threshold for CM than PbSe nanocrystals (~ 2.5 vs. ~ 2.9 energy gaps), which can be explained using simple carrier effective-mass arguments. Furthermore, we observe a monotonic increase in QE with increasing excess energy above the CM threshold up to $\sim 700\%$ in PbSe nanocrystals and $\sim 150\%$ in CdSe nanocrystals; and we expect that these values can be increased further by using still higher photon energies and/or by decreasing the energy

gap. High exciton multiplicity produced by a single light quantum can find numerous applications in physics and chemistry ranging from high-efficiency photovoltaics and single-photon oxidation of water molecules (water splitting) to low-threshold lasing and generation of entangled photon pairs.

11:00 AM P10.7

Nanoscale Single Quantum Dot Light Emitting Devices at 1300 nm. *Christelle Monat*, Carl Zinoni, Blandine Alloing, Lianhe H. Li and Andrea Fiore; SB-IPEQ-LPDS, EPFL, Lausanne, Switzerland.

Quantum cryptography allows unconditionally-secure exchange of cryptographic keys by the transmission of optical pulses each containing exactly one photon. Whereas single-photon pulses can be obtained by exciting any single quantum system (atom, molecule), solid-state systems, and especially single semiconductor quantum dots (QDs), are more promising candidates for any practical application. The electronic confinement within the nanometer scale islands results in a discrete energy spectrum, and in strong carrier correlation effects, making the energy of each electronic configuration easily distinguishable. While each QD can emit several photons after the excitation, a single-photon pulse can be obtained by spectrally isolating the last emitted photon. For fiber-based quantum cryptography systems, the technology of practical single-photon sources is needed. The fabrication of efficient single-QD Light Emitting Diodes (LEDs), at telecom wavelengths, is required. First, they should operate under electrical pumping. Secondly, the device should comprise only one or few QDs in its active region. This can be achieved by combining a low QD density with a technology enabling either the selection of the emission arising from a few QDs or the current injection towards only a few QDs. Here we report the first demonstration of a single-QD LED operating in the 1300 nm wavelength region. The MBE growth of sparse arrays (a few QDs/ μm^2) of self-organized InAs/GaAs QDs emitting at 1300 nm at low temperature has been optimized [1]. Sub-micrometer oxidized current apertures have been realized within LED structures [2]. A careful control of current spreading associated to the small diffusion length in QDs ensure a restricted injection area close to the aperture area. This results in excitation of one or few QDs. Low temperature electroluminescence measurements show narrow spectral lines (linewidth $<200 \mu\text{eV}$) which can be attributed to emission from single QDs. As compared to other approaches to single-photon LEDs (spatial selection through metal apertures), this one provides a much higher external efficiency (extracted photons / injected electrons) The efficiency of the device should further benefit from its integration with a wavelength-scale high quality factor microcavity. The coupling of the QD emission with an appropriate microcavity mode enables to redirect the emitted photons in the same mode, easy to collect. Furthermore, under some conditions, the enhancement of the spontaneous emission of the QD in the microcavity mode is expected. We have thus combined the LED structure with a micropillar cavity, while keeping the oxidized current aperture for both the lateral optical confinement and the restriction of the current injection in the device. We will report preliminary results from this approach, which may provide efficient single QD LEDs. [1] B. Alloing et al., Appl. Phys. Lett. 86, 101908 (2005) [2] A. Fiore et al., Appl. Phys. Lett. 81, 1756 (2002)

11:15 AM P10.8

Near-field measurement of spectral anisotropy and optical absorption of isolated ZnO nanorod single-quantum-well structures. *Takashi Yatsui*¹, Tadashi Kawazoe¹, Jinkyong Yoo^{4,3}, Sung Jin An^{4,3} and Gyu-Chul Yi^{4,3}; ¹SORST, JST, Machida, Tokyo, Japan; ²School of Engineering, the University of Tokyo, Bunkyo-ku, Tokyo, Japan; ³National CRI Center for Semiconductor Nanorods, Pohang, Kyungbuk, South Korea; ⁴Department of Materials Science and Engineering, POSTECH, Pohang, Kyungbuk, South Korea.

ZnO nanocrystallites are promising material for realizing nano-scale photonic devices at room temperature, owing to their large exciton binding energy. Furthermore, ZnO/ZnMgO nanorod heterostructures were fabricated and the quantum confinement effect even from the single-quantum-well structures (SQWs) was successfully observed. Here we report low-temperature near-field spectroscopy of isolated ZnO SQWs. ZnO/Zn_{0.8}Mg_{0.2}O SQWs (well width of 3.75 nm) was fabricated on the ends of a ZnO nanorods with a mean diameter of 40 nm. They were grown vertically from the sapphire (0001) substrate using catalyst-free metalorganic vapor phase epitaxy, in which the ZnO nanorod was grown in the c orientation. After growing the ZnO/ZnMgO nanorod SQWs, they were dispersed so that they were laid down on a sapphire substrate to isolate them from each other. We used a collection-mode near-field optical microscope using a He-Cd laser ($\lambda = 325 \text{ nm}$) for excitation, and an apertured (diameter of 30 nm) UV fiber probe. In addition to the PL measurements, absorption spectra were obtained using a halogen lamp. First, we obtained near-field PL spectra with polarization perpendicular to the c-axis. At the ZnO nanorod, the single emission peak was observed at 3.365 eV

which correspond to the neutral-donor bound exciton (DOX). However, at the well layer, the emission from DOX was suppressed, while blue-shifted PL emission peak was emerged at 3.444 eV (I_{1a}^{QW}). The value of the blue shift was consistent with the theoretical prediction using finite square-well potential of the quantum confinement effect in the ZnO well layer. The spectral width (3 meV) of peak from the SQWs was much narrower than those of the far-field PL spectra (40 meV). Furthermore, the Stokes shift of 3 meV was much smaller than the reported value (50 meV) in ZnO/ZnMgO superlattices. The small Stokes shift may result from the decreased piezoelectric polarization effect by the fully relaxed strain for the ZnO/ZnMgO nanorod quantum structures in contrast to ZnO/ZnMgO heteroepitaxial multiple layers. Second, we obtained polarization-dependent PL spectrum of isolated ZnO SQWs. In contrast to the near-field PL spectra obtained with perpendicular polarization, a new peak at 3.483 eV (I_{1b}^{QW}) was observed in the PL spectrum with parallel polarization. By considering the valence band anisotropy of ZnO owing to the wurtzite crystal structure and the energy difference between Γ_5 and Γ_1 in the center of the zone around 40 meV for bulk material, emission peaks I_{1a}^{QW} and I_{1b}^{QW} are allowed for the exciton from Γ_5 and Γ_1 , respectively. This successful observation of a Γ_1 exciton in a PL spectrum originates from the enhancement of the exciton binding energy owing to the quantum confinement effect. The results shown here provide criteria for realizing nano-scale photonic devices using a two-level system.

11:30 AM P10.9

Probe of the Interaction Dynamics of Optically Excited Si-nc and Er-ions in Silica by Use of a Tuneable Double Pulse Set-up. *Elisabetta Borsella*¹, M. Falconieri², G. Franzo^{3,5}, F. Priolo³, F. Iacona⁴, F. Gourbilleau⁵ and R. Rizk⁵; ¹Applied Physics, ENEA, Frascati (Rome), Italy; ²Materials and New Technologies, ENEA, Casaccia (Rome), Italy; ³Physics and Astronomy, Univ. of Catania, Catania, Italy; ⁴IMM, CNR, Catania, Italy; ⁵SIFCOM, ENSICAEN-CNRS, Caen, France.

The process of energy transfer (ET) from optically excited Si-nc to Er-ions is of huge interest not only for the promising applications in optoelectronics and photonics, but also as a model case for studying the interaction between a quantum confined electronic system (excitons and carriers in Si-nc) and impurity ions in a dielectric host (Er-ions in silica). This subject has been investigated by many researchers upcoming to well assessed results such as the increase by more than three order of magnitude in the effective excitation cross section of Er-ions through energy transfer from optically excited Si-nc. However a deep understanding of the whole process is still lacking since most of the papers only deal with the detection of PL (photo-luminescence) emitted by Er-ions at 1540 nm after optical excitation of Si-nc, thus overriding many dynamical aspects of the interaction: how is affected the Si-nc decay by the ET process? are there one or more energy transfer times? to which Er levels is the energy transferred? which is the fraction of excited Er ions? how is influenced the ET process by Auger processes? We try to give a novel contribution to answering these questions by looking at the ET process from a complementary point of view. In our experiments, a first powerful ns pulse and a subsequent pulse, whose delay is varied with great precision, are shone on the Er and Si-nc co-doped samples and the 1540 nm PL emission is detected. The use of a tuneable ns double pulse set-up allows us to design experiments to follow either the dynamics of Si-nc recovery (by degenerate two-beam excitation) or the dynamics of Er depletion and recovery (by probe of the number of Er ions left or returning to the ground state through resonant Er excitation). At variance with most of the published papers, our approach offers the possibility to follow the dynamics of Si-nc recovery also in the case of amorphous Si clusters that do not emit radiation. Furthermore, in the case of Si nanocrystals, we have tried to complement data existing in the literature by following the Si-nc recovery dynamics through detection of near-IR PL emission after double pulse excitation at variable delay. The main results of our investigation are: the determination of a fast recovery of the sensitizers (few hundred ns) in samples containing large and well defined Si-nc, which is related to a fast energy transfer process to the first (luminescent) Er level; the occurrence of slower ET times (500-900 ns) to the first and possibly to the second excited level in samples containing small (less than 1 nm) Si-nc; the evidence for a considerable depletion of Er ions; the occurrence of Auger quenching processes between excited centres which limit the number of excited ions especially in samples containing large clusters; the determination of Auger processes impact on the the Si-nc de-excitation.

11:45 AM P10.10

Sensitization of Nanoporous TiO₂ Electrodes With HgTe Nanocrystals. *Serap Gunes*¹, Pinar Senkarabacak¹, Helmut Neugebauer¹, Niyazi Serdar Sariciftci¹, Jurgen Roither², Maksym Kovalenko², Georg Pillwein² and Wolfgang Heiss²; ¹Physical Chemistry, Linz Institute for Organic Solar Cells (LIOS), Johannes Kepler University Linz, Linz; ²Institute For Semiconductor and Solid

Nanocrystals of inorganic semiconductor materials have been a topic of intensive research over the last decade. Due to quantum confinement in particles with dimensions smaller than the extension of the excitonic wavefunction, the emission and absorption of semiconductor nanocrystals can be tuned by changing the average particle size. Flexibility by the solution processability gives the opportunity to utilize these nanocrystals in different optoelectronic devices as selective absorbers/emitters. In conjunction with organic polymeric semiconductors or as nanoporous electrodes these semiconductor nanoparticles can be used to produce photovoltaic solar cells in all-solid-state as well as electrolyte based architectures. Inorganic and organic materials are used in their photo- and electroactive layer and are therefore dubbed "hybrid solar cells", combining the unique properties of the two classes of materials. In this work we present hybrid solar cells using HgTe semiconductor nanocrystals for improving the photovoltaic performance by mixing them into a conjugated polymer, and/or by addition to a nanoporous TiO₂ films, used as electrodes. Our devices make use of two solar cell concepts: 1.) a solid state nanocrystal sensitized solar cell combined with 2.) a nanocrystal/polymer blended solar cell. HgTe nanocrystals are demonstrated to increase the photon harvesting efficiency of hybrid solar cells over a broad spectral region between 350 nm and 1500 nm. The devices give incident photon to current efficiencies up to 10% and short circuit current densities of 2 mA/cm² under AM 1.5 (100 mW/cm²) illumination.

SESSION P11: In-Room Poster Session I
Chairs: Khaled Karrai and Richard Schaller
Thursday Morning, December 1, 2005
8:30 AM - 12:00 PM
Room 210 (Hynes)

P11.1

Ge nanoparticles in GeO₂ and GeO₂-SiO₂: natural or artificial? Nan Jiang, Physics, Arizona State University, Tempe, Arizona.

Ge nanoparticle embedded into a dielectric matrix has attracted much attention due to its intense photoluminescence. Various methods have been claimed to be able to fabricate Ge nanoparticles, usually in amorphous SiO₂. The most popular method involves depositing GeO₂-SiO₂ on substrates (usually Si and SiO₂), either by co-sputtering GeO₂ and SiO₂ or by oxidizing epitaxial Si_{1-x}Gex films, following by post annealing processes. However, there is controversy over the post annealing treatments. Some studies reported that annealing environment must include reduction agent such as H₂, while the inactive agent such as N₂ plays no known role. On the contrary, other studies claimed that Ge nano-particles can be obtained by isothermal annealing in N₂ gas ambient, and even in an Ar atmosphere. Although the diffusion of Si from the substrates may provide reductant to reducing Ge from GeO₂, some experiments were using fused quartz (amorphous SiO₂) rather than Si as substrates. The evidences of existing Ge nano-particles in the most of previous studies were from TEM images. However, none of them have ever mentioned how electric field created by fast electron affects their observations. Here, we demonstrate, using spatially-resolved electron energy-loss spectroscopy (EELS) in a TEM, that Ge nano-particles can be precipitated in GeO₂ and GeO₂-SiO₂ efficiently by the high-energy electron beam of a TEM. The formations of nanoparticles in these oxides are observed from the TEM images in real time. These particles are Ge, which were concluded from both electron diffraction and EELS analyses. We suggest that the mechanism involving the nucleation and growth process on surfaces is responsible for the precipitation of Ge in GeO₂. The mechanism of precipitations in GeO₂-SiO₂ is probably related to such a tendency that electron irradiation eliminates M⁺ O⁻ Si (M represents cation) configuration in complex glasses, and decompose the phase into cation rich and poor regions. This is relevant to TEM characterization of luminescent Ge nanoparticles in silicate glasses, which may produce artificial results.

P11.2

Water-induced Structural Transformation of Metastable Zinc Sulfide and Cadmium Sulfide Nanocrystallites. Navendu Goswami and P. Sen; School of Physical Sciences, Jawaharlal Nehru University, New Delhi, India.

Hexagonal ZnS and cubic CdS are thermodynamically unstable crystalline phases [1-3]. Typically, the stable structure of most ZnS nanoparticles prepared at room temperature is zinc blende, with few evidences of stable wurtzite ZnS [2, 3]. We have devised a non-equilibrium process to fabricate the metastable phases of nanocrystalline ZnS and CdS with enhanced surface states. In our novel process, we employ the potential of the electro-explosion of wire (EEW) method to produce copious amount of ZnS and CdS

nanoparticles by explosion of Zn and Cd wires in a cell filled with sulfide ions [4]. Moreover, this method of preparation, in principle, has opened up the possibility to synthesize a variety of technologically important semiconductor nanoparticles of the type ME (M=Zn, Cd, Pb and E= S, Se, Te). The non-equilibrium nature of synthesis favors the formation of rare unstable phases of ZnS and CdS nanocrystallites. The ZnS and CdS nanoparticles are initially obtained as free-standing colloidal particles. To study the properties of the nanocrystalline ZnS and CdS synthesized by our novel technique we characterize the colloidal as well as powder samples by atomic force microscopy (AFM), x-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy and x-ray photoelectron spectroscopy (XPS) etc. An extensive study of the size, crystallinity and surface structure of these nanoparticles was performed. Here we present the direct evidence of the water-induced structural buildup and stabilization of nanocrystalline ZnS and CdS. The colloidal suspensions containing the ZnS and CdS nanoparticles clearly show a visible gradual change in their color with evolution of time. Although the rate of structural transformation is different for nanocrystalline ZnS and CdS, both the systems demonstrate irreversible phase transitions. The evolution of crystallinity and structure is primarily driven by the strong interaction at the interface of water and the semiconductor nanoparticles. The water-driven structural transformation of the metastable phases of ZnS and CdS nanocrystallites with enhanced surface states make these materials ideal for water sensing applications. References: [1] X. Zhong, S. Liu, Z. Zhang, L. Li, Z. Wei and W. Knoll, *J. Mater. Chem.*, 14, 2790-2794 (2004) and references therein. [2] C. Ma, D. Moore, J. Li and Z. L. Wang, *Adv. Mater.*, 15 (3), 228 (2003) and references therein. [3] S. B. Qadri, E. F. Skelton, D. Hsu, A. D. Dinsmore, J. Yang, H. F. Gray, and B. R. Ratna, *Phys. Rev. B*, 60 (13), 9191-9193 (1999) and references therein. [4] N. Goswami and P. Sen, *Solid State Commun.* 132, 791-794 (2004) and references therein.

P11.3

Tabular Gold Sulfide Nanostructures. Jiajie Diao, Jaime B. Hutchison and Mark E. Reeves; Physics, The George Washington University, Washington, District of Columbia.

We report the nanoscale growth of hexagonal tabular crystals of a gold compound, most likely gold sulfide - a preliminary identification based upon TEM, EDAX, and optical absorption measurements. High resolution TEM and EDX will be completed by the time of the presentation of this result. This morphology is observed in nature, occurring in gold telluride, the mineral calaverite, which usually has a prismatic monoclinic structure, and is only rarely found in tabular form. Less rare is the silver analogue, tabular silver halide, which is widely applied in the manufacture of photographic emulsions because of its advantageous sensitivity to photons absorbed in the (111) crystallographic direction. We will present the method of synthesis and characterization, as well as a summary of the physical properties of these new materials.

P11.4

Characterisation of II-VI Semiconductor Quantum Nanoparticles Produced Using Plant Tissue Culture. Katie J. Levick¹, Marion A. Stevens-Kalceff¹, Hongqing Zhao² and Pauline M. Doran²; ¹School of Physics, University of New South Wales, Sydney, New South Wales, Australia; ²School of Biotechnology and Biomolecular Sciences, University of New South Wales, Sydney, New South Wales, Australia.

Nanometer sized crystallites of wide band gap II-VI semiconductor materials (typically <20nm in diameter) have unique physical and optical properties that differ from the properties of bulk crystals. The properties of nanoscale materials differ from those of bulk materials due to the large surface to volume ratio and/or quantum confinement effects. The useful physical and optical properties of nanoscale materials can be directly engineered by changing the size of the nanocrystals. Many new applications of quantum nanoparticles are now being developed in areas such as medical imaging, diagnostics, targeted therapies, high-throughput screening, optical encoding of biomolecules, photonics and microelectronics. Currently, disperse nanocrystals (quantum dots) are most commonly produced using chemical methods involving crystal nucleation in organic or aqueous solvents. Biological synthesis methods may permit the mass production of monodispersed nanocrystals while minimizing particle instability and aggregation. Cells which can be considered as microscopic reaction chambers intrinsically provide the space confinement conditions needed to restrict the dimensions of the generated nanoparticles. To date very little work has been carried out to investigate the potential of large-scale cell culture as a biological source of quantum nanocrystals, although some yeast and a plant species have been reported to contain nanocrystals after exposure to heavy metal. In these cells, the normal response to heavy metals includes the formation of metal-sulfur complexes that are capped with short chelating peptides known as phytochelatins. As well as

protecting the organism from metal toxicity, peptide binding provides a biological ligand for nanoparticle functionalization and has the potential to control crystal growth, improve particle stability and passivate the nanocrystal surfaces. These are significant advantages compared with non-biological methods for quantum nanoparticle synthesis. In this work, the properties of cadmium sulphide (CdS) quantum nanoparticles produced using hairy root plant tissue culture grown in Cd-containing medium have been investigated. The resultant semiconductor CdS nanoparticles have been investigated using a combination of electron microscopy techniques including imaging, electron diffraction, cathodoluminescence spectroscopy, energy dispersive x-ray microanalysis, and other analytical techniques including photoluminescence and X-ray diffraction.

P11.5

Dynamics of Photoinduced Charge Ejection of CdSe Nanocrystals in Dielectric Environments. Abey Issac, Christian von Borczyskowski and Frank Cichos; Institute of Physics, Chemnitz University of Technology, Chemnitz, Germany.

Fluorescence intermittency (blinking) of single CdSe/ZnS quantum dots (QDs) obeys power law statistics for the lifetime of the dark states. This power law distribution is supposed to be related to a distribution of states located outside the QDs, which are able to trap charges ejected from the QDs. We present for the first time direct evidence, that blinking is affected by the polarity of the surrounding medium. The higher the dielectric constant of the medium, the higher will be the probability for long off times. To explain the observed results we propose a simple self-trapping model for the ejected charges. The interaction of the reaction field, induced by the ejected charge in the matrix, with the ejected charge stabilizes the charge against a fast return to the ionized particle. On the other hand, the lifetime statistics of the bright periods (on times) is unaffected by the dielectric environment and shows a turnover between two power laws. We relate this turnover to an intermediate step during the ionization of the QDs involving surface states.

P11.6

Electron donor/acceptor effects on etching of CdSe nanocrystals in amines. Rongfu Li¹, Kushan Biswas¹ and Fotios Papadimitrakopoulos^{1,2}; ¹Institute of Materials Science, Polymer Program, Univ. of Conn., Storrs, Storrs, Connecticut; ²University of Connecticut, Storrs, Connecticut.

The chemical etching of CdSe nanocrystals (NCs) in 3-amino-1-propanol mixture at 80 Celsius degree has been reported previously.[1] This is evidenced not only by the stepwise blueshift in UV/Vis and PL emission peak position, but also by their shape transformation from spherical to Cd-terminated faceted pyramidal morphology. Two competitive processes take place on the surface of these CdSe NCs: (i) oxidation of the exposed Se-sites to acidic SeOx entities, that are readily solubilized in the basic APOL/H2O mixture, and (ii) coordination of the underlying Cd-sites with both amines and hydroxyl moieties to temporally impede NC dissolution. One issue that is currently unclear involves the question on why this chemical etching process decelerates as opposed to accelerate with decreasing NC size. Band-gap involvement of the CdSe NC into one or more chemical reactions associated with this etching technique might be able to provide an answer to this unusual phenomenon. For this, we have conducted a series of etching experiments utilizing different electron donors and acceptor organic reagents. Electron acceptors generally accelerate this etching process, while donors decelerate or arrest it completely. These findings have enabled us to provide an initial understanding on the interactions between semiconducting nanocrystals and organic redox reagents. [1] R. Li, J. Lee, B. Yang, D. Horspool, M. Aindow, F. Papadimitrakopoulos, J. AM. CHEM. SOC. 2005, 127, 2524-2532

P11.7

Near-field scanning photocurrent microscopy of a nanowire photodetector. Yi Gu¹, Eun Soo Kwak², Jessica L. Lensch¹, Jonathan E. Allen¹, Teri W. Odom² and Lincoln J. Lauhon¹; ¹Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois; ²Department of Chemistry, Northwestern University, Evanston, Illinois.

One-dimensional nanomaterials are being considered as the basis of a variety of device technologies. Semiconductor nanowires and carbon nanotubes, for example, have been used to make nanoscale photodetectors with reasonable efficiencies and unique features such as polarization-sensitive detection. The mechanisms of carrier photogeneration have been addressed in a number of studies, but charge transport and collection in nanowire/nanotube photodetectors have received comparatively little attention and are not well understood. In this regard, photoconductivity measurements employing uniform illumination (spot size larger than the device) may be insufficient to establish the operational principles of nanowire

devices because (1) unlike the illumination, the internal electric fields may be highly non-uniform, especially near the metal contacts and (2) similarities between conventional and nanowire device characteristics may be fortuitous. To understand the global response and the ultimate potential of nanowire photodetectors, an understanding of the photoresponse on a smaller length-scale is desirable. We have developed a new technique, near-field scanning photocurrent microscopy (NSPM), to explore the local photoresponse of semiconductor nanowire devices. A near-field scanning optical microscope (NSOM) was used to image the photocurrent induced by local illumination along the length of a metal-semiconductor-metal (MSM) photodetector made from an individual CdS nanowire. Under uniform monochromatic illumination, the MSM photodetectors exhibited photocurrents $\sim 10^5$ larger than the dark current (< 2 pA). Under local illumination (excitation spot size less than device size), the response of the devices was limited to regions near the M-S contact. Analysis of the spatial variation and bias dependence of the local photocurrent allowed the mechanisms of photocarrier transport and collection to be identified. In these devices, the photocurrent is limited by the majority (minority) carrier diffusion when the reverse (forward)-biased M-S contact region is under local illumination. For local illumination in the middle of the NW, the absence of an electric field indicates that photo-generated electrons and holes are not separated and recombine rather efficiently. As a result, no photocurrent is observed. Experiments to determine the effects of channel length and contact Schottky barriers on nanowire photodetector operation are ongoing and will also be discussed. The NSPM techniques we describe can be readily extended to other NW-based devices with similar geometries, including transistors, sensors, and light emitting diodes, and provide insight into the operation principles of these devices. NSPM therefore has the potential to significantly advance the understanding and development of NW device technology.

P11.8

Lasing characteristics of a ZnO nanostructure studied by near-field scanning optical microscopy (NSOM). Dake Wang¹, Heewon Seo¹, Yonhua Tzeng², Michael Bozack¹, Chin-Che Tin¹, John Williams¹ and Minseo Park¹; ¹Department of Physics, Auburn University, Auburn, Alabama; ²Department of Electrical and Computer Engineering, Auburn University, Auburn, Alabama.

Zinc oxide (ZnO) nanostructure is a promising material for nanophotonic application. In the present investigation, the ZnO nanostructures were synthesized at low temperature using a thermal chemical vapor deposition. The morphology of the sample was studied using scanning electron microscopy. Nanostructures with a nail- and a bone-shaped morphology were obtained by employing different processing parameters. The room photoluminescence (PL) spectra were collected using a pulsed UV laser as excitation. The near-band-edge emission spectra were collected by using a near-field optical scanning microscope (NSOM), which enables the spectrum collection of a single nanostructure when NSOM tips with an aperture size of 300 nm or smaller are used. Very sharp peaks (FWHM=0.1 nm) associated with lasing action are observed under high pumping power density. The intensity dependency of laser emission characteristics were studied by varying the pumping power density.

P11.9

Photoluminescence of Charged CdSe Quantum Dots. Praket Prakash Jha and Philippe Guyot-Sionnest; Chemistry, University of Chicago, Chicago, Illinois.

The photoluminescence (PL) of singly and doubly charged TOP/TOPO capped CdSe quantum dots has been investigated. The electrochemical injection of charge in the dots leads to PL quenching which is seen to be persistent well after the removal of electrons(1). The fluorescence quenching, attributed to the nonradiative recombination surface sites, does not follow the kinetics of charging and discharging. PL quenching is reduced at lower temperatures and can be associated with an energy barrier. Further lowering of temperature to freeze the electrolyte is expected to increase the electrochemical stability of the film, reduce the build-up of the trap states, and enhance the fluorescence of the dots. (1) Wang, C.; Wehrenberg, B. L.; Woo, C. Y.; Guyot-Sionnest, P., J. Phys. Chem. B, 2004, 108, 9027.

P11.10

The Location and Nature of CdS Nanoparticles Encapsulated within Zeolite. Nak Cheon Jeong¹, Hyun Sung Kim¹, Se Ahn Song² and Kyung Byung Yoon¹; ¹Chemistry, Sogang University, Seoul, South Korea; ²Samsung Advanced Institute of Technology, Gyeonggi-Do, South Korea.

Zeolites are potentially ideal hosts for the generation of quantum dots (QDs) in uniform sizes, organization of them into regular arrays, and stabilization of them for extended periods of time since the sizes and

shapes of the produced QDs are governed by the zeolite pores which are highly uniform in size and shape when they are produced within zeolites, the generated QDs automatically form regular arrays within the framework with very precise spacing between the QDs, and the stability of the QDs can be increased significantly if they can be protected from the attack by moisture and oxygen by confining them within the inert zeolite framework. However, there are still much to be done in the area of characterization of zeolite-encapsulated QDs before seeking practical applications of the zeolite-encapsulated QDs. Most of all, there are still unresolved controversies over the location and the nature of networking between the QDs within zeolites A and Y consisting of α and β cages. We will report that in the case of intrazeolite CdS QDs, they exist within α cages, and they form quantum wires (QWs) by connecting through the window. X-ray analyses revealed that while the structures of intrazeolite QDs and QWs were hexagonal, those of the large extraframework QDs were cubic.

SESSION P12: Silicon Nanocrystal and Nanowires
Chairs: Philippe Fauchet and Victor Klimov
Thursday Afternoon, December 1, 2005
Room 210 (Hynes)

1:30 PM *P12.1

Light Emitting Devices and Lasers with Silicon Nanostructures. Philippe M. Fauchet, ECE, Univ. of Rochester, Rochester, New York.

Silicon quantum structures with at least one dimension ranging from ~ 10 nm to smaller than 2 nm have been synthesized using a variety of techniques. Thanks to engineering of the electronic wavefunction and to the elimination of most bulk or surface defects, these structures can photoluminesce from the near infrared throughout the visible and the near ultraviolet with quantum efficiencies that may exceed 10%. The luminescence wavelength range can be extended to longer wavelengths by the addition of selected impurities such as light-emitting rare earths including erbium. Light emitting devices (LEDs) have been fabricated and their performance is starting to approach those of direct bandgap semiconductor or organic LEDs. A search for a silicon quantum dot-based laser is even under way. In this presentation, a critical overview of the state-of-the-art in the materials science, physics and device development of luminescent silicon quantum structures is provided.

2:00 PM P12.2

Abstract Withdrawn

2:15 PM P12.3

Impact of Nanocrystal Size and Density on Performance of Silicon Nanocrystal Memories. Rajesh A. Rao, Horacio Gasquet, Ramachandran Muralidhar, Robert Steimle, Glenn Rinkneberger, Sherry Straub, Bruce Hradsky, Steve Anderson, Jane Yater, Michael Sadd, Bryan Acred, Craig Swift, Erwin Prinz, Juan Carlos Ledezma, John Hamilton, Jerry Peschke, Bruce White and Ko-Min Chang; Technology Solutions Organization, Freescale Semiconductor, Austin, Texas.

Silicon nanocrystals provide an attractive option to scale down voltages and improve reliability of floating gate non-volatile memories (NVM). This is because, charge is stored in nanocrystals that are electrically isolated from one another and this mitigates charge loss to defects in underlying oxide. A key aspect governing the performance of charge trapping memories such as nanocrystal and SONOS is the stack balance or the device geometrical aspects. In SONOS, for example, thicknesses of tunnel and control oxides as well as the nitride layer dictate the relative importance of electron emission from the nitride, hole injection from substrate and electron back injection from the gate during erase operations and manifests in the well understood erase saturation phenomenon. In nanocrystal memories, the memory window and program/erase speed is determined primarily by nanocrystal size and number density in the device. This is because, charge confinement or Coulomb blockade effects become more pronounced as the size decreases and manifest in device performance even at room temperature. Additionally, the fractional area that the nanocrystals occupy influences the lateral conductivity of this charge storage layer and hence reliability. In this paper, we systematically study the impact of nanocrystal size, density and area fraction on device characteristics using single bit memory devices as well as 4Mb memory arrays. We show that Coulomb blockade effects manifest at room temperature and that optimal nanocrystal characteristics are desired from this point of view. Additionally, using data from 4Mb memory arrays, we show that lateral charge transport can be negligible over a range of nanocrystal properties.

2:30 PM P12.4

Optical Activation of Silicon Nanowires. Heon-Jin Choi¹, Hee-Chul Han¹, Kiseok Seo², Jung H. Shin², Lingling Ren³ and

Won-Young Jeong³; ¹School of Advanced Materials Science and Engineering, Yonsei University, Seoul, South Korea; ²Department of Physics, Korea Advanced Institute of Science and Technology, Daejeon, South Korea; ³Materials Science and Technology Division, Korea Institute of Science and Technology, Seoul, South Korea.

Semiconductor nanowires have great potential in the fabrication of optoelectronic 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. Meanwhile, a great interest lies in developing the efficient Si-based light emitting materials that could enable integration of photonics with Si technology. Recently, much progress has been made with Er doping of silicon-rich silicon oxide (SRSO), which consist of nanocluster Si embedded inside an SiO₂ matrix. However, isolation of nanocluster Si inside the SiO₂ matrix makes current injection into SRSO difficult, which raises questions about the realization of such devices. Such problems, however, may be solved by using Si nanowires. It has diameters in the range of 10-100 nm and with length exceeding 1 mm and, thus, provides a very high areal density of Er³⁺ ions in case of Er-doping. Furthermore, electrical doping, transport, and fabrication of active electronic devices based on Si nanowires have been reported, demonstrating the ease of injection into, and transport along, the Si nanowires. Herein we report the optical activation of Si nanowires by ex-situ Er-doping (i.e., Er doped sol-gel coating of the grown nanowire in a post process) or in-situ Er-doping (i.e., Er-Si-O layer coating in a growth process). We obtain strong room temperature 1.54 μ m luminescence with a luminescence lifetime of 6.9 msec and a nearly complete suppression of the temperature quenching of the Er³⁺ luminescence in ex-situ Er doped Si nanowires. It indicates that Er³⁺ ions in the nm-thin silica shell around Si nanowires are excited via energy transfer from carriers in the Si nanowires, indicating the possibility using silica sol-gel activated Si nanowires to develop a new material platform for Si-based photonics that can achieve both high excitation and luminescence efficiency of Er³⁺ while providing a high areal density of Er³⁺ and ease of carrier injection. We also obtained luminescence from the in-situ Er doped Si nanowires. In these nanowires, novel coaxial Er-Si-O/Si heterostructure generated on a nano meter scale with self organization mode provides luminescence with a very narrow peak width. Based on the experimental, the possible application as building blocks for optical devices of Er-doped Si nanowires will be discussed.

2:45 PM P12.5

Nanoscale Strain Engineering using Ge Quantum Dots on Ultrathin Silicon-on-Insulator(100). Eli Sutter¹, Young-suk Choi¹, Toma Stoica², Lili Vescan² and Peter Sutter¹; ¹Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York; ²Institut fuer Schichten und Grenzflaechen, Forschungszentrum Juelich GmbH, Juelich, Germany.

The growth of heteroepitaxial materials on engineered composite substrates such as silicon-on-insulator (SOI) opens a new route for controlling the structural and electronic properties of materials at the nanoscale. SOI is a composite material in which a thin monocrystalline Si 'template' is bonded to a conventional Si 'handle' wafer via a layer of amorphous SiO₂, that has recently been developed into a viable substrate for very-large scale integrated circuits. Ge quantum dots (QDs) form spontaneously via lattice-mismatch strain-induced self-assembly during heteroepitaxial Ge growth on bulk Si(001) as well as SOI(001). For Ge quantum dots on bulk substrates, mismatch strain is concentrated in the epitaxial QDs and studies typically focus on the electronic properties of the Ge dots themselves. Growing Ge on ultrathin (< 8 nm) SOI allows us to use the QDs as nanoscale epitaxial stressors that generate a well-defined strain field and associated band-structure changes in the underlying ultrathin Si substrate. We have shown that local lattice strain induced by Ge quantum dots grown coherently on SOI causes significant local distortion in the ultrathin Si template [1]. Using a combination of atomic force microscopy and cross-sectional transmission electron microscopy we quantify the Ge stressor-induced deformation profile of the Si template as a function of the Si template thickness. Measurements of the strain-induced bandgap narrowing by photoluminescence spectroscopy directly demonstrate the extent of the nanoscale band structure changes induced by the localized strain field of the epitaxial Ge stressors. [1] P. Sutter, E. Sutter, P. Rugheimer, and M. G. Lagally, Surf. Sci. 532, 789 (2003).

3:15 PM P12.6

Field Effect Electroluminescence in Silicon Nanocrystal Arrays. Robert J. Walters¹, Josep Carreras², George Bourianoff³ and Harry A. Atwater¹; ¹Applied Physics, California Institute of Technology, Pasadena, California; ²Universitat de Barcelona, Barcelona, Spain; ³Intel Corporation, Hillsboro, Oregon.

We have recently reported on the operation of a novel light emitting

device termed a "Field Effect Light Emitting Device" (FELED) that enables electrical pumping of silicon nanocrystal arrays.⁽¹⁾ These devices consist of MOS transistors with an embedded floating gate comprised of $\sim 5 \times 10^{12}$ silicon nanocrystals/cm² (2-4nm diameter) isolated from the channel by an ~ 4 nm tunnel oxide and isolated from the gate contact by an ~ 8 nm thick control oxide layer. The gate contact is designed to be optically transparent at the emission wavelength of the nanocrystals (~ 780 nm). In contrast to traditional LEDs in which charges are driven into an active region by a constant current, the charges in this device are injected sequentially into the silicon nanocrystal array from the channel of the transistor by an alternating gate potential. Excitons are thus formed only at bias transitions. Time resolved electroluminescence measurements show rise times of order 100nsec and EL decay times of ~ 30 usec for abrupt changes in gate bias (~ -6 Volts). These measurements are consistent with a charge injection model based on Coulomb-field enhanced Fowler-Nordheim tunneling. We will present new observations of light emission from a prototype FELED device, including wavelength resolved emission traces, EL emission spatial maps, and optical measurements of charge injection and retention processes in the nanocrystal array. We will additionally comment on the prospects for efficient light emission in optimized FELED structures. (1) R. J. Walters, G.I. Bourianoff and H.A. Atwater, *Nature Materials*, 4, 143 (2005)

3:30 PM P12.7

Enhanced photoluminescence from silicon nanocrystals coupled to plasmonic materials. Julie Suzanne Biteen¹, Hans Mertens², Domenico Pacifici¹, Nathan S. Lewis¹, Albert Polman² and Harry A. Atwater¹; ¹California Institute of Technology, Pasadena, California; ²AMOLF, Amsterdam, Netherlands.

We report local-field-enhanced light emission from silicon nanocrystals close to nanostructured noble metals and attribute the enhanced photoluminescence result to local electric field effects at the silicon nanocrystal emitter location. Upon coupling to nanoporous gold, the silicon nanocrystal luminescence enhancement results from concomitant increases in the coupled silicon nanocrystal/nanoporous gold absorbance cross section, radiative decay rate and quantum efficiency. We resolve photoluminescence as the gold-Si nanocrystal separation distance is varied between 0 and 20 nm, and observe an up to 8-fold luminescence intensity enhancement dependent on pump power and separation distance. A detailed analysis of emission in the 760 - 800 nm range indicates the radiative decay rate is enhanced more than 4-fold (to 57.5 kHz), the absorbance cross section is more than doubled (to 3.1×10^{-16} cm²), and the quantum efficiency is enhanced more than 2-fold (to 58%). Quantitative modeling that accounts for the depth-resolved distribution in silicon nanocrystal density indicates that the optimal silicon nanocrystal/nanoporous gold spacing is 1.6 nm, and this analysis determines that local-field enhanced emission dominates at intermediate distances, on and off the plasmon resonance, while luminescence-quenching processes dominate at small gold-nanocrystal separations. The enhancement effects also depend strongly on the metal nanostructure/Si nanocrystal geometry, and we will report on the consequences of using a variety of additional metal structures, including lithographically defined silver particle islands and self-assembled monolayers of colloidal gold particles. The effects of changing the metal structure, as well as the result of altering the size, pitch, and aspect ratio of the arrays, will be discussed.

3:45 PM P12.8

Time-resolved Photoluminescence Studies of Energy Transfer from Excitons in Si Nanocrystals to Oxygen Molecules. Minoru Fujii¹, Shingo Minobe¹, Shinji Hayashi¹ and Dmitri Kovalev²; ¹Department of Electrical & Electronics Engineering, Faculty of Engineering, Kobe University, Kobe, Japan; ²Physics Department, Technical University of Munich, Garching, Germany.

It has been demonstrated recently that Si nanocrystals can act as a photosensitizer for the generation of active oxygen species - singlet oxygen molecules (¹O₂). Singlet oxygen is an electronically excited state of oxygen molecules and is a very important substance in biology and chemistry because it mediates important processes in organic molecules. One of the most important applications of ¹O₂ is a photodynamic therapy of cancer. Thus the capability of Si nanocrystal to generate ¹O₂ is an interesting prospective for new applications of the most commonly used semiconductor in chemistry, biology and medicine. From detailed spectroscopic studies of oxygen-adsorbed Si nanocrystals, the energy transfer from excitons to oxygen molecules was shown to be governed by electron exchange mechanism. Electrons are exchanged between triplet excited states of energy donors, i.e., Si nanocrystals, and triplet ground states of energy-accepting oxygen molecules. During this process oxygen molecules are excited to either a first-excited ¹Δ state (0.98 eV from the ground state) or a second-excited ¹Σ state (1.63 eV) depending on the bandgap energies of Si nanocrystals responsible for energy transfer. The coupling of excitons to the ¹Σ state is much stronger

than that to the ¹Δ state. Below the ¹Σ state energy, excitons can couple weakly to the ¹Δ state. The weak coupling results in partial quenching of exciton luminescence (PL). By analyzing partially quenched spectra, the mechanism of energy transfer to the ¹Δ state has been studied in detail. On the contrary, the strong coupling to the ¹Σ state results in almost complete suppression of exciton PL above the ¹Σ state energy, and thus specific energy transfer-related spectral signatures are absent. This hinders detailed studies of energy transfer mechanism to the ¹Σ state. In this work, we investigate time-dependent coupling of excitons confined in Si nanocrystals to the ¹Σ state of oxygen molecules and to dimers of oxygen molecules (O₂)₂ using time-dependent analysis of energy transfer-related PL features at low temperatures. This study allows us to discuss detailed mechanism of the energy transfer to the strongly coupled ¹Σ state. We will show that the energy transfer time is the shortest for the resonant energy transfer and the involvement of one transverse optical phonon for energy conservation results in about 40 % increase of the time. The energy transfer time to the first excited ²1Δ state of (O₂)₂ dimers was on the same order of that to the ¹Σ state of O₂ monomers. Temporal analysis of energy transfer-related spectral signatures evidences that Si nanocrystals with the bandgap energy of 1.95 eV still retain indirect bandgap nature of bulk Si crystals.

4:00 PM P12.9

Nano-Si Quantum Dot for Flash Memory Applications. Tingkai Li, Sheng Teng Hsu, Lisa Stecker and David Evans; PTL, Sharp Labs. of America, Inc., Camas, Washington.

Nanocrystal Si quantum dots embedded in silicon dioxide have been made using multi-layer CVD poly-Si and thermal oxidation processes. By controlling the poly-Si thickness and post-oxidation processes, the nano-Si particle size from 1 nm to 5 nm can be obtained. The x-ray and PL measurement confirmed the formation of the nanocrystal Si quantum dots. In order to improve the properties of flash memory devices, the nanocrystal Si quantum dots have been integrated into flash memory devices. For flash memory, the problem is due to the non-uniformity of the oxide. If there is a weak spot such that the leakage current density at that spot is larger it leaks all stored charges in the floating gate. This problem increases with the thinning of the oxide thickness. If the floating gate is replaced with nano particles the weak spot only affect one nano particle and has no effect on the other storage particles. Therefore, the thickness of both tunnel oxide and inter-level oxide can be reduced without sacrificing the memory retention time. The nanocrystal Si quantum dot flash memory devices show excellent memory working functions. The memory windows are about 5 to 12 V, and the ratios of on current to off current are about 4 to 6 orders. The experimental data also show the operation voltage increases and the memory retention also improves with increasing tunneling oxide thickness. The integration processes are also discussed in this paper.

4:15 PM P12.10

Light Emission from Silicon Nanocrystals: Probing a Single Quantum Dot. Ilya Sychugov, Jan Linnros and Jan Valenta; Material and Semiconductor Physics, Royal Institute of Technology, Stockholm, Sweden.

Semiconductor quantum dots have aroused much interest during the last ten years due to their electronic and optical properties where quantum size effects are readily observed. In particular spectroscopic studies of single quantum dots have revealed unexpected new physics such as blinking, spectral diffusion etc., which may not be observed in ensemble studies. For silicon, an optically inactive material due to its indirect bandgap, the discovery of the strong luminescence from porous silicon in 1990 stimulated a new research field. Despite the long lifetime of excitons in silicon nanocrystals (4-5 orders of magnitude larger than in some direct bandgap quantum dots), interest in them is promoted by the well-developed VLSI technology. Also, the quantum efficiency of such nanocrystals is comparable to the one of their direct bandgap counterparts. In this work we fabricate individual silicon quantum dots using electron-beam lithography, plasma etching and subsequent size-reduction by oxidation. The photoluminescence from individual dots at various temperatures is detected and spectrally resolved using a sensitive CCD camera imaging system. The objectives of the study are to unravel the physics of the luminescence mechanism on a single dot level and to understand the intriguing phenomenon of on/off blinking. Much variation between dots has been observed. The parameters of luminescence, such as homogeneous linewidth, quantum efficiency, characteristic blinking times, may vary from dot-to-dot significantly. Such differences highlight the need for both structural and electronic configuration characterization of a single silicon nanocrystal in order to shed some light on the origin of the variations. The regular arrangement of individual nanocrystals used in this work enables combined high-resolution transmission electron microscopy and low-temperature photoluminescence characterization of the same single quantum dot.

4:30 PM **P12.11**

CO₂ laser printing of silicon quantum dot solids. Martien den Hertog, Anna Tchebotareva, Rob van Loon and Albert Polman; Center for Nanophotonics, FOM-Institute AMOLF, Amsterdam, Netherlands.

Si nanocrystals show quantum-confined radiative emission at a rate and quantum efficiency much higher than bulk silicon. Optically active Si nanocrystals could serve as the light source in CMOS compatible opto-electronic circuits. They also find applications as sensitizer for optically active ions such as rare earth ions, and may also be used as bio-compatible, non-bleaching biomarkers. In addition, electrically isolated Si nanocrystals can serve as the charge storage medium in MOS non-volatile memories. Here, we present a new method of locally creating Si nanocrystals on a planar substrate using CO₂ laser irradiation. A thermally grown SiO₂ film on a Si substrate is implanted with Si to excess concentrations as high as 10 at.%. Subsequently, this supersaturated solution is irradiated using a short (~ 100 μs) CO₂ laser pulse. This leads to the local nucleation and growth of Si nanocrystals. After passivation using a 500 or 800 °C anneal under forming gas, clear photoluminescence from Si nanocrystals is observed, with a wavelength and luminescence lifetime characteristic of quantum-confined emission from 3-4 nm diameter nanocrystals. Spectroscopic ellipsometry shows that the laser annealed quantum dot solid has a slightly lower refractive index than the Si-rich oxide starting material. We show experimental data on the optimization of the laser anneal parameters (pulse duration in the range 0-200 μs, power in the range 0-25 W) and find these in agreement with finite-element heat flow calculations of the time- and depth-resolved temperature profiles in the irradiated oxide film. The calculations show that thermal isolation by the thick oxide substrate is essential to achieve the high near-surface temperature required for the nanocrystal formation, with the final temperature then determined by the laser pulse duration. As the CO₂ laser anneal can be applied locally, this novel technique enables the fabrication of a wide array of functional geometries, including LED pixel arrays, MOS memories, optical waveguides and other passive and active optical structures. As an example, we show fluorescent line and ring quantum dots solid geometries made using laser irradiation using a scanning sample stage, imaged with two-dimensional confocal microscopy.

4:45 PM **P12.12**

Theoretical Investigation of the Electronic, Vibrational, and Optical Properties of Silicon Nanowires. Li Yang and Mei-Yin Chou; School of Physics, Georgia Institute of Technology, Atlanta, Georgia.

Semiconductor nanowires have potential applications in many fields such as optoelectronics, photovoltaic cells, and especially device miniaturization. We have performed calculations of the electronic, vibrational, and optical properties of silicon nanowires using first-principles approaches. Structure relaxation and lattice vibrations are studied within the framework of the density functional theory. The quasi-particle spectra are evaluated using the many-body perturbation theory with the GW approximation. Excitonic effects are included by solving the Bethe-Salpeter equation. We have studied the structural, electronic, and optical properties of hydrogen-passivated silicon nanowires along [110] and [111] directions with a diameter up to 4.2 nm. The size and orientation dependence of the band gap is investigated. Quantum confinement becomes significant for $d < 2.2$ nm, where new low-energy absorption peaks start to appear in the imaginary part of the dielectric function for polarization along the wire axis [1]. We further investigated the lattice vibrations for silicon nanowires along the [110] direction and the distribution of phonon modes at the Gamma point for nanowires of various diameters. Two different frequency shifts are found for the optical modes and the collective modes, respectively. When the size of nanowires decreases, the frequencies of optical modes are red-shifted, while the frequencies of collective modes are blue-shifted. We provide an explanation for these trends based on different quantum confinement effects. In addition, the controversy over clamped and free boundary conditions is resolved in light of our first-principles calculations. The relative Raman scattering activity and its size-dependence in a small nanowire are evaluated. We also find that quantum confinement considerably changes the sound velocity, which has a significant effect in the studies of transport properties in nanostructures. Finally, we report the effect of electron-hole interaction on the optical spectra. Due to quantum confinement and reduced screening, a large exciton binding energy of the order of 1 eV is found. The excitonic effect also creates some strong absorption peaks in silicon nanowires. We acknowledge the collaboration with C. D. Spataru and S. G. Louie. [1] X. Zhao, C. M. Wei, L. Yang, and M. Y. Chou, Phys. Rev. Lett. 92, 236805 (2004).

SESSION P13: Poster Session III
Chairs: Philippe Guyot-Sionnest, Margaret Hines and Hedi Mattoussi
Thursday Evening, December 1, 2005
8:00 PM
Exhibition Hall D (Hynes)

P13.1

Temperature Dependent X-ray Excited Optical Luminescence (XEOL) Studies on Si Nanocrystals. Yimin Chao¹, Jianhua Yang^{2,3}, Lidija Siller², Nigel R. J. Poolton⁴, Andrew Houlton¹ and Ben R. Horrocks¹; ¹School of Natural Sciences, University of Newcastle upon Tyne, Newcastle upon Tyne, United Kingdom; ²School of Chemical Engineering and Advanced Materials, University of Newcastle upon Tyne, Newcastle upon Tyne, United Kingdom; ³School of Sciences, University of Nantong, Nantong, China; ⁴Daresbury Laboratory, CCLRC, Warrington, United Kingdom.

Nanometresized silicon quantum dots capped with an alky monolayer (SiNCs), were prepared by electrochemical method and their soft x-ray excited optical luminescence (XEOL) behavior was investigated using synchrotron radiation to access a range of excitation photon energies and temperatures. At 8 K two PL emission bands were found at 430 ± 10 nm (blue) and 600 ± 10 nm (orange). As the X-ray excitation energy increased from 5.1 to 22.5 eV, the intensity of the blue emission increased while the orange emission intensity remained constant. Further, the blue band appeared strongly enhanced with excitation energies greater than 8.7 eV which corresponds to the SiO₂ indirect bandgap. Optically detected NEXAFS data showed that in the Si L_{2,3} region there are two absorption edges at 100 eV and 104 eV corresponding to Si and SiO₂ respectively, depending on the detection of particular emission band (orange vs. blue, respectively). This has led to the assignment that orange and blue bands correspond primarily to excitation from Si and SiO₂, respectively. At an excitation energy of 21.2 eV, the intensity of the blue emission decreased monotonically over the temperature range of 8 K to 150 K and above 150 K no blue emission could be detected. This can be explained as temperature quenching in a two-level system. Below 150 K both PL emission peak wavelengths are insensitive to temperature, but from 150 K to room temperature, the orange peak position shifted to longer wavelengths, from 600 ± 10 nm to 630 ± 10 nm. The orange emission intensity also gradually increases as the temperature decreased from room temperature (ca. 290 K) until about 150 K after which the intensity falls as the temperature drops further. The value at 290 K is about 50% of that at 150 K. The results imply the dominant physical process controlling orange PL properties at high temperatures is different from that at low temperatures. The temperature behaviour of the orange emission intensity can be explained by a competition between radiative and non-radiative recombination processes [1], while the temperature behaviour of the orange PL peak wavelength results from localized tail states formed by the disordered potential at the surface due to the surface roughness and variations in surface stoichiometry. [1] A.G.Cullis, L.T.Canham and P.D.J.Calcott, J.Appl.Phys. **82**, 909 (1997)

P13.2

Photochemical etching of Silicon using hard x-rays. In Hwa Cho, Do Hyung Kim, Sang Hoon Nam and Do Young Noh; Materials Science and Engineering, Gwangju Institute of Science and Technology, Gwangju, South Korea.

Photochemical wet etching of n-Si (100) was carried out using high-energy x-rays from synchrotron radiation. HF (49%) solution was used as the etching solution. Under the illumination of intense white x-rays, silicon was electropolished with the etching rate of about ~ 1.7 nm/min. On the other hand, porous silicon was formed under the illumination of relatively less intense monochromatic x-rays. The porous silicon is studied by SEM cross-section imaging and PL. The major difference between the electropolishing and the formation of porous silicon is the intensity of x-rays. Porous silicon was also formed as the concentration of HF solution was reduced even under the illumination of white x-rays.

P13.3

Synthesis and Investigation of Thin p-Type ZnO Films on Si Substrates Obtained by Ultrasonic Spray Pyrolysis. Irina Victorovna Khvan, Shavkat Uzgenovich Yuldashev and Rafael Aydinovich Nusretov; Heat Physics, Academy of Sciences of Uzbekistan, Tashkent, Uzbekistan.

Thin p-type ZnO films were deposited on the Si n-type substrates with different conductivities (up to 10⁻³ Ohm*cm⁻¹) from zinc nitrate (Zn(NO₃)₂) and ammonium acetate (NH₄CH₃COO) aqueous solutions by the ultrasonic spray pyrolysis method at various temperatures of synthesis and subsequent annealing. The investigations of structural (SEM, XPS) and optic (photoluminescence) properties of the obtained films, as well as study

of Hall effect were carried out. Scanning electron microscopy studies showed that the obtained films have dense polycrystalline surface with crystallite sizes about 60 nm. ZnO film thickness was about 160 nm. Hall effect measurements indicated high concentration of p-type carriers (up to 10^{18} cm⁻³) in some samples. We have revealed a strong correlation between concentration of holes in the synthesized ZnO films and conductivity values of Si substrates. It was found that with the increasing of Si substrate conductivity the concentration of p-type carriers in ZnO films increases. The results of photoluminescence, Hall effect and XPS measurements of the produced samples correspond to the primary position of N atoms as substitutional impurity of oxygen in thin ZnO films, and which are acceptor dopants in these ZnO/Si heterostructures.

P13.4

Structure of hydrogenated Silicon nanowires.

Cristian V. Ciobanu¹ and Mihail M. Popa²; ¹Division of Engineering, Colorado School of Mines, Golden, Colorado; ²School of Automation, Computers and Electronics, University of Craiova, Craiova, Romania.

In an effort to explain recent experiments that show very few preferred orientations (such as [112], [110], or [111]) for hydrogenated silicon nanowires, we have studied how the wire structure and energetics is affected by the crystallographic orientation of the axis. At a given orientation, we also show the effect of the hydrogen supersaturation on the wire surface, and show that novel structures can evolve in the low-thickness regime. The approach that we take is based on global structural optimization via a genetic algorithm. The algorithm is coupled with highly optimized empirical potentials for Silicon, which help build databases of structural candidates for the most favorable nanowire configurations. The models in the database are further optimized at the level of density functional theory (DFT) calculations in order to gain an accurate understanding of their energetic ordering. These studies explain the experimentally observed structures through a competition between the chemical potential of Hydrogen, the quantum-chemical bonding at the surface, and stress release in the wire. The results presented here serve as basis for further investigations of electrical transport and mechanical properties in nanowires with different axis orientations.

P13.5

Large Influence of Strain on the Variation of the Band-Gap Pressure Coefficients of InAs/GaAs Quantum Dots with Different Sizes.

Christian Kristukat¹, Quincy K. K. Liu² and Christian Thomsen¹; ¹Institute of Solid State Physics, Technical University Berlin, Berlin, Germany; ²SF5 (Theory), Hahn-Meitner-Institut, Berlin, Germany.

In the last few years many different kinds of strained and unstrained heterostructures have been systematically studied by means of optical spectroscopy under high hydrostatic pressure. The strained InAs/GaAs is one of the most popular material systems for the growth of quantum dots, exhibiting strong luminescence in the infra-red region. The pressure coefficients of the direct band-gap of all InAs/GaAs quantum dot samples measured so far are remarkably lower than that of both InAs and GaAs bulk and, moreover, exhibit a linear dependency on the emission energy which is directly related to the size of the quantum dot. While the former is mostly due to the difference in bulk modulus of InAs and GaAs, the size dependence is not understandable at first sight. We present results from continuum elasticity and atomistic force-field calculations for different quantum dot shapes and sizes which show that the pressure inside the dot and therefore the band-gap energy depends on its size.

P13.6

Bipolaronic phase in polar semiconductor quantum dots: An all-coupling approach.

Phani Murali Krishna Ravuri¹, Soma Mukhopadhyay² and Ashok Chatterjee¹; ¹School of Physics, University of Hyderabad, Hyderabad, Andhra Pradesh, India; ²Department of Physics, Shadan Institute of PG Studies, Hyderabad, Andhra Pradesh, India.

An all-coupling variational calculation has been performed to explore the formation and stability of a bipolaron in a polar semiconductor quantum dot. It has been shown that quantum confinement in general leads to a broadening of the bipolaron stability region. It has been furthermore shown for the first time that stable bipolarons can exist in realistic parabolic quantum dots of polar semiconductors like GaAs, CdS, CdTe and CdSe if they are fabricated in certain range of sizes.

P13.7

Luminescence property of RGB luminescent nanocrystalline silicon embedded in glass.

Yosuke Sasaki, Keisuke Sato and Kenji Hirakuri; Department of Electronic and Computer Engineering, Faculty of Science and Engineering, Tokyo Denki University, Hatoyama, Saitama, Japan.

Luminescent color of nanocrystalline silicon (nc-Si), with visible emission from red light up to blue light, has been strongly dependent on particle size. We have fabricated SiOx glass films which included nc-Si particles, which emits a red/green/blue light in order to realize the white light source based on the nc-Si. In this paper, we report on the luminescence property of the glass film with the nc-Si particles. Moreover, the correlation between the film thickness of the glass film and luminescence intensity will be discussed. The glass film embedding the nc-Si was prepared by radio-frequency magnetron sputtering method with silicon/silicondioxide targets and post-annealing treatment in argon gas atmosphere. Each luminescence of the nc-Si in the glass film was tuned by changing the sputtering conditions, which can freely control the particle size. The glass film was estimated by using scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and photoluminescence (PL) measurements. The glass films exhibited very broad spectra with a peak from 400nm to 800nm. The films emitted white light when the glass films were irradiated by optical light from a xenon lamp through an optical band-pass filter of 313nm. The intensity of white luminescence was dependent on the film thickness of the glass. The intensity of the white luminescence doubled with an increase of the film thickness from 0.69 μ m to 1.12 μ m.

P13.8

Optical Signature of Aharonov-Bohm Phase in Multilayer Structures with Type-II Quantum Dots.

Igor L. Kuskovsky¹, Weldon MacDonald², Maria C. Tamargo³, Alexander O. Govorov⁴ and Xing Wei⁵; ¹Physics, Queens College of CUNY, Flushing, New York; ²Physics, Queens College of CUNY, Flushing, New York; ³Chemistry, The City College of CUNY, New York, New York; ⁴Physics and Astronomy, Ohio University, Athens, Ohio; ⁵National High Magnetic Field Laboratory, Tallahassee, Florida.

We report magneto-photoluminescence study on multilayer Zn-Se-Te structures with type-II (ZnTe/ZnSe) quantum dots in magnetic fields up to 25T, confirming theoretical predictions [1] that the intensity of the excitonic photoluminescence (PL) from type-II quantum dots is dependent on the magnetic flux via the Aharonov-Bohm (AB) effect. Recently we have shown [2] that quantum islands with type-II band alignment are formed in Zn-Se-Te multilayers with sub-monolayer insertion of Te. The resultant ZnTe/ZnSe type-II hetero-structures are characterized by strong confinement of holes (about 1eV, see e.g. Ref. [3]) within ZnTe-rich islands, whereas electrons, attracted by holes via the Coulomb potential, are located within ZnSe spacer (barrier) regions. The multilayer character of our samples ensures the electron motion within the x-y plane. We thus observed strong oscillations in the integrated PL intensity with the period of Φ/Φ_0 ($\Phi_0 = h/e$ is the flux quantum) in an agreement with theories [1, 4] based on the Aharonov-Bohm effect. We have observed up to 7 trapped fluxes. The strongest (first) signature has been observed at fields as low as $B \sim 0.8T$, corresponding to the effective island diameter of $\sim 85nm$. We explain such a strong AB signature in terms of the circular motion of electron around a stack of quantum dots, since in our structures, the distance between quantum dots in the z-direction (3 nm) is much smaller than the in-plane diameter of a quantum dot. In our model the hole in the exciton is strongly localized in one of the quantum dots whereas the electron is free to rotate around a stack of quantum dots. We note that our experimental results are in qualitative agreement with the theoretical predictions of Ref. [4] for magneto-excitons in a system of stacked quantum dots. [1] A.B. Kalametsev, V.M. Kovalev, and A.O. Govorov, JETP Lett. **68**, 669 (1998). [2] Y. Gu, Igor L. Kuskovsky, M. van der Voort, G.F. Neumark, X. Zhou, and M.C. Tamargo, Phys. Rev. B **71**, 045340 (2005). [3] S.-H. Wei and A. Zunger, Phys. Rev. B **53**, 10457 (1996). [4] L.G.G.V. Dias da Silva, S.E.Ulloa, and A.O.Govorov, Phys. Rev. B **70**, 155318 (2004). [5] K. L. Janssens, B. Partoens, and F.M. Peeters, Phys. Rev. B **69**, 235320 (2004).

P13.9

Collective excitations in charged nanocrystals.

Christophe Delerue¹, Yann-Michel Niquet² and Guy Allan¹; ¹ISEN, IEMN, Villeneuve d'Ascq Cedex, France; ²DRFMC, CEA, Grenoble, France.

Close-packed arrays of semiconductor nanocrystals presently receive a growing interest due to their optical and electrical properties. Here we consider theoretically the case where all the nanocrystals are charged by one or two electrons. By using self-consistent tight binding calculations, we demonstrate that the charging profoundly affect the optical properties in the infrared range due to strong collective electronic effects. In a single dot, we show that at the resonance with the S to P transition, the dipole induced by the additional electron(s) oscillates in opposite phase with respect to the dipole induced by the plasma of valence electrons. In a close-packed array, we predict an important change of the refractive index near the resonance and also an energy region where the dielectric constant is negative. Transverse and longitudinal excitations are found with frequencies obeying the Lydanne-Sachs-Teller equation. Consequences of these predictions on

possible applications of these systems will be discussed.

P13.10

Implantation-defect-mediated intermixing of InAs/InP quantum dot and InAs/InGaAsP/InP QDs lasers.

Carolyne Dion¹, Sylvain Raymond², Philip Poole², Francois

Schiettekatte³, Martin Chicoine³ and Patrick Desjardins¹;

¹Department of Engineering Physics, Ecole Polytechnique de Montreal, Montreal, Quebec, Canada; ²Institute for Microstructural Sciences, National Research Council of Canada, Ottawa, Ontario, Canada; ³Department of Physics, Universite de Montreal, Montreal, Quebec, Canada.

The reduced dimensionality provided by quantum dots (QDs), which leads to atom-like discrete energy levels and δ -function-like density of states, offers possibilities for considerable improvements in optoelectronic device applications. However, the use of these nanostructures relies on achieving precise tunability of QDs luminescence emission. For that reason, we have investigated the effect of post-growth P implantation followed by rapid thermal annealing (RTA) on the low-temperature photoluminescence (PL) spectra of self-assembled InAs/InP(001) QDs grown by chemical beam epitaxy and metal-organic vapor phase epitaxy. Low implantation energies were selected such that the InAs QDs were not damaged. In untreated samples, threshold temperature for intermixing was found to be 725 °C with blueshifts of the PL peaks of up to 90 meV after RTA at 800 °C for 210 s, while preserving emission bandwidth. Implantation with fluence as low as 10^{12} P/cm² followed by annealing at 500 °C were sufficient to induce a 275 meV blueshift, however the overall emission bandwidth became larger by about 140 meV. Towards the application of ion implantation for the fabrication of monolithically integrated devices, we also studied implantation-defect-mediated intermixing for wavelength tuning of p-i-n InAs/InGaAsP/InP QD lasers diode structures. Laser structures showed thermal stability up to 700 °C. PL shift of 20 and 150meV were obtained after RTA at 750 °C for 60 s, respectively for untreated and implanted sample with fluence of 10^{14} P/cm². These observations provide important insights into the role of defects generated in InP-based structures on the As/P intermixing in InAs QDs.

P13.11

Zn Nanocrystal Formation by Photo-MOCVD Method.

Keen Bang, Sangsu Kim and Koengsu Lim; Electrical Engineering and Computer Science (Division of Electrical Engineering), Korea Advanced Institute of Science and Technology, Daejeon, South Korea.

Recently, nanocrystal memories employing discrete traps as a charge storage media have attracted a lot of research attention as the promising candidates to replace conventional DRAMs or Flash memories. DRAMs allow fast write/erase operation, but suffer from high power consumption incurred by the constant refresh operations due to their short retention time. It is also very difficult to fabricate high-density DRAMs because a large capacitor is necessary for charge retention. In case of Flash memories which have long retention time, they have the drawbacks of high operation voltage and slow write/erase operation due to relatively thick tunnel oxide. Until now, for nanocrystal floating gate memory fabrication, most researches are focused on Si or Ge nanocrystal memories. However, in order to maintain good retention characteristics in nanocrystal memories, the programming voltages (write and erase) cannot be scaled down easily. Interface and dopant fluctuations at the Si/Ge nanocrystal interface also cause device design difficulty. On the other hand, metal nanocrystals have many advantages over the semiconductor counterparts including high density of states around the Fermi level, stronger coupling with the conduction channel, a wide range of available work functions, and smaller energy perturbation due to carrier confinement. Metal nanocrystals also provide a great degree of scalability for the nanocrystals size. However, most researches to fabricate metal nanocrystals are concentrated on evaporation or sputtering, followed by thermal annealing. These methods are complicated and time-consuming. In this paper, new method for metal nanocrystal fabrication will be introduced by using Zn with the photo-MOCVD method. Photo-MOCVD is based on photo-chemical process involving photo-dissociation. In this system, diethylzinc (DEZ) which is liquid source is used to fabricate Zn nanocrystals and decomposed by the UV source with the wavelength at 254nm. DEZ source is heated in the thermostat to 20 °C and carried from source cylinder to the reactant chamber by Ar gas. Fundamentally it is not physical vapor deposition but chemical vapor deposition method. Hence, there are several parameters to adjust for optimal condition such as chamber pressure, flow rate of carrier gas and substrate temperature. In the experiment, DEZ thermostat is set to 20 °C, substrate temperature is set to 150 °C and flow rate of carrier gas is changed from 20 sccm to 50 sccm. Thereafter, Zn nanocrystal shape is investigated with the process time varied. AFM (Atomic Force Microscope) and SEM (Scanning Electron Microscope) are used to identify the Zn nanocrystal. As a result, dense Zn nanocrystals were

obtained when the chamber pressure is 2 Torr, the substrate temperature is set to 150 °C, flow rate of carrier gas is set to 30 sccm, and the process time is 1 min. Dense Zn nanocrystals fabricated by photo-MOCVD can be easily applied to the Zn nanocrystal memory.

P13.12

Enhancing Memory Efficiency of Si Nanocrystals Floating Gate Memories with High- κ Gate Oxides.

Prakaipetch Punaichetch¹, K. Ichikawa¹, H. Yano¹, T. Hatayama¹, Y. Uraoka¹, T. Fuyuki¹, E. Takahashi², T. Hayashi², K. Ogata² and S. Horii³; ¹Department of Materials Science, Nara Institute of Science and Technology, 8916-5 Takayama Ikoma, Nara 630-0192, Japan; ²R&D Laboratory, Nissin Electric Co. Ltd, Umezu-Takase-cho, Ukyo-ku, Kyoto 615-8686, Japan; ³Hitachi Kokusai Electric Inc, 2-1 Yasuuchi, Yatsuo-Machi, Nei-gun, Toyama 939-2393, Japan.

Silicon nanocrystals floating gate memories have attracted considerable attention due to its low power consumption, small devices size, high density integration, and compatibility to conventional ULSI process [1-2]. However, the improvement in term of short memory window and retention time is the critical issues and important for further studies. The high quality Si nanocrystal dots prepared by side-wall type plasma enhanced CVD method could confirm the stable memory efficiencies for floating gate MOSFET [3]. In this study, the advantages of suppressed leakage current with low operating voltage by using high- κ gate film was studied as compared to SiO₂ film. The SiO₂ tunnel and control oxide were replaced with Hf-based dielectric films with dielectric constant about 15. The thicknesses of tunnel oxide and control oxide are 4 and 17 nm, respectively. Larger capacitance density with stable charging-discharging characteristic was observed in the case of high- κ gate oxide devices, as compare to SiO₂ gate oxide. Additionally, larger hysteresis shift due to larger electron confinement were observed in high- κ film devices. This improvement is owing to larger capacitance density which could enhance more electron confinement probability toward Si nanocrystal dots. Therefore, Si nanocrystal dots with high- κ dielectric films could be useful for the future memory devices. [1] S. Tiwari, F. Rana, H. Hanafi, A. Hartstein, E.F. Crabbe, and K. Chan, Appl. Phys. Lett. 68 (1996) 1377. [2] H. I. Hanafi, S. Tiwari, I. Khan, IEEE TED 45 (1996) 1553. [3] P. Punaichetch, K. Ichikawa, H. Yano, T. Hatayama, Y. Uraoka, T. Fuyuki, E. Takahashi, T. Hayashi, K. Ogata, submitted.

P13.13

The Effect of Hydrogen Passivation on Si Nanocrystals

Embedded in a SiO₂ Matrix. Young-Kwan Cha¹, Sangjin Park¹,

Youngsoo Park¹, Daigil Cha², Jung H. Shin² and In-Kyeong Yoo¹;

¹Devices lab, Materials and Devices Research Center, Samsung Advanced Institute of Technology, Suwon, South Korea; ²Department of Physics, Korea Advanced Institute of Science and Technology, Daejeon, South Korea.

In this work, we investigated the effect of hydrogenation on electronic properties of Si nanocrystals embedded in a SiO₂ matrix. Si-rich oxide and SiO₂ control oxide were grown by ICP-CVD using SiH₄ and O₂ as precursor gas and depending on the gas flux ratio, the value of x varied from 2 to 0.76. After the control oxide growth, annealing and hydrogenation were performed respectively, and sequentially. It is shown that as-deposited and annealed samples were able to store carriers, but the hydrogenation effects of each sample were quite different. After hydrogenation, the memory window of as-deposited sample is improved but that of the annealed sample was reduced regardless of the value of x. We analyzed C-V behavior on MOS structure and FT-IR signals in terms of structural and electronic modification induced by hydrogenation.

P13.14

The Electronic Structure of Diamondoids Using Synchrotron

Radiation. Trevor Willey¹, Christoph Bostedt², J. E. Dahl³, Thomas

Moeller², R. M. K. Carlson³, S. G. Liu², E. J. Nelson¹, T. van Buuren¹, R. W. Meulenberg¹ and L. J. Terminello¹; ¹Lawrence Livermore National Laboratory, Livermore, California; ²Technische Universitat, Berlin, Germany; ³MolecularDiamond Technologies, Chevron-Texaco Technology Ventures, Richmond, California.

Although the Group IV semiconductors Si and Ge show quantum confinement effects in nanoparticles, diamond particles a few nanometers in size do not show this increase in band-gap. However, various calculations on diamond predict increasing HOMO-LUMO gap as the diameter decreases below 1 nm. We have tested this hypothesis and will present the first measurements of the electronic structure of diamond in this near- and sub-nanometer size regime using synchrotron radiation techniques. Pure, defect-free, hydrogen-terminated diamondoids were investigated in the gas phase to eliminate particle-particle interaction and ensure measurement of pristine molecules. X-ray absorption probes the unoccupied electronic states; the Carbon K-edge reveals rich electronic structure in these

materials. We will present our analysis showing the emergence of a diamond-like band structure and a comparison to the predicted change in HOMO-LUMO gap from several calculations and our own recent X-ray absorption and emission measurements on solid-state diamondoids.

P13.15

Prediction of strong absorption in GaInNAs quantum wires. Andrea Feltrin, Andenet Alemu and Alex Freundlich; Center for Advanced Materials, University of Houston, Houston, Texas.

The incorporation of small amounts of nitrogen in III-V semiconductor produces a large reduction of the optical band gap with a huge bowing parameter. This behavior has been explained in terms of a band anti-crossing (BAC) model. In this picture the band gap reduction is caused by the interaction between localized nitrogen states and extended conduction band electron states of the host material. A further consequence of this interaction is the modification of the electron dispersion in the reciprocal space and the increase of the conduction band electron effective mass. Masses as high as 0.4 free electron mass have been measured in quantum confined structures and calculations seem to support these first experimental results. The properties associated with this unusually high electron effective masses points to promising applications in the optical domain for dilute nitride nanostructured materials encompassing ternaries or quaternaries such as GaNAs and GaInNAs. In order to gauge quantitatively these anticipated benefits, in this work, we carry out a systematic comparison between the quantum wire absorption spectrum of two material systems, GaInAs and GaInNAs, having the same optical band gap. The calculations are carried out in the dipole and effective mass approximation, using parabolic dispersions and take into account both, the strain induced modifications of heavy and light hole valance sub-bands. We compute the single particle allowed transitions and take into account consistently the Coulomb interaction between electrons and holes for each of these transitions. The inclusion of excitonic features in our model leads to the well-known appearance of an excitonic resonance below the single particle transition energy and to the disappearance of the divergence of the absorption at single particle transition energy. We show that the larger electron mass in dilute nitride materials such as GaInNAs leads to an enhanced exciton binding energy and absorption strength in such well material. The advantages of these enhancements are twofold. A larger electron mass implies not only an increase of the optical density of states and thus of the absorption strength in comparison to GaInAs quantum wires but also an increased number of confined electron states and hence dipole allowed optical transitions. An additional enhancement of the absorption strength is thus obtained over the integrated quantum wire absorption spectrum.

P13.16

Fast and Slow Luminescence in Three-dimensional Si/SiGe Nanostructures. Leonid Tsybeskov¹, Boris Kamenev¹, Jean-Marc Baribeau² and David Lockwood²; ¹ECE, NJIT, Newark, New Jersey; ²IMS, National Research Council of Canada, Ottawa, Ontario, Canada.

We report the first experimental observation of both a fast (~0.01 ms) and a slow (~10 ms) photoluminescence (PL) that co-exist in Ge-rich (>50%) island-like, three-dimensional Si/SiGe nanostructures. We present a quantitative model that explains the observed PL lifetime dependence on carrier concentration, temperature and detection wavelength. The PL dynamics are found to be determined by the excess carrier concentration: the fast PL is associated with a dynamic type I and the slow PL with a type II energy band alignment in Ge-rich Si/SiGe nanostructures.

P13.17

Radiative Quantum Efficiency of Si Nanocrystals from Local Density of Optical States. Robert J. Walters¹, Jeroen Kalkman², Nick Chiang¹, Albert Polman², Harry A. Atwater¹ and Michiel de Dood³; ¹Applied Physics, California Institute of Technology, Pasadena, California; ²FOM-AMOLF, Amsterdam, Netherlands; ³University of Leiden, Leiden, Netherlands.

Researchers have long speculated that the internal quantum efficiency of well passivated silicon nanocrystals may be near unity. We have measured the decay rate of silicon nanocrystals as a function of the local optical density of states in order to examine this proposition. Silicon nanocrystals are prepared by Si ion implantation into oxide layers of various thicknesses (10nm - 1um) at low energy (5keV) and subsequent thermal annealing (1100C). This procedure creates a layer of 2-4nm diameter silicon nanocrystals centered at the projected implantation range of 10nm from the oxide surface. Many different oxide thicknesses are created on the same sample by etching back an initially grown thick oxide to form a "staircase" structure prior to implantation. This ensures that the nanocrystal populations we are comparing have been created through identical processing. The

optical density of states is calculated as a function of the distance from the nanocrystals to the high index silicon substrate. In accordance with the model, the decay rates of the silicon nanocrystals is observed to vary between 10 and 50 kHz, in proportion to the local optical density of states. The data are fit to measure the vacuum radiative recombination rate of silicon nanocrystals (10.5kHz) and the ensemble quantum efficiency (70%) at the peak emission wavelength of 750nm.

P13.18

X-ray Diffraction Investigation of the Shapes of Buried Ge Nanowires on Si(124). Yang Da^{2,1}, Heedon Hwang^{2,1}, Ross Harder^{3,1} and Ian Robinson^{3,1}; ¹Materials Research Laboratory, Urbana, Illinois; ²Materials Science and Engineering, University of Illinois, Urbana, Illinois; ³Physics, University of Illinois, Urbana, Illinois.

In this work, we employ the natural tendency of vicinal surfaces to form nanoscale facets to engineer an array of parallel nanowires of Ge on Si. Si (124) substrates are found to spontaneously form facets of {113} and {157} directions, making a small angle to the (124) normal direction. Gas-source molecular beam epitaxy (MBE) gives rise to Ge nanowires which are 50-100nm in diameter along a certain spatial direction. They are subsequently buried in Si to prevent oxidation. These can be imaged by AFM for exposed surfaces, but are difficult to image when buried. The study addresses the question of the structure of the wires before and after burial using coherent X-ray diffraction at sector 34 of the Advanced Photon Source, Argonne National Lab. The diffraction pattern of a long crystalline wire is like a thin sheet perpendicular to the wire direction. From our coherent X-ray diffraction data we have made the 2-D reciprocal lattice map (RLM) of diffraction pattern intensity distribution in order to understand the cross-sectional shape of wires. By using a high-Q Bragg peak for the RLM, we can also study the Strain in the nano heterostructure. Visualization of the 3D lattice maps in a skewed coordinate system is facilitated by coordinate transformations and rendering with Mayavi software.

P13.19

ZnO nanopillars on Si grown with Au catalysts: Details of the growth process and luminescence properties. Yujie Li¹, Martin Feneberg¹, Anton Reiser¹, Martin Schirra¹, Rainer Enchelmaier¹, Andreas Ladenburger¹, Andre Langlois¹, Jun Cai², Hubert Rauscher², Rolf Sauer¹ and Klaus Thonke¹; ¹Abt. Halbleiterphysik, Universitaet Ulm, Ulm, Germany; ²Oberflaechenchemie und Katalyse, Universitaet Ulm, Ulm, Germany.

The growth of ZnO nanopillars on silicon substrates via the catalyzed vapor-liquid-solid (VLS) mechanism involves many more complications than the VLS growth on insoluble substrates like sapphire. We have studied in detail the initial steps of ZnO nanopillar growth on Si substrates. We find that in the initial growth stage the substrate surface is melt and partially oxidized, and that alloys with different compositions of Au, Si, Zn, and ZnO_x are formed. In an atmosphere with low O₂ partial pressure, Zn rich alloys instead of ZnO are first deposited on the SiO₂ covered Si substrates and form poly-crystalline broad bases for the growing pillars. The difficulty of ZnO to nucleate on SiO₂/Si is another reason preventing ZnO nanopillars to grow epitaxially on the substrates. Defects, steps, and/or stress on the substrate surfaces support the nucleation process and thus influence the initial growth stage and the control of the growth orientation of the pillars. By scratching the Si substrates and avoiding the formation of the initial polycrystalline bases, well-aligned ZnO nanopillars were obtained both on Si (111) and (100) surfaces. Sharp photoluminescence peaks of bound exciton emissions and free exciton emission were detected at low temperature, indicating perfect crystalline quality of the nanopillars.

P13.20

Electronic Properties of Wurtzite-based Nanowires, Nanorods, and Nanodots. Lok C. Lew Yan Voon¹, Calin Galeriu², Benny Lassen³, Morten Willatzen³ and Roderick Melnik⁴; ¹Physics, Wright State University, Dayton, Ohio; ²Physics, Worcester Polytechnic Institute, Worcester, Massachusetts; ³University of Southern Denmark, Sonderborg, Denmark; ⁴Laurier University, Waterloo, Ontario, Canada.

In recent years, the experimental study of semiconducting nanowires and nanorods has garnered a lot of interest due, in part, to new growth methods [1] and the demonstration of lasing [2]. In this talk, we propose a theoretical framework for studying the increased functionality that is being experimentally explored via the effect of size and shape of nanorods [3] and of the crystallographic growth direction of a nanowire array [4]. Specifically, we have calculated the electronic structure of wurtzite-based nanowires, nanorods, and nanodots using the k.p method. The generalization of the bulk Rashba-Sekha-Pikus Hamiltonian with Burt-Foreman boundary

conditions for nanostructures is used [5]. For nanostructures with cylindrical symmetry, we have developed a Vahala and Sercel transformation [6] which we have found to be exact, as opposed to the corresponding result for zincblende-based nanostructures [6]. Implementation of our formulation for GaN nanodots is shown to be two orders of magnitude more efficient (i.e., less memory and compute time) than without the Vahala and Sercel transformation. We will also present data on the dimensionality and valence-band level crossing problems for CdSe nanorods [3]. Comparison with zincblende-based nanorods will be given [3,7]. For nanowires grown along different directions and with various cross-sectional shapes [4], we have implemented the k.p theory using MAPLE and FEMLAB so that we can easily treat any growth direction by rotating the Hamiltonian. Comparison with the experimental data of Kuykendall et al. [4], and to our previous calculations for zincblende-based nanowires [8], will be given. Work supported by NSF DMR 0454849, Wright State University and Ohio Board of Regents. [1] Duan and Lieber, *Adv. Mater.* 12, 298 (2000); Yang, Wu, and Fan, *Int. J. Nanoscience* 1, 1 (2002). [2] Huang et al., *Science* 292, 1897 (2001); Johnson et al., *Nature Materials* 1, 106 (2002); Duan et al., *Nature* 421, 241 (2003). [3] Hu et al. *Science* 292, 2060 (2001); Katz et al. *Phys. Rev. Lett.* 89, 086801 (2002). [4] Kuykendall et al. *Nature Materials* 3, 524 (2004). [5] Mireles and Ulloa, *Phys. Rev. B* 60, 13650 (1999). [6] Vahala and Sercel, *Phys. Rev. Lett.* 65, 239 (1990). [7] Kan et al., *Nature Materials* 2, 155 (2003); Lew Yan Voon et al., *Nano Letters* 4, 289 (2004); Steiner et al., *Nano Letters* 4, 1073 (2004). [8] Lassen et al., *Solid State Commun.* 132, 141 (2004).

P13.21

The strong size dependence in crystal growth orientation of GaN nanowires. Jung-Chul Lee¹, Yun-Mo Sung¹ and Dae-Hee Kim²; ¹Materials Sci. & Eng., Korea University, Seoul, South Korea; ²Materials Sci. & Eng., Daejin Univ., Pochun-si, South Korea.

GaN in two-dimensional multi-quantum well structure has been successfully applied for blue light emitting diode (LED), laser diode (LD), and photodetector (PD) applications due to its wide energy band gap and direct transition characteristics. Recently, GaN in one-dimensional nanowire forms has brought much attention due to superior light emitting properties compared to that in thin film forms, arising from reduced defect density and size confinement effect. In this study GaN nanowires were grown on GaN/AlN/Si substrates via vapor-liquid-solid (VLS) mechanism using chemical vapor deposition (CVD). The GaN/AlN double buffer layers with the growth direction of <002> were formed on Si wafers using reactive RF-sputtering and employed to minimize the lattice mismatch between GaN nanowires and Si wafers. The crystal growth orientation of GaN nanowires has been investigated with the variation in the diameter of nanowires. X-ray diffraction (XRD) and transmission electron microscopy (TEM) selected area electron diffraction (SAED) were used for this purpose. The GaN nanowires with the diameter larger than 50 nm showed preferably <002> growth, while those with that less than 50 nm showed strong <101> growth. The growth orientation difference was discussed based upon the surface energy and interfacial energy differences. Also, it was suggested that the GaN nanowires showing <101> growth would show the formation of two <100> and <001> interfaces with liquid Ni catalysts. The small GaN nanowires with <101> growth were almost defect free, showing high photoluminescence (PL) intensity. Also, they showed almost negligible intensity of yellow luminescence.

P13.22

Molecularly-Mediated Assembly of Metal Nanoparticles. I-Im Stephanie Lim, Lingyan Wang, Jin Luo, Wui Ip and Chuan-Jian Zhong; Chemistry, State Univ. of New York at Binghamton, Binghamton, New York.

Nanostructures have received enormous attention due to their unique physical/chemical properties and promising applications in the fields of sensors and catalysis. While the optical, magnetic, catalytic, and electronic properties of nanoparticles and nanostructures are highly interesting, many applications are hampered by the lack of ability to assemble nanoparticles with controllable sizes, shapes, and interparticle spatial properties. This presentation reports the results of an investigation of the viability of using multifunctional sites of supramolecules (e.g., fullerenes, dyes, proteins, and DNAs) as a mediator for the assembly of metal nanoparticles. Water-soluble gold nanoparticles (1-100 nm) are studied as a model system. The combination of these building blocks allows the creation of an entirely new array of nanostructures with desired sizes and shapes. Characterizations of the nanostructured assemblies using various spectroscopic and microscopic techniques will be discussed. One important finding is that the interparticle spatial properties of the network nanostructures can be finely tuned, which could find potential applications in biological/chemical sensing, controlled drug delivery, micro/nano electronics, and photosensitive or luminescent devices.

P13.23

Rapid Thermal Crystallization of amorphous SiGe nanoparticles deposited by Low Pressure Chemical Vapour Deposition. Maria Isabel Ortiz¹, Andres Rodriguez¹, Jesus Sangrador¹, Tomas Rodriguez¹, Angel Prieto², Juan Jimenez² and Carmen Ballesteros³; ¹Tecnologia Electronica, Universidad Politecnica Madrid, Madrid, Spain; ²Fisica Materia Condensada, Universidad de Valladolid, Valladolid, Spain; ³Fisica, Universidad Carlos III, Madrid, Spain.

SiO₂ / SiGe nanoparticles / SiO₂ structures to be used in nanomemories have been deposited onto Si wafers in a continuous process at 390 oC. A commercial low pressure vapour deposition reactor operating in batch mode has been used. Germane (GeH₄) and disilane (Si₂H₆) were used as precursor gases for the SiGe nanoparticles deposition, while the SiO₂ was deposited from Si₂H₆ and O₂. The GeH₄ to Si₂H₆ flow ratio was kept at 0.82 and the total pressure in the chamber was 50 mTorr. These low values of pressure and temperature result in a reduced deposition rate (in the 5 nm / hour range) that ensures an easy control of the amount of deposited material. The SiGe nanoparticles were obtained by stopping the deposition before the coalescence of the growth nuclei. After the deposition, the nanoparticles were crystallized by RTA at different temperatures from 750 to 950 oC and for different times from 0.5 to 10 minutes. The thickness of the top and bottom oxides, the effect of the deposition time on the size of the nanoparticles and the effect of the annealing temperature and time on their crystallization have been characterized by FTIR spectroscopy, UV (325 nm) Raman spectroscopy and cross-sectional Transmission Electron Microscopy equipped with EDX and Z-contrast imaging in STEM mode. The characteristics of the deposited and annealed SiO₂ are similar to those of thermal SiO₂. The as-deposited SiGe nanoparticles are amorphous and spherical, with diameters ranging from 2 to 5 nm depending on the deposition time and their density is around 1012 cm⁻². The Raman spectra and TEM pictures show that the amorphous nanoparticles with diameter around 5 nm are crystallized at temperatures as low as 750 oC and times of 0.5 minutes, being necessary higher temperatures to crystallize the smaller ones.

P13.24

Significant Blue Shift of Luminescence in InGaN/GaN Nano-posts. Horng-Shyang Chen¹, Dong-Ming Yeh¹, Cheng-Yen Chen¹, Yen-Cheng Lu¹, Chi-Feng Huang¹, Tsung-Yi Tang¹, Chih-Chung Yang¹, C. S. Wu² and C. D. Chen²; ¹Institute of Electro-Optical Eng., National Taiwan University, Taipei, Taiwan; ²Institute of Physics, Academia Sinica, Taipei, Taiwan.

Three-dimension (3-D) quantum confinement in semiconductor can lead to good carrier confinement and enhance the quantum efficiency of photon emission. For implementing the 3-D confinement, the fabrication of nano-posts on quantum well structures is an attractive method. Several fabrication methods have been used for implementing nano-posts with the diameter ranging from 60 to 200 nm. In this research, we use the electron-beam lithography and inductively-coupled plasma dry etching to fabricate nano-posts on InGaN/GaN quantum well (QW) structures to achieve the smallest diameter near 10 nm. The QW structure consists of five pairs of 3 nm-thick In_{0.15}Ga_{0.85}N well and 20 nm-thick GaN barrier. To understand the effects on photon emission, we perform photoluminescence (PL) measurements with relatively high excitation intensity. At room temperature, with the excitation intensity at 0.4 W/cm², the PL spectral peak of the 10 nm nano-posts blue shifts by 22.5 nm or 121.8 meV and the 40 nm nano-posts blue shifts by 18 nm or 96.65 meV, when compared with that of the un-patterned sample. When the excitation intensity is increased to 3.5 W/cm², the PL spectrum of the 10 nm nano-posts blue shifts by only 12 nm or 67.1 meV. Also, the 40 nm nano-posts blue shifts by only 10.5 nm or 58.5 meV. In other words, when we increase the excitation intensity from 0.4 to 3.5W/cm², the variations of the PL spectral peak positions of nano-posts are smaller than that of the un-patterned sample. In this excitation intensity range, the un-patterned MQW PL shifts by 13 nm, the 40 nm nano-posts shifts by 5.5 nm, and the 10 nm nano-posts shifts by 2.5 nm. To confirm the 3-D quantum confinement in the nano-posts, we perform numerical calculation for the effective band gap of a nano-post. We solve the Schrodinger equation in the cylindrical coordinates. In the calculations, the following parameters are used: In composition is 15 %, the electron effective mass of GaN is 0.176421m₀ and that of InN is 0.103228m₀. The hole effective mass of GaN is 1.713018m₀ and that of InN is 1.639008m₀. The results show that the effective band gap shifts by 58.6 meV when post diameter is 10 nm. In our experiment, the blue shift range of the nano-post PL spectrum is larger than the theoretical result. This result might be due to the release of the strain field when the sample becomes so thin. The release of the strain field leads to further PL blue shift.

P13.25

Quantum Confinement Effect and Manipulation of Si

Nanowires Synthesized by Laser Ablation and Self-limiting Oxidation. Naoki Fukata^{1,3}, Takashi Oshima², Naoya Okada², Tokushi Kizuka⁴, Takao Tsurui⁵, Shun Ito⁵, Takashi Sekiguchi¹ and Kouichi Murakami^{2,3}; ¹Nanomaterials Laboratory, National Institute for Materials Science, Tsukuba, Japan; ²Institute of Applied Physics, University of Tsukuba, Tsukuba, Japan; ³Special Research Project on Nanoscience, University of Tsukuba, Tsukuba, Japan; ⁴Institute of Materials Science, University of Tsukuba & PREST JST, Tsukuba, Japan; ⁵Institute for Materials Research, Tohoku University, Sendai, Japan.

Silicon nanowires (SiNWs) are of great interest in the fields of both fundamental and application research. For the realization of nanoscale quantum devices and bio/chemical sensors, it is necessary to investigate physical properties such as quantum size effects emerged in nanoscale and to develop the manipulation method of SiNWs. In order to investigate them, SiNWs were synthesized by laser ablation of a Si target with Ni catalyst which was placed in a quartz tube heated at 1000-1200°C in a flowing Ar gas. The effect of phonon confinement depending on the diameter of SiNWs was investigated by micro-Raman measurements. The Si optical phonon peak showed a downshift and an asymmetric broadening with the decrease in the synthesis temperature or increase in the oxidation temperature, namely, the decrease in the diameter of SiNWs [1]. This is well explained by the phonon confinement effect. The excess oxidation showed an upshift and further broadening of optical phonon peak [1]. This is caused by the compressive stress due to the progress of surface oxidation. The peak shift and broadening due to continuous oxidation are the first experimental findings obtained so far for the phonon confinement effect and subsequent compressive stress. The self-limiting oxidation effect was also observed for thermally oxidized SiNWs, i.e., the compressive stress significantly decreased the oxidation rate. This result shows that it is possible to control the diameter of Si core in SiNWs by using this effect. Manipulation of SiNWs was performed under scanning electron microscope observation. By changing the degree of charge-up for the free-standing adjacent SiNWs, the distance and speed of opening motion of them could be controlled. This motion is probably caused by the Coulomb repulsive interaction between them. Electron spin resonance, photoluminescence, and cathodoluminescence measurements are now in progress to investigate the P doping effects and the optical properties of SiNWs. [1] N. Fukata et al., Appl. Phys. Lett. 86, 213112 (2005).

P13.26
Controlled Embedding of Multiple Semiconductor Quantum Dots in Silica Colloids. Sofia Dembski, Christina Maria Graf and Eckart Rühl; Institut fuer Physikalische Chemie, Universitaet Wuerzburg, Wuerzburg, Germany.

Semiconductor quantum dots (QD) are attractive systems for numerous applications including bio labeling or they are contained in tracers in diffusion studies. This is mostly due to their distinct optical properties. High quality CdSe-ZnS nanoparticles are usually obtained from syntheses based on the high temperature thermolysis (200-360°C) of organometallic precursors in the presence of stabilizing agents (triethylphosphine oxide/triethylphosphine). These organic ligands render the QD hydrophobic, while most applications require water-soluble or at least polar systems. Furthermore, such particles are cytotoxic. Therefore, the QD have to be covered by a more polar and protective coating or they are embedded in suitable matrices. Up to now several approaches have been presented, were either single QD are coated with protective shells or multiple QD are randomly dispersed in matrices. The proper adjustment of the size of the tracer over a wide range is an important issue for many applications. Furthermore, the interparticle distance has to be adjusted in order to retain the optical properties of the QD in the matrix. We present a novel method for the controlled embedding of multiple semiconductor quantum dots (2 to 5 nm in diameter) in silica colloids in the range from 20 nm to 1000 nm. In a first step the amphiphilic polymer polyvinylpyrrolidone (PVP) is reversibly adsorbed on organic stabilized CdSe-ZnS core shell QD. These functionalized particles are subsequently homogeneously adsorbed on the surface of amino-functionalized silica spheres. The lateral distance between the single QD on the silica surface can be adjusted by variation of the polymer length. The QD-labeled colloids are directly covered with a silica shell by a Stober-like growth process. The size of the silica core and the thickness of the outer shell are adjustable over a wide range (from 5 nm to several 100 nm). It is also possible to add a second layer of QD in a well-controlled distance from the first layer. The particle size and structure of the multi-core particles are characterized by transmission electron microscopy (TEM). The influence of the polymer coating and the silica environment on the optical properties of the QD are studied by optical absorption and photoluminescence spectroscopy. Furthermore, the multi-core particles are soluble in water and various organic solvents, which is due to their outer silica shell. The distance between the QD in the silica matrix and the particles size can be easily controlled. Therefore, these species are also

of interest to fundamental studies on distance and matrix dependent properties of QD. Furthermore, such particles have also the potential to be used as building blocks for photonic crystals.

P13.27
Dynamical Quantum Properties of Electrons Controlled by Time-Dependent External Field. Masakazu Muraguchi¹, Yusuke Asari², Yusuke Otuka¹, Tetsuro Satake¹ and Kyozauro Takeda¹; ¹Waseda University, Tokyo, Japan; ²Institute of Industrial Science, University of Tokyo, Tokyo, Japan.

Electrons controlled externally by the time-dependent (TD) field, such as the ac electric or electromagnetic field, have lots of quantum effects applicable to semiconductor devices. In meso-scopic systems, an electric field having a tera-hertz-order frequency causes these quantum phenomena efficiently while the electron wave function changes significantly within an extremely short time of few pico-seconds. Thus, in order to discuss these ultra-fast TD phenomena, it is crucial to solve the TD Schrodinger equation. We, here, focus on the TD phenomena of electrons in the resonant tunneling structure (RTS) under the presence of the TD electric field. By injecting an electron wave packet into the RTS, we theoretically study the tunneling processes within the finite lifetime and discuss how the electron-photon interaction changes the TD phenomena of the resonant transition among the resonant levels. We employed the finite difference method both in the real space and real time, and solved the TD Schrodinger equation numerically in the scheme of Hartree-Fock approximation. We decomposed the time evolution operator by Suzuki's exponential product theory, and calculated those decomposed terms individually in real space. In order to discuss the stability of the electron in the RTS, we introduced the effective lifetime τ and obtained its spectrum against the amplitude and frequency of the external field. The resulting τ spectrum reveals that the photon absorption reduces the lifetime while the emission elongates it. This spectrum analysis also elucidates that the lifetime causes a non-linear change against the amplitude of the applied electric field because of Rabi oscillation. According to the energy dependence of the spectrum, we can easily find the multi-photon (absorption/emission) processes in addition to the one-photon processes. We further extended our consideration to such RTS having a two-dimensional structure. Our calculated results demonstrate that an increase in the spatial freedom works as an elastic scattering for the electron injected into the potential interface while the photon absorption and/or emission works as an inelastic scattering in the RTS. We found that the former elastic scattering renews the selection rule and the novel transition paths are generated in the photo-assisted RTS. We will further report our result of inter-electron interaction via the TD phenomena of the electron-hole exciton confined in the RTS.

P13.28
Nanostructural investigation of ferric oxide and oxyhydroxides nanorods. Alexandre Gloter^{1,2} and Lionel Vayssieres¹; ¹ICYS, NIMS, Tsukuba, Japan; ²Laboratoire de Physique des Solides, CNRS UMR 8502, 91405 Orsay, France.

Preparation of akaganeite (β -FeOOH) by forced hydrolysis in aqueous solutions and its transformation into hematite (α -Fe₂O₃) is a well known phenomenon being reported for several decades. Oriented hematite nanorod arrays have been obtained by taking advantage of such process. First, the stabilization of the beta phase is obtained by strict control of the chemical composition as well as the nucleation and growth kinetics and thermodynamics resulting in nanorod bundles with controlled orientation onto various substrates. Hematite nanorods are subsequently obtained by heat treatment and crystal phase transition of the thin films. In this presentation, we will first discuss the influence of the synthesis conditions on the size, morphology, orientation and structural properties of the oriented akaganeite nanorods. In particular, we will report on the complex porosity of such structure by direct observation at nanometer scale by high angle annular dark field microscopy and energy filtered electron microscopy of as-grown and transverse cross sectional samples. Thereafter, the role of such porosity as well as the structural relationship between nanorods within a bundle will be demonstrated for a fine tuning of the final size of the hematite nanorod arrays. Finally, electron energy loss spectroscopy data will be presented to probe and better understand the chemical stoichiometry, the iron valence state and the band gap of such purpose-built nanorods of the thermodynamically stable of iron oxide.

P13.29
A single-chip two-wavelength switchable strained-type-II -Si_{1-x}Ge_x/Si-quantum-well LED. Nozomu Yasuhara¹ and S. Fukatsu^{1,2}; ¹Graduate School of Arts and Sciences, The University of Tokyo, Tokyo, Japan; ²PRESTO, Japan Science and Technology Agency (JST), Saitama, Japan.

Wavelength-switchable light emitting diodes (LEDs) find a broad

range of applications although wavelength switching in an LED of a single-chip format is hard to achieve in general. Alternate approaches toward wavelength selection using LEDs are that one of many LEDs running in parallel is turned on at a time, or that one puts a broad-band LED in front of the entrance slit of a monochromator. In this work, we demonstrate that choosing type-II $\text{Si}_{1-x}\text{Ge}_x/\text{Si}$ -based heterostructures allows us to switch the emission wavelengths at ease, as apposed to III-V-based LEDs, simply by controlling the density of only one type of the carriers (electrons) in the two or more active regions through longitudinal electric field. Importantly, bipolar EL operation is warranted by utilizing the impact ionization that occurs in a reverse-biased Si and SiGe. Sample was a nominally-undoped strained $\text{Si}_{1-x}\text{Ge}_x/\text{Si}$ double quantum well (DQW) grown on on-axis p-type Si(001). Recently, we have performed a proof-of-principle experiment to demonstrate voltage-controlled emission wavelength switching (VCEWS) of photoluminescence (PL) in a strained $\text{Si}_{1-x}\text{Ge}_x/\text{Si}$ DQW by modulating local electron densities through longitudinal electric fields applied across the DQW. Strained $\text{Si}_{1-x}\text{Ge}_x/\text{Si}$ QWs with $x < 0.3$ are known to have a small conduction band offset, $\Delta E_c < 15\text{meV}$, and the confinement of the electrons in the QW is not as strong as that of the holes ($\Delta E_v > 100\text{meV}$ for $x > 0.1$). The only binding force is the Coulomb interaction between the hole and the electron ($\approx 10\text{-}30\text{meV}$). As such, the electrons are easy to be ionized and begin to drift under longitudinal electric fields. The physics and principle of two-wavelength switching in the EL mode is similar to that in the PL mode. 1) The loosely bound electrons in the QW on the higher energy side for the electrons (negative electrode side) begin to drift toward the other QW on the lower energy side (positive electrode side) upon application of longitudinal electric fields. 2) The electrons tend to build up in the hole-rich QW because the electrons are only weakly bound to the QW through the Coulomb interaction between the electron and the quantum-confined hole. Either of the two QWs which is located in the upstream of the hole current (positive electrode side) captures more holes than the other since hole collection efficiency is sufficiently high ($\approx 70\%$). For these reasons, the hole-rich QW on the positive electrode side collects more electrons and exclusively emits EL. The situation is more complicated in the reverse bias conditions where carriers are generated not by injection but by impact ionization. An extinction ratio more than 100 was obtained in the cw mode at 10 K. Dynamic response and issues such as operation temperature will also be discussed. The delayed impact ionization, characteristic of type-II strained $\text{Si}_{1-x}\text{Ge}_x/\text{Si}$ QWs caused by dynamic screening, is invoked to account for and improve the temporal switching dynamics.

P13.30
Efficient Infrared Photo-Luminescence from Sputtered SiO_2 Films with Ge-Rich Nanoparticles and Er Ions. J. Mayandi¹, C. L. Heng¹, S. Foss¹, T. G. Finstad¹ and H. Klette²; ¹Centre Mat. Sci. and Nanotech. and Dept. of Physics, University of Oslo, Oslo, Norway; ²Materials and Chemistry, SINTEF, Oslo, Norway.

We have reported strong photoluminescence (PL) from an (Er, Ge) co-doped SiO_2 film deposited by rf-magnetron sputtering before [1]. The structure of samples prepared with different sputtering conditions and subjected to different heat treatments have been studied by several material characterizing techniques and the PL yield has been correlated with the structure of the samples. It has been found that the PL as well as the structure of the films are sensitive to preparation techniques. For example there is a large difference in the PL intensity and its dependence on the annealing temperature for samples prepared using Ar plasma during sputtering and those prepared with Ar+O₂ plasma. The luminescence is correlated with the microstructure of the films. The PL intensity increases for situations yielding Ge-rich nanoclusters, while the development of these varies with the fabrication of the film. These conclusions are based upon studies by high-resolution transmission electron microscopy (TEM) with energy dispersive analysis of emitted X-rays and energy loss spectroscopy, X-ray photoelectron spectroscopy (XPS) analysis and Fourier Transform Infrared Spectroscopy (FTIR). Some preparation instances results in films, which have nanovoids. The PL from these have been very strong while the annealing behavior has the same characteristics as those without voids sputtered in Ar plasma: the PL intensity increases with annealing temperature and has a sharp maximum at 700 C and then falls off. We have studied the time evolution of the films for the 700 C annealing. The results indicates that several processes having an effect upon the luminescence occur simultaneously; The luminescence intensity as a function of annealing time reaches a maximum point after 30 min and then falls rapidly followed by a slow increase and a very high apparent value after 540 min. We will present correlations between this annealing behavior of the PL and the microstructure evolution. By FTIR we have observed that the Si-O stretching mode peak around 1100 cm^{-1} becomes sharper and increases in wave number upon annealing. This is interpreted as being due to densification of the oxide film with annealing. The LO₃ shoulder at around 1250 cm^{-1} vanishes after oxygen gas annealing or for films sputtered in an Ar+O₂ plasma. It is

speculated that it is related to the Ge-rich clusters as their occurrence is correlated. The PL is very weak after annealing in an O₂ ambient. [1] C.L. Heng, T.G. Finstad, P. Storaas, Y. Li, A.E. Gunnaes, O. Nilsen, Appl. Phys. Lett. 85, 4475 (2004)

P13.31
Enhanced Energy Transfer between Colloidal Semiconductor Quantum Dots in an Optical Microcavity. Li Guo¹, Carl Poitras² and Xiaowei Teng³; ¹Chemistry, University of Rochester, Rochester, New York; ²Electrical and Computer Engineering, Cornell University, Ithaca, New York; ³Chemical Engineering, University of Rochester, Rochester, New York.

Nonradiative energy transfer via resonant dipole-dipole interactions (RDDI) is potentially an important communication and energy transport mechanism at the nanoscale. Although experimental investigations have shown that the relative efficiency of energy transfer from a donor to an acceptor can be modified by optical microcavities, the question of whether the microcavity modifies the RDDI is still not answered. We will present studies of nonradiative energy transfer between colloidal CdSe/ZnS semiconductor nanocrystals (NCs) inside a one-dimensional optical microcavity. We have found that the microcavity can enhance the fluorescence intensity from a monolayer of NCs by a factor of 4.8 compared with an identical sample measured in free space. At the same time, the fluorescence linewidth is decreased from 33nm to 5.5nm due to coupling between the cavity mode and the NC emission. Deposition of two different sized NCs (ratio of 4:3 smaller to larger) inside the microcavity allows for the study of cavity mediated energy transfer from the smaller NCs to the larger NCs. We observed that the integrated fluorescence intensity from the larger NCs is increased by a factor of 2.7 compared with a layer of purely large NCs inside the cavity, which indicates that significant energy transfer is taking place. Also, the smaller NCs are well coupled to the cavity, as we observe no fluorescence from these particles when the cavity mode resonance does not overlap with the NC fluorescence spectrum. The implication of these findings regarding the effect of the microcavity on the RDDI will be discussed.

P13.32
Studies on the electrostatic potentials within core/shell nanowires by electron holography. Jayhoon Chung and Lew Rabenberg; Material Science and Engineering, University of Texas at Austin, Austin, Texas.

Devices based on semiconductor nanowires are currently being investigated for applications such as transistors and sensors. Production of the active devices based on nanowires requires that controlled interfaces be created within the nanowires. Of the various interfaces, the semiconductor-oxide interface is of greatest interest because of its critical role in field effect devices and because it is formed naturally when large-surface-area nanowires are exposed to oxygen in the environment. Charged states at a semiconductor-oxide interface, or in the oxide itself, produce electric fields that affect charge distributions and transport within the nanowires. Clearly, charge transport in the nanowire devices will depend on the electrostatic potentials near the electrical junction and interface as well as their dopant distributions. Engineering useful devices from such nanowire devices will require quantitative measures of the dopant concentrations and potential distributions within them. Electron holography in the transmission electron microscope (TEM) is a technique that records the phase shifts imposed on an electron wave as it propagates through a solid. Since the phase shift at each point in the hologram depends on the local potential, holography can be used to image the distribution of electrostatic potentials within a solid. In this paper, phase profiles within core-shell nanowires, composed of intrinsic germanium cores and shells of germanium oxide and/or doped germanium, were imaged using electron holography in a transmission electron microscope. Germanium nanowires were grown using a supercritical fluid-liquid-solid (SFLS) technique. The nanowires were converted to core/shell structures by radial deposition of amorphous p-type germanium shell layers using remote plasma chemical vapor deposition (RPCVD). First, accurate mean inner potentials for germanium and its oxide were determined from phase data obtained from experimental electron holography with knowledge of the thickness profile of the nanowire. Using measured and simulated phase profiles, it was possible to determine the dopant concentration within a shell of doped germanium around an intrinsic germanium core. Secondly, using the cross-section analysis, the surface potential, screening length, and doping concentration for the doped germanium shell were determined quantitatively from the two-dimensional potential image. These characteristics were compared with values obtained from a numerical solution of Poisson's equation. The potential distribution resulting from interface charges as well as dopants was successfully imaged.

P13.33
First-principles study of photoinduced defect formation in

silica glass. Shoji Ishibashi¹, Tomoyuki Tamura¹ and Masanori Kohyama²; ¹RICS, AIST, Tsukuba, Ibaraki, Japan; ²UBIQEN, AIST, Ikeda, Osaka, Japan.

Synthetic SiO₂ glass is a key optical material for deep ultraviolet and vacuum ultraviolet lasers because of high optical transparency. It is known that the laser irradiation leads to the formation of defects, which gives degradation of materials functions. Therefore, control of the formation of photoinduced defects is expected to enhance the performance of SiO₂ glass as a photonic material. SiO₂ glass contains two types of structural disorder. One is a point defect defined as chemical disorder and the second is physical disorder, which results from a wide distribution of Si-O-Si bond angle and the size of (Si-O) ring structure. Recently, the effects of the physical disorder on the formation process of photoinduced defects have attracted much interest [1]. It was experimentally proposed that strained Si-O-Si bonds such as small (three- or four-membered) ring structures are chemically excited (reviewed in Ref. [2]). However, there exist few detailed theoretical studies of the physical and chemical response of strained bonds. In order to understand the effects of the physical disorder on the photoinduced defect formation, we performed first-principles simulations of the dissociation of Si-O bonds with an averaged Si-O-Si bond angle and a heavily strained one. The calculations were based on the density functional theory with the local spin density approximation. Total energies and structures were calculated using the projector augmented wave (PAW) method implemented in the program package QMAS (Quantum Materials Simulator) developed by our group. We used a periodic cubic cell of amorphous SiO₂ containing 32 Si and 64 O atoms [3]. The simulation was performed on the neutral ground state and a positively charged state corresponding to a photoionization process. We obtained a new metastable configuration via the migration of Si-DB (dangling bond) and the formation of an alternative Si-O bond with a nearby O atom. We have proposed that the origin of chemical reactivity of strained bonds is high ionicity resulting from the charge transfer from Si to O. This work was performed as a part of National Research Grid Initiative (NAREGI) Nanoscience project by Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. [1] H. Hosono, Y. Ikuta, T. Kinoshita, K. Kajihara, and M. Hirano, *Phys. Rev. Lett.* 87, 175501 (2001). [2] K. Awazu and H. Kawazoe, *J. Appl. Phys.* 94, 6243 (2003). [3] T. Tamura, G.-H. Lu, R. Yamamoto, and M. Kohyama, *Phys. Rev. B* 69, 195204 (2004).

P13.34

Retention characteristics for nonvolatile memory based on metal nanocrystals and carbon nanotube FET with CVD SiO₂ and ALD HfO₂ tunneling dielectrics. Udayan Ganguly¹, Raghav Sreenivasan², Paul McIntyre² and Edwin C. Kan³; ¹Materials Science and Engineering, Cornell University, Ithaca, New York; ²Materials Science and Engineering, Stanford University, Palo Alto, California; ³Electrical and Computer Engineering, Cornell University, Ithaca, New York.

Non-volatile memory devices based on carbon nanotube field effect transistor (CNTFET) with ultra-narrow channels are promising for high-density, low-voltage and low-power applications [1, 2]. CNTFET memory using metal nanocrystals for charge storage has been recently demonstrated with a large memory window and single electron sensitivity at cryogenic temperatures (10K) [1]. However, the memory characteristics at room temperature were not acceptable for realistic applications due to the lack of a reliable tunneling dielectric with process/material compatibility to the CNTFET. Although the evaporated SiO₂ used previously [1] was benign to the single walled nanotubes (SWNT), the high trap density enabled hopping-based charge leakage paths that severely deteriorated charge retention at room temperature. Top-gate CNTFET logic devices have been demonstrated previously with improved switching characteristics using PECVD (plasma enhanced chemical vapor deposition) SiO₂ [3] and atomic layer deposition (ALD) Zr₂O₃ [4]. Here we present the process development and electrical evaluation of reliable tunneling dielectrics using low pressure chemical vapor deposition (LPCVD) SiO₂ and ALD HfO₂ on SWNT for enhanced charge retention at room temperature. ALD HfO₂ and LPCVD SiO₂ were deposited in layers of 3-7 nm thickness on back-gated CNTFETs [1] for different process splits. Au nanocrystals were then self-assembled from a thin 1.2 nm evaporated layer, followed by passivation with evaporated SiO₂ or PECVD SiO₂. The measurement pads were exposed by reactive ion etching (RIE) the passivation SiO₂ layer. Physical and electrical characterization techniques are used to study the devices. Retention measurements at different temperatures are used to extract retention time for different tunneling dielectrics. We found that ALD HfO₂ can significantly improve the memory characteristics. The effect of the choice of source/drain metals was also compared from the points of view of process compatibility and sensing FET characteristics. References [1] U. Ganguly, E.C. Kan and Y. Zhang, "Carbon nanotube based non-volatile memory with charge storage in metal nanocrystals," *Applied Physics Letters*, (accepted), 2005. [2] G.

Molas, B. De Salvo, G. Ghibaudo, D. Mariolle, A. Toffoli, N. Buffet, R. Puglisi, S. Lombardo, S. Deleonibus, *IEEE Trans. Nanotech.* 3, 42 (2004). [3] S.J. Wind, J. Appenzeller, R. Martel, V. Derycke and P. Avouris, "Fabrication and electrical characterization of top gate single-wall carbon nanotube field-effect transistors," *Journal of Vacuum Science & Technology B (Microelectronics and Nanometer Structures)*, vol. 20, pp. 2798-801, 11/. 2002. [4] A. Javey, Hyoungrub Kim, M. Brink, Qian Wang, A. Ural, Jing Guo, P. McIntyre, P. McEuen, M. Lundstrom and Hongjie Dai, "High- κ dielectrics for advanced carbon-nanotube transistors and logic gates," *Nature Materials*, vol. 1, pp. 241-6, 12/. 2002.

P13.35

Silicon Nanostructures for Third Generation Photovoltaics. Richard Paul Corkish^{1,2}, Gavin Conibeer², Martin A. Green², Young Cho², Eun-Chel Cho^{2,3}, Thipwan Fangsuwannarak², Edwin Pink², Yidan Huang², Tom Puzzer², Thorsten Trupke², Avi Shalav² and Kuo-Lung Lin^{2,4}; ¹Centre for Photovoltaic Engineering, University of New South Wales, Sydney, New South Wales, Australia; ²Centre of Excellence in Advanced Silicon Photovoltaics and Photonics, University of New South Wales, Sydney, New South Wales, Australia; ³Now with Corporate R&D Center, Samsung SDI Co., Yongin-Si, Gyeonggi-do, South Korea; ⁴Now with Origin Energy, Regency Park, South Australia, Australia.

Solar cell technologies can be conceptually grouped into generations, with the first generation being cells made from self-supporting wafers of a single semiconductor, principally silicon in practice. The second generation includes thin films of a single semiconducting material on a low-cost substrate or superstrate. UNSW has commercialised silicon technologies for both first and second generation cells. Both these generations of technologies have efficiencies restricted by the Shockley-Queisser limit (around 30 percent without concentration). Third generation photovoltaics concepts are intended to significantly increase device efficiencies, using thin film processes and abundant, non-toxic materials, avoiding the Shockley-Queisser limit for single band gap devices. This requires the use of multiple energy thresholds. UNSW is using the energy confinement of silicon based quantum dot nanostructures to engineer wide band gap materials to be used as upper cell elements in Si based tandem cells. HRTEM data shows silicon nanocrystal formation in oxide and nitride matrices with a controlled nanocrystal size, grown by both layered reactive sputtering and layered PECVD. Photoluminescence (PL) evidence for quantum confinement in the Si quantum dots in oxide shows an increase in PL energy with reduction in dot size. We are investigating junction formation in these materials. We are also applying silicon quantum dot structures in double barrier resonant tunnelling structures for use in hot carrier solar cell contacts. Hot carrier cells are intended to collect energetic carriers prior to their relaxation to the band edges. These contacts must collect carriers over a limited energy range. To date and subject to confirmation, apparent negative differential resistance has been observed in room temperature I-V on these samples, a necessary proof of concept for selective energy filter contacts.

P13.36

High Quality Quantum Dots: Synthesis and Water-Solubility for Biological Application. William W. Yu and Vicki L. Colvin; Department of Chemistry, Rice University, Houston, Texas.

Novel strategy for the synthesis of monodisperse nanocrystals was developed. This new method is cheap, reliable, safe and environmentally benign. The nanocrystals synthesized by this new method, including semiconductor nanocrystals (quantum dots) CdS, CdSe, CdTe, PbSe, and magnetic nanocrystals, Fe₃O₄ (magnetite), have wider size range, and narrower size distribution (less than 10%). Through this new method, one can control the size, shape, and crystal structure of the aimed nanocrystals by simply changing the ligands used in the synthesis. With the high quality nanocrystals, some basic physical constants, such as extinction coefficients of semiconductor nanocrystals were accurately measured. A simple method was also developed to transfer the above-mentioned organic-media synthesized high quality nanocrystals to aqueous media (pure or buffered water). The water-soluble nanocrystals keep their original properties in organic media. For example, water-soluble semiconductor nanocrystals have the same absorption and emission spectra, the same quantum yield, and the same size and size distribution as the ones dispersed in chloroform. The water-soluble nanocrystals are stable in pure water and conventional biological buffers.

SESSION P14: Nanorods, Nanocrystals and Carbon Nanotubes (CNT)
Chairs: Rachel Goldman and Philippe Guyot-Sionnest
Friday Morning, December 2, 2005
Room 210 (Hynes)

8:30 AM P14.1

Directed Seeding of Semiconductor Nanopillars. Weifeng Ye,

Xiaojun Weng, John F. Mansfield and Rachel S. Goldman; Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan.

The directed self-assembly of low-dimensional semiconductor structures has been achieved using a variety of approaches to producing topographical patterns. However, an approach for producing highly ordered arrangements of nanostructures with well-controlled shapes and size distributions has yet to be developed. Therefore, we are exploring the seeded-assembly of semiconductor nanopillars on substrates topographically patterned using a focused-ion-beam (FIB). We have already seeded ordered arrays of holes with controlled concentrations of Ga droplets using FIB implantation. These holes have nearly uniform sizes and shapes. By controlling the ion beam energy, current, and size, hole arrays with various sizes, depths, and periodicities may be produced. Interestingly, after scanning the ion beam over the patterned area, Ga dots form at the centers of the holes, resulting in the formation of ordered arrays of nearly uniformly sized Ga dots. The Ga dot formation is likely due to the preferential agglomeration of the excess Ga in the holes. We will discuss the mechanisms of Ga droplet formation and present real-time studies of the interaction of various gases with the droplets. In addition, we will discuss the use of these ordered arrays of Ga dots as catalysts for vapor-liquid-solid growth of a variety of semiconductor nanopillars.

8:45 AM P14.2
Growth of Highly Ordered InAs/GaAs Quantum Dots on Nonlithographically Patterned Substrates by Molecular Beam Epitaxy. Rodney S. Guico, Wei Guo, J. Roderic Beresford and Jimmy Xu; Engineering, Brown University, Providence, Rhode Island.

Despite years of effort leading to improvements in the control of the dimensions and size dispersion of self-assembled epitaxial quantum dots, there has been no effective approach with rational control for producing highly ordered arrays of quantum dots, which is seen as important for many applications. The absence of ordering in the conventional self-assembled growth is fundamental and rooted in the lack of a feedback mechanism between the adjacent growing dots. We have recently reported a novel nonlithographic patterning method for InAs/GaAs quantum dot growth using self-organized nanopore arrays in anodized aluminum oxide (AAO) membranes for patterning the growth sites[1]. The InAs dots grow on the nanopore-patterned substrates by a surface topology pattern-driven mechanism. This method is inherently parallel and scalable, and has already produced size dispersions that rival that reported in the literature for the best electron-beam lithographically patterned substrates[2]. In the present work, we further extend this method to a SiO₂ passivated GaAs substrate in order to better preserve the crystallinity of the GaAs surface while still providing the surface topology pattern-driven growth mechanism. We compare the highly-ordered growth behavior of InAs dots on GaAs substrates with and without a deposited nanopore-patterned SiO₂ film, which influences the growth selectivity. Scanning electron microscope (SEM) and atomic force microscope (AFM) are used to study the InAs dots. Uniformly distributed and densely-packed dots as defined by the AAO pore array are obtained. The hexagonal array period is uniform within each sample and can be controllably varied from 50 nm to 420 nm. The size of the dots can be controlled by the growth time and the pore size and depth, and range from a few monolayers to several tens of monolayers. Different growth temperatures and growth rates are found to affect selectivity of the quantum dot growth sites on the patterned surface. The quantum dot growth window on the GaAs nanopored surfaces has been determined and the surface-curvature driven mechanism has been observed at different stages of the growth. The use of SiO₂ nanopatterns on GaAs(100) substrates as a template for direct growth of the InAs dots is successful as well. We investigate the different InAs selectivity mechanism for the SiO₂ patterns, which is improved compared to GaAs. GaAs capping layers have also been produced in order to ensure efficient photoluminescence from fully clad highly ordered dots. In addition to providing highly ordered arrays of dots, the pattern-assisted growth method has a range of control over dot parameters that is potentially much larger than that for the self-assembled method, and it is applicable to forming quantum dots with a wider range of materials systems. 1 J. Liang, H. Luo, R. Beresford, and J.M. Xu, Appl. Phys. Lett. 85, 5974 (2004). 2 H. Heidemeyer, C. Müller, and O.G. Schmidt, Physica E 23, 237 (2004).

9:00 AM P14.3
Quantum Confinement Effects in 0-D and 1-D Metal Oxide Semiconductor Arrays. Lionel Vayssieres, ¹ICYS, National Institute for Materials Science, Tsukuba, Japan; ²Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California.

A thermodynamical growth concept, based on chemical and electrostatic lowering of the interfacial energy and a resulting thin film processing technique are presented. Such strategy allows the

generation, at large scale and low cost, of novel thin film materials and arrays. Advanced metal oxide nanostructures consisting of oriented multidimensional arrays featuring building-blocks of controlled morphologies, sizes, aspect ratios and orientations are genuinely fabricated without template, surfactant, undercoating or applied field directly onto various substrates of large physical areas from the hydrolysis-condensation and heteronucleation of aqueous metal salts solutions at mild temperatures. In-depth investigations of their electronic structure performed at synchrotron radiation facilities by x-ray absorption and emission spectroscopies, including polarization dependent experiments and resonant inelastic x-ray scattering revealed important insight of direct relevance for semiconductor technology. For instance, confinement effects in alpha-Fe₂O₃ oriented quantum rods and TiO₂ quantum dot arrays grown on transparent conducting substrate as well as the determination of orbital symmetry and orbital character of the conduction band of ZnO oriented nanorod-arrays will be presented. Finally, innovative advances in the design of 1-D semiconductor nanostructures have been developed very recently in our laboratories and will be presented and their characteristics demonstrated.

9:15 AM P14.4
Abstract Withdrawn

9:30 AM P14.5
Morphology and Self-Assembling of SiGe/Si Islands Grown by Liquid Phase Epitaxy in the Near- and Far Non-equilibrium Growth Limits. Michael Hanke¹, Torsten Boeck², Anne-Kathrin Gerlitzke², Frank Syrowatka³ and Frank Heyroth³; ¹Department of Physics, Martin-Luther-University Halle-Wittenberg, Halle /Saale, Germany; ²Institute of Crystal Growth, Berlin, Germany; ³Center of Materials Science, Halle /Saale, Germany.

Liquid phase epitaxy (LPE) serves as a growth method which usually operates closer to thermodynamical equilibrium than any other growth technique. We first discuss a characteristic shape transition of SiGe/Si(001) Stranski-Krastanov islands and the evolution of lateral positional correlation in a near-equilibrium LPE experiment, and relate these findings to the three-dimensional strain distribution as revealed by diffuse x-ray scattering and finite element calculations. Extended island rows forming a chess-board like formation indicate a nucleation scenario governed by a long-range strain interaction of, at least, the second last island in a chain. The reduced symmetry of Si(113) substrates, on the other hand, results in a unidirectional ordering of the SiGe islands. An initial homoepitaxial layer grown from indium solution at 930°C yields a perfectly linear pattern which serves in the subsequent heteroepitaxial growth from a bismuth solution at a considerably lower temperatures of 590°C as a natural template for island nucleation. Generally the applied lattice mismatch restricts the final dimensions to a certain minimal value. Thus, several attempts are directed to further shrinking of the island size. Applying energy dispersive x-ray microanalysis we could prove that in the far non-equilibrium limit of LPE, using an exceptional high cooling rate of 10K/min, the final island size does not depend on the lattice mismatch within a given concentration window. Moreover it shows a way to drop down the island size below the strain restricted value by more than a factor of two. Lateral positional correlation exclusively happens by next-to-island interactions forming square-like island configurations with subsequently smaller islands outwards. Eventually subsequent island stages indicate a morphological transition with decreasing facet angles from steep whisker-like objects towards island with flatter facets.

9:45 AM P14.6
GaAsSb/InGaAs quantum dots with room temperature emission at 1.6 microns. Jose M. Ripalda¹, Daniel Granados¹, Yolanda Gonzalez¹, Ana M. Sanchez², Sergio I. Molina² and Jorge M. Garcia¹; ¹Instituto de Microelectronica de Madrid, Tres Cantos, Madrid, Spain; ²Ciencia de los Materiales e I.M. y Q.I, Universidad de Cadiz, Cadiz, Cadiz, Spain.

In the last few years there has been a strong interest in expanding the usable wavelength range of GaAs based optoelectronic devices towards 1.5 micrometers and beyond.[1] Room temperature photoluminescence at 1.6 micrometers is demonstrated from InGaAs quantum dots capped with an 8 nm GaAsSb quantum well. Results obtained from various sample structures are compared, including samples capped with GaAs. Capping of InAs QDs with pure GaSb has also been studied, resulting in high intensity room temperature photoluminescence at 1.3 micrometers. The photoluminescence data suggests separate confinement for electrons and holes in these nanostructures, and type II spatially indirect recombination. The observed redshift in samples capped with Sb is attributed mostly to a beneficial modification of growth kinetics, apparently preventing the common self-disassembly of the dots during the initial stages of capping. The sample structure is discussed on the basis of transmission electron microscopy results and in situ Reflection High

10:30 AM P14.7

Conductance in multiwall carbon nanotubes and semiconductor nanowires. Travis Lee Wade¹, Jean-Eric Wagrowe¹, Jean-Francois Dayen¹, Xavier Hoffer¹, Dider Privat² and Anna Romyantseva¹; ¹Laboratoire des Solides Irradies, ECOLE Polytechnique, Palaiseau Cedex, France; ²Laboratoire de Physique des Interfaces et Couches Mines, ECOLE Polytechnique, Palaiseau, France.

We compare the electronic transport in an ensemble of multiwall carbon nanotubes and semiconductor nanowires. The nanotubes and nanowires were obtained by template synthesis in nanoporous membranes, and are contacted in a current perpendicular to the plane geometry using different methods [1]. The carbon nanotubes are obtained by CVD, and the semi-conductor nanowires are electrodeposited tellurium, and CVD-grown single crystalline Si. The contacts are metallic (Ni,Co,Au,Cu) with different crystallinity, and superconducting (Pb). In all cases, the non-ohmic behavior of the conductance, the so-called zero bias anomaly, shows a temperature dependence that scales with the voltage dependence. The conductance $G(V,T)$ is described by a single scaling coefficient a . A universal law as a function of a was found for all samples [2]. The origin of the universal law is investigated using magnetoresistance measurements and superconducting contacts. Weak localization effects, and superconducting proximity effects with reentrance gave information about the transparency of the barrier. The observed behavior can be understood in terms of coulomb blockade theory, providing that a hypothetical universal tunnel barrier is present, with a resistance of about 4 kOhm and a capacitance of 1018 Farad. References [1] T. Wade; J.-E. Wagrowe, European Physical Journal, Appl. Phys. 29 (2005) 3. [2] J.-F. Dayen, et al. ArXiv, cond-mat/0412316.

10:45 AM P14.8

Nanofabrication of Top Gated Carbon Nanotube-Based Transistors: Probing Electron-Electron Interaction in One-Dimensional Systems. Zvonimir Z. Bandic¹, Joseph Albert Sulpizio², Charis Quay² and David Goldhaber-Gordon²; ¹Research, Hitachi San Jose Research Center, San Jose, California; ²Department of Physics, Stanford University, Stanford, CA, California.

Carbon nanotubes are interesting for studying the remarkable electronic properties of one-dimensional systems. Electron flow in such systems is not expected to be describable with Fermi liquid theory - restricted dimensionality leads to the appearance of collective excitations, or *Luttingerliquid* behavior. Previous studies have probed Luttinger liquid behavior by tunneling into or between one dimensional systems. We extend these studies by using a narrow top gate to introduce a tunable tunnel barrier within a nanotube. We report on the fabrication of carbon nanotube-based transistors with sub-30 nm wide Pd nanowire top gates. We use electron beam lithography (with a Leica VB6 tool) to create carbon nanotube transistors with source-drain spacings down to 200 nm and with sub-30 nm Pd metal nanowire top gates acting as tunable tunnel barriers. The top metal gate is isolated from the nanotube by a thin Aluminum Oxide layer deposited by atomic layer deposition. We fabricate chips with 98 devices using multiple electron beam lithography alignment steps and achieve overall placement better than 30 nm. The details of the top-gated carbon nanotube transistor fabrication will be presented, as well as initial results on probing the electronic properties of one-dimensional electronic liquids.

11:00 AM P14.9

CdSe nanoparticles photosensitize C60 crystals. Andreas Biebersdorf¹, A. S. Susha¹, A. L. Rogach¹, T. A. Klar¹, J. Feldmann¹, D. V. Talapin² and H. Weller²; ¹Photonics and Optoelectronics Group, Physics Department and CeNS, Ludwig-Maximilians-Universitaet Muenchen, 80799 Munich, Germany; ²Institute of Physical Chemistry, University of Hamburg, 20146 Hamburg, Germany.

C₆₀ has been used as a component in solar cells [1] or as a photosensitizing material for conducting polymers [2]. In both cases electron hole pairs are generated by the absorption of light and subsequently dissociated. In the case of a solar cell both types of charge carriers are extracted from the device. Contrary, in case of the photoconducting polymer, the electrons are trapped on the C₆₀ and the holes in the polymer lead to a unipolar current. In our work we use the C₆₀ not as photosensitizers but show for the first time that C₆₀ crystals can be photosensitized by CdSe nanoparticles. Needle like crystals of C₆₀ covered with CdSe nanoparticles show a photocurrent increased by 3 orders of magnitude as compared to needles of C₆₀ without CdSe nanoparticles. The photocurrent spectrum closely follows the absorption spectrum of the CdSe nanoparticles and can be tuned by the size of the CdSe nanoparticles.

The samples are prepared by dropcasting a mixed solution of C₆₀ molecules and CdSe nanoparticles onto interdigitating gold contacts. During evaporation of the solvent, the C₆₀ forms crystalline needles which bridge the gap between the gold electrodes while the CdSe nanoparticles are distributed around the needles. After photoexcitation of the CdSe nanoparticles, the holes remain trapped in the CdSe nanoparticles while the electrons are transferred to the C₆₀ crystals causing photocurrent. Under illumination, we observe a nonlinear I/V characteristic due to electronic disorder in the C₆₀ crystals. We discuss this behaviour in terms of localized / delocalized states and a related mobility edge. Our findings are relevant for possible applications of C₆₀ / CdSe mixed films as photoconductors, materials for photocopiers, or as components in solar cells. [1] Sariciftci, N. S., Appl. Phys. Lett. 62, 585 (1993). [2] Wang, Y., Nature, 356, 585 (1992).

11:15 AM P14.10

Vibrational Properties of Small Diameter Single-Wall Carbon Nanotubes: a Comparative Study of the Symmetry-Adapted Force-Constant Model vs. Resonance Raman Spectroscopy Measurements. Georgii Samsonidze¹, Riichiro Saito², Jie Jiang², Hyungbin Son¹, Eduardo Barros¹, Shin Grace Chou³, Gene Dresselhaus⁴ and Mildred Dresselhaus^{1,5}; ¹Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts; ²Department of Physics, Tohoku University and CREST JST, Sendai, Japan; ³Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts; ⁴Francis Bitter Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts; ⁵Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Single-wall carbon nanotubes of less than 1 nm in diameter provide a good prototype for studying physical properties of one-dimensional semiconductor quantum wires. Recent advances in nanotube characterization by photoluminescence and Raman scattering techniques indicate extremely strong excitonic effects and exciton-phonon coupling in these materials. The conventional tight-binding and force-constant models that well describe the electronic and vibrational properties of bulk carbon materials fail to predict the experimentally observed exciton and phonon spectra in small diameter carbon nanotubes. In this work, we introduce the symmetry-adapted modifications to the conventional tight-binding and force-constant models that directly incorporate the helical symmetry of the nanotube into the picture. The symmetry-adapted tight-binding model has already been shown to accurately predict the energies of excitonic transitions observed in photoluminescence spectra of small diameter carbon nanotubes. In a similar fashion, we compare the predictions from the symmetry-adapted force-constant model against resonance Raman spectra taken with a tunable Raman system from individual small diameter carbon nanotubes of various chiralities dispersed on the substrate. We find that the symmetry-adapted approach closely reproduces the frequencies of the vibrational modes observed by Raman scattering. Strong dependence of the phonon frequencies on the nanotube chirality in the small diameter limit predicted from the symmetry-adapted force-constant model is confirmed by Raman measurements. The symmetry-adapted force-constant model presented here improves characterization technique of carbon nanotube samples by resonance Raman spectroscopy.

11:30 AM P14.11

Quantized Bimolecular Auger Recombination of Excitons in Single-walled Carbon Nanotube. Libai Huang and Todd Krauss; Department of Chemistry, University of Rochester, Rochester, New York.

Understanding the impact of a strong electron-hole interaction on the electronic structure of SWNTs is important, since excitons play an important role in influencing the properties and potential applications of quantum confined materials. We will present quantitative studies of Auger recombination in isolated single-walled carbon nanotubes (SWNTs) using femtosecond transient absorption spectroscopy. Auger recombination between discrete electron-hole pairs was observed and Auger recombination lifetimes for 2 and 3 electron-hole pair states (τ_2 and τ_3 , respectively) are determined. Auger recombination in SWNTs is extremely fast, with typical recombination lifetimes of only a few ps. The τ_2/τ_3 ratio in SWNTs is 1.5, which shows an excellent agreement with the theoretical value for two-particle Auger recombination in 1D exciton systems. Further, the transient dynamics at high excitation intensity further validates this bimolecular nature of Auger recombination in SWNTs. Our experiments directly probe that the nature of the optically excited exciton state in SWNTs, since free electrons would lead to a three-particle Auger process that does not agree with our data.

P15.1

Cone-Stack carbon nanotubes: Fabrication, microstructure, Raman spectroscopy. Chih-Hsun Hsu, Sylvain Cloutier, Teng-Fang Kuo and Jimmy Xu; Division of Engineering, Brown University, Providence, Rhode Island.

Carbon structures can take a surprising large variety of shapes and forms, of which carbon nanotubes have been particularly popular subject of research. Other new Carbon structures also exist, though not yet attracted as much attention, despite their possibly new and interesting properties unavailable in the carbon nanotube. The cone-stack carbon nanotube stands out as a prominent example. It was accidentally made and found in some carbon nanotube synthesis processes, and has largely remained in the same state in fabrication and study. In this work, we report on controlled fabrication of the cone-stack carbon nanotube, with a high yield, ~50%, one that is many times greater than that of prior findings. The controlled fabrication was achieved in a CVD process with sol-gel dispersion of iron nanoparticles as catalyst. The solution based iron catalyst and sol-gel mixture spin coated on silicon substrate provides a matrix for generating separate iron nanoparticles required for the growth. Conventional thermal furnace was employed to grow the free-standing cone-stack carbon nanotubes using methane as precursor at 800~900°C. Electron microscopic studies revealed that the as-grown nanotubes are hollow in core with a fully graphitized cone-stack structure as the outer shell. The resultant tube outer diameter is around 10 nm, straight, and as long as tens of micrometers on average. The classic graphitic D-band and G-band peaks are observed in Raman spectroscopy with spectral width and peak similar to commercial graphite micro powder confirming its highly graphitized nature as observed in transmission electron microscopy.

P15.2

Resonant Raman Scattering Intensities of Suspended Individual Carbon Nanotubes. Yan Yin¹, Andrew Walsh¹, Stephen Cronin², Alexander Stolyarov², Michael Tinkham², Anthony Vamivakas³, Selim Unlu^{3,1}, Bennett Goldberg^{1,3} and Anna Swan³;
¹Physics Department, Boston University, Boston, Massachusetts;
²Physics department, Harvard University, Cambridge, Massachusetts;
³Electrical and Computer Engineering Department, Boston University, Boston, Massachusetts.

Kataura plots are for resonant Raman scattering what photoluminescence excitation (PLE) maps are for photoluminescence; the information provides characteristic patterns where the locations of the Resonant Raman Scattering (RRS) peaks or PLE peaks can be used to identify the carbon nanotubes (n,m) species and study the optical transition energies. In ensemble measurements, the intensity of a particular peak is given both by the relative abundance of that species, and of the strength of the optical transition. In contrast, intensity measurements from one tube at a time can directly yield, for example, the intensity dependence of the chiral angle. The information from this more labor intensive type of study could be valuable to evaluate electron-phonon coupling matrix elements, and could provide a tool to understand electron-phonon coupling process in carbon nanotubes and 1-dimensional systems in general. In this report, individual single wall carbon nanotubes (SWNTs) in air are studied with tunable Resonant Raman spectroscopy. The individual SWNTs are deposited by chemical vapor deposition onto a quartz substrate with pre-etched trenches. The resonant Raman profile of the radial breathing mode intensities from different individual SWNTs (n,m) species are studied. The results show that there is a weak intensity dependence on chirality, but that the variation of Raman intensity for a given species is larger than the chirality dependency. The experimental results suggest similar chirality tendency as reported in previous work for resonant Raman scattering [1]. RRS intensity profiles of different Raman modes from the same individual carbon nanotube, independently measures the active optical resonance energy. This information experimentally proves that different Raman modes indeed have the same optical resonance energy E_{ii} . The relative electron-phonon coupling efficiencies (matrix elements) for different Raman modes are derived from the experimental results of tunable RRS intensity profiles. RRS intensities from the same carbon nanotubes in different humidity conditions are also under investigation. In conclusion, we have found that while the optical transition energy E_{ii} remains nearly identical for different CNTs of the same (n,m) species, the tunable RRS intensities can vary an order of magnitude. This variation is possible the result of growth quality (defects) and environmental factors. Compared such variation, the RRS intensity chirality dependency is a much weaker effect at individual carbon nanotube level. The experimental results give the

relative electron-phonon coupling efficiencies for different Raman modes and offer important information in understanding the RRS process. I. H. Telg, J. Maultzsch, S. Reich, F. Hennrich and C. Thomsen, Phys. Rev. Lett. 93, p. 177401.

P15.3

Dielectric properties of carbon nanotubes from first principles. Boris Kozinsky¹ and Nicola Marzari²; ¹Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts; ²Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

We study the response of single-wall carbon nanotubes to static uniform electric fields. Polarizability tensors for metallic and semiconducting carbon nanotubes are computed using density-functional perturbation theory and compared to analytical predictions of the random phase approximation and classical electrostatics. We find that the longitudinal polarizability of semiconducting nanotubes is inversely proportional to the square of the band gap. The transverse polarizability, on the other hand, is independent of the gap and chirality of the nanotube of a given radius. These dependencies have practical implications for selective growth of different types of nanotubes using aligning fields as well as for methods of separating different kinds of nanotubes in solutions. We also predict that the transverse polarizability of multiwall nanotubes is strongly dominated by the outermost tube. In the regime of strong transverse electric fields we find a weak suppression of the gap in semiconducting nanotubes. We compare our results to earlier tight-binding calculations of polarizabilities as well as gap suppression.

P15.4

Y-junction Single Wall Carbon nanotube and its electrical characterization. Jun Huang, Bangalore K. Rao, Do Hyun Kim and WonBong Choi; Mechanical and Materials Engineering, Florida International University, Miami, Florida.

The Y-junction single wall carbon nanotubes (SWNTs), which have three terminals with different electrical properties, can be used as nanoscale field-effect transistor or interconnect. We have demonstrated Y-SWNTs synthesis using methane CVD method by adding Mo or Zr doped Fe particle catalysts. Most of the synthesized SWNTs have branches at Mo/Zr catalyst position, forming Y-junctions. Raman spectroscopy and Transmission electron microscopy (TEM) images provide evidence that Y-SWNT consists of three isolated SWNTs with different diameters. These results are indicative of the possible formation of three terminal nanostructures with different electrical properties. Two terminal I-V measurement show that one branch of Y-SWNT is metallic while the other one is semiconducting. By varying gate voltage applied at the metallic branch, the electrical transport across semiconducting nanotube demonstrates p-type and n-type behavior under forward and reverse bias respectively, i.e. ambipolar characteristics. This observed unusual gate response could be explained by the gate bias-dependent Fermi level alignment between metallic and semiconducting SWNT related with the small band gap of carbon nanotube. Y-junction SWNTs enable us to make a nano junction device in which the electron transport of semiconducting SWNT can be controlled by applying voltage of metallic SWNT. In this paper we will discuss the crucial issues for Y-SWNTs synthesis, and their electrical property together with potential applications of for future electronics.

P15.5

C₆B Carbon Nanotubes. Ling Wang¹ and Linda E. Jones²;

¹School of Engineerings, Alfred University, Alfred, New York; ²Picker Engineering Program, Smith College, Northampton, Massachusetts.

A novel carbon, C₆B, having a substitutional boron concentration of 17 at.% is being catalytically synthesized into nanotubes via a CVD reaction between benzene and BCl₃. Modeling has indicated that the composition is C₅B not C₆B as described in the literature. The influence of deposition condition on tube structure and boron content is being explored. Multiwalled nanotubes and filaments are produced on nickel or chromium coated fused silica substrates. Compared to pure carbon nanotubes grown under the same condition, C₅B nanotubes have larger diameters in the range of 80-300 nm. Boron substituted in the C₅B lattice produces distortion in the structure by modifying both bond angles and interatomic distances. With the help of computer simulation, using both molecular mechanics and quantum mechanics, an out-of-plane distortion deflection as much as 0.7 Å as well as a bond length strain of 4% are realized. This material may yield a unique absorption surface and volume for H₂ storage. At the same time, the high boron concentration leads to a lowering of the Fermi level and improves the electronic structure related properties, such as oxidation resistance and electrical conductivity. C₅B survives at 600°C for 12 hours under 93.3kPa air. The electrical conductivity is in the range of 5-8×10⁴ (Ω m)⁻¹. Additionally, the novel carbon nanotubes are expected to have superior mechanical properties as well

as improved electronic behaviors.

P15.6

Manipulation of the Electronic Structure of Suspended Carbon Nanotubes. Andrew Walsh¹, Y. Yin¹, S. Cronin², A. N. Vamivakas³, B. Allen⁴, M. Tinkham², S. Unlu^{3,1}, B. Goldberg^{1,3} and A. Swan³; ¹Physics, Boston University, Boston, Massachusetts; ²Physics, Harvard University, Boston, Massachusetts; ³Electrical and Computer Engineering, Boston University, Boston, Massachusetts; ⁴Physics, Alabama A&M University, Huntsville, Massachusetts.

We systematically vary the environment surrounding CVD grown carbon nanotubes suspended over trenches on quartz substrates. We then use tunable resonant Raman spectroscopy to study the resultant effect on the underlying electronic structure. Since each carbon atom in a nanotube lies at the surface, carbon nanotubes are inherently very sensitive to changes in their environment. Furthermore, the one dimensional nature of carbon nanotubes is responsible for very weak intrinsic screening and large Coulomb interactions are anticipated. Indeed, recent two-photon absorption experiments have definitively shown that the spectra of carbon nanotubes arise from the presence of excitons with large binding energies.^{1,2} Therefore, due to the weak intrinsic screening in nanotubes, modulation of the surrounding dielectric constant significantly alters the strength of the Coulomb interactions and thus leads to changes in the exciton binding energy and band-gap renormalization. These changes are reflected in the resulting spectra.³ Until recently, carbon nanotubes were primarily studied in bulk, in suspensions, and/or coated in surfactants. In an earlier study⁴, we investigated the intrinsic electronic structure of individual nanotubes free from perturbations by their environment, including other nanotubes, by suspending them in air over trenches. Comparisons with other studies of nanotubes in solutions and/or in bulk show that increased dielectric constant leads to substantial blue shifts (70-90 meV). In this study, using tunable resonant Raman spectroscopy, we create resonance excitation profiles (REPs) where the intensity of either the Stokes or anti-Stokes Raman peak is plotted as a function of excitation wavelength. We vary both the temperature and humidity of the environment and immerse the nanotubes in water and oil. We look for spectral shifts of the peak of the REP for both the radial breathing mode (RBM) and G-Band mode with changing dielectric constant. We thereby directly measure the dependence of the renormalized band-edge and exciton binding energy with dielectric constant. 1. F. Wang, G. Dukovic, L. Brus, T. Heinz, *Science*, 308, 838 (2005) 2. J. Maultzsch, et. al., arXiv, 0505150 (2005) 3. V. Perebeinos, J. Tersoff, P. Avouris, *Phys. Rev. Lett.* 92, 257402 (2004) 4. Y. Yin et. al., arXiv, 0505004 (2005)

P15.7

Carbon Nanotube Field Effect Transistors for High Speed Electronics. Hong Zhang, James E. Baumgardner, Aaron A. Pesetski, James M. Murduck, Erica Folk, John D. Adam and John X. Przybysz; Northrop Grumman, Linthicum, Maryland.

Carbon nanotube field effect transistors (CNT FETs) are being developed as potential replacements for silicon and III-V semiconductor devices for high frequency electronics applications. CNT FETs have demonstrated the highest carrier mobility at room temperature of any known material and high electrical and thermal conductivity, along with their small size and low parasitic resistances, making them ideally candidates for miniaturized, low-power devices that are capable of operation up to THz frequencies. The development of CNT FETs that operate at high frequencies enables a wide variety of new applications, from high-speed digital logic to spectroscopy of biological molecules. In this presentation, we will report on our development of CNT FETs, including the device design, growth, fabrication and characterization. We have used proper microwave design techniques to build top-gated CNT FETs on insulating substrates capable of operating at microwave frequencies. Our unique approach includes the fabrication of CNT FETs from carbon nanotubes grown via chemical vapor deposition (CVD) on quartz substrates. The CVD process is capable of producing long and straight nanotubes with high crystalline quality while quartz substrates minimize loss at microwave frequencies. Metal contacts were formed from a titanium/gold metal bilayer, using a standard optical lithography lift-off process. This bilayer adheres both to the nanotube and to the substrate, while maintaining high electrical conductivity and chemical stability. We will include our experimental results on device measurements such as linearity, mobility, noise, and breakdown voltage. We will also report our recent breakthrough in the demonstration of the frequency-independent performance of a CNT FET. Our demonstration marks a crucial step in the development of tomorrow's advanced high speed electronics.

P15.8

Production of Nitrogen Endohedral Fullerenes as Quantum Bits. Chao Liu¹, Xingcheng Xiao¹, Frank Y. Fradin¹, John A. Schlueter¹, Orlando Auciello^{1,2} and John A. Carlisle^{1,2}; ¹Material

Science Division, Argonne National Laboratory, Argonne, Illinois; ²Center for Nanoscale Materials, Argonne National Laboratory, Argonne, Illinois.

It has been demonstrated that endohedral fullerenes are one of the most promising candidates for the construction of a quantum computer. The fullerene molecule is a fantastic trap for atoms, for instance, atomic nitrogen and phosphorus, at room temperature. These atoms exhibit long electron spin phase coherence time and strong dipolar spin-spin coupling between two adjacent endohedral molecules. The concept of using endohedral fullerenes as quantum bits (Qubits) in a spin quantum computer has also been reported. In this study, as the first step of experimental realization of a quantum spin computer, nitrogen endohedral C60 (N@C60) molecules are synthesized using an ion beam bombardment method. A Kaufman ion source is used to generate atomic nitrogen ions, which are accelerated and bombard onto a layer of C60 molecules deposited onto a silicon substrate. Various irradiation currents and acceleration voltages are used in order to maximize the production efficiency of endohedral fullerenes. The samples are subsequently investigated with electron paramagnetic resonance (EPR). The absolute number of N@C60 is calculated based upon EPR spectra with a standard DPPH sample as reference. Enrichment of the endohedral fullerenes is performed in a high performance liquid chromatography (HPLC) system with a BuckyPrep column. UV/Vis absorption properties of N@C60/C60 mixture, as well as those of pure C60, are studied in a spectrophotometer, which gives a good indication of the proper wavelength used during the HPLC purification process to detect the C60 and N@C60 peaks. EPR spectra are obtained previous to and after the HPLC process. The enrichment of N@C60 in the solution is indicated by the increase of the line width of the 14N+ triplet in the EPR spectra due to the stronger dipole/dipole interaction of randomly oriented N@C60 neighboring sites. In order to improve the efficiency of endohedral fullerene production, open-caged C60 derivatives with an 8-membered ring-opening on each molecule are chemically synthesized. Preliminary results of producing N@C60 out of the open-cage C60 derivative are presented. This work is supported by the US Department of Energy, BES-Materials Sciences, under Contract W-13-109-ENG-38.

P15.9

Quantum Transport through Carbon Nanotubes near a Conducting Plate: Vacuum Fluctuations and Decoherence. Pier Giuseppe Gabrielli¹ and Simone Gabrielli²; ¹MAT, ENEA, Rome, Italy; ²Physics, Univ, di Roma La Sapienza, Rome, Italy.

The process of environmental decoherence is seen to occur when we include the quantum dynamics of a system and its environment: the innovative idea is that environmental degrees of freedom are relevant even though the coupling to them is only weak. The effect of vacuum fluctuations on electron coherence is known: the time-varying electromagnetic field produces a time-varying Aharonov-Bohm phase. It is well known that a conducting boundary modifies the properties of the zero-point fluctuations and therefore could affect the electronic transport properties in a carbon nanotube via interaction with a time-varying electromagnetic field. We shall go to discuss a situation in which a quantum-mechanical system, the ballistic electrons in nanotube, is disturbed not just by a classical system but another quantum-mechanical system, the vacuum fluctuations due to conducting plate, about which there are statistical uncertainties.

P15.10

Raman Characterization of Single-Walled Carbon Nanotube Samples With Tunable Laser Excitation. Hyungbin Son, Alfonso Reina Cecco, Jing Kong and Mildred S. Dresselhaus; Massachusetts Institute of Technology, Cambridge, Massachusetts.

An ensemble of individually addressable single-walled carbon nanotubes (SWNTs) were characterized using a high-throughput tunable laser Raman spectrometer at different laser excitation energies from 1.5eV to 2.6eV. The nanotubes were synthesized by chemical vapor deposition (CVD) method on pre-patterned substrates. The diameter and chirality distributions of a SWNT sample were estimated by counting the number of Raman spectra representing each type of SWNT. All the Raman spectra taken from a sample was integrated to simulate a bulk measurement, i.e. a Raman spectrum taken from a large number of SWNTs at one integration. By comparing the chirality distribution and the simulated bulk measurement, we provide a basis for interpreting a bulk measurement. The chirality distribution obtained from our measurements provide further understanding in how various parameters in the CVD synthesis influence the growth result. Alfonso Reina Cecco thanks the support from MARCO Interconnect Focus Center.