

Nanometer-scale Science and Technology

Room: 12 - Session NS-MoM

Nanoparticles and Quantum Structures

Moderator: G.S. Herman, Oregon State University

8:40am **NS-MoM2 Synthesis of Visible Light Emitting Self-assembled Ge Nanocrystals Embedded within a SiO₂ Matrix and Post-annealing Effects**, A. *Hernández-Hernández*, F. *De Moure-Flores*, J.G. *Quiñones-Galván*, CINVESTAV-IPN, Mexico, L.A. *Hernández-Hernández*, ESFM-IPN, Mexico, J. *Santoyo-Salazar*, M. *Meléndez-Lira*, CINVESTAV-IPN, Mexico

As-grown light emitting self-assembled Ge nanocrystals (Ge-NCs) embedded in a SiO₂ matrix were produced by a sequential deposition process of SiO₂/Ge/SiO₂ layers employing reactive radio frequency sputtering technique. Obtained Ge-NCs shown a crystallographic phase whose proportion, size, quality and specific orientation are determined by the oxygen partial pressure. Photoluminescence (PL) spectra indicate that the size distribution of Ge-NCs is reduced and centered at around 8 nm when higher oxygen partial pressure is employed; the formation of Ge-NCs is corroborated by transmission electron microscopy (TEM) measurements, their sizes are consistent with estimates from PL measurements. After vacuum annealing it is observed the elimination of an instable high pressure tetragonal phase of germanium present in as-grown samples. It is possible that this phase is related to the SiO₂ matrix stress on the Ge-NCs. In addition, the PL peaks shifted to higher energies indicating the formation of Ge-NCs probably from Ge dispersed within SiO₂ matrix. It was also found that the PL intensity increases drastically after annealing process. The strong size dependence of the PL spectra indicates that the observed PL originates from the recombination of electron-hole pairs confined in Ge-NCs.

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9:00am **NS-MoM3 A Single Atom Transistor**, M.Y. *Simmons*, University of New South Wales, Australia **INVITED**

Over the past decade we have developed a radical new strategy for the fabrication of atomic-scale devices in silicon [1]. Using this process we have demonstrated few electron, single crystal quantum dots [2], conducting nanoscale wires with widths down to ~1.5nm [3] and most recently a single atom transistor [4]. We will present atomic-scale images and electronic characteristics of these atomically precise devices and demonstrate the impact of strong vertical and lateral confinement on electron transport. We will also discuss the opportunities ahead for atomic-scale quantum computing architectures and some of the challenges to achieving truly atomically precise devices in all three spatial dimensions.

[1] F.J. Rueß et al., *Nano Letters* 4, 1969 (2004).

[2] M. Fuchsle et al., *Nature Nanotechnology* 5, 502 (2010).

[3] B. Weber et al., *Science* 335, 64 (2012).

[4] M. Fuchsle et al., accepted for *Nature Nanotechnology* (2012).

9:40am **NS-MoM5 Transforming Luminescent Silicon Nanocrystals Into a Direct-Bandgap Semiconductor via Surface-Capping-Induced Strain**, P. *Hapala*, P. *Jelinek*, K. *Kusova*, I. *Pelant*, Institute of Physics of ASCR, Czech Republic

We report combined experimental and theoretical work pointing out the possibility to convert Silicon Nanoparticles (SiNcs) to a luminescing direct-band gap material via the concerted action of the quantum confinement and tensile force induced by proper surface passivation.

The transformation of silicon, originally a very poor light emitter due to indirect band gap, into a light-emitting medium is key challenge from the application point of view. One promising way to achieve this ultimate goal is through dramatic shrinkage in the size of the crystal down to nanoscale. The observation of an efficient room-temperature luminescence [1] from SiNcs initiated the debate about the nature of their band structure. The most common silicon-oxide-capped SiNcs maintain the indirect band gap showing long radiative lifetimes (>100 µs) [2].

Beside the size of the nanocrystal, a proper surface also plays an important role in the light emission process. Recently we have shown that SiNcs sized 2.5-3 nm with methyl-based surface passivating layer [3] exhibit luminescence properties (short radiative lifetime ~10 ns and enhanced quantum yield ~20%) analogical to direct-band gap semiconductor. This property is further supported by single-crystal luminescence experiment

giving emission pattern very similar to that observed in direct-band gap CdSe nanoparticles [4].

To understand the impact of surface passivation on the electronic structure of SiNcs we performed large-scale total energy DFT calculations including up to 1500 atoms and different functional surface groups (-H,-CH₃,-OH). Our calculations show that the presence of methyl group leads to significant elongation of the Si-Si distance in core region. Further we restore band structure of SiNc mapping real space molecular orbitals into the momentum space [6].

The resorted band structure clearly shows, that combination of tensile stress and the quantum confinement strongly modifies dispersion of the conduction band along the Γ -X direction, with significant lowering of the Γ 15 even as lifting the conduction minimum band Δ 1.

References

[1] L. Canham, *App. Phys. Lett.* 57, 1046 (1990).

[2] D. Kovalev et al, *Phys. Rev. Lett.* 81, 2803 (1998).

[3] K. Kůsová et al *ACS Nano*, 4(8), 4495 (2010).

[4] X. Wang et al *Nature* 459, 686 (2009).

[5] K. K. Kůsová et al (submitted).

[6] P. Hapala and P. Jelinek (ArXiv:cond-mat/1204.0421).

10:00am **NS-MoM6 Plasma Synthesis and Hydrosilylation of Silicon Nanoparticles**, S.L. *Weeks*, S. *Agarwal*, Colorado School of Mines, B. *Macco*, Eindhoven University of Technology, the Netherlands

Silicon nanoparticles (NPs) are of interest in a variety of optoelectronic applications due to the observation of multiple exciton generation, room temperature photoluminescence, size tunable band gap, and optical gain. Design of any device employing Si NPs requires control over both the size and interfacial passivation as these parameters dictate the electronic properties of the NPs. Our synthesis process employs a capacitively-coupled tubular Ar/SiH₄ plasma to produce H-terminated Si NPs. The surface composition and functionalization of the Si NPs was characterized via *in situ* attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy. Organic passivation of the H-terminated Si NPs was achieved through a two-stage gas-phase hydrosilylation process using 1-alkynes with different numbers of C atoms that led to surface coverages comparable to the thermodynamic limit for alkenyl monolayers on bulk H:Si(111) surfaces. The hydrosilylation reaction requires abstraction of a surface hydride to stabilize an intermediate surface radical formed upon absorption of the 1-alkyne. Injection of H₂ into the afterglow region of the synthesis plasma was employed to manipulate the surface hydride composition, which led to an increase in the relative fraction of SiH_x (x = 2, 3) species on the surface compared to SiH. The impact of these higher hydrides on the hydrosilylation reaction of 1-alkynes was investigated through *in situ* ATR-FTIR spectroscopy. Finally, using *in situ* photoluminescence measurements, we also determined the effect of the various hydrosilylation processes on the relative quantum yield from these Si NPs.

10:40am **NS-MoM8 Exchange Bias in Pure and Core/Shell Structured γ -Fe₂O₃-based Nanoparticles**, P. *Lampen*, H. *Khurshid*, M.H. *Phan*, H. *Srikanth*, University of South Florida

Iron oxide nanoparticles, Fe₃O₄ and γ -Fe₂O₃, are of great interest for applications in high-density magnetic recording media, sensor technology, and biomedicine. These systems are also excellent candidates for probing fundamental properties due to well-established synthesis methods that yield uniform, high quality particles with good control over size and shape. It has recently been shown by polarized small angle neutron scattering that Fe₃O₄ nanoparticles possess a chemically uniform, but magnetically distinct, core and canted-spin shell structure [1]. While many similarities exist in the magnetic and microstructural properties of γ -Fe₂O₃ and Fe₃O₄, the exchange bias that can be observed in nanoparticles of γ -Fe₂O₃ [2] is not present in similarly sized Fe₃O₄ [3]. Therefore, an investigation of the evolution of spin canting angle and shell thickness with temperature in γ -Fe₂O₃ is expected to yield valuable information about subtly altered spin geometries that can be correlated with the presence of exchange bias in this nanoparticle system.

In order to compare results for both chemically distinct and chemically uniform exchange-biased systems, we report the synthesis and characterization of γ -Fe₂O₃ and core/shell Fe/ γ -Fe₂O₃ nanoparticles. The particles used in the present study were synthesized by high temperature decomposition of iron organometallic compounds. X-ray diffraction and transmission electron microscopy techniques were used to study the structural and microstructural properties of the nanoparticles, which confirmed the presence of bcc iron and fcc γ -Fe₂O₃ in these particles. High-

resolution TEM images evidenced monodisperse products with particle diameters of 9 ± 0.8 nm in the pure $\gamma\text{-Fe}_2\text{O}_3$, while the core/shell particles showed 9.8 ± 0.7 nm Fe cores surrounded by a shell of $\gamma\text{-Fe}_2\text{O}_3$ with 2 ± 0.4 thickness. The DC magnetic properties of the samples were characterized using a vibrating sample magnetometer over a temperature range of 5-300 K, revealing a superparamagnetic behavior. Pronounced exchange bias of up to ~ 4100 Oe was confirmed in these particles using cooling fields of up to 5T. While the spin-glass-like phase associated with disordered surface spins in $\gamma\text{-Fe}_2\text{O}_3$ plays an important role as a fixed phase in both systems, providing the pinning force to the reversible spins, the frozen spins at the interface between Fe and $\gamma\text{-Fe}_2\text{O}_3$ are also shown to contribute to EB in the core/shell Fe/ $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles.

11:00am **NS-MoM9 Magnetic Polymer Nanocomposites with Tunable Microwave and RF Properties**, K. Stojak, S. Chandra, H. Khurshid, S. Pal, C. Morales, J. Dewdney, J. Wang, T. Weller, M.H. Phan, H. Srikanth, University of South Florida

There has been much interest in magnetic polymer nanocomposites (MPNCs) recently due to potential applications for EMI shielding, tunable electromagnetic devices and flexible electronics. We report synthesis, structural, magnetic and RF characterization on MPNCs ranging from 30-80wt-% loadings of uniformly dispersed CoFe_2O_4 nanoparticles (~ 10 nm) in a high-temperature, thermosetting resin from the Rogers Corporation (RP). Nanoparticles were synthesized by thermal decomposition and structurally characterized by XRD and TEM. Magnetic properties were studied using a Quantum Design PPMS. MPNCs displayed characteristic features of superparamagnetism at room temperature and blocking at low temperature. A blocking temperature (T_B) of ~ 298 K was observed for all weight percentages. The saturation magnetization (M_S) was found to increase with increasing weight percentages of CoFe_2O_4 , from 9.7 emu/g for 30wt-% to 28.5 emu/g for 80wt-%. A large value of coercivity (H_C), ~ 18.5 kOe, is observed at 10K and is not affected by various loadings of CoFe_2O_4 . Microwave transmission/reflection studies were done using a linear microstrip resonator. Strong tunability in the microwave absorption was observed, particularly in the 80wt-% sample and the quality factor shows a strong enhancement with applied magnetic field. We extend our study to include nanoparticle-filled multi-walled carbon nanotubes (CNTs) synthesized by CVD. These high-aspect ratio magnetic nanostructures, with tunable anisotropy, are of particular interest in enhancing magnetic and microwave responses in existing MPNCs. The CNTs have an average diameter and length of 300nm and $2\mu\text{m}$, respectively and are partially filled with CoFe_2O_4 nanoparticles (~ 7 nm) [2]. When comparing the CoFe_2O_4 nanoparticles to the CoFe_2O_4 -filled CNTs, T_B increases from 224K to 264K, and M_S increases from 36 emu/g to 37.1 emu/g. These results indicate that enclosing the nanoparticles within the CNTs enhances interparticle interactions, which is also independently confirmed with frequency-dependent AC susceptibility. This trend is also observed with NiFe_2O_4 and Fe_3O_4

nanoparticle fillers.

11:20am **NS-MoM10 Factors Controlling Thermodynamic Properties at the Nanoscale: Ab Initio Study of Pt Nanoparticles**, G. Shafai, M. Alcántara Ortigoza, T.S. Rahman, University of Central Florida

We analyze via density-functional-theory calculations how factors such as size, shape, and hydrogen passivation influence the bond lengths, vibrational density of states (VDOS), and thermodynamic quantities of 0.8-1.7 nm diameter Pt nanoparticles (NPs), whose shape was previously characterized via extended X-ray absorption fine structure spectroscopy (EXAFS) [1]. For a given shape, unsupported NPs display increasingly broader bond-length distributions with decreasing size. Since the VDOS is remarkably non-Debye-like (even for the largest NPs), the VDOS and the thermal properties are not correlated as they are in the bulk. Generally, the fundamental vibrational frequency of a NP is associated with the shape and decreases with increasing size, as in macroscopic systems. Not surprisingly, we find that the frequency of this fundamental mode largely characterizes the thermal properties. We demonstrate that the qualitative difference between the atomic mean-square-displacement and the corresponding mean bond-projected bond-length fluctuations should be taken into account when interpreting the Debye-Waller factor of NPs measured by X-ray (or neutron) scattering or EXAFS. We find that in H-passivated Pt NPs, H desorption with increasing temperature explains the appearance of negative thermal expansion.

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[1] B. Roldán Cuenya, M. Alcántara Ortigoza, L. K. Ono, F. Behafarid, S. Mostafa, J. R. Croy, K. Paredis, G. Shafai, T. S. Rahman, L. Li, Z. Zhang, and J. C. Yang, PRB 84, 245438 (2011)

[2] G. S. Shafai, M. Alcántara Ortigoza, and T. S. Rahman; J. Phys.: Condens. Matter 24, 104026 (2012)

11:40am **NS-MoM11 Fabrication of Fe Doped Nano-engineered Matrix for Cholesterol Biosensor**, R.R. Pandey, C. Kant, CSIR-National Physical Laboratory, National Physical Laboratory, India, M. Dhayal, CSIR Centre for Cellular and Molecular Biology (CCMB), India, K.K. Saini, CSIR-National Physical Laboratory, National Physical Laboratory, India

In recent years, sol-gel chemistry has been a subject of intense investigations in the fields of chemical sensors and biosensors as it offers a cost effective route the fabrication of high surface area plate forms for sensitive biosensors. The inherent low temperature process of the technology, provide an attractive way for the immobilization of heat-sensitive biological entities (enzyme, protein, and antibody). This class of sol-gel silica (TiO_2) matrix possesses chemical inertness, non-toxic, physical rigidity, tunable porosity, high photochemical and thermal stability, and optical transparency.

Nanostructured nature of the metal-oxides films have been extensively reported, we have utilized this property of the material for effective enzyme adsorption per unit area to develop high sensitivity biosensors. We have further improved the matrix property to alter the surface properties (microstructure and charge transport) by Fe doping in the TiO_2 film. The modified matrix has been characterized by XRD, XPS, FTIR, SEM. The Fe^{3+} ion doped TiO_2 matrix successfully introduces redox property in the electrode and provides enhanced electron communication features. Sensing response obtained by the bioelectrocatalytic oxidation of cholesterol by cholesterol oxidase. Chox/ Fe^{3+} ion doped TiO_2 /ITO electrode was studied using cyclic voltammetry (CV). These studies reveal that the Chox/ Fe^{3+} ion doped TiO_2 /ITO bio-electrode exhibits improved biosensing response as compared to Chox/ Undoped TiO_2 /ITO electrode. The results confirm promising application of the Fe^{3+} ion doped TiO_2 thin film matrix for the realization of efficient cholesterol biosensor.

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