SYMPOSIUM S

Magnetic Nanoparticles and Nanowires

March 29 - April 1, 2005

Chairs

D. Kumar

Dept. of Mechanical & Chemical Engineering North Carolina A&T State University Greensboro, NC 27411 336-256-1151

I. W. Boyd

Electronic & Electrical Engineering University College London Torrington Pl. London, WC1E 7JE United Kingdom 44-0-207-679-7307

L. Kurihara

Naval Research Laboratory Code 6363 Washington, DC 20375 202-767-2563

G. Duscher

Dept. of Materials Science & Engineering North Carolina State University Raleigh, NC 27695 919-515-1104

V. Harris

Dept. of Electrical & Computer Engineering Northeastern University 440 Dana Research Center 360 Huntington Ave. Boston, MA 02115-5000 617-373-7603

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^{*} Invited paper

SESSION S1/AA1: Joint Session: Self-Assembly of Magnetic Nanoparticles Chairs: Dhananjay Kumar and Ralph Nuzzo Tuesday Morning, March 29, 2005 Room 3005 (Moscone West)

8:00 AM *S1.1/AA1.1

Multi-Component Nanocrystal Assembly: A Route to Multi-Functional Nanomaterials. Christopher Bruce Murray¹ and Elena Shevchenko^{2,1}; ¹IBM, T. J. Watson Research Center, Yorktown Heights, New York; ²Department of Applied Physics and Applied Mathematics., Columbia University, New York, New York.

Collodial nanocrystals with controlled crystal shape, structure and surface passivation are now increasingly available. This talk will focus on the interesting superlattice systems that can be built with two types of these these "artificial atoms". We combine a high temperature solution phase synthesis with size selective processing techniques to produce organically passivated magnetic and semiconducting nanocrystals with size distributions less than 5%. Procedures have been developed for Co, Ni, FePt, CoPt3, Fe3O4 and Fe2O3 magnetic nanocrystals as well as for CdSe, PbSe, PbS, PbTe and semiconductor quantum dots. Examples of bianry superlattices with AB13, AB2 and AB5 structures will be discussed allow with other potenial structure encorporating 2 distinct types of nanocrystals as the building blocks.

8:30 AM *S1.2/AA1.2

Arrays of Magnetic Nanowires via Block Copolymer Templates. Thomas P. Russell¹ and M. Tuominen²; ¹Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts; ²Physics Department, University of Massachusetts, Amherst, Massachusetts.

Arrays of magnetic nanowires and nanowire devices were fabricated using nanoporous templates derived from self-assembling diblock copolymer films. Poly(styrene-methacrylate) (PS-PMMA) diblock copolymers as porous templates that were used to fabricate hexagonal arrays of vertical nanowires with densities of exceeding 1x10¹² square inch. Electrodeposition within the template produces 10nm-scale magnetic cobalt nanowire arrays that exhibit large perpendicular coercivity and remanance making them potential candidates for ultrahigh-density perpendicular magnetic storage media. The internal crystal morphology of the nanowires, and consequently magnetic properties, can be manipulated and tuned by electrodeposition process parameters. The copolymer templates have been patterned laterally using conventional lithographic exposure to fabricate novel 3D magnetic nanowire devices. This includes current-in-plane magnetoresitive devices and current-through-wire switching field devices. Anisotropic magnetoresistance measurements show a sharp and complete magnetization reversal, indicating single-domain nanowire switching behavior. Such properties offer promising potential for new magnetic nanodevices built upon on single-domain elements. This work is supported by National Science Foundation Nanoscale Interdisciplinary Research Team, Materials Research Science and Engineering Center and the Department of Energy.

9:00 AM S1.3/AA1.3

From Self-Ordering Towards Imprint Lithography: Large Scale Periodic Nickel and Permalloy Nanowire Arrays. Kornelius Nielsch¹, Woo Lee¹, Ralf B. Wehrspohn², David Navas³, Manuel Vazquez³ and Ulrich Goesele¹; ¹Max Planck Institute of Microstructure Physics, Halle, Germany; ²Department of Physics, University of Paderborn, Paderborn, Germany; ³Instituto de Ciencia de Materiales de Madrid, CSIC, Madrid, Spain.

In this paper, we will analyze the impact of the nanowire arrangement on the total anisotropy of magnetic nanowire arrays and the deviation of the switching fields of individual nanowire inside magnetic arrays for nickel and permalloy nanowire arrays with a disordered, polycrystalline and monocrystalline hexagonal arrangement of the nanowires. Ni and Ni₈₀Fe₂₀ is used for the nanowires due to its small magneto-crystalline anisotropy and small magnetic moment which lead to weak dipolar interactions inside the arrays and a large anisotropy resulting from the nanowire shape which en-ables these materials as suitable materials for patterned per-pen-dicular magnetic media. Self-or-dered alu-mina pore channel arrays are used as tem-plates for the fabrication of magnetic nanowire arrays with a perio-dicity of 65 nm (180 Gbit/in²), 100 nm (75 Gbit/in²) and 500 nm (3 Gbit/in²). A nearly per-fect hexagonal arrangement for the columns occurs only inside very narrow process win-dows for periodic distances of 65, 100 and 500 nm, and a degree of pore filling of almost 100% was achieved. In analogy to polycrystallites, the nanowires are hexagonally arranged in domains, which are extended over more than ten lattice periods. We obtain a perfect hexagonal or monocrystalline arrange-ment on a ${\rm cm}^2$ -scale, when we introduce imprint lithography in the fabrication process of our magnetic arrays. For the disordered

arrays the standard deviation of the nanowire diameter is >20% and for the polycrystalline and monoystalline arranged samples <10% and <2%, respectively. We observe that the total magnetic anisotropy increases by either reducing the deviation in nanowire diameter or by improving the ordering of the nanowire arrangement. In the case perfect ordering, we have detected the highest coercivity (1200 Oe) and total anisotropy (100% squareness) reported for a high-density Ni nanowire array with 100 nm periodicity and a column diameter of 30 nm. This work was funded by the German Federal Ministry of Education and Science (BMBF Nachwuchswettbewerb Nanotechnolgie, Grant No. BMBF 03N8701).

9:15 AM *S1.4/AA1.4

Polar-surface Induced Novel Growth Configurations of Piezoelectric Nanobelts. Zhong L. Wang, School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia.

The wurtzite structure family has a few important members, such as ZnO, GaN, AlN, ZnS and CdSe, which are important materials for applications in optoelectronics, lasing and piezoelectricity. The two important characteristics of the wurtzite structure are the non-central symmetry and the polar surfaces. The structure of ZnO, for example, can be described as a number of alternating planes composed of tetrahedrally coordinated O2- and Zn2+ ions, stacked alternatively along the c-axis. The oppositely charged ions produce positively charged (0001)-Zn and negatively charged (000-1)-O polar surfaces, resulting in a normal dipole moment and spontaneous polarization along the c-axis. This polar surface gives rise a few interesting growth features. In this presentation, we will focus on a few growth phenomena that are closely related to the polar surface. The growth mechanisms and the explaination about the growth features will be presented. Some details will be given about the analysis of the presented. Some details will be given about the analysis of the nanobelt based materials. [1] Z.W. Pan, Z.R. Dai and Z.L. Wang, Science, 209 (2001) 1947. [2] X.Y. Kong and Z.L. Wang, Nano Letters, 2 (2003) 1625 + cover. [3] Z.L. Wang, X.Y. Kong and J.M. Zuo, Phys. Rev. Letts. 91 (2003) 185502. [4] Nanowires and Nanobelts - materials, properties and devices; Vol. I: Metal and Semiconductor Nanowires, Vol. II: Nanowires and Nanobelts of Functional Materials, edited by Z.L. Wang, Kluwer Academic Publisher (2003). [5] X.Y. Kong, Y. Ding, R.S. Yang, Z.L. Wang, Science, 303 (2004) 1348. [6] Y. Ding and Z.L. Wang, J. Phys. Chem. B, 108 (2004) 12280. [7] Please visit http://www.nanoscience.gatech.edu/zlwang/ for more information.

9:45 AM S1.5/AA1.5

Magnetic Rings: Influence of Asymmetry. Vitali Metlushko¹, U. Welp², V. Vlasko-Vlasov², G. Crabtree², M. Grimsditch², N. Zaluzec², B. Ilic³, J. Bekaert⁴, V. V. Moshchalkov⁴, Y. Bruynseraede⁴, Xiaobin Zhu⁵, P. Grutter⁶, A. Imre⁷, G. Csaba⁷, G. H. Bernstein⁷ and W. Porod⁷; ¹ECE, UIC, Chicago, Illinois; ²MSD, ANL, Argonne, Illinois; ³Cornell University, Ithaca, New York; ⁴Katholieke Universiteit Leuven, Leuven, Belgium; ⁵University of Alberta, Edmonton, Alberta, Canada; ⁶McGill University, Montreal, Quebec, Canada; ⁷University of Notre Dame, Notre Dame, Indiana.

Recent studies on Co and permalloy rings have shown that a totally flux-closed magnetic vortex state could be stable at remanence. The two chiralities of the vortex, clockwise and counterclockwise, have been proposed as the carriers for the stored information. Our in-field magnetic imaging demonstrated that on subsequent field cycles the chirality of the large portion of individual rings was fixed. Earlier, we suggested that the shape effects are responsible for the vortex formation and chirality in circular elements. Furthermore, using micromagnetic modeling, we have ascertained that small asymmetry in the shape of ring is sufficient to produce preferential chirality. The modern microfabrication techniques allow us to produce systematic shape changes. The results show that with the knowledge of the asymmetry present, we can predict the switching direction accurately.

SESSION S2: Self-Assembly of Magnetic Nanoparticles $$\operatorname{II}$$

Chair: Dhananjay Kumar Tuesday Morning, March 29, 2005 Room 3005 (Moscone West)

10:30 AM *S2.1

Magnetic Nanoparticles Made using Block Copolymer Templates. <u>Caroline Ross</u>, Filip Ilievski and Joy Cheng; Massachusetts Institute of Technology, Cambridge, Massachusetts.

Applications such as patterned media require precisely controlled arrays of magnetic nanoparticles on a surface. One way to achieve this is to use a self-assembling system such as a block copolymer as a sacrificial mask for forming magnetic nanoparticles. In this work, a polystyrene-20% polyferrocenyldimethylsilane (PS-PFS) block

copolymer was spin-coated onto a substrate and annealed to form a monolayer of closepacked PFS spheres within a PS matrix. The sphere pattern was transferred into an underlying CoCr(22%)Pt(12%) magnetic film deposited over a 5 nm Ti underlayer, using a series of etching steps to form an array of 25 nm diameter and 50 nm period magnetic dots. 10 - 20 nm thick CoCrPt dot arrays have an out of-plane anisotropy and show thermally-assisted reversal with switching volumes similar to their physical volume, indicating relatively weak interparticle magnetostatic interactions. This is in contrast to the interactions in in-plane-magnetized 5 - 20 nm thick, 35 nm diameter, 56 nm period NiFe or Co dot arrays, which are strong enough to cause collective reversal of groups of nanoparticles (Phys. Rev. B70 064417 2004). The CoCrPt arrays have a perpendicular coercivity of up to 2000 Oe, depending on their thickness, considerably higher than that of the unpatterned CoCrPt films. Although the magnetic dot arrays have good short range order, they lack long range order. To impose long range order, the substrate can be patterned chemically or by etching shallow grooves in it to form coarse templates of dimensions ~100 nm and above, which control the positions of the PFS spheres. For example, in shallow parallel-sided grooves, the closepacked directions of the arrays of spheres line up with the edges of the grooves. These ordered polymer arrays can be used to form arrays of magnetic nanoparticles with long range order. Both periodic and aperiodic arrays can be formed by appropriate choice of the template geometry (Nature Mats. 3 823 2004), allowing a variety of nanoparticle array geometries to be created.

11:00 AM S2.2

Hcp-Co Nanoparticles and Crystallographic Alignment During Self-Assembly. Shihai Kan, Madhur Sachan and Sara Majetich; Physics, Carnegie Mellon University, Pittsburgh, Pennsylvania.

The ability to prepare self-assembled magnetic nanoparticle arrays with crystallographic alignment has been elusive, either because the nanoparticles have cubic crystal structures, and therefore a low magnetcrystalline anisotropy K, or as in the case of FePt, the high anisotropy phase is developed by heating after self-assembly. Here we report on the alignment of spherical hcp Co nanoparticles, and the competitive Neel and Brownian rotation processes which control it. A uniform external field applied during self-assembly will exert a torque on the nanoparticle moment, tending to align it parallel to the field. In order to crystallographically orient the particles, Brownian rotation must dominate Neel rotation during array formation. The Neel relaxation rate is proportional to exp[KV/kT], where V is the particle volume and kT is the thermal energy. The Brownian relaxation rate is proportional to the effective viscosity and to V/kT. Monodisperse Co nanoparticles (6 to 12 nm) were prepared via heterogeneous nucleation and high temperature solution chemistry techniques. The resulting particles form stable dispersions in toluene. Transmission electron microscopy (TEM), shows that these particles form arrays rather than chains when the solvent is evaporated, indicating that nonmagnetic forces dominate self-assembly. The particles are nearly spherical though some facets are evident. Powder x-ray diffraction confirmed the presence of the hcp phase. In addition to varying the particle size, we also self-assembled arrays at different temperatures (\sim 200-300 K), in order to vary the relative importance of the Neel relaxation mechanism. No significant changes in morphology of the self-assembled arrays were seen because of the low temperature or magnetic field. The remanent to saturation magnetization ratios show significant increases when the particles are self-assembled in a field, for larger particle sizes. X-ray diffraction is used to quantify the degree of crystallographic alignment.

11:15 AM S2.3

Synthesis and Self-Assembled Ring Structures of Ni Nanocrystals. Guangjun Cheng 1.2, Victor Puntes 3.4 and Ting Guo²;

¹Physics, NIST, Gaithersburg, Maryland; ²Chemistry, University of California, Davis, Davis, California; ³Chemistry, University of California, Berkeley, Berkeley, California; ⁴Physics, University of Barcelona, Barcelona, Spain.

Ni nanocrystals with a face-centered cubic (fcc) structure were synthesized via rapid thermo-decomposition in the presence of the surfactants in organic solvents. Transmission electron microscopy (TEM) and X-ray diffraction (XRD) were used to characterize these nanocrystals. It was found that the solvents determined the rate of the decomposition of Ni precursors, while the surfactants controlled the size and shape of Ni nanocrystals. Three-step process for the synthesis was discussed. The as-prepared Ni nanocrystals can form micrometer-sized ring strctures on TEM grids by evaporating from hexanes after purification, and magnetic field can increase the number of the ring.

11:30 AM <u>S2.4</u>

Self-Assembled Single Crystal Ferromagnetic α -Fe and Co Nanowires formed by Decomposition.

Ladan Mohaddes-Ardabili^{1,2}, H. Zheng^{1,2}, S. B. Ogale^{1,3}, F. Zavaliche^{1,2}, T. Zhao^{1,2}, S. Y. Yang^{1,2}, D. G. Schlom⁴ and R. Ramesh²; ¹Materials Science and Engineering, University of Maryland, College Park, Maryland; ²Materials Science and Engineering, University of California, Berkeley, California; ³Physics, University of Maryland, College Park, Maryland; ⁴Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania.

A novel approach to create self-assembled ferromagnetic nanostructures for new magnetic recording media with high storage capacity is reported, which involves spontaneous phase decomposition of a single-phase perovskite oxide during film growth. We are exploring the stability in a nominally single phase LaSrTMO3 (TM=Fe, Co, Mn) system as a function of oxygen pressure, using thin film heteroepitaxy as the processing route. We find that the film structure and microstructure depends systematically on the oxygen pressure during deposition. Deposition under reducing environments, leads to the formation of self-assembled arrays of nanowires. Specifically, in the case of Fe and Co system the deposition under reducing conditions leads to spontaneous formation of an array of single crystalline ferromagnetic α -Fe and Co nanowires embedded in an antiferromagnetic matrix with nominal compostion of LaSrFeO4 $\,$ and LaSrCoO4, respectively. The diameter of both α -Fe and Co nanowires is controlled by growth temperature and the height is controlled by film thickness. In the case of $\alpha\text{-Fe}$ at growth temperatures of 840 C, square shaped $\alpha\textsc{-}\mathrm{Fe}$ pillars with a lateral width of d = 50-60 nm are formed. As the deposition temperature is reduced the diameter of the nanowires is progressively reduced to $4\text{-}6~\mathrm{nm}$ for the growth at 560 C and the shape is circular. In the case of Co the growth temperature window is smaller and the nanowires with d = 60-70 nm are formed at around 700 C. The magnetic properties of these nanowires are both dependant on the average diameter and also the height of nanowires. For iron nanowires maximum coercivity of Hc = 3000 (Oe) is achieved for 200 nm thick nanowires with average diameter of 15-20 nm grown at 760 C (M = 0.95 Msat). The magnetic properties of α -Fe and Co with different diameters are measured at 300, 100 and 5 K and the trend is discussed. Transmission Electron Microscopy (TEM) and Magnetic Force Microscopy (MFM) data is also reported. The large remanence and sizable coercivity of the nanowires make them desirable for high-density data storage and other magnetic device applications. This work is supported partly by NSF-MRSEC under contract No. DMR-00-80008 and by an ONR MURI program under contract No. N000140110761.

11:45 AM <u>S2.5</u>

Field-driven Self-assembly of Magnetic Nanocolloidal Particles. Stefan Kooij, Aurelian Galca, Herbert Wormeester and Bene Poelsema; MESA+ Institute for Nanotechnology, Univ. Twente, Enschede. Netherlands.

The behaviour of magnetic nanoparticles suspended in a polar or nonpolar solvent (frequently referred to as a ferrofluid) has been studied for centuries and a lot of intriguing effects have been observed. One example which has found its way to practical applications is the tunable viscosity of these liquids by external fields. Most often, ferrofluids are treated in terms of fluid mechanics without considering the magnetic behaviour of the individual magnetic nanoparticles. In our work we investigate the response of individual magnetic nanoparticles to the influence of external magnetic fields and especially focus on magnetophoretic deposition. For this, a description of the characteristics on a single-particle level is a prerequisite. Different forces act on a suspended magnetic nanocrystal when it is subjected to an external magnetic field. A homogeneous magnetic field induces an alignment parallel to the magnetic field. Sufficiently strong particle-particle interactions will give rise to chaining of nanoparticles due to alignment of individual dipole moments. In addition to the orientation, an inhomogeneous field will lead to movement of the particles in these fields. To lower their energy, particles will migrate towards regions where the field line density is highest. Competing with the orientation and the movement of magnetic nanocrystals in a suspension is the Brownian motion of the particles. Two types of Brownian motion can be distinguished: (i) the rotational motion which competes with the alignment in the magnetic field, and (ii) the translational Brownian diffusion which competes with the migration due to inhomogeneous magnetic fields. To enable quantitative studies on magnetophoretic deposition, we present finite element calculations of a number of possible magnet geometries. Based on the results, we determine the forces acting on suspended nanoparticles. In situ experiments on true magnetophoretic deposition using inhomogeneous fields will be presented. Furthermore, the alignment and chaining of individual particles is studied in very dilute suspensions using transmission ellipsometry. Finally, we will show anomalous flow behaviour observed in oil-based ferrofluids in nearly homogeneous fields.

SESSION S3: Nanoscale Charactrization and Nanosystems Chair: Jagdish Narayan Tuesday Afternoon, March 29, 2005 Room 3005 (Moscone West)

1:30 PM *S3.1

Single Atom Imaging and Spectroscopy through Aberration-Corrected Scanning Transmission Electron Microscopy. Stephen J. Pennycook, Matthew F. Chisholm, Andrew R. Lupini, Albina Y. Borisevich, Maria Varela, Yiping Peng and Klaus Van Benthem; Condensed Matter Science Division, Oak Ridge National Lab, Oak Ridge, Tennessee.

The successful correction of electron microscope aberrations has doubled the achievable resolution in the last few years. Our VG Microscopes' 300 kV scanning transmission electron microscope (STEM) equipped with a Nion aberration corrector achieves direct sub-Angstrom imaging of a crystal lattice with a resolution of 0.06 nm. The small beam size also gives increased sensitivity, allowing low-Z columns such as oxygen can be imaged adjacent to high-Z columns. Individual high-Z atoms can be imaged on or within specific columns of a crystal and analyzed spectroscopically by simultaneous electron energy loss spectroscopy. A previously unanticipated advantage of aberration correction is the reduced depth of focus. It is now possible to perform optical sectioning in the STEM simply by changing the focus of the beam, allowing a three-dimensional reconstruction with sub-Angstrom lateral resolution and nanometer depth resolution. Applications of these techniques will be presented to nanocrystals, nanowires and device structures.

2:00 PM *S3.2

Formation and Structural Evolution of Haxagonal Close-Packed Ni Nanoparticles on (001) MgO by in situ Ultra-High Vacuum TEM. Xiaoqing Pan¹, Haiping Sun¹, Wei Tian¹, Yanbin Chen¹, Jinhai Yu², Chris Boothroyd², Mark Yeadon² and Roy Clarke³: ¹Materials Science and Engineering, University of

and Roy Clarke³; ¹Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan; ²Institute of Materials Research and Engineering, Singapore, Singapore; ³Department of Physics, University of Michigan, Ann Arbor, Michigan.

3d transition metals exist in three closely related crystallographic phases in nature, namely face-centered cubic (fcc), body-centered cubic (bcc), and hexagonal close-packed (hcp) phase. Due to a small difference in the lattice energies of these crystallographic phases, the structures of transition metals can be tuned among these phases by varying the temperature and pressure, or by structural stabilization through heteroepitaxial growth. Ni, Fe, and Co are among the particularly important 3d transition metals, because they all show ferromagnetism. Co undergoes a structural phase transformation from hcp to fcc at 425°C at ambient pressure, while bcc Co has been formed by heteroepitaxial growth on GaAs and Cr. Fe possesses bcc and fcc structures at ambient pressure, and hcp Fe exists at high pressure. While Ni is fcc at ambient pressure up to its melting point, bcc Ni was also formed by heteroepitaxial growth. In this paper, we report the in-situ transmission electron microscopy observation of an unnatural phase of Ni, a highly strained hexagonal close-packed (hcp) form which we believe is stabilized by heteroepitaxial growth on the (001) face of MgO. We find that the nanosized hcp nickel islands transform into the normal face-centered cubic structure when the size of the islands exceeds a critical value (about 2.5nm thick with a lateral size of ~5nm). The structural transition proceeds via a Martensitic change in the stacking sequence of the close-packed planes. The formation of hcp Ni nanostructures with an unusually large crystallographic c/a ratio (\sim 6% larger than ideal hcp) is very interesting for spintronic and recording applications where large uniaxial anisotropies are desirable.

2:30 PM <u>S3.3</u>

Characterizing the Microscopic Switching Behaviour of CoPt Nanoparticles with High Resolution Magnetic X-ray Microscopy. Peter Fischer¹, Dong-Hyun Kim¹, Bosun Kang¹, Elke Arenholz¹ and Manfred Albrecht²; ¹CXRO, LBNL, Berkeley, California; ²Dept. Physics, U Konstanz, Konstanz, Germany.

Magnetic nanoparticles are currently attracting significant physical and technological interest as being potential candidates for high density magnetic storage media [1-3]. However, a thorough understanding of characteristic magnetic properties on a microscopic length scale is inevitably for future developments. Of particular interest is the switching behaviour and the switching distribution of individual nanoparticles located in a dense packed array of neighboring elements. We utilized analysis techniques based on X-ray magnetic circular dichroism to determine these properties in CoPt nanoparticle systems (Co 0.3nm/Pt 1nm)x8 + 1nm Pt capping layer) with particles sizes below 250nm. Element-specific in-situ hysteresis loops of the Co component were derived from magnetic absorption

spectroscopy at the Co L3 edge measured in transmission mode at BL4 at the Advanced Light Source in Berkeley CA [4], which clearly indicate the onset of magnetization reversal already at very small applied magnetic fields. Detailed studies of the underlying microscopic switching behaviour were obtained by recording high resolution images with magnetic transmission X-ray microscopy (MTXM) [5] at the XM-1 beamline at the ALS, Berkeley CA. The lateral resolution provided by Fresnel zone optics can be as low as 13nm [6] and the field of view extends up to about 20mum, thus allowing to record a large set of nanoparticles under identical conditions, e.g. external magnetic field. We observe the flipping of individual magnetic particles and are able to derive the switching field distributions and the stochastical character of the magnetisation reversal process by analysing the obtained images by correlation techniques. Comparing the MTXM results with Magnetic force microscopy results indicate the influence of the magnetic stray field of the tip to the switching of individual particles. In future X-MCD based analytical tools will contribute significantly to the understanding of magnetic nanoparticles providing non-ambigous element-specific information on the nanometer length and sub-ns time scale. [1] S. Sun et al, Science, 287 (2000) 1989 [2] S. Anders et al, J Appl Phys 93 (2003) 7343 [3] MH Kryder, DIGEST Joint [NA]PMRC 2003 IEEE Piscataway, NJ USA (2003) 68 [4] AT Young et al, Surface Review & Letters, 9 (2000) 549 [5] P. Fischer, Current Opinion in Solid State and Materials Science 7 (2003) 173 [6] W. Chao et al, (2004) to be published

2:45 PM <u>S3.4</u>

Controlled Synthesis and Characterization of $Co_{core}Au_{shell}Nanoparticles$ with Tailored Optical and Magnetic Properties. Yuping Bao and Kannan M. Krishnan; Materials Science & Engineering, University of Washington, Seattle, Washington.

Core-shell nanoparticles have received considerable attention recently because their physical and chemical properties can be tuned by controlling their chemical composition and the relative sizes of the core and shell. In this context, we have developed a reliable method for the reproducible synthesis of $Co_{core}Au_{shell}core$ -shell nanoparticles by slowly reducing an organo-gold compound onto pre-made ϵ -Co seeds with a weak reducer at mild condition (85-105¢C). For the first time, these core-shell nanoparticles are generated in non-polar solvent in a controlled manner. Subsequently, these nanoparticles are made water-soluble by functionalizing them with hydrophilic thiol-containing surfactants through the specific binding between gold and thiols. These Co_{core}Au_{shell}core-shell nanoparticles have been extensively characterized by a wide range of transmission electron microscopy methods. Routine transmission electron microscopy (TEM) images clearly show the core-shell structure based on the diffraction contrast from Co and Au. High resolution TEM image show a single crystal Co core surrounded by multiple gold grains, suggesting that gold has multiple nucleation sites on cobalt seeds during synthesis. Electron energy-loss spectroscopy and z-contrast imaging also independently confirm the spatial distribution of the two elements: a Co center with a more or less homogeneous coating of Au. Bulk structural and magnetic properties of these nanoparticles were investigated on powder form samples by x-ray diffraction and superconducting quantum interference device and the optical properties in solution form by UV-Visible spectrophotometery. θ -2 θ x-ray scans demonstrate a high degree of crystallinity and uniform particle size of these core-shell nanoparticles. Magnetically, these particles are superparamagnetic at room temperature with a blocking temperature of 55K, and at lower temperatures (5K) the nanoparticles show hysteresis behavior consistent with the ferromagnetic state. Optically, the Au shell absorbance of UV-visible spectrum shows a red shift from 520nm to 680nm, compared to similar size individual gold nanoparticles. Our ongoing work is focused on combining this well-characterized core-shell nanoparticles synthesis with well-understood gold-thiol chemistry, which provides a variety of surface functionalization opportunities, for biomedical applications where their dual magnetic and optical properties provide novel detection and sensing functionalities in diagnostics. This work is supported by NSF/DMR DMR-0203069 and the Campbell Endowment at UW

3:30 PM $\underline{*S3.5}$

Magnetic Oxide Heterostructures for Interface Characterization. Jochen Mannhart¹, Andreas Schmehl¹, Stefan Thiel¹, Akihito Sawa² and John R. Kirtley³; ¹EKM; Institute of Physics, University of Augsburg, Augsburg, Germany; ²Correlated Electron Research Center (CERC), National Institute of Advanced Science and Technology (AIST), Tsukuba, Japan; ³IBM T.J. Watson Research Center, Yorktown Heights, New York.

The active components of many magnetic oxide devices are embedded interfaces. Therefore we have explored techniques to analyze with high resolution the transport properties of such interfaces. For this, we are developing novel heterostructures that allow to precisely measure the

interface characteristics in a current-perpendicular plane geometry. This approach is applied to magnetic oxides, for which first results will be presented.

4:00 PM *S3.6
Itinerant Ferromagnets: The Role of Disorder in the Suppression of Long-Range Magnetic Order in Nanoscale Systems. Arthur F. Hebard and Partha Mitra; Physics, University of Florida, Gainesville, Florida.

As nanoparticles and ultra thin films decrease in size, the surface-to-volume ratio increases and magnetic ordering becomes increasingly dominated by interfaces. To help understand these effects we phrase a simple question, i.e., what happens in a simple band ferromagnet such as iron when the ability of the itinerant electrons to transfer spin is compromised by disorder? We present the results of a study in which in situ magnetoresistance and Hall effect studies are made on pure and composite films with Fe thicknesses as small as 6 angstrom. We use the sheet resistance as a measure of disorder and correlate this quantity with the saturation field, the saturated moment and the carrier concentration as derived from Hall effect measurements. We find that in the weakly disordered regime where logarithmic temperature dependences dominate, that there is a noticeable but weak suppression of the saturated moment. Surprisingly, in the strongly disordered regime where the sheet resistance at low temperatures (~5 K) is approaching 300,000 Ohms per square (a value well above the quantum limit) the saturated moment is still remarkably robust. In this regime the temperature dependence of the resistance deviates strongly from the logarithmic dependence of the weakly localized regime. We also present scaling dependences of our resistivity and conductivity matrices and find that they are in disagreement with the predictions of interaction theory. Our results will be compared to the results of other investigators for both one and two-dimensional structures. The implications of these experiments for understanding magnetism in nanoscale structures will also be discussed.

4:30 PM <u>S3.7</u>

Sensitive Measurement of Parallel and Transverse Susceptibility in Magnetic Nanoparticles by Alternating Gradient Magnetometry. <u>Mladen Barbic</u> and Mary Brady; Physics and Astronomy, California State University, Long Beach, Long Beach,

Reversible susceptibility tensor measurements reveal important information about the switching fields and anisotropies of magnetic nanoparticles. We show that a simple reconfiguration of an alternating gradient magnetometer can be used to measure both reversible parallel and transverse susceptibilities with high sensitivity. It is demonstrated that positioning the sample off-axis with respect to the magnetometer gradient field coils results in a signal at twice the frequency of the gradient field that is directly proportional to the reversible susceptibility. Offsetting the sample along the x-axis results in a sensor signal proportional to the reversible parallel susceptibility, while rotating the sample holder by 90 degrees and offsetting it along the y-axis results in a sensor signal proportional to the reversible transverse susceptibility. Examples of reversible parallel and transverse susceptibility measurements of aligned nanoparticle systems will be demonstrated.

4:45 PM S3.8

Room-temperature Ferromagneticsm in Nanostructured Co-doped ZnO. Ming Wei, N Khare, K. A. Yates, A. Venimadhav, D. Zhi, R. E. Dunin-Borkowski, M. G. Blamire and J. L. MacManus-Driscoll; Material Science and Metallurgy, University of Cambridge, Cambridge, United Kingdom.

Nanosized Co-doped ZnO samples were synthesized using an ultrasonic spray assisted chemical vapour deposition method. Microstructural and magnetic properties of these samples were studied. The room-temperature ferromagnetism was observed in the Co-doped ZnO. Also, x-ray analysis revealed a wurtzite ZnO structure with a small change of the lattice constants due to the doping of Co in ZnO. Raman spectroscopy of the Co-doped ZnO films indicated direct substitution of Co. Scanning electron microscopy showed nanostructured Co-doped ZnO with a ring or cup shape. Transmission electron microscopy analysis revealed nano grains within the rings of an average diameter of around 10 nm. Both energy dispersive spectroscopy and energy-filtered transmission electron microscopy indicated a uniform distribution of Co.

> SESSION S4: Magnetic Nanoparticles and Properties I Chair: A. Gupta Wednesday Morning, March 30, 2005 Room 3005 (Moscone West)

8:00 AM <u>*S4.1</u>

Fabrication of Multifunctional Magnetic Nanoparticles. Jian-Ping Wang, The Center for Micromagnetics and Information Technologies (MINT), Department of Electrical and Computer Engineering, University of Minnesota, Minneapolis, Minnesota.

Magnetic nanoparticles with size from 1 nm to 100 nm have unique physical properties compared with their counterpart of bulk materials. They have broad range applications in extremely high density magnetic recording, biomedicine, catalysts, biosensor, and ferrofluid, etc. Single crystalline magnetic nanoparticles are especially important because they carry the highest magnetic magnetization and magnetic crystalline anisotropy and free of microstucture. Meanwhile, the hybrid structured magnetic nanoparticles (e.g. core-shell type) are receiving a lot of attention because this heterostructure offers opportunities to develop devices and materials with multi-function or new functions for bio and medical applications. Both chemical and physical protocols are being used in fabricating magnetic nanoparticles. The latter one has the merits of materials independence, ease of purity and composition control, process simplicity, etc. However, its dynamic nature makes the particles crystallization hard to achieve without further processing like post-annealing. The as-formed particles are generally in polycrystalline or even amorphous state. Here we report a protocol that employs nanocluster generation, on-line heating and on-line shell coating techniques to directly fabricate multifunctional crystalline magnetic nanoparticles. Magnetic nanoparticles were generated by gas-phase aggregation using a magnetron sputtering based nanocluster source and flying through the deposition system by pressure differential driving-force. An infrared light on-line heater was applied to crystallize the in-flight particles in vacuum prior to substrate landing. Both evaporation source and sputtering gun are used for the nanoparticles shell coating. Various magnetic materials such as FeCo, FePt and CoPt were investigated for the particle generation and Au, Ag and C were used as the nanoparticle-shell materials. Single crystalline phase was achieved by in-situ phase formation and characterized by transmission electron microscope (TEM). Tetragonal phase FeCo nanoparticles with novel hard magnetic properties were achieved for the first time and will be discussed in the full paper. FeCo and FePt nanoparticles with various shapes (e.g. cubic, spherical, etc) and their effects on magnetic properties will be reported too.

8:30 AM *S4.2

X-doped $\overline{\mathrm{Gd}_5\mathrm{Ge}_2\mathrm{Si}_2}$ Alloys (X=Fe, Co, Mn, Cu, Ga) with Large Magnetocaloric Effects and Little Hysteresis Due to the Formation a Nanocomposite Structure. V. Provenzano, R. D. Shull and A. J. Shapiro; Magnetic Materials Group, National Institute of Standards and Technology, Gaithersburg, Maryland.

Upon the application of a magnetic field to a material, the resulting magnetic spin alignment represents a decrease in the material's magnetic entropy (ΔS). If the application of the field is performed adiabatically, so that the total entropy change is zero, then the reduced magnetic entropy is offset by an equal increase in lattice entropy, resulting in an increase in the temperature (ΔT) of the material. This $\Delta \bar{S}$ is called the magnetocaloric effect, and it is a property of the material and its magnetic state. Similarly, when the field is removed the magnetic entropy is increased and the material cools. Field cycling a magnetic material forms the basis for a magnetic refrigerator. In assessing the usefulness of a material as a magnetic refrigerant, equally important to the magnitude of its magnetocaloric effect is the magnitude of its magnetic hysteresis. Since the hysteresis is the cost in energy to make a single cycle in the field, it represents an energy loss that must be properly accounted for in computing the usefulness of that material as a magnetic refrigerant. This is not an important consideration if the refrigerants are either paramagnetic or superparamagnetic materials since they have no magnetic hysteresis. However, for ferromagnets, the hysteresis loss becomes an important parameter. Here we report on such data and analysis for the ${\rm Gd_5Ge_2Si_2compound}$, a material exhibiting a large magnetocaloric effect (the "Giant Magnetocaloric Effect") as well as large hysteretic losses and show that when this material is doped with about one atom percent of either Fe, Co, Mn, Cu, or Ga the material possesses very little magnetic hysteresis losses and the resulting ΔS value is smaller while its peak value is shifted from 275K to 305 K, compared to the doped-free compound[1]. The greatly reduced hysteretic losses are believed to be due to the formation of a magnetic nanocomposite structure in the doped alloy. This nanocomposite structure gives rise to a supermagnetic behavior in the temperature range where the doped alloys exhibit their large magnetocaloric effects. These results clearly show that, compared to the basic Gd₅Ge₂Si₂ alloy, one atom percent metal doping, changes the alloy magnetocaloric response in a very profound way. Possible mechanisms to explain theses significant changes will be presented. [1] V. Provenzano, A.J. Shapiro, and R.D. Shull, Nature 429, 853 (2004).

9:00 AM <u>**S4.3**</u>

Formation of Monolayer Arrays of Magnetic Nanoparticles Using a Non-Aqueous Langmuir Layer Method. <u>Julie Gardener</u>, Yuhang Cheng, Stephen Garoff and Sara Majetich; Physics, Carnegie Mellon University, Pittsburgh, Pennsylvania.

Large area ordered monolayer arrays of nanoparticles are desirable for studies of magnetic interactions and for magnetoelectronic measurements. It is particularly challenging to prepare monolayer arrays of air-sensitive materials such as iron and cobalt, which should have the strongest magnetostatic interactions for a given particle size. Here we describe a method for forming well-ordered monolayer arrays of air-sensitive nanoparticles and transferring them onto different substrates. Langmuir layers of surfactant-coated nanoparticles have previously been formed using an aqueous underlayer and nanoparticles that were not particularly air-sensitive. However, when applying this technique to magnetically interesting materials such as bcc Fe and hcp Co, care must be taken to avoid corrosion and oxidation. We modified the standard procedure by replacing the aqueous subphase with anhydrous ethylene glycol and by preparing the Langmuir layer under argon in a glove box. Glass is used to contain the subphase instead of the standard material (Teflon) to prevent leakage of the surfactant chains coating the nanoparticles onto the barrier and to alter the curvature of the meniscus. Several drops of a nanoparticle solution in hexane are gently introduced to the ethylene glycol surface, and allowed to disperse. The monolayer film is visible to the naked eye, and the onset of multilayer formation can be distinguished by the appearance of a dark ring. Langmuir-Blodgett and Langmuir-Schaefer techniques are used to transfer the monolayer onto thin substrates of various kinds (amorphous C, SiOx, SiNx and Pt). The morphologies are then studied using transmission electron microscopy (TEM), and the uniformity of the nanoparticle ordering is related to the monolayer transfer technique and the surface energy of the substrate. The magnetic properties of Fe and Co nanoparticle monolayers are compared with those of multilayer arrays and nanoparticle crystals.

9:15 AM S4.4

Synthesis of Highly Magnetic Iron Nanoparticles Using a Beta-Diketone Surfactant. <u>Dale L. Huber</u>, Eugene L. Venturini, James E. Martin and Paula P. Provencio; Sandia National Laboratories, Albuquerque, New Mexico.

Iron nanoparticles have been synthesized with the frequently used iron carbonyl decomposition, but using a novel beta-diketone surfactant that has yielded nanoparticles with very high saturation magnetization. Literature reports of iron nanoparticles often show reduced magnetic response, particularly for particles less than 5 or 6 nm in diameter. This reduction in magnetism is generally agreed to be due to surface effects, and is likely caused by interactions with surface bound surfactants. Beta-diketones are a class of weak surfactants whose interactions with the iron surface do not tend to disturb the particle magnetism greatly. We have measured a saturation magnetization of greater than 200 emu/g for oxide-free, 6 nm iron nanoparticles. This represents greater than 90% of the value for bulk iron. These particles also possess a very high magnetic susceptibility, and tend to magnetically agglomerate even in the absence of a magnetic field. Smaller particles, while still highly magnetic, do not have this strong tendency to agglomerate. We have also achieved excellent reproducibility and control of the size of the iron nanoparticles. Both TEM and magnetic measurements demonstrate that these particles have low polydispersity. We believe that this procedure is an ideal method for synthesizing a well-defined system to investigate isolated and collective magnetic behaviors of iron nanoparticles. This work was supported by the Division of Materials Sciences and Engineering, Office of Basic Energy Sciences, United States Department of Energy. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

9:30 AM <u>S4.5</u>

Size Dependence of Phase Transformation in FePt Nanoparticles. Sara Majetich and Yi Ding; Physics, Carnegie Mellon University, Pittsburgh, Pennsylvania.

A key advantage of using self-assembled nanoparticle arrays in data storage media would be the high degree of uniformity in the grain size and position. However, FePt nanoparticles as made have the fcc structure, which must be annealed to transform into the high anisotropy L10 phase. Sintering occurs because the surfactant coating around the particles decomposes around 400 degrees Celsius. Without the steric barrier, the particles coalesce below temperatures sufficient for the L10 phase transformation [1]. High coercivities have been reported only in samples where the particles have at least partially sintered. This raises the questions of whether there is a threshold size needed for the L10 phase to be stable, and whether the degree of ordering and transformation temperatures may be size dependent. To

address these issues, monodisperse FePt nanoparticles (3 to 12 nm) were prepared using standard high temperature chemical methods. The synthesis parameters were adjusted so that the average Fe:Pt ratio determined by calibrated x-ray fluorescence was close to 50:50. Monolayer films of the nanoparticles were deposited on thinned silicon nitride windows, so that the particle size distribution could be determined after annealing in flowing H2 at different temperatures (400 to 700 degrees Celsius). After annealing the room temperature coercivity was measured with an alternating gradient magnetometer, and the chemical order parameter was determined from the ratio of the (110) and (111) x-ray diffraction peak intensities. We find that small sintered regions can dominate the coercivity even when the average size is much smaller. The measured size distributions are to model how the coercivity evolves with particle size. The coercivities and ordering fractions as a function of particle size and annealing temperature are reported. 1. Y. Ding, S. Yamamuro, D. Farrell, and S. A. Majetich, J. Appl. Phys. 93 (2003) 7411.

9:45 AM S4.6

Thermodynamic Properties of Antiferromagnetic Clusters. Florentino Lopez-Urias¹ and Gustavo M. Pastor²; ¹Advanced Material Department, Instituto Potosino de Investigacion Cientifica y Tecnologica (IPICYT), San Luis Potosi, Mexico; ²Laboratoire de Physique Quantique, Centre National de la Recherche Scientifique, Universite Paul Sabatier, Toulouse, France.

The finite-temperature properties of magnetic clusters motivate a considerable interest in current research on low-dimensional magnetism. Antiferromagnetic clusters are a major theoretical challenge in this field due to the complex competition between the itinerant and localized behavior of the electrons and the resulting strong electron-correlation effects. In this work, the thermodynamic properties of clusters having N ≤ 9 atoms are systematically investigated in the framework of the Hubbard model with nearest-neighbor hopping t and on-site Coulomb repulsion U. A complete optimization of the topological structure of the clusters is performed. The ground-state and excited-state electronic energies, the corresponding wave functions, and the total spin are calculated exactly by using a full-many-body numerical-diagonalization method. The spin-resolved specific heat, magnetic susceptibility, and spin-spin correlation functions between sites i and j are obtained from the canonical partition function. Finally, the effects of temperature induced fluctuations of the cluster structure are discussed.

10:30 AM <u>*S4.7</u>

Formation of Epitaxial Nanodots/Nanocrystals by Domain Matching Epitaxy. Jagdish Narayan, Materials Sc & Eng, N C State University, Raleigh, North Carolina.

This paper reviews recent developments in thin film growth and formation of three-dimensional epitaxial nanostructures, grown by a new paradigm of domain matching epitaxy (DME). The $\widecheck{\mathrm{DME}}$ involves matching of integral multiples of lattice planes (diffracting as well as nondiffracting) between the film and the substrate, and this matching could be different in different directions. We focus special attention on the formation of epitaxial nanodots/ nanocrystals in crystalline matrices such as MgO and TiN. The formation Ni nanocrystals inside MgO involves lattice misfit ranging from 3.0% to 31.3%, and the formation of Ni nanocrystals in TiN has misfit of about 17%. To form epitaxial nanodots, we utilize DME framework to grow nanodots inside crystalline matrices. The DME principles are applied to grow self-assembled epitaxial nanodots using pulsed laser deposition. By controlling the clustering kinetics, it is possible to obtain a uniform distribution of epitaxial nanodots and overcome thermodynamically driven Ostwald ripening. This process allows the formation of epitaxial nanostructures via three-dimensional self-assembly of nanostructured materials processing, leading to unique and novel properties. We discuss unique modifications in optical, mechanical and magnetic properties produced by nonodots. For nanostructured magnetic materials, coercivity and blocking temperature can be considerably enhanced by controlling the orientation for magnetic memory and storage applications among others.

11:00 AM <u>S4.8</u>

Structural and Magnetic Properties of Iron Nanoparticles prepared by Chemical Vapor Synthesis. Thorsten Enz^{1,3}, Branko Stahl^{1,3}, Sarbari Bhattacharya¹, Markus Winterer², Gerhard Miehe¹, Keir Foster³, Claudia Fasel¹ and Horst Hahn^{1,3}; ¹Institute of Materials Science, Darmstadt University of Technology, Darmstadt, Germany; ²School of Engineering, Nanoparticle Process Technology, University Duisburg-Essen, Duisburg, Germany; ³Institute of Nanotechnology, Forschungszentrum Karlsruhe, Karlsruhe, Germany.

Particles of metallic iron with a mean diameter of 3 nm have been produced by Chemical Vapor Synthesis (CVS). A detailed structural, electronic and magnetic characterization has been attained by various methods. Structural analysis of the powder was performed using

X-ray diffraction (XRD), high resolution transmission electron microscopy (HR-TEM) and extended X-ray absorption fine structure (EXAFS) analysis. Small angle X-ray scattering (SAXS) was applied to determine the morphological length scales of the nanomaterial. Differential thermal analysis (DTA), thermogravimetry (TG) and combustion analysis were applied to reveal the phase stability and carbon content. The samples were magnetically characterized by magnetometry and Mössbauer spectroscopy. The atomic arrangement of the as prepared particles is both strongly affected and stabilized by the incorporation of excess carbon and furthermore influenced by the exceptionally small size. Due to the in-situ formation of a carbonaceous shell the particles are stable against oxidation at ambient conditions. Despite the high concentration of carbon there are no detectable amounts of iron carbides. The particles exhibit superparamagnetic behavior with a blocking temperature of 30 K. The complex electronic structure results in an average magnetic moment per iron atom of approximately 1.8 μ_B . The formation of microcrystalline particles that serve as a substrate for the growth of large carbon nanotubes is observed as a side-effect of the synthesis.

11:15 AM S4.9

Monte Carlo Simulations of Thermodynamic Properties of FePt Nanoparticles. <u>Michael Mueller</u> and Karsten Albe; Institute of Materials Science, TU Darmstadt, Darmstadt, Germany.

Nowadays, a number of experimental routes for synthesizing FePt nanoparticles are available. Depending on the process conditions, the particle size distribution, stoichoimetry and structure can vary significantly and it is still unclear, whether it is for kinetic or thermodynamic reasons that the disordered phase is often observed even at low temperatures. Therefore, a detailed investigation of the thermodynamic properties of nanoalloys, especially phase segregation and order-disorder phenomena as function of particle size and temperature, would provide important information. In this work we have chosen a lattice Monte-Carlo model combined with a spin-1/2 Ising model including nearest and next nearest neighbor interactions. The parameters of the model were fitted to the FePt bulk phase diagram and experimental data on Pt surface segregation. By using this model, we have systematically explored the influence of particle size and chemical composition on the ordering temperature as well as the segregation of Fe and Pt in ordered particles. In general we find no evidence for a considerable decrease of the ordering temperature with particle size. On the other hand, a lowering of the ordering temperature with increasing deviation from stoichiometry could clearly be observed. This effect was found to be strongly assymetric with respect to compositions enriched with Fe or Pt, which can be explained by differences in the segregation behaviors of the two elements at the surface.

11:30 AM <u>S4.10</u>

Effects of Crystal Size in Nanoparticles of ABO₃-type Magnetoelectric Spintronic Oxides. Shishir K. Ray¹, Mark Williamsen¹, Vaijayanti R. Palkar² and Prasenjit Guptasarma¹;

¹Department of Physics, University of Wisconsin - Milwaukee, Milwaukee, Wisconsin;

²Tata Institute of Fundamental Research, Mumbai, India.

Magnetoelectric perovskite oxides are a rare and fascinating class of materials which show a coexistence of magnetism and ferroelectricity via what appear to be coupled ground states. Such materials have potential applications in future spin based electronic devices, where the electric field could be used as a means to control spin. Of special interest in such future devices, where the material is likely be structured with dimensions on the order of tens of nanometer, is the question of whether limiting crystal size could have an effect on long-range ordered correlated electron phenomena. We report our recent work in the fabrication and characterization of nano-sized crystals (size \sim 20nm, 33nm, 56nm and 80nm) of the ABO $_3$ family of oxides. We have examined structural and magnetic properties, as well as electronic structure and the phonon spectrum, and report changes of properties with crystal size which mostly arise from a change in lattice symmetry in this size range.

11:45 AM <u>S4.11</u>

Size Effects on the Electronic Structure of Magnetic Nanoparticles. Keith Gilmore¹, Damon Resnick¹, Adam McClure¹, Yves U. Idzerda^{1,4}, Michael T. Klem², Mark Allen², Trevor Douglas², Mark Young³ and Joe Dvorak^{1,4}; ¹Department of Physics, Montana State University, Bozeman, Montana; ²Department of Chemistry, Montana State University, Bozeman, Montana; ³Department of Plant Sciences, Montana State University, Bozeman, Montana; ⁴National Synchrotron Light Source, Brookhaven National Lab, Upton, New York.

A primary interest in nanomaterials is the emergent properties they exhibit. Nanoparticles exist in the 0-dimensional limit of the particle diameter becoming smaller than relevant electronic and magnetic

lengthscales. Therefore, it is not reasonable to expect these systems to behave identically to their bulk counterparts. Determining how size and surface effects govern the properties of systems at this scale is of fundamental importance if one hopes to fabricate novel materials. X-ray spectroscopy is ideally suited for the study of the electronic structure and magnetic characterization of nanoparticles. The greatest advantage of x-ray spectroscopy is that it provides element specific measurements. Standard x-ray absorption spectroscopy provides a direct probe of the electronic structure of materials. The complimentary x-ray absorption fine structure measurement is used to determine lattice spacings and the distortion of the lattice at the surface. A third technique, x-ray absorption magnetic circular dichroism, provides a spin-resolved picture of the electronic structure of materials allowing absolute measurement of the separate spin and orbital magnetic moments of constituent ions. We investigate size effects on the electronic and magnetic structure of nanoparticles. The materials studied are cobalt-oxide and iron-oxide particles grown inside protein cages. The protein cages (Listeria, Ferritin, and CCMV) constrain the size of the spherical particles to 5, 8, and 20 nm in diameter, respectively. The electronic structure and magnetic properties of these systems are mapped out as a function of size.

> SESSION S5: Magnetic Nanoparticles and Properties II Chair: Ian Boyd Wednesday Afternoon, March 30, 2005 Room 3005 (Moscone West)

1:30 PM <u>*S5.1</u>

The Role of Surface Crystallography in the Magnetic Response of NiZn Ferrite Nanoparticles.

Michael Edward McHenry and Rajasekaran Swaminathan; MSE, Carnegie Mellon University, Pittsburgh, Pennsylvania.

The study of magnetic nanostrucutres is rich because many important magnetic length scales are on the order of 10 - 100 nm and ingenious engineering of magnetic nanostructures allows for the tailoring of properties [1,2]. Ferrite nanomaterials have been investigated in recent years because of their potential applications in high-density magnetic recording, ferrofluid technology, magnetocaloric refrigeration, magnetic resonance imaging enhancement, and magnetically guided drug delivery. NiZn ferrites are the most important materials for high frequency (100 MHz - 1 GHz range) power applications because of their large resistivities, low conductive losses and high permeabilities. In ferrite nanoparticles, the crystallography of terminating faces determines the symmetry of atomic environments at the surface. Oxygen mediated A-B and B-B superexchange bonds determine the temperature dependence of the magnetization and whether the alignment of cation magnetic dipole moments is collinear or non-collinear. The symmetry of surface polyhedra also determines surface magnetic anisotropy. Two important observations pertinent to the faceted nanoparticles are (1) the ratio of the number A-B to B-B exchange bonds at the (111) surfaces is smaller than in the bulk, and (2) the 4-fold screw axis symmetry of the bulk crystal is broken to yield linear chains of octahedra at (100) terminated faces of nanoparticles The former coupled with a higher concentration of non-magnetic Zn atoms on surface A-sites of the (111) terminated surfaces gives rise to non-collinear triangular spin configurations and the latter yield a uniaxial surface magnetic anisotropy in the large nanoparticles. We will review TEM and HRTEM observation polyhedral surface structure of polydisperse NiZn ferrite nanoparticles synthesized using an RF plasma torch. The nanoparticles exhibit truncated cuboctahedral morphologies with more (111) surface area than (100). The critical nucleus shape is a perfect octahedron, while growth forms assume Wulff shapes. The relationship between morphology and the atomic structure of the faceted nanoparticles has been studied using Mossbauer spectroscopy and Extended Absorption Fine Structure (EXAFS) analysis. The contribution of the faceting to the surface magnetic anisotropy of the (100) and the (111) surface will be used to interpret the dynamic transverse susceptibility and low temperature static magnetic measurements in these systems. A surface structural model is proposed to explain surface spin canting and magnetic anisotropy for the observed (100) and (111) nanoparticle surfaces in the polydisperse and size-selected monodisperse nanoparticles 1. M. E. McHenry and D. E. Laughlin, Nano-scale materials development for future magnetic applications. Acta Materiala (Millenium Issue) 48 (2000) 223.

2:00 PM <u>S5.2</u> Defects in CoO Dominate Exchange Biasing in Co(core)/CoO(shell) Nanoparticles. <u>Joseph B. Tracy</u> and Moungi G. Bawendi; Chemistry, MIT, Cambridge, <u>Massachusetts</u>.

We have investigated two effects of pinning the Co core in Co(core)/CoO(shell) nanoparticles which cause exchange biasing: (1) the CoO lattice and (2) defects in the CoO shell. Stoichiometric and

crystallographic defects in CoO give rise to a paramagnetic response that freezes at low temperature below the Neel temperature of CoO. In this experimental investigation, we switched the biasing field during cooling at an intermediate temperature above the freezing temperature of the defect moments, so that the orientation of the defect pinning could oppose that of the CoO lattice pinning. As the sample was heated, the exchange field changed sign before vanishing. Therefore, at low temperature, the CoO defects are the stronger pinning mechanism and dominate exchange biasing. At higher temperatures, the CoO defects are paramagnetic and cannot contribute to pinning, and the CoO lattice controls exchange biasing. These results support the domain state model for exchange biasing.

2:15 PM <u>S5.3</u>

Synthesis and Magnetic Properties of MnP and MnAs Nanoparticles: Implications for Spintronics. Kanchana Somaskandan¹, Kristy A. Gregg¹, Georgy Tsoi³, Lowell E. Wenger³, Gavin Lawes² and Stephanie L. Brock¹; ¹Chemistry, Wayne State University, Detroit, Michigan; ²Physics, Wayne State University, Detroit, Michigan; ³Physics, University of Alabama, Birmingham, Birmingham, Alabama.

The manganese pnictides (pnicogen = Group 15 element) exhibit complex magnetochemical properties that have yet to be systematically investigated on the nanoscale, despite implications that nanoparticulate MnP and MnAs are playing a role in the ferromagnetic properties of several Mn-doped III-V semiconductors currently being evaluated as spintronic materials. In the bulk, MnP exhibits a low temperature helimagnetic structure that transforms to a ferromagnet near 50 K; MnAs undergoes a phase change near room temperature from the NiAs structure (high spin, ferromagnetic) to the MnP structure type (low spin, antiferromagnetic), then returns to the NiAs-type above 400 K. These phase changes in MnAs are accompanied by large magnetostrictive, magnetocaloric, and magnetooptical effects and depend sensitively on pressure and composition. We have developed a synthetic methodology for the preparation of transition metal pnictide nanoparticles based on the reaction of zero-valent metals with phosphines or arsines in coordinating solvents. In this paper, the preparation of spherical and rod, and ellipsoidal particles of MnP and MnAs of size 4-30 nm and with low polydispersities will be presented. The role of crystallite size and shape on magnetic phase transitions will be evaluated, and the potential contribution of manganese pnictide nanoparticles to the magnetic properties of phosphide and arsenide based diluted magnetic semiconductors, discussed.

2:30 PM <u>S5.4</u>

Magnetic Nanoparticle Aggregation States in Ag_{100-x}Fe_x Cosputtered Granular Films Investigated by Magnetic and Magnetotransport Measurements. Paolo Allia¹, Federica Celegato¹, Marco Coisson², Paola Tiberto², Franco Vinai² and Federico Spizzo³; ¹Physics, Politecnico di Torino, Torino, Italy; ²IEN Galileo Ferraris, Torino, Italy; ³Physics, University of Ferrara, Ferrara, Italy.

Cosputtered bimetallic granular films of composition $Ag_{100-x}Fe_x$ with varying Fe-atom concentration (10 \leq x \leq 30) provide a unique opportunity to study the effect of nanoparticle interactions with changing particle size, number and average distance. Combining magnetic and magnetotransport measurements, a self-consistent, unequivocal picture of the magnetic aggregation level of Fe nanoparticles can be experimentally obtained. $Ag_{100-x}Fe_x$ films, of thickness 250 nm, were prepared by dc plasma cosputtering deposition on Si in inert gas atmosphere. Magnetic measurement techniques included: SQUID magnetometry (up to 50 kOe, 4 to 270 K); VSM (up to 20 kOe, 100 to 300 K); extraction magnetometry (up to 70 kOe, 4 to 300 K). Isothermal magnetization, ZFC/FC curves, and static initial susceptibility were obtained by proper combination of magnetic techniques. Magnetotransport measurements were performed between 4 and 270 K by means of the four-contact method with soldered electrical contacts, under a maximum applied field of 70 kOe. The surface topography of films was obtained by conventional AFM technique. Isothermal magnetization curves exhibit an apparent superparamagnetic behavior at low Fe concentration (x = 10%, 14%), while at higher Fe content a behavior similar to a frustrated ferromagnet is observed. Even at the lowest Fe concentration, however, nanogranular films are better described as interacting superparamagnets (ISP) rather than as a pure superparamagnets [1]. Below x = 14%, magnetic measurement analysis is sufficient to provide a good estimate of the actual nanoparticle size and distance. All films display a negative magnetoresistance with unsaturating behavior at high fields. Low-temperature magnetoresistance values range between 8% for $\rm Ag_{70}Fe_{30}$ and 25% for $\rm Ag_{86}Fe_{14}.$ Magnetoresistance vs.magnetization curves were analyzed in terms of a simple model allowing a magnetic correlation range to be obtained as a function of temperature and applied field [2]. At each temperature, the zero-field magnetic correlation length steadily increases with increasing Fe

content, starting from a value slightly higher than the electron mean free path λ for x = 10, and reaching a value hundreds of times higher than λ for x = 30. The following picture of the magnetization process Ag Fe nanogranular system emerges: even for low Fe content (x \leq 14%), the magnetic ordering entities are not single nanoparticles, but small nanoparticle clusters containing strongly correlated moments; these magnetic ordering entities grow in size with increasing x, finally resulting, for x = 30%, into a magnetic response arising from the entire Ag Fe matrix. The behavior of magnetoresistance with Fe concentration, displaying a maximum shifting from x = 14% to x = 26% as a function of measuring temperature, can be explained in terms of the above picture. [1] P. Allia et al., Phys. Rev. B64, 144420 (2001) [2] P. Allia et al., Phys. Rev. B67, 174412 (2003)

2:45 PM S5.5

Synthesis and Magnetic Multiplex Separation of Superparamagnetic Magnetite Nanocrystals. <u>Cafer T. Yavuz</u>¹, J. T. Mayo², William Yu¹, Joshua C. Falkner¹ and Vicki L. Colvin¹; ¹Chemistry Dept., Rice University, Houston, Texas; ²Chemistry Dept., University of St. Thomas, Houston, Texas.

Uniform size and highly monodisperse ($\sigma=5\text{-}10\%$) magnetite (Fe3O4) nanocrystals were synthesized utilizing two different solvothermal reactions of iron (III) species (FeOOH and Fe(acac)3). Wide range of sizes (4, 6, 8, 11, 12, 14, 20, 26, 33 nm) achieved, characterized and used for further applications. Size dependent magnetic separation was studied and applied to polydisperse samples successfully. Iron content of effluents was determined by ICP-AES. Magnetic field strength vs. percent retention of individual sizes reported. Magnetic multiplex separation method is created and proposed for bio-magnetic separations. Superparamagnetic limit for magnetite (Rc = 34 nm at RT) is experimentally reported for the first time. Arsenic adsorption to nanosize magnetite is shown and compared to bulk material as a proof of wide variety of applications. 3D arrays of ultrafine magnetite nanocrystals with different nanosized materials (i.e. CdSe, C60, TiO2) are also being tested.

3:30 PM <u>*S5.6</u>

Pulsed Laser Assisted Fabrication of Self-Assembled Iron Nanoparticles in Epitaxial TiN Thin Film Matrix. Shri Dana¹, Dhananjay Kumar¹, Jag Sankar¹, Albert A. Gapud² and David K. Christen²; ¹Center for Advanced Materials and Smart Structures, Mechanical Engg, North Carolina A&T State University, Greensboro, North Carolina; ²Solid State Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Nanodimensional iron particles were embedded in epitaxial TiN thin film matrix using a pulsed-laser deposition processes. TiN was chosen for the following reasons(i) it can be grown epitaxially at low temperatures on Si, (ii) it has excellent diffusion barrier characteristics, and (iii) it has excellent electrical conductivity. Iron nanodots were embedded into the matrix by careful adhesion of iron foil (10mm x 5mm) to the TiN target and changing the laser repetition rate. These films were characterized using x-ray diffraction, high resolution transmission electron microscopy, and superconducting quantum interference device magnetometer. The size of Fe magnetic nanoparticles was controlled by varying laser repetition rate from 5 Hz to 15 Hz keeping the thickness of spacer-layer same. The uniformity in Fe particle size distribution was manipulated by the competition between the thermodynamic instability and kinetic effects. The coercivity of Fe-TiN thin film nanocomposites were found to be in the range of ~550 Oe at 10 K to ~90 Oe at 300 K.

4:00 PM <u>S5.7</u>

Superparamagnetic Flexible Substrates based on Submicron Electrospun Estane Fibers Containing MnZnFe-Ni Nanoparticles. Pankaj Gupta¹, Ramazan Asmatulu², Rick Claus² and Garth Wilkes¹; ¹Chemical Engineering, Virginia Tech, Blacksburg, Virginia; ²Fiber and Electro Optics Research Center, Virginia Tech, Blacksburg, Virginia.

Estane, a segmented polyester based segmented polyurethane that is elastomeric in fibrous form, was dissolved in dimethylene acetamide, DMAc, at a concentration of 20wt%. Superparamagnetic ferrite nanoparticles (ca. 14 nm) based on MnZnFe-Ni and dispersed at 10wt% in ethanol were mixed into the 20 wt% Estane solution at wt% different concentrations of the nanoparticles. These solutions were then electrospun at 17-20 kV, 20 cm and 3 ml/h for 20 min to produce fine fibrous mats that were collected on a steel wire mesh target. After easy removal from the target, the fibrous mats were subsequently dried in a vacuum oven for 8h at 60 oC to minimize any residual solvent. The flexible mats were characterized in terms of fiber morphology and magnetic properties. Field Emission Scanning Electron Microscopy (FESEM) indicated that the diameter of these composite fibers was ca. 300-500 nm. Furthermore, the back-scattered electron FESEM images indicated regions where some agglomeration of the nanoparticles at higher wt% (ca 17-26 wt%) loading on the

electrospun fibers was apparent. Characterization of the magnetic properties was conducted by measuring the induced specific magnetization upon application of an external magnetic field at 300 K. The induced specific magnetic saturation and the relative permeability was found to increase linearly (R2=0.999) with increasing wt% loading of the ferrite nanoparticles on the submicron electrospun fibers. A specific magnetic saturation of 1.7 - 6.3 emu/g and relative permeability of 1.8-6 at 300 K indicated superparamagnetic behavior of these composite electrospun substrates.

4:15 PM <u>S5.8</u>

Oxide Shell Formation in CoNi/Oxide Core/Shell Nanoparticles. Jalpa Patel¹, Dorothy Farrell², Ivan P. Parkin¹ and Quentin A. Pankhurst²; ¹Dept. of Chemistry, University College London, London, United Kingdom; ²Dept. of Physics and Astronomy, University College London, London, United Kingdom.

The polyol method of synthesis for submicron particles is well established, and in the last decade modifications of the technique have been used to produce monodisperse nanoparticles of numerous magnetic metals (e.g., Fe, Co, Ni, FeCo, CoNi). Stable dispersions of high quality CoNi nanoparticles are synthesized by the reduction of hydrated cobalt and nickel acetate salts in high boiling point organic solvents in the presence of a surfactant, with the final alloy composition determined by the [Co]:[Ni] precursor ratio. Previous work using oleic acid (OA) as the surfactant with a 3:1 [OA]:[Co + Nil molar ratio suggests that each particle consists of an oxide shell around an alloy core. The core/shell morphology leads to exchange anisotropy in the particles and therefore enhanced coercivity, and the core/shell composition is stable for up to one year [1]. The magnetic properties of the particles depend on the exchange coupling between the oxide shell and alloy core, allowing tuning of the magnetic properties via control of the oxide shell. To better understand the formation of the oxide shell, reactions with varying heating rates and different surfactant head groups and concentrations have been studied. Replacement of oleic acid by hexadecylamine (HDA) under otherwise identical reaction conditions greatly promotes particle agglomeration, indicating weak binding of the amine headgroup to the particle surface. Additionally, particle formation, as evidenced by the reaction medium changing color from violet to black, occurs at lower temperature in the presence of HDA (~ 160 °C versus ~ 215 °C with OA). UV-Vis absorption spectra of aliquots of reaction media extracted throughout the synthesis reaction show a shift in the dominant absorption peak to lower energy when OA is replaced with HDA. Even with OA as surfactant, particle aggregation results from rapid heating of the reaction mixture, with the most stable dispersions synthesized after first maintaining the reaction above the acetate salt dissolution temperature, but below the particle formation temperature (i.e., 120 - 160 $^{\circ}$ C), for at least an hour. These results indicate the formation of cobalt- and nickel-surfactant complexes which act as the particle precursors and determine the particle formation temperature and reaction kinetics. Further studies on the particles, particularly with high resolution transmission electron microscopy (HRTEM) and SQUID magnetometry, will determine the effects of the different formation temperatures, as well as the different binding strengths of the head groups to the particles, on the oxide shell thickness and stability. 1. C. Luna, M. del Puerto Morales, C. J. Serna, and M. Vazquez, Nanotechnology, 15, 2004, S293.

4:30 PM <u>S5.9</u>

Growth Mechanisms and Oxidation-Resistance of Gold-Coated Iron Nanoparticles. Sung-Jin Cho¹, Juan-Carlos Idrobo², Justin Olamit², Kai Liu², Nigel D. Browning^{3,4} and Susan M. Kauzlarich¹; ¹Department of Chemistry, University of California, Davis, California; ²Department of Physics, University of California, Davis, California; ³Department of Chemical Engineering and Material Science, University of California, Davis, California; ⁴National Center for Electron Miscroscopy, Lawrence Berkeley National Laboratory, Berkeley, California.

Core-shell structured magnetic nanoparticles have attracted a lot of interest as a new type of multifunctional heterostructure. Here we report the chemical synthesis of Fe-core/Au-shell nanoparticles by a reverse micelle method, and the investigation of their growth mechanisms and oxidation-resistant characteristics. The core-shell structure and the presence of the Fe & Au phases have been confirmed by transmission electron microscopy, energy dispersive spectroscopy, X-ray diffraction, Moessbauer spectroscopy, and inductively coupled plasma techniques. Additionally, atomic-resolution Z-contrast imaging and electron energy loss spectroscopy (EELS) in a scanning transmission electron microscope (STEM) have been used to study details of the growth processes. Interestingly, the Au-shell grows by nucleating at selected sites on the Fe-core surface before coalescing. The jagged surface could compromise the oxidation-resistance of the Au shell. Indeed, the magnetic moments of such nanoparticles, in the loose powder form, do decrease over time due to oxidation. However,

in the pressed pellet form, electrical transport measurements show that the particles are fairly stable, as the resistance of the pellet does not change appreciably over time. These results shed lights on new synthesis routes to achieve truly air-tight Au-shells over Fe-cores.

4:45 PM <u>S5.10</u>

Carbon Encapsulated Magnetic Nanoparticles Produced by a Catalytic Disproportionation Of Carbon Monoxide.

<u>Eugene A. Katz</u>¹, Oleg Prilutskiy², Alex Shames³, Emma Mogilko⁴
and I. Bruckental⁴; ¹Inst. for Des. Res., Dept. of Solar Energy and Evironmental Physics, Ben-Gurion University of the Negev, Sede Boqer, Israel; ²CMC Ltd, Ofakim, Israel; ³Department of Physics, Ben-Gurion University of the Negev, Beer-Sheva, Israel; ⁴Department of Physics, Bar-Ilan University, Ramat-Gan, Israel.

Carbon nanotubes produced by various catalytic methods are known to be decorated by catalyst metal particles and spherical carbon nanocapsules with a catalyst metal core. Here we report the serendipitous discovery of the fact that, using catalytic disproportionation of carbon monoxide with a Fe2O3 initial catalyst powder, quasi-spherical highly crystalline magnetic nanoparticles can be effectively synthesized and collected separately from the other products of the reaction. XRD patterns for this nanomaterial was found to include reflections from polycrystalline magnetite (Fe3O4) together with (0002) graphite peak from the carbon shells. HRTEM revealed that the material consists of quasi-spherical nanoparticles with a diameter from 5 to 30 nm. Some of the particles are encapsulated by 1 - 2 carbon shells. Lattice imaging demonstrated defect-free crystalline structure of the nanoparticles. Selective area electron diffraction supports the conclusion that every such nanoparticle is a Fe3O4 single nanocrystal. Energy Dispersive Spectrum (EDS) analysis confirmed presence of iron, oxygen and carbon. A possible mechanism for a formation of the nanocapsules is suggested. The encapsulating carbon shells of the Fe3O4 nano-clusters are stable in air at room temperature, but do not prevent them at high temperatures. Accordingly, these nanoparticles may also act as catalysts for the corresponding production of carbon nanomaterials via carbon monoxide disproportionation. For example, we have demonstrated the corresponding transformation from Fe3O4 core to a nanoparticle of the iron carbide (Fe5C2) with a simultaneous formation of additional encapsulating carbon layers. The distance between the carbon layers are found to be close to that of graphite, 0.34 nm. DC magnetization characterization of the both materials revealed clearly resolved hysteresis loops. However characteristic S-shape of the loops (magnetization is still not saturated at 16 kOe) points out some superpamagnetic effects driven by the nano-size origin of the samples. Room temperature ESR spectrum of the ${\rm Fe}3{\rm O}4$ nanoparticles consists of a singlet line with a g-factor g = 2.008 and line width of 1042 Oe, whereas EPR spectrum of the Fe5C2@C consists of two overlapping lines: broad one with g=2.55 and line width of 1832 Oe and narrow one with g = 2.06 and line width of 220 Oe. Analysis of the temperature dependence of magnetization and ESR spectra provides an additional insight to the coexistence of the magnetic phases in the synthesized nanomaterials.

> SESSION S6: Poster Session: Magnetic Nanoparticles and Nanowires Chairs: Dhananjay Kumar and Lynn Kurihara Wednesday Evening, March 30, 2005 8:00 PM Salons 8-15 (Marriott)

S6.1

Surface Effects on the Magnetic Behavior of Nanocrystalline Nickel Ferrites: The Effect of Surface Roughness and Dilution. Devesh K. Misra¹, <u>Harish Nathani</u>¹ and W. F. Egelhoff²; ¹Chemical Engineering, University of Louisiana at Lafayette, Lafayette, Louisiana; ²Magnetic Materials Division, National Insitute of Standards and Technology, Gaithersburg, Maryland.

The paper describes the surface roughness and dilution effects on the magnetic behavior of nanocrystalline nickel ferrites studied by SQUID magnetometer. Two different kinds of measurements were performed: (a) zero-field cooling (ZFC) and field cooling (FC) magnetization versus temperature and (b) magnetization as a function of the applied field. The analysis of magnetic measurements indicate that while the superparamagnetic behavior is retained by the nanocrystalline ferrites of different surface roughness (8-18 Angstroms) at 300K, the hysteresis loop at 2K becomes non-squared and the coercivity increases with increase in surface roughness. This behavior is discussed in terms of broken bonds and degree of surface spin disorder. In diluted dispersion systems containing 10-40% nickel ferrite in a polyethylene matrix, the interparticle attractions continue to be dominant even when the concentration of nickel ferrite is 10 wt. % in the diluted system. The general magnetic behavior of diluted dispersion system is

similar to the undiluted system; however, coercivity, remanence, and saturation magnetization are altered. These changes in the magnetic data are ascribed to magnetization interactions that encourage flux closure configuration. * Corresponding author (dmisra@louisiana.edu)

S6.2

Sintering Behavior of NiZn Ferrite Nanoparticles Interpreted in a Surface Structure Model. Rajasekaran Swaminathan¹, Scott Calvin², Rameil Jacob¹ and Michael E. McHenry¹; ¹Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania; ²Physics, Sarah Lawrence College, Bronxville, New York.

The sintering behavior of RF plasma synthesized NiZn ferrite nanoparticles was studied to evaluate their potential in compacted cores for use in high frequency magnetic applications. The BET measured specific surface area of the as-synthesized nanoparticles was 26.42m²/g with a TEM estimated average particle size of 12-15 nm. The as-synthesized nanoparticles have been modeled as having a core-shell structure with a richer Zn concentration on the surface as compared with the core of the nanoparticle (with Zn occupying surface tetrahedral sites). Evidence of the core-shell structure was observed in the high-resolution TEM and the truncated Fourier transformed Zn-edge EXAFS (extended X-ray absorption fine structure) [1]. The core-shell is further modeled using fits to the EXAFS data, suggesting that different degrees of disorder for different cations in the ferrite. Most Zn cations occupy bulk tetrahedral sites typical of zinc ferrites, while some of the Zn cations appear in tetrahedral sites in a (111) surface layer in the form of ZnO. Ni and Fe cations show no evidence of such disorder; both are consistent with observations for pure-phase spinel structure. The preference for ZnO at the surface is of added importance in the sintering process. NiZn ferrite nanoparticles were compacted using a Carver press and heat treated in air at temperatures between 300°C-1100°C. XRD studies on the sintered nanoparticle compacts showed an evolution of a two-phase mixture of the ferrite + ZnO with increasing sintering temperature. ZnO is observed to appear at about $500^\circ C$ (for a 1-hour sintered sample) and its fraction increases until it becomes the majority phase at 1100°C. Although there was significant sintering shrinkage of the compacts at temperatures greater than 900°C, the average ferrite particle (estimated from the Scherrer broadening of XRD peaks) suggested that the nanoparticle size of the ferrite was preserved up to sintering temperatures of 1100°C. The observed sintering effects are interpreted in light of a surface structure model proposed to explain the effects of (111) and (100)-type surfaces on the structural [1] and magnetic [2] properties of as-synthesized nanoparticles. The core-shell model suggests that the ZnO shell contributes to the sintering process by surface diffusion while acting as a barrier for the growth of the ferrite particles. Magnetization data indicated that the saturation magnetization and the Curie temperature were reduced as a function of the sintering temperature. The reduction in magnetic moment is explained by Zn diffusing from the core depleting the ferrite and increasing the amount of non-magnetic ZnO in the shell. 1.R.Swaminathan, M.E.McHenry, S.Calvin, M.Sorescu and L.Diamandescu. Journal of American Ceramic Society, accepted for publication in 2005. 2.R.Swaminathan, M.E.McHenry, P.Poddar and H.Srikanth, Journal of Applied Physics, accepted for publication in 2005.

S6.3

Static and Dynamic Response of Isolated and Structured Iron Nanoparticles. Eugene Venturini, Dale Huber, James Martin and Paula Provencio; Sandia National Laboratories, Albuquerque, New Mexico.

We present experimental data on the magnetic properties of Fe nanoparticles with diameters between 2 and 6 nm and superparamagnetic blocking temperatures from 12 to above 250 K. Particle synthesis employed Fe carbonyl decomposition in dioctyl ether with pentanedione surfactant to prevent oxidation. Particle size was varied systematically by changing Fe and surfactant concentrations. The isolated particles exhibit saturation magnetization up to 90% of bulk Fe and have the bcc structure from TEM selected area diffraction. Magnetic and TEM sizes are in good agreement and there is no evidence for oxidation in the high-resolution images. AC susceptibility data suggest Arrhenius kinetics for blocking; however, the effective magnetic anisotropy is two orders of magnitude greater than that of bulk Fe for the smaller nanoparticles. The saturation magnetization decreases more rapidly with increasing temperature than bulk Fe. Static and AC magnetic fields assemble the larger nanoparticle solutions into 1D chain-like structures or 2D sheets with strong dipolar coupling. These structured nanocomposites, frozen in dioctyl ether, exhibit greater than 20-fold enhancement and nearly 3-fold suppression of the magnetic susceptibility just above blocking for specific orientations. Compared to isolated Fe nanoparticles, the collective dipolar interactions in structured samples produce shifts in the blocking temperature and

significant changes in coercivity and remanence below blocking. Current efforts are focused on reproducing these structures in polymers. This work was supported by the Division of Materials Sciences and Engineering, Office of Basic Energy Sciences, United States Department of Energy. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

S6.4

Amorphous Se: A New Platform for Synthesizing Superparamagnetic Colloids with Controllable Surfaces. Unyong Jeong and Younan Xia; Chemistry, University of Washington, Seattle, Washington.

We have successfully incorporated iron oxide nanoparticles into monodispersed amorphous selenium (a-Se) colloids by regulating the reaction temperature during the synthesis of a-Se. The surfaces of these a-Se colloids could be coated with conformal and smooth shells made of noble metals and SiO2. The Se cores could then be removed by etching with hydrazine. The spherical morphology and superparamagnetism were maintained in all these synthetic steps. The presence of noble metals and SiO2 on the outer surfaces of these colloidal particles allows one to readily control their surface functionalities by using thiolate. This presentation will explicitly discuss the synthesis of the magnetic colloids and the coatings. And I will also discuss the use of the colloids to immobilize biomolecules.

$\underline{\mathbf{S6.5}}$

Transferred to S5.3

Fabrication of Core-shell Type Nanoparticles. <u>Jianmin Bai</u>, Yunhao Xu and Jianping Wang; MINT & Dept. of Electrical and Computer Engineering, University of Minnesota, Minneapolis,

The fabrication of core-shell type nanostructures is receiving a lot of attention, because that their composition, small size (several nanometers to several tens of nanometers) and special structure offer opportunities to develop devices and materials that provide new capabilities for magnetic, electrical, optical, chemical, medical and biochemical applications. In this study, we fabricated several kinds of Core-shell type nanostructures, such as FeCo/FeCoOx, FeCo/Au, and so on. We used nanocluster gun to produce nanoparticles of CoFe as core. The shell layer was either on-line oxidized or sputtered by using a target of Au. The target of shell material was placed between the source orifice and substrate, and inversed to the flying direction of nanoparticles. The thickness of shell is related closely on the velocity of nanoparticles, density of atom cloud of shell material, partial pressure of oxygen, and flying time of nanoparticles. The size of nanoparticles (core) is controllable from several nanometers to several tens of nanometers through changing preparation conditions of nanoparticles source, such as target-to-orifice distance, sputtering power, carrier gas flow rate, and diameter of orifice. The atom density of shell material is adjustable by controlling sputtering power and sputtering gas pressure. TEM observations showed that the FeCo cores are single crystals and the shells are also crystallized.

S6.7

Synthesis and Frequency Dependent Properties of Core/Shell Magnetic Nanoparticles. Christy Vestal¹ and Max Alexander²;

¹Universal Technology Corporation, Dayton, Ohio; ²Air Force Research Laboratory, Wright-Patterson AFB, Ohio.

The development of materials with high permeability, high permittivity and with low loss is of interest due to their application in microelectronics and microwave communication systems. Although ferromagnetic materials display high permeabilities, they have limited applications in microwave applications due to their large conductivities that limit the ability of microwaves to penetrate into bulk materials. One approach commonly taken to overcome the limitations of bulk ferromagnetic materials is to disperse ferromagnetic inclusions in an insulating matrix (i.e. a dielectric material). Measurements of the permeability and permittivity of micron-sized core/shell-type materials show improved properties compared to the solid particulates. Here we report the synthesis of core/shell nanoparticles with a non-magnetic core and magnetite shell as a model system to evaluate the potential of nano-sized core/shell materials. The magnetic properties and frequency dependent permeability and permittivity will be discussed.

86.8

Supercritical Hydrothermal Synthesis of MgFe₂O₄
Nanoparticles. Takafumi Sasaki, <u>Seiichi Takami</u>, Satoshi Ohara,
Mitsuo Umetsu and Tadafumi Adschiri; Institute of Multidisciplinary
Research for Advanced Materials, Tohoku University, Sendai, Miyagi,

Japan.

We report the synthesis of MgFe₂O₄ nanoparticles by supercritical hydrothermal reaction. The mixed aqueous solution of iron and manganese ions was heated in a pressure-resistant vessel to produce MgFe₂O₄ nanoparticles. The solid products were collected and then characterized by transmission electron microscopy and X-ray diffraction (XRD). The average diameter of the synthesized nanoparticles was $10{\sim}20$ nm. XRD measurement indicated that the nanoparticles were mainly composed of MgFe₂O₄, containing Fe₂O₃ and Mg(OH)₂ as impurities. The products did not dissolve in nitric acid, preserving the main XRD peaks of MgFe₂O₄.

S6.9

Ferromagnetic Resonance of Iron Nanoparticles Formed by Sonoelectrochemical Precipitation. Tamara Gharibyan, Arshack Khachatryan, Varya Minasyan and Vahe Khachatryan; Kinetics and Catalysis, Institute of Chemical Physics of NAS of Armenia, Yerevan, Armenia.

Ferromagnetic resonance (FMR) experiments at 9.26 GHz in suspensions of iron nanoparticles are performed as a function of temperature (77-300 K) and particle diameter (7-28nm). The nanostructural iron powders with controlled the average dimension are obtained by changing the components of the ultrasonic field during electrochemical reduction in non-aqueous solutions (sample I-28nm, sample II-17nm, sample III-7nm). The observed EPR spectra are changed from isotropic line at 300 K to anisotropic one at 77 K, with a behavior consistent with a system of particles that undergoes superparamagnetic relaxation. The blocking temperatures: 50 K - 80 K - 100 K are obtained. Analysis of the temperature dependence of the distance between EPR line extrema, under the view of two theoretical models, allowed the evaluation of magnetic parameters, particulary of anisotropy energies (KV). The analysis of temperature dependence of the resonant magnetic field give an average value (KV) of $(0.21\pm0,018)\times10$ -14 erg, in agreement with that one obtained from the linewidth analysis.

S6.10

Production and Magnetic Properties of Ni Nanoparticles. Gang Ho Lee and <u>Yoon Tae Jeon</u>; Chemistry, Kyungpook National University, Taegu, South Korea.

We produced nanometer size Ni nanoparticles and investigated their magnetic properties. We characterized their diameters with HRTEM, magnetic properties with MPMS, and structure with XRD. The blocking temperatures increased with increasing particle diameters. They were superparamagnetic at room temperature.

86.11

Monodisperse Magnetic Iron Oxide Nanocrystals: Synthesis and Application. William W. Yu and Vicki L. Colvin; Chemistry (MS60), Rice University, Houston, Texas.

High quality iron oxide (magnetite) nanocrystals with monodisperse size distribution were synthesized by simple thermolysis of iron carboxylic salts. Several other methods with modification were also test for making magnetite nanocrystals. Prelimary application in seperation was studied.

S6.12

In Situ Synthesis of Nickel and Zinc Ferrite Particle/Organic Hybrid. Toshinobu Yogo, Yasuaki Hayashimoto and Wataru Sakamoto; EcoTopia Science Institute, Nagoya University, Nagoya University, Nagoya, Aichi, Japan.

Functional inorganic nanoparticle/organic hybrid materials have attracted attentions because of their benefitical properties of each phase. Magnetic nanoparticle/organic hybrid materials have various applications, such as recording media, printing agent, ferrofluid, magnetic resonance imaging, hyperthermia. The authors reported the synthesis of spinel ferrite particle/organic hybrid through hydrolysis of iron- and metal-organic compound below 373K [1]. This paper describes in situ synthesis of nickel- and zinc ferrite particle/polymer hybrid under controlled conditions. Spinel particle/organic hybrid was synthesized from iron acetylacetonate derivative and metal acetylacetonate (metal=Ni, Zn) below 373K. XRD analysis revealed the formation of crystalline spinel particles in the organic matrix. The crystallinity of spinel particles was dependent upon the processing conditions, and increased with increasing hydrolysis water and time. The dispersion of crystalline particles below 10 nm in the organic matrix was confirmed by TEM and SAD. The chelated bond of organic ligands to metal was observed by IR spectroscopy. The magnetic properties of the hybrids were analyzed by VSM and SQUID. The BH curve of the nano-sized spinel oxide particle/organic hybrid showed no remanence at room temperature. 1. T. Yogo, T. Nakamura and W. Sakamoto, Nanotech 2004, Vol. 3, 296 (2004).

S6.13

Synthesis and Magnetic Properties of CoPt(Ag)
Nanoparticles Assembly. Xiangcheng Sun¹, Yunhe Huang²,
Zhiyong Jia³, J. W. Harrell³ and D. E. Nikles³; ¹Department of
Nuclear Engineering, University of Michigan, Ann Arbor, Michigan;
²Physics, University of Delaware, Newark, Delaware; ³Center for
Materials for Information Technology, University of Alabama,
Tuscaloosa, Alabama.

CoPt(Ag) nanoparticles have been synthesized by high temperature polyol reduction of cobalt, platinum and silver reagents in the presence of oleic acid and oleyl amine. The effects of the addition of Ag on the magnetic and structural properties have been investigated. By varying the reaction conditions, particles with different sizes and shapes can be obtained, including some particles with cubical shape. The as-prepared CoPt(Ag) particles were well dispersed in hydrocarbon solvents, and self-assembled particles arrays were formed when deposited on Si substrates for magnetic measurements and on carbon coated grids for TEM studies. The as-prepared particles showed disordered face-centered cubic (fcc) lattice with an average diameter over 10 nm and were superparamagnetic at room temperature. The ordered face-centered tetragonal (fct) CoPt structure could be obtained by annealing at temperatures ranging from 550C to 700oC under Ar and H2 atmosphere. The coercivity of the annealed samples increased with increasing heat treatment temperatures and times. XRD patterns showed a possible mixture of ordered fct CoPt and fcc CoPt3 phases after annealing, and Ag was observed to segregate at temperatures above 500oC. The addition of Ag did not promote the phase transformation, although it did have a strong effect on the microstructure. This is in contrast to the case of chemically synthesized FePt(Ag) nanoparticles and sputtered CoPt(Ag) films where the additive Ag significantly lowered the phase transformation temperature. The shapes of the hysteresis loops including large remanence (Mr/Ms) values for the samples annealed at high temperatures suggested exchange interactions as a result of particle sintering during annealing.

S6.14

Fabrication of Uniform Metal Nanowire Arrays. Kun Yang and W. J. Yeh; Physics, University of Idaho, Moscow, Idaho.

Nickel nanowire arrays with high aspect ratio and large packing densities have been grown in thin nanochannel glass template by an electrochemical deposition method. The template initially was polished and etched to obtain parallel, uniform, hollow channels. One of surfaces of a template was then coated with a copper film layer of around 150 nm in thickness to provide an electrode to drive the electrochemical deposition. The pH value of NiSO4 aqueous solution was set to be 1 to 2 and the deposition potential was to be 1.2 V versus the saturated Calomel electrode. Obtained nickel wires were uniform and circular with diameter of down to 80 nm, depending on the size of nanochannel itself. The length of wires was controlled, typically about 140 um, depending on the deposition time. Finally, scanning electron microscopy (SEM) has been used to characterize the structures of nanowires. Magnetic properties of nickel nanowire arrays have been also investigated using a superconducting quantum interference device magnetometer (SQUID). In this paper, the authors also presented some results of cobalt nanowire arrays grown by superfluid deposition. This work was supported by NSF grant EPS-0132626 and ONR grant N000140210925.

$\underline{\mathbf{S6.15}}$

Fabrication of Vertically Well-Aligned Ferromagnetic (Zn,Mn)O Nanorods. Jeong Min Baik¹, Yoon Shon², Tae Won

Kang² and Jong-Lam Lee¹; ¹Materials Science and Engineering, Pohang University of Science and Engineering, Pohang, South Korea; ²Quantum Functional Semiconductor Research Center, Dongguk University, Seoul, South Korea.

In the past two decades, the diluted magnetic semiconductors (DMSs) have attracted much attention due to their physical properties and potential spintronic device applications, such as spin light-emitting diode, spin field effect transistor, and magnetic sensor. Many DMSs including (Ga,Mn)N, (Ga,Mn)As, and (Zn,Mn)O have been fabricated for device applications. However, no results on ferromagnetic properties of nanometer-sized materials have been reported. Ferromagnetic nanowires have considerable potential as high intensity data storage devices and nano bio-sensors due to their nanosize and anisotropic magnetic response. In this paper, we have fabricated vertically well-aligned ferromagnetic (Zn,Mn)O nanorods. Microstructural, magnetic, and optical properties of nanorods were investigated. (Zn,Mn)O nanorods were grown on 30Å-Au-coated c-plane sapphire by the reaction of pure Zn metal and MnCl₂ powder in a horizontal CVD chamber under a flow of argon gas of 100 sccm. The nanorods were grown at temperature of 700 °C and at operating pressure of 50 torr. SEM images showed that (Zn,Mn)O nanorods

have lengths up to hundreds of micrometers and diameters ranged from 100 to 200 nm. Only ZnO (00·l) and Au peaks were observed in XRD measurement, meaning that nanorods were grown with a c-axis orientation. ZnO (002) peak shifted to lower angle by 0.05° in (Zn,Mn)O nanorods. This was due to the increase of lattice constant by Mn doping to ZnO nanorods. No secondary phases were observed in HR-TEM images of (Zn,Mn)O nanorods. The hystersis loops of nanorods showed clear ferromagnetic behaviors. When magnetic fields were applied vertically to the sample plane, the coercive field increased by the factor of 35 %. In Raman spectra, E2 longitudinal optical (LO) modes were observed and shifted toward the higher energy side of the spectra by Mn incorporation.

S6.16

Ferromagnetic Mn-Doped GaN Nanowires for

Nanospintronics. <u>Doo Suk Han</u>, Chan Woong Na, Woo Sung Jang, Seung Yong Bae and Jeunghee Park; Korea University, Seoul, South Korea

Diluted magnetic semiconductors (DMS) are recently the subject of intense research because of high Curie temperature. We report Mn-doped GaN nanowires exhibiting ferromagnetism even at room temperature. The growth of single-crystalline wurtzite structured GaN nanowires doped homogeneously with about 5 atomic % Mn was achieved by chemical vapor deposition using the reaction of Ga/GaN/MnCl2 with NH3. The ferromagnetic hysteresis at 5 and 300 K and the temperature-dependent magnetization curves suggest the Curie temperature around 300 K. Negative magnetoresistance of individual nanowires was observed at the temperatures below 100 K.

S6.17

Alignment of the Cobalt Layered Nanotubes Using Magnetic Field. Daekyun Jeong, Taekwan Oh, Hyunjung Shin, Jaegab Lee and Jiyoung Kim; Advanced Materials Engineering, Kookmin University, Seoul, South Korea.

One dimensional nanostructures, such as nanowires and nanotubes, have been considered as one of the most important materials to build a block for the next generation nanosystems. However, it is not fully understand how to align them properly. In this presentation, we will demonstrate how to form one dimensional nanotube array using self-assembled monolayers(SAMs) and magnetic field on Si wafer. We fabricated zirconium oxide hybrid nanotubes on novel soluble nano-templates polycarbonate using conformal and selective deposition techniques atomic layer deposition (ALD) with SAM (Self-Assembled Monolayers). We consecutively deposited metal cobalt on the inner wall of the zirconia nanotubes. It will be also reported how to fabricate Co/ZrO2 double wall nanotubes through modification of conventional nanotemplate methods. In order to align the metal/oxide nanotubes which were separated with nanotemplate, they were wetted with hydrophilic SAMs (hexadecanthiol:HDT). Then, we patterned different types of SAMs (Octadesyl-tetrachlorosilane: OTS) which had hydrophobic property on Si wafer. OTS lines with 3μ m width were patterned by micro-contact printing on top of SiO2/Si substrate. Hydrophilic nanotubes were arrayed on Si wafer line (Si area without SAM covering), otherwise there was no nanotubes on OTS line patterns. Nanotubes were formatted to the same direction. Afterward, zirconia nanotubes with the cobalt ends were perfectly positioned with magnetic fields. The various properties of the resultant metal oxide nanotube were examined with a number of techniques of HR-TEM, FE-SEM, EDX, and AFM. We also observed nanotube direction with FE-SEM and AFM.

$\frac{S6.18}{5}$

Formation of 2-D and 3-D Arrays of Colloidal Co Magnetic Nanoparticles. Eva Majkova¹, Yuriy Chushkin¹, Livia Chitu¹, Stefan Luby¹, Alexander Satka², Vaclav Holy³, Jozef Ivan⁴, Michael Giersig⁵, Michael Hilgendorff⁵, Helmuth Metzger⁶ and Oleg Konovalov⁶; ¹Institute of Physics SAS, Bratislava, Slovakia; ²International Laser Center and Faculty of Electrical Engineering and Informatics STU, Bratislava, Slovakia; ³Institute of Condensed Matter Physics, Masaryk University, Brno, Czech Republic; ⁴Institute of Materials and Machine Mechanics SAS, Bratislava, Slovakia; ⁵Caesar Research Center, Bonn, Germany; ⁶European Synchrotron Radiation Facility, Grenoble, France.

Self-assembling of colloidal metallic nanoparticles is of considerable technological interest because of the possibility to synthesize new artificial materials with unique properties. In this work we report on the formation of ordered 2- and 3-dimensional arrays of magnetic colloidal Co nanoparticles on silicon wafer covered by 300 nm thick Si3N4 layers. Samples were prepared by deposition of Co nanoparticles (10 nm diameter) in external magnetic field up to 1 T applied perpendicular or parallel to the substrate surface. The structure of nanoparticle arrays was studied by transmission electron microscopy, high resolution scanning electron microscopy and grazing incidence small angle X-ray scattering (GISAXS) performed at ID01

and ID10 B beamlines at ESRF. In external magnetic fields (B=0.26-1 T) the Co nanoparticles form a monolayer composed of ordered 2dimensional hexagonal closed-packed arrays separated by disordered inclusions. The ordered arrays have various orientation to each other and form an in-plane mosaic structure. At appropriate colloid concentrations and in magnetic fields (B=0.26-1 T) formation of 3D superstructures (rods) composed of nanoparticles was observed. The rods 300-400 nm in diameter and several micrometer in length are aligned with the field direction. The structures of 2-D arrays and 3-D rods were studied by GISAXS. For the quantitative analysis of GISAXS spectra the distorted wave Born approximation (DWBA) approach has been applied. From the simulations of measured spectra the particle radius, the mean spacing between particles and the type of ordering were determined. Distribution of the particles in monolayers was described by a 2-D paracrystal of hexagonal symmetry and in rods by a 3-D close packing of hard-spheres models. The formation of 3-D structures in external magnetic fields could be of some importance in preparation of ordered mesomagnetic structures. The formation of rods is discussed within the framework of ferrofluid arrangement mechanism. However, the results of magnetic field formed self-assemblies of magnetic colloidal particles are dependent on the solvent evaporation time.

S6.19

Directed Self-Assembly of Nanopore Arrays and Fabrication of Nanowires with Long Range Order. Liwen Tan¹, Jia Zou², Nahyoung Kim² and Bethanie J. H. Stadler²; ¹Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota; ²Electrical and Computer Engineering, University of Minnesota, Minneapolis, Minnesota,

The fabrication of nanoparticles and structured arrays has been extensively studied in recent years for potential applications in electric, optoelectric, biological and magnetic devices[1,2]. Template synthesis has proven to be a low cost and high yield technique for producing large areas of nanowire arrays. In particular, nanoporous aluminum oxide (AAO) is ideal for the fabrication of nanowires due to its stability against high temperature and organic solvents and its compatibility with CMOS processing. [3] In this work, AAO templates with different lattice constants were prepared by directed self-assembly using stamp imprinting and anodization. The master nanoimprint stamps were Si3N4 posts that were fabricated using a simple process. First, a 100nm Si3N4 films were deposited on Si substrates by LPCVD. Second, electron beam lithography was used to define 2D hexagonal. Third, reactive ion etching (RIE) was used to remove all of the Si3N4 except for posts defined by the 2D arrays. The resulting stamp was then imprinted onto an electrochemically-polished aluminum sheet using an up to 1000lb of force. Atomic force microscopy (AFM) was used to observe that the patterns of the master stamps were transferred onto the aluminum sheet after the imprinting. Next, anodization was carried out in 1wt% phosphoric acid under varied applied voltages for different lattice constants. Scanning electron micrographs (SEM) showed that perfectly ordered porous arrays were obtained with center-center spacings of 100-500nm. Various magnetic nanowires were then grown into these ordered porous templates, including Co of various crystalline anisotropies and Co/Cu multilayers for magnetoelectronics. The magnetotransport properties of the nanowires were studied as a full array, in separate lines via patterned electrodes and individually by removal of nanowires onto separate interdigitated electrodes. These measurements enabled the separation of magnetic effects, such as shape anisotropy, crystalline anisotropy, and magnetostatic interactions of the nanowires. 1. Calvin, S., Carpenter, E.E.; Harris, V.G.; Morrison, S.A., Appl. Phys. Let, 81,3828 (2002) 2. S. Y. Chou, M. S. Wei, P. R. Kruss and P. B. Fisher, J. Appl. Phys. 76, 6673(1994) 3. Das B and Mcginnin S P Appl. Phys. A. Mater. 71, 681 (2000) Symposium S

S6.20

Self-Assembling Magnetic Nanostructures: Wires, Helices, Nanotubes of Ni Nanoparticles. Vladimir V. Kislov¹, Yury V. Gulyaev¹, Igor V. Taranov¹, Vadim V. Kashin¹, V. M. Kozhevin², D. A. Yavsin², M. A. Zabelin² and P. A. Tretyakov²; ¹Institute of Radioengineering & Electronics, Russian Academy of Sciences, Moscow, Russian Federation; ²Ioffe Physico-Technical Institute, Russian Academy of Sciences, St. Petersburg, Russian Federation.

Molecular nanoclusters (MNC) are playing increasingly important role as building blocks for electronic, catalytic, medical applications [1, 2]. The formation of self-assembling structures of magnetic nanoparticles has been discovered [3, 4] by scanning probe microscopy when depositing Ni nanoclusters on conducting (gold on HOPG) substrates. In this case magnetic Ni nanoparticles formed by laser electrodispersion technique (size of particles $\sim 2.5~\rm nm)$ form highly ordered superstructures, including helical (double helix with outer diameter $\sim 10~\rm nm$, distance between sequences $\sim 5~\rm nm$, length of such

helix is typically hundreds of nm), linear (chains of clusters) and nanotubes. The results of calculations for dipole-dipole and exchange interaction of magnetic nanoparticles support such formation of helix-like structures. The structures discovered were investigated also by STS methods, with clear demonstration of Coulomb blockade effect over single nanoclusters. Therefore, we have experimentally observed strong self-ordering effects and structure formation, including helical nanostructures and linear chains due to magnetic interaction of Ni nanoparticles with very well defined size. We have also observed nanotube-like superstructures of magnetic Ni nanoparticles. References [1] V.V.Kislov, Yu.V. Gulyaev, V.V.Kolesov, I.V.Taranov, S.P.Gubin, G.B.Khomutov, E.S.Soldatov, I.A.Maximov, L.Samuelson, "Electronics of Molecular Nanoclusters", International Journal of Nanoscience, 3, No. 1, (February 2004). [2] S.P.Gubin, Yu.V.Gulyaev, G.B.Khomutov., V.V.Kislov, V.V.Kolesov, E.S.Soldatov K.S.Sulaimankulov., A.S.Trifonov, Nanotechnology, 13, 185, (2002). [3] V.Kislov, Yu.Gulyaev, I.Taranov, V.Kashin, V.Kozhevin, D.Yavsin, M.Zabelin, P.Tretyakov and S.Gurevich, SCANNING PROBE MICROSCOPY - 2004, 2 - 6 May, Nizhny Novgorod, Russia. [4] V. V. Kislov, S. A. Gurevich, et al., Self- Assembling Magnetic Nanostructures: Chains, Helices, Nanotubes of Ni-Nanoparticles, 7-th International Conference on Nanostructured Materials, June 20 - 24, 2004, Wiesbaden, Germany.

S6.21

Transferred to S3.7

S6.22

Investigations on the Magnetic Properties of High-Coercivity Nd40Fe30Co15Al10B5 Bulk Amorphous Alloys.

<u>Lotfi Bessais</u>^{1,3}, Catherine Djega-Mariadassou¹ and N.X. Phuc²;

¹UPR209, LCMTR - CNRS, Thiais, France; ²Institut of Materials Science, NCST, Hanoi, Viet Nam; ³IUFM, Creteil, France.

The Nd-based bulk-amorphous have attracted much attention as they were regarded as new type of clustered amorphous alloys with interesting ferromagnetic properties at room temperature. Together with their good mechanical properties, these glass-forming alloys appeared as promising candidates for permanent magnet applications. In this study our objective is to improve the hard magnetic properties of the bulk amorphous Nd40Fe30Co15Al10B5 by a controlled nanocrystallization of the as-milled alloys and understand the nature of the entities responsible for this improvement. Besides Curie temperature and hysteresis loop measurements, we have carried out structural investigations by careful powder x-ray diffraction (XRD) analysis with Rietveld refinements, electron micros-copy coupled with energy dispersive x-ray (EDX) analysis, and Mossbauer spectroscopy. Nd40Fe30Co15Al10B5 bulk amorphous shows a coercivity of 650 kA/m with a Curie temperature of 645 K. The controlled nanocrystallization enhances the coercivity to 1600 kA/m and the remanence ratio is equal to 0.59. The coexistence of two crystalline magnetic phases, ferromagnetic (F) Nd2(Fe,Co,Al)14B and antiferromagnetic (AF) Nd6(Fe,Co,Al)14 are revealed by x-ray diffraction, high-resolution transmission electron microscopy, magnetization measurements, and Mossbauer spectrometry. The grain size for optimal magnetic properties is around 30 nm. The high coercivity is explained by several effects: the exchange coupling F-AF, a low dipolar interaction, and a low value of the effective demagnetizing factor.

86.23

Magnetic Susceptibility of Montmorillonite: Tri-axially Reinforced Nanocomposites from Uniaxial Magnetic Fields. Hilmar Koerner¹, Zafer Turgut², Lawrence Drummy³, Peter Mirau³ and Richard Vaia³; ¹Nonmetallic Materials Division, Univ of Dayton Res Inst, Dayton, Ohio; ²UES Inc., Dayton, Ohio; ³Materials and Manufacturing Directorate, AFRL, WPAFB, Ohio.

Phyllosilicates (smectites, 2:1 layered silicates) are important to a broad range of technologies, including viscosity and filtration control, water based drilling muds, bonding agents, pelletisation of stockfeeds, dam sealants, moisture absorbent and oil, fat or solvent refinement. Most recently, they are the foundation of polymer nanocomposite technology, with numerous products in the market place. Smectites, such as montmorillonite (MMT), consist of parallel stacks of covalent sheets comprised of a layer of octahedrally coordinated Mg and Al that is sandwiched between two layers of tetrahedrally coordinated silicon. The magnetic response is primarily determined by the concentration and distribution of paramagnetic impurities, such as 1-4% iron (Fe(II) and Fe(III)), within the two-dimensional aluminosilicate crystal structure. Depending on the geological source of the MMTs though, the layers may align parallel or perpendicular to an external magnetic field. This behavior cannot be ascribed to a simple paramagnetic response. Super Conducting Vibrating Sample Magnetometer (VSM) data indicate that the magnetic mass susceptibility χ ($\sim 7 \times 10^{-6} \text{ emu/gOe}$) of these highly purified MMTs is in good agreement with literature. However, a hysteresis indicates

the presence of antiferro- and ferrimagnetic inclusions with a remnant magnetization M_F ($\sim 0.0055~\mathrm{emu/cm^3})$ and a Curie temperature, T_C , greater than $500^{\circ}\mathrm{C}$. The macroscopic response of the system implies these must be intimately associated with every aluminosilicate layer. The implications of these observations to compositional heterogeneity within a montmorillonite layer as well as potential inorganic manipulation of the aluminosilicate layers to impart novel properties for both processing and performance will be discussed. For example, by exploiting the orthogonal magnetic susceptibility of the aluminosilicate sheet of MMTs from different deposits, a three-dimensionally reinforced morphology comprised of orthogonal alignment of aluminosilicate layers is generated from a mixture of MMTs and a uniaxial external magnetic field, opening the avenue toward directing polymer nanocomposite morphology rather than accepting shear induced or random nano-filler distributions.

S6.24

Structural and Magnetic Properties of Granular Co-ZrO₂ Films. Zorica Konstantinovic¹, Bart J. Hattink¹, Montserrat Garcia del Muro¹, Xavier Battlle¹, Amilcar Labarta¹ and Manuel Varela²; ¹Departament de Fisica Fonamental, Universitat de Barcelona, Barcelona, Spain; ²Departament de Fisica Aplicada i Optica, Universitat de Barcelona, Barcelona, Spain.

The rapid development of several film preparation techniques provides magnetic granular systems with a very well controlled nanostructure and thus, promising technological applications depending on basic properties of magnetic nanoparticles [1]. In particular, the granular films composed of Co clusters embedded in various insulating matrix are very active research topics, where the interplay between the structure and magnetism can be studied [2]. We present here ${\rm Co\text{-}ZrO_2}$ granular films growth by laser ablation [3]. By varying the preparation conditions, we are able to get wide range of Co concentration. The average composition of the samples is determined by x-ray photoemission spectroscopy and microprobe results. High resolution transmission electron microscopy (TEM) shows existence of very well define crystalline Co particles embedded in amorphous zirconia with no detectable interdiffusion boundaries. Moreover, the amorphous matrix tends to coat the metallic particles, preventing the formation of large aggregates. The mean particle size and the size distribution were determined directly from TEM images as well as by fitting low-field magnetic susceptibility and the isothermal magnetization in the paramagnetic regime to a distribution of Langevin functions. The evolution of structural and magnetic properties with Co concentration is discussed and compared with properties of Co nanoparticles in various matrices, prepared by usual sputtering technique. [1] for a review see X. Batlle, and A. Labarta, J. Phys. D: Appl. Phys. 35, 15 (2002). [2] M. Ohuma et al., J. Appl. Phys. 82, 5646 (1997); R. H. Kodama and A. S. Edelsetein, J. Appl. Phys. 85, 4316 (1999); S. Sankar et al., J. Magn. Magn. Mater. 221, 1 (2000); M. Jamet et al., Phys. Rev. B 62, 493 (2000); S. Sankar, A. E. Berkowitz, and D. J. Smith, Phys. Rev. B 62, 14273 (2000); F. Luis et al., Phys. Rev. B 65, 94409 (2002). [3] B. J. Hattink et al., Phys. Rev. B 67, 033402 (2003).

86.25

Magneto-Transport and Neutron Diffraction Studies of a Short Range Ferromagnetic Order in Amorphous Gd_xSi_{1-x} Alloys. Nikolai Chumakov¹, Victor Tugushev¹, Stanislav Gudenko¹, Olga Nikolaeva¹, Valery Ozhogin¹, Pavel Alekseev¹, Vladimir Lazukov¹, Igor Goncharenko¹, Erik Helgren² and Frances Hellman²; ¹RRC Kurchatov Institute, Moscow, Russian Federation; ²Department of Physics, University of California, Berkeley, California.

Recently, the microscopic model of compositional disorder in amorphous Gd_xSi_{1-x} alloys has been presented, describing the peculiarities of electron transport in frame of a short range ferromagnetic (FM) order and local FM transition. This approach takes into account the large non-uniformity of amorphous systems and assumes the appearance of regions with high electron concentration (drops) around the regions with enhanced Gd concentration (core droplets). Local magnetic ordering in the drops at temperatures below 50K was supposed to be experimentally observed from the conductivity on temperature dependences [1]. Magneto-transport measurements were performed at temperatures 5K - 300K in magnetic field up to 4 T. The simple assumption was made, that components of the magneto-resistivity tensor R_{xy} , R_{xx} are determined by the itinerant electron concentration n and by local field B_{in} in the region where the current flows: $1/R_{xx} \sim n$, $R_{Hall} = R_{xy}/B_{in} \sim 1/n$. This relations allow to draw the dependence of the inner $B_{in} \sim R_{xy} / R_{xx}$ acting on itinerant electrons vs. external magnetic field. The experimentally determined dependence of the $B_{in}(H)$ is in good qualitative agreement with the theoretical one, proposed within the model of a short range ferromagnetic ordering inside the drops. We estimate the mean number of Gd atoms forming the droplet ~ 10 and the saturated magnetization to be about 2.5T. This suggests that local concentration of Gd atoms inside the drops is about of five times higher than the averaged one in the matrix. Thus, the itinerant

electron transport is determined by the regions with enlarged Gd concentration, possibly by GdSi₂ nano-wires formed during sample preparation process. Neutron diffraction measurements were performed in temperature range 1.7 K - 80 K. At T < 15 K ferromagnetic (FM) correlations between Gd ions with correlation length ~ 5 A and Gd ion distances ~ 2 A have been observed. At T=1.7 K antiferromagnetic (AFM) correlations with correlation length as ~ 15 A take place. But the best fit for T = 1.7 K was obtained under an assumption that AFM and FM correlations coexist. Thus, the presented data give the direct experimental evidence that the drops with FM short-range correlations indeed exist at T < 15Kand provide an increasing of magnetization. The following strong magnetization decrease on cooling is connected with the AFM correlations between FM drops, as was observed at T < 4.2K. Analysis of neutron-inelastic-magnetic-scattering intensity allows us to conclude that almost all Gd ions are involved into the AFM correlations. In brief, we suppose that amorphous Gd_xSi_{1-x} can be considered as a new type of magnetic material, having physical properties of both disordered alloys and nano-composites. The studied system shows a conductivity of percolation type over a network of nano-wires formed by the FM drops embedded into the matrix with the much lower Gd concentration. 1. N.K.Chumakov, et. all, JMMM, V.272, p.1351.

$\frac{\underline{S6.26}}{\text{Transferred to S4.3}}$

S6.27

Magnetoresistance and TEM Characterization of MnAs/AlCrN/GaN and GaMnN/AlCrN/GaN TMR Structures. Sang Youn Han¹, Rachel Frazier¹, Brent Gila¹, Andrew Herrero¹, C. R. Abernathy¹, S. J. Peartton¹, Josh Kelly² and A. F. Hebard²; ¹Department of Materials Science and Engineering, University of Florida, Gainesville, Florida; ²Department of Physics, University of Florida, Gainesville, Florida.

Dilute magnetic semiconductors (DMS) materials have potential for use as ultra-low-power switching elements, where the bit state of the device is determined through control of electron spin. Furthermore, these materials may also allow for the integration of photonic (laser and light-emitting diodes), electronic (field-effect and bipolar transistors) and magnetic (information storage) devices on a single substrate, leading to a new class of electronic devices that offer multi-purpose functionality. Device operation using DMS structures requires two basic criteria, injecting spin polarized charge and manipulating this charge between two bands of different spin. Room temperature ferromagnetism has been reported in both GaN and AlN doped with transition metals such as Mn or Cr. However, spin injection efficiency in these systems has proven difficult to measure due to the short spin relaxation time in InGaN/GaN quantum wells in standard GaN-based light emitting diodes. An alternative method uses tunneling magnetoresistance (TMR). Control structures exhibit spin-independent tunneling, i.e a constant magnetoresistance. Replacing the insulator with a nitride-based DMS seeks to demonstrate spin-dependent tunneling using an all-semiconductor TMR stack. We have examined MR and TEM of two types of structures, using either MnAs or GaMnN room temperature ferromagnets as the injector layer and AlCrN as the insulator, grown on GaN on sapphire. The Hc of the MnAs was 500 Oe , the AlCrN: $70\,$ Oe and the GaMnN 100Oe. The MR of structures wire-bonded to reduce total resistance will be reported, along with an investigation of the interface quality that defines the ease of spin injection through the insulator.

S6.28 Abstract Withdrawn

S6.29 Abstract Withdrawn

S6.30

DNA Separation Using Gold/Magnetic Iron-oxide Composite Nanoparticles. Takuya Kinoshita¹, Satoshi Seino², Yohei Otome¹, Yoshiteru Mizukoshi³, Takashi Nakagawa¹, Tadachika Nakayama², Tohru Sekino², Koichi Niihara² and Takao A. Yamamoto¹; ¹Graduate School of Engineering, Osaka University, Suita, Osaka, Japan; ²The Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka, Japan; ³Osaka Prefectural College of Technology, Neyagawa, Osaka, Japan.

We have synthesized gold/magnetic iron-oxide composite nanoparticles and evaluated the amounts of thiol-modified single-strand oligonucleotides adsorbed onto gold. The composite nanoparticles were obtained by immobilizing single-nanosized gold grains onto nanoparticles of magnetic iron-oxide, $\gamma\text{-Fe}_2\text{O}_3$, with an average diameter of 26-nm. This immobilization was induced by irradiation with ^{60}Co gamma-rays. Fluorescein-labeled thiol-modified

oligonucleotides (15 mer) were added to an aqueous suspension containing the composite nanoparticles and allowed to be adsorbed onto the gold nanograins via S-Au bonds. After a stirring, the nanoparticle-oligonucleotide conjugates were collected by a magnet. The amount of the excess oligonucleotides remaining in the supernatant was measured using a spectrofluorometer to determine the adsorbed amount, X, as a concentration decrement. Mercaptoethanol (ME) was added to the nanoparticle-oligonucleotide conjugates redispersed in PBS in order to desorb the thiol-modified oligonucleotides from the nanoparticles. After a magnetic separation, the amount of the displaced oligonucleotides from the nanoparticles, Y, was determined by the spectrofluorometry. The amounts of the oligonucleotide adsorbed onto the nanoparticles were X=5.2 and Y= 4.8 nmol/nanoparticles-mg, respectively, which agree well with each other, which indicates that almost all the oligonucleotides connected to gold were desorbed by ME. These results show that the oligonucleotides were adsorbed onto the gold/magnetic iron-oxide composite nanoparticles via S-Au bonds and picked up by the magnet. Our composite nanoparticles are very promising for the various applications such as screening and analysis of biomolecules containing mercapto group.

S6.31

Synthesis of Different Shape Nanoparticles of Iron Oxides for Biomedical Applications. P. E. Garcia-Casillas¹, Carlos A. Martinez-Perez¹, Eduardo Perez-Eguia², Jose A. Matutes-Aquino³ and Humberto A. Monreal³; ¹Instituto de Ingenieria y Tecnologia, Universidad Autonoma de Cd. Juarez, Juarez, Chihuahua, Mexico; ²Instituto de Ciencias Biomedicas, Universidad Autonoma de Cd. Juarez, Juarez, Chihuahua, Mexico; ³Division de Ceramicos, Centro de Investigacion en Materiales Avanzados, Chihuahua, Chihuahua, Mexico.

Deoxyribonucleic acid (DNA), lineal polysaccharide and goethite were use as template to obtained different shape nanoparticles of iron oxides. The development of diversity shape particle and their magnetic properties which can lead to range for a new biomedical and biotechnology application, such as drug delivery, cell separation techniques, hyperthermia anti-cancer strategy, enzyme immobilization and biological lakes. The super paramagnetic particles were study by Transmission electron microscopy (TEM). The images showed the different morphologies such as spherical, cylindrical and rods with a diameter range between 50 to 700 nm. The values of saturation magnetization were 50 to 68emu/g. The coercivity of these particles were study by vibrating sample magnetometer (VSM). The x-ray diffraction patterns and Rietveld refinement were obtained for each sample.

86.32

Soft Magnetic Vapor Phase Co-Deposited Polymer-Metal Nanocomposites for High Frequency Applications.

Henry Greve¹, Abhijit Biswas³, Michael Scharnberg¹, Vladimir Zaporojtchenko¹, Franz Faupel¹, Michael Frommberger² and Eckhard Quandt²; ¹Chair for Multicomponent Materials, Faculty of Engineering of the Christian-Albrechts University, Kiel, Germany; ²Smart Materials Group, CAESAR, Bonn, Germany; ³Applied Science Laboratory, Institute for Shock Physics, Spokane, Washington.

Recent growing markets for mobile communication handsets and portable information tools demand new requirements for further miniaturization and lower insertion lossess for inductive components installed in Monolithic Micowave Integrated Circuits (MMIC). The possible carrier frequency range is from 800 MHz to 3 GHz including audio and intermediate frequencies. Magnetic thin-film inductors will be advantageous over currently used air-core spirals if loss generation in the magnetic film is low at the frequency of interest. Besides parasitic effects due to the design of the magnetic device, two main loss mechanisms limit the applicability of soft magnetic films at very high frequencies (> 1 GHz): (a) Eddy currents give rise to losses due to the conductivity of the materials and determine the cutoff frequency f_w together with the resistivity ρ of the material and the film thickness d. (b) Ferromagnetic resonance (FMR) occurs when the frequency of the applied rf-field matches the characteristic precession frequency of the spins. The FMR frequency is proportional to the product of the saturation magnetization \mathcal{M}_s and the in-plane anisotropic field H_k . Further, as the relation $\mu = M_s/H_k$ goes, a trade-off is required between H_k and the permeability μ . The principle requirements for such high frequency applications are therefore a large saturation magnetization M_s , a high resistive material and a low but finite anisotropic field H_k , in order to shift the FMR frequency and hence the cut-off frequency in the GHz frequency regions. Two component nanocomposites of fine mixtures of magnetic nanoparticles protected in insulating polymer matrices are promising candidates and could play important roles particularly in such magnetic high frequency applications. Appropriately volume filled isolated magnetic nanoparticles dispersed 3-dimensionally in an insulating polymer matrix possess good potential to generate quite

high Ms alongwith significantly minimised eddy current lossess due to the surrounding highly insulating zones. However, there is no easy synthesis route existing to prepare such nanocomposites. Moreover, generating appropriately high magnetic volume of such non-interacting nanoparticles in organic matrix while keeping narrow size distribution is a conflicting process and a technological challange from the preparation point of view. Here, we present a simple and one-step vapor phase co-deposition of polymer and a ternary alloy to produce softmagnetic nanocomposites with thicknesses of hundreds of nanometers of Teflon AF containing Fe-Ni-Co single domain nanoparticles. The structure of the films strongly depend on the ratio between evaporation rates of metal and polymer and also on the substrate temperature. The filling factors of the films were determined by EDX measurements and the structure observed by TEM images. We achieved a quite high M, of nearly 2 Tesla and we will also present the high frequency behaviour of the permeabilities.

> SESSION S7: Nanowires and Applications Chair: Gerd Duscher Thursday Morning, March 31, 2005 Room 3005 (Moscone West)

8:30 AM <u>*S7.1</u>

Magnetic Oxide Nanotubes for Spintronic Applications. Arunava Gupta, University of Alabama, Tuscaloosa, Alabama.

The emerging field of spintronics aims to exploit the electron spin, in addition to its charge, to create a new class of devices that scale down to much smaller dimensions. Of particular relevance are novel magnetic structures and devices that can provide additional functionality. Nanostructured materials in the form of tubes or wires can potentially open up new applications for magnetic tunnel junction (MTJ) devices consisting of two ferromagnetic electrodes separated by an insulating barrier. Most of the studies on MTJs have thus far focused on using transition metal ferromagnets (Fe, Ni, Co) and their alloys - typically with spin polarization values less than 50% - where the maximum observed tunneling magnetoresistanse (TMR) is limited to about 40-50% at room temperature. There is obvious interest in further enhancing the TMR by using materials with a higher degree of spin polarization. Half-metallic oxide systems, such as the mixed-valence manganites ($\text{La}_{1-x}A_x\text{MnO}_3$, A=Ba, Sr, or Ca), magnetite (Fe₃O₄), and chromium dioxide (CrO₂), which contain a gap in one spin band at the Fermi level and no gap in the other spin band, are expected to have a spin polarization value approaching 100%. We have reported in the past on the properties of MTJ structures fabricated using these half-metallic materials in the form of standard thin film stacks. We have now started work on the synthesis of nanotubes of these oxides with the goal of fabricating 3D MTJ nanostructures. As part of this effort we have successfully synthesized CrO₂ nanotubes by CVD using SnO₂ nanowires as a template. The ${\rm SnO_2}$ nanowires are grown by a vapor process involving the VLS method using gold as a catalyst. The structural characteristics of the CrO₂ nanotubes and their magnetic and transport properties will be reported.

9:00 AM S7.2

Two-Mode Magnetic Switching of a Ferromagnetic Nanowire-Granule-Array Embedded in a Porous Silicon Matrix. Klemens Rumpf, Petra Granitzer and Heinz Krenn; Institute of Experimental Physics, University of Graz, Graz, Austria.

Media of perpendicular magnetic anisotropy promise a wide field of applications (e.g. in magnetic storage), but their fabrication is much more complicated than that of in-plane magnetized films. Therefore a low-cost method was developed to produce metallic, vertically oriented ferromagnetic nanowires embedded in a silicon skeleton. Mesoporous silicon consisting of highly oriented (partly selforganized) channels of diameters around 60nm and depths of 30 micrometer is formed by an electrochemical etching process. In a second electrochemical process Ni is incorporated into these nanochannels by varying the electrolytic loading conditions to build a magnetic nano-wire array. Particularly the bimodal growth of pores and granules causes a peculiar two-mode magnetic switching which originates from the interplay between the strong dipolar interaction between the wires of extraordinary high aspect ratio (1:1000) and the coherent magnetization rotation of the granules. The hysteresis branches show a further steep ascent at a second rather large switching field HSW2=5.2~T. The data gathered by SQUID magnetometry are compared with calculations of this dipolar coupling field between antiparallel wires with the result HSW2 4.9 T. Measurements of the magnetization for different field directions (in the field range -7 T to +7 T) demonstrate a change of the easy axis from in-plane to perpendicular due to the morphology of the Ni wires. The filament structure of the samples is imaged by SEM, and profiles of chemical composition are scanned by EDXS and AES. The oriented and Ni-filled pores terminate abruptly at a very sharp

boundary to bulk silicon. Such interfaces may act as spin-injectors into silicon where the spin life-time is increased. The incomplete filling of the silicon skeleton with Ni opens the possibility to observe Faraday rotation in the transmitted infrared beam probed by an FTIR spectrometer.

9:15 AM <u>S7.3</u>

Dilnted Magnetic Semiconductor Mn:GaN Nanowires. Heon-Jin Choi¹, Han-Kyu Sung^{1,2}, Yun-Ki Pyun², Young-Mi Paik², Joonyeon Jang², Yong-Ju Park², Rongrui He³ and Peidong Yang³; ¹School of Advanced Materials Science and Engineering, Yonsei University, Seoul, South Korea; ²Materials Science and Technology Division, Korea Institute of Science and Technology, Seoul, South Korea; ³Department of Chemistry, University of California, Berkeley, Berkeley, California.

Diluted magnetic semiconductors (DMSs) represent the most promising candidates for simultaneously manipulating both charge and spin in a single semiconductor medium that leads to the exciting area of spintronics. Theoretical studies indicate that transition metal doped GaN possesses ferromagnetic transition temperature higher than room temperature by hole mediated ferromagnetism that would be advantageous for many of the proposed spintronic applications. Many experiments have already been carried out to demonstrate such hypothesis, however, significant controversy exists over the possible magnetic impurity phase separation for many of these thin-film studies. Moreover, nonequilibrium molecular beam epitaxial growth process of thin-film results many defects that act as a hurdle to realize the hole mediated ferromagnetism. Herein we report on the fabrication of single crystalline diluted magnetic semiconductor nanowires Ga1-xMnxN by in-situ doping. The nanowires, which have diameters of 50 - 100 nm and lengths of up to tens of micrometers, show ferromagnetism with Curie temperature above 300 Kelvin. Yielding magnetoresistance (MR) up to 200 K from single nanowire transistor structures, p-n junction characteristics and electroluminescence (EL) from nanowire-based light emitting diode structures indicates the unique characteristics of p-type Mn:GaN diluted magnetic semiconductor nanowires. Based on the experimental results, the possible application as building blocks for spintronic devices as well as fundamental aspect of DMS Ga1-xMnxN nanowires will be discussed.

9:30 AM <u>S7.4</u>

Synthesis of Magnetic Self-Assembled Nickel-Rich Oxide Nanowires using a Novel Electrochemical Process.

Yash Bhargava¹, Shawn Thorne¹, Todd Mintz¹, Velimir Radmilovic², Yuri Suzuki¹ and Thomas Devine¹; ¹Materials Science and Engineering, UC Berkeley, Berkeley, California; ²National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, Berkeley, California.

We present a novel self-assembly nanowire synthesis technique capable of producing nickel-rich oxide nanowires of lengths up to 20um and diameters as small as 5nm. The method was discovered inadvertently while examining stress corrosion cracking of Alloy 600 (nickel- 15.5a/o Cr, 8a/o Fe) in a PWR reactor environment. The nanowires have been grown on substrates of Alloy 600 and 70-30 nickel-chromium exposed to oxidizing conditions in 1500psi pressurized water with 2ppm lithium and 1200ppm boron at temperatures ranging from 238°C to 288°C. Oxidizing conditions can be controlled in one of two ways: by controlling the dissolved oxygen concentration, or by use of a potentiostat. Nanowires, of metal-oxide composition in particular, have generated interest lately because of their wide range of applications including gas sensors, optoelectronic devices, and biodetection agents. Clearly, synthesis techniques which make use of self-assembly are attractive for the production of these nanowires, however, the wires must also incorporate properties that can be functionalized in potential applications. Consequently, the nanowires that we have been able to synthesize are exciting for their functional properties. Compositional studies performed via energy dispersive spectroscopy (EDS) using a transmission electron microscope indicate the content of the nanowires grown on Alloy 600 to be 49a/o oxygen, 47a/o Ni, and 4a/o Fe. Their oxide composition gives the nanowires an inherent resistance to aggressive environments, such as ones found in the body or other aqueous solutions, in contrast to simple metal nanowires, which are susceptible to corrosion in such environments. Most importantly, analysis with a SQUID magnetometer indicates that the wires are ferrimagnetic. Hysteresis curves verify their ferrimagnetic nature and shows that they have a coercivity of approximately 80 Oe and a remnant field of 0.027 A*m2/kg (or emu/g). Our current research is focused on the expansion of this growth technique to other substrate compositions in order to achieve control over electrical, magnetic, and electrochemical properties of the nanowires.

9:45 AM <u>S7.5</u>

Self-Assembly Synthesis and Characterization of FePt Nanowires. Yanglong Hou¹, Hiroshi Kondoh¹, Renchao Che², Erika,

O. Sako¹, Masaki Takeguchi² and Toshiaki Ohta¹; ¹Department of Chemistry, School of Science, The University of Tokyo, Tokyo, Japan; ²National Institute for Materials Science, Tsukuba, Japan.

One-dimensional (1D) magnetic nanoscale materials have become the focus of intensive research due to their promising applications in high-density data storage and nanoelectronics. Here we present the one-step synthesis of free-standing FePt nanowires by means of the reduction of platinum complexes and the thermodecomposition of iron pentacarbonyl in a solvothermal process. The as-synthesized FePt nanowires have a diameter tunable in the range of 40-60 nm and a length of several micrometers, depending on the crystallization temperature and reaction time. The formation mechanism and evolution of nanowires are discussed. The magnetic investigation indicates that as-synthesized FePt nanowires are superparamagnetic at room temperature. Annealing at elevated temperatures, in which no noticeable sintering was observed, made each wire have a dense structure with a smooth surface and well crystalline characteristic, and enhanced their room temperature coercivity up to ~ 2.8 kOe. The morphology evolution of nanowires in in-situ annealing process was also observed by a transmission electron microscope (TEM). The FePt nanowires are expected to be used as blocks for magnetic storage devices due to their high magnetocrystalline anisotropy and flexibility for manipulation.

10:30 AM *S7.6

Multifunctional Magnetic Nanowires for Biotechnology and Biomagnetics Applications. <u>Daniel H. Reich</u>, Physics and Astronomy, Johns Hopkins University, Baltimore, Maryland.

Nanoscale magnetic particles are playing an increasingly important role as tools for manipulating and studying biological systems. With appropriate surface functionalization, they enable the selective application of magnetic forces to a wide range of cells, sub-cellular structures and biomolecules. The majority of nanoparticles currently in use for biomagnetic applications are spherical in shape, but a promising new approach is to use asymmetric, multisegment magnetic nanoparticles, such as electrodeposited nanowires. These nanowires are highly elongated rod-shaped particles, with diameters from 10 nm to 1 micron, and lengths up to tens of microns, whose magnetic and other physical properties can be tuned by controlling the size, shape composition, and juxtaposition of the segments. They can be given multiple and spatially resolved chemical specificity through the use of ligands that bind selectively to the different segments. I will discuss our recent results on fabrication and design of multicomponent nanowires, selective functionalization, and manipulation and assembly of nanowires for applications including magnetic separations, biosensing, cell patterning, tissue engineering, and targeted intracellular delivery.

11:00 AM S7.7

Self-assembled Iron Nanowires: Electrical and Magnetic Properties. Tim Patrick Huelser^{1,2}, Hartmut Wiggers², Joerg Knipping² and Axel Lorke¹; ¹Dept of Physics, University Duisburg-Essen, Duisburg, NRW, Germany; ²Dept of Mechanical Engineering, Institute of Combustion and Gasdynamics, Duisburg, NRW, Germany.

We report on the self-assembled formation of iron nanowires from iron nanoparticles. The particles with a diameter of about 35 nm are synthesized by thermal decomposition of iron pentacarbonyl Fe(CO)5, in a hot wall reactor [1]. The size is chosen to produce single domain ferromagnetic particles. As a result, the magnetic forces between the particles dominate the collision behavior, leading to iron nanowires of up to of 300 μm length. HRTEM and EELS investigations give detailed morphological, structural and chemical information. They reveal the presence of an iron oxide shell with a thickness of 3-4 nm at the particle surface, originating from self limiting oxidation under ambient conditions. For electrical characterization, single iron wires have been thermophoretically sampled on interdigital capacitors. For the investigation of collective properties, larger amounts of material were pressed into discs. Both systems of iron nanowires have been measured under ambient gas atmospheres and various temperatures using impedance spectroscopy and DC measurements methods. Magnetic investigations were made using SQUID magnetometry. Impedance spectroscopy on single nanowires indicates both capacitive and ohmic contributions to the overall conductivity. The data have been analyzed for different temperatures using R-RC elements for fitting. The resistance of a 20 μm long wire consisting of 35 nm sized particles was $5\cdot 10^5\Omega$ at room temperature corresponding to a specific resistance of $3.2\cdot 10^{-5}$ ohmm. Impedance measurements of the discs show ohmic behavior in the temperature range between 323 K and 523 K. Investigations in H_2 atmosphere at 673 K exhibit increasing conductivity due to sintering and reduction of the oxidic shell, as also confirmed by scanning electron microscopy. Magnetization measurements reveal a saturation magnetization of 160 emu/g at 5 K, which is more than 70% of the iron bulk value and is comparable to

iron particles investigated by Huber et al. [2]. The magnetic and morphologic data are in good agreement when the magnetic moment of the oxidic shell is taken into account. [1] J. Knipping, H. Wiggers, B.F. Kock, T.P. Huelser, B. Rellinghaus and P. Roth Nanotechnology 15 (2004) 1665-1670 [2] D.L. Huber, E.L. Venturini, J.E. Martin, P.P. Provencio and R.J. Patel; Journal of Magnetism and Magnetic Materials 278 (2004) 311-316

11:15 AM $\underline{S7.8}$

Formation and Characterization of Magnetic Multilayer Ni/Cu Nanoanowires. Ru-Shi Liu^{1,2}, Sung-Chun Chang¹, Shu-Fen Hu^{2,3} and Chao-Yuan Huang^{2,4}; ¹Department of Chemistry, National Taiwan University, Taipei 106, Taiwan; ²Taiwan Spin Research Center, National Chung Cheng University, Chia-Yi 621, Taiwan; ³National Nano Device Laboratories, Hsinchu 300, Taiwan; ⁴Institute of Materials Manufacturing, Chinese Culture University, Taipei 111, Taiwan.

A highly ordered composite nanowires with multilayer of Ni/Cu, have been fabricated by pulsed electrodeposition into nanoporous alumina membrane. The diameter of wires can be easily controlled by pore size of alumina, ranging from 30 to 100 nm. The applied potential and the duration of each potential square pulse determine the thickness of the metal layers. The nanowires have been characterized by transmission electron microscopy (TEM), magnetic force microscopy (MFM), and vibrating sample magnetometry (VSM) measurements. From the result of MFM analysis, the magnetic multilayer nanowire indicates unique magnetic property. The MFM images indicate that every ferromagnetic layer separated by Cu layer was present as single-domain magnet. Due to the existence of those magnets, the nanowires can orient and spin in circles as nano stir-bar by applied magnetic fields. This technique has potential for use in the measurement and application of magnetic nanodevices.

11:30 AM <u>S7.9</u>

Magnetoresistive La0.67Sr0.33MnO3 Nanowires. <u>Chao Li</u>, Bo Lei and Chongwu Zhou; Dept. of EE, Univ. of Southern California, LA, California.

We report the synthesis of novel La0.67Sr0.33MnO3 nanowires and the observations of intriguing magnetoresistance phenomena, including colossal magnetoresistance, anisotropic magnetoresistance and low-field magnetoresistance. These nanowires were synthesized by depositing an epitaxial shell of La0.67Sr0.33MnO3 onto MgO nanowires, thereby rendering single-crystalline MgO/La0.67Sr0.33MnO3 core-shell structures. Transport studies on these nanowires have revealed a remarkable metal-insulator transition at 325 k, accompanied by room-temperature colossal magnetoresistance $\sim 10\%$ under a one-Tesla magnetic field. In addition, anisotropic magnetoresistance was observed at room temperature with a 1.4% resistance variation between magnetic fields parallel and perpendicular to the nanowire. Furthermore, polycrystalline La0.67Sr0.33MnO3 have been obtained by tuning the synthesis condition, leading to a low-field magnetoresistance up to 16 % at 0.06 T. This is attributed to the spin-dependent scattering of polarized electrons at the grain boundaries, with underlying physics similar to the giant magnetoresistance. Our study demonstrates the advantages of one-dimensional magnetic oxide nanowires and may lead to novel applications in the near future.

11:45 AM S7.10

Magnetite (Fe3O4) One-dimensional Nanowires and Nanotubes: Synthesis and Magnetoresistance. Daihua Zhang, Zuqin Liu, Song Han, Chao Li, Bo Lei and Chongwu Zhou; EEEP, University of Southern California, Los Angeles, California.

Fe3O4 possesses a variety of intriguing properties such as 100% spin polarization and ultrahigh Curie temperature. Nanostructures based on Fe3O4 may provide ideal template model for fundamental research and find potential applications in nanoelectronics and spintronics. We present our recent studies on the synthesis and magnetoresistance of single crystalline Fe3O4 core-shell nanowires and nanotubes. Homogeneous Fe3O4 nanowires/tubes with controllable length, diameter and wall thickness were synthesized via pulsed laser deposition technique. The material composition and stoichoimetry have been carefully examined and confirmed with a variety of characterization techniques including X-ray diffraction, transmission electron microscopy, energy-dispersive X-ray spectroscopy and X-ray photoelectron spectroscopy. These novel structures have rendered unique opportunities to investigate the transport behavior and magnetoresistance property of Fe3O4 in its one-dimensional form. Room temperature magnetoresistance of $1\sim2\%$ was observed in the Fe3O4 nanowire/tubes under a magnetic field of B = 1.8 T, which has been attributed to the tunneling of spin-polarized electrons across the anti-phase boundaries.

SESSION S8: Biomagnetic Materials and Applications I Chair: Lynn Kurihara Thursday Afternoon, March 31, 2005 Room 3005 (Moscone West)

1:30 PM *S8.1

Synthesis and Surface Modification of Monodisperse Magnetic Nanoparticles for Biological Applications. Shouheng Sun^{1,2}, Hao Zeng², Heng Yu², David Robinson³, Guanxiong Li³, Shan Wang³ and Robert White³; ¹Department of Chemistry, Brown University, Providence, Rhode Island; ²IBM T. J. Watson Research Center, Yorktown Heights, New York; ³Stanford University, Stanford, California.

We present chemical synthesis and surface modification of monodisperse magnetic nanoparticles for potential applications in bio-recognition. Biocompatible dispersions of magnetic nanoparticles have been used widely in bimolecular labeling and biological imaging, sensing and separation in recent years. These applications require that the particles be superparamagnetic at room temperature, and monodisperse for uniform biodistribution, bioelimination and contrast effects. The Co and Fe based magnetic nanoparticles, including metallic Co, Fe, CoFe and oxide MFe2O4 nanoparticles, have high magnetic moment, and thus sufficient sensitivity for magnetic detection. With proper functionalization, they can be useful candidates as magnetic probes for biomolecule identification. We have developed various synthetic procedures for making monodisperse magnetic nanoparticles. Using a combination of surfactants, such as oleic acid/oleyl amine, to control nanoparticle growth and stabilization, we can tune the size of the nanoparticles to obtain an optimum magnetic signal for sensor detection. By controlling particle surface chemistry and synthetic conditions, we can also produce multi-functional nanoparticles with either core/shell-structured particles, such as Fe3O4/AgSe or Fe3O4/FePt, or dumbbell-structured particles, such as Fe3O4-Ag. We can further transform the oleic acid/oleylamine capped, hydrophobic nanoparticles into hydrophilic ones by using tetramethylammonium hydroxide, bi-functional thiol molecules, or multi-functional polymeric molecules. These hydrophilic nanoparticles are both chemically and magnetically stable in phosphate buffer solution at neutral pH, and can withstand DNA denaturing and hybridization conditions. They are suitable as magnetic probes for highly sensitive bio-detection. Acknowledgement: The work is supported in part by DARPA under grant No. N00014-01-1-0885.

2:00 PM <u>*S8.2</u>

Novel Medical Ferrite Nanobeads with Bioactive Molecules Immobilized Strongly onto the Surfaces. Masanori Abe¹, Nobuhiro Matsushita¹ and Hiroshi Handa²; ¹Department of Physical Electronics, Tokyo Institute of Technology, Tokyo, Japan; ²Department of Biological Information, Tokyo Institute of Technology, Yokohama, Japan.

At as low as 4-25°C and on nearly neutral conditions (pH=7~9), we successfully immobilizes bioactive molecules onto surfaces of Fe-ferrite (an intermediate between ${\rm Fe_3O_4}$ and $\gamma{\rm -Fe_2O_3}$) nanobeads ($\sim\!10{\rm nm}$ in size) during the synthesis of the ferrite beads from an aqueous solution containing ${\rm Fe^{2+.3+}}$ ions and the bioactive molecules. We found that the molecules were fixed onto the ferrite surface intermediated by particular amino-acid or similar-structured molecules having a pair of COOH groups per molecule. We called such molecules "connector" molecules. The COOH pairs of connector molecules made strong chemical bonds with ferrite surface. We established a methodology to fabricate medical ferrite nanobeads with physiologically active molecules (e.g. antibodies, anticancer drugs, DNA's, proteins, etc.) strongly immobilized on the ferrite surface intermediated by the connector molecules. Innovative, medical applications of our novel nanobeads will be presented.

2:30 PM S8.3

A Nanoscale, Magnetism-Based Platform for Kinetic Studies of Biomolecular Binding Events at Surfaces. Marc P. Raphael, Lynn K. Kurihara, David J. Pena, Michael M. Miller, Joseph A. Christodoulides and Jeff M. Byers, Code 6363, Naval Research Laboratory, Washington, District of Columbia.

From biosensors to signal transduction at the cellular membrane, there is scarcely a problem in biology that would not benefit from a deeper understanding of the kinetics of binding events between biomolecules. The stochastic nature of these events, often on millisecond timescales, make them particularly difficult to study with the more traditional techniques developed around the optical microscope. To this end, we are working to develop a nanoscale interface between molecular biology and electronics which is based upon the manipulation of biofunctionalized magnetic particles. Polyol chemistry and electrochemistry have been utilized to grow magnetic particles of varying compositions (Co, Fe, Ni, FeCo) ranging in

diameter from tens of nanometers to microns. The particles are biofunctionalized with a protein and can be positioned on a substrate by the use of lithographically-patterned, current-carrying wires. Actuation of the protein-tagged particles across a current-carrying wire is readily recorded by using fluorescently-tagged proteins and far-field fluorescence microscopy. Furthermore, we demonstrate the ability to place the proteins corresponding ligand within 50 or $200~\mathrm{nm}$ of the lithographically defined electronics by means of either dip-pen nanolithography or electron-beam nanolithography, respectively. This geometry will allow for the forming and breaking of receptor-ligand bonds by the actuation of the protein-tagged magnetic particle to and from the vicinity of the ligand. Current work includes optimization of particle actuation using biotinylated surfaces and avidin-tagged particles, as well as the fabrication of Hall-cross magnetometers beneath the surface for electronic detection of the receptor-ligand binding event.

2:45 PM <u>S8.4</u>

Attenuating Protein Adsorption with Vibrating Nanowires as a way to Inhibit In Vivo Biofouling of Implanted Sensors. Kristy Ainslie¹ and Michael Pishko¹.².³; ¹Chemical Engineering, Penn State, University Park, Pennsylvania; ²Material Science, Penn State, University Park, Pennsylvania; ³Chemistry, Penn State, University Park, Pennsylvania.

The research described here investigates the hypothesis that nanoarchitecture contained in a nanowire array is capable of attenuating the adverse host response, biofouling, generated when a medical devices are implanted in the body. This adverse host response generates an avascular fibrous mass transfer barrier between the device and the analyte of interest, disabling the sensor. Numerous studies have indicated that surface chemistry and architecture modulated the host response. These findings lead us to hypothesize that nanostructured surfaces will significantly inhibit the formation of an avascular fibrous capsule. We are investigating whether vibrating magnetostrictive nanowires, formed in nanowire arrays, can prevent protein and cell adhesion. Magnetostrictive nanowires are fabricated by electroplating a ferromagnetic metal alloy into the pores of a nanoporous alumina template. The ferromagnetic nanowires are made to vibrate by altering the magnetic field surrounding the wires. Enzyme-linked immunosorbent assay (ELISA) and other protein assays were used to study protein adhesion on the nanowire arrays. These results display a reduced protein adhesion per surface area of static nanowires. The vibrating nanowires show a further reduction in protein adhesion, compared to static wires. Studies were also preformed to investigate the effects nanoarchitecture has on cell adhesion. These studies were performed with both static and vibrating nanowires. Protein adhesion studies have shown that nanostructures wire arrays modulate protein adhesion in vitro.

3:30 PM <u>*S8.5</u>

Designing Magnetically "Colorful" Nanolabels for Biochemical Sensors. Mark Tondra, NVE Corporation, Eden Prairie, Minnesota.

Magnetic nanoparticles have been used as labels in a wide variety of biochemical assay applications. Their role is to be bound to the species of interest (e.g. DNA strand or an e-coli bacterium) through a defining biochemical bond. The nanoparticle, once bound, serves as a magnetically detectable and quantifiable object which enables the detection of the species of interest by making a magnetic measurement. NVE and others have been especially interested in adapting spintronic detectors to this type of assay. Spintronic detectors have several potential advantages for consumer and commercial biosensor diagnostic devices, including cost, size, power, ruggedness, and usability. All of these magnetic techniques are competing against the dominant optical methods. These involve capturing photons emitted by bound labels. The photons can be generated through fluorescence, reflection, radiation, and so forth. One advantage of optically based systems, for some applications, is the ability to have optical labels that give off different colors. Specifically, the optical detection system can simultaneously measure the quantity of several different assay species in the same sample. It may be possible for properly designed magnetic nanoparticles to fill in this technology gap, or even go beyond what optical labels can do. This paper will discuss the prospects for using magnetic labels with "colors". The operation of real spintronic detectors, particularly the modes of magnetic excitation and field distribution at the detectors, will be described. Key parameters are the excitation field orientation, frequency, and amplitude. This magnetic system description will form the basis for identifying properties of magnetic nanoparticles that make them distinguishable in a simultaneous assay. Promising distinguishing magnetic "color" properties include total moment, remenance, anisotropy, shape and size.

4:00 PM S8.6

Enzymatic Clipping of DNA Wires Coated with Magnetic

Nanoparticles. Joseph Kinsella and Albena Ivanisevic; Purdue University, West Lafayette, Indiana.

This study describes how ss-DNA coated with magnetic nanoparticles remains biologically active and accessible to the BamH1 restriction enzyme. Long DNA molecules were coated with 2-pyrolidinone capped Fe₂O₃ magnetic nanoparticles in solution using the electrostatic interactions between the negative charge along the phosphate backbone of the DNA and the positive charge of the nanoparticles. The resulting DNA templated magnetic nanowires were stretched onto either silicon oxide or dip-pen nanolithography patterned polyelectrolyte templates using a receding meniscus procedure. The coated, stretched and surface bound wires were incubated with the BamH1 restriction enzyme which specifically recognizes any strand containing the GGATCC base sequence and clips the DNA at that position. We show that, despite the presence of the nanoparticles along the length of the DNA, the enzyme is still able to recognize the cleavage sites and effectively clip the wire at these locations. This has been confirmed via atomic force microscopy (AFM) studies as well as magnetic force microscopy (MFM) studies.

4:15 PM <u>S8.7</u>

A TEM Study Biological Distribution of Superparamagnetic Iron Oxide Nanoparticles. Jikou Zhou¹, Lauren Heyward¹, Carola Leuschner², Challar Kumar³, Josef Hormes³ and Wole O. Soboyejo¹; ¹Mechancial and Aerospace Egnineering, Princeton University, Prineton, New Jersey; ²Pennington Biomedical Research Center, Louisiana State University, Baton Rouge, Louisiana; ³Center for Advanced Microstructures and Devices, Louisiana State University, Baton Rouge, Louisiana.

A TEM study is carried out to investigate the biological distribution of Superparamagnetic Iron Oxide Nanoparticles (SPION) and SPION conjugated with Luteinizing Hormone and Releasing Hormone (LHRH) that are injected into nude mice bearing MDA-MB-435S.luc tumors for thirty days. After sacrificing the mice, tumors and periphery organs including livers, lungs and kidneys are collected for transmission electron microscopy (TEM) analysis. These show that LHRH conjugated SPIONs are distributed mainly in tumors, and associated metastases developed in the lungs in this study. The TEM analysis is consistent with results obtained through Prussion Blue Reaction. The results suggest that LHRH conjugated SPION can be used to target both primary cancer cells and their metastases in vivo.

4:30 PM <u>*S8.8</u>

Properties, Surface Functionalization and Cytotoxicity of Chemically Synthesized Iron Oxide and Nickel Ferrite Nanoparticles. Gan-Moog Chow, ¹ Molecular Engineering of Biological and Chemical Systems, Singapore-Massachusetts Institute of Technology Alliance, Singapore, Singapore; ²Department of Materials Science, National University of Singapore, Singapore, Singapore, Singapore.

Nanoparticles find many potential biomedical applications including cell labeling, drug targeting, gene delivery, hyperthermia therapy and biosensors. Often the surfaces of nanoparticles are functionalized using surfactants in order to achieve the desirable properties in various applications. Recent highlights on potential environmental and health impacts of nanoparticles have raised concerns of toxicity being a critical factor on evaluating their applications. In this talk, examples of some of our work on magnetic nanoparticles for biomedical applications are presented. Nanoparticles of ferrimagnetic iron oxide and nickel ferrite were synthesized using solution chemistry. The surfaces of these nanoparticles were functionalized with either carboxyl group or oleic acid. The degree of adsorption of anticancer drug (carboplatin) on nanoparticles was controlled by varying surfactant chemistry and solution pH. The dependence of magnetic properties on surface functionalization was studied. The effects of size and surface properties of these nanoparticles on cytotoxicity were also investigated.

SESSION S9: Biomagnetic Materials and Applications II Chair: Marc Raphael

Chair: Marc Raphael Friday Morning, April 1, 2005 Room 2020 (Moscone West)

9:00 AM *S9.1

Effect of Magnetic Nanoparticles and Their Surface Terminiations on Alignment of Biological Molecules. L. J. Martinez-Miranda¹, I. Koh², S. Ehrman² and T. Pulliam-Holoman²; ¹Department of Materials Science and Engineering, University of Maryland, College Park, Maryland; ²Department of Chemical Engineering, University of Maryland, College Park, Maryland,

We have observed the effects of adding magnetic nanoparticles consisting of $\mathrm{SiO_2/Fe_2O_3}$ to E.coli and how it responds to an applied magnetic field when combined with the particles, compared to how it responds alone. The purpose of this work is to investigate if we can use the magnetic nanoparticles to target specific sites in the cell so they can be opened selectively. To look at the magnetic response we use x-ray scattering. The response to the magnetic field with the magnetic nanoparticles is at least one order of magnitude smaller than when the E.coli is all alone. By varying the surface termination we have found out that we can vary the intensity and the sign of the response. The same effect can be seen if we study a liquid crystal with different magnetic nanoparticles and surface terminations.

9:30 AM <u>S9.2</u>

In Vitro Analysis of Magnetic Field-Induced Superparamagnetic Nanoparticle Dynamics in Extracellular Matrix. Sam J. Kuhn¹, Chun-Cheng R. Chen¹, Dennis E. Hallahan^{2,1} and T. D. Giorgio^{1,3}; ¹Biomedical Engineering, Vanderbilt University, Nashville, Tennessee; ²Radiation Oncology, Vanderbilt University, Nashville, Tennessee; ³Chemical Engineering, Vanderbilt University, Nashville, Tennessee.

Dispersion of large therapeutic constructs such as gene therapy vectors or radiotherapy seeds poses a significant barrier to successful treatment of solid tumors. Intratumoral injection of gene therapy vectors results in transgene expression along the needle track. We propose the use of intratumorally delivered therapy linked to superparamagnetic (SPM) nanoparticles (NPs) in conjunction with an external magnetic field as a means to modulate tissue biodistribution. We have demonstrated magnetically induced mobility of SPM NPs in an in vitro extracellular matrix (ECM) system. The mobility characteristics of 250nm diameter SPM NPs were studied in an in vitro model system consisting of purified extracellular matrix (ECM) from murine sarcoma. SPM NPs were layered onto the surface of purified ECM in a glass vial. The glass vial was placed on the surface of a NdFeB 1T surface strength magnet. SPM NP velocity was calculated from contrast-based tracking of SPM NP mobility by digitally captured, time-lapse optical imaging. The magnetic field was mapped in space throughout the experimental field at a resolution of 1.5 mm. The diameter of the SPM NPs utilized in this study is near the pore size of the ECM collagen fibers. A porous media model, the traditional representation for studying nanostructure mobility in the interstitial space, poorly models NP mobility at or near the matrix pore size. SPM NPs in the absence of an external magnetic field were unable to enter the ECM gel. PEG coating of the NPs increased the velocity of the NPs three fold through the ECM when compared to NPs with a silica-dextran surface. NP velocity was dependent on the concentration of NPs applied to the system, suggesting that a single-NP theoretical model may not appropriately model NP-ECM interactions. Our data suggests that SPM NP mobility at or near the pore size of the ECM matrix is best approximated by modeling the SPM NP behavior as a Stokesian droplet. The NPs introduced into the system appeared to form a loose aggregate capable of deforming the ECM gel, allowing transit of the NPs. The velocity of the PEG-coated NPs under the influence of an external magnetic field (1T, -140mT gradient) was approximately 2 mm / hr. This velocity was sufficient to provide distribution of SPM NPs through a significant tissue volume within a clinically relevant time frame of 12 to 24 hours.

10:15 AM *S9.3

Magnetic Nanoparticles for Biotechnology and Biomedicine. Quentin Pankhurst, London Centre for Nanotechnology, University College London, London, United Kingdom.

The physical principles underlying some current biotechnological and biomedical applications of magnetic nanoparticles will be reviewed. Starting from well known basic concepts, and drawing on examples from biotechnology and biomedicine, the relevant physics of magnetic materials and their responses to applied magnetic fields will be surveyed. The way these properties are controlled and used will illustrated with reference to: (i) magnetic separation of labelled cells and other biological entities; (ii) therapeutic drug, gene and radionuclide delivery; (iii) radio frequency methods for the catabolism of tumours via hyperthermia; (iv) contrast enhancement agents for magnetic resonance imaging applications; and (v) the role of biogenic magnetic iron compounds in neurodegenerative diseases such as Alzheimer's disease and Huntington's disease. Future prospects for applications involving the use of magnetic nanoparticles will also be discussed.

10:45 AM S9.4

Gold/Magnetic Iron-oxide Composite Nanoparticles for Biological Applications. <u>Takao A. Yamamoto</u>¹, Takuya Kinoshita¹, Satoshi Seino², Yohei Otome¹, Yoshiteru Mizukoshi³, Takashi Nakagawa¹, Tadachika Nakayama², Tohru Sekino² and Koichi Niihara²; ¹Graduate School of Engineering, Osaka University, Suita, Osaka, Japan; ²The Institute of Scientific and Industrial Research,

Osaka University, Ibaraki, Osaka, Japan; ³Osaka Prefectural College of Technology, Neyagawa, Osaka, Japan.

We have developed original techniques for immobilizing gold nanograins onto the surface of magnetic iron-oxide nanoparticles by stimulating reduction of aqueous gold ions with gamma-rays or ultrasonics. TEM observation indicated that many single-nanosized gold grains surround each iron-oxide nanoparticle. A reddish color due to the surface plasmon absorption of nano-sized gold was attracted by a magnet, which indicates an intimate connection of gold and iron-oxide. We have confirmed that our nanoparticles adsorb mercapto groups and are magnetically attracted by executing separation tests employing glutathione as a test molecule including mercapto group. In addition, two amino acid possessing sulfur, cystine and methionine, were selectively adsorbed via S-Au bonds and separated from the other amino acids without sulfur. These results indicate that our composite nanoparticles would be suitable materials for biological applications such as screening of biomolecules, cell separation and drug delivery because its ability to bind to biomolecules via S-Au bonds without any linker compounds.

11:00 AM <u>S9.5</u>

Manipulation of Non-Magnetic Materials in Ferrofluid Containing Media. Derek S. Halverson¹, B. B. Yellen^{2.1} and G. Friedman¹; ¹Electrical & Computer Engineering, Drexel University, Philadelphia, Pennsylvania; ²Division of Cardiology, Children's Hospital of Pennsylvania (CHOP), Philadelphia, Pennsylvania.

While robotic assembly has been very effective in manufacture of systems consisting of many different components on the macroscopic scale, it is difficult to extend this technique to micro- and nano-scale. Techniques inspired by self-assembly of structures in natural settings appear to be a promising alternative. Massively parallel assembly methods based on laser tweezing, electric and ultrasonic fields, gravitation, flow, morphological templates and chemical recognition have been explored. Among all these different assembly methods few offer the possibility of programmable assembly and manipulation of micro- or nano-components. Dielelectrophoretic manipulation is one of the methods particularly suitable to programmable manipulation of components. However, methods involving charged surfaces [1] place restrictions on the chemistry that can be used with them. A novel method of massively parallel programmable manipulation and assembly of non-magnetic components such as colloidal particles will be discussed in this presentation. In this method, non-magnetic components are dispersed inside ferrofluid (with 1% volume concentration of magnetic nanoparticles). A pattern of magnetic field maxima and minima on a surface is created using a pattern of magnetized thin Co islands and an external uniform magnetic field. Non-magnetic particles are attracted to regions of magnetic field minima through a process that can be called negative magnetophoresis forming highly ordered patterns. The pattern of magnetic field minima can be re-arranged though re-magnetization of magnetic islands on the surface or through changing the direction of the external uniform magnetic field. Rotation of the uniform magnetic field can also cause movement of the pattern of the magnetic field minima resulting in controlled massively parallel movement of non-magnetic colloidal particles. This allows for dynamic control of objects in a massively parallel or individual manner based on the needs of the user. This work investigates the effectiveness of above massively parallel programmable manipulation and assembly method as the size of colloidal particles is reduced to the 100 nanometer scale. Magnetic islands on the order of 200 nanometers square to 2.2 micron by 200 nanometers are fabricated in different patterns to evaluate their capabilities to array fluorescent nanoparticles and move them in specific directions along the surface. It also tests their ability to create convergent and divergent flow for the collection or separation of nanoparticles. It also investigates the possibility to prevent the passage of particles into specific locations on a surface such as would be needed in various lab-on-a-chip sorting applications. [1] Hau W.L.W., Trau D., Sucher J., Wong M., Zohar Y, Micro Flow Patterns on Demand Using Surface Chemistry Technology, Proceedings of the IEEE-2002, 475-478, 2002

11:15 AM <u>S9.6</u>

Use of Ferrofluid Patterns as Diffusion Masks.

<u>Derek S. Halverson</u>¹, B. B. Yellen^{2.1} and G. Friedman¹; ¹Electrical and Computer Engineering, Drexel University, Philadelphia, Pennsylvania; ²Division of Cardiology, Children's Hospital of Pennsylvania (CHOP), Philadelphia, Pennsylvania.

Patterning surfaces by different materials has been the subject of significant interest in connection with combinatorial chemistry and material studies. Commercially important examples of such patterned substrates are bio-molecular micro-arrays such as DNA and protein chips. Fabrication of such devices has focused primarily on two techniques: photolithographically enabled in-situ synthesis and ink jet type printing technology. Photolithography is capable of producing

small spot size and high resolution. However, it is an expensive process requiring multiple masking steps with accurate masking registration and alignment. The type of molecules that can be synthesized in photolithographic fabrication is also limited. Printing provides greater flexibility in the choices of molecules that can be deposited on the substrate. However, it is limited by a relatively large spot size and resolution. A new method to selectively mask local deposition of molecules on a surface will be described in this presentation. This method is based on using the phenomenon of controlled aggregation of magnetic nanoparticles in aqueous solution (ferrofluid). In this method a pattern of magnetizable islands on a solid surface in conjunction with externally applied uniform magnetic field is used to create strong magnetic field maxima and minima on the surface. Ferrofluid aggregation in the regions of local magnetic field maxima will be shown to mask diffusion of molecular species to the surface and their subsequent binding. Repeating the process of ferrofluid aggregation with different molecular species after changing the pattern of magnetization on the surface through magnetic recording techniques, it is possible to pattern mutually aligned spots of different molecules on the surface without the use of chemical solvents, heat, UV radiation or other potentially harmful influences typically involved in photolithographic patterning. In the work presented here, magnetic patterns are first prepared in the form of rectangular Co islands of micrometer dimensions. These islands are subsequently magnetized in the same direction. The glass substrate between the Co islands is functionalized with biotin and placed inside a 1% by volume commercially available ferrofluid solution. Application of external uniform field is shown to cause aggregation of ferrofluid nanoparticles between the islands. Fluorescent streptavidin is then placed into the solution. It is shown that fluorescent molecules attach to the biotinylated substrate only in those regions that remain unmasked by the ferrofluid aggregates. The results demonstrate feasibility of ferrofluid masking technology.