Thursday Afternoon, October 18, 2007

Magnetic Interfaces and Nanostructures

Room: 619 - Session MI-ThA

Magnetic Semiconductors II

Moderator: J. Shen, Oak Ridge National Laboratory

2:00pm **MI-ThA1 Ferromagnetism and Dopant Ordering in Semiconducting, Epitaxial Ti-doped α-Fe_2O_3 Hematite**, ***T.C. Droubay***, Pacific Northwest National Laboratory, *A. Celik-Aktas*, University of Wisconsin-Milwaukee, *K.M. Rosso*, Pacific Northwest National Laboratory, *S.M. Heald*, Argonne National Laboratory, *S.H. Cheung, C.M. Wang*, Pacific Northwest National Laboratory, *M. Gadjardziska-Josifovska*, University of Wisconsin-Milwaukee, *S.A. Chambers*, Pacific Northwest National Laboratory

The classical visualization of a ferromagnetic semiconductor is the random substitution of a fraction of the original atoms within the semiconductor lattice with magnetic atoms, most commonly transition metal ions. An alternate approach which has not garnered much attention until recently is the ordered substitution of non-magnetic metal ions into an otherwise antiferromagnetic semiconductor lattice. Ti-doped α-Fe_2O_3 has been suggested as such a material if Ti(IV) substitutes preferentially in one magnetic sublattice, effectively creating a ferrimagnetic semiconductor. To examine the ordering more fully, we have used oxygen plasma-assisted MBE to grow Ti-doped hematite on α-Al_2O_3(001) for various dopant levels between the endpoints Fe_2O_3 and $FeTiO_3$. Excellent heteroepitaxy was achieved by first growing a Cr_2O_3 buffer layer to grade the lattice mismatch. Fe was predominantly found to be in the +3 charge state by Fe K-shell XANES and Fe 2p photoemission, except at concentrations nearing x = 0.15. Ti was found to be exclusively in the +4 charge state and to uniformly substitute for Fe(III) in the hematite lattice by Ti K-shell XANES and EXAFS, accompanied by a significant site distortion. The resultant epitaxial films for low dopant concentration are magnetic at room temperature albeit with a fraction (~0.5 μ_B/Ti atom) of the 4 μ_B/Ti saturation magnetization expected if a magnetic ordered phase had nucleated exclusively. DFT predicts that the magnetically ordered and magnetically random structures are nearly iso-energetic which explains the weak normalized moment. We have investigated the atomic structure of the low-doped epitaxial ferromagnetic films using high-resolution TEM and electron diffraction analysis. HRTEM and electron diffraction confirm the lack of long-range chemical ordering of Ti along the [001] direction. HRTEM images show weak but discernable lines in $(Ti_xFe_{1-x})_2O_3$ along the growth direction with an average in-plane periodicity of ~0.94nm. Electron diffraction patterns corroborate this ordering by displaying additional diffraction spots perpendicular to the growth direction. These satellite spots are suggestive of Ti dopant ordering in the basal plane. A proposed atomic model of the dopant ordering including DFT calculations will be discussed in relation to the observed experimental electronic and magnetic properties.

2:20pm **MI-ThA2 Carrier-Dopant Exchange Interactions in Colloidal Mn^{2+}:ZnO Quantum Dots**, ***S.T. Ochsenbein***, *K.M. Whitaker, W.K. Liu, D.R. Gamelin*, University of Washington

Magnetically doped semiconductor nanocrystals present an interesting motif for possible spintronics applications. In such so-called diluted magnetic semiconductors (DMSs) the interaction between charge carriers and the dopant ions is the key factor defining their spintronics functionality. Ferromagnetism in some DMSs is attributed to carrier-mediated interaction between the dopant ions for example,[1] and thus depends strongly on carrier-dopant interactions. The effect of quantum confinement in DMS nanostructures on carrier-dopant interactions has been the subject of theoretical considerations,[2] but experimental investigations are scarce. We present experimental results addressing electron-Mn^{2+} interactions in colloidal Mn^{2+}:ZnO nanocrystals. Photochemical injection of conduction band electrons[3] allows the interaction between these quantum confined electrons and the Mn^{2+} ions to be studied by electron paramagnetic resonance (EPR) spectroscopy and magnetic measurements. The microscopic origins of the resulting perturbed magnetic properties will be described.

[1] Dietl, T.; Ohno, H.; Matsukura, F., Phys. Rev. B 2001, 63, 195205.
[2] Bhattacharjee, A. K., Phys. Rev. B. 1998, 58, 15660.
[2] Liu, W. K.; Whitaker, K. M.; Kittilstved, K. R.; Gamelin, D. R., J. Am. Chem. Soc. 2006, 128, 3910. .

2:40pm **MI-ThA3 Growth and Properties of Epitaxial Co- and Mn-doped ZnO Films**, ***T.C. Kaspar***, *T.C. Droubay, Y.J. Li, M.H. Engelhard, P. Nachimuthu, V. Shutthanandan, Z. Zhu*, Pacific Northwest National Laboratory, *S.M. Heald, D.J. Keavney*, Argonne National Laboratory, *C.A. Johnson, D.R. Gamelin*, University of Washington, *S.A. Chambers*, Pacific Northwest National Laboratory

Doping ZnO with transition metal ions may be a promising route to realize dilute magnetic semiconductors which are ferromagnetic above room temperature. Although several groups have reported room temperature ferromagnetism in both Co:ZnO and Mn:ZnO, significant controversy persists as to whether the observed ferromagnetism is intrinsic to doped ZnO or is due to extrinsic factors such as secondary phase formation. Of particular concern is the formation of ferromagnetic Co metal clusters in Co:ZnO, and potentially ferromagnetic Zn-Mn oxides in Mn:ZnO. The difficulty lies in the small quantity of secondary phase required to explain the observed weak ferromagnetism, often comprising less than 5% of the dopants (which themselves are generally only 10% or less of the total cations in the material). Conventional materials characterization techniques, such as x-ray diffraction (XRD) and transmission electron microscopy (TEM), can be insensitive to the small volume fraction of secondary phase involved, making detection difficult. Spectroscopic techniques, particularly x-ray absorption (XAS), can provide much more information on the charge state and local environment of the dopant. However, the detection limit at the K-edge is about 5% of the dopants for metal formation; oxide secondary phases can be more difficult to detect. A related issue concerns the determination of the location and role of p-type dopants in ZnO, since ferromagnetic ordering is only expected in Mn:ZnO when the material is p-type. Here we present a detailed study of Co:ZnO and Mn:ZnO thin films deposited by pulsed laser deposition. The ZnO quality and majority dopant behavior were probed by conventional characterization techniques such as XRD, TEM, and XAS, which indicated dopant substitution for Zn in ZnO. The possibility of a small fraction of secondary phase formation was investigated with several techniques including x-ray linear dichroism, Raman spectroscopy, and x-ray photoelectron spectroscopy (XPS) sputter depth profiling. In Co:ZnO, localized Co metal formation at the film surface under reducing conditions was not detectable by K-edge XAS but was clearly observed by XPS sputter depth profiling. The presence and location of the potential p-type dopants N and Li were investigated by secondary ion mass spectrometry and nuclear reaction analysis. The implications of secondary phase formation on ferromagnetism in Co:ZnO and Mn:ZnO will be discussed.

3:00pm **MI-ThA4 Manipulating Ferromagnetism in Co^{2+}:ZnO by Controlling Interstitial Zinc Concentrations**, ***C.A. Johnson***, *D.R. Gamelin*, University of Washington

Demonstration of reproducible intrinsic high-temperature ferromagnetism in diluted magnetic semiconductors (DMSs) is an important step toward their use in devices. Recently it has become apparent that understanding the defects in Co^{2+}:ZnO is paramount to understanding the microscopic origins of its ferromagnetism. We will describe that Co^{2+}:ZnO films can be made ferromagnetic by annealing under Zn vapor to create the Zn_i lattice defect.[1] Oxidation of the Zn-treated Co^{2+}:ZnO films at elevated temperatures results in a controlled quenching of the ferromagnetism as the Zn_i migrates out of the lattice and is oxidized.[2] These changes can be followed kinetically using both magnetic measurements and magnetic circular dichroism spectroscopy. These results demonstrate that ferromagnetism of Co^{2+}:ZnO thin films can be controlled by controlling Zn_i concentrations and provide new insights into the microscopic origins of this interesting magnetism.

[1] Schwartz, D.A. and D.R. Gamelin, Adv Mat, 2004. 16 2115-2118.
[2] Kittilstved, K.R., Schwartz, D.A., Tuan, A.C., Heald, S.M., Chambers, S.A., Gamelin, D.R., Phys Rev Let, 2006. 97 0372203.

3:40pm **MI-ThA6 Optimal Dopant Control of High-Tc Diluted Magnetic Semiconductors via Subsurfactant Epitaxy or n-p co-doping***, ***Z. Zhang***, Oak Ridge National Laboratory and University of Tennessee **INVITED**

Recent developments of diluted magnetic semiconductors (DMS) seem to suggest that one must rely on nano-phase separations inside the DMS films of III-V and column-IV semiconductors in order to achieve high magnetic ordering temperatures (Tc>300K). Here we present two conceptually new and intriguing approaches to enhance substitutional doping of Mn in Ge and Si, based on first-principles calculations. One is via subsurfactant epitaxy, the other is via n-p co-doping. In the former case, the resultant materials exhibit homogeneous distributions of substitutional Mn dopants with Tc>300K, as observed experimentally. In the latter case, we find that co-doping faciliates the efficiency of Mn substitutional occupation, and

observe dramatically enhanced anisotropy in the ferromagnetic coupling between the dopants. These results will be compared in connection with the recent developments of the field emphasizing the importance of nano-columns within the DMS.

*Work done in collaboration with Wenguang Zhu, Hanno Weitering, Changgan Zeng, Enge Wang, Tim Kaxiras, Mina Yoon, Klaus van Benthem, and Matthew Chrisholm. Supported by US. NSF (Grant No. DMR-0606485), the NSF of China, and by the Division of Materials Sciences and Engineering, Office of Basic Energy Sciences, US Department of Energy, under contract DE-AC05-00OR22725 with ORNL, managed and operated by UT-Battelle, LLC.

4:20pm **MI-ThA8 Formation Mechanism of Self-assembled Nanocolumns in (Ge,Mn) Epitaxial Films***, ***W. Zhu***, University of Tennessee, *M. Yoon,* University of Tennessee and ORNL, *Z. Zhang*, ORNL and University of Tennessee

The spatial distribution of magnetic dopants in diluted magnetic semiconductors is critical in determining the magnetic property of the materials. Traditionally, the magnetic dopants were viewed to be homogeneously distributed in the host semiconductors. Recently, self-assembled Mn-rich nanocolumns were observed experimentally in (Ge,Mn) epitaxial films, which exhibit remarkable magnetic properties.[1] Here, we propose a microscopic formation mechanism for the nanocolumns, involving the interplay between the electrostatic attractions of oppositely charged Mn ions and effective long-range repulsions due to elastic effect. Based on first-principles calculations and kinetic Monte Carlo simulations, we show that the proposed mechanism can successfully explain the formation of the self-assembled Mn-rich nanocolumns in the (Ge,Mn) epitaxial systems. We also discuss the potential applicability of the proposed model to other related systems.

*Work supported by US. NSF (Grant No. DMR-0606485), and by the Division of Materials Sciences and Engineering, Office of Basic Energy Sciences, US Department of Energy, under contract DE-AC05-00OR22725 with ORNL, managed and operated by UT-Battelle, LLC.

[1] M. Jamet et al., Nat. Mater. 5, 653 (2006); A. P. Li et al., Phys. Rev. B 75, 201201(R) (2007).

4:40pm **MI-ThA9 Ferromagnetism in Mn Doped Ge Thin Films**, ***J. Yu***, *J. Lu, K.G. West, L. He, R. Hull, S.A. Wolf*, University of Virginia

Ferromagnetism in Group IV semiconductors produced by transition metal doping is of great interest due to their potential applications in spintronics. In this study, we use ion implantation to introduce Mn ions into Ge. 0.5~4 at. % Mn ion was implanted into 200 nm Ge thin films. Both single implantation and dual implantation were used to prepare samples. The dual ion implantation was performed at 75 °C to improve the uniformity of Mn distribution and avoid formation of a ferromagnetic Mn5Ge3 phase which forms at higher implant temperatures. The implantation damage to Ge was healed by rapid thermal annealing at temperatures ranging from 300 to 800 °C in forming gas. Moment vs. Temperature showed that the ferromagnetic transition temperature was ~ 60 K for 4% samples annealed at 300 °C for 1.5 minutes. The saturation moment at 5K is 0.12 Bohr magnetons per Mn. Transport measurements using the Van der Pauw method were performed to study the correlation between the magnetization and resistivity of Mn:Ge. Significant magnetoresistance and anomalous Hall effect were observed on samples annealed at 300 °C for 1 and 1.5 minutes. The normal and anomalous Hall coefficients are both calculated and confirmed with transport measurement. Cross-section TEM study is underway to determine the phase composition and the distribution of Mn ions in this dual implanted sample annealed at 300°C.

5:00pm **MI-ThA10 Atomic and Electronic Structure of Manganese Alloys on Ge(100) Surface**, ***H. Kim***, *G.E. Jeong, K.H. Chung, S.-J. Kahng*, Korea University

Ferromagnetic metals on semiconducting surfaces are promising for spintronics application. The surface structures of Mn5Ge3(111) alloy on Ge(100) surfaces were studied with scanning tunneling microscope. The plateau structures of Mn5Ge3 were prepared by solid phase epitaxy. Clear hexagonal atomic structures were observed on top of the plateau structures. In support of diffraction experiments and previous theoretical predictions, we were able to confirm that the plateau structures are Mn5Ge3 alloys with the top surfaces along (111) directions. Several atomic patterns, with strong bias-energy dependence, were observed in topography images. As the patterns are compared with theoretical predictions, it is believed that the atomic structures of second layers were observed at certain energy levels. Three types of defect structures were observed in STM images, whose atomic structures will be discussed.

Authors Index

Bold page numbers indicate the presenter