# Dilute Magnetic Semiconducting Oxide Thin Films and Nanostructures

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***Project Summary:***

We have initiated a multidisciplinary project to investigate the growth, properties and optimization of dilute magnetic semiconducting oxides for spintronics applications. Specifically, our efforts are focused on transition metal-doped ZnO and anatase ($TiO_2$) thin films and heterostructures. At the same time that our individual JIN applications were funded last year, four of the PIs involved (Krishnan, Gamelin, Olmstead and Chambers) also submitted a coordinated proposal to the NSF in response to a national initiative on Spin Electronics. This proposal entitled "Varied synthetic approaches to the development of room-temperature ferromagnetic and semiconducting oxide nanostructures for silicon-based spintronics" was also funded. Naturally, there is now significant synergy between the JIN activity and the NSF-funded research. However, there is one principal difference. The NSF activity will eventually focus on the integration of such oxide films with silicon whilst the JIN activity will continue to explore new methods of growing a viable room-temperature dilute magnetic semiconductor. Fundamental magnetic/transport measurements, structural characterization and the role of dimensionality are being initially emphasized. In keeping with our educational mission a graduate student (Brad Roberts) has been brought on board. He is being trained and will eventually take over this project as part of his doctoral dissertation in MSE.

In a search for new methods for growing diluted magnetic semiconductors (DMS), superlattices of Co/ZnO, with varying nominal thickness of metal (2-10Å) and semiconductor (2-20Å), were prepared by ion beam sputtering. The films were characterized by x-ray diffraction/reflectivity, Rutherford back-scattering and x-ray photoelectron spectroscopy. Magnetic, transport and magneto-transport measurements were carried out over a temperature range of 2.5-300K. With decreasing Co thickness and increasing ZnO thickness in the multilayer stack, the properties of the samples undergo a crossover from those of granular metallic Co/semiconductor multilayers to a DMS superlattice.

RBS studies showed the Co/Zn atomic ratio in the range from 0.1 to 1.25, a slight excess of oxygen compared to stoichiometric ZnO, and about 5% of aluminum (donor dopant). Fig. 1 shows an XRD pattern for a $(ZnO_{20Å}Co_{2Å})_{25}$ sample on a glass substrate, which reveals the nano-crystalline structure of ZnO, and no peaks of metallic Co. Samples with larger relative Co content indicated diffuse Co reflections. Fig. 2(a-d) show the zero field cooled and field cooled magnetization measurements as a function of temperature in a field of 20 Oe for samples with fixed Co layer thickness and varying ZnO thickness. Because of the limited solubility of metal, higher relative content of Co results in a granular multilayer structure, which demonstrates magnetic blocking phenomena and superparamagnetism. Magnetic blocking results in separation of the ZFC and FC curves, and a maximum in the ZFC susceptibility near the blocking temperature (Fig. 2a,b). The sample with the thickest ZnO layers behaves as a diluted magnetic semiconductor, i.e. its magnetization does not go to zero at high T, and remains approximately constant in the temperature range 40-300 K (Fig 2d). M vs H dependences for this sample are hysteretic both at 10 K and 300 K as shown in Fig. 2(e), where the slope at large fields is dominated by the substrate. While closed loops with no hysteresis typical of superparamagnetic materials are observed in samples a-c above the blocking temperature. Analyses of the temperature dependences of resistivity (Fig. 3 (a-d)) for these multilayers indicate a crossover from dominating 2D variable range hopping (VRH) conduction via metallic granules ($\ln R \sim 1/T^n$, $n>1/2$) to 3D VRH ($n<1/2$) to VRH with no single exponent in the whole temperature range, close to that of Al-doped ZnO film with no Co added (not shown here). Magnetoresistance was measured with magnetic field perpendicular to the film plane. These measurements also show a

crossover from negative magnetoresistance in superparamagnetic state (Fig. 4(a-b)) to a behavior typical of doped semiconductors with positive magnetoresistance (Fig. 4(d)).

In summary, we have managed to prepare ZnO:Co DMS films, with the Curie temperature higher than room temperature, by alternating deposition of ZnO and Co multilayers on the atomic scale. We have also studied the properties of superparamagnetic granular multilayers and observed a 2D-3D transition in both VRH and magnetization in these films. Further studies will include modification of the films by thermal treatment in controlled atmosphere, optimization of the sputtering process and advanced measurements (optical MCD and synchrotron radiation experiments) in collaboration with the other members of our team.

***Publications, Presentations and Proposals:***

1. A.B. Pakhomov, Bradley Roberts and Kannan M. Krishnan, Dimensional transitions in granular magnetic Co/ZnO multilayers, Phys. Rev. B, in preparation
2. Diluted magnetic semiconductor Zn(Co)O superlattices by ion beam sputtering deposition, Appl. Phys. Lett., in preparation.

**Figures:**

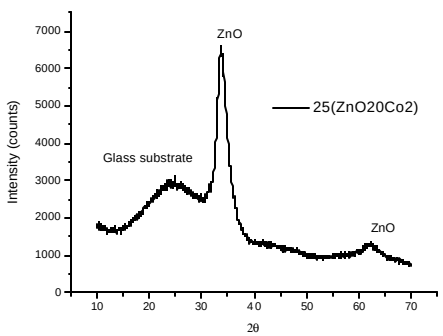


**Fig. 1. XRD pattern for sample 25(ZnO20/Co2).**

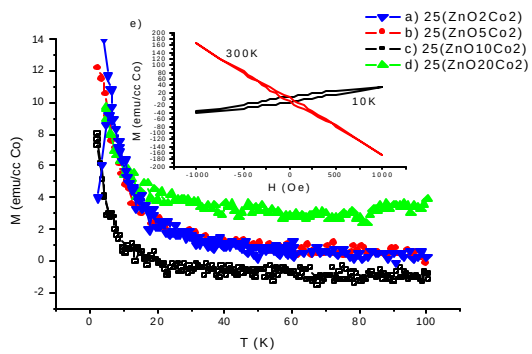


**Fig. 2. (a-d) ZFC and FC magnetization at 20 Oe, (e) Hysteresis loops for sample (d).**

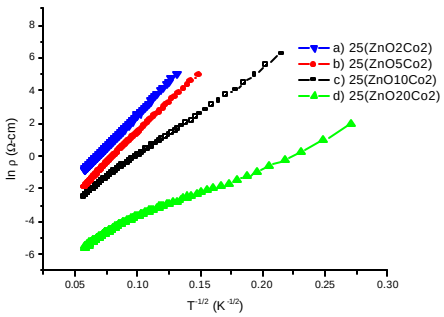


**Fig. 3. Temperature dependences of resistivity.**

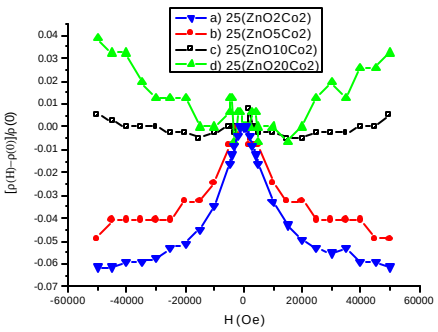


**Fig. 4. Magnetoresistance for different compositions at low temperature.**