Synthesis, Magneto-Optical and Electronic Spectroscopies of Nanocrystalline Ferromagnetic Oxide Semiconductors

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Project Summary:

Recent promising work in the field of spintronics has shown that internal incorporation of cobalt into TiO_2 *(anatase),* grown by high-vacuum Oxygen Plasma Assisted Molecular Beam Epitaxy (OPA-MBE), results in a ferromagnetic dilute magnetic semiconductor (DMS) above room temperature. Such a high Curie temperature material would be quite useful for controlling the electron spin state in future generation spin dependent computation. However, solution chemistry offers a complementary technique and alternative approach to such spintronics materials. We propose developing and studying a colloidal solution chemical approach which has the added benefits of: 1) dopant ion oxidative state control achieved through Sol-Gel chemical techniques 2) accessibility of ultraviolet-visible (UV-VIS) characterization probes able to elucidate dopant speciation and 3) the low cost of sol-gel chemical precursors and equipment. Nanophase doped samples offer the unique processability of colloidal samples along with possessing the potential to be used as nanoscale building blocks for larger hetero-structures.

We have used Sol-Gel micellar nanoreactors to synthesize doped TiO_2 colloids. Because the initial hydrolysis step of the Sol-Gel process, through the nucleophilic addition of water, is so rapid, internalization of a dopant species may only be achieved by slowing down the hydrolysis step via limiting the number and type (free or bound) of water molecules present. Pressure treatment of the doped nanoparticles yields nanocrystalline material as seen in figure 1. Fitting the width of the (101) peak in the spectrum at $2\theta=25.2°$ using the scherrer relation yields an average particle diameter of 4 nm. The crystallinity of the nanophase doped titania and the crystallite size is further verified by Transmission Electron Microscopy (TEM) *taken at PNNL* shown in figure 2.

The magnetic properties of these nanocrystals were measured to investigate their DMS behavior. Ferromagnetism has been observed in these samples as evidenced by the room temperature hysteresis of the magnetic moment shown in figure 3. The saturation moment of the Co is lower than that of the thin film indicating a large concentration of paramagnetic Co ions. However, this behavior is to be expected, as the inter-granular electronic coupling between nanocrystallites is significantly weaker than the homogenous OPA-MBE grown thin films. The coupling can be increased by high temperature sintering of the particles into larger crystallites. This is demonstrated in figure 3 where the saturation moment is increased by a near order of magnitude upon sintering the particles from an average 4 nm to an average 22 nm. Such an electronic coupling between Co ions is thought to be necessary for the itinerant electron exchange interaction resulting in ferromagnetism. Tuning such an interaction will be important for the rational design of DMS hetero-structures. The ligand field absorption spectroscopy and magneto-optic circular dichroism spectroscopy is shown in figure 4. The chemical doping procedure significantly changes the band structure of the TiO_2 shifting the absorption bandgap edge from UV into the visible region resulting in a light orange-brown color of the doped colloidal samples. The inflection change in the doped absorption spectra between 16 000 and 24000 cm^{-1} are the *d-d* or ligand-field bands of the Co dopant. These bands appear to be obscured by the bandgap absorption edge extending into the visible, likely a result of sub-bandgap defect states arising in the perturbed TiO_2 band structure. The Magnetic Circular Dischroism (MCD) is also shown in figure 4. This data, taken at 5 K, verifies the existence of the ligand-field bands and the feature shows an increasing intensity with increasing field. This mixing verifies that the Sol-Gel derived $Co_{0.023}Ti_{0.97}O_2$ nanocrystals are indeed dilute magnetic semiconductors. Shown in figure 5 is the absorption and MCD spectra of $Zn_{1-x}Co_xO$ grown by MOCVD at PNNL by A. Tuan and S. Chambers. The saturation magnetization fit inset shows the spin state (S=3/2) and magnetization of the charge-transfer transition illustrating magnetization of the ZnO band states by the dopant and therefore DMS behavior.

Publications, Presentations and Proposals:

1) J. Daniel Bryan, Daniel R. Gamelin, *Manuscript in Preparation for the Journal of the American Chemical Society,* May 2003.
2) A. Tuan, S. Chambers, J. D. Bryan, D. R. Gamelin, et al. *Phys Rev. B.* Submitted 2003.
2) Proposal citing this work submitted to the American Chemical Society- Petroleum Research Fund-Alternative Energy Research Post-Doctoral Fellowship. – *Proposal chosen for funding.*

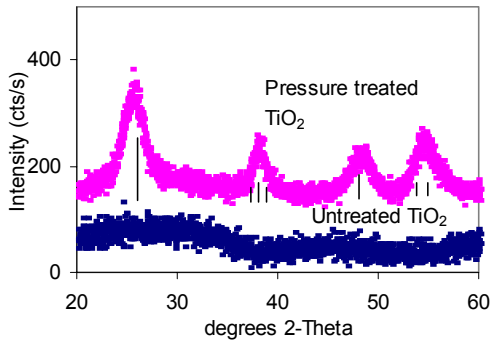

Figure 1. Powder X-Ray diffraction of untreated and pressure treated nanocrystalline $Co_{0.023}Ti_{0.097}O_2$. Vertical lines represent position of bulk anatase peaks

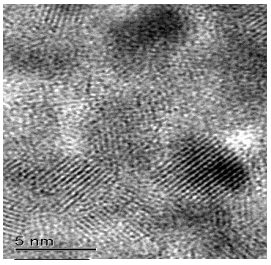

Figure 2. TEM image of $Co_{0.023}Ti_{0.97}O_2$ nanocrystals *taken at EMSL-PNNL*

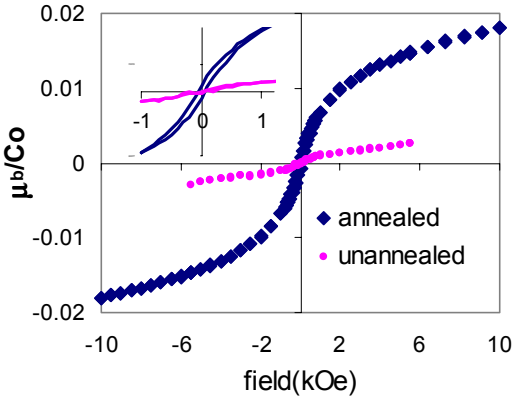

Figure 3. 300 K hysteresis loop for $Co_{0.023}Ti_{0.097}O_2$. The annealed sample was heat treated in air at 600 C for ½ hour, XRD analysis gave particle sizes ~20 nm.

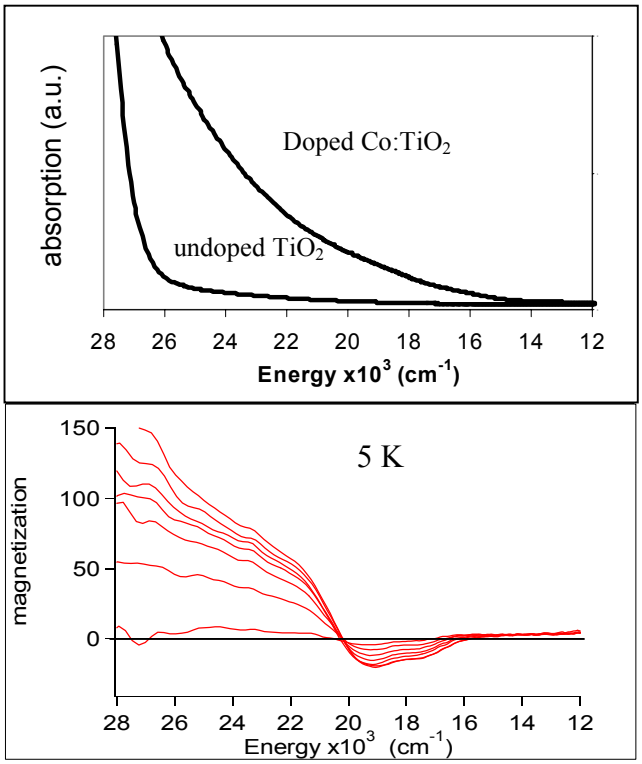

Figure 4. Electronic absorption (upper) and magnetic circular dichroism (lower) spectrum of $Co_{0.023}Ti_{0.97}O_2$.

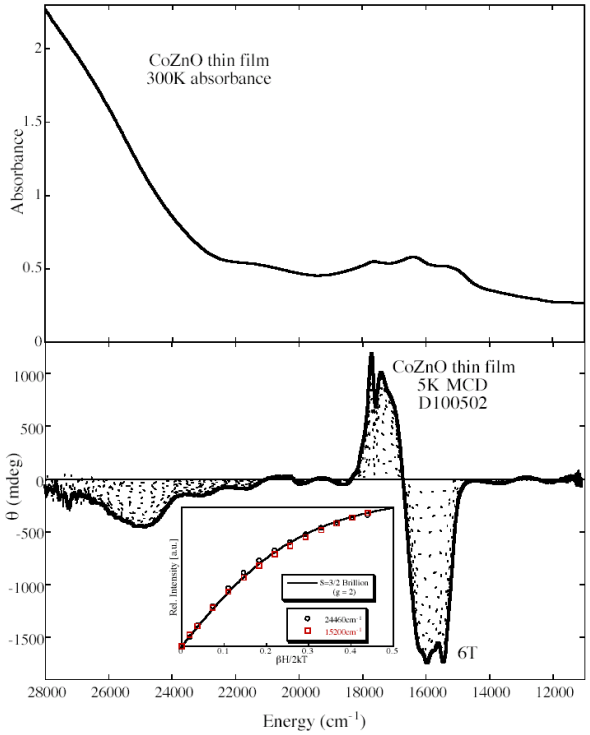

Figure 5. Absorption (upper) and MCD spectra (lower) of Co:ZnO thin film.Inset shows magnetization saturation for 24460 cm^{-1} and 15200 cm^{-1} fit to a spin 3/2 Brilluoin function