Synopsis

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Thesis Title: Microstructural, Magnetic, Optical and Transport Studies of Nanostructured Diluted Magnetic Semiconducting $Zn_{1-x}TM_xO$ (TM = Co, Mn, Fe, Ni) and Manganite $La_{0.7}Ba_{0.3}MnO_3$ Spintronic Oxides

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In **chapter 1,** *Spintronics*, or *spin electronics*, refers to the study of the role played by electron (and more generally nuclear) spin in solid state physics, and possible devices that specifically exploit spin properties instead of or in addition to charge degrees of freedom. For example, spin relaxation and spin transport in metals and semiconductors are of fundamental research interest not only for being basic solid state physics issues, but also for the already demonstrated potential these phenomena have in electronic technology. The prototype device that is already in use in industry as a read head and a memory-storage cell is the giant – magneto-resistive (GMR) sandwich structure, which consists of alternating ferromagnetic and nonmagnetic metal layers. Depending on the relative orientation of the magnetizations in the magnetic layers, the device resistance changes from small (parallel magnetizations) to large (antiparallel magnetizations). This change in resistance (also called magneto-resistance) is used to sense changes in magnetic fields. Recent efforts in GMR technology have also involved magnetic tunnel

junction devices where the tunneling current depends on spin orientations of the electrodes.

Major challenges in this field of *spintronics* that are addressed by experiment and theory include the optimization of electron spin lifetimes, the detection of spin coherence in nanoscale structures, transport of spin-polarized carriers across relevant length scales and heterointerfaces, and the manipulation of both electron and nuclear spins on sufficiently fast time scales. In response, recent experiments suggest that the storage time of quantum information encoded in electron spins may be extended through their strong interplay with nuclear spins in the solid state. Moreover, optical methods for spin injection, detection, and manipulation have been developed that exploit the ability to precisely engineer the coupling between electron spin and optical photons. It is envisioned that the merging of electronics, photonics, and magnetics will ultimately lead to new spin-based multifunctional devices such as spin-FET (field effect transistor), spin-LED (light-emitting diode), spin RTD (resonant tunneling device), optical switches operating at terahertz frequency, modulators, encoders, decoders, and quantum bits for quantum computation and communication. The success of these ventures depends on a deeper understanding of fundamental spin interactions in solid state materials as well as the roles of dimensionality, defects, and semiconductor band structure in modifying these dynamics. If we can understand and control the spin degree of freedom in semiconductors, semiconductor heterostructures, and ferromagnets, the potential for high-performance spin based electronics will be excellent.

In **chapter 2**, we have discussed about the fabrication of dc resistivity set – up and complex impedance measurement set – up, fabricated in our laboratory. Additionally,

a brief discussion about the fabrication of room temperature home made vibrating sample magnetometer (VSM) set – up (actively involved during fabrication) and pulsed laser (excimer laser, KrF) deposition thin film unit (actively involved during development) was also presented. We have presented some characterization techniques, such as x - ray diffraction (XRD), transmission electron microscopy (TEM), high - resolution field emission scanning electron microscopy (FE-SEM), energy dispersive analysis of x-ray (EDAX), thermo gravity analysis (TGA), differential thermal analysis (DTA), x-ray photoelectron spectroscopy (XPS), electron paramagnetic resonance (EPR), Mössbauer study etc. All the above mentioned techniques are mainly employed in characterizing our nanostructured DMS and manganite samples, prepared through low temperature chemical pyrophoric reaction technique. We have also presented in details about magnetic measurement techniques, electrical - transport measurement techniques and optical measurement technique, employed for studying magnetic, electrical as well as optical properties of our structurally well characterized DMS and manganite samples.

In **chapter 3** we have shown from x - ray diffraction (XRD) studies on bulk amount of chemically prepared nanocrystalline powder of $Zn_{1-x}TM_xO$ (TM = Co, Mn, Fe, Ni), that the evolution of secondary phases (Co_3O_4, Mn_3O_4, Fe_3O_4 or NiO) along with the single phase $Zn_{1-x}TM_xO$ in wurtzite ZnO structure strongly depend on growth temperature (T_g) and doping concentration (x). We have established experimental phase diagram for each TM, which shows the relation between growth parameters (T_g and x) and single/multiple phases of $Zn_{1-x}TM_xO$. At the lowest T_g (300^0C) of our experiment, the highest solubility limits of Co, Mn, Fe and Ni in ZnO are 30%, 30%, 20% and 3% (at. wt.), respectively. The magnetization measurements using SQUID magnetometer show

that the secondary phase formation reduces the magnetization of single phase $Zn_{1-x}TM_xO$. This destructive role of secondary phase on magnetization may be the important clue to realize that any hidden (hardly detectable) secondary phase cannot be the source of magnetic property observed for $Zn_{1-x}TM_xO$ in single phase.

In **chapter 4**, we have investigated structural, magnetic, optical and electrical transport properties of 3d-transition metal (TM) doped $Zn_{1-x}TM_xO$ (TM = Co, Mn) diluted magnetic semiconducting nanoparticles for different doping concentrations ($0 \leq x \leq 0.4$) synthesized by chemical "pyrophoric reaction process". From x-ray diffraction (XRD) measurements the solubility limits of Co and Mn in ZnO nanoparticles are found to be strongly dependent on growth (calcinations) temperature (T_g). The highest solubility limit of both Co^{2+} and Mn^{2+} in ZnO at $T_g \sim 300^0$C are found to be ~ 30%. High resolution transmission electron microscopy (TEM) studies show that $Zn_{1-x}TM_xO$ particles are single crystalline of high quality with a wide particle size distribution in nanometric regime. The non-mean-field like very strong concave nature of temperature dependent magnetization curves are observed at very low temperature in both the systems without showing any distinct magnetic transition. The magnetic behavior of those Mn^{2+} and Co^{2+} doped ZnO semiconducting nanoparticles are observed to be quite different. The magnitude of net magnetization at a field of 5000 Oe for $Zn_{1-x}Mn_xO$ system is found to grow with the dopant concentration (x) in sharp contrast to the case for $Zn_{1-x}Co_xO$ where it is found to decrease. From mean-field Curie-Weiss fit as well as from the calculated values of effective exchange interaction constants (J_{ex}), which is found to be negative, we can assert that the ground state of both of these systems are antiferromagnetic (AFM) for the entire series. In the case of $Zn_{1-x}Mn_xO$ samples the magnitude of J_{ex} is found to

decrease with the increase in Mn^{2+} ion concentrations whereas for $Zn_{1-x}Co_xO$ samples the magnitude of J_{ex} is found to increase. These typical variations of J_{ex} with AFM interaction have been best explained through the magnetic polaron – polaron interactions model [P. A. Wolff *et al.* J. Appl. Phys. **79**, 5196 (1996) and A. C. Durst *et al.* Phys. Rev. B **65**, 235205 (2002)]. The semiconducting band gap of those nanoparticles has been estimated using recorded absorbance spectra. The electrical behaviors of those samples have been investigated over the wide temperature and frequency range using ac complex impedance spectroscopy and dc technique.

In **chapter 5**, we have investigated magnetic properties of Fe - doped ZnO nanocrystals, which are successfully synthesized and structurally characterized by using x - ray diffraction and transmission electron microscopy. Bulk magnetization measurements reveal a para to ferromagnetic phase transition at a temperature of > 320 K followed by a low - temperature transition from ferromagnetic to spin - glass state due to canting of the disordered surface spins in the nanoparticle system. Local magnetic probes like EPR and Mössbauer studies indicate the presence of Fe in both valence states Fe^{2+} and Fe^{3+}. We argue that the presence of Fe^{3+} is due to the possible hole doping in the system by cation (Zn) vacancies.

In **chapter 6**, we have investigated the ground state magnetic phase and the optical band gap of chemically synthesized $Zn_{0.85}Fe_{0.15}O$ diluted magnetic semiconducting nanoparticles (7 nm). The temperature dependent magnetization study shows strong irreversibility along with a cusp-like anomaly, which is ascribed to a freezing to a cluster glass-like magnetic ground state. This assignment is further established by Arrott-Belov-Kouvel plots along with *S*-like non-saturating magnetization

versus field curves. The finite size ferromagnetic clusters which are formed due to an enhanced grain surface effect in the system undergo random dipolar intercluster interactions, giving rise to strong competitive ferromagnetic and antiferromagnetic interactions, finally leading to the freezing of those clusters.

We have also investigated the magnetic, optical and electrical transport properties of $Zn_{1-x}Fe_xO$ (x = 0.05, 0.10 and 0.15) diluted magnetic semiconducting nanoparticles (~ 7 nm) synthesized through same low temperature chemical pyrophoric reaction process. Fe (x) doping in ZnO, i.e., $Zn_{1-x}Fe_xO$ leads us to the most desired room temperature ferromagnetism for a typical dopant concentration of x = 0.10, as strongly supported by finite coercive field (~ 94.4 Oe) and remanent magnetization (0.011 μ_B/Fe ion) from strong hysteretic magnetization versus magnetic field curve at room temperature. The Curie temperature of this x = 0.10 sample has been estimated to be ~ 388 K. The existence of room temperature ferromagnetic phase is further established by convex nature of ABK plots with spontaneous magnetization, whereas absence of ferromagnetism is observed in x = 0.05 and 0.15 samples. These observed magnetic behaviors for different x have been best explained through magnetic polaron model.

In **chapter 7**, we have investigated structural, magnetic, optical and transport properties of $Zn_{1-x}(Mn_{x/2}Co_{x/2})O$ (x = 0.1 and 0.2) diluted magnetic semiconducting nanoparticles synthesized by similar chemical "pyrophoric reaction process". X-ray diffraction analysis clearly shows that the samples are single phase in ZnO wurtzite structure, where the average crystallite sizes of samples are found to be in nanometric regime (~ 10 nm). From the Curie - Weiss fit, as well as, from the calculated value of effective exchange constant (J_{ex}), which is found to be negative, we can assert that the

nature of magnetic ground state of both these samples are antiferromagnetic (AFM). This is further established by concave nature of isothermal Arrott - Belov - Kouvel plots at the ground state (5 K) without having any spontaneous magnetization in both the samples. When both Mn and Co dopant concentration (x) are increased in ZnO matrix, the magnitude of AFM interaction (J_{ex}) is found to enhance. This observed magnetic behavior has also been best explained through the bound magnetic polaron - polaron interactions model. The semiconducting band gap of those nanoparticles has been estimated using recorded optical absorbance spectra. Electrical transport property has been investigated through complex impedance technique.

We have also investigated structural, magnetic, optical and electrical transport properties of $Zn_{0.9-x}Fe_{0.1}(Co/Mn)_xO$ (x = 0.05, 0.1 for Co and x = 0.1 for Mn) diluted magnetic semiconducting nanoparticles synthesized through same low temperature chemical process. From transmission electron micrograph particles size are found to be in nanometric regime (~7 nm) and single crystalline in nature. The magnetization measurements reveal that doping of Co or Mn ions in ZnFeO nanometric matrix decreases the values of coercive field and average magnetization, not due to the just increasing the total dopant concentration. It has been attributed to the formation of antiferromagnetic or paramagnetic states in ferromagnetic infinite cluster (spanning of magnetic polarons) by doping of Co or Mn ions. The strong irreversibility has been observed to persist at and above room temperature in magnetization versus temperature curve. The semiconducting band gap of those nanoparticles has been estimated using recorded absorbance spectra. The electrical behaviors of those samples have been

investigated over the wide temperature and frequency range using ac complex impedance spectroscopy.

We have also investigated microstructural, magnetic, optical and electrical transport properties of $Zn_{1-x}Fe_{x/2}Co_{x/2}O$ (x = 0.1 and 0.2) diluted magnetic semiconducting nanoparticles synthesized through low temperature same chemical process. From TEM and FE-SEM micrographs the particle sizes are found to be in the nanometric regime. The strong irreversibility between zero field cooled and field cooled conditions in concave nature of magnetization versus temperature curves persists at even room temperature without showing any distinct magnetic phase transition. x = 0.2 sample shows finite coercive field and remanent magnetization in magnetization versus field curve at room temperature resembling a ferromagnetic feature, whereas absence of ferromagnetism is observed in x = 0.1 sample. The observed ferromagnetic like behavior may be attributed to the formation of higher defect states at particle/particle interfaces acting large volume magnetic polaron which couple the spins. The semiconducting band gap of those nanoparticles has been estimated using recorded absorbance spectra at room temperature. Electrical properties of those nanometric DMS particles are investigated using complex impedance spectroscopic technique and dc resistivity technique as mention earlier.

In chapter 8, we have discussed microstructural, magnetic and optical properties of high quality epitaxial thin films of diluted magnetic semiconductor $Zn_{1-x}Mn_xO$ ($0.01 \leq x \leq 0.25$) grown on (0001) sapphire substrate (α-Al_2O_3) by pulsed laser deposition technique. Seven (01-10) planes of ZnMnO film are found to match with six (-12-10) planes of sapphire substrate through excellent domain matching epitaxy by 30^0 rotations

of ZnMnO unit cell about c - axis with respect to the sapphire unit cell. From high resolution transmission electron micrograph image the misfit dislocations are observed at the interface of sapphire and ZnMnO film growth plane. The insulating $Zn_{0.82}Mn_{0.18}O$ epitaxial thin film showed ferromagnetic behavior (hysteretic) with coercive field ~ 6.2 mT, and a maximum saturation moment of 0.42 μ_B/Mn^{2+} ion at a field of 0.5 T at lowest attainable temperature (T = 10 K). The strong concave behavior of magnetization as a function of temperature curves in this strongly insulating ferromagnetic diluted magnetic semiconductor film has been best explained through non- mean - field polaron percolation - theory. The increase of band gap from bulk ZnO with dopant concentration (x), observed from absorbance spectra, has been attributed to the sp - d spin - exchange interaction between the band electrons and localized d electrons of Mn^{2+} ions of $Zn_{1-x}Mn_xO$ films in presence of tetrahedral crystal field interaction.

In **chapter 9**, we have investigated the effect of nanometric grain size on electrical - and magneto-transport properties of single phase, highly spin-polarized, half-metallic spintronic oxide $La_{0.7}Ba_{0.3}MnO_3$ (LBMO) manganite nanoparticles having average grain size in the nanometric regime (21- 35 nm). We have observed that both metal - insulator transition temperature (T_P) and the para - ferromagnetic transition temperature (T_C) shifts to lower temperature with decrease in average grain size. For the entire series of sample, a distinct minima in resistivity at a temperature (T_{min}) followed by an upturn at very low temperature ($\leq$ 47 K) regime is observed. We have attributed the steeper low temperature (~ 47 K) resistivity upturn in smaller grain size sample than that of larger grain size sample below at T_{min} to the increased value of charging energy (E_C). E_C has been estimated to be 1.3 K for 21 nm sample, 0.56 K for 25 nm sample and 0.04 K

for 30 nm sample. Magneto-transport measurements show that the magnitude of low field MR (LFMR) (sharp drop at low field of MR) varies with average grain size. In order to investigate the MR behavior of LBMO nanoparticles, we have analyzed our data in the light of a phenomenological model, based on spin-polarized transport of conduction electrons at the grain boundaries. Typical LFMR at 1 kOe is found to be ~ 15 %, whereas at 50 kOe the HFMR at 4 K is found to be about ~ 40 % for LBMO nanoparticles. Magneto-transport measurements show that the magnitude of low field MR (LFMR), as well as of high field MR (HFMR) remains constant up to sufficiently high temperature (~ 50 K) and then drops sharply with temperature. We found that this strange temperature dependence of MR is decided predominantly by the nature of the temperature response of surface magnetization (M_S) of nanosize magnetic particles.

The final chapter, **Chapter 10,** discusses the conclusions and Scope of Future Work of the thesis.