STUDY OF STRUCTURAL, ELECTRICAL AND MAGNETIC PROPERTIES OF TRANSITION ELEMENT DOPED DILUTE MAGNETIC SEMICONDUCTOR NANOPARTICLES

THESIS ABSTRACT

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Abstract
Dilute Magnetic Semiconductors (DMS), defined as a diamagnetic semiconductor doped with few atomic percent of metal ions with unpaired $d$ electrons have become one of the emerging field of nanoscale electronics and condensed mater physics in recent years. Doping of transition metal ions into a non-magnetic semiconducting system not only induces ferromagnetism but also maintains its semiconducting property. The magnetic interaction between the magnetic impurities is supposed to be mediated via charge carriers. SnO$_2$ based DMS material exhibits remarkable behaviour because of its wide band gap, high electrical conductivity, optical transparency, presence of native oxygen vacancies and high chemical and thermal stabilities. It has generated huge interest among scientific community due to its wide application in photovoltaic cells, liquid crystal displays, gas sensors, thin films resistors, optoelectronic devices, Li-ion batteries and transparent conduction coatings. The present thesis contains the synthesis and characterization of SnO$_2$ based dilute magnetic semiconductor nanostructures. The structural, electrical and magnetic properties of the samples in nanoparticle and thin film form were studied. The thesis is divided into eight chapters, which can be read independently. Chapter wise details are as follows:

**Chapter 1** puts forward the basic understanding and history of DMS in general, and transition metal doped SnO$_2$ in particular. Different theoretical models that were used to explain different properties of SnO$_2$ based DMS material are also described in detailed.

**Chapter 2** covers necessary theoretical background about the various experimental techniques used for the synthesization and characterization of SnO$_2$ based DMS nanoparticles and thin films.

In **chapter 3** SnO$_2$ nanoparticles were synthesized using citrate gel auto-combustion method and annealed at 500°C, 700°C, 900°C, 1100°C and 1300 °C. The structural and compositional analysis were carried out using X-ray diffraction (XRD), Raman spectroscopy, field emission scanning electron microscopy (FESEM), energy dispersive X-ray spectroscopy (EDX), high resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED). The XRD graph revealed that all the samples have single- phase tetragonal rutile structure. The average crystallite size was observed to increase from 15 nm to 46 nm as the
annealing temperature was increased. In Raman spectra, the intensity of E\textsubscript{g} peak is decreasing with the increase in annealing temperature, indicating the decrease in the concentration of the oxygen vacancies (V\textsubscript{o}) or defects. The room temperature dielectric constant (\(\varepsilon'\)), loss tangent (\(\tan\delta\)) and ac conductivity (\(\sigma_{\text{ac}}\)) were studied as a function of frequency and the behaviour has been explained on the basis of Maxwell–Wagner model. It is also observed that all the dielectric parameters show their maximum values for as synthesized SnO\textsubscript{2} nanoparticles. Complex impedance measurement was used to separate the grain and grain boundary contribution in the system which suggests the dominance of grain boundary resistance in all the samples.

For electrical transport properties of as synthesized and annealed nanoparticles, dc resistivity measurement was carried out in between the temperature range of 297-400 K which confirmed the semiconducting behaviour of as synthesized and annealed nanoparticles and showed dependence of resistivity on crystallite size. Magnetic measurements were performed at 300 K and 5 K for all the samples using VSM which show that none of the samples exhibit ferromagnetism at room temperature. However, at 5 K, it was observed that as synthesized and annealed SnO\textsubscript{2} nanoparticles show ferromagnetism and the value of saturation magnetization and coercivity decreases with the increase in annealing temperature.

Chapter 4 presents the synthesis and characterization of Sn\textsubscript{1-x}Fe\textsubscript{x}O\textsubscript{2} (0.0 ≤ x ≤ 0.05) nanoparticles synthesized through citrate-gel method. X-ray diffraction analysis shows that all the samples were single phase and rutile tetragonal in structure. The average particle size calculated from the XRD data is between 3 nm to 5 nm. FESEM showed that with increasing the dopant level grain size decreases. In EDX spectra, peaks corresponding to Sn and O have only been detected in pure SnO\textsubscript{2}, while additional Fe peaks were observed in doped samples. Dielectric permittivity, ac conductivity and complex impedance for all the samples were evaluated as a function of frequency and composition at room temperature. The frequency response of \(\varepsilon'\), \(\tan\delta\) and \(\sigma_{\text{ac}}\) show dispersion that is due to Maxwell-Wagner type of interfacial polarization and these parameters decrease with progressive doping of Fe ions in the investigated samples. Complex impedance spectroscopy measurement was used to evaluate the conduction mechanism in the studied samples using non-linear least square fitting (NLLS). Nyquist plots show that the conductivity takes dominantly through grain boundary. No other contribution through the grains was resolved to
predominance of grain boundary resistance. Resistivity measurements in the temperature range of 297-400 K show that all the samples behave like a semiconductor and the value of resistivity increases with the increase in Fe contents. The M-H loops were obtained for all Fe doped SnO$_2$ nanoparticles using vibrating sample magnetometer (VSM) at room temperature. It was observed that pure SnO$_2$ nanoparticles show paramagnetic behaviour which disappears at higher degree of magnetic field. In case of doped samples, the saturation magnetization increases up to 3% and decreases with further increase in Fe concentration.

In chapter 5 nanoparticles of basic composition Sn$_{1-x}$Co$_x$O$_2$ (x = 0.00, 0.01, 0.03, 0.05 and 0.1) were synthesized and characterized for investigating their structural, electrical and magnetic properties. XRD analysis of the powder samples sintered at 500 °C for 12 hours showed single phase rutile type tetragonal structure and the crystallite size decreased as the cobalt content was increased. FT-IR spectrum displayed various bands that came due to fundamental overtones and combination of O-H, Sn-O and Sn-O-Sn entities. The effect of Co doping on the dielectric and magnetic properties was studied using dielectric spectroscopy and VSM at room temperature. The dielectric parameters ($\varepsilon'$, tan\(\delta\) and $\sigma_{ac}$) show their maximum value for 10% Co doping. The dielectric loss shows anomalous behaviour with frequency where it exhibits Debye relaxation. The variation of dielectric properties and ac conductivity with frequency reveals that the dispersion is due to Maxwell-Wagner type of interfacial polarization in general and hopping of charge between Sn$^{2+}$ and Sn$^{4+}$ as well as between Co$^{2+}$ and Co$^{3+}$ ions. The complex impedance analysis showed that the conduction process in grown nanoparticles takes place predominantly through grain boundary volume. The resistivity measurement confirmed semiconducting behaviour of Co doped SnO$_2$ nanoparticles. It is also observed that the dc resistivity decreased as Co doping was increased. Hysteresis loops were observed clearly in M-H curves from 0.01 to 0.1% Co doped SnO$_2$ samples. The saturation magnetization of the doped samples increased slightly with increase of Co concentration. However pure SnO$_2$ displayed paramagnetism which vanished at higher values of magnetic field.

Chapter 6 describes the effect of co-doping on structural, electrical and magnetic properties of SnO$_2$. Nanostructures (NSs) of basic composition Sn$_{1-x}$Fe$_{x/2}$Co$_{x/2}$O$_2$ with $x = 0.00, 0.04, 0.06, 0.08$ and $0.1$ were synthesized by citrate-gel route. X-ray
diffraction and Raman spectroscopy were used to confirm the formation of single phase rutile type tetragonal structure. The crystallite sizes calculated by using Williamson Hall equation were found to decrease with increasing doping level. In addition to the fundamental Raman peaks of rutile SnO$_2$, the other three weak Raman peaks at about 505, 537 and 688 cm$^{-1}$ were also observed. Field emission scanning electron microscopy studies showed the emergence of structural transformation. Electric properties such as dc electrical resistivity as a function of temperature and ac conductivity as a function of frequency were also studied. The variation of dielectric properties with frequency reveals that the dispersion is due to Maxwell-Wagner type of interfacial polarization in general. Hysteresis loops were clearly observed in M-H curves of Fe and Co co-doped SnO$_2$ NSs. However, pure SnO$_2$ nanoparticles (NPs) showed paramagnetic behaviour which vanished at higher values of magnetic field. The grain and grain boundary contribution in the conduction process is estimated through complex impedance plot fitted with NLLS approach which shows that the role of grain boundaries increases rapidly as compared to the grain volume with the increase of Fe and Co ions in to system.

Chapter 7 includes the SnO$_2$ thin film deposition on quartz substrates using pulse laser deposition (PLD) technique. The thickness of as-deposited SnO$_2$ thin films was about 150 nm and the samples were annealed at different temperature ranging from 600 °C to 900 °C for 1 hour with 100 °C variation per sample respectively. The phase formation and crystallographic structure of all SnO$_2$ thin film samples annealed at different temperatures were analyzed by XRD. The XRD spectra show that as deposited thin film was completely amorphous and do not reflecting any diffraction peak corresponding to rutile phase of SnO$_2$ while XRD peaks of annealed SnO$_2$ thin films were randomly oriented polycrystalline in nature and correspond to the rutile phase and space group P4$_2$/mm. The average crystallite size estimated using Scherrer and Williamson-Hall equations was found to increase from 6 nm to 19 nm with annealing temperature. In addition to the three fundamental Raman peaks at 473 cm$^{-1}$ ($E_g$), 627 cm$^{-1}$ ($A_{1g}$) and 766 cm$^{-1}$ ($B_{2g}$) corresponding to the tetragonal rutile phase of SnO$_2$, two more weak Raman bands were observed at 500 cm$^{-1}$ $A_{2u}$ (TO) and 690 cm$^{-1}$ $A_{2u}$ (LO), both of which are IR active, whereas the band at 544 cm$^{-1}$ was a Raman forbidden $B_{1u}$ mode. The dc resistivity measurements were performed in the
temperature range of 297-400K which showed semiconducting behaviour of all film samples. Dielectric properties at room temperature of the films were studied using dielectric spectroscopy in the 42 Hz to 5 MHz frequency range. All the film samples show dispersion which is explained in the light of Koop’s theory based on Maxwell-Wagner two-layer model. The dielectric parameters ($\varepsilon'$, tan$\delta$ and $\sigma_{ac}$) show their maximum value for SnO$_2$ film sample annealed at 600 °C. The dielectric loss shows anomalous behaviour and exhibits relaxation peaks (Debye peaks) at lower and middle frequency. Complex impedance plots (Nyquist plots) for SnO$_2$ thin films annealed at 600 °C, 700 °C, 800 °C and 900 °C show two well-resolved semicircles corresponding to two different electrical transport mechanisms stands for grain and grain boundary. It is observed that the contribution of grains in the conduction process is dominating over the grain boundary as the annealing temperature is increasing. To check if the single phase thin films are showing room ferromagnetism (RTFM), M-H loop was measured for all annealed SnO$_2$ thin films. It is clear that all the single phase thin films were ferromagnetic at room temperature and the value of saturation magnetization and coercivity show its maximum for SnO$_2$ film annealed at 600 °C.

**Chapter 8** presents an overview of results concluded from all previous chapters and scope of future work on the studied materials.

**Keywords:** SnO$_2$; nanoparticles; thin films; XRD; FESEM; TEM; FT-IR; Raman; dielectric properties; resistivity; magnetic properties.