Abstract

This thesis describes the investigations of Mn-doped, Mn-Co co-doped, and Cd doped nanocrystalline SnO_2 diluted magnetic semiconductors with varying concentrations of dopants. The nanocrystalline samples were synthesized by the co-precipitation technique. The context of the thesis has been divided into seven chapters, and the chapter-wise details are given below.

Chapter 1 includes an overview and history of the traditional diluted magnetic semiconductors in chronological order. The detailed literature review of transition metal-doped metal oxide semiconductors is also carried out. Further, the idea, innovation, and motivation for switching towards the metal oxide-based diluted magnetic semiconductors are discussed. An essential introduction and the reason for choosing SnO_2 among all other metal oxides as our investigating material is also given. Several reports on transition metal doped SnO_2 and related key findings are involved. Some crucial reports about Mn, Co, and Cd doped SnO_2 published by other researchers and corresponding noteworthy results are also included. The mechanisms of ferromagnetism in transition metal-doped diluted magnetic semiconductors are also explained.

Chapter 2 comprises of the synthesis and characterization techniques. The procedure and execution detail of the co-precipitation synthesis method has been discussed. The basic principle with a brief explanation of characterization techniques used in the present study, namely X-ray diffraction, FTIR spectroscopy, Raman spectroscopy, UV Visible spectroscopy, photoluminescence, SEM, EDX, TEM, two probe method, LCR meter, VSM, and SQUIDs have been also included.

Chapter 3 is based on the study of various physical properties of nanocrystalline pure and doped $Sn_{1-x}Mn_xO_2$ (with x= 0, 0.01, 0.03, 0.05) samples. The tetragonal phase of the synthesized powder samples was confirmed by X-Ray diffraction measurement. FTIR spectra were recorded to reveal the functional groups in as-synthesized powder samples. The average crystallite size was calculated by the Debye-Scherrer formula by taking into consideration the most intense XRD peak and found to be in the range of 21.8 to 32.2 nm. The optical band gap was found in the range of 3.80 to 3.91 eV showing a small redshift in UV-Vis absorption spectra. Photoluminescence spectra revealed the presence of defects

like oxygen vacancies in the materials. The dielectric properties such that dielectric constant, dielectric loss, and ac conductivity with frequency have been studied in the frequency range of 42Hz-5MHz. Impedance spectroscopy revealed the behavior of grains and grain boundaries parameters. The ferromagnetic behavior of pure and Mn-doped SnO_2 diluted magnetic semiconductor have also been discussed in detail.

In **chapter 4**, the structural, electrical, and optical properties of Mn-Co co-doped SnO_2 nanocrystallites by fixing Mn concentration (5%) and varying Co concentration (0%, 1%, 3%, and 5%), have been studied. The structural properties and surface morphology were studied using an X-ray diffractometer (XRD) and scanning electron microscopy (SEM), respectively. Composition analysis of the samples has been carried out from EDX data. XRD pattern emphasized that all the samples are in the rutile tetragonal crystalline phase. The lattice parameters and the average crystallite size decrease with increasing concentration of Co due to the smaller ionic radius of Co^{2+} compared to Sn^{4+}. Optical properties were studied using reflectance spectroscopy in the wavelength range of 200-800 nm. Reflectance spectra revealed that the bandgap of prepared samples changes with doping concentration and found to be in the range 3.91eV to 3.95eV. Fourier-transform Infrared (IR) spectra describe the different modes of vibrational and rotational band related to functional groups present in the materials. Mn and Mn-Co doped SnO_2 exhibit very strong emission near the wavelength 413 nm and 434 nm. DC resistivity measurement shows that the activation energy increases with increasing concentration of dopant and can be attributed to the reduced transportation ability of the ions in the co-doped systems.

Chapter 5 is based on the comprehensive investigation of Raman modes, magnetic, and temperature-dependent dielectric properties of Mn-Co co-doped SnO_2 nanoparticles. High-resolution transmission electron microscopy analysis gives evidence that the pre-synthesized Mn-Co co-doped SnO_2 powder samples contain nanoparticles of particle size 24.5 nm and 14.5 nm for 5% Mn-doped SnO_2 and 5% Mn + 5% Co co-doped SnO_2 respectively. These nanoparticles exhibit a very strange ferromagnetic to superparamagnetic transition, and the superparamagnetic phase of the samples grows on increasing Co content. This improved superparamagnetic phase in Mn-Co co-doped SnO_2 nanoparticles may offer ferrofluids and several biomedical applications like the contrast in MRI, drug delivery, hyperthermia, etc. The origin of electric polarization in the Mn-Co co-

doped SnO_2 nanoparticles has been explained on the basis of dielectric permittivity and typical dielectric dispersion. The small polaron hopping and correlated barrier hopping were found as a dominating ac conduction mechanisms in 5% Mn-doped SnO_2 and heavily (5% Mn + 5% Co) co-doped SnO_2. The typical increasing behavior of ac activation energy with frequencies in Mn-Co co-doped SnO_2 samples have also been depicted.

Chapter 6 covered a study of the structural, optical, and dielectric properties of Cd assimilated SnO_2 nanoparticles with varying concentrations of Cd. The structural properties were probed by XRD and FTIR Spectroscopy. XRD patterns disclosed the rutile tetragonal polycrystalline phase, and FTIR spectra provide significant information about functional groups in the pure and Cd-doped SnO_2 samples. As-synthesized nanoparticles were examined to study their morphology, shape, and average particle size by Transmission electron microscopy (TEM). The average crystallite size calculated by XRD and the average particle size obtained from TEM were found to be consistent and below 50 nm for all samples. The optical properties were studied by diffuse reflectance spectroscopy, and the optical band gap of as-synthesized powder was found in the range of 3.76 to 3.97 eV. Dielectric properties such as complex dielectric constant and ac conductivity were investigated by LCR meter. The study of frequency-dependent dielectric constant demonstrated the typical dielectric dispersion. The grain boundary parameters such that R_{gb}, $C_{gb,}$ and τ were evaluated using impedance spectroscopy.

Finally, **chapter 7** has an important summary and key findings of all the chapters. It also contains future work plans.