CHAPTER 2

LITERATURE REVIEW

Semiconductor nanoparticles especially dilute magnetic semiconducting materials (DMS) gain more significance in research and technology because of their exciting magnetic properties with optical properties which are important for nano electronics, spintroincs and antibacterial activities for biological applications. Among the most studied transparent conducting oxides are tin oxide. SnO_2 is a widely used semiconductor oxide in most of the applications such as gas sensors and transparent conducting electrodes, transistors etc. An extensive research is going on to modify the physical and chemical properties of SnO_2 NPs by incorporating transition metal ions in order to satisfy the specific needs and extended applications. In this chapter the various fields where the SnO_2 NPs are being used and several features especially the optical and magnetic properties explored by the researchers have been reviewed in detail.

Krishnakumar et al. [1] prepared tin oxide nanoplatelets (SnO) and nanoparticles (SnO_2) by microwave assisted technique. They have studied the effect of microwave radiation on SnO powder which had been synthesized by precipitation technique using water as medium. They showed that microwave treatment of an aqueous solution containing hydrated tin oxide species leads to the formation of crystalline nearly monodisperse SnO nanoplatelets and also analysed their morphological, structural properties and annealing behavior leading to crystalline SnO_2 for temperatures as low as 300 °C .

Zhang et al. [2] synthesized nanostructured SnO_2 powders by sol-gel process using the precursors tin tetrachloride and ethylene glycol. Compared to sol-gel process using metal alkoxides as precursors, the sol solution was extremely stable even in the presence of high concentration of hydrochloride and the kinetics of the gelation process was not susceptible to Cl^- ions. In their work, ethylene glycol is not only as a complexion agent to form a polymeric network but also as a spacer to modulate the distance between metal ions, preventing metal oxides from aggregation during earlier stage of organic removal.

Małgorzata Norek et al.[3] investigated the photoluminescence (PL) properties of tin oxide nanostructures of different morphologies such as non-continuous nanoporous layer, irregular nanoparticles of the size of 50–100 nm and regular equi-lateral triangles of the sides length of 110 nm induced by ALD process and the nanoporous anodic aluminum oxide (AAO) sub-strate. Two intense PL peaks were observed in all studied samples centered at about 540 and 620 nm due to the recombination of electrons from the conduction band and shallow trap levels to the surface oxygen vacancy levels.

Zulfiqar et al.[4] reported the effect of oxygen vacancies on band gap narrowing, enhancement in electrical conductivity and room temperature ferromagnetism of SnO_2 nanoparticles synthesized by chemical precipitation method. The oxygen content is increased steadily with increasing calcinations temperature, with the Sn:O atomic ratio very near to the stoichiometric value of 1:2 at high temperatures suggesting the low density of defects. The optical band gap energies of all SnO_2 nanoparticles were in the visible light region decreasing from

2.89 to 1.35 eV, while room temperature ferromagnetism and electrical conductivity were enhanced with reduced temperatures.

El-Shazly et al. [5] reported the formation of curved nanoribbon, wedge-like tinoxide nanowires and star-like nanowires. The photoluminescence (PL) measurements for the tinoxide nanowires indicated that there were three stable emission peaks centered at wavelengths 630, 565 and 395nm due to nanocrystals inside the nanobelts or the occurrence of Sn or O vacancies during the growth which can induce trapped states in the bandgap.

Ni-doped SnO_2 nanostructures which are synthesized using different techniques suggest that with increasing Ni doping the particle size gets reduced. Ahmed et.al.[6] synthesized Ni-doped SnO_2 nanoparticles using sol–gel route along with the reduction in particle size. They also observed the decrease in bandgap when the dopant Ni content is increased. Similar results were also obtained by Liu et. al.[7].

Kuppan et al.[8] investigated the optical and magnetic studies on nickel (Ni) doped SnO_2 powder samples prepared by solid-state reaction with dopant concentrations in the range of 3 at.% to 15 at.%. They observed the enhancement in the ferromagnetic signal up to 10 at.% of dopant with increased saturation magnetic moment due to substitution of Ni^{2+} with Sn^{4+} which favours an increase of oxygen vacancies available for electron trapping. But ferromagnetism has been observed even at higher Ni doping levels with decreased saturation magnetic moment at

higher dopant levels (15 at.%). They also analysed the optical band gap which was decreased from 3.76 eV to 3.70 eV with the increase of Ni from 3 at.% to 15 at.%.

Mousa Aliahmad et al.[9] reported the existence of superparamagnetic properties on their prepared samples Ni-doped SnO_2 nanocrystalline powders by the co-precipitation method. Their magnetic studies revealed no hysteresis loops for their samples and the magnetization curve displayed zero remanence and coercivity which proved that nanoparticles had superparamagnetic properties and they were single-domain nanoparticles.

Chen et.al.[10] reported that Ni-doped SnO_2 catalyst has photocatalytic activity in the degradation of RhB under visible light irradiation. The doped Ni played a key role in narrowing the band gap and reducing the recombination rate of photon-generated carriers, thus promotes the activity and stability of the catalyst.

Yogamalar et.al.[11] and Pascariu et.al.[12] reported that the improvement of the green emission band in the PL for the Ni-doped SnO_2 nanocrystals due to the increased defect sites. The magnetic measurements also made by Pascariu et.al. showed that the magnetization measured at H_{max} was increased with doping level due to a larger amount of induced defects and oxygen vacancies formed in the Ni-doped SnO_2 samples.

Ahmad et.al.[13] synthesized Ni-doped SnO_2 nanoparticles by the modified solvothermal method. High surface area of 680 m^2/g, paramagnetic behavior with antiferromagnetic interactions were observed for synthesized Ni-doped samples.

Similar results were obtained by Aragon et.al.[14], ~3 mol% Ni favoured defect-related ferromagnetism, doping with Ni content above 3 mol% favoured the stabilization of a paramagnetic phase. They suggested that in the low Ni content region, the substitution of Sn by Ni ions occurs near the particle surface which increases the oxygen vacancies available for the electron trapping and thus the associated ferromagnetism is enhanced.

Fan et.al.[15] reported Ni-doped SnO_2 powders with the tuneable room-temperature ferromagnetic response as a function of the Ni loading. The ferromagnetic response was attributed to both the Ni doping and the formation of oxygen vacancies and to the occurrence of uncompensated spins at the surface of the NiO nanocoating.

Sato et al. [16] studied the magnetic properties on II-VI-based DMSs $Cd_{1-x}Mn_xTe$. This DMS material has the capability to accommodate a high percentage of Mn atoms (as high as 77%) and its suitable energy gap for optical application. The ferromagnetic properties were controlled by electric gating and the motion of magnetic domain walls. It was reported by Parkin et al. [17] in their research work. This leads to the next generation of storage devices.

Aragon et al. [18] performed the Mossbauer investigation of oxygen-vacancy formation on doped substitutional solution of $Sn_{1-y} M_y O_2$ (M = Al, Fe, Ce and Er) nanoparticles. In their experimental work, they explained the rise of the oxygen-vacancy population while increasing the content of dopant ions (M) which are assessed from Mossbauer spectroscopy data. They have also analyzed the dependence of the structural, electronic and hyperfine properties on the oxygen-

vacancy concentration through first-principles calculations of the SnO_{2-x} (where x varies from 0 to 0.25) system. They found an increase of the unit-cell volume with the increase of oxygen vacancy (V_o), while the bulk modulus showed a linear decrease with V_o. They concluded that the experimental findings for pure and transition-metal-doped SnO_2 systems for which the presence of the oxygen vacancies play a key role.

Anandan et al. [19] reported the room temperature ferromagnetism (RTFM) in Mn (1, 2 and 3 mol %) doped SnO_2 nanoparticles prepared by precipitation process. The saturated magnetizations (M_s) of the samples doped with different concentrations (1–3 mol %) were measured as $278.18x10^{-6}$, $151.90x10^{-6}$ and $75.17x10^{-6}$ emu/g respectively. The reduction of the saturated magnetization has already been observed in Mn-doped SnO_2 samples with large Mn concentrations, and it decreases the saturated magnetization with the decreasing grain size of the Mn-doped SnO_2 nanocrystals [20]. They reported that the ferromagnetism in the nanoparticles of SnO_2 was confined to the surface of the nanoparticles due to oxygen vacancies. They found that the particle size decreases when the band gap increases; the increase in the band gap suggests that the size of the nanoparticles influences the optoelectronic properties of the materials and also observed strong visible emission peak at 449 nm due to the structural defects or luminescent centers in the SnO_2 nanoparticles.

Saravanakumar et al. [21] prepared the nano sized $Sn_{1-x}Mn_xO_2$ powders using the sol–gel technique. They indicated that Mn doped SnO_2 in the nano form exhibit

paramagnetic (PM) order upto the concentration level x=0.03 and becomes diamagnetic when x increases from 0.05 to 0.09. They conveyed the message that the dilution of Mn in the host matrix is still possible more than 9%, but in the nano form the Mn doped SnO_2 cannot possibly produce the ferromagnetic order since the disorder and defect chemistry dominate more in the prepared nanosystems.

Fitzgerald et al. [22] reported that the RTFM was exhibited by $Sn_{1-x}M_xO_2$ (M=Mn, Fe) but Co-doped samples were paramagnetic at room temperature. They observed the room temperature saturation magnetization of 0.2 and 1.8 Am^2kg^{-1} for $Sn_{0.95}Mn_{0.05}O_2$ and $Sn_{0.95}Fe_{0.05}O_2$ respectively, corresponds to a moment of 0.11 or 0.95 mB per Mn or Fe atom. They also suggested that the magnetization could not be attributed to any identified impurity phase.

In contrast, the absence of ferromagnetism in Mn doped SnO_2 nano particles synthesized by chemical co-precipitation method were reported by Vivek Agrahari et al.[23]. The exact origin of ferromagnetism in magnetic Mn ions doped SnO_2 based DMSs is controversial. But they observed the room temperature ferromagnetism in SnO_2 nanoparticles due to the presence of defects and oxygen vacancies while the Mn doped SnO_2 nanoparticles exhibit room temperature paramagnetism. They have found 2.81 eV band gap for undoped SnO_2 nanoparticles and it decreases continuously with the increase of Mn doping in SnO_2. Their product showed the strong optical absorption with weak magnetic properties at room temperature.

Percy et al.[24] reported the existence of room temperature ferromagnetism in nanocrystalline $Sn_{1-x}Co_xO_2$ (x = 0, 0.01, 0.03 and 0.05) synthesized under

microwave irradiation. They revealed that the substitution of Co^{2+} in Sn, introduced number of free charge carriers and oxygen vacancies to maintain charge neutrality leading to the formation of BMP (Bound Magnetic Polarons) and the interaction between these BMP with the available neighboring Co^{2+} ions produced the ferromagnetic behavior. PL studies showed the emission peaks which correspond to band edge emission and defects states that are present in pure and doped SnO_2.

Srinivas et al. [25] used the tartaric acid gel route to prepare the nanocrystalline Co doped SnO_2 diluted magnetic semiconductors subjected to different annealing temperature. Their studies also proved the room temperature ferromagnetism in Co doped SnO_2 for the annealing temperature from 300^oC to 600^oC. They concluded that the ferromagnetic properties depend on the factors like surface diffusion of Co ions, the distribution of defects such as oxygen vacancies or vacancy clusters, nanometric size of the materials and their surface conditions. From PL study, they noticed that the emission spectral intensity increases gradually with decreasing particle size of Co doped SnO_2 except in the sample annealed at temperature 300^oC and the observed behaviour can increase the number of luminescence centres by increasing the ratio of surface area and concentration of oxygen vacancies.

In Bouaine et al.[26] work, they observed the absence of ferromagnetism in polycrystalline Co-doped SnO_2 diluted magnetic semiconductors synthesized by coprecipitation technique. Their magnetization measurements revealed a mixture of paramagnetic and antiferromagnetic behavior for Co-doped SnO_2 with no sign of

ferromagnetism. They concluded that the absence of ferromagnetism could be due to the absence of free carriers which mediate the interaction between magnetic ions.

Sakthiraj et al. [27] reported the nanocrystal of $Sn_{1-x}Cu_xO_2$ with x=0.00, 0.02, 0.03 and 0.04 synthesized by sol-gel route. In their work, undoped SnO_2 showed RTFM where as Cu doped sample illustrated the diamagnetic property at higher fields. The diamagnetic property on doping was arised due to the structural disorder, electronic structural modifications and surface nature of the nanocrystallites. They also showed the variation of band gap values of 2-4% Cu doped samples from 3.21 to 3.50 eV, which ensured that the optical properties varied with respect to the quantum confinement effect in nanocrystal. The PL intensities are increased with increasing Cu concentration

Johari et al. [28] reported the room temperature ferromagnetism (RTFM) in Cu doped SnO_2 nanowires grown on silicon substrate using thermal evaporation process at atmospheric pressure and they explained that the origin of RTFM was both surface defects and oxygen vacancies. Since Cu has a very good electrical property and improves the structural and morphological properties of the host material, it is used as doping element.

Nilavazhagan et al. [29] synthesized $Sn_{0.97-x}Ni_{0.03}Cu_xO_2$ (x = 0, 0.01, 0.02) nanoparticles by employing co-precipitation method. They investigated the change in crystallite size and optical properties such as absorption, transmittance and band gap based on Cu concentration and density of defect states. Their results showed the lower optical absorption and higher transmittance of $Sn_{0.96}Ni_{0.03}Cu_{0.01}O_2$

nanoparticles, the shift of band position towards lower wave number side and the decrease in the intensity of fourier transform infrared spectra peaks due to the presence of Cu in Sn–Ni–O lattice.

Pulsed laser deposited Co-doped SnO_2 thin films with Co content in the range of 5–27% were reported to show room temperature ferromagnetism (RTFM) [30]. RTFM was also observed in Co-doped SnO_2 powders, but in these samples the phenomenon was strongly dependent on the dopant content, such that RTFM was only observed for concentrations lower than 1 mol% and the ferromagnetism was destroyed for higher Co^{2+} contents [31, 32]. Similarly to Co-doped SnO_2, pulsed laser deposited Ni-doped SnO_2 thin films (~8% Ni) grown on different substrates also show room temperature ferromagnetism [33]. Khaled Melghit et al. [34] reported the weak ferromagnetic character at room temperature Fe–SnO_2 sample and mixture α-Fe_2O_3–SnO_2 sample.

Vidhu et al.[35] successfully prepared SnO_2 nanoparticles by biogenic synthesis method using Saraca indica flower extract as reducing agent. They investigated the antibacterial activity of the as-prepared sample against gram negative bacterium *E. Coli*. They observed that the active oxygen species produced due to the presence of SnO_2 nanoparticles which was interacted with bacterial membrane cell, allowed the penetration of nanoparticles into the cell and inactivated the bacteria. Yu et al. [36] investigated the thermal conductivity and viscosity of ethylene glycol (EG)-based ZnO nanofluid while a similar investigation on SnO_2/EG nanofluid has been done by Mariano et al. [37].

Manjula et al.[38] studied the magnetic and antibacterial properties of Zr-doped SnO_2 nanopowders synthesized by soft chemical route adding various concentrations of zirconium (0, 5, 10 and 15 wt%). They observed the diamagnetic behaviour in pure SnO_2 nanopowders which become ferromagnetic with Zr doping. They suggested that the ferromagnetic behaviour observed for the doped samples is due to the large defect density (oxygen vacancies) and substitution of Sn^{2+} ions by Zr^{4+} ions interstitially. With increasing Zr content these defects mostly existed at the grain boundaries or at the interfacing sites between the nanopowders but the reduction in the ferromagnetic ordering for the 15 wt% Zr-doped sample which was due to the direct Zr–Zr paramagnetic or anti-ferromagnetic exchange coupling between the neighbouring Zr ions through O ions. They also tested the antibacterial activities of the Zr-doped SnO_2 nanopowders by disc diffusion method against *K.pneumoniae* (gram −ve) bacteria. All the doped SnO_2 nanopowders showed the enhanced bacterial retardant behavior compared to the undoped sample against the tested pathogenic microorganism

The electrical, optical, and microstructural properties of SnO_2 nanomaterials were tailored by doping with metal cations which was proved to be a successful tool by researchers. The luminescence of pure SnO_2, observed in the UV and/or visible region (350–550 nm) is generally correlated with the presence of crystalline defects resulting from the various synthesis processes [39,40]. The literature agrees towards the oxygen vacancies as the most probable candidates for the recombination centres in the emission processes of SnO_2. Of the various metal dopants of SnO_2, the Ce^{3+} Mn^{2+} [39,40], Co^{2+} [41], Ni^{2+} [6] or Cr^{3+} [42] exposed significant information on the

relationships between doping, defects related luminescence, surface effects, changes in morphology and particle size.

Kim et.al.[43] successfully prepared core-shell nanowires, in which outer Cu metal layers were deposited on SnO_2 nanowires through plasma sputter coating using a pure Cu target, followed by thermal annealing at 300 °C. This was formed in cluster-like structures including a Cu_2O phase. The enhancement of ferromagnetic properties with Cu sputtering and subsequent thermal annealing was attributed to the generation of Cu_2O phase, Cu-doping into the SnO_2 and the generation of oxygen vacancies in the SnO_2 lattice core.

The work on dilute magnetic semiconductor was started on 1960s and was expanded in 1980s with II-VI semiconductors. It was realized that a small percentage of magnetic impurities would not affect the optical and electronic transport properties of the host, but would also simultaneously introduce large magnetic field effects. In 1996, Hideo Ohno et.al proved the ferromagnetic order in Gallium manganese arsenide (Ga Mn As) with a curie temperature T_C of 110 K [44] which, with improvements in the control of the material quality when T_C was risen to ~ 170 K.

The physical properties of magnetic semi-conductors, such as magnetic red shift of the absorption edge and huge negative magnetoresistance (MR) around the curie temperature were discovered in the first-generation materials europium chalcogenides [45] and chalcogenides of chromium with spinel-type crystal structures [46,47].

Sawicki et al. [48] reported the strong temperature and magnetic field dependence of the conductivity in the semi-magnetic semiconductor $Cd_{0.95}Mn_{0.05}Se$ doped with indium (In), whereas no such behaviour was detected in pure CdSe. They reported that the influence of the s-d exchange interaction on the conductivity in the weakly localized regime is responsible for this semi-magnetic nature.

In 1980s, it was demonstrated that the semi-magnetic semiconductors exhibit the properties giant magnetoresistance [49] and insulator to metal transition on increasing magnetic field [50] or temperature [51]. These findings helped to understand the effect of sp-d exchange interaction on transport phenomenon and provided the experimental verification of theoretical ideas on electron transport in disordered systems [52].

Wojtowicz et al. [53] observed millikelvin conductivity of semi-magnetic n-$Cd_{0.95}Mn_{0.05}Se$ and p- $Hg_{0.915}Mn_{0.085}Te$ in the region of the insulator to metal transition induced by magnetic field. The magnetic properties of these materials are either paramagnetic or spin glass. The material prepared in their research work also exhibits a good optical property that leads to its application in optical isolators.

Zener proposed his model to explain the ferromagnetism for transition metals in 1950 [54]. He described the role of the carriers which was the important parameter in his model, i.e. the magnetic properties can be tuned by changing the carrier density in the materials, for example through external gating as reported by Ohno et al. [55]. They reported the field effect device using (In, Mn) as dilute magnetic semiconductor.

III-V-based diluted semiconductors have been extensively used for high speed electronic devices and optoelectronic devices. In this class of DMSs, magnetic properties have been found to be strongly dependent on the carrier concentration in the material. Since III-V compound semiconductors are widely used in electronic devices, the III-V-based DMSs are inherently capable of device-integration. The discovery of hole mediated ferromagnetism in (Ga, Mn)As [56] and the heterostructures based on it paved the way for the wide range of possibilities for integrating magnetic and spin-based phenomenon with the mainstream microelectronics and optoelectronics as well as taking advantage of the already established fabrication processes [57]. Much attention has been paid to the generation of DMSs due to their ferromagnetism, which has close relation to electric transport and can be controlled by external parameters [58].

Naseem Ahmad et al. [59] successfully synthesized Cd assimilated SnO_2 nanoparticles using precipitation route and investigated the structural, optical and dielectric properties. They attained average crystallite size and average particle size below 50 nm for all samples. The optical band gap of their powder samples from absorption study was in the range of 3.76 to 3.97 eV.

S. Mathews et al. [60] reported a ferroelectric field effect device with $La_{0.7}Ca_{0.3}MnO_3$ as the semiconductor and $PbZr_{0.2}Ti_{0.8}O_3$ as the ferroelectric gate exhibited a modulation in channel conductance of at least a factor of 3 and a retention loss of 3% after 45 minutes without power. The compromise on the origin of ferromagnetism in DMSs has not been reached till the date [61].

There are large number of papers in literature reporting ferromagnetism at or above room temperature, particularly in oxides [62]. Ferromagnetic semiconductors can provide fundamental insight into phenomena that when present in other types of materials, like some ferromagnetic metals are highly relevant for spintronic applications [63].

Chetri et al. [64] demonstrated that the decrease of crystallite size by increasing Cu-doping in SnO_2 is due to the formation of defects (holes or oxygen vacancies) which make the charge imbalance between the dopant and host ion. Aragon et al. [65] studied the thermal-annealing effects on the structural and magnetic properties of 10 % Fe-doped SnO_2 NP synthesized by a polymer precursor method. He assigned the thermal relaxation features observed in DC and AC susceptibility measurements to the formation of clusters of spins likely at the particle surface which show cluster-glass behaviour. These spin clusters seem to be formed due to the out diffusion of iron ions from the core of the SnO_2 matrix caused by the annealing process.