Chapter: 1

Introduction and Aim

In this chapter, a brief introduction to the present work is given. Glimpse of the problems and debates surrounding the dilute magnetic semiconductors (DMS) in general, and transition metal doped SnO$_2$ in particular is presented. Different theoretical models that were used to explain different properties of SnO$_2$ based DMS material are also described in detail. Finally, the importance of the work carried out for this thesis is emphasized.
1.1. GENERAL INTRODUCTION

We are living in an era where digital technology has huge influence in the everyday life and it is difficult for us to grasp life without it. Devices based on digital technology store information in the form of 0 or 1 and then process the information in the way they want. With the rapid growth of this digital world the demand for smaller devices is increasing with every passing day. Newer approaches have been continuously explored for miniaturization of these devices. However, there is a limit to go down in physical dimensions of solids as further reduction in size will make the material to start behaving as molecules and they can no longer be characterized as solids. One such approach is to utilize spin of the charge carriers in addition to their charge in devices and the field which uses this approach for device fabrication is known as spintronics. There are two potential advantages of this approach, the first being the ability of magnetic materials to remember their spin state for a finite period of time without any refresh, which could allow us to integrate logic and storage processes and potentially lead to "instant-on" computers, where no boot up is required. The other advantage is that relatively lower energy is required to manipulate the orientation of spin of a carrier, which could allow development of low power spintronic devices [1.1]. Chart 1.1 depicts the technology tree for spintronics and their potential applications. Spintronics has already revolutionized the field of data storage in the form of giant magnetoresistance (GMR) effects which was discovered by Alfert Fert and Peter Grunberg in 1998 [1.2]. With the discovery of this effect in multilayers, the size of the real heads was reduced to nano-dimensions and has also lead to decrease in the cost of the storage/MB. Key requirements for developing the devices based on spin and charge of the electrons are that the host material should be ferromagnetic above room temperature and it should have an efficient spin-polarized carrier. The most critical step in the functioning of spintronic device is the injection and detection of spin-polarized carriers at the semiconductor interface. Achieving efficient spin injection is a difficult and challenging task for the scientific community; however, two approaches used by different research groups have resulted in an efficient spin injection. One approach to achieve spin injection is to create built-up super lattices (SLs) of alternating magnetic and non-magnetic materials. This
attempt has been tried by different research groups [1.3-1.4]. In 2009, Zaoui et al. [1.5] made an attempt through ab initio electronic structure calculations for one monolayer (ZnO)$_1$(CuO)$_1$ SL, with the aim of obtaining a half–metallic behaviour material, since they are 100% spin polarized at the Fermi level and thus appear ideal for the well-defined carrier spin injection.

Later on in 2011, Pablo D. Borges et al. [1.3] studied the magnetic and electronic properties of (CrO$_2$)$_n$(SnO$_2$)$_n$ SL (1 ≤ n ≤ 10) with the same aim. They observed a half metallic behaviour for all the samples and suggested that (CrO$_2$)$_n$(SnO$_2$)$_n$ SL's may be applied to spintronic applications as they provide efficient spin-polarized carriers. Continuous attempts are made by material scientists using this approach with the aim of utilizing investigated properties in the field of device application [1.6]. For gaining a handle on the properties of the magnetic materials, the number of charge carriers should

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**Chart 1.1: Technology tree for spintronic devices and their potential applications** [1.7]
be comparable to that of semiconductors which can be then manipulated using methods which are employed in the present day semiconductor devices.

*Figure 1.1: (a) Magnetic semiconductor, (b) Diluted magnetic semiconductor, and (c) non-magnetic semiconductor.*

It has been turned out that it is not possible to have a magnetic semiconductor where every cation is a magnetic ion [Figure 1.1(a)]. So, to have a magnetic semiconductor, a non-magnetic semiconductor is doped with transition metal ions to achieve magnetism [Figure 1.1(b)]. Further, it was found that the transition metal cation impurity is of dilute concentration. Due to this reason such materials are called as diluted magnetic semiconductors (DMSs). This is the second approach that has been used widely due to
their potential as the source of spin polarized carrier and easy integration in semiconductor devices. These materials promise to provide a wide range of applications in various fields like logics, storage, communications, quantum computations and multifunctionality on the same chip [1.8]. Since ferromagnetism in DMS is related to the carriers in the semiconductors, ferromagnetic order can be disturbed thus gives rise to new possibilities such as optical manipulation of magnetic behaviour of DMS [1.9] or gate controlled ferromagnetism [1.10]. Apart from the present day application of DMS in the field of spintronics, these materials are of interest to the physics community due to the rich variety of physics they exhibit.

1.2. LITERATURE REVIEW

The field of DMSs originated in the late 1960s and was developed in the 1980s with work on II-VI semiconductors, when it was realized that a small percentage of magnetic impurities would not only deteriorate the optical and electronic transport properties of the host, but would also simultaneously introduce large magnetic field effects. DMSs came into the focus of scientific community in 1996, when Hideo Ohno’s group demonstrated ferromagnetic order in Gallium manganese arsenide (Ga, Mn)As with a curie temperature ($T_C$) of 110 K [1.11] which, with improvements in the control of the material quality, has subsequently risen to ~170 K. The first-generation materials studied intensively in the late 60s and early 70s were europium chalcogenides [1.12] and chalcogenides of chromium with spinel-type crystal structures [1.13-1.14]. Interesting 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 at that time. However, scientific community lost interest in these materials because their low Curie temperatures were far below the room temperature and growth of good-quality single crystals was very difficult. The second-generation materials are II-VI-based DMSs [1.15], among which Cd$_{1-x}$Mn$_x$Te was extensively studied due to its capability to accommodate a high percentage of Mn atoms (as high as 77%) and its appropriate energy gap for optical application [1.16]. Several other II-VI-based DMSs were also investigated at that time. M. Sawicki et al. [1.17] reported the strong temperature and magnetic field dependence of the conductivity in the semi-magnetic semiconductor Cd$_{0.95}$Mn$_{0.05}$Se
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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 difference. T. Wojtowicz et al. [1.18] presented 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 most of these materials are either paramagnetic or spin-glass. Although the controllability of transport properties is relatively poor, the material shows a good optical property that led to its application in optical isolators. At that time, it was demonstrated that the semi-magnetic semiconductors exhibit a number striking properties in the vicinity of the Anderson-Mott transition [1.19], such as giant magnetoresistance [1.20-1.23] and insulator to metal transition on increasing magnetic field [1.24] or temperature [1.25]. These findings helped to understand that effect of \( sp-d \) exchange interaction affects the transport phenomenon to some extent but was not satisfactorily solved, but provided a novel tool for experimental verification of theoretical ideas on electron transport in disordered systems [1.26]. However, the low critical temperature and to some extent the difficulty in doping these II-VI based DMSs, \( p \) and \( n \)-type made these materials less attractive for applications [1.27]. The third-generation materials are III-V-based diluted semiconductors, which have been widely 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 [1.28]. 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 [1.29] 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 [1.27]. Much attention has been paid to this generation of DMSs due to their ferromagnetism, which has close relation to electric transport and can be controlled by external parameters [1.30]. However, extensive studies on control of ferromagnetism are still under debate [1.28]. Scientists have proposed different models explaining this ferromagnetic behaviour of DMSs which are discussed in section 1.5 of this chapter.
Zener proposed his model for explaining ferromagnetism for transition metals in 1950 [1.31], the role of the carriers is a crucial aspect of this model, as it implies that 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. [1.32]. They reported a field effect device using a (In, Mn) as dilute magnetic semiconductor. S. Mathews et al. [1.33] 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. Still, even after so many years of intense research, consensus over the origin of ferromagnetism in DMSs has not been reached [1.34-1.35]. The Zener model explains most of the prominent features, but some of the fundamental aspects are still controversial. There are large numbers of papers in literature reporting ferromagnetism at or above room temperature, particularly in oxides [1.36]. The strive for improving the quality of the materials has led to high control of the growth processes and to the development of dedicated characterization techniques, primarily based on electron microscopy or X-rays. These advanced techniques have made it now possible to visualize the formation of magnetic ion clusters, which may one day be used to fabricate structures in which the magnetic properties of the semiconductors are controlled by purposefully designed magnetic clusters, rather than isolated ions at 190 K. However, 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 [1.37]. These include the control of ferromagnetic properties by electric gating and the motion of magnetic domain walls that has been proposed as the basis of the next generation of storage devices [1.38]. Even though investigation of electrical properties $SnO_2$ is of technological importance there are very few papers in literature reporting its electrical dielectric properties. In 1977 J.C. Manifacier et al [1.39] reported the resistivity of $5 \times 10^3 \Omega$ and $2 \times 10^5 \Omega$ in $SnO_2$ thin films deposited by two different techniques. M.P. Lopez-Sancho et al [1.40] studied the effect of ferromagnetic order on electrical properties of diluted magnetic semiconductors. Over the last decade there have been reports in literature focused on electric properties of DMS [1.41-1.42] however there is tremendous need for investigation of effect of induced ferromagnetic behaviour on
electrical properties of DMS from application point of view. The origin of room temperature ferromagnetism (RTFM) in semiconductors is still a controversial issue; however, these materials have already generated interesting physics and served as model systems for the study of phenomena of interest for application.

1.3. SYNTHESIS OF NANOSTRUCTURED DILUTE MAGNETIC SEMICONDUCTORS

Bulk DMSs systems possess very low Curie temperature ($T_c$) which limits their technological applications. Synthesis of DMSs based structures with room temperature $T_c$ and higher is the first requirement and one of the central issues for application of DMS based materials in novel spintronics. The properties of materials remain similar to that of bulk up to micrometer length scale; however, change drastically when dimensions are further reduced within nanoscale region. The field of nanotechnology has grown from several decades due to their fundamental technological importance for miniaturization of devices and in biomedical application. Nanostructures are generally considered to be a number of atoms or molecules bonded together with a radius of $< 100$ nm. Such materials and systems can be synthesized to exhibit novel and significantly improved physical and chemical properties, and also the phenomenon as a result of the limited size of their constituent particles or molecules. The main reason for the interesting and useful behavior is due to their characteristic structural features, which are intermediate in extent between isolated atoms and bulk macroscopic materials. Thus the nanostructured materials display physical attributes substantially different from those displayed by either atoms or bulk and hence leading to new technological opportunities as well as challenges [1.43-1.44]. The synthesis methods may be grouped in two streams: top down and bottom up approach of nanofabrication. In the top down approach nanomaterials are derived from a bulk substrate and obtained by progressive removal of material, until the nanomaterial is obtained. However, in Bottom up approach nanomaterials are obtained from the atomic or molecular precursors and gradually assembling it until the desired structure is formed. Among the two, bottom-up approach has become favored, as steady improvement in the synthetic protocols over the past 20 years have resulted in particle synthesis that are highly controllable [1.45]. A number of specific methods based on
bottom-up approach of synthesis method have been developed, among which those broadly in used for metal oxide based DMSs preparation are:

1.3.1. Wet Chemical Processes

i) **Sol-gel processing**: It is a wet chemical process which prepares DMSs nanostructures (metal oxides) through hydrolysis of precursors, usually alcoxides in alcoholic solution, resulting in the corresponding oxo-hydroxide. Condensation of molecules by giving off water leads to the formation of a network of the metal hydroxide: Hydroxyl-species undergo polymerization by condensation and form a dense porous gel. Appropriate drying and calcination lead to ultrafine porous material [1.46], which is further ground to get the desired nanostructure.

ii) **Co-precipitation method**: This method involves dissolving a salt precursor (chloride, nitrite etc.) in water or other solvents to precipitate the oxo-hydroxide form with the help of a base. The prepared precipitate is filtered followed by proper calcination and grinding leads to the formation of desired nanostructures.

iii) **Micro-emulsion technique**: This technique represents an approach based on the formation of micro/nano- reaction vessels under a ternary mixture containing water, a surfactant and oil. Metal precursors on water will precede precipitation as oxo-hydroxides within the aqueous droplets, typically leading to monodispersed materials with size limited by the surfactant–hydroxide contact [1.47].

iv) **Hydrothermal method**: This method of synthesis involves use of solvents under high pressure to dissolve and recrystallize material [1.48]. The use of the technique in preparing metal oxide based DMSs has become a recent trend because the resultant powder is prepared at low temperature which avoids nanoparticles from re-clustering and from being contaminated.

v) **Auto-combustion method**: This method is one of the widely useful methods for the preparation of DMS based nanomaterials. This is the combustion synthesis route using a fuel. The fuel used may be glycine, citric acid or urea. It involves exothermic and self-sustaining thermally induced anionic redox
reaction of xerogel, which is obtained from aqueous solution containing desired metal salts (oxidizer) and organic complexant (reductant) [1.49].

1.3.2. Thin Film Deposition

For any technological application integration of materials into the thin films is a first step towards its realization. Thin films have immense importance in the study of their properties, primarily because compared to the synthesisization of nanocrystals and bulks, thin films can be easily produced in single crystal form. Various deposition techniques are known to deposit high quality thin films like, pulse laser deposition (PLD) [1.50], DC and RF sputtering [1.51], molecular beam epitaxy (MBE) [1.52], thermal evaporation etc. The basic process involved almost in all the techniques is to evaporate the material, to provide atomic or molecular species in sufficient background pressure and carry them to the properly heated substrate of choice. The substrate is kept at elevated temperatures which influence the nucleation process and the mobility of the deposit across the substrate for good crystallinity. The choice of substrate is guided by the lattice parameter of the compound and substrate as well as the orientation of the substrate. The lattice mismatch between the substrate and the film can lead to compressive/tensile strain which may affect its different properties as well as its epitaxial nature. Therefore, this brings out the limitations in the choice of the substrate for the thin film deposition. The percentage lattice mismatch ($\sigma$) between the film and the substrate is evaluated as:

$$\sigma = \frac{(a_{\text{substrate}} - a_{\text{film}}) \times 100}{a_{\text{substrate}}}$$  \hspace{1cm} (1.1)$$

where, $a$ is lattice parameter. The positive value of $\sigma$ corresponds to the tensile strain whereas the negative value of $\sigma$ corresponds to the compressive stress. Stress and strain can highly affect the M-O-M bond angle and bond length causing concomitant change in electrical as well as the structural property in DMS based oxides.

1.4. INTRODUCTION TO DIELECTRIC SPECTROSCOPY

Dielectric Spectroscopy (DS) is a powerful and easy tool used to investigate dielectric properties of materials as a function of frequency which are based on interaction of electric dipole moment with external field. We have chosen this technique for
investigating electrical properties of pure and transition metal (TM) doped SnO$_2$ nanoparticles and pristine SnO$_2$ thin films, because of its sensitivity to any weak change in structure and dynamics.

This technique operates in a wide range of frequencies ($10^{-6} - 10^{12}$ Hz); however, all frequency ranges have not been equally available for measurement as it requires a complex and expensive equipment. The study of dielectric properties of nanosized materials is important for both fundamental and application oriented research. The morphology and the connectivity of random network of random nanoparticles influence both the mechanical restoring force and transport properties [1.53]. Enhanced electric properties of nanosized materials compared to their bulk counterparts are reported in literature [1.54-1.55]. Grains and grain boundaries present in nanosized materials play important role in determining their electrical properties. Majority of atoms reside in the grain boundary or within a few atomic layers from the boundary. The interface regions are bound to contain a large concentration of vacancies, vacancy clusters, dangling bonds etc. which can control different properties of these materials. Investigation of dielectric properties of nanomaterials is of tremendous interest among scientific community which is obvious from some of the reviews done by Lewis [1.56] and Frechette [1.57]. In the writing of this section of thesis our aim is to demonstrate some of the basic concepts used to explain dielectric properties of investigated samples.

Any material that resists to the electric field from passing through it and has ability to support an electrostatic field while dissipating minimal energy in the form of heat is a dielectric material. When this material is placed in an electric field it gets polarized and the polarization $P$ of the sample is given by

$$P = \frac{\langle M \rangle}{V}$$  \hspace{1cm} (1.2)

Where $\langle M \rangle$ is the macroscopic dipole moment of the whole sample of volume $V$. Here brackets $\langle \rangle$ denote ensemble average. In the linear approximation the macroscopic polarization of the dielectric sample is proportional to the strength of the applied external electric field $E$ [1.58]:
\[ P_i = \varepsilon_0 \chi_{ik} E_k \]  \hspace{1cm} (1.3)

Where, \( \chi_{ik} \) is the tensor of the dielectric susceptibility of the material and \( \varepsilon_0 = 8.854 \times 10^{-12} \) F/m is the permittivity of the vacuum. Now, if the dielectric is isotropic and uniform, \( \chi \) is scalar and Eq. 1.3 will be reduced to:

\[ P = \varepsilon_0 \chi E \]  \hspace{1cm} (1.4)

According to the macroscopic Maxwell approach, matter is treated as a continuum and the field in the matter in this case is the direct result of the electric displacement vector \( D \), which is the electric field corrected for polarization [1.59]:

\[ D = \varepsilon_0 E + P \]  \hspace{1cm} (1.5)

Substituting Eq. 1.4 in 1.5 we get

\[ D = \varepsilon_0 (1 + \chi) E = \varepsilon_0 \varepsilon E \]  \hspace{1cm} (1.6)

Where, \( \varepsilon = 1 + \chi \) is the relative dielectric permittivity and is also called as dielectric constant.

1.4.1. Types of Polarization

When an electric field is applied to across the faces of parallel plate capacitor containing a dielectric, the atomic and molecular charges in the dielectric are displaced from their equilibrium positions and thus the material is polarized through following mechanisms:

i) **Electronic polarization:** This type of polarization is due to the displacement of nuclei and electrons in the atom under the influence of external electric field. As electrons are very light they have a rapid response to the field changes; they may even follow the field at optical frequencies.

ii) **Ionic polarization:** This type of polarization is caused by relative displacements between positive and negative ions in ionic crystals. When an electric field is applied to ionic lattice, the positive ions are displaced in the direction of an applied field while the negative ions are displaced in opposite
directions giving a resultant dipole moment to the whole system. This type of polarization demonstrates only weak temperature dependence and is determined mostly by the nature of the interface where the ions can accumulate. Ionic polarization causes ferroelectric transition as well as dipolar polarization.

iii) **Orientation polarization:** The applied electric field tends to direct the permanent dipoles. The rotation is counteracted by the thermal motion of the molecules. This type of polarization is, therefore, strongly dependent on the frequency of applied field and on the temperature.

iv) **Space charge (interfacial) polarization:** This type of polarization arises from accumulation of charge at interfaces in a heterogeneous material consisting of more than one phase having different resistivity.

### 1.4.2. Dielectric Properties of Dilute Magnetic Semiconductors (DMSs)

i) **Dielectric constant:** It is a property of dielectric materials that measures the ability of a dielectric material to store electric charge in an electric field. In an ac field dielectric constant becomes imaginary and is represented by

\[ \varepsilon = \varepsilon' - j\varepsilon'' \]  \hspace{1cm} (1.7)

Where, \( \varepsilon' \) is the real part of dielectric constant which describes the stored energy and \( \varepsilon'' \) is the imaginary part of dielectric constant describing the dissipated energy. The value of dielectric constant was calculated using the relation:

\[ \varepsilon' = \frac{C_p \times d}{\varepsilon_0 A} \]  \hspace{1cm} (1.8)

Where, \( \varepsilon_0 \) is the permittivity of free space, \( d \) is thickness of pellet; \( A \) is the cross sectional area of the flat surface of the pellet and \( C_p \) is the capacitance of the specimen in Farad (F). For the proposed work the interpretation and explanation of variation of dielectric constant with frequency was based on Koop’s model [1.60]. In this model, the dielectric materials with heterogenic structure is assumed as the systems consisting of highly conducting grains
(with $\varepsilon_1$, $\sigma_1$ and thickness $d_1$) separated by highly resistive thin grain boundaries (with $\varepsilon_2$, $\sigma_2$ and thickness $d_2$). He assumed that $x = \frac{d_2}{d_1} \ll 1$, $\sigma_2 \ll \sigma_1$ and $\varepsilon_1 \sim \varepsilon_2$ so the dielectric constant is given by

$$
\varepsilon' = \varepsilon_1 \sim \varepsilon_2
$$

(1.9)

Behavior of dielectric constant ($\varepsilon'$) is controlled by grain boundaries at low frequencies while at higher frequencies grains control it. Higher the dielectric constant thinner will be the grain boundary. At lower frequencies the grain boundaries are more effective than the grains in electric conduction. The higher values of dielectric constant at low frequencies were explained on the basis of interfacial space charge polarization also called as Maxwell/Wagner/Sillars (MWS) polarization. This type of polarization occurs at inner dielectric boundary layers on a mesoscopic scale or at the external electrode-sample interface on a macroscopic scale and leads to the separation of charges. As the frequency increases any species contributing to polarizability are bound to be lagging behind the applied field at higher frequencies. There are two dielectric polarization mechanisms that contribute to the enhanced dielectric behavior of nanomaterials: rotation direction polarization (RDP) process and space charge polarization (SCP) process. Mainly, RDP process plays an important role for higher values of $\varepsilon'$. As for the typical n-type semiconductor, there are a large amount of oxygen vacancies acting as shallow donors (SnO$_2$ in present case), resulting in a lot of oxygen vacancies existing in the interfaces of n-type semiconductor nanostructures (NSs) [1.61-1.62]. Positive oxygen vacancies together with negative oxygen ions give a large amount of dipole moments. These dipole moments will rotate in an external electric field, which leads to the rotation direction polarization occurring in the interfaces of n-type NSs. On the other hand, SCP process can also occur in the sample. Generally, nanostructured materials have about $10^{19}$ interfaces/cm$^3$, much more than those of bulk solids [1.31]. The interfaces with a large volume fraction in the nanostructure
sample compacted under high pressure (50 MPa) contain a large amount of defects, such as micro-porosities, dangling bonds and vacancy clusters. These defects can cause a change of positive and negative space charge distributions in interfaces [1.63- 1.64]. Negative and positive space charges at interfaces move towards positive and negative poles of the electric field respectively. As they are trapped by defects, dipole moments will form and SCP process will occur in the sample. Because the volume fraction of the interfaces of sample in nano range is larger than that of bulk materials, SCP is stronger than that in the bulk materials. Thus, \( \varepsilon' \) of the SnO\(_2\) NSs is higher than that of bulk. Nevertheless, in the high frequency range, dielectric response of RDP and SCP cannot keep up with the electrical field frequency variation, resulting in the rapid decrease of \( \varepsilon' \) in SnO\(_2\) NS’s.

ii) Dielectric loss (\( \tan\delta \)): Dielectric loss or loss tangent is caused by the domain wall which represents the energy dissipation in the dielectric system. At higher frequencies the losses are found to be low since domain wall motion is inhibited and magnetization is forced to change rotation. Since \( \tan\delta \) is directly proportional to the imaginary part of dielectric constant according to equation:

\[
\varepsilon'' = \varepsilon' \tan\delta
\]  

(1.10)

It, therefore exhibits similar dispersion behavior. This is because of the fact that at lower frequencies the trend is due to space charge polarization which was explained through Shockley-Read mechanism [1.65]. According to this mechanism, it is given that at low and middle order frequencies the impurity ions in the bulk crystal matrices capture the surface electron, causing the space charge polarization at the surface. Relaxation peaks observed at higher frequency are due to the fact that jumping frequency of localized electric field carriers is approximately equal to external applied ac field. Increased intensity of relaxation peak can be explained with the help of Rezlescu model [1.66] according to which these relaxation peaks occur due to the collective contribution of both n-type and p-type charge carriers [1.67]. Since the
direction of displacement of electrons is opposite to that of holes under the application of external field, the mobility of holes is relatively very small with respect to that of electrons. The resultant polarization of both types of charge carriers will give peaking behavior of $\tan\delta$ with frequency.

iii) **ac conductivity:** The total conductivity is the sum of the band and hopping part [1.68]

\[
\sigma_{\text{tot}} = \sigma_0(T) + \sigma(\omega, T)
\]

(1.11)

Where, $\sigma_0(T)$ is the dc conductivity due to the band conduction, it is frequency independent and $\sigma(\omega, T)$ is the pure ac conductivity due to the hopping process and is related to the dielectric relaxation caused by the localized electric charge carriers which obeys empirical power law

\[
\sigma(\omega) = B\omega^n
\]

(1.12)

Where, $B$ and $n$ are constants that depend on both temperature and composition, $n$ is a dimensionless quantity and $B$ has the dimensions of electric conductivity. The behavior of $\sigma_{\text{ac}}$ was explained on the basis of hopping model. At low frequencies the conductivity is constant; the transport takes place on infinite paths. But for the frequency dependent conductivity, the transport is through the hopping of the charge carriers.

iv) **Impedance analysis:** Dielectric response of a material is due to the contribution from various microscopic elements such as the grain, grain boundary, and electrodes [1.69]. One of the important factors, which influence the impedance properties of ferrimagnetic nanoparticles, is the nano or microstructural effect. The complex impedance measurement gives us information about the resistive (real part) and reactive (imaginary part) components in the material. The complex impedance plot known as the Cole-Cole or Nyquist plot can give three semicircles, depending upon the electrical properties of the material. Since the ionic polarization is not present in the investigated samples, we have only two semicircles because of the space charge and orientation polarization in the studied samples. The complex
impedance plot can be represented in terms of any of the five possible complex formalisms, the permittivity ($\varepsilon^*$), the admittance ($Y^*$), the electric modulus ($M^*$), the impedance ($Z^*$) and the loss tangent ($\tan\delta$). These parameters are related with each other by the formula:

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} = \frac{M''}{M'} = \frac{Z'}{Z} = \frac{Y'}{Y}$$

(1.13)

where as the real and imaginary parts of the complex impedance are given by

$$Z' = \frac{R_g}{(1+\omega C_g R_g)^2} + \frac{R_gb}{(1+\omega gb C_gb R_gb)^2}$$

(1.14)

$$Z'' = -\frac{R_g^2\omega C_g}{1+(R_g\omega C_g)^2} + \frac{-R_g^2\omega gb C_gb}{1+(R_gb\omega gb C_gb)^2}$$

(1.15)

Where, the terms $R_g$ and $C_g$ represents the resistance and capacitance of the grain, while $R_gb$ and $C_gb$ represent the corresponding terms for the grain boundary volume. The resistance value for the grain and grain boundary have been calculated from the intercepts on the real part of $Z (Z')$ on X-axis, whereas the capacitance values have been calculated from the frequency peaks of the semi-circle arcs. Since the value of $Z' = -Z''$ at the maximum, we have;

$$C_g = \frac{1}{\omega R_g}$$

(1.16)

$$C_gb = \frac{1}{\omega gb R_gb}$$

(1.17)

Also, the relaxation times $\tau_g$ and $\tau_gb$ have been calculated from the frequency peaks using the equations:

$$\tau_g = \frac{1}{\omega} = R_g C_g$$

(1.18)

$$\tau_gb = \frac{1}{\omega gb} = R_gb C_gb$$

(1.19)
1.5. Models for Exploring Ferromagnetism in Dilute Magnetic Semiconductors (DMSs)

Discovery of RTFM in (Ga, Mn) by Hileo Ohno et al. [1.70] triggered a considerable number of investigations of magnetic properties in oxide based DMS such as transition metal doped SnO$_2$ [1.71], ZnO [1.72], Cu$_2$O [1.73] and In$_{1.8}$Sn$_{0.2}$O$_3$ [1.74].

<table>
<thead>
<tr>
<th>S. no.</th>
<th>Material</th>
<th>$E_g$ (eV)</th>
<th>Doping percentage</th>
<th>Magnetic moment $\mu_B$</th>
<th>Curie temp. $T_C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>SnO$_2$</td>
<td>3.5</td>
<td>5% Fe</td>
<td>1.8</td>
<td>610</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5% Co</td>
<td>7.5</td>
<td>650</td>
</tr>
<tr>
<td>2.</td>
<td>ZnO</td>
<td>3.3</td>
<td>4% Co</td>
<td>6.1</td>
<td>&lt; 280</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1% C</td>
<td>5.1</td>
<td>790</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5% C</td>
<td>7.1</td>
<td>300</td>
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<td></td>
<td></td>
<td></td>
<td>15% V</td>
<td>0.5</td>
<td>&gt; 350</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5% Fe</td>
<td>0.75</td>
<td>550</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1% Cu</td>
<td>2.0</td>
<td>280-330</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10% Co</td>
<td>0.06</td>
<td>&gt; 300</td>
</tr>
<tr>
<td>3.</td>
<td>TiO$_2$</td>
<td>3.2</td>
<td>1-2% Co</td>
<td>0.3</td>
<td>&gt; 300</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7% Co</td>
<td>1.4</td>
<td>650-700</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2% Fe</td>
<td>2.4</td>
<td>&gt; 300</td>
</tr>
<tr>
<td>4.</td>
<td>GAN</td>
<td>3.4</td>
<td>0.9% Mn</td>
<td>0.9</td>
<td>940</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.9% Cr</td>
<td>0.9</td>
<td>&gt; 400</td>
</tr>
<tr>
<td>5.</td>
<td>AlN</td>
<td>4.3</td>
<td>7% Cr</td>
<td>1.2</td>
<td>&gt; 600</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5% V</td>
<td>4.2</td>
<td>&gt; 400</td>
</tr>
<tr>
<td>6.</td>
<td>In$<em>{1.8}$Sn$</em>{0.2}$O$_3$</td>
<td>3.8</td>
<td>5% Mn</td>
<td>0.8</td>
<td>&gt; 300</td>
</tr>
<tr>
<td>7.</td>
<td>Cu$_2$O</td>
<td>2.0</td>
<td>5% Co and 0.5% Al</td>
<td>0.2</td>
<td>&gt; 300</td>
</tr>
</tbody>
</table>

*Table 1.1: Literature review of oxide based DMSs [1.75]*

Table 1.1 summarizes the magnetic moment and curie temperature reported in literature for these oxide based DMSs. Although a number of different models have been
proposed, the mechanism responsible for the origin of ferromagnetism in oxide based DMS is not fully understood and explained yet. Different theoretical models that have been commonly used to explain ferromagnetism in DMS are discussed below along with the concepts involved.

1.5.1. Carrier mediated exchange model

Zener [1.31] argued that the magnetic ordering in DMS is governed by the competition between three interactions and this net spin coupling energy is a combination of three terms and based his model on three simple assumptions:

i) The interaction between the incomplete $d$ shell of the transition metal is insufficient to disrupt the coupling between the $d$ electrons in the same shell.

ii) The exchange integral between the $d$ shell of the neighboring atoms is always the same and favors anti-ferromagnetic ordering of spins.

iii) The spin of the incomplete $d$ shell is strongly coupled with the conduction electrons. Dominance of this coupling over the direct exchange makes ferromagnetism possible.

Combining these three couplings, the spin coupling energy is given by

$$E_{spin} = \frac{1}{2} a S_d^2 - \beta S_d S_c + \frac{1}{2} \gamma S_c^2$$ (1.20)

Here first term is the direct exchange between incomplete $d$ shell electrons while second is the exchange between $d$ shell electrons and the conduction electrons. The third term denotes the Fermi Kinetic energy of the conduction electrons, where $S_d$ and $S_c$ are the net spin polarizations of the d shell electrons and conduction electrons respectively. The sign of $E_{spin}$ determines the nature of magnetic order, while the positive sign indicates the anti-ferromagnetic order, a negative sign indicates ferromagnetic order. One of the major shortcomings of this model is that it does not take into consideration the Friedel oscillations of the electrons spin polarization, as is done in the Ruderman-Kittel-Kasuya (RKKY) model. However, in case of semiconductors, the mean distance between the carriers is greater than that between the spins [1.76], the effect of Friedel oscillations
averages to zero. Thus the Zener model becomes equivalent to RKKY model in case of semiconductors. In case of DMS materials, as doping of the TM ions is very dilute, the antiferromagnetic interaction between them is greatly reduced due to the smaller overlap of the $d$ shell and the ferromagnetic interaction among the localized spin and the charge carriers dominate resulting in RTFM.

Figure 1.2 (a): Direct super exchange interaction: Antiferromagnetic coupling of adjacent TM cations through shared ions.

Figure 1.2 (b): Indirect super exchange interaction: Ferromagnetic coupling of localized spins through the conduction electrons.

Figure 1.2(a) and 1.2(b) shows the schematic representation of Direct super exchange interaction: Antiferromagnetic coupling of adjacent TM cations through shared ions and Indirect super exchange interaction: Ferromagnetic coupling of localized spins through the conduction electrons.
1.5.2. The Bound Magnetic Polaron (BMP) Model

The exchange interaction between localized magnetic moments and charge carriers within the material leads to polarization of the localized moment in the vicinity of charge carriers. This type of organization is called a magnetic polaron. The localized moments then, in turn produces an effective field on the charge carriers and hence polarize them. This self-trapping process of carrier spins produces a magnetic potential well resulting in the formation of a magnetization cloud. In case of magnetic semiconductors BMP model was first introduced in Eu-rich EuO [1.77] to explain the low temperature metal-insulator transition. In BMP model for DMS, an itinerant electron is considered to be orbiting around the donor impurity in a large radius molecular orbit with several tens to hundreds of localized spins. The exchange interaction between the localized spins of the doped magnetic ion and the electron in the hydrogen-like orbit aligns the magnetic ions ferromagnetically. The radius of the donor electron is given by

\[ r_H = \varepsilon \frac{m}{m^*} a_0 \]  

(1.21)

Where \( \varepsilon \) is the high frequency dielectric constant, \( m \) and \( m^* \) are respectively the electron mass and effective mass of donor electron respectively and \( a_0 \) is the Bohr radius.

If \( n_d \) is the donor concentration and \( n_o \) is the oxygen density then, the defect density is given by

\[ \vartheta = \frac{n_d}{n_o} \]  

(1.22)

As \( \vartheta \) increases these orbitals start to overlap. At the beginning the electrons will remain localized due to correlation and potential fluctuations in the narrow band. With increase in the number of charge carriers, the band width of the impurity band increases and after a certain critical value \( n_o^{crit} \), insulator to metal transition takes place. Figure 1.3 depicts the interaction in oxides, where defects such as oxygen vacancies act as a source of electrons.
Figure 1.3: Schematic diagram for the magnetic polaron and the various possibilities in transition metal doped oxide. Cation sites are shown by small circles. Oxygen is not shown; the unoccupied oxygen sites are presented by the squares [1.78].

1.6. MOTIVATION AND OUTLINE OF THE PRESENT WORK

Silicon-based conventional semiconductor devices have been developed for many decades, in which electrical switching and signal amplification were controlled through electron charge under the influence of external electric fields. With the evolution of information technology, information processing devices are required to operate at an elevated speed whereas the physical dimensions of the device shrink to the atomic scale. However, there are two major basic obstacles for continuing down the pathway of silicon technology. Primarily, as Moore’s law predicts, the number of transistors per chip doubles every eighteen months. This causes the heat generated per chip to increase dramatically and at a certain point it will be too intense to be drained off the circuit. Secondly, the shrinkage of device dimensions brings up new challenges as quantum confinement effects become more significant. As a result, it is of tremendous interest, for
both semiconductors technology and fundamental science to seek for alternative electronic materials and devices, combating over the old problems of balancing speed and power consumption.

One of the alternatives is the emerging field of spin electronics or “Spintronics” which can be defined as the technology that exploits both the spin and charge of the electrons via external magnetic or electric field. With its operation based on the manipulation, transport, and detection of spin-polarized carriers, spintronics is expected to improve upon traditional electronic and photonic devices in terms of reduced power consumption, lesser heat generation, faster device operation, and new forms of information computation [1.79]. In order to realize the widespread application of these devices such as: spin-polarized LEDs, spin-field effect transistors (FETs), and spin-based qubits for quantum computation. Multifunctionality is also expected to improve overall device performance, for example by integrating magnetic (spin-related) and electronic (charge-related) operations on the same chip. Since the electron spin is fundamentally a “binary” quantity (spin-up or spin-down), spintronics materials may also be used in fast rewritable memory which is nonvolatile. For this range of applications, it is essential that new materials systems be developed for the fabrication of spintronics devices. One solution is to incorporate ferromagnetism into semiconductors to polarize the carrier’s spin for further manipulation; often achieved by doping the diamagnetic host semiconductor with a dilute concentration of magnetic ions, from which the concept of “dilute magnetic semiconductor” (DMS) is raised. For spintronic devices to be functional at ambient, it is also crucial for the developed DMS materials to possess RTFM. There are two essential roles for DMSs in spintronic devices.

i) The ferromagnetic DMS supports the transport of spin polarized current through the device.

ii) The semiconducting nature of the DMS facilitates signal amplification and switching application as in traditional semiconductor devices.
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DMS materials in recent year have become an intensively focused research field across several disciplines, including material science and engineering, chemistry, experimental and theoretical physics. The ongoing efforts aim to address the following problems:

i) Theoretical explanation for the origin of ferromagnetism in DMSs which is a quantum many-body system problem, treated in various ab initio and phenomenological approaches.

ii) Material preparation for DMS samples in various morphologies, focused on non-equilibrium growth of doped DMS crystals and defect engineering to control the magnetic ion and carrier concentrations.

iii) Material characterization techniques, such as measuring the structural, magnetic, optical and electrical properties, with various standard and unique methodologies. However, this proves rather challenging due to low concentration of magnetic ions.

The major challenge at the present stage of developing functional DMS materials is to achieve intrinsic ferromagnetic ordering in DMS above room temperature. This requires a deep understanding of the magnetic interactions between the doped magnetic ions and host materials in addition to the subtle effect of native point defects and impurity contamination of the host materials.

The aim of the work is to present a systematic study of structural, electrical and magnetic properties of DMS materials based on wide band gap semiconductor stannic oxide (SnO$_2$), that have a potential application in technology. The better understanding of its structural properties with varying particle size, electrical and magnetic behavior with different doping concentrations may help us to explore the materials capabilities in the futuristic applications. SnO$_2$ is one of the most promising candidates for DMS material which shows RTFM. SnO$_2$ has a tetragonal structure and the unit cell contains two Sn and four O atoms. Each Sn atom is at a centre of six O atoms placed approximately at the corners of the regular octahedron, while each oxygen atom is surrounded by three Sn atoms at the corners of an equilateral triangle. The total energy is minimized by the geometry optimization and optimized values of its structural parameters are,
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\[a = b = 4.673 \, \text{Å}, \, c = 3.148 \, \text{Å}\]. Figure 1.4 shows the systematic representation of rutile SnO\(_2\) [1.80].

![Systematic representation of rutile SnO\(_2\).](image)

**Figure 1.4: Systematic representation of rutile SnO\(_2\).**

SnO\(_2\) based materials constitute an important component for optoelectronic application by combining high electric conductivity with optical transparency in the visible range of optical spectrum. Optoelectric properties of SnO\(_2\) have been investigated in number of applications, notably as electrode material in solar cells [1.81-1.82], light emitting diodes [1.83-1.84], flat displays [1.85], and other optoelectronic devices where an electric contact needs to be made without obstructing photons from either entering or escaping the optical area [1.86]. Gas sensor is another application of SnO\(_2\). A lot of research efforts have been dedicated to the development of miniature gas sensing devices particularly for toxic gas detection and for pollution monitoring. SnO\(_2\) dominates over other metal oxides that have been extensively studied for sensing application. The well-known advantages of this material include low cost and high selectivity for different gas species.
As an n type wide band gap, multi-functional semiconductor material, SnO$_2$ based DMS is becoming one of the most important host systems for 3d element after the first report of high temperature ferromagnetism in SnO$_2$ thin films by Ogale et al. [1.87] in 2003 reported giant magnetic moment of $7\pm 0.5 \mu_B$/Co, with a curie temperature close to 650 K in 5%Co doped SnO$_2$ thin films. After that, a series of works on realization of ferromagnetism in SnO$_2$ doped with different 3d elements such as Fe, Ni, Cr etc. have been reported [1.88-1.91].

As mentioned, SnO$_2$ is a unique material in which gas sensing effect, optical transparency semi conductivity and ferromagnetism can be combined simultaneously. In most applications, SnO$_2$ is modified by additives to increase the charge carrier concentration by donor atoms or incorporate ferromagnetic property by transition metal doping. The effect of doping on structural, electrical and magnetic properties has been systematically studied in the present work. Furthermore, mechanism behind the unexpected high temperature ferromagnetism in transition metal atom is still an open question. In this scenario it is highly desirable to establish a systematic study of structural electrical and magnetic properties of SnO$_2$ based DMSs as a function of doping and annealing temperature. The unique features of DMSs [1.92] which has opened doors for device applications and made them as interesting grounds for various theoretical ideas can be summarized as:

a. The existence of magnetic phenomenon in a host with a simple band and crystallographic structure.

b. The possibility of reliable control of stoichiometry as well as of carrier impurity and magnetic ion concentration.

c. Their excellent optical and transport properties enabling application of the most powerful methods that have been developed for the studies of canonical semiconductors.

Our objective revolves around studying different properties of pure and transition metal (TM) doped SnO$_2$ based diluted magnetic semiconductor nanostructures (NSs) and SnO$_2$ thin films. NSs were synthesized using citrate gel method and the polycrystalline SnO$_2$
thin films were grown using Pulsed Laser deposition techniques. The structural, electrical, and magnetic characterizations of the prepared samples have been performed using different techniques such as X-Ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM), Energy Dispersive X-ray Spectroscopy (EDS), Transmission Electron Microscopy (TEM), Selected Area Diffraction (SEAD), Raman Spectroscopy, Fourier Transform Infrared Spectroscopy (FTIR), Dielectric Spectroscopy, Impedance Spectroscopy and Vibrating Sample Magnetometer (VSM) etc. In the first chapter of the thesis an overview of general introduction and the existing, unresolved, issues in DMS systems are also briefed along with different theoretical models used in thesis. At last, we have addressed to the motivation for choosing tin oxide as a host material for its synthesis and to perform various experiments. Chapter 2 of the thesis covers the necessary experimental details of various techniques used to investigate structural, morphology, electrical and magnetic properties of the systems studied. Chapter 3 comprises all the experimental results of un-doped SnO$_2$ nanoparticles annealed at different temperatures synthesized by the citrate gel method. In chapter 4, we explored the DMS nature of Fe doped SnO$_2$ nanoparticles using different sophisticated experimental techniques followed by chapter 5, in which different properties of Co doped SnO$_2$ nanoparticles were investigated. Chapter 6 includes the structural electrical and magnetic studies done on Fe/Co co-doped SnO$_2$ nanostructures. In chapter 7 different properties of SnO$_2$ thin films deposited using Pulse Laser Deposition Technique (PLD) and annealed at different temperatures is presented. Chapter 8 presents an overview of the results, concluded from all previous chapters, and scope of future work on the studied materials.
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