

CHAPTER 1

INTRODUCTION TO MAGNETIC SEMICONDUCTORS

The term magnetic semiconductor represents the semiconducting materials with spin as a new degree of freedom and expected to be a promising material for next generation spintronic devices. The motivation behind the study of magnetic semiconductors is to combine semiconducting and magnetic behavior in a single material and such combination will facilitate the integration of compatible semiconductor-ferromagnetic interfaces. Hence, the ferromagnetic semiconductor is viewed as a promising candidate in the field of magnetoelectronics (Chambers et al. 2006, NicoloSpaldin 2003). However, the need for basic research in magnetic semiconducting materials is to explore the origin of ferromagnetism and simultaneously utilize their unique properties in spin based electronic devices (Wolf et al. 2001). The materials challenge is great due to the requirement of magnetic and electronic doping and the interaction between spins and free carriers must be engineered. Hence, it is proposed that the magnetic dopant should possess unpaired d electrons in order to exhibit net spin. Further, the ferromagnetic alignment of these spins throughout the material is to be brought by spin polarization and interaction with free carriers. Hence, the associated spin-polarized current gives new and novel functionality in spintronic devices.

Conventional electronics is based on electronic charge and its transport whereas the up gradation in electronic industry provides spin of electron as additional degree of freedom or by using the spin alone is called magnetoelectronics or spintronics. It was also identified that the addition of spin as a degree of freedom to conventional semiconductors enhances the



performances of electronic devices. The first generation spintronics devices were made from alloys of ferromagnetic 3d metals. The development of passive magnetoresistive sensors and memory elements was enhanced by the discovery of giant magnetoresistance effect in $(\text{Fe/Cr})_n$ multilayers and tunneling magnetoresistance (Zutic et al. 2004). The next generation spin based devices will involve manipulation of spin polarized electrons in semiconductors (Zutic et al. 2004, Baibich et al. 1989). The functionalities of electronic and photonic devices can be enhanced by injection, transfer and detection of spin at and above ambient temperature. The major advantages of these new devices would be non- volatile, increased speed of data processing, less power consumption and increased integration densities compared with conventional semiconductor devices (Binasch et al. 1989).

The key challenges in spintronics is to optimize stability and lifetime of electron's spin, detection of spin coherence in nanoscale structures, transport of spin polarized carriers and the manipulation of electrons (Prinz et al. 1998). Recent experiments suggest that the storage time of quantum information encoded in electron spins may be extended through their strong interplay between the nuclear spins in solid state. Further, optical methods for spin injection, detection and manipulation have been developed to exploit the ability of coupling the electron spin and optical photons (Wolf et al. 2001). It is visualized that the merging of electronics, photonics and magnetism will lead to new spin based multifunctional devices such as spin Field effect transistor (FET), Spin-Light Emitting Diodes (LED), spin-Resonant tunneling devices (RTD), optical switches, modulators, encoders, decoders and quantum bits for quantum computing and communication (Tsang et al. 1994, Fiederling et al. 1999, Jonker et al. 2000). However, the successes of these ventures depend on understanding the fundamentals of spin interaction in materials, the role of dimensionality, defects and semiconductor band structure. Therefore,



the design of materials merging semiconducting and ferromagnetic properties turns to be vital role in the development of spintronics devices.

1.1 MAGNETIC SEMICONDUCTORS

Magnetic semiconductors (MS) are the class of material exhibiting both semiconducting and magnetic properties simultaneously. The fascinating physical property of semi-magnetic semiconductors creates much attention towards magnetic semiconductors to explore the potential utilization of spin and charge in materials that may lead to the development of novel multifunctional devices (Fukumura et al. 2005, Prinz 1998, Wolf et al. 2001). Magnetic semiconductors are found to be attractive because of their high temperature magnetic ordering and structural compatibility.

Magnetic semiconductors are broadly classified as concentrated magnetic semiconductors (CMS) and dilute magnetic semiconductors (DMS). The naturally existing ferromagnetic semiconductors are known as concentrated magnetic semiconductors and are found to have very low Curie temperature (T_C) below room temperature. In order to achieve the room temperature ferromagnetism in semiconductors various non-magnetic semiconductors have been investigated by doping fractional amount of magnetic elements which is known as dilute magnetic semiconductor (DMS).

1.1.1 Concentrated Magnetic Semiconductors (CMS)

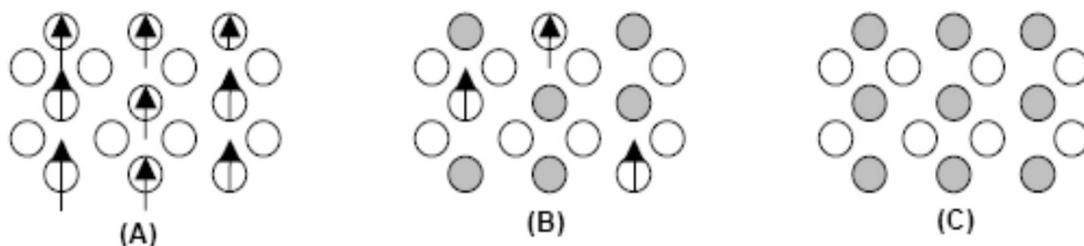
Semiconducting materials those possess intrinsic magnetic moment are called Concentrated Magnetic Semiconductors (CMS) in which all the constituent cations have individual magnetic moment. However, most of the CMS are found to be ferromagnetic well below the room temperature which imposes restriction for practical application (Matthias et al. 1961). In addition, it is also found that the materials doped with foreign (impurity) elements could not cause significant changes in the intrinsic physicochemical characteristics



of CMS. Extensive research works on magnetic semiconductors especially on CMS were done in late 1960's to early 1970's (Holtzberg et al. 1964). The exchange interactions between the electrons in semiconducting band and localized electrons at the magnetic ions leads to number of peculiar and interesting properties (Von Molnar & Methfessel 1967). However, it was found that the crystal growth of such materials is very difficult and imposes severe restrictions on using CMS in semiconductor devices. Further, the Curie temperature (T_c) of such ferromagnetic semiconductors is well below the room temperature (RT) and found inappropriate for spintronic devices.

1.1.2 Diluted Magnetic Semiconductors

Diluted Magnetic Semiconductors (DMS) are non-magnetic semiconductors doped with few percent of magnetic elements and are expected to be easily integrated with existing semiconductors. The discovery and understanding of DMS materials are proving the magnificent challenges in solid-state sciences. The great challenge is that both magnetic and electronic doping is required and the interaction between dopant spins and free carriers must be engineered to obtain thermally robust dopant spin-carrier coupling (Chambers et al. 2006). The schematic representation of magnetic materials with respect to the availability of magnetic moments are shown in Figure 1.1



(Source: Chambers et al. 2006)

Figure 1.1 Schematic illustrations of (A) magnetic, (B) non-magnetic and (C) Diluted magnetic semiconductors

In the preliminary stage of identifying DMS materials, the work was mainly focused on Mn-doped Group II-VI compound semiconductors



(Furdyna et al. 1988, Ferrand et al. 2001, Macet et al. 1993, Lijuan Zhao et al. 2006) and then it was shifted to Group III-V (GaAs, GaP, GaN, GaSb, InAs, InP, InSb) (Ohno 1999 & 2000, Dietl et al. 2000, Story et al. 1993), Group IV-IVc compounds (PbS, PbSe, PbTe) (Story et al. 1993) and even in elemental semiconductors (Si, Ge). The Curie temperature (T_C) of these compounds was found below the room temperature and restricts the technological interest (Ohno 1999). In II-VI semiconductors, divalent magnetic ions would easily occupy the Group-II cation sites of the host lattices and results in antiferromagnetic (AFM) or spin glass ordering at higher concentrations (Furdyna et al. 1988). Evidence of ferromagnetism was observed in highly doped p-type ZnTe films ($T_C \sim 30$ K) (Ferrand et al. 2001) and it was noted that the Mn doped GaAs compounds exhibit highest Curie temperature around 110 K (Ohno 1999 & 2000).

The major breakthrough in the field of DMS emerged in the year 2000, when Dietl et al. (2000) successfully explained the ferromagnetic ordering in Mn doped ZnO. In addition, it was predicted that the transition metal doped wide band-gap oxide semiconductors could be a promising candidate to exhibit high T_C ferromagnetism. Further, the theoretical calculation also proves the stable magnetic ordering in DMS materials (Sato & Katayama-Yoshida 2000) and these theoretical predictions opened the pathway of Oxide Diluted Magnetic Semiconductors (O-DMS). The experimental observation of room temperature ferromagnetism in Co: TiO₂ thin films (Matsumoto et al. 2001) has stimulated considerable interest in investigations on other oxide based DMS such as transition metal doped ZnO and SnO₂ (Wang et al. 2004, Rahman et al. 2008). Further, the room temperature ferromagnetism was also identified in ABO₃ structured nano materials such as SrTiO₃, BaTiO₃, PbTiO₃ etc., (Sundherson et al. 2009). The occurrence of ferromagnetism in these materials was explained on the basis of mediated carriers which modify the magnetic behaviour by charge manipulation. The continuous search for materials with high T_C and carrier



mediated ferromagnetism reveals that the oxide based DMS materials would play key role in the development of spintronic devices.

1.2 WIDE BANDGAP OXIDE SEMICONDUCTORS

Semiconducting materials with energy gap greater than 3.0 eV are generally called as wide bandgap semiconducting materials. They are optically transparent in the visible region and suitable for shorter wavelength light applications. The most common examples for such oxide semiconductors are ZnO, TiO₂, SnO₂, In₂O₃ and ATiO₃ (where A= Ba, Sr, Pb) and AMO₄ (where A = Sr, Pb, Ba and M = W, Mo). These wide band gap DMS materials have the following advantages;

- (1) Optical Transparency
- (2) High carrier concentration
- (3) Ecological safety
- (4) Durability and low cost

In addition, the large electronegativity of oxygen is expected to produce strong p-d exchange coupling between band carriers and localized spins (Mizokawa et al. 2002). Wide band gap semiconductors are the prime candidates for various multifunctional applications such as in transparent electronics, UV light emitters, gas sensors, varistors and surface acoustic wave devices. Adding spin functionality to these materials, it could be useful to produce magnetic FETs and low threshold spin-lasers (Gurzhi et al. 2003, Rudolph et al. 2003).

1.2.1 Perovskite Structured Compounds

The ideal perovskite compounds with general formula of ABO₃ where A is the larger cation and B is the smaller cation possess cubic crystal structure (Ishihara et al. 2007). In that perovskite structure, the B cation has



6-fold coordination and the A cation has 12-fold coordination with oxygen anions. The corner sharing octahedra forms the skeleton of the structure, in which the center position is occupied by A cation. Alternatively, the perovskite structure can be viewed by placing B cation in the center of octahedron and A cation in the center of cube. Hence, the perovskite (ABO_3) structure is a superstructure with ReO_3 -type framework built up by the incorporation of A cations into BO_6 octahedra. The simple perovskite structure may be appropriately modified by incorporating B site ions with suitable size and charge. The most frequent substitutions are the equiatomic proportions of the two ions at the B-site, for which the general formula of the perovskite is $A_2BB'O_6$ (or $AB_{0.5}B'_{0.5}O_3$). If the charge of B and B' are different, in the ordered structure the oxygen's are slightly shifted towards the more charged cation although the octahedral symmetry of B and B' cations are preserved.

The distorted structure may exist at room temperature, but it transforms to cubic structure at high temperature. The deviations from cubic perovskite structure may proceed from a simple distortion of the cubic unit cell or an enlargement of cubic unit cell or a combination of both (Galasso 1990, Ishihara et al. 2007).

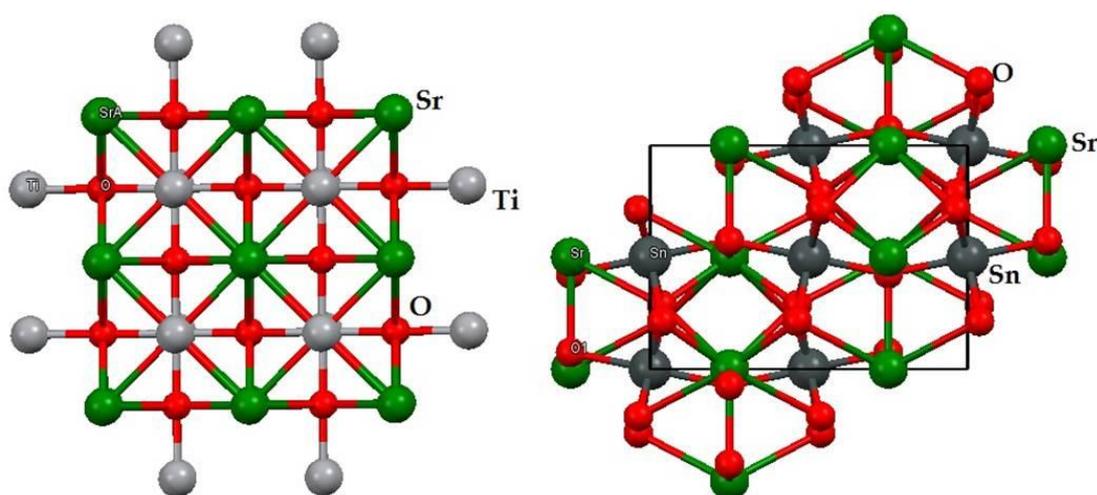


Figure 1.2 Crystal structures of $SrTiO_3$ and $SrSnO_3$ perovskite compounds

Distorted perovskites with reduced symmetry was found important for their magnetic and electric properties. Examples of perovskite based compounds are SrTiO_3 , BaTiO_3 , SrRuO_3 and LaFeO_3 . The crystal structures of the perovskite based SrTiO_3 and SrSnO_3 compounds focused for the present investigation were given in Figure 1.2. Further, the perovskites structured materials display several interesting physical properties such as ferroelectricity (BaTiO_3), ferromagnetism (SrRuO_3), weak ferromagnetism (LaFeO_3), superconductivity ($\text{YBa}_2\text{Cu}_3\text{O}_7$), large thermal conductivity due to exciton transport (LaCoO_3), insulator-to-metallic transitions (LaCoO_3), a fluorescence compatible with laser action ($\text{LaAlO}_3:\text{Nd}$) and transport properties of interest for high temperature thermoelectric power (La_2CuO_4).

1.2. 2 Scheelite Structured Compounds

Scheelite compounds have been referred with the general molecular formula of ABO_4 , (where A = Ca, Ba, Pb and Sr, B = W or Mo) (Cavalli et al. 2010). The compounds with large divalent ions exhibit Scheelite structure with tetragonal symmetry and those compounds having smaller metal ions such as Zn, Mn, or Fe are found to have Wolframite structure (monoclinic). The crystal structure of the scheelite based SrMoO_4 and SrWO_4 compounds studied in the present work is given in Figure 1.3. The Scheelite structure was characterized by tetrahedrally coordinated $(\text{WO}_4)^{2-}/(\text{MoO}_4)^{2-}$ group positioned at four corners of the unit cell. The divalent cation is located at the body centre position of the unit cell which is octahedrally coordinated with oxygen ions (Gurmen et al. 1971, Botella et al. 2014). These minerals glow with bright sky-blue colour while exposed to ultraviolet radiation. Occasionally green color fluorescence is also observed in the presence of molybdenum trace impurities. Well-formed crystals are occasionally fashioned into gemstones when they are free of flaws.



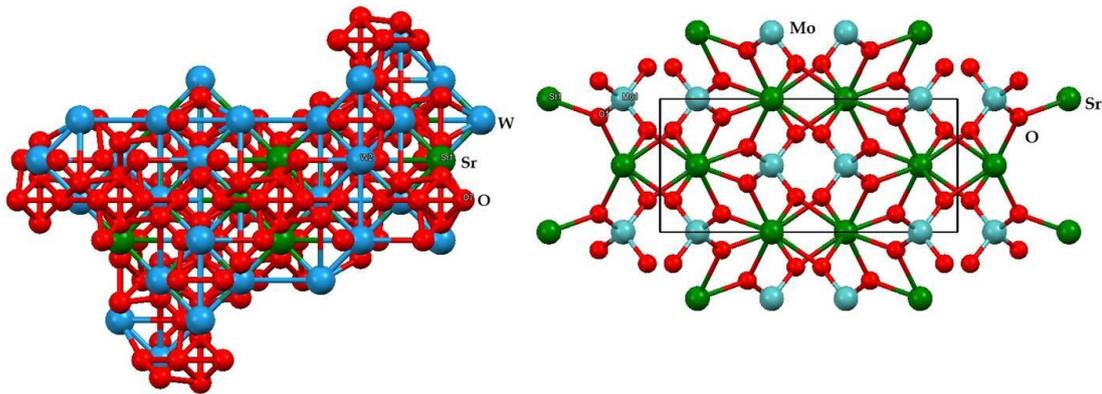


Figure 1.3 Crystal structures of SrWO₄ and SrMoO₄ Scheelite compounds

The robust lattice structure makes these compounds suitable for intrinsic scintillators to detect the very high energy radiation (Ninković et al. 2005) and can be utilized as laser-host materials (Faure et al. 1996), detectors for X-rays and γ -rays in medical applications (Mahlik et al. 2012) and in optoelectronic devices (Brenier et al. 2004).

1.3 ORIGIN OF FERROMAGNETISM IN DILUTED MAGNETIC SEMICONDUCTORS

The origin of ferromagnetism is believed to be an intrinsic property of a material due to the interactions mediated by charge carriers or from extrinsic sources, by which the magnetic impurities or secondary magnetic phases segregate in oxide materials. Both theoretical predictions and experimental analysis have been carried out for the analysis of structural, magnetic and electronic transport properties of DMS materials to determine the mechanism responsible for room temperature ferromagnetism. According to that, several models have been proposed to explain the origin of ferromagnetism in wide bandgap oxide materials, such as superexchange interactions, indirect exchange mechanisms, double exchange, Ruderman-Kittel-Kasaya-Yosida (RKKY) model and bound polaron model. However, the contradictory results made it difficult to draw definitive conclusions. Structural defects such as oxygen vacancies, interstitial atoms, presence of

amorphous phases and grain boundaries have been considered as an important factor which influences the magnetic properties. Further, the origin of high temperature ferromagnetism in diluted magnetic oxides is related to the transition metal dopants which have unfilled d-shell and thus carry magnetic moment due to unpaired electrons.

On the other hand, the spins of electron align with each other and exhibit ferromagnetic behaviour even in the absence of magnetic field. This may happen when the density of states of spin up electrons is more while comparing to spin down states. Therefore, an interaction between the spins must exist. This interaction depends on orientation of spins and charge distribution between magnetic ions separated by a non-magnetic ion. In the second case, the direct exchange interaction arises due to direct Coulomb interaction between the electrons from two ions. Hence the magnetic ions interact with each other via electrons originating from common non-magnetic neighbour and have been described as superexchange interaction (Anderson 1955). The possible spin pinning on non magnetic materials have been proposed by various models and discussed as follows:

1.3.1 The Double Exchange Interaction (DE)

The double exchange interaction is an indirect type exchange mechanism that occurs in solids when the concentrations of magnetic ions are larger than the number of carriers. The indirect exchange interaction is due to the presence of mobile carriers that can mediate the interactions between magnetic spins. The double exchange model was proposed by Zener (1951) to describe the magnetic interactions taking place in transition metals.

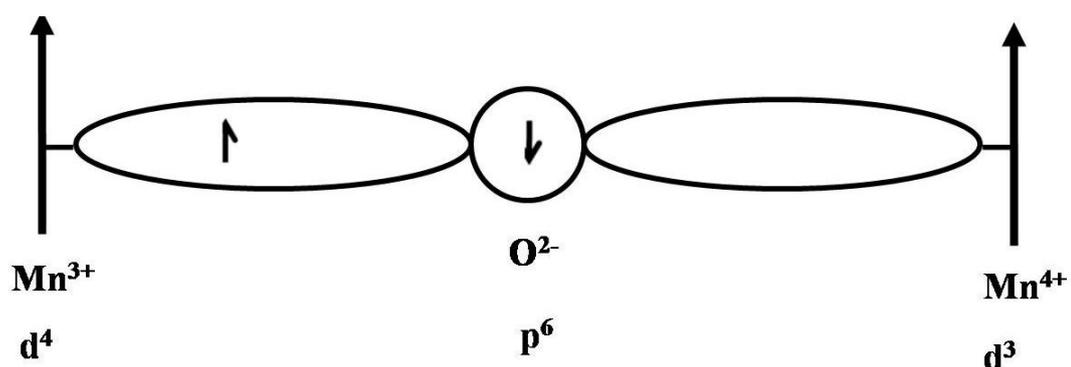
- 1) Coupling due to direct exchange between incomplete d shells of transition metal ion and completely filled p orbitals of the anion.
- 2) Coupling due to indirect exchange interaction between the localized d-shell electrons and delocalized conduction



electrons which tends to align the spins of transition metals and thus creating a long range ferromagnetic ordering in the solid. Ferromagnetism is possible only when neighboring incomplete d-shells are sufficiently far apart so that the indirect exchange through conduction electrons dominates the antiferromagnetic exchange interaction. Thus, conduction electrons are necessary to provide the ferromagnetic coupling.

- 3) The third coupling was related to Fermi kinetic energy of the conduction electrons.

Zener (1951) argued that the carriers do not change their spin orientation during hopping process. This case may be possible only when the spins of two magnetic ions are parallel. This model has been applied to Europium salts and Manganites in order to explain the ferromagnetism and conductivity. Zener (1951) described the exchange interaction between neighboring Mn^{3+} and Mn^{4+} ions, separated by a closed shell neutral O^{2-} atom as shown in Figure 1.4. An electron from Mn^{3+} ion is transferred to O^{2-} ion and then the electron can further move from O^{2-} to Mn^{4+} (Coeys et al. 2009)



(Source: Zener 1951)

Figure 1.4 Schematic representation of double-exchange interaction in manganites

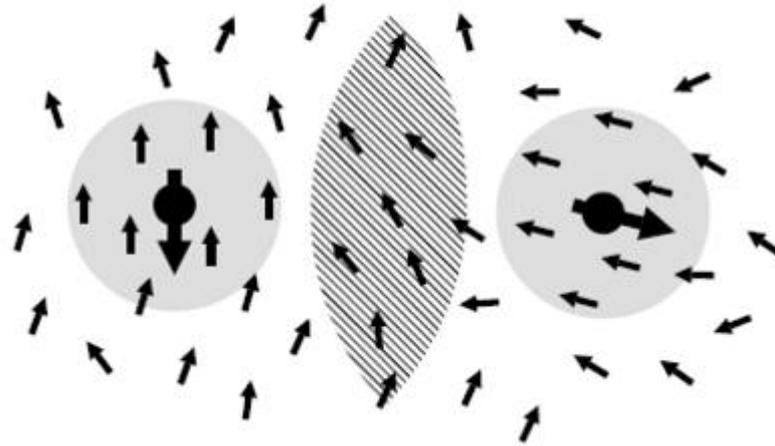
1.3.2 The Bound Magnetic Polaron Model

The bound magnetic polaron (BMP) model was introduced to explain the low temperature metal to insulator transition in oxygen deficient EuO compound (Torrance et al. 1972). By this model, it was noted that the oxygen vacancies can act as electron donors, and results the possible electron trapping mechanism to maintain insulating behavior. Each trapped electron couples the local moments of host lattice that lie within its orbit ferromagnetically and leads to a bound polaron with large net magnetic moment. If neighbouring polaron does not interact strongly, paramagnetic or insulating phase results. However, for certain polaron distances and electron-local moment exchange constants, the polaron couples ferromagnetically (Durst et al. 2002, Angelescu & Bhatt et al. 2002). The critical distance above which the exchange between two BMPs becomes ferromagnetic is typically of the order of few Bohr radii (Angelescu & Bhatt 2002). It was also found that the amplitude of exchange interaction drops rapidly with respect to the distance. Above critical electron density, the attractive potential of vacancy is screened by which the donor electrons become unbound and the system becomes metallic (Kubler & Vigren 1975).

When the transition metals doped with oxide semiconductors, there could be a possible formation of shallow donors due to defects formation (Forro et al. 1994, Tuan et al. 2004). Moreover, the local exchange between carriers and magnetic ions allow the formation of an impurity band. Electrons will be localized due to electrostatic interaction with certain defects (e.g. oxygen vacancy in oxides). The electrons bound to the defect, interacts with surrounding impurity spins to produce local ferromagnetic interaction which is also described as bound magnetic polaron (Torrance et al. 1972, Das Sarma et al. 2003, Berciu et al. 2003). The illustration about the interaction between two bound polaron is shown in Figure 1.5. In the Figure, the small arrows represent



the spin of impurity atom and large arrows indicate the spin of hole (Kaminski & Das Sarma 2002). The shaded region designates overlap affected by fields.



(Source: Kaminski & Das Sarma 2002).

Figure 1.5 Interaction between two bound magnetic polaron (BMP)

In BMP model, the oxygen defects are responsible for shallow donors to strongly stabilize the ferromagnetic ground state. The oxygen vacancies were documented for TiO_2 (Yahia et al. 1993) and ZnO (Kohan et al. 2000). For ZnO, Zn interstitials (Zn_i) are reported as a shallow donor (Look et al. 1998). By *ab initio* calculations, it was predicted that the Co-doped TiO_2 has more oxygen vacancies than the undoped ones (Errico et al. 2005). Further, it was also suggested that the oxygen vacancies in adequate portion can provide necessary carriers to stabilize the ferromagnetic state. By the electronic structure calculations, it was reported that the oxygen vacancy with half spin strongly promote ferromagnetic coupling of Co ions in Co-doped ZnO compound (look et al. 1999, Lee et al. 2002). At the same time, Calderon & Das Sarma (2007) argued that the bound magnetic polaron mechanism can be explained the low temperature magnetic ordering in dilute magnetic semiconductors, but it is not sufficient to explain high T_C in oxide materials.

1.3.3 The RKKY Model

The Ruderman- Kittel-Kasuya-Yosida (RKKY) interaction theory was developed to explain the indirect exchange coupling of nuclear magnetic moments by conduction electrons (Cullity & Graham 2009, Rath & Callaway 1973). The RKKY model describes the magnetic interaction between localized magnetic ions and delocalized conduction band electrons. Due to this interaction, the conduction electrons close to magnetic ions get magnetized and act as an effective field to influence the polarization of nearby magnetic ions. Hence the process leads to polarization decay in an oscillatory manner and the oscillation mediates either ferromagnetic or antiferromagnetic exchange coupling depends on the separation between magnetic ions. In rare-earth metals and alloys of magnetic ions in a non-magnetic metallic host, the magnetic ions are too far to interact directly with each other. However, a long-range of interaction can occur via non-magnetic conduction electrons. Essentially, a magnetic ion polarizes the surrounding electrons with respect to delocalization and distance between magnetic ions. Hence the interaction between the magnetic ions can be either ferro or antiferromagnetic, depending upon the distance between the ions. The RKKY model is efficient when high concentration of delocalized carriers is present in the host material (Yosida 1996, Kaminski & Das Sarma 2002, Pintu Das et al. 2012). This type of interaction is specific to ferromagnetic metals due to spin imbalance that occurs due to exchange interactions between 3d electrons and conduction electrons.

1.3.4 d^0 Ferromagnetism in Oxide Semiconductors

The occurrence of unexpected ferromagnetism in non-magnetic semiconductors would be explained on the basis of absence of magnetic d-block ions and is called as “ d^0 ferromagnetism”. In this model, it was suggested that the defects such as cation or anion vacancies, grain boundaries



and interfaces play a crucial role in inducing ferromagnetism in oxide materials, even though the d or f shells of anions or cations of the material is empty or completely filled. The observed d^0 ferromagnetism in HfO_2 system open up new challenges for the theory of magnetism and also the possibility of designing new class of spintronic oxide-based materials (Venkatesan et al. 2004).

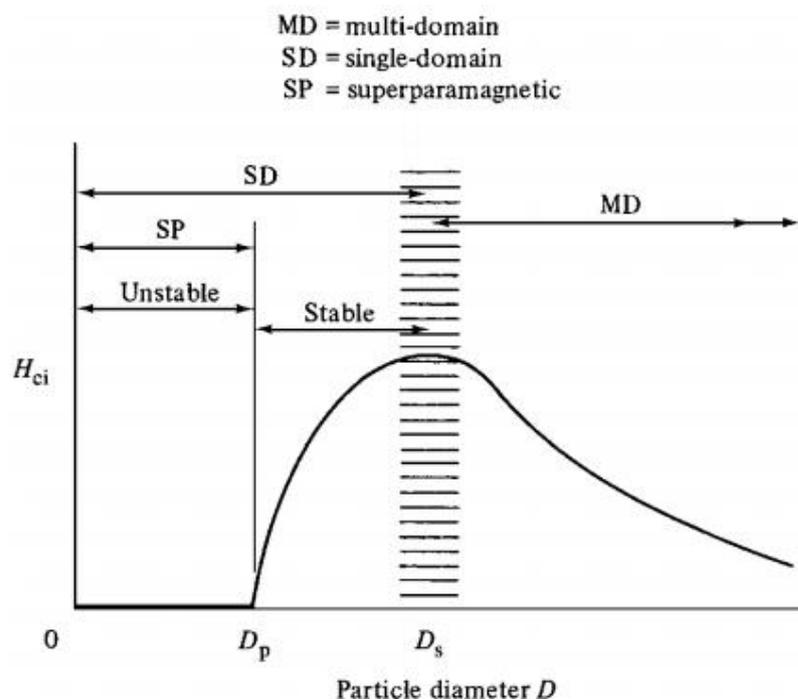
Defects in magnetic and nonmagnetic oxides during the growth process, structural defects such as cation vacancy, oxygen vacancy, interstitials, antisite defects, grain boundaries and interfacial defects would be stabilized within the materials. These type of defects are known to control various intrinsic or extrinsic properties such as optical, luminescence, magnetic, electrical conductivity etc. However, the investigations on local magnetic properties of these defects become essential after the observation of unexpected ferromagnetism in HfO_2 thin films (Venkatesan et al. 2004). Among various defects, cation vacancy (e.g. Zn vacancy in ZnO, Sn vacancy in SnO_2 , Hf vacancy in HfO_2 , Zr vacancy in ZrO_2 and Ca vacancy in CaO) was found to induce localized magnetic moment which originates from 2p state of electrons from nearest oxygen atoms (Wang et al. 2004, Chan et al. 2009, Rahman et al. 2008, Pemmaraju & Sanvito 2005, Elfimov et al. 2002) etc.). On the other hand, oxygen vacancy within oxide materials can capture one or two electrons and will be stabilized in three different ionized states such as double ionized oxygen vacancy (VO^{++}), single ionized oxygen vacancy (VO^+) and neutral oxygen vacancy (VO^0). However, the theoretical investigation have shown that only single ionized oxygen vacancy (VO^+) i.e. F^+ centre has local magnetic moment of $1\mu\text{B}$ which originates due to trapping of an electron (Coey et al. 2005, Venkatesan et al. 2006). Besides intrinsic defects, the substitutional defects arise by doping of C, N at oxygen site are also found to induce magnetic moment in non-magnetic oxides (Gu et al. 2009, Yu et al. 2007). In addition, vacancy-induced ferromagnetism in oxides show that the cationic substitution of Group-I elements such as Li, Na, K, Cs



etc. in II-VI and IV-VI oxides can stabilize the ferromagnetic ordering (Bouzerar&Ziman 2006).

1.3.5 Grain Boundaries, Spin Glasses, Magnetic Clusters

The microscopic spin distributions in solids are great of interest while dealing with spin-dependent transport mechanism. In general, coercivity is defined as the reverse field that must be applied to the magnetically saturated material in order to completely demagnetize it. Coercivity values of the magnetic specimen are depends on size and dimensionality of the system. The coercive field was determined by the factors such as shape and size of the particles and crystalline anisotropy. The study of coercivity in thin films is a complicated issue due to magnetic and structural inhomogeneities in thin films. Moreover, grain boundaries also contributing to the anisotropies associated with the crystal.



(Source: Cullity 2009)

Figure 1.6 Dependence of intrinsic coercivity (H_{ci}) with particle size

Many reports suggest that the details of grain boundaries as well as the formation of magnetic nanoparticles or spin glass structures would be useful to explain the high temperature ferromagnetism in DMS (Coey et al. 2010). In fine magnetic nanoparticles, it was experimentally proved that the coercivity value increases with respect to decrease in particle size and reaching its maximum (Luborsky 1961). Then it was found that the H_c value decreases to zero with further decrease of particle size. Figure 1.6 reveals the effect of size of particles with coercivity values. The regions to be specified for the conditions are follows:

- 1) Region-I: Particle size smaller than D_p (threshold critical radius) are to be unstable single domain particles. For single domain particles, below critical volume, the magnetization can randomly flip its direction between easy axes under the influence of temperature due to the energy barriers are comparable with thermal energy.
- 2) Region-II: The critical volume of particles between D_s to D_p ; which leads the particles become stable single domain particles.
- 3) Region-III: Multi domain particles exist above the critical diameter of the particle.

In reality, small particles interact with each other; therefore there will be a distribution in size of particles as well as distribution in local environments of particles in the host matrix.

In Superparamagnetic region, the size of particles are smaller than threshold (D_p) value in which the coercivity is zero, In stable single domain region, the coercivity increases with particle size, whereas the multi domain region was characterized by decrease of coercivity value with the increase of particle size (Cullity 2009).



1.4 TRANSITION METAL-DOPED OXIDE SEMICONDUCTORS

Following the theoretical prediction about the possibility of achieving high T_C ferromagnetism in wide band semiconducting oxides, many efforts have been carried out to prepare oxide-based DMS compounds by doping various transition and rare earth elements (Dietl et al. 2000). The first principle calculations reveals that the ferromagnetic ordering in transition metal ion doped ZnO matrix is stable (Sato & Katayama Yoshida 2001). Magnetic properties of transition metal ion doped oxides also depend on sample preparation conditions and indicate that the doped transition metal 3d electrons may not be responsible for the origin of ferromagnetism in such oxides. In most of the cases, small amount of the presence of TM impurity secondary phases or defects has been identified as the origin of observed ferromagnetism (Kaspar et al. 2005).

Straumal et al. (2009) reported that the grain boundaries and related vacancies are the intrinsic origin for room temperature ferromagnetism in Mn doped ZnO compounds whereas Liu et al. (2007) reported that ferromagnetism in V:ZnO powder is highly correlated with structural defects rather than V^{5+} ions. In addition, the perovskite structured $ATiO_3$ (A= Ba, Sr, Pb) compounds doped with magnetic elements such as Fe, Ni, Co, Mn and Cr exhibits the room temperature ferromagnetism. Alternatively, oxygen vacancy induced ferromagnetism also reported in titanate based compounds. In order to explore the origin of ferromagnetism in oxide DMS, a systematic study with careful identification of crystalline phases and microstructures are needed. Hence, the present investigation is focused on effect of TM (Cr) ion doping in the magnetic property of wide bandgap semiconducting materials.



1.5 NEED FOR HIGH TEMPERATURE (T_C) MAGNETIC OXIDE SEMICONDUCTORS

The observation of room temperature ferromagnetism (RTFM) in pure HfO_2 thin film (Venkatesan et al. 2004) has opened up a new challenge to explain the origin of magnetism in the absence of any d or f orbital electrons. Different oxide thin films and nanostructures such as ZnO , SnO_2 , TiO_2 , In_2O_3 and ATiO_3 compounds were found to exhibit ferromagnetism in their purest phase or using non-magnetic dopants (Gacic et al. 2007, Kaspar et al. 2005, Straumal et al. 2009, Hong et al. 2006, Gao et al. 2010, Sundaresan et al. 2006). The theoretical calculations were also performed to reveal the origin of ferromagnetism in these oxides and it was found that the localized cation vacancies may induce the magnetic moment. Further, Sundaresan et al. (2007) reported that the ferromagnetism in oxide nanostructures was due to oxygen vacancy (VO) and defects. However, Density Functional Theory (DFT) based first principle calculations show that neutral oxygen vacancy is non-magnetic whereas Zn and Sn vacancy in ZnO and SnO_2 have magnetic moment, which originates from unpaired 2p state of Oxygen atom in the vicinity of cation vacancy site (Wang et al. 2008, Rahman et al. 2008). Therefore, proper realization of defects and defect-dynamics within the oxides can provide exciting opportunities to achieve the goal of high T_C ferromagnetic oxide semiconducting materials.

1.6 AIM OF THE PRESENT WORK

From the above perspective, the present work deals with search of high temperature (T_C) oxide DMS materials. The peculiar magnetic properties of transition metal doped oxide DMS materials impose serious restriction to find applications. In fact, the presence and/or absence of intrinsic ferromagnetism in transition metal doped wide bandgap oxides is a controversial issue and to overcome, there is a need for systematic investigation on various parameters such as synthesis process, dimensionality,



crystallite size and surface morphology which influence the physical properties of the compounds. The motivation of present work is to investigate the origin of magnetism in transition metal doped wide bandgap oxide semiconductors correlating with their optical properties. The realization of multifunctional properties would be possible only through proper understanding of role of defects and charge carriers in the host lattice. Therefore, the motivation behind the present work is as follows;

- Synthesis and characterization of structural, optical and magnetic properties of pure and Cr doped SrTiO_3 compounds.
- Synthesis and characterization on structural, optical and magnetic properties of pure and Cr doped SrSnO_3 compounds.
- Synthesis, characterization and studies on structural, optical and magnetic properties of pure and Cr doped SrMoO_4 compounds.
- Synthesis and characterization of structural, optical and magnetic properties of pure and Cr doped SrWO_4 compounds.

