CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION OF DILUTED MAGNETIC SEMICONDUCTORS

In order to achieve higher speeds, size of devices is diminishing continuously. As a result of this shrinkage, design parameters are impacted in such a way that materials in present use are pushed to their limits [1]. The alternative would be to exploit multifunctional properties of materials. Today, one of the hot topics among researchers is to use other unexploited degree of freedom, the spin of electrons or ions to gain new functionalities in electronics. The electronic charge, spin and mass form the pillar of present IT industry. ICs made of semiconductors utilize the electronic charge. On the other hand the information storage is done by magnetic recording using electronic spin in a ferromagnetic metal [1, 2]. But, in future, information technology may see semiconductivity (charge) and magnetism (spin) combined in a single device by exploiting both charge and spin to process and store the information. Such a device is called as “Spintronic device”. It is difficult to realize such a device because semiconductors currently used in integrated circuits, transistors and lasers, such as silicon and gallium arsenide are nonmagnetic. Moreover, the magnetic fields that would be required to have a useful difference in the energy between the two possible electron spin orientations (up and down) are too high for everyday use [3]. So, the creation and control of spin-polarized currents in semiconductor is important. The integration of spintronics into existing semiconductor devices provided by ferromagnetic semiconductors is relatively easy. For instance, highly efficient spin injection is possible between semiconductor/semiconductor interface, whereas, due to conductivity mismatch, very less spin polarizations (a few percent) are possible between a ferromagnetic metal/semiconductor interface [4]. However, for realization of semiconductor-based spintronics, significant challenges related to the lifetime, control and detection of spin polarized carriers in semiconductors must be seriously addressed. Thus, semiconductors that can retain their ferromagnetism above room temperature are crucial to the practical applications of spintronic devices. There are semiconductors with, a periodic array of magnetic elements (Europium, chalcogenides and semiconducting spinels) but their crystal structure is different from the conventional
semiconductors Si and GaAs, which are generally used in electronics. Their crystal growth is very difficult too. Hence, these are not the ideal candidate for spintronic applications [5].

Since late 1980s, scientists have found that, in many semiconducting crystals, substitution of transition metals (TM) adds local magnetic moments to the system’s low energy degree of freedom [6]. These doped semiconducting materials are called diluted magnetic semiconductors (DMSs), where usually a small fraction of TM is substituted on the host semiconductor. Figure 1.1a illustrates a nonmagnetic semiconductor like GaAs or ZnO which is composed of two nonmagnetic elements (yellow and green). A contrast, ferromagnetic semiconductor is shown in figure 1.1c in which one of the two elements has local magnetic moment. Now, figure 1.1b shows the desired DMS in which few atoms of a non-magnetic semiconductor are substituted by atoms (TM) possessing local magnetic moments.

![Figure 1.1. Illustration of (a) nonmagnetic semiconductor, (b) a diluted magnetic semiconductor and (c) a magnetic semiconductor [7].](image)

Metals used as magnetic atoms in DMS are transition metals with partially filled d states (Ti, V, Cr, Mn, Fe, Co, Ni and Cu) and rare earth elements with partially filled f state (eg. Eu, Gd and Er) [5]. Partially filled d or f states containing unpaired electrons, are responsible for magnetic behaviour in DMSs. In DMSs, delocalized conduction band electrons and valence band holes interact with localized magnetic moments of magnetic atoms. Generally, substitution of 3d transition metal ions for host cations, influences the electronic structure by strong hybridization of the 3d orbitals of magnetic ions and mainly p orbitals of the neighbouring host anions which gives rise to the strong magnetic interaction between localized 3d spins and carriers in the host valence band [8]. The availability of high quality samples have flowedished the study of DMS. The DMS offers a possibility of studying
magnetic phenomenon in crystals with a simple band structure and excellent magneto optical and transport properties. Also, existing high quality techniques for semiconductor heterostructure formation enable incorporation of layers of DMS into transistors, quantum wells, electro-optical devices etc, in which the spin splitting also be tuned by the confinement of energy and the size quantization. The most challenging task for potential applications is to find diluted magnetic semiconductor operating at room temperature.

The III-V and II-VI DMSs have attracted the researchers due to their potential ability. As a consequence of 3d transition-metal substitution for host cations, the electronic structure of 3d transition-metal is influenced by two factors which are competing: (1) strong 3d-host hybridization and (2) strong Coulomb interactions between 3d-3d electrons. Multiplet structures in d-d optical-absorption spectra are due to Coulomb interaction between 3d-3d electrons. On the other hand, the hybridization between the transition-metal and the host valence band gives rise to the magnetic interaction between localized 3d spins and carriers in the host valence band [9]. To search new functionalities, it is important to look the evolution of semiconductors Figure 1.2.

![Semiconductor periodic table of element needed for spintronics.](Figure 1.2)

Recently, observations of high temperature magnetic transitions in III-V and II-VI semiconducting materials at relatively high temperature (100 K) [10-15] have attracted the scientific community. The demonstration of spin-coherence in semiconducting materials [16] and the development of the storage technology using ferromagnetic metals have heightened the activities in this field. As, these semiconductors can be manipulated easily to act as an appropriate heterostructure with doping, the actual fabrication of RTFM semiconductors remains attractive for device applications.
1.2 SPINTRONICS AND NEED OF MAGNETIC SEMICONDUCTORS

The conventional electronics relies on the transport of charge of the electron in a semiconductor and ignores its spin which provides an opportunity to explore the future of information technology. Until 1970’s, electronic components circuits were compacted into integrated circuits in semiconducting chips. Since then, information industry got momentum in the development and maintaining Moore’s law [17], which summarizes the development of semiconductor and information industry which compacts a huge electronic computer to be a part of our everyday life. As, a transistor cannot be smaller than an atom, it becomes an insurmountable obstacle in the modern industry. As the size of the transistor decreases classical physics no longer applied and quantum effects come to the picture. So, it will be necessary to understand and overcome the quantum mechanical limitations. When people began to think about the future semiconductor industry, it is surprisingly found that almost all electric products just ignore the intrinsic quality spin of an electron. In contrast, magnetic materials are utilized on the basis of spin of electron. Thus, the advance in electronics which is called spintronics combines both features of the electron: the charge and the spin. The spin of electron carrying the information can be utilized as an additional degree of freedom basic electronic devices. Thus, the development of functional ferromagnetic semiconductors is a key to the development of the spintronics (or spin based electronics) [18], which will certainly be the devices of future. The advantage of spin over the charge is that spin can be easily manipulated by externally applied magnetic fields. Another significant property of spin is its long coherence, unlike charge states, which are easily destroyed by scattering or collision with defects, impurities or recombination [19]. Such characteristics of spin open the possibility of developing new devices that could be much smaller, consume less power and will be more powerful for certain types of computations which is not possible with electron-charge-based systems. It is widely expected that new functionalities for electronics and photonics can be derived if injection, transfer and detection of carrier spin can be controlled above room temperature [20].

Thus, spintronics is a branch of science dealing with the active manipulation of spin degree of freedom of electrons in semiconducting materials. The science has a long tradition starting with Mott’s theoretical work in 1936 on spin polarized transport [21]. But, interest in this field was developed after the work of groups of Albert Fert in Paris and Peter Grnberg in...
Julich [22]. The field has seen an explosive growth since the discovery of Giant Magneto Resistive (GMR) material which has found successful commercial applications [23].

Spintronics consist of, spin generation, transport and detection [24]. For the generation of polarized spins in the semiconductor, ferromagnetic metals were applied first as a source, but there is a large mismatch of the resistance between metals and semiconductors [25]. A more efficient way for the spin injection is making the semiconductor ferromagnetic as suggested by H. Ohno [5].

First generation spintronic devices were based on passive magnetoresistive sensors and memory elements using electrodes made from alloys of ferromagnetic 3d metals which was later boosted by the discovery of GMR in (Fe/Cr)n multilayer and tunnelling magnetoresistance [26]. Future generation spin-based devices will necessarily comprise the creation and manipulation of spin-polarized electrons in a host semiconductor [27, 28]. To resize an operational device, spin-polarized electrons need to preserve their polarization as they travel through the semiconductor. The most obvious way for spin injection would be injection from a FM metal in a metal/SC junction. Such type of heterostructures have been extensively studied; however, it has been shown that due to the large mismatch in electrical conductivity between two materials it is difficult to preserve the electron spin across the interface [29]. On the other hand, magnetic semiconductors should allow easier integrability with the existing semiconductor technology, and would be crucial for signal amplification with highly spin-polarized carriers. Therefore, a real challenge for material scientist is to design materials containing both semiconducting and ferromagnetic properties which will be crucial in the development of such devices. It was in this context that the concept of DMS emerged which are non-magnetic semiconductors doped with a few percent of magnetic elements TM, and are expected to be not only easily integrable with existing semiconductors but also highly spin-polarised. However, the discovery and understanding the mechanism of origin of magnetism in such materials are proving to be a grand challenge in solid state science. Indeed, one of the 125 critical unanswered scientific questions raised in a commemorative issue of Science magazine [30, 31], asks, “Is it possible to create magnetic semiconductors that work at room temperature?”.
1.3 BASICS OF MAGNETISM

The story of magnetism begins with a mineral called magnetite (Fe₃O₄), which is the first magnetic material known to us. The early history of magnetism is obscure, but its power of attracting iron was certainly known 2500 years ago.

The first truly scientific study of magnetism was made by the Englishman William Gilbert (1540–1603), who experimented with lodestones and iron magnets, cleared away many superstitions that had clouded the subject and formed a clear picture of the Earth’s magnetic field.

The type of magnetism is generally associated with three main categories of materials diamagnetic, paramagnetic and ferromagnetic; in addition, antiferromagnetism and ferrimagnetism are considered to be subclasses of ferromagnetism. The behaviour of magnetic materials depends on the response of electron and atomic magnetic dipoles to an externally applied magnetic field.

1.3.1 DIAMAGNETISM

Diamagnetism is the weakest form of magnetism i.e. non-permanent, induced by a change in the orbital motion of the electron due to an applied magnetic field. The magnitude of the induced magnetic moment is extremely small and is in the direction opposite to that of the applied magnetic field. Thus, the diamagnetic material exhibits a negative and an extremely small magnetic susceptibility of around 10⁻⁵ and relative permeability less than unity. A perfect diamagnetic material could offer maximum resistance to an external magnetic field with zero permeability. Schematic atomic magnetic dipole configurations for a diamagnetic material in the presence and absence of applied magnetic field are shown in figure 1.3.
The property of diamagnetism is observed in all materials; but as is so weak and is observed if others are absent. As Michael Faraday showed that all substances can be magnetized in sufficient magnetic field. Materials such as gold, silver, mercury, quartz and graphite, the noble gases and the majority of organic compounds are all diamagnetic in nature.

1.3.2 PARAMAGNETISM:

It occurs in materials having atoms or molecules with permanent dipole moment. In absence of field, these atomic dipoles are oriented randomly i.e. no magnetization.

The susceptibility of paramagnetic substances are small and positive of the order of the $10^{-3}$ to $10^{-5}$. Atomic dipoles are permanently free to rotate and paramagnetism results when they...
preferentially align, by rotation with an external magnetic field as shown in figure 1.4. Paramagnetism is found in magnesium, molybdenum, lithium, and tantalum etc.

1.3.3 FERROMAGNETISM:

Ferromagnetic materials have a spontaneous magnetization in the absence of the external field and manifest very large and permanent magnetization. Permanent magnetic moments in these materials result from atomic magnetic moments due to un-cancelled electron spins. There is also small orbital magnetic moment contribution in comparison to the spin moment. Furthermore, in a ferromagnetic material, coupling interaction causes net spin magnetic moments of adjacent atoms to align to one another, even in the absence of an external magnetic field which is schematically illustrated in figure 1.5.

![Figure 1.5: Schematic representation of spin alignment in a ferromagnetic material.](image)

The origin of these coupling forces is not completely known, but it is thought to rise from electronic structure of the metal. This mutual spin alignment exists over relatively large volume regions of the ferromagnetic crystal called domains. So, Ferromagnetic crystals are composed of tiny domains inside which atoms exhibit parallel magnetization. In fact, the magnetic moments of each atom can align themselves spontaneously within these domains, even in the absence of an external field. Magnetic susceptibility of ferromagnetic substances is positive and very high of the order of $10^6$. The value of the susceptibility of ferromagnetic substance changes with temperature in a complicated manner. Above a particular temperature called Curie temperature, the spontaneous magnetization vanishes.

So, any ferromagnetic material at temperature below $T_c$ have small domains which are spontaneously magnetized (Figure 1.6a) and are separated by domain wall, across which the
spin gradually changes as shown in figure 1.6b. The domain size may vary from \(10^{-6}\) cm to the entire volume of the crystal.

\[\text{Figure 1.6 (a): Schematic depiction of domains in a material; arrows represent atomic magnetic dipoles.}\]

Initially, moments of domains are randomly oriented giving no net magnetization (Figure 1.7). As the external field is applied, domains which are oriented in the direction of the applied field grow at the expense of those which are not favourably oriented (inset B through D). This process continues with increasing field until the macroscopic specimen becomes a single domain (inset E). Saturation is achieved when domains, by means of rotation become oriented with the field (inset F).
Figure 1.7: The M-H behavior for ferromagnetic material that was initially unmagnetized. Domain configurations during several stages of magnetization are represented [33].

When a ferromagnetic material is magnetized in one direction with the help of the external field, it will not relax back to zero magnetization when the applied field is removed.

Figure 1.8: A schematic of the magnetization versus field curves expected for ferromagnetic, paramagnetic, and diamagnetic materials.
The magnetization may be driven back to zero by a magnetic field in the opposite direction. If an alternating field is applied to the ferromagnetic material, its magnetization traces out a loop called hysteresis loop. According to the domain concept, applied external field triggers domain wall movement that tends to strengthen the applied field. If the field exceeds a certain value then it diminishes the domain walls which cannot fully reverse back to their original positions which results in remanent magnetization. From the figure 1.8 it is clear that if the field \( H \), is reduced by reversal of direction, magnetization does not retrace its original path. At zero field there exists a residual magnetization called remnance. In order to cancel out the magnetization within the specimen, field is to be applied in the opposite direction which is known as coercive field \( H_c \), and this phenomenon is called coercivity (figure 1.8). For diamagnetic and paramagnetic materials, the observed magnetization, at low fields, is linear with the applied field and returns to zero after removal. The slope of the diamagnetic signal is small and negative; for a paramagnetic substance it is small but positive. Ferromagnetic materials can be easily identified by hysteresis.

1.3.4 ANTIFERROMAGNETISM AND FERRIMAGNETISM

The phenomenon of ferromagnetism is based on the fact that quantum mechanical exchange interactions produce large internal fields due to which the neighbouring dipoles tend to align parallelly in the same direction. When the distance between interacting dipoles is very small, the exchange force tends to produce antiparallel alignment of the neighbouring spin dipoles; which is called as antiferromagnetism. The spin arrangement for antiferromagnetic substance is schematically presented in figure 1.9a. Conclusively, there is no net magnetic moment; the alignment of the various spins will cancel out and there are equal numbers of atoms with opposite spins. The characteristic signature of a polycrystalline antiferromagnetic substance is that its susceptibility shows a maximum as a function of temperature.
Figure 1.9: Schematic representation of spin alignment: (a) Antiferromagnetic and (b) ferrimagnetic materials.

In ferrimagnetic materials, moments of two sublattices which are aligned antiparallel to each other produce a total moment equal to the difference between their individual moments. The macroscopic magnetic characteristic of ferromagnets and ferrimagnets are similar, the distinction lies in the source of net magnetic moments. The temperature dependence of magnetization of ferrimagnet is quite different to ferromagnetic materials due to the difference in their internal structure but the external behaviour is similar. The schematic of the spin alignment in ferrimagnetic materials is illustrated in figure 1.9b. Ferrimagnetic materials are of great technical importance because they exhibit a spontaneous magnetic moment below a curie temperature just as iron, cobalt and nickel but they are poor electrical conductors.

The familiar example of ferromagnetic material is magnetite, the formula for prototype ferrite is Fe$_3$O$_4$, the mineral magnetite. The formula Fe$_3$O$_4$ may be written as Fe$^{2+}$O$^{2-}$ - (Fe$^{3+}$)$_2$(O$^{2-}$)$_3$. A net spin magnetic moment exist for each Fe$^{2+}$ and Fe$^{3+}$ ions, which corresponds to 4 and 5 Bohr magnetrons, respectively for the two ion types. Furthermore, the O$^{2-}$ ions are magnetically neutral. An antiparallel spins coupling interaction exists between Fe ions, similar to antiferromagnetism. However, the net ferromagnetic moment exists due to from the incomplete cancelation of spin moments.
1.4 Theoretical Models for Explaining Ferromagnetism in DMS

1.4.1 THE RKKY MODEL

The RKKY (Ruderman-Kittel-Kasuya-Yosida) model [34] explains the magnetic interaction between a single localized magnetic ion and delocalized conduction band electrons. Due to RKKY interaction, conduction electrons close to the magnetic ion get magnetized and act as an effective field to influence the polarization of neighbouring magnetic ions, with the oscillatory polarization decaying with distance from the magnetic ion and causing indirect super exchange interaction (RKKY) between two magnetic ions on nearest or next nearest magnetic neighbours. This coupling results in a parallel (ferromagnetic) or an anti-parallel (antiferromagnetic) setting of moments dependent on separation of the interacting atoms. This RKKY model is efficient when a high concentration of delocalized carriers is present in the host material.

1.4.2 THE MEAN FIELD ZENER MODEL

This model is proposed by Dietl et al. [35] and is based on the original model of Zener [36] and the RKKY interaction. In this model, the delocalized hole carriers mediate a RKKY-like interaction among localized TM ions resulting in ferromagnetism. As compared to the RKKY interaction, this theory takes into account the complex valence-band structure of zinc-blende ferromagnetic semiconductors. In the process, it reveals the important effect of the spin-orbit coupling in the valence band in determining the magnitude of the Curie temperature $T_C$ and the direction of the easy axis in p-type ferromagnetic semiconductors. Most importantly, this theory predicts that Mn-doped p-type GaN and ZnO are ferromagnetic with $T_C$ values above room temperature as shown in Figure 1.10. Even though this model indicates the dominance of hole exchange of Sato et al. [37] which predicts that the high Curie temperature ferromagnetism could also be stabilized in n-type ZnO.
The double exchange mechanism proposed by Zener [36] explains the experimentally observed ferromagnetism in manganite materials. This interaction is explained by hopping of electrons between two neighbour TM ions. In DMS materials, 3d levels of TM ions split by the crystal field into lower energy doublet i.e. and higher energy triplet t 2g levels. The spin-up (↑) and spin-down (↓) states also split by the exchange splitting. In Co-doped ZnO, low energy spin up Co 3d-states are strongly hybridized with oxygen 2p states [39, 40]. Besides that, high energy spin-down states of Co ions are located close to the conduction band of host ZnO. If the magnetic moments of neighboring Co ions are aligned parallaly, electrons in the partially filled 3d-orbitals of the Co ions are allowed to hop from one ion to the other and stabilize the ferromagnetic ground state (Figure 1.11).
Figure 1.11: Ferromagnetic coupling of nearby Co$^{2+}$ (3d$^7$) ions via double exchange interaction [36].

1.4.4 BOUND MAGNETIC POLARON THEORY

The bound magnetic polaron theory (BMP) model is an important tool to explain the ferromagnetic ordering in the transition metal doped ZnO. A bound magnetic polarons (BMP) is a collection of electrons (or holes) bound to impurity atoms through exchange interactions within an orbit [41]. These interactions are responsible to render carriers parallel or anti-parallel to the magnetic impurity, depending upon the system. The parallel & anti parallel configurations differ in energy, and result in a non-zero spin flip energy that is a characteristic of BMPs. The net energy of the system can be lowered by parallel alignment of ions, since they all interact with carriers the same way. At low temperatures, the s-d exchange energy exceeds $K_B T$, so mutual alignment of ions and carriers results in a ferromagnetic “bubble. However at higher temperatures however, the spins of magnetic ions are not constant
anymore. A nonzero magnetization results from spin fluctuations within any carrier orbit. While, the former instance comprises the “collective” regime, the latter is a characteristic of the “fluctuation” regime.

The temperature up to which a BMP can facilitate magnetic ordering depends upon the nature of interactions between atomic spins and the charge carriers. The net exchange has been computed by Durst et al [42] based on the polaron-pair model which considers the interaction between a pair of BMPs via a shared interstitial area, where magnetic ions interact with carriers belonging to both the polarons. Such an area is crucial for carrier mediated ordering of individual polarons. Fig. 1.12 shows a schematic of the polaron-pair model.

Donor bands are relatively large and s-d interactions are weak. Therefore, if these are involved in the formation of BMPs, the collective phase can be observed only at low temperatures. On the other hand, when more localized valence bands are involved, the p-d interaction is strong enough to sustain collective phase even at higher temperatures.

Coey et al [43] have proposed a model for n-type DMS materials which is based on exchange interaction between highly correlated narrow impurity bands and the atomic spin
moment on dopant ions. Figure 1.13 shows a schematic of the interaction in oxides, where defects such as oxygen vacancies act as a source of electron. As the concentration of these $e^-$, which are lying in hydrogenic orbitals with characteristic Bohr radii increases, their individual orbits extend out into narrow impurity bands. Electrons interact with all magnetic ions that lie within their orbit. If there is enough number of magnetic spins within the orbital, the electron is completely spin polarized. Furthermore, the atomic magnetic moments have an indirect exchange interaction mediated by carriers, resulting ferromagnetic ordering.

Figure 1.13: Representation of Magnetic Polarons in a semiconductor lattice [17].

1.5 INTRODUCTION OF ZINC OXIDE

Zinc Oxide is one of the most important wide bandgap (3.37 eV at 300K) semiconductors for today’s research. The lack of a centre of symmetry in wurtzite structure, combined with large electromechanical coupling results in strong piezoelectric and pyroelectric properties and the
consequent use of ZnO in mechanical actuators and piezoelectric sensors [44]. Some optical properties of ZnO overlap with GaN which is another wide band gap semiconductor used in production of ultraviolet, blue, green and white light emitting devices. But ZnO have some advantages over GaN which include a large exciton binding energy (\(\sim 60\) meV), higher radiation hardness, availability of fairly high quality ZnO bulk single crystals and relatively low cost for ZnO based devices [45].

1.5.1 STRUCTURE OF ZnO

ZnO is a II-VI binary compound semiconductor which follows the hexagonal wurtzite structure and belongs to P63mc space group symmetry. Crystal structures shared by ZnO are wurtzite, zinc blende, and rocksalt, as schematically shown in Figure 1.14 (a, b and c). At ambient conditions, the thermodynamically stable phase of ZnO is wurtzite. The zinc-blende structure can be stabilized only by growth on cubic substrates, and the rocksalt structure may be obtained at relatively high pressures.

![Figure 1.14: Representation of ZnO crystal structures: (a) cubic rocksalt, (b) cubic zinc blende, and (c) hexagonal wurtzite. The shaded gray and black spheres denote Zn and O atoms, respectively [45].](image)

The crystal structure of ZnO as shown in the figure 1.14c (the wurtzite hexagonal structure) has two variable lattice parameters a=b (=3.2495 Å) and c (= 5.2069) in the ratio of c/a = \((8/3)^{1/2}\) and the density of 5.605 gcm\(^{-1}\) [46]. The structure is composed of two interpenetrating
hexagonal closed packed (hcp) sublattices, each of which consists of one type of atom displaced with respect to each other along the threefold c-axis by the amount of $u=3/8$ (for ideal condition). A schematic representation of the wurtzite ZnO structure is also shown in Figure 1.15. In ZnO hexagonal closed packed structure, the individual type of ions form a sublattice with a ABAB stacking sequence. Oxygen fills half of the tetrahedral position in the Zn sublattice making every Zn ion tetraherally coordinated by four oxygen ions and vice versa. This tetrahedral coordination gives rise to polar symmetry along the hexagonal axis which is responsible for a number of the properties of ZnO, including its piezoelectric and spontaneous polarization. It is also a key factor in crystal growth, etching and defect generation. Aside from causing the inherent polarity in the ZnO crystal, the tetrahedral coordination of this compound is also a common indicator of sp³ covalent bonding.

![Schematic representation of a wurtzite ZnO structure. The black and grey spheres denote Zn and O atoms, respectively [45].](image)

**Figure 1.15:** Schematic representation of a wurtzite ZnO structure. The black and grey spheres denote Zn and O atoms, respectively [45].

### 1.5.2 BASIC PHYSICAL PARAMETERS OF ZnO

Basic physical properties of ZnO are listed in table 1.1. Some of the properties for example thermal conductivity, the mobility of holes and its effective mass are still debatable. Values
for carrier mobility were undoubtedly increased as more control is gained over compensation and defects in the material.

Table 1.1: Basic physical parameter at room temperature [47]

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Lattice Constant</td>
<td>a=3.2495 Å, c=5.2069 Å</td>
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<tr>
<td>2.</td>
<td>Density</td>
<td>5.67526 g/cm³</td>
</tr>
<tr>
<td>3.</td>
<td>Molecular mass</td>
<td>81.389 g/mol</td>
</tr>
<tr>
<td>4.</td>
<td>Band Gap at 300K</td>
<td>3.37 eV</td>
</tr>
<tr>
<td>5.</td>
<td>Melting Point</td>
<td>2250 K</td>
</tr>
<tr>
<td>6.</td>
<td>Electron Mobility</td>
<td>~210 cm²/Vs</td>
</tr>
<tr>
<td>7.</td>
<td>Electron Effective Mass</td>
<td>0.28 m₀</td>
</tr>
<tr>
<td>8.</td>
<td>Hole Effective Mass</td>
<td>0.59 m₀</td>
</tr>
<tr>
<td>9.</td>
<td>Static Dielectric Constant</td>
<td>8.656</td>
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<tr>
<td>10.</td>
<td>Refractive Index</td>
<td>2.008, 2.029</td>
</tr>
<tr>
<td>11.</td>
<td>Exciton Binding Energy</td>
<td>60 meV</td>
</tr>
<tr>
<td>12.</td>
<td>Thermal Conductivity</td>
<td>0.6-1.16 W/Km</td>
</tr>
<tr>
<td>13.</td>
<td>Specific Heat</td>
<td>0.125 cal/g°C</td>
</tr>
<tr>
<td>14.</td>
<td>Thermal Constant at 573 K</td>
<td>1200 mV/K</td>
</tr>
<tr>
<td>15.</td>
<td>Intrinsic Carrier Concentration</td>
<td>(&lt;10^6 \text{ cm}^{-3}) (max n-type doping(&gt;10^{18} \text{ cm}^{-3}) electrons; max p-type doping(&lt;10^{17} \text{ cm}^{-3}) holes)</td>
</tr>
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1.5.3 OPTICAL PROPERTIES OF ZnO

The band gap engineering of doped ZnO plays an important role to design ZnO based LEDs and other optoelectronic devices. In recent years, optical properties of ZnO have been in focus among researchers due to their wide band gap (3.37 eV) and high exciton binding energy (60 keV) which is much larger than GaN (25 meV), and make it promising material for photonic applications in the UV and blue electromagnetic range. Its efficient excitonic emission at
room temperature, makes it interesting and efficient material for optoelectronic device applications.

1.5.4 DEFECTS IN ZnO

Semiconductors are so useful for electronic devices because their properties can be modified significantly by incorporation of impurities or defects. The quantity of defects necessary for the required property is often considerably less than one defect atom per million host atoms.

Defects include vacancies, interstitials and antisites. The common vacancy states in ZnO are oxygen and zinc vacancies depending upon the synthesis parameters involved. In particular, oxygen vacancies ($V_\text{O}$) have lower formation energy than that the zinc interstitial ($Zn_\text{i}$) and hence are more abundant in Zn-rich conditions. However, under oxygen rich conditions, zinc vacancies ($V_{Zn}$) dominate.

The origin of intrinsic emission of ZnO is debatable due to defects in the structure. Whose origin is still a topic of debate [48, 49]. Zinc Vacancies which are widely studied and reported by Reynold et al. [50] are expected to be one of the sources of green emission (2.4-2.6 eV) below the conduction band in ZnO. Some additional reports on green emission claim the green emission to be due to the oxygen vacancies [51]. Beside this, Willander et al. [52] reported that the oxygen interstitials and extrinsic deep level defects are responsible for green emission in ZnO. Recently, it has been reported that many deep level defects are responsible for the green emission in ZnO along the $V_\text{O}$ and $V_{Zn}$ [53, 54]. The recombination process between the $Zn_\text{i}$ energy level to Zn energy level is also responsible for the blue emission and this corresponds to $\approx 2.84$ eV (436 nm) [55]. Typically, zinc interstitial defects positioned at 0.22 eV below the CB play important part to visible emission in ZnO due to the recombination process among $Zn_\text{i}$ and different defects that exists in the deep level like oxygen and zinc vacancies, oxygen interstitials which are the main source for the different colour emission such as blue, red, and green emission in ZnO [56]. Oxygen interstitials normally positioned at 2.28 eV below the CB generate the orange red emission in ZnO [53, 54]. Oxygen interstitial defects are also responsible for the yellow emission as reported by Reynold et al. [59]. Transitions corresponding to defect levels are shown in the figure 1.16. [58].
1.6 RECENT RESEARCH IN ZnO

As we discussed earlier, ZnO is an attractive material for applications in electronics, photonics, acoustics and sensing, therefore it has a strong potential for various short-wavelength optoelectronic devices. While, to obtain high quality ZnO based p–n junctions is one of the key steps of its optoelectronic applications. Despite the significant efforts, there are still a number of important issues to be resolved before it to complete commercially with GaN, which is established in terms of devices. ZnO exhibits enormous scope on spintronics simultaneously with optical properties. Transition metal doped ZnO based diluted magnetic semiconductors (DMSs) are potential candidates for next generation of spintronic devices. But, the reproducibility in such systems has shown to be difficult resulting in a large range in reported values. Such spread in reported results and a lack of understanding of the mechanism of magnetism in TM doped ZnO have cast doubt over the origin of ferromagnetism in these systems. In this section, recent progress in optical and magnetic properties of ZnO is discussed and a review of critical issues for realization of ZnO-based devices is also given.
1.6.1 CURRENT EXPERIMENTAL STATE OF OPTICAL PROPERTIES OF ZnO

As we know that GaN based short wavelength light emitting diodes (LEDs) and lasers have changed our life in various ways. While, ZnO has a potential of replacing GaN in semiconductor light emitting devices owing its fundamental advantages over GaN like its more efficient exciton emission at room temperature than GaN [61, 62] and wide band gap (3.32 eV). However, pure ZnO do not meet the practical needs as a photocatalytic material, as activation of ZnO catalyst necessitate high-energy UV light, resulting to low efficiency in the visible and near infrared regions [63]. The rapid recombination of photogenerated electron-hole pairs is another limiting factor that impedes the photocatalytic activity of ZnO [64]. To overcome these limitations, considerable efforts have been made on the improvement of the photocatalytic activity by means of semiconductor combination, transition-metal doping or metal deposition [65-67]. Several studies have been reported on optical properties of pure, transition and non transition metal doped ZnO, which were prepared by different techniques and interesting outcomes were observed.

The metal doping of ZnO could change its properties; doping with the Group II elements, (Cd, Mg) may change the value of the optical band gap and also change the UV luminescence intensity [68], doping with group III elements (Al, Ga and In) could affect the optical and electrical properties of ZnO [69]. This raises the possibility of band gap engineered heterostructures for potential optoelectronic applications in the UV range.

There are several reports available on the growth and properties of Mg doped ZnO nanostructures prepared by various techniques [70, 71]. Zn$_{1-x}$Mg$_x$O ternary alloy semiconductors were used as barrier layers for carrier confinement in highly efficient ZnO-based visible to near-UV quantum-well LEDs [72-74]. There is also a large potential for the development of LEDs operating in the UV to deep-UV range using Zn$_{1-x}$Mg$_x$O ternary alloy semiconductors as an active layer in quantum-well structures [75, 76]. Thus, the study of photoluminescence (PL) of highly excited Zn$_{1-x}$Mg$_x$O is of considerable importance. One of the important issues that limits the synthesis of Mg alloyed ZnO is the solubility of Mg in ZnO which is limited to about ~4% [77]. It has been claimed that using the vapour phase route such as pulsed laser deposition, it is possible to incorporate Mg up to ~ 40% [78]. Thus, study on pure and Mg doped ZnO systems synthesized at low temperature is important not only to understand the excitonic transitions but also to create its new forms which could open more frontiers for its applications.
Some reports on doped ZnO with other metals (Al$^{3+}$, In$^{3+}$, Ga$^{3+}$ etc) indicate that the doping affects the optical and electrical properties of ZnO [79-81]. Among these metal dopants, Al is the most efficient material for improvement of optical and electrical properties of ZnO. Kadam et al. [82] studied the grain size related optical band gap changes in ZnO nanocrystals, Lo et al. [83], studied the raman scattering of Al doped ZnO nanoparticles synthesized by chemical colloid process, while Lai et al. [84] studying the thickness dependent optical band gap shift in Al doped ZnO thin film prepared by spray pyrolysis. Gondoni et al. [85] studied the structural dependent optical and electrical properties of Al doped ZnO nanostructures and the formation of Al$^{3+}$ doped ZnO nanowires and nanotubes with high conductance and high crystal quality. It seems that, there are no significant reports available on the detailed structural analysis of Al doped ZnO nanoparticles up to high level of doping concentration.

In transition metal ions, Cr$^{3+}$ has several advantages as a dopant for Zn$^{2+}$. Ionic radius of Cr$^{3+}$ is less than Zn$^{2+}$ which makes it easy to incorporate into ZnO crystal structure and also enhances the green emission [86-88]. Singh et al. (2008) [88] studied the micro structural, optical and electrical properties of Cr-doped ZnO micro particles and observed show that doping did not induce any phase transition. Liu et al. [87] studied optical properties of Cr-doped ZnO using the density functional theory. The calculated optical properties indicate that the optical band-gap is increased after Cr doping and strong absorption band found in the visible-light region originating from the intraband transition of Cr$^{3+}$ bands and conduction bands.

However, despite various studies, the mechanism behind the visible luminescence has still not been established. Much of the research on the luminescence of ZnO is performed on single crystalline powders or single crystals [89]. Two emission bands are usually found in photoluminescence (PL) spectrum of ZnO; a near-band-edge UV emission and a broad defect related visible emission. A relatively weak and narrow UV emission band is observed around 380 nm (3.25 eV), just below the onset of absorption which is due to the radiative annihilation of excitons with a short lifetime of the order of several tens to hundreds of picoseconds [90]. The defect-related visible emission is most commonly green luminescence, though other emissions such as yellow or blue have also been observed [91]. For high efficiency UV light emitting devices, it is important to suppress the visible emission. In spite of numerous studies [92–96] on the green luminescence its origin is still controversial, and a number of suggestions have been proposed. The green luminescence has been attributed to various type
of defects such as oxygen vacancies [92–95], zinc vacancies [89], as well as donor–acceptor pairs [56, 96].

1.6.2 CURRENT EXPERIMENTAL STATE OF ZnO AS DMS

Early studies on DMS materials began with Mn-doped II-VI alloys of the form AII BVI$_{1-x}$Mn$_x$ (where AII = Zn, Cd, Hg and BVI = S, Se, Te) in 1980s [5, 9]. It is worthwhile to review few aspects of these materials since ZnO also belongs to the II-VI family of semiconductors. The high solubility of Mn in host materials while maintaining the zincblende or wurtzite structures is possible, which is thought to arise from the chemical similarity of Mn$^{2+}$ to group II elements [97]. In earlier studies, it was observed that magnetic properties of these alloys are the consequence of exchange interactions between local moments of atoms (provided by the Mn) and sp-band electrons and have dramatic impact on optical and electrical properties of the material, such as giant Faraday rotation and bound magnetic polaron formation [98]. Driven mostly by super-exchange mechanisms, an indirect exchange interaction mediated through the anion, these systems exhibit low temperature spin glass phase, high temperature paramagnetism and type III antiferromagnetic ordering [99]. However, recently, ferromagnetic ordering with low Curie temperature (Tc < 2 K) has been achieved in low-dimensional quantum wells driven by hole-mediated exchange [100]. An additional challenge of II-VI materials is the capability of bipolar doping (both n-type and p-type). Again, these materials are not practical since materials that did show ferromagnetism were restricted to low ordering temperatures (T$_c$ just a few degrees above 0 K) [101, 102].

A technological breakthrough in the advancement of DMS occurred in the early 1990s, with the discovery of ferromagnetism up to 35 K in Mn-doped InAs [5], which is an established III-V compound semiconductor material. The demonstration of ferromagnetism in InMnAs offered the intriguing opportunity to study spin-based phenomena in these well-established semiconductor devices.

In 2003, Sharma et. al. [17] first time observed room temperature ferromagnetism (RTFM) in Mn doped ZnO samples. After this letter number of researchers observed the RTFM in ZnO with the doping of different transition metals by different preparation routes [103-109]. But, the lack of reproducibility is a huge issue in these systems. Also, the mechanism behind the ferromagnetism in these systems is controversial and debatable.
After the breakthrough by Sharma et al. [17], Kundaliya et al. [103] followed the same route and observed ferromagnetic ordering at room temperature for 2 at.% Mn-ZnO bulk sample which supports the previous result but there is a little bit of confusion over the mechanism behind the ferromagnetism as it may be due to Mn$_2$O$_3$ phase or due to some other phase. To check the reproducibility, Garcia et al. [104] also followed the same preparation technique and observed that increasing the annealing temperature above 600°C resulted to a decrease of the FM signal at room temperature that completely disappeared after annealing at 800°C. They concluded that the coexistence of Mn$^{3+}$ and Mn$^{4+}$ is responsible for FM via the double-exchange mechanism. After this, number of similar results supporting the decrease of ferromagnetism with increase in sintering temperature were reported, but the limiting sintering temperature to observe ferromagnetism is still not clear [105]. Thus, upto now, two outcomes are in focus that the RTFM is either due to the Zn$_{1-x}$Mn$_x$O$_4$ spinal phase or coexistence of both oxidation states (Mn$^{2+}$ and Mn$^{3+}$), giving rise to a double-exchange mechanism. Contrary to a RTFM, Kolesnik et al. [106] showed no bulk ferromagnetism for single-phase Mn doped ZnO materials which show paramagnetic Curie–Weiss behaviour. Cong et al. [107] explained the observed ferromagnetism in Mn doped ZnO nanoparticles on the basis of RKKY interaction which is quite different from previously reported literature. Wang et al. [108] found that the ferromagnetism of Zn$_{1-x}$Mn$_x$O strongly related to defect states. Yan et al. [109] propose that the Zn vacancy can induce the RTFM in Mn-doped ZnO, which provides the new pathway on the description of origin of ferromagnetism in ZnO. Z. Wang et al. [108] observed room-temperature ferromagnetism in the hydrogenated Zn$_{0.98}$Mn$_{0.05}$O nanopowders prepared at high temperature (700 °C), which originated from the lattice defects such as oxygen vacancies and Zn interstitials. Jing et al. [110] explained the paramagnetic behaviour of samples upto high doping levels and observed the coexistence of ferromagnetism and paramagnetism in the 5% Mn-doped ZnO sample at room-temperature, which may arise from ferromagnetic exchange interaction as well as small secondary phases.

One of the early works on another most common, cobalt-doped ZnO DMS was by Ueda et al. [111]. They reported the material to be ferromagnetic below RT with the curie temperature ~280 K for 5-25% Co without observing any secondary phases. Again, results conflict with reports of ferromagnetism in phase pure films [102], ferromagnetism from clusters [112], and no observed ferromagnetism [113]. Polyakov et al. [114] found RTFM in bulk Mn and Co-doped ZnO crystals for TM concentrations of 1 at. %. At higher
concentrations, films become paramagnetic due to direct coupling between the transition metal ions. Experimental results on magnetic properties regarding RTFM in Co doped ZnO systems, in thin films, bulk, polycrystalline and nanocrystalline samples differ widely. In case of thin films, there are many reports of RTFM, some of which attribute the observed RTFM to Co clustering [115, 116] and in some cases it is thought to be intrinsic in nature [116-118]. Double exchange interaction has also been proposed as an alternative explanation of RTFM [119]. In the case of polycrystalline bulk samples, prepared by the solid-state reaction method, many groups have reported paramagnetic (PM) behaviour at RT [119-120]. In the recent work, Carvalho et al. [121] and Pal et al. [122] worked on the Co doped ZnO systems, prepared by the solid state reaction route and observed totally different behaviour. No Co-rich nanoclusters or segregated secondary phases were observed in the samples and magnetization measurements reveal a Curie-Weiss behavior of the susceptibility at high temperatures characterized by the antiferromagnetic interaction between Co ions. Pal et. al [122] prepared nanocrystalline ZnCoO by simple ball milling and found that BMP model fitting to experimental M-H data leads to a low concentration of BMPs to give rise to large magnetization value. Though, the exact mechanism for the observed FM is not clear, possible pairing of the Co$^{2+}$ and extended defects may be responsible for the observed FM at and above RT.

Ni doped ZnO is another prime candidate from the view point of transparency and magnetism for potential monolithic optical integrated circuit (OIC) and optical application in short wavelength field [123]. From the research point of view, the magnetic properties of the Ni doped ZnO are not very well understood. In 2001, Ueda et al. [124] observed spinglass behavior of Ni doped ZnO thin films grown by PLD on sapphire substrate with very poor reproducibility of the method [124]. Yin et al. reported the paramagnetism in Ni-doped ZnO films [124]. On the other hand, ferromagnetism was observed at room temperature in Ni-doped ZnO nanorods [125], films [126] and nanowires arrays [127], Ni- doped ZnO quantum dots with Curie temperature ($T_c$) up to 350 K [128-130].

Mao et al. [131] found RTFM with saturation magnetization of 0.01 emu/g and Curie temperature above 340 K for Ni concentration of 0.01% in atomic ratio in Ni-doped ZnO nanocrystals synthesized by wet chemical reaction method. Mao et al. [131] have also obtained RT ferromagnetic Ni-doped ZnO samples prepared by solid state reaction, but FM originates from the nanosized Ni clusters formed from the decomposition of NiO during
calcination. Snure et al. [132] found that ZnO:Ni films deposited under $10^{-6}$ torr of pressure shows hysteresis at room temperature. From the literature, it is observed that there are only a few studies on Ni doped ZnO system, in which diverse magnetic properties have been reported [133]. Besides, successful incorporation of Ni$^{2+}$ into ZnO host matrix, only paramagnetic behaviour was observed [134]. Liu et al.[134] reported that defect states are responsible for the RTFM in Ni doped ZnO system. On the other hand, Tong et al. [135] explained enhancement of the RTFM by H$_2$ annealing.

Among all the known TM doped ZnO systems, Ni-based materials are probably the most controversial. There is a great deal of conflict and controversy over the origin of ferromagnetism in these materials and the reported diversity in magnetic moments.

Besides, the Mn, Co and Ni doped ZnO systems, Cr doping is also attractive because theoretical calculations [136, 137] suggested that the ferromagnetic (FM) state in it could be more stable and energetically favorable than other studied systems. Though, the work of Ueda et al. [137] suggested no indication of FM in Cr doped ZnO films deposited by pulsed laser deposition [136], Roberts et al. [138] observed a RTFM in Cr doped synthesized by co-sputtering. Liu et al. [139] also reported in RT-FM in co-sputtered Cr doped films Zn$_{1-x}$Cr$_x$O but paramagnetism (PM) in sol-gel prepared powders, and they explained the role of zinc interstitial in the FM of films. Wang et al. [140] suggested that FM observed in Cr (2%) doped ZnO nanowires is due to the presence of V$_o$. Zhuge et al. [141] predicted charged zinc vacancies (V$_{Zn}^+$) or zinc vacancies (V$_{Zn}^-$), which were accepters in intrinsic n-type ZnO [141], are responsible for the origin of FM in Zn$_{1-x}$Cr$_x$O thin films. They also observed that intensity of photoluminescence due to V$_{Zn}$ decreased with concentration of Cr resulting a decrease in magnetization of films.

In spite of various reports on ZnO-based DMSs, there is no unanimous agreement on the nature and origin of magnetic properties of samples prepared by various methods and different groups. It is a matter of current debate that whether the FM in transition metal doped ZnO is related to TM doping or due to intrinsic defects. Few studies suggested that clusters or extrinsic defects (such as oxygen vacancies) are the reason for FM signal. These controversial results suggest that properties of these materials seem to be very sensitive to synthesis routes processing parameters.
1.7 SPINTRONIC DEVICES

Spintronic devices came into existence after the discovery of “Gaint magneto resistance (GMR)” in 1988 by French and German physicists. The GMR effect was reported by P. Grunberg [141] and A. Fert [142] in 1988 for layered alternating layers of ferromagnetic and nonmagnetic layers. When magnetizations of ferromagnetic layers are parallel, materials show very low resistance (figure 1.17a) and if the magnetizations of ferromagnetic layers are antiparallel (figure 1.17b), material shows high resistance due to carriers. In the metal-based spintronics, people are now trying to improve GMR devices by developing new materials with enhanced spin-polarization and better spin filtering.

![Diagram of GMR sandwich structure](image)

**Figure 1.17:** A GMR sandwich structure, consisting of alternating magnetic and nonmagnetic metal layers [144].

Similar rapid development is expected from tunneling magnetoresistance (TMR) devices composed of two ferromagnetic layers separated by a thin insulating metal-oxide layer. In these devices, electrons can easily tunnel through the insulating layer depending on the relative magnetization of the two ferromagnetic layers and the fact that the spin of electrons are preserved during their passage through the barrier. In 1995 Moodera et al. [145] demonstrated TMR room temperature. Less than a decade later, Motorola, IBM and Infineon started manufacturing fast magnetic storage devices by incorporating dense arrays of TMR elements, known as magnetic random access memory (MRAM) [146, 147]. In semiconductor-based spintronics, a lot of efforts focus on producing RTFM in semiconductors. Such new class of spintronic devices could be integrated with conventional semiconductor technology. In this section, some potential semiconductor-based spintronic devices are briefly summarized.
1.7.1 SPIN VALVE

In spintronic devices, there is an important role of magnetized ferromagnets which affect the flow of electrons (Figure 1.18). Particles which can pass through the ferromagnetic layer, are those having the spin in the direction of the spin of states available at the Fermi level; all other are reflected back at the fermi surface. If the incident current is unpolarized, electrons passing through the magnetized layer acquire this same spin bias and the ferromagnetic layer acts as spin polarizer.

Figure 1.18: Spin Valve action. Spin polarized transport through a sandwich consisting of layer of ferromagnetic metal, normal metal and ferromagnetic metal (a) when magnetic moments in the ferromagnetic layer are parallel, and (b) when they are anti parallel [145].
On the other hand, the completely polarized current will pass through if the spins of the carriers are parallel with those of atoms in the layer; otherwise its passage will be hindered. Now, the ferromagnetic layer operates like a spin analyzer. So, for a complete polarized current, a ferromagnetic material can function either as a conductor or an insulator, depending on whether its direction of magnetization is aligned parallel or anti parallel to the spin polarization of the current [145].

1.7.2 Magnetic Bipolar Diode:

Magnetic bipolar diode (MBD) was first proposed in 2002 by Zutic et al. [147], which is a p-n junction diode with one or both regions magnetic. A scheme of an MBD is shown in Figure 1.19.

The p region is magnetic i.e. it has a spin-split conduction band with the spin splitting (Zeeman or exchange) $2q\zeta \sim k_B T$. Zeeman splitting can be enhanced significantly by increasing $g^*$ factors of narrow-band-gap semiconductors. The region n is non magnetic. The inreplay of equilibrium of polarization in p region, and the nonequilibrium spin polarization source in n region, at the edge of the depletion layer, determines the I-V characteristics of bipolar diodes [148]. Nonmagnetic bipolar spintronic devices are the spinpolarized p-n
junction [149] and the spin solar cell [24] which offer opportunities for effective amplification of spin amplification, injection of spin [150].

### 1.7.3 SPIN TRANSISTOR

Spin transistor can be defined in two ways: one in analogy with the bipolar transistor and the other one in analogy with field effect transistor. Bipolar transistor consists of a semiconductor emitter, a magnetic semiconductor base, and a semiconductor collector as shown in the figure (1.20).

![Spin transistor diagram](image)

**Figure 1.20:** Spin transistor.

The emitter and collector are non-magnetic n-type semiconductors and the base is a p-type magnetic semiconductor, in which the conduction band is split due to the exchange interaction. The emitter-base junction is connected in forward bias while the junction between the base and collector is reversed biased.

If non-equilibrium is produced in the emitter, spin-polarized electrons will flow towards the base where few electrons will recombine with holes to produce base current. The remaining spin-polarized electrons will flow through the thin base to the collector. The current amplification factor $\beta$ (the ratio of the collector current to the base current) will have different
values for positive and negative non equilibrium polarisation. Such a transistor has not yet been realized.

The second transistor is Datta-Das spin field effect spin transistor, a conceptual diagram of this transistor is shown in figure (1.21).

![Figure 1.21: Scheme of the Datta-Das spin field-effect transistor (SFET). The source (spin injector) and the drain (spin detector) are ferromagnetic metals or semiconductors, with parallel magnetic moments [151].](image)

The scheme is similar to usual FET, having a drain, source, channel, and a current controlling gate. The gate either allows either flow (ON) the current or does not (OFF). A spin transistor also controls the current through the narrow channel. However, the physical realization controlling the current is different in SFET. In SFET the source (injector) and drain (detector) are ferromagnets which injects and detects electron spins. In a simplified way if the spin of electron is aligned to spin of drain, it enters the drain (ON). Otherwise it will be is scattered (OFF). The the gate is to generate an effective field parallel to $\Omega$ in (Figure 1.21).
1.7.4 SPIN LIGHT EMITTING DIODE (LED)

In spin light emitting diodes (LED), spin-polarized holes from a DMS and unpolarized electrons from a nonmagnetic semiconductor are injected from either side to recombine in a quantum well. The polarization of injected holes can be measured by comparing the intensity of the right- and left-circularly polarized light of the emitted electroluminescence (EL). Efficient spin injection has been demonstrated in spin-LEDs by using a spin-polarized DMS as the injector [152]. In Figure 1.22, the sample structure of a GaAs-based spin-LED proposed by Y. Ohno et al. [45] is represented.

![Figure 1.22: Injection of spin-polarized holes into a light emitting p–n diode using a DMS (Ga, Mn)As [153].](image)

The structure of GaAs-based spin-LED consists of a p-type ferromagnetic semiconductor (Ga, Mn)As and n-type non-magnetic semiconductor GaAs, which were epitaxially grown by molecular beam epitaxy (MBE). Since a spontaneous magnetization occurs below Tc in the p-type (Ga, Mn)As DMS which gives possibility to inject spins without requiring a magnetic field. When a forward bias is applied, spin polarized holes from the (Ga, Mn)As are injected through a spacer layer into the nonmagnetic region and recombine with spin unpolarized electrons injected from the n-type GaAs in a nonmagnetic (In, Ga)As quantum well, producing polarized electroluminescence. Injected spin-polarized electrons can be detected as circularly polarized light emission from the quantum well, which corresponds to the magneto-optical Kerr effect loops. The presence of spin-polarization can
be confirmed by observation of hysteresis in the polarization of the emitted light as a function of the magnetic field. Since the $T_c$ of (Ga, Mn)As is much below room temperature, the main issue now is to find a proper DMS material that can inject a spin-polarized current efficiently at room temperature. Realization of such spin-LEDs would eliminate the need for the polarizing filters that are presently inserted into conventional devices.

1.7.5 MAGNETIC SWITCH

Recently, Ohono et al. [154] designed a magnetic switch, which has a layer of indium manganese arsenide, ((In,Mn)As), material added within a FET. A positive voltage on the metallic gate electrode creates electric fields (shown by arrows in figure 1.23) that repels holes causing the Mn moments to orient randomly [155]. However, negative voltage on the gate electrode creates electric fields that attract holes, causing the Mn magnetic moments to align. A schematic of the magnetic switch is shown in figure 1.23.

In order to realize the spintronic devices in practice, ferromagnetic semiconductors functional at room temperature are needed. The search for suitable materials started in 1960s and several promising materials have been found and the search is still on.

Chapter II describes synthesis routes used during the present work which includes the standard solid state route for Mn and Ni doped ZnO systems, sol-gel route for Mn, Ni and Co doped ZnO systems and thermal decomposition method for preparation of nanoparticles of Cr,
Al, Mg and Ba doped ZnO. The chapter also covers a comprehensive discussion of different experimental techniques used for the characterization in the present work. The characterization techniques include X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infra-red (FTIR) spectroscopy, superconducting quantum interference device (SQUID), UV–Visible spectrometer, luminescence spectrophotometer etc.

Chapter III deals with a comparative study of two systems of Mn doped ZnO systems which were prepared by solid state and sol-gel route. The refinement of the unit cell parameters revealed that cell parameters slightly increased with Mn concentration, indicating the substitution of divalent Mn$^{2+}$ (0.66 Å) ions on Zn$^{2+}$ (0.60 Å) ions in ZnO crystal lattice for both series. The band gap increased monotonically with Mn concentration for both series which can be explained by the Burstein-Moss effect. PL spectra show that the vacancy states have increased for series which can strongly affect magnetic properties. Weak hysteresis loops were observed for all samples with the lower Mn concentration which manifest the slight ferromagnetic ordering at room temperature. However, ferromagnetism completely disappeared for the sample with 6% Mn concentration. Magnetic measurements clearly indicate that samples prepared by sol-gel route show better magnetic properties in comparison to samples prepared by the solid state route. The MH curves of the series Mn doped ZnO samples prepared by sol-gel route were tried to fit on the BMP model, but the calculated concentration of BMP ($\sim 10^{14}$ cm$^{-3}$) appears to be quite low to achieve percolation. For further investigations of magnetic ordering in samples prepared by sol-gel route, we tried to explore it with the help of modified Curie Weiss law and observed some antiferromagnetic ordering in the samples.

Chapter IV presents the synthesis and characterization of Co doped ZnO samples prepared by sol-gel route. The X-ray diffraction, X-ray photoelectron spectroscopy and UV–visible spectroscopy confirmed the substitution of Co ions on Zn sites without changing the wurtzite structure. No segregated secondary phases or Co rich clusters were detected. Optical absorption spectra of the samples exhibit a blue shift in the absorption band edge with increasing dopant concentration. Photoluminescence measurements show a blue shift in UV emission peak with the increase in Co concentration and a slight shift in the green emission band at around 509 nm which gets suppressed for higher sintering temperature. The field dependence of magnetization observed at room temperature exhibits clear ferromagnetic behavior. Efforts have been made to fit the experimental M–H data using the magnetic
polarons model (BMP) which involves localized carriers and magnetic cations. The calculated concentration of the BMPs is found to be below the typical percolation threshold in ZnO. Thus BMP model alone is not sufficient to explain the RTFM behaviour in ZnO. To know the exact magnetic ordering in the system, we also attempted to fit temperature dependent magnetization curves with the Curie–Weiss Law which shows antiferromagnetic ordering in all samples.

In Chapter V, Ni and Cr doped ZnO systems were studied in detail. X-ray diffraction pattern of Ni doped ZnO suggested an appearance of a secondary phase of NiO only in 6% Ni doped sample. Phonon modes in Ni doped ZnO nanoparticles were studied through FTIR measurements. Furthermore, the enhancement in optical band gap with Ni doping from 3.29 to 3.32 eV has been observed through UV-visible spectroscopic analysis. Photoluminescence spectra of $Z_{1-x}Ni_xO$ show the UV-emission peak showing the blue shift with increase in doping concentration followed by broad visible (blue) emission corresponding to the defect emission whose intensity decreased with increasing Ni concentration. A clear RTFM is observed in all samples but saturation magnetization decreased with increasing Ni content. The suitability of bound magnetic polarons (BMP) model is checked and numbers of BMPs are found to be of the order $10^{15}$ per cm$^3$, which is very small for the percolation in ZnO. In the present case, oxygen rich stoichiometry with enhanced Zn-O bonding favours the indirect Ni-O-Ni ferromagnetic exchange coupling and reduction of oxygen vacancies leading to strong hybridization of Ni in ZnO host matrix responsible for RTFM.

Interestingly, band gap decreased with Cr doping from 3.23 to 3.04 eV, this band gap narrowing has been interpreted in terms of the s, p–d spin-exchange interactions between delocalized s- or p-type band electrons of Zn and O atoms, respectively and localized d electrons of transition metal replacing the cation. This shift is most probably occurs due to band structure deformation by Cr ions doping in the lattice of ZnO structure. The estimated number of BMPs is higher than earlier observed values in other TM doped systems and it is above the threshold of percolation in DMS and this is quite likely due to the high value of magnetization of the present system.

In Chapter VI, our main focus was on the structural and optical properties of alkaline metal (Al, Mg) doped ZnO nanoparticles prepared by thermal decomposition method. X-ray diffraction studies confirmed the substitution of Al and Mg on Zn sites without changing the hexagonal structure of ZnO. Also, lattice parameters, the crystallite size and other physical
parameters such as strain, stress and energy density were calculated from various modified form of W-H equations and their variation with the doping of Al is discussed. A blue shift in the energy band gap attributed to increase in carrier concentration (Burstein Moss Effect) is observed by absorption spectra with Al and Mg. Photoluminescence studies show a strong and dominant peak corresponding to the near band edge emission in ultra violet range and a broad band in the range 420-700 nm corresponding to defects and oxygen vacancies. From the FTIR spectra, we observed that the effective mass of Zn (Al)-O bond decreased with Al substitution because of lower atomic weight of Al than Zn. Also, the average force constant decreased with Al substitution which results an increment in the average Zn (Al)–O bond length. Besides that, opposite behaviour was obtained in the FTIR measurement of Mg doped ZnO nanoparticles. The tunability of the band gap of ZnO nanoparticles could eventually be useful for potential optoelectronic applications.

Chapter VII is devoted to the dielectric and ferroelectric properties of Ni and Ba doped ZnO samples prepared by different routes.

X-ray diffraction confirmed the appearance of NiO phase for 6% Ni doping. Significant blueshift with Ni doping was observed in UV–visible studies, strongly supported by photoluminescence spectra that show a high intensity UV emission peak followed by the low intensity green emission band corresponding to oxygen vacancies and defects. The photoluminescence analysis suggested that doping of Ni can affect defects and oxygen vacancies in ZnO and give the possibility of band gap tuning for applications in optoelectronic devices. High values of dielectric constant at low frequency and a strong dielectric anomaly around 320°C were observed.

The substitution of Ba on Zn sites of the wurtzite structure of ZnO was also observed by XRD pattern. FESEM images show some structural transformation in the morphology of nanostructure with Ba doping. The IR bands corresponding to Zn show a variation in the vibrational frequencies after Ba doping which may be due to the difference in ionic radii of Zn and Ba as well the structural changes induced due to doping. Band gaps are observed to be 3.18 eV for pure and 3.14 eV for 5% Ba doped ZnO, respectively. Red shift in band gap is observed in the UV-Visible spectra after Ba doping, supported by photoluminescence spectra and showing enhanced defect states with Ba doping. In dielectric studies, high value of dielectric constant and transition temperature at (~ 330°C) were observed. High value of
remnant polarization (1.01 µCcm\(^{-2}\)) and low value of coercive field (2.02 kVcm\(^{-1}\)) were also observed in ferroelectric studies which can be useful for potential applications.

In Chapter VIII, a summary of research work is given.