CHAPTER 1

INTRODUCTION

Study on optical materials provides the possibility of many applications in the emerging field of optoelectronic devices. The area of optical materials is an integral part of material science that enriches next-generation technology. The basic physics of optical materials is based on the interaction between material and light. In order to get the desired optical properties, one can control the interaction between material and light by tuning size, morphology and structure. Among all materials, semiconductors in low dimensional states have been approved as a prominent material for spintronics and optical devices. Owing to new developments in materials science, zinc oxide nanoparticles and thin film have emerged as a prospective material in the world of nanotechnologies for instance. ZnO nanostructure in different morphology holds significant potential for addressing the demand of semiconductor devices.

1.1 LOW DIMENSIONAL MATERIALS

The low dimensional materials can fulfill the current requirement of small, lightweight, cost effective and highly efficient devices. By dimension, materials can be classified into four parts, namely zero-dimensional (0D) one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D) materials as shown in Figure1.1. The typical dimension of bulk materials is in the range of micrometer scale. The distribution of low dimensional materials is based on the scale of dimension. If, all the dimensions (x, y, z) of the material are at nanoscale then, it is considered as zero-dimensional material. The most common representation of zero-dimensional material is nanoparticles. The nanoparticles can be amorphous or crystalline, single crystalline or polycrystalline and exhibit various shapes. In case of 1D material, two dimensions (x, y) are at the nanoscale and one dimension is outside the nanoscale. The examples of such systems are nanowire, nanorod and nanotube. The shape of such systems is needle-like. In case of the 2D materials, one dimension is at the nanoscale and two dimensions are not confined in nanoscale. 2D materials exhibit plate-like shapes. The examples of 2D material are thin films and nanolayers. Thin films exhibit thickness of the film at the nanoscale. Three-dimensional nanomaterials are not confined to the nanoscale in any dimension. These materials have three arbitrary dimensions above 100nm.

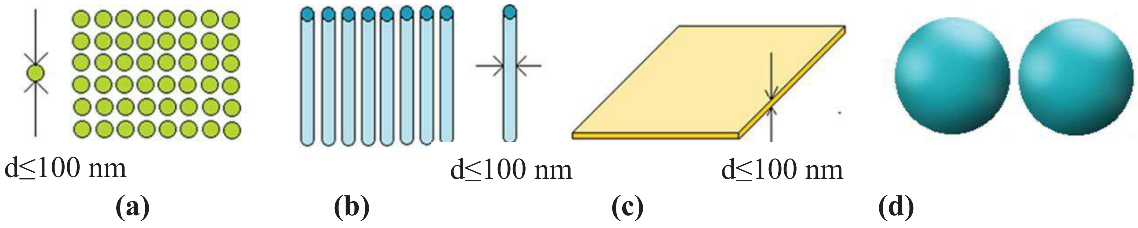

Figure 1.1: The low dimensional materials **(a)** Nanoparticles (0-D) **(b)** Nanorod (1-D) **(c)** Thin film (2-D) **(d)** 3D materials

The properties of materials are significantly different in bulk as compare to properties in low dimensional states. It was found that low dimensional material based devices have several advantages such as, small in size, requires fewer amounts of raw material, cost effective large scale production, several morphology etc. These advantage leads toward highly efficient practical devices. Thus, we are focussed in the low dimensional state. The subject of transition metal and rare earth doped semiconductors in low dimensional states have attracted lots of attention in last few decades due to their unique optical and magnetic properties, which leads toward wide variety of applications in optoelectronic and spintronics devices [1–4].

1.2 SEMICONDUCTOR

The semiconductor can be defined as “A material having electrical conductivity value falling in between conductor and insulator”. It can also classify on the basis of band gap i.e. “A material having band gap value falling in between conductor and insulator”. Typically, the band gap value of conductor is less than 1eV and semiconductors have the band gap in the range of 1-4eV. The materials having the band gap greater than semiconductor are named as insulators.

1.2.1 Types of Semiconductor

The semiconductor is generally classified in two categories, intrinsic and extrinsic semiconductors. The intrinsic semiconductor is also named as pure semiconductor, undoped semiconductor and *i*-type semiconductor. A pure semiconductor (intrinsic semiconductor) is similar to an insulator except with a smaller gap, so that electron can be excited across the band gap at room temperature. The intrinsic semiconductor is neither a very good insulator nor a very good conductor. It exhibit equal number of electron and hole. The doped semiconductor is known as an extrinsic semiconductor. The presence of dopant significantly influences the optical, electrical and magnetic properties of the semiconductor. The induced dopant ions in the host change the electrons and holes concentration of the semiconductor. The selection of appropriate dopant ions leads toward various applications of extrinsic semiconductor. Semiconductors doped with donor and acceptor impurities are known as *n*-type and *p*-type semiconductor respectively. The *n*-type and *p*-type designations indicate majority carrier in the semiconductor. The concentration of minority carrier is much lower than majority carrier.

1.2.2 Diluted Magnetic Semiconductors (DMS):

The diluted magnetic semiconductors (DMS) materials have attracted considerable attention due to combination of both semiconducting and magnetic properties within the same materials. DMS has potential applications in optoelectronics and spintronics devices. DMS exploit both the electron spin in magnetic materials and the charge of an electron in semiconductors for device application. The Figure 1.2 clearly defines the diluted magnetic semiconductors.

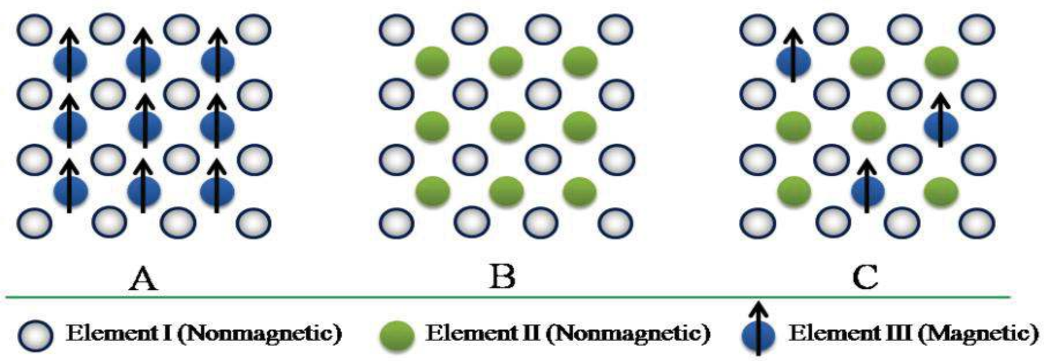

Figure 1.2: (a) Magnetic semiconductor (b) Non-magnetic semiconductor (c) Diluted magnetic semiconductor

Diluted magnetic semiconductor [Figure1.2(c)] or semi-magnetic semiconductor can be considered as an alloy between a magnetic semiconductor, in which a periodic array of the magnetic element is present [Figure 1.2(a)] and a nonmagnetic semiconductor, which contains no magnetic ions [Figure 1.2(b)]. The host in such system is a semiconductor and presence of magnetic dopant ions induced the magnetic properties in the system. In DMS, spin degree of freedom (quantum spin state of up or down) of electron carries the information and can be used as an additional degree of freedom for novel spintronics (spin-based electronics) applications. Zinc oxide is considered as a most suitable DMS for different dopant ions due to its unique optical and magnetic properties and exceptional applications[5-6].

1.2.3 Properties of Semiconductor

(a) Optical Properties

The phenomenon which involves the interaction between electromagnetic radiations with the semiconductor is considered as optical properties. This includes absorption, emission diffraction, polarisation, reflection, refraction and scattering of light. The study of optical property lies under the area of optical spectroscopy. The spectroscopy investigations reveal the information about the optical property as well as the structure of atom and defects present in the system. The study of optical property is essential to acquiring a systemic fundamental understanding about semiconductor and deeply rooted in the foundation of modern solid state physics.

(b) Energy Band of Semiconductors

The energy band gap can be defined as the band gap between conduction band and valence band. It gives information about absorption of photon and probability of electronic transitions. The conservation of energy and momentum is essential for the transition of an electron between conduction and valence band. By band structure, the semiconductors can be divided into two parts, namely direct bandgap semiconductor and indirect bandgap semiconductor. Figure1.3 shows the direct and indirect band gap semiconductor. A direct bandgap semiconductor exhibit band edge aligned in *k* i.e. maximum of the valence band is below the minimum of the conduction band. In such system, an electron can make a transition for recombination with holes without involvement of any phonon. In case of indirect bandgap semiconductor, band edge is not aligned in *k*, therefore direct transition of an electron is not allowed and phonon is involved in the process of electron transition.

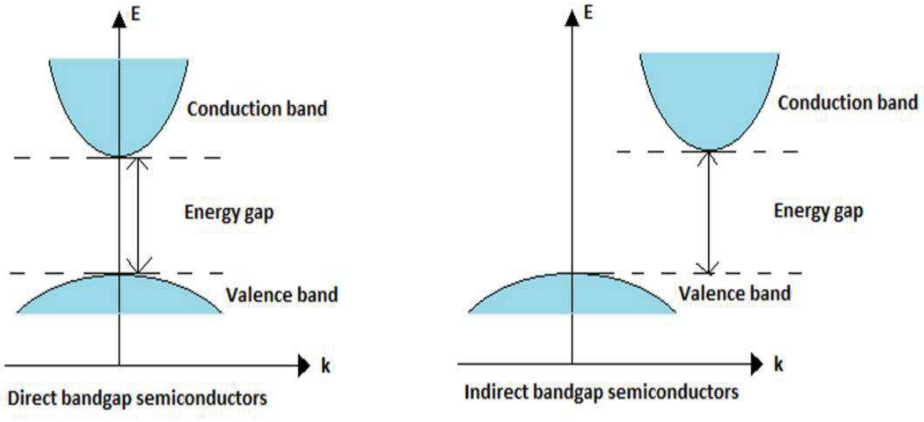

Figure 1.3: Direct and indirect band gap semiconductor

(c) Absorption

Absorption of electromagnetic radiation is a phenomenon in which photon (having energy greater than band gap) transferred its energy to an electron and creates electron-hole pair. The photon gets absorbed during this process. If the energy of the photon is less than the bandgap, it will not absorb. There are two ways of electron transition from valence band to conduction band in indirect bandgap as shown in Figure1.4.

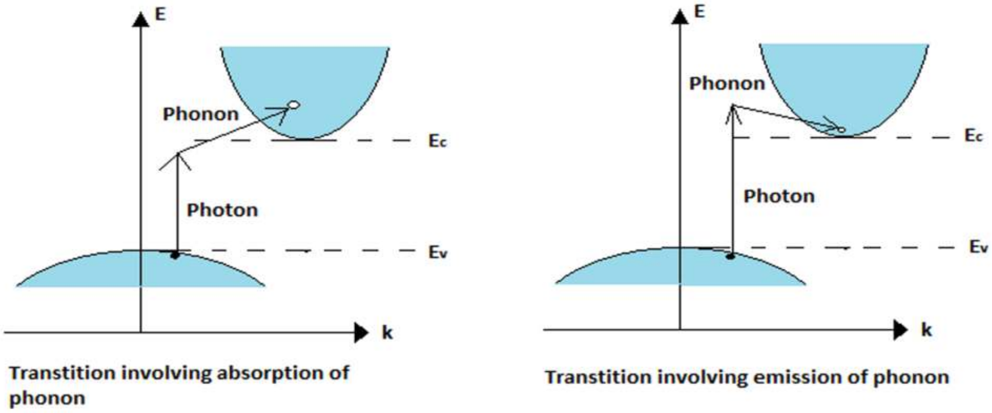

Figure 1.4: Electron transition from valence band to conduction band in an indirect band gap semiconductor.

(d) Luminescence

The phenomenon of light emission as a consequence of an atomic or molecular excitation is known as luminescence. It is often described as “cold light” to distinguish it from incandescent light emission. By mode of excitation, luminescence can be categorised as- Photoluminescence, Chemiluminescence, Electroluminescence, Mechanoluminescence, Radioluminescence and Thermoluminescence etc. The photoluminescence deals with light emission from the material after the photon absorption. In this process, photon excited the electron to a higher energy level, after excitation-relaxation photons are re-radiated. The time period between absorption and emission is very small. The diagram for excitation-relaxation process of photoluminescence is shown in Figure1.5. Photoluminescence is an important technique for optical characterization and to get information about disorder present in the system.

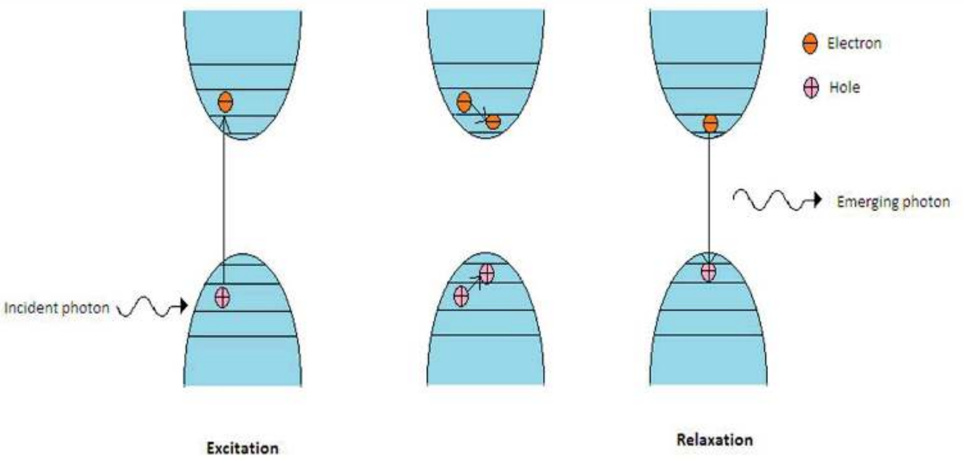

Figure 1.5: Excitation-relaxation process of photoluminescence.

(e) Ferromagnetism

The Ferromagnetic material exhibits a spontaneous magnetic moment i.e. magnetic moment even in the absence of an applied magnetic field. The presence of spontaneous magnetic moment is due to the arrangement of electron spin and magnetic moment in a regular manner. The origin and behaviour of ferromagnetism have been explained in the literature with the help of various theories, such as- Mean field theory, different types of exchange interactions [7-8]. The BMP model has been also employed to explain the phenomenon of ferromagnetism [9]. The Theory of s-d exchange involves the coupling of *d* electron spins with the conduction electron spins, which leads toward ferromagnetic ordering. The Mean field theory was proposed by Pierre Weiss in 1906[10]. The basic idea was, there is an internal molecular field which is proportional to the magnetization of the ferromagnet. It was found that magnetic behaviour depends on the type of interaction between atoms, which is influenced by the distance between two atoms in the crystal. The ferromagnetic behaviour observed for direct exchange interaction between atoms at a particular distance. When the separation between atoms is very small, the interaction becomes anti-ferromagnetic. Subsequent researcher did further modification in the theory.

The various types of exchange interactions based theories have also been employed to explain the concept of ferromagnetism. The direct exchange and super-exchange interactions did not involve any carriers. The direct exchange has short range and strong coupling, which depends on the separation between ions. In case of a direct-exchange, the wave function overlaps due to very small separation. The super-exchange involves in such a system where the direct-exchange is not possible due to large separation between ions. In this case, ions are coupled through a non-magnetic material over a relatively long distance i.e. the magnetic interaction is mediated by intermediate anions. The carrier-mediated exchange/indirect exchange are based on the interaction between localized magnetic moments that are mediated by free carriers in the system. This type of interaction is also known as RKKY (Ruderman-Kittel-Kasuya-Yosida) interaction [3]. The RKKY exchange coefficient oscillates from positive to negative as the separation between ions changes, which leads to ferromagnetic or anti-ferromagnetic behaviour. The spin polarisation induced by a magnetic ion is felt by the moment of the other magnetic ions, which leads to an indirect coupling.

1.2.4 Ferromagnetism in DMS: Bound Magnetic Polarons (BMP) Model

The coupling between impurity charge carriers and localized spins leads to the formation of a bound state in a DMS i.e. bound magnetic polarons (BMP)[11]. The role of oxygen vacancies in the BMP model is quite interesting. It can bind electron and maintain the insulating behaviour due to its dual action i.e. as an electron donor and electron trap. The large magnetic moment bound polarons are generated due to coupling between trapped electrons and local moment of the host lattice. The ferromagnetic behaviour arises due to the interaction between polarons separated by a certain distance (order of few Bohr radii)[12]. The long-range ferromagnetic ordering in BMP model can be formed by either direct overlap between BMP or indirect BMP-magnetic impurity-BMP interactions. In the first case the distance between polarons is smaller than polaron radius, while in the latter case, separation is greater than polaron diameter[13].

1.3. ZINC OXIDE: AN OVERVIEW

Zinc oxide has a very rich and interesting history in various applications. ZnO has attracted research attention for a long time due to its unique optical, electrical and magnetic properties. The semiconducting behaviour of zinc oxide was first observed in the 1920s[14]. The study on synthesis and characterization of ZnO was reported on 1935[15]. Further investigations on different preparation technique of ZnO have been carried out to explore new morphology, structure and interesting properties. Among all semiconductor, ZnO has been recognized as most promising material for optoelectronics and spintronics applications[16]. ZnO exhibit several advantages over other wide bandgap semiconductor such as, it has large excitation binding energy (60meV) as compared to GaN (25meV) [17- 18], which indicate that free exciton is stable at 300K. The higher excitation binding energy increases the stability of exciton and luminescence efficiency by increasing the radiative recombination probability.

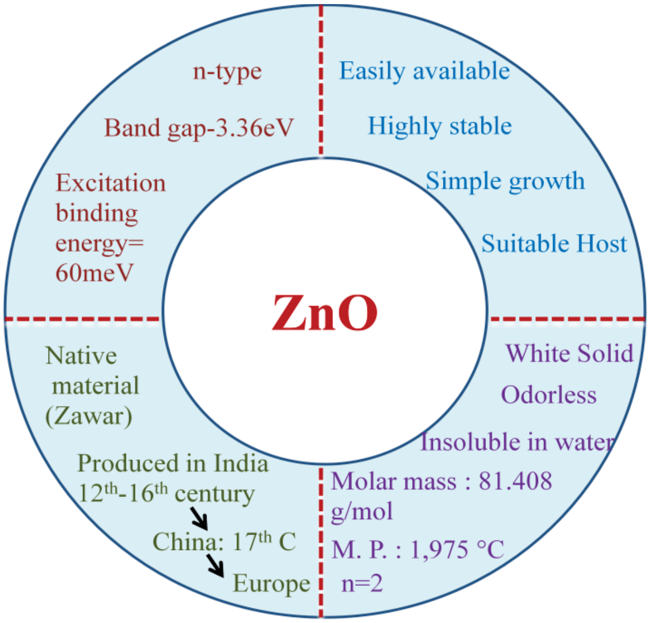

Figure 1.6: An overview of ZnO material properties.

Overview of ZnO material properties is shown in diagram and can be explained as:

- ZnO is an *n*-type semiconductor.
- It is a wide band gap material having band gap value 3.3eV.
- Large excitation binding energy (60meV). The free exciton is stable at 300 K.
- Large size single crystal substrates are available.
- The high chemical, physical and thermal stability of ZnO make it useful host.
- It is biocompatible.
- It has a lower power threshold for optical pumping and lasing.
- Suitable host for transition metal and rare earth doping.
- ZnO also has much simpler crystal-growth technology, results a potentially lower cost for ZnO-based devices.
- It has a greater resistance to radiation damage.
- ZnO is a white odourless solid, which is insoluble in water.

- ZnO exhibit molar mass=81.408g/mol, melting point $=1975^0$C and refractive index=2
- ZnO is a native material.
- From the 12th to the 16th century zinc and zinc oxide were recognised and produced in India using a primitive form of the direct synthesis process. From India, zinc manufacture moved to China in the 17th century. In 1743, the first European zinc smelter was established in Bristol, United Kingdom.

1.3.1. Crystal Structure of ZnO

Zinc oxide exhibit three types of crystal structure, hexagonal wurtzite, zinc blende and rock salt. The hexagonal wurtzite crystal structure is a most stable structure at normal temperature and pressure. The zinc blende is stable only in cubic form and rock salt structure exists at higher pressure (<10GPa) [19]. The structure of wurtzite ZnO is shown in Figure1.7. The lattice structure of ZnO is belonging to space group $P6_3mc$. It is characterised by the interconnection of two sub-lattices made of Zn^{2+} and O^{2-} in such a way that each Zn^{+2} ions is surrounded by four O^{2-} ions and vice-versa. The lattice constant is a=3.25Å and c=5.206Å [20]. The bond distance for the tetrahedral bond parallel to c-axis is 1.992Å, while in other three directions it is 1.973Å. This indicates slightly distorted tetrahedron with c/a =1.633(ideal HCP c/a= 1.60) due to different electronegativity of Zn and O. The ionicity of bonds lies between covalent and ionic semiconductor. The native point defects in a semiconductor are very important factor, and it often influences the optical, electrical and magnetic properties of the semiconductor. Therefore, a meticulous study of defects is essential for the development of novel devices. Zinc oxide is n-type semiconductor due to native doping. Oxygen vacancies and Zn interstitial are often considered as a source of n-type conductivity [21-22]. Zinc oxide mainly exhibits six types of defects, namely, zinc interstitials (Zn_i), zinc vacancies (V_{zn}), zinc antisites (O_{Zn}), oxygen interstitials (O_i), oxygen vacancies (V_O) and oxygen antisite (Zn_O). By their donor and accepter nature, the defects can be categorised into two groups, the donor defects and acceptor defects. The donor defects include V_O, Zn_i and Zn_O, while O_i , O_{Zn} and V_{zn} can be put in accepter defects group. The concentration of these defects significantly controls the emission intensity, compensation and other properties of a semiconductor. The presence of dopant ions affects the concentration of these defects.

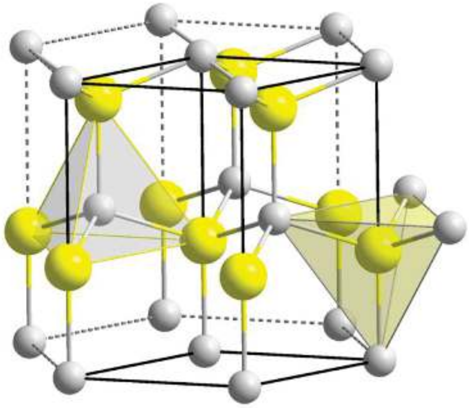

Figure 1.7: ZnO wurtzite structure.

1.3.2. Optical Properties

The band structure of semiconductor plays a crucial role to control the optical properties of semiconductor materials. Zinc oxide is considered as wide band gap semiconductor with direct band gap 3.37eV [17]. In such systems, the bottom of the conduction band and top of valence band lies at the same point in the Brillouin zone (i.e. at Γ point). Where crystal momentum K=0. The electronic band structure of ZnO is shown in Figure 1.8(a). The bottom of the conduction band is made of empty 4s states of Zn^{+2} or the anti-binding sp^3 hybrid states, while valence band formed by the occupied *2p* orbital of O^{2-} or the binding *sp3* orbital. The bottom of the conduction band has Γ_1 and Γ_7 symmetry without spin and with spin respectively. The valence band splits into two states Γ_1 and Γ_5 without spin due to effect of hexagonal crystal field, while with spin it further split into three two-fold-degenerated sub-valence bands. The higher to lower energies of valence band are labelled as A, B, C bands and corresponding band gaps are 3.445eV, 3.448eV and 3.487eV respectively. The ordering of valence band is a topic of discussion. The three main opinions about ordering included, the normal form (AΓ_9, BΓ_7, CΓ_7), negative spin-orbit splitting(AΓ_7, BΓ_9, CΓ_7) and inverted ordering of the top two valence band [23-24].

The typical absorption spectra of ZnO is shown in Figure1.8(b) [25]. Generally, zinc oxide absorbs UV light with the wavelength ≤ 385nm. As we know that 45% of solar spectrum is included in visible light. Therefore, for better photo-catalytic properties and many practical applications, it is desired that ZnO should absorb visible light. The visible light absorption can be achieved by narrowing the band gap or split it into several sub-gaps, which can be obtained by doping of suitable materials.

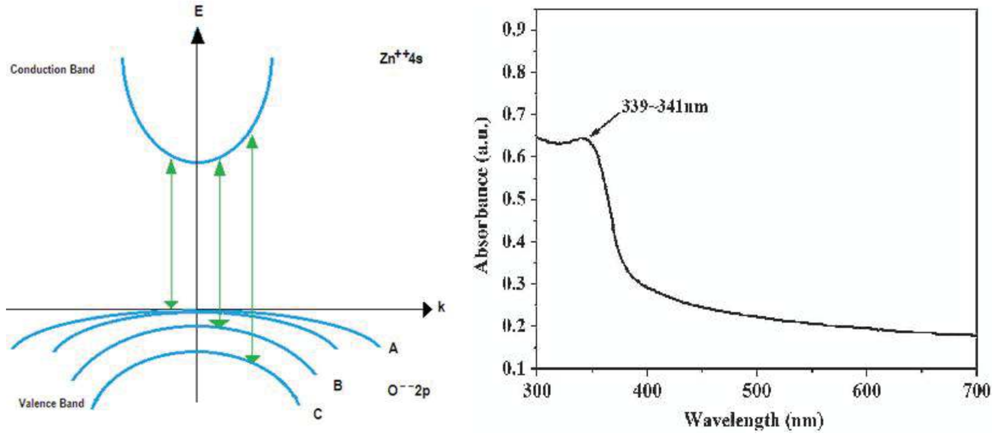

Figure 1.8 (a) Band structure of ZnO **(b)** Typical ultra violet-visible (UV-Vis) spectrum of ZnO nanoparticles

The typical photoluminescence emission spectra of pure ZnO with excitation wavelength 320 nm is shown in Figure1.9 [26]. Usually, zinc oxide has emission in the visible region with a prominent peak at violet colour. The PL spectra showed in Figure 1.9 exhibits five peaks around 380, 410, 434, 464 and 525nm. The spectra indicate that defect-related emission dominated the band edge emission of ZnO and therefore, band edge emission (380nm) is weakly resolved. The observed peaks can be assigned in spectrum colour as, peaks in the ultraviolet region, violet, violet-blue, blue and green region respectively. The peak arises around 398 nm can be attributed to near band edge emission (NBE). The recombination of an excited electron localized below the conduction band with holes in the valence band is responsible for NBE emission. The energy interval between the bottom of the conduction band and the zinc vacancy (V_{Zn}) level (~3.06eV) tells that the violet emission around 410 nm may be related to zinc vacancies. The energy interval between interstitial Zn level (Zn_i) and the valence band is consistent with the energy (~ 2.9eV) of the violet-blue emission at 434 nm observed in that experiment. This emission at 434 nm comes from the radiative transition between this level related to at grain boundaries and the valence band. The weak blue emission around 464 nm may be attributed to the defect-related positively charged Zn vacancies and green band (~525 nm) emission is attributed to the oxygen vacancies (V_o), which arises due to the recombination of electrons with photo-generated holes trapped in singly ionized oxygen vacancies.

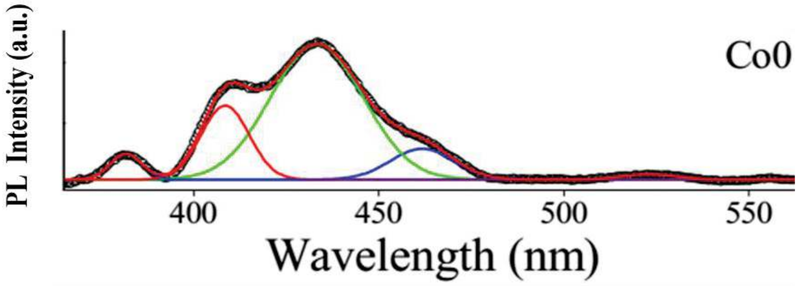

Figure 1.9: Deconvoluted Photoluminescence emission spectra of ZnO at λ_{ext}=320 nm.

The assignment of emission peaks explains that defect is an important parameter, which controls emission of ZnO. Thus proper engineering of defect is essential for desire emission in the visible region. Moreover, incorporation of the rare earth creates the new emission wavelength. Thus the selection of appropriate dopant leads to enhancement in emission peak and can be useful for ZnO based luminescent devices.

1.3.3. Magnetic Properties

The renewed interest in zinc oxide is fuelled and fanned by prospects of its spintronics applications owing to its RTFM properties. The magnetic behaviour of zinc oxide is significantly influenced by preparation method, defect concentrations and size. ZnO in bulk form often shows diamagnetic behaviour [27], while several reports on ZnO nanostructure experimentally reveals its ferromagnetic nature [28-29]. The ferromagnetism in ZnO nanostructure is control by defect concentrations [30-31]. In case of ZnO, point defects, namely Zn and O vacancies and interstitials have been considered for ferromagnetism [32]. The presence of magnetic ions (dopant) induces magnetism in semiconductor but ferromagnetism in absence of *d* electron has challenged the conventional thinking about the origin of magnetism. The magnetism arises in undoped ZnO due to defects is also called as defect–induced *d0* ferromagnetism. The origin of *d0* ferromagnetism is quite controversial and rooted in nature of native defects. Theoretical investigations indicate that short range (super-exchange interaction between O interstitials and double exchange interaction between Zn vacancies) interactions are responsible for ferromagnetism in pure ZnO [31]. The rigorous study on magnetic nature of pure ZnO with experimental techniques and theoretical analysis ascertain that *d0* ferromagnetism is due to structural defects, non-stoichiometric chemical composition or dangling bonds. Thus, in principle, the enhancement in RTFM can be achieved by stabilizing native defects in ZnO without deteriorating the crystalline quality. Suitable dopant ions can also support the enhancement in RTFM. The RTFM study enriches the applicability of ZnO based devices.

1.4. TRANSITION METAL DOPED ZnO

Transition metal doped ZnO continues to be topic of interest since the shrinkage of the current predominating semiconductor (ZnO) nanomaterials is tending towards limited functionality. The element of periodic Table whose atom has partially filled *d* sub-shell is known as the transition metal. These elements are also called as a *d*-block element. Due to their partially filled *d* sub-shell, transition metals exhibit several unique and interesting properties. For example, they form colour compound due to *d-d* transition and exhibit different oxidation states due to the low energy gap between different possible oxidation states. The manipulation of ZnO properties is required to perform the faster device operation with enhanced optical and magnetic properties, which can be achieved by incorporation of a suitable host in ZnO. Transition metal doped ZnO are promising materials for spintronic devices such as- spin polarised LEDs and spin field effect transistor. The one aspect of spintronics deals with creation and control of spin polarised current in a semiconductor. Other work of renewed interest is the development of DMS by doping of small amount of dopant ions in a non-magnetic semiconductor. The study on transition metal doped ZnO was carried out using different transition metals[33-34]. Among all, Mn and Co have attracted considerable attention because they offer a viable means of tuning the ferromagnetic property, optical band gap, have small ionic radius mismatch and the high solubility limit [26,35-36]. The practical application of spintronics device depends on RTFM property of DMS. Thus, much attention has been paid to develop the doped ZnO with RTFM. Consequently, the origin of ferromagnetism becomes a topic of discussion. The authors have reported different magnetic behaviour using different preparation method. For example, *Ahmed et al.* [37] found RTFM in Co doped ZnO, while *Rao et al.* [38] observed absence of ferromagnetism in Co doped ZnO. *Cong et al.* [39] showed RTFM in Mn doped ZnO, while *Tamura et al.* [40] could not get

RTFM in Mn doped ZnO. Some results on co-existence of paramagnetic and ferromagnetic have also been reported [41]. Thus, in spite of the exciting experimental result, the doubt about the origin of ferromagnetism in DMS still creates debate. The concentration of dopant ions is always well below the percolation limit.

1.5. RARE EARTH DOPED ZnO

Rare earth ions are an integral part of luminescent materials. The daily life of humans is surrounded by several luminescent devices, such as fluorescent lamps, light emitting diodes (LED), high definition television (HDTV) screens and commercial display panels. The rare earth ions exhibit sharp emission bands, high luminescence efficiencies with up-conversion and down-conversion property. The group of fifteen lanthanides with scandium and yttrium, i.e. seventeen chemical elements in the periodic Table are known as rare earth elements. The word *Rare* itself indicate the importance of such elements available in small quantity. The rare earth elements exhibit some interesting properties such as a substantial range of coordination number (*6-12*), small crystal field splitting and outer most *f* orbital are shielded, as a result, optical and magnetic properties are not much affected by the host. The incorporation of one or more than one rare earth ions gives the emission at a selective wavelength. The partially filled *f* orbital in the rare earth are involved in radiative transition as well as carry the magnetic moment and control both luminescence and magnetic properties. The benefit of doping rare earth ions into ZnO is that we get enhancement in optical properties coupled with unique properties of the semiconductor. The energy transfer process between rare earth ions in solids significantly affects the luminescence of material. The energy transfer can take place in several ways such as resonant radiative energy transfer, resonant non-radiative energy transfer, phonon assist energy transfer and ion pair emission. Rare earth ions (Eu, Yb, Er, Ho, Tm, and Tb) doped light-emitting semiconductor materials have been studied for optoelectronics applications [19,42]. Moreover, higher ionic radius, unsuitable energy level position of rare earth ions as compared to Zn ions, makes the doping very challenging task.

1.6. THIN FILM

The thin film can be defined as "a layer of material having the thickness in the range of nanometre to micrometre." The thin film is considered as two-dimensional materials with a dimension of the substrate in micrometre and thickness of the film in nanometre scale. Thin film technology improves the performance of practical devices with a very small amount (mass) of optical material. The properties of the thin film are controlled by thickness of the film, roughness, morphology and annealing temperature. The thickness of the film can be tuned by changing molarities of solution and number of deposited layers. The film with small roughness value is required for better performance. The film is deposited on the substrate to get better properties compared to bulk materials. The main application of thin film includes but not limited to the solar cell, electronic semiconductor device, UV detectors, optical coating and sensors etc. The nanostructure thin film enhances the efficiency of device with a reduced cast. The pivotal role of thin film technology is to improve and enrich the area of microelectronics, integrated optics, optoelectronics, spintronics, optical coating, thin film superconductivity, quantum engineering, surface science, nanomagnetism, biosensors and metallurgical coating [43-44]. ZnO thin film has attracted immense interest due to their potential application as transparent conducting oxide (TCO) in hetero-junction solar cell and piezoelectric devices. The unique properties of zinc oxide remain in thin film structure. ZnO thin film exhibits merits over other TCO like, easy and number of technique for cost-effective fabrication. The properties of thin film are also affected by preparation method. Transition metal and rare earth doped ZnO have been studied extensively for different application purpose. Recently, *J. Gosh et al.* have reported Al-doped ZnO thin film grown by radiofrequency magnetron sputtering for its application in label-free detection of glucose based on fluorescent quenching [45]. *J. Dong et al.* have investigated the feasibility of Al-doped ZnO as an active layer of thin film transistor and found that electrical properties (saturation mobility, sub-threshold swing and on to off ratio) are improved [46]. This indicates Al-doped ZnO have huge potential to be the active layer of thin film transistor. *N. Narayanan et al.* reported enhancement in photocatalytic activity of ZnO thin film via Cu doping [47]. In addition, ZnO based thin film UV detector is a subject of paramount interest, and several efforts have been made to improve its performance.

1.7. APPLICATIONS OF ZnO

Zinc oxide is widely used in many industries due to its diverse properties (physical and chemical). The broad industrial applications include rubber, pharmaceutical, cosmetic, textile and electronics industry etc. as shown in Figure1.10. Apart from that, ZnO exhibit several applications electronic devices including UV detector, sensors, solar cell, LED, TCO, Spin polarised LED, spin transistors and photocatalyst etc. Here we discuss few important applications.

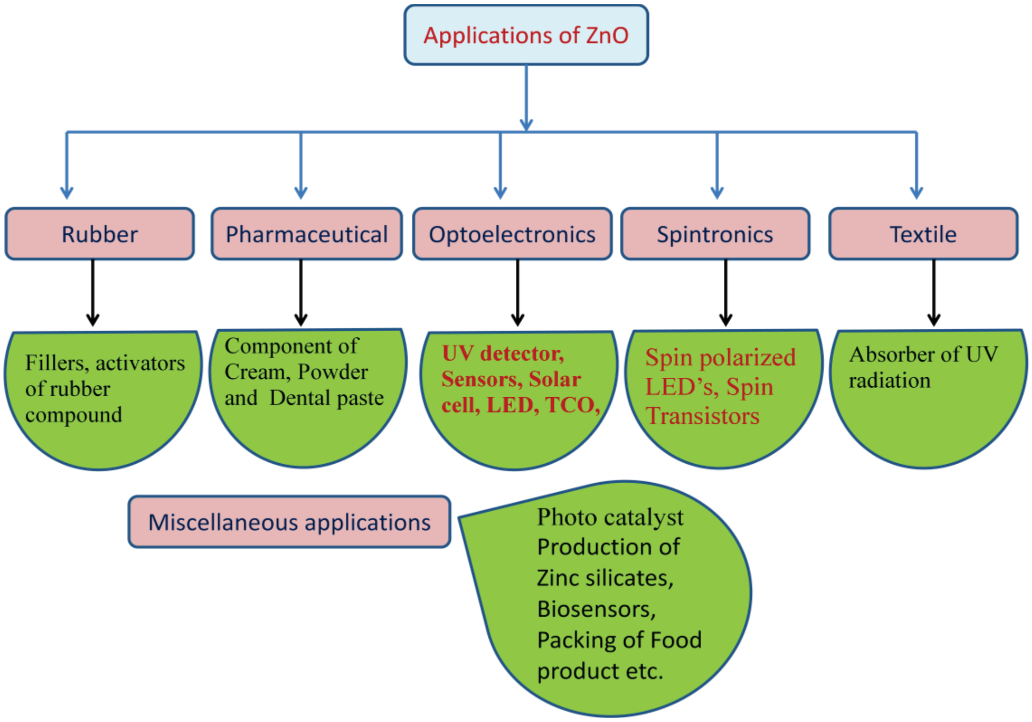

Figure 1.10: Diagram of ZnO versatile applications.

The pure silicon exhibit low thermal conductivity and can be improved by adding certain thermal conducting fillers. Different thermal conducting powder has been used for this purpose. It was found that ZnO improves the thermal conductivity of typical pure silicon rubber as well as retain the high electrical resistance. ZnO is also used as cross-linking agent for carboxylate elastomers [48]. ZnO is widely used in pharmaceutical and cosmetic industries due to its disinfection, antibacterial and dry properties [49]. It is used in an ointment, creams and lotion to protect against sunburn by UV light because it absorbed UV radiation without creating any irritation on skin [50]. It is also used as a component of baby powder and barrier cream to treat diaper rashes, anti-dandruff shampoos and antiseptic ointment. The textile industry offers many applications for nanostructure ZnO due to its biocompatibility, air permeability and efficient UV blocking properties. The investigations on self-cleaning, water repellent and UV blocking textile are continued to benefit textile industry [48]. ZnO offers unique photocatalytic properties which can be useful in degradation process of various substances [51]. *Li et al.* reported degradation of rhodamine (RhB) by ZnO nano-sphere with high photocatalytic activity below the UV range [52]. *Ma et al.* observed ZnO nanorods and nano-flower are better than ZnO particle for photocatalytic performance with methyl orange (MO)[53]. ZnO nanowire is found suitable for degradation of stearic acid. The study on doped ZnO was carried out to enhance the photocatalytic properties of ZnO.

In addition, ZnO exhibit several other applications such as it is used in the production of water and fire resist zinc silicates (act as a binder in paints), methanol (as an active component), typographical ink, car lubricant oils and packing of the food product. Some emerging optoelectronics and spintronics application of ZnO, driven by specific structural, optical and magnetic properties are listed here-

1.7.1. Solar cell

ZnO can be used as TCO, the hole blocking layer, active layer, photoanode, a buffer layer and the intermediate layer in the solar cell by doping of suitable material to tailor the material properties for specific applications [54]. Due to high bulk electron mobility and different stable nanostructure, ZnO was the first metal oxide that used in dye sensitised solar cell (DSSC). *J. Dong et al.* reported enhancement in average power conversion efficiency of perovskite solar cell using Al-doped ZnO nanorods [55]. Eu doped ZnO bi-functional layer has been used as a spectral conversion layer as well as an electron transport layer by *Wu et al.*[56]. *Anta et al.* also supported the fact that ZnO is suitable for DSSC [57]. Recently, *J. Luo et al.* studied the importance of ZnO nanostructure in perovskite solar cell and suggested the need of buffer layer or passive layer between perovskite and ZnO surface [58]. *B. Boro et al.* pointed out the use of TiO_2/ZnO nanostructure as photoanode in DSSC [59]. They have highlighted that rapid electron transfer rate, slower charge recombination rate, and a higher surface area can be achieved in DSSC using three dimensional and hybrid nanostructure (nano-donuts, nanoflower and 3D hierarchical hetero-structure) of TiO_2 and ZnO. *R. Vittal et al.* also pointed out the need of ZnO photoelectrode with new architectures and prevention of Zn^{+2}/dye aggregation [60]. They found that vertically aligned 1-D nanostructure (nanotube and nanowire) facilitate fast electron transfer as well as reduce the recombination rate. The Li doped ZnO has been proposed as cathode buffer layer to improve the photovoltaic performance of inverted polymer solar cell [61].

1.7.2. Light Emitting Diodes (LED)

ZnO based blue; UV and white light emitters are the favourite topics for many researchers due to large excitation binding energy (60meV) of zinc oxide. The production of reliable, low resistive *p*-type ZnO is required for ZnO based LED. The unintentional *n*-type nature of ZnO creates an issue in preparation of *p*-type ZnO. The *p*-type ZnO can be prepared by doping of group I elements (Li, Na and K) at Zn site or group V elements (N, P, As and Sb) at oxygen site [62]. The high brightness in UV LED has been obtained by growth of vertically aligned ZnO nanorod on a *p*-type GaN substrate without any interface layer and using a polyvinyl alcohol seed layer [63]. *H. Huang et al.* reported fairly pure UV emission peak at 370 nm with a line width less than 8 nm using ZnO based structure (metal-insulator-semiconductor diode on n^+ GaN substrate) [64]. ZnO based UV LED using hetero-structure (*n*- ZnO/AIN/GaN) has been reported by *D. You et al.*[65]. *X. M. Zhang et al.* have reported high brightness blue LED using ZnO nanowire on *p*-GaN [66]. *Y. J. Lu et al.* have improved the performance of ZnO *p-n* homo-junction LED up to three orders of magnitude by introducing hole injection layer [67]. The reports on colour switchable LED based on solution growth *n*-type ZnO on *p*-GaN/*n*-GaN hetero-junction is also available [68]. This smart dual colour LED emits red light with a peak at 692 nm and green light under reverse bias. The bias polarity controls the switching of two different light colours. In addition, several results on ZnO based LED indicates the importance of ZnO for UV, blue and white LED [69–74].

1.7.3. Sensors

Zinc oxide based various chemical and gas sensors have been demonstrated using pure and doped ZnO with the different nanostructure. Recently, *L. Meng et al.* reported 20fold increase in the sensitivity of ZnO micro-wire gas sensor towards NO_2[75]. The enhanced sensitivity was observed by the surface etching method, which leads to increase in adsorption site for gas molecule due to increase in surface area and surface density. *M. Poloja et al.* found improvement in ammonia gas sensing property of pure ZnO and ZnO/CuO by doping of aluminium [76]. The high response, good stability and fast recovery time was observed for Al-ZnO/CuO nano-composite. *M.M. Hassan et al.* reported two times enhancement in ethanol sensing of ZnO by doping of Cr [77]. The surface to volume ratio plays an important role in sensitivity and control adsorption of a gas molecule at the surface. The ethanol sensor was also reported by *X. Deng et al.* using NiO/ZnO nano-composite [78]. *E. Wongrate et al.* found that coating of Pt and Nb on ZnO nanostructure enhances the acetone gas sensing property of ZnO [79]. The highly sensitive and fast response carbon monoxide optical gas sensor based on ZnO thin film was reported by *A. Paliwal et al.*[80] The several results on room temperature sensing property of ZnO nanostructure indicates its importance for sensor applications [1,81-82].

1.7.4. UV- Detectors

UV detection field has attracted considerable attention due to its tremendous demand in scientific as well as the commercial area. UV detectors exhibit important applications in blood gas monitors, computed tomography, high-temperature flame detection, ozone layer monitoring, optical communications and missile warning system[83-84]. Zinc oxide is extensively used material in the field of UV detection due to its band gap. The intrinsic impurity of ZnO, as well as suitable dopant ions, significantly influences the quality of a detector. ZnO based photodetector have been prepared by different techniques, such as lithography, aerosol deposition, sol-gel, spray pyrolysis etc. [83]. *S. Patra et al.* reported ZnO polymer composite based UV photodetector [85]. *J. Sun et al.* observed 1020% enhancement in responsivity under external compressive strain for photodetector based on ZnO nano-arrays/NiO structure [86]. They claimed that response of the photodetector could be effectively enhanced using piezo-phototronic effect. *N. Yu et al.* suggested that ZnO micro-wall is a superior material for UV detection [87]. The ultra-fast photoresponse was observed using ZnO micro-wall grown along the cracks of GaN/Si. Hydrothermally synthesised ZnO nanorod detector has been reported for wearable computing devices by *T. H. Eom et al.*[88]. The effort has been made by the different researcher to improve the performance of ZnO based UV detector using different technique [89-90]. In conclusion, we can say, several efforts to enhance the sensitivity and responsivity of ZnO based UV detector indicate its importance for UV detection application. This area is still emerging and need sincere effort to improve the performance via rare earth doping and controlled impurity engineering in ZnO based UV detector.

1.8. THE MOTIVATION OF THESIS

The thesis work is directed along study of transition and rare earth metal doped zinc oxide in low dimensional state, namely nanoparticles and thin films. The improvement in optical absorption, emission and RTFM properties of ZnO is required, which can be achieved by incorporation of suitable dopant ions. The regions of RTFM in transition metal-doped ZnO are not clear yet and still a topic of discussion. The global success of spintronics is still waiting for strong RTFM in DMS. Therefore, to shed more light on the correlation between structural optical and magnetic properties of transition metal doped ZnO, we have systematically change the doping percentage of Co and Mn to study its effect on optical absorption, emission and RTFM properties for optoelectronics and spintronics applications.

Most of the work in rare earth doped ZnO is focused on optical emission property. The easy way to enhance the luminescent property of rare earth is tuning of doping concentration. But enhancement in rare earth-related luminescent with a higher doping concentration of rare earth leads towards impurity formation as well as distortion of host crystal structure. Therefore, we have studied rare earth doped ZnO with small doping concentration (1%) of Eu and Tb and tried to improve its optical property via different concentration of Li co-doping (0.25-1.00%) using charge compensation phenomenon. Moreover, the extensive study of magnetic behavior for rare earth doped ZnO is still required. In this thesis, we have put sincere effort to investigate the local structure, optical and magnetic property of Eu, Li co-doped ZnO and Tb, Li co-doped ZnO via various characterization techniques.

In order to fulfill the demand for highly sensitive and fast response ZnO based UV detector, we have investigated the structural, optical and electrical properties of rare earth doped ZnO. The sol-gel method has been employed to prepare the Dy doped ZnO and Co doped ZnO thin film. We found that Dy doped ZnO is best suitable material for ZnO based UV detector.