CHAPTER 1

INTRODUCTION

Nanotechnology is broadly defined as the manipulation of matter on a molecular scale. This refers to the production of structures and even devices, called nanomaterials, in the size range of 1 to 100 nm in any dimension (Nel et al 2006). The ever-increasing demand for the miniaturization of technology has resulted in an explosion in nanotechnology research. The range in use of products containing nanomaterials are wide; nanotechnology has made its way into cosmetics, sunscreen, clothing, electronics, appliances, filtration, medicine, and even food products (Sozer & Kokini 2009). Silver nanoparticles (NP) are currently the most heavily used, being incorporated for their antimicrobial properties in clothing, upholstery, pillows, food storage containers, and even toys for children (Schrand et al 2010).

In 1959, physicist Richard Feynman gave a talk at the American Physical Society entitled “There’s Plenty of Room at the Bottom” in which he discussed the possibilities of directly manipulating single atoms and molecules in structures. He also highlighted that these materials may behave differently on such a small scale. For instance, gravity would hold less sway, while Van der Waals forces would become more important. The lecture had little effect over the subsequent 20 years, but has been looked at in hindsight as that which sparked the move toward nanotechnology development that now encompasses different types of nanomaterials utilized in many different areas.
Though the physical and chemical properties of substances have been well characterized, an intriguing facet of nanotechnology is that materials reduced to the nanoscale in size begin to display different physical and chemical properties. This can include changes in optical properties, such as color and light diffraction, solubility, hardness and strength, magnetism, heat, and electrical conductivity, and surface reactivity (Schrand et al. 2010). As NP size is reduced, the surface area-to-volume ratio increases, and a large number of the atoms composing the particle are found on the particle surface (Nel et al. 2006). This can render substances previously thought inert suddenly highly reactive. These changes in properties mean that researchers cannot rely upon expectations of chemical behaviour based upon the previously understood characteristics of these substances. This has profound impacts upon toxicology; it cannot be assumed that substances that are safe on the bulk (micron) scale will be so when reduced to nano size. Different properties also open new doors for utility, and are being exploited for applications such as imaging and cosmetics.

Different types of nanomaterials are now being synthesized from a variety of different substances. Carbon nanotubes (CNT) are studied heavily due to their strength, hardness, heat, and electrical conductivity (Lacerda et al. 2006). Scientists have found that carbon nanotubes can be engineered harder than diamonds, and are looking at them with increasing interest as scaffolds for tissue regeneration (Blank et al. 1998, Saito et al. 2009). Many other substances including gold, silver and semiconducting materials such as metal oxides have also been used to form nanorods and NP (Schrand et al. 2010). Nanoparticles are those with diameters of 1-100 nm and those made of semiconducting materials sized approximately 10 nm or less behave as quantum dots, in which the band gap can be modified with NP size (Medintz et al. 2005). The band gap is the amount of energy required for an electron in the material to be liberated from the allowed valence band and become a
charge carrier. If enough energy is supplied, an electron jumps from the valence band to the conductance band, leaving behind a vacancy called an electron “hole” in the valance band (Mansur 2010). In NP, a large portion of the atoms are found at the surface, and consequently so too are the highly reactive valence electrons and holes. This has strong implications for the potential of NP to have toxic reactivity in biological systems.

1.1 WIDE BAND GAP SEMICONDUCTOR

ZnO was one of the first semiconductors to be prepared in rather pure form after silicon and germanium. It was extensively characterized as early as the 1950’s and 1960’s due to its promising piezoelectric/acoustoelectric properties. Wide band gap semiconductors have gained much attention during last decade because of their possible uses in optoelectronic devices in the short wavelength and ultraviolet (UV) portion of the electromagnetic spectrum. These semiconductors such as ZnSe, ZnS, GaN and ZnO have shown similar properties with their crystal structures and band gaps. Initially, ZnSe based devices and the GaN based technologies obtained large improvements such as blue and UV light emitting diode and injection laser. ZnSe has produced some defect levels under high current drive. No doubt, GaN are considered to be the best candidate for the optoelectronic devices. However, ZnO has great advantages for light emitting diodes (LEDs) (Look et al 1998) and laser diodes (LDs) (Tang et al 1998) over the currently used semiconductors.

Recently, it has been introduced that ZnO as II–VI semiconductor is promising for various technological applications, especially for optoelectronic short wavelength light emitting devices due to its wide and direct band gap. The most important advantage is the high exciton binding energy (60 meV) giving rise to efficient exitonic emission at room
temperature. Since ZnO and GaN have almost identical lattice parameters and the same hexagonal wurtzite structure, ZnO can satisfactorily be used as lattice matched substrate in GaN based devices or vice versa. ZnO has excellent radiation hardness among all other semiconductors. This property supplies the uses of ZnO based devices in space applications and high energy radiation environments. Bandgap energy can be varied from 3.3 eV up to 4.5 eV with alloying process. Hence it can be used as an active layer in the doubly confined hetero-structured LEDs and quantum well lasers. These unique nanostructures unambiguously demonstrate that ZnO is probably the richest family of nanostructures among all materials, both in structure and properties (Ozgur et al 2005).

1.2 ZINC OXIDE (ZnO)

The unique and fascinating properties of II-VI compound semiconductors have triggered tremendous motivation among the scientists to explore the possibilities of using them in industrial applications. Zinc oxide (ZnO) is a piezoelectric, dielectric, transparent, semiconducting oxide, with a direct band gap of 3.37 eV at room temperature and a large excitation binding energy (60 meV) (Klingshirn 1975), which is 2.4 times the effective thermal energy (kBT =25 meV) at room temperature and de-excitation energy is 15 meV. This is one of the key parameters that ZnO exhibits near-UV emission, transparency, conductivity and resistance to high temperature electronic degradation. As expected, quantum dots of ZnO have electronic structures between those bulk and molecular materials and quantum confinement effects should be evident by a blue of the absorption edge with decreasing particle size. In addition, ZnO is the hardest of the II-VI semiconductors due to the higher melting point (2248 K) and large cohesive energy (1.89 eV) (therefore more resistant to wear), as well as one of the most piezoelectric semiconductors (d= 12.2 × 10-12 C/N) with good piezoelectric coefficient.
KL = 0.27 and its high adherence on various substrates (Ozgur et al 2005, Ferblantier et al 2005).

There are also possible applications of ZnO in microelectromechanical systems (MEMS), both in sensors, actuators and in the fabrication of acoustic and electro-optical devices. In particular, it can be used as bulk acoustic wave (BAW) resonators and as thin film bulk acoustic wave (FBAR) resonators or surface acoustic wave (SAW) resonators (Chopra 1983; Carlotti et al 1987, Bose & Barua 1999, Kim et al 2000). It is commonly used as a catalyst, piezoelectric transducer and photonic material. ZnO has several fundamental advantages over its chief competitor GaN and SiC. In fact, its free exciton is bound with 60 meV, much higher than that of GaN (21–25 meV); high energy radiation stability and amenability to wet chemical etching (although both are much better than Si or GaAs).

Furthermore several experiments verified that ZnO is very resistive to high energy radiation, making it suitable candidate for space applications (Kucheyev et al 2003). It can be easily etched in all acids and alkalis. Due to this reason it can be used in the fabrication of small size devices e.g. transparent electrodes, window materials for displays and solar cells (Keis et al 2002). Moreover it is used in a variety of technical applications, including porcelain enamels, heat resisting glass, an activator in vulcanization, an additive for rubber and plastics, pigment in paints with UV-protective (Smij & Pavel 2011) and fungistatic properties, spacecraft protective coatings, a constituent of cigarette filters, healing ointments, in optical waveguide and many more (Hirchwald 1985). ZnO has played an important role in the fabrication of transparent thin film transistors (TFT), by depositing channel layer on a flexible substrate through low temperature processes, realizing transparent TFTs and achieving extra functions such as photo detections using ZnO channel.
The films of Zinc oxide (ZnO), indium tin oxide (ITO) and cadmium oxide (CdO) have been investigated in recent years as transparent conducting oxide (TCO) due to their good electrical and optical properties in combination with large band gap (>3eV), abundance in nature, optical transmittance (>80%) in visible region and absence of toxicity. Besides, this zinc oxide has received particular attention as a promising substrate material due to its isomorphic structure. Low conductivity ZnO single crystal substrates have numerous advantages for both nitride and oxide based devices in base station wireless power amplifier applications. Low substrate defect density coupled with the isomorphic wurtzitic lattice with respect to GaN result in films that reward device manufacturers with better performance. The semi insulating property of the substrate prevents parasitic currents in field effect transistors as well as permitting direct electrical characterization of epitaxial films especially in thin film form, since bulk ZnO is quite expensive and unavailable in large wafers for the time being, interfacial energy between ZnO and sapphire or other oxide substrate is such like that it always favoured two-dimensional growth, which results in high quality film at lower temperatures (less than 700ºC) (Pearston et al 2003).

ZnO is a promising material for spintronics applications because of theoretical predictions of room temperature ferromagnetism, for example Curie temperature of > 300K for Mn-doped p-type ZnO and n-type doping in Fe, Co or Ni alloyed. ZnO have gained intense attention in the searching for high temperature dc Curie (Tc) ferromagnetic diluted magnetic semiconductors (DMS) materials, which are based on ZnO. DMSs could exhibit ferromagnetism above room temperature upon doping with transition elements (Ozgur et al 2005).
1.3 FUNDAMENTAL PROPERTIES OF ZnO

1.3.1 Crystal Structure of ZnO

Most of the group II-VI binary compound semiconductors crystallize in either cubic zinc-blende or hexagonal wurtzite structure where each anion is surrounded by four cations at the corners of a tetrahedron, and vice versa. This tetrahedral coordination is typical of sp³ covalent bonding, but these materials also have a substantial ionic character. ZnO is a II-VI compound semiconductor whose ionicity resides at the borderline between covalent and ionic semiconductor. The crystal structures shared by ZnO are wurtzite, zinc blende, and rocksalt. At ambient conditions, the thermodynamically stable phase is wurtzite, as schematically shown in Figure 1.1. The zinc-blende ZnO structure can be stabilized only by growth on cubic substrates, and the rocksalt (NaCl) structure may be obtained at relatively high pressures.

![Image of ZnO crystal structure]

Figure 1.1 Crystal Structure of hexagonal wurtzite ZnO
1.3.2 Lattice Parameters

Lattice parameters are considered important, when one has to develop semiconductors devices. There are mainly four factors which determine the lattice parameters of the semiconductors. (i) Free-electron concentration which affects the potential of the bottom of conduction band normally occupied by electrons. (ii) Concentration of impurities and defects and the difference in ionic radii between these defects and impurities with respect to substituted matrix ions. (iii) External strains (for example, those induced by substrate) (iv) temperature. On the other hand, the strict periodicity of the lattice is disturbed by many imperfections or defects. These imperfections or defects have a considerable, controlling influence on mechanical, thermal, electrical and optical properties of semiconductors. They determine the plasticity, hardness, thermal and electrical conductivities. Commonly the lattice parameters of any crystalline material are measured accurately by high-resolution x-ray diffraction (HRXRD).

The wurtzite structure has a hexagonal unit cell with two lattice parameters a and c in the ratio of $c/a = \sqrt{8}/3 = 1.633$ (in an ideal wurtzite structure) and belongs to the space group $C_{6h}^{d}$ in the Schoenflies notation and P6$_{3}$mc in the Hermann–Mauguin notation. The structure is composed of two interpenetrating hexagonal close 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 $u = 3/8 = 0.375$ (in an ideal wurtzite structure) in fractional coordinates. The internal parameter $u$ is defined as the length of the bond parallel to the c-axis (anion–cation bond length or the nearest-neighbor distance) divided by the c lattice parameter. The basal plane lattice parameter (the edge length of the basal plane hexagon) is universally depicted by $a$; the axial lattice parameter (unit cell height), perpendicular to the basal plane, is universally described by $c$. Each sublattice includes four
atoms per unit cell, and every atom of one kind (group II atom) is surrounded by four atoms of the other kind (group VI), or vice versa, which are coordinated at the edges of a tetrahedron.

1.3.3 Physical parameters of ZnO

Table 1.1 shows a compilation of the basic physical parameter for ZnO. Still some uncertainty exists in these values. For example, in few reports it has been mentioned physical properties of only p-type ZnO and therefore the hole mobility and effective mass are still in debates.

1.4 PROPERTIES OF ZINC OXIDE

There are number of properties are associated with wurtzite ZnO namely optical, magnetic, thermal, mechanical, electrical etc. In this section we are discussing the basic principles of two ZnO properties which is studied in the present investigation.

1.4.1 Optical Properties

The optical properties of a semiconductor are associated with both intrinsic and extrinsic effects. Intrinsic optical transitions take place between the electrons in the conduction band and holes in the valence band, including excitonic effects due to the coulomb interaction. The main condition for exciton formation is that the group velocity of the electron and hole is equal. Excitons are classified into free and bound excitons. In high quality samples with low impurity concentrations, the free exciton can also exhibit excited states, in addition to their ground-state transitions.
Table 1.1 Basic physical properties of wurtzite ZnO

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice parameters at 300 K</td>
<td></td>
</tr>
<tr>
<td>$a_0$</td>
<td>0.32495 nm</td>
</tr>
<tr>
<td>$c_0$</td>
<td>0.52069 nm</td>
</tr>
<tr>
<td>$a_0/c_0$ (ideal hexagonal structure shows 1.633)</td>
<td></td>
</tr>
<tr>
<td>$u$</td>
<td>0.345</td>
</tr>
<tr>
<td>Density</td>
<td>5.606 g cm$^{-3}$</td>
</tr>
<tr>
<td>Stable phase at 300 K</td>
<td>Wurtzite</td>
</tr>
<tr>
<td>Bond length</td>
<td>1.977μm</td>
</tr>
<tr>
<td>Melting point</td>
<td>1975°C</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>0.6, 1–1.2</td>
</tr>
<tr>
<td>Linear expansion coefficient (/C)</td>
<td></td>
</tr>
<tr>
<td>$a_0$: 6.5 × 10$^{-6}$</td>
<td></td>
</tr>
<tr>
<td>$c_0$: 3.9 × 10$^{-6}$</td>
<td></td>
</tr>
<tr>
<td>Static dielectric constant</td>
<td>8.656</td>
</tr>
<tr>
<td>Refractive index</td>
<td>2.008, 2.029</td>
</tr>
<tr>
<td>Energy gap</td>
<td>3.4 eV, direct</td>
</tr>
<tr>
<td>Intrinsic carrier concentration $&lt;10^6$ cm$^{-3}$</td>
<td></td>
</tr>
<tr>
<td>Breakdown voltage (106 V cm$^{-1}$)</td>
<td>5.0</td>
</tr>
<tr>
<td>Saturation velocity (107 cm$s^{-1}$)</td>
<td>3.0</td>
</tr>
<tr>
<td>Exciton binding energy</td>
<td>60 meV</td>
</tr>
<tr>
<td>Electron effective mass</td>
<td>0.24</td>
</tr>
<tr>
<td>Electron Hall mobility at 300 K for low n-type</td>
<td>200 cm$^2$ V$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>conductivity</td>
<td></td>
</tr>
<tr>
<td>Hole effective mass</td>
<td>0.59</td>
</tr>
<tr>
<td>Hole Hall mobility at 300 K for low p-type</td>
<td>5–50 cm$^2$ V$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>conductivity</td>
<td></td>
</tr>
<tr>
<td>Knoop hardness</td>
<td>0.5N/cm$^2$</td>
</tr>
<tr>
<td>Minimum pressure at melting point</td>
<td>7.82 atm</td>
</tr>
<tr>
<td>Ionicity</td>
<td>62%</td>
</tr>
<tr>
<td>Heat capacity $C_p$</td>
<td>9.6 cal/molK</td>
</tr>
<tr>
<td>Heat of crystallization $\Delta H_l$s</td>
<td>62KJ/mol</td>
</tr>
<tr>
<td>Young’s modulus $E$ (bulk Zno)</td>
<td>111.2±4.7 GPa</td>
</tr>
<tr>
<td>Bulk modulus, B (Polycrystalline Zno)</td>
<td>142.2 Gpa</td>
</tr>
<tr>
<td>Spontaneous polarization (C/m$^2$)</td>
<td>-0.057</td>
</tr>
</tbody>
</table>
Extrinsic properties are related to dopants or defects, which usually create discrete electronic states in the band gap and therefore influence both optical absorption and emission processes. As we mentioned above, that ZnO is a direct band semiconductor and a transparent conductive material. ZnO films are transparent in the wavelength range of 0.3 and 2.5 μm and plasma edge lies between 2 and 4 μm depending on the carrier concentration. It is well known that a shift in the band gap edge appears with an increase in the carrier concentration. This shift is known as Burstein-Moss shift. Optical transitions in ZnO have been studied by a variety of experimental techniques such as optical absorption, transmission, reflection, spectroscopic ellipsometry, photoluminescence, cathode luminescence, calorimetric spectroscopy etc.

Room temperature PL spectrum of ZnO is usually composed of a near UV emission band (375 nm) and a green emission band (510 nm) although a yellow-orange band (610 nm) can also be observed in some situations. The near UV-band is closely related to the excitonic nature of the material and may be superposed with the free exciton emission, its phonon replica, bound exciton emission, as well as biexciton emission. The observation of luminescence from exciton is usually difficult even at low temperatures. This comes from a lot of factors (Stolt et al 1993), first, the efficiency of radiative emission is low even for direct gap semiconductors, which is often found to be $10^{-1}$ to $10^{-3}$. A large part of the radiative emission comes from bound-exciton complexes and defect centers. Second, exciton emission is limited by the internal reflection of the exciton and the small escape length. As a quasi-particle exciton moves with their group velocity through the semiconductor. During its movement exciton can be trapped or scattered by impurities and phonons. When it eventually reaches the surface of the semiconductor, in most cases, it will be reflected back into the semiconductor. Except the internal reflection, the radiative combination yield
from free-exciton is also limited by the small escape length, which is defined as the depth from which exciton can reach the surface. Only the free-exciton inside the escape length can have the contribution to the luminescence.

The research interest for the green band emission in ZnO can be traced back to the early stage of last century. Due to this green emission, ZnO is considered as an important luminescent material for the planar display and short-decay cathode luminescence screens. Unfortunately, the mechanisms behind this emission band are still unclear even though the researches on this topic have been lasted for many years. Green band emission was first attributed to an excess of zinc. Almost all the proposed mechanisms about the green emission are attributed to the native lattice defects except the one that is based on the divalent Cu impurities (Stolt et al 1993).

1.4.2 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, 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.
1.4.2.1 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.

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 organic compounds are all diamagnetic in nature.

1.4.2.2 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. Paramagnetism is found in magnesium, molybdenum, lithium, and tantalum etc.

1.4.2.3 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.

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.

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. 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 1.2, it is clear that if the field \( H \), is reduced by reversal of direction, magnetization does not retrace its original path. At zero fields 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 1.2). 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.
1.4.2.4 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. 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.

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. 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.

1.5 DOPING AND DEFECTS IN ZnO

As wide band gap ZnO is gaining much importance for the possible application due to the capability of ultraviolet lasing at room temperature and possibilities to engineer the band gap. In order to attain the potential offered by ZnO, both high-quality n- and p-type ZnO are essential. But it is very difficult to obtain the bipolar carrier doping (both n and p types) in wide-
band-gap semiconductors such as GaN and II-VI compound semiconductors including ZnS, ZnSe, and ZnTe. Unipolar doping has not been a surprising issue in wide-band-gap semiconductors: ZnO, GaN, ZnS, and ZnSe are easily doped to n-type, while p-type doping is difficult. All undoped ZnO to date has been found to be n-type, with donor concentrations typically around $10^{17}$ cm$^{-3}$ for present-day, high-quality material, but sometimes as high as $10^{21}$ cm$^{-3}$, for doped material. The situation is opposite for ZnTe where p-type doping is easily obtained, while n-type doping is difficult. The main characterization techniques used to find the shallow electrical defects in semiconductor materials are photoluminescence and temperature dependent Hall Effect measurements. Zn$_i$ and V$_{Zn}$ are the zinc interstitial and zinc vacancy respectively while O$_i$ and V$_o$ denote the oxygen interstitial and vacancy respectively. Impurity atom X can occur either as interstitials X$_i$ or substitutionals X$_{Zn}$ and X$_o$ on zinc and oxygen sites respectively. D and A denote that the relevant impurity is expected to be donor or acceptor respectively. X does not have to be a foreign atom. A Zn-on-O anti site can for example also occur.

1.5.1 n-Type Doping

ZnO has wurtzite structure, excess zinc is always found in ZnO. Due to this zinc excess, ZnO is a non-stoichiometric compound and n-type semiconductor. Undoped ZnO shows intrinsic n-type conductivity with high electron densities of about $10^{21}$ cm$^{-3}$. Zinc interstitials Zn$_i$ and the oxygen vacancy V$_o$ are known the dominant native donor in unintentionally ZnO film. But still it is debatable issue. Photoluminescence and temperature dependent Hall studies of electron irradiated ZnO have shown that Zn$_i$ is the most likely candidate for purely lattice-related dominant shallow donor, with an activation energy about 30-50 meV. It has been argued that the n-type conductivity of unintentionally doped ZnO film is only due to hydrogen (H),
which is treated as a shallow donor with activation energy of 31 meV instead of Zn$_i$. This assumption is valid because hydrogen (H) is always present in all growth methods and can easily diffuse into ZnO in large amounts due to its large mobility (Look et al 1999). Hydrogen has been considered as a shallow donor candidate, much research has been done on hydrogen (H) in ZnO. During seeded chemical vapor transport (SCVT) growth of ZnO, it has been shown that hydrogen with activation energy 39 meV acts as main donor. n-type doping of ZnO is relatively easy as compared to p-type doping. Group III elements Al, Ga and In as substitutional elements for Zn and group-VII elements Cl and I as substitutional elements for O can be used as n-type dopants. Doping with Al, Ga, and In has been attempted by many groups, resulting in high-quality, highly conductive n-type ZnO films. Al-doped ZnO films were grown by MOCVD. The films obtained through this method is high by conductive with minimum resistivity as compared to Ga-doped ZnO films by Chemical-vapor deposition (Özgür et al 2005).

### 1.5.2 p-Type Doping

It is very difficult to obtain p-type doping in wide band gap semiconductors. Acceptors in ZnO can also take place from both lattice defects and impurity atoms. The oxygen interstitial O$_i$ and zinc vacancy V$_{Zn}$ are both known to be acceptors in ZnO. Deep impurity level can also be source of doping problem, causing large resistance to the formation of shallow acceptor level.

P-type doping in ZnO may be possible by substituting either group-I elements (Li, Na, and K) for Zn sites acting as shallow acceptors and group-V elements (N, P, and As) are found to act as deep acceptors on O sites. It was shown that group-I elements could be better p-type dopants than group-V elements in terms of shallowness of acceptor levels. However, group-I
elements tend to occupy the interstitial sites, due to their small atomic radii, rather than substitutional sites, and therefore, they act as donors instead of acceptors. Moreover, significantly larger bond length for Na and K than ideal Zn–O bond length (1.93 Å) induces lattice strain, increasingly forming native defects such as vacancies which compensate the shallow dopants. These are among the many causes leading to difficulties in attaining p-type doping in ZnO (Jagadish & Pearton 2006 and Park et al 2002). Group V elements (N, P, As) except N, both P and As, have a larger bonds lengths. That’s why they are likely to form antisites to avoid the lattice strain. Unfortunately for p-conduction these elements have a tendency towards antisite formation, i.e. they can substitute not only oxygen but also zinc atoms, in which case they act as donors. Nitrogen (N) appears to be good candidate for a shallow p-type dopant in ZnO with smallest ionization energy, although N is not soluble in ZnO, and doping can be achieved by ion implantation (Özgür et al 2005 and Tüzemen & Emre 2007).

1.6 METHODS OF PREPARATION OF NANOMATERIALS

The preparation of nanomaterials with well defined size and morphology is an important challenge. A variety of techniques have been used for the synthesis of nanomaterials which depends on the material of interest and the size range involved. The basic principle for the synthesis of nanomaterials is to produce a large number of nuclei and to inhibit the growth and aggregation of grains. Different metals, metal oxides, sulfides, polymers and composite nanomaterials can be prepared using a number of synthetic techniques, which are broadly classified into two categories, namely, physical methods and chemical methods.
1.6.1 Physical Methods

Since past few decades, various methods have been used for the synthesis and commercial production of various nanomaterials, thin films and nanocomposite. Brief and concise descriptions of most of the physical pathway used for the synthesis of nanomaterial are as follows.

1.6.1.1 Laser ablation method

In the laser ablation technique, a high power laser pulse was used to vaporize carbon from a target at high temperature. This method is useful for depositing nanocrystalline thin films and powder. As a result, a supersonic jet of particles (plume) is ejected normal to the target surface. The plume expands away from the target with a strong forward directed velocity distribution of different particles. This ablation process takes place in a vacuum or in presence of some background gases. The substrate temperature has to be sufficiently large (700-800°C). This method is applicable to high melting point elements and transition metals. Iron, gold, palladium and compounds of sulphides have been prepared by this method. This method is also suitable for highly toxic and radioactive materials, often in trace amounts. The advantage of this method is that the rate of production of materials is high usually 2-3 gm/min. Nanocrystalline NiO thin-film electrodes were prepared by reactive pulsed laser ablation of a metallic Ni target in oxygen ambient (Wang & Qin, 2002). Laser ablation of gold dipped in liquid alkanes from n-pentane to n-decane produced Au sol with varying results (Compagnini et al 2003, Dahl et al 2007).

1.6.1.2 Inert gas condensation method

Gas condensation was the first technique used to synthesize nanocrystalline metals and alloys. In this technique, the evaporation of a
material takes place in presence of a cool inert gas, usually He or Ar, at low pressure condition, in the order of 1 mbar. This method is also called as ‘inert gas evaporation’ process. The evaporated atoms or molecules undergo a homogeneous condensation to form nanoclusters via collisions with gas atoms or molecules. In this technique, a metallic or inorganic material is vaporized using thermal evaporation sources such as Joule heated refractory crucibles, electron beam evaporation device in an atmosphere of 1-50 m bar. According to researchers’ gold/ palladium nanoparticles were fabricated by inert-gas condensation on a sputtering reactor, where they found the particle are icosahedral in shape and there is no evidence of a core-shell structure (Pérez-Tijerina et al 2008).

1.6.1.3 High energy ball milling method (Mechanical alloying method)

This is a top-down approach for nanomaterial synthesis. This method has been used for the generation of magnetic and catalytic nanoparticles. Ball milling and subsequent annealing is a simple method for the large production of various nanopowders. Here elemental blends, prealloyed powders and ceramics are milled to achieve alloying at the atomic level. This method consists of placing graphite powder into a stainless steel container along with four hardened steel balls. Argon is purged into the container (Shah & Ahmad 2010). The milling is done for longer period of time, which is followed by annealing in inert atmosphere at 1400°C. The mechanism of this process is still not known. It is suggested that the alloy generated due to collision of balls resulting in continuous fragmentation, coalescence events of the alloy at the collision site are the procedure of mechanical alloying. Recently, Mg₂Ni was synthesized by a solid state reaction from the constituent elemental powder mixtures via mechanical alloying (Iturbe-García et al 2010).
1.6.1.4 Chemical vapour deposition method

Chemical vapour deposition (CVD) is a widely used materials-processing technology. It is a process in which a substrate is exposed to one or more volatile precursors, which react and/or decompose on the substrate surface to produce a non-volatile solid deposit or thin film. The majority of its applications involve formation of solid thin-film coatings to surfaces, but it is also used to produce high-purity nano materials and powders, as well as fabricating composite materials via infiltration techniques (Creighton et al 2001). Because of versatile nature of CVD, the chemistry is very rich and various types of chemical reactions are involved. General experience is that low temperature CVD (600-900°C) yields MWNTs, whereas higher temperature (900-1200°C) reaction favours SWNT growth. Sometimes carbon nanofibers and nano beads are also formed depending upon the nature of the source materials (Bhattacharjee et al 2012). Recently, a group found that single-walled carbon nanotubes (SWNTs) with highly graphitized structure were synthesized by thermal chemical vapor deposition method using an improved nitrogen-pretreatment Fe-Mo/MgO catalyst. From the whole observation they inferred that nitrogen pretreatment enhances the catalytic activity and promotes the growth mechanism to yield longer SWNTs. It also produced long length, highly graphitized SWNTs (Patil et al 2012).

1.6.1.5 Electro-deposition method

Template-assisted electrodepositing is an important technique for synthesizing metallic nanomaterials with controlled shape and size. The development of materials science has brought great momentum to applied electrochemical fields. Arrays of nanostructured materials with specific arrangements can be prepared by this method, employing either an active or restrictive template as a cathode in an electrochemical cell. Preparation of
oxide films by electro deposition from aqueous solution presents several advantages over other techniques; this method presents interesting characteristics for large-area, low-cost, and generally low-temperature and soft processing of materials. The electro deposition process involves the formation of either an instantaneous or a progressive nucleation. Synthesis of ZnO nanoparticles and electrodeposition of polypyrrole/ZnO nanocomposite film is studied by Moghaddam et al. (2009). Li et al. (2013) also developed a new facile synthesis method of polyaniline nanoparticles (PANI) by an in-situ electro deposition technique. The morphology of PANI nanoparticle was controlled by the growth time during the electro deposition process.

1.6.2 Chemical Methods

Although the bottom up approach is nothing new it plays an important role in the fabrication and processing of nanostructures and nanomaterials. This approach refers to the building-up of materials from the bottom: atom by atom, molecule by molecule or cluster by cluster. Nanoparticles of various oxides can also be synthesized by confining chemical reaction, nucleation and growth process. Various synthesis methods can be grouped into two categories: thermodynamic approach or kinetic approach.

In the thermodynamic approach, synthesis process consists of (i) generation of super saturation, (ii) nucleation, and (iii) subsequent growth. In kinetic approach, formation of nanoparticles is achieved by either limiting the amount of precursors available for the growth or confining the process in a limited space. A brief and concise description of most of the chemical methods for nanomaterial synthesis is as follows:
1.6.2.1 Hydrothermal method

Hydrothermal method can be defined as a method of synthesis of single crystals which depends on the solubility of minerals in hot water under high pressure. Since ionic product of water (Kw) has a maximum value of around 250-300°C, hydrothermal synthesis is usually carried out below 300°C. The crystal growth is performed in an apparatus consisting of a steel pressure vessel called autoclave, in which a nutrient is supplied along with water. The contribution of the dielectric constant to the reaction rates becomes remarkable based on the electrostatic theory. The dielectric constant of water is 78 at room temperature, in which polar inorganic salts can be soluble in water. The dielectric constant of water decreases with increasing temperature and decreasing pressure (Hayashi & Hakuta 2010). This method has the capability to create crystalline phases which are not stable at the melting point and is also suitable for the growth of large good-quality crystals while maintaining good control over their composition.

The formation mechanism of metal oxide particles from metal salt solution is as follows: first hydrated metal ions are hydrolyzed to metal hydroxide. Then, metal hydroxides proceed to precipitate as metal oxides through dehydration. Hydrolysis is regarded as an electrostatic reaction between metal ions and hydroxyl ions. This method has proved to be efficient both in search of new compounds with specific physical properties and in the systematic physicochemical investigation of intricate multi component systems at elevated temperature and pressure. Crystalline nanotubes of \( \gamma \)-AlOOH and \( \gamma \)-Al\(_2\)O\(_3\) have been synthesized by hydrothermal method and its formation mechanism and catalytic performance has been studied (Lu et al 2009). Similarly, synthesis of alpha alumina by hydrothermal method and its surface characterization with controlled chemical composition has been observed by Suchanek et al (2010).
Solvothermal synthesis is also a similar type of synthesis, where different organic solvents are used in place of aqueous medium (Li et al 2010). Recently, ultra small Tungsten Oxide nanoparticles were synthesized by solvothermal method. Here a one-pot, two precursor synthesis route was adopted in which a polyoxometalate salt is decomposed thermally in a high boiling organic solvent oleylamine. These findings provide a new method to control the size and shape of transition metal oxide nanoparticles, which will be especially useful in catalysis (Soultanidis et al 2012).

1.6.2.2 Sonochemical method

Sonochemistry is a process in which molecules undergo a chemical reaction due to the application of powerful ultrasound radiation having frequency in the range of 20 KHz-10MHz. The ultrasonic vibrations are intensified and focused through an ultrasonic probe in a very intense flow. The stream passes through the liquid causing alternatively a compression and a relaxation of the liquid. This change in pressure leads to the emergence of microscopic bubbles (cavities) that expand during the decompression phase and implode violently during the compression phase. The cavitations are a quenching process, and hence the composition of the particles formed is identical to the composition of the vapour in the bubbles, without phase separation (Shafi et al 2001).

Sonochemistry has been used to prepare various kinds of nanostructured materials magnetic which include materials of metal alloy, metal oxide, ferrite, nitride and so on (Nguyen et al 2012, Ziylan et al 2013). Synthesis of silver nanoparticles by sonochemical method was studied by Manoiu et al (2010), where they found spherical shape and uniform size. A novel method for sonochemical preparation of nanosized hollow iron oxide using carbon nanoparticles as template has been demonstrated by Bang &
Suslick (2007). Nano-sized metal-organic lead(II) polymer is used as precursor for the preparation of nano-structured lead(II) iodide and lead(II) oxide by sonochemical method was studied by Aslani et al (2009).

1.6.2.3 Co-precipitation method

Co-precipitation synthesis involves dissolution of compound salt precursor in aqueous media and subsequent precipitation from the solution by pH adjustment. The co-precipitation technique is a useful method for the preparation of ceramics and metal oxide powders. Apart from its simplicity, atomic mixing of the constituents by chemical co precipitation yields a final product of near-perfect stoichiometry without high-temperature treatment. Wang et al (2009) have synthesized highly photocatalytic ZnO/In$_2$O$_3$ heteronanostructures by co-precipitation method. Jadhav et al (2009) have studied on effect of different surfactants on the size and optical properties of Y$_2$O$_3$: Eu$^{3+}$ nanoparticles prepared by co-precipitation method. A cost effective co precipitation method has also been used by Wang et al (2010) for the synthesis of indium tin oxide nanoparticle without chlorine contamination. Recently, Kim et al (2013) have investigated on characterization of as-synthesized FeCo magnetic nanoparticles by using co precipitation method.

1.6.2.4 Electrospinning method

A large number of advanced techniques have been employed to fabricate 1-D nanostructure, but electrospinning seems to be the simplest and most versatile method. Electrospinning is a broadly used technique for electrostatic fiber formation. In this method electrical force is utilized to produce polymer fibers with diameters ranging from few nanometers to several micrometers using polymer solutions of both natural and synthetic polymers (Bhardwaj & Kundu 2010). It is the process by which continuous nanofibers are produced with high surface area-to-volume ratio. Basically, an
electrospinning system consists of three major components: a high voltage power supply, a spinneret (e.g., a pipette tip) and a grounded collector (usually a metal screen, plate, or rotating mandrel) and utilizes a high voltage source to inject charge of a certain polarity into a polymer solution or melt, which is then accelerated towards a collector of opposite polarity (Liang et al 2007). In this process, a polymer solution is injected from a needle in the presence of electric field.

A DC voltage in the range of several tens of kVs is necessary to generate electric field during the electrospinning. When the applied electric field overcomes the surface tension of the liquid a continuous jet is ejected which upon subsequent solvent evaporation and bending produces nanofibers on the collector surface (Greiner & Wendorff 2007). This method has following advantages: (i) the ability to produce thin fibers with diameters in the micrometer and nanometer ranges; (ii) one-step forming of the two-or three dimensional nanofiber network assemblies and (iii) applicability for a broad spectrum of molecules, such as synthetic and biological polymers (Matsumoto & Tanioka 2011). Recently, various applications of electrospun fibers are being carried out, as these fibers have high surface to volume ratio, very high porosity and enhanced physico-mechanical properties. Thavasi et al (2008) have reviewed on electrospun nanofibers in energy and environmental applications. Applications of electrospun nanofibers in drug delivery and tissue engineering have also been investigated by Sill et al (2008). Agarwal et al (2008) have investigated on the use of electrospinning technique for biomedical applications.

Similarly, Dong et al (2011) have studied on the use of electrospinning to create materials suited for four major energy-related applications i.e. fuel cells, dye-sensitized solar cell, Li-ion batteries and super capacitors. Teo & Ramakrishna (2009) have reviewed on electrospun
nanofibers as a platform for multifunctional, hierarchically organized nanocomposite. Ceramic nanofibers have great potential in various applications such as photonics, nanoelectronics, data storage, catalysis, adsorption studies and many more (Formo et al 2009, Biswas et al 2012). These ceramic nanofibers can be amorphous, polycrystalline, dense, porous or hollow (Sigmund et al 2006). Recently, electrospinning technique has been used to prepare various ceramic nanofibers (Dai et al 2011, Wu et al 2012). In a review article Ramaseshan et al (2007) have reported the fabrication and usefulness of various nanostructured ceramics by electrospinning method. They have also highlighted some important applications and the physicochemical properties of nanostructured ceramics material.

1.6.2.5 Sol-gel method

Sol-gel method involves the formation of a concentrated suspension of a metallic oxide or hydroxide (sol), which is subsequently dehydrated by evaporation or solvent extraction, resulting in a semi-rigid mass (gel). This method is carried out in solution, tailoring of certain desired structural characteristic such as compositional homogeneity, grain size, particle morphology and porosity is possible. A uniform distribution of the particles is important for optimal control of grain size and micro structure to maintain high reliability (Shah & Ahmad 2010). A wide range of pure and mixed oxides can be produced on controlled heating of this gellated material. In a typical sol-gel method, a colloidal suspension or a sol is formed from hydrolysis and polymerization reactions of precursors, which are usually inorganic metal salts or metal organic compounds such as metal alkoxide. The characteristics and properties of a particular sol-gel network are related to a number of factors that affect the rate of hydrolysis and condensation reactions, such as: pH, temperature and time of reaction, reagent concentration, nature and concentration of catalyst, $H_2O/M^+$ molar ratio,
aging temperature and time and drying. Nickel oxide was prepared by modified sol-gel method and spherical NiO nanoparticles were obtained by Wu et al. (2007). In this paper, influence of some parameters on the synthesis of nanosized NiO materials has produced spherical nanoparticle. Similarly, many more metal oxides like SnO$_2$ (Aziz et al. 2013), TiO$_2$ nanoparticle (Hema et al. 2013) were also synthesized by sol-gel method.

The sol-gel process is a versatile soft chemical process, widely used for synthesizing metal oxides, ceramic and glass materials. Sol-gel chemistry has opened a new opportunity in the field of materials science. Sol-gel method normally involves the use of metal alkoxides or organometallic inorganic salts as precursors. In this process, the precursor’s undergoes a series of hydrolysis and polycondensation reaction to form a colloidal suspension or a sol. The sol-gel process involves the transition of a system from a liquid “sol” (mostly colloidal) into a solid “gel” phase (Chaudhury et al. 2007, Mourad et al. 2009). Then drying of the gel followed by calcination at different temperatures to obtain the metal oxide nanopowder. In sol-gel method it is possible to control the shape, morphology and textual properties of the final materials. That shows the versatility of the sol gel process. In contrast to high-temperature processes, Sol-gel method has large advantages such as possibility of obtaining metastable materials, achieving superior purity and compositional homogeneity of the products at moderate temperature. Furthermore, this process also influences the particle morphology during the chemical transformation of the molecular precursor to the final oxidic network.

The sol-gel method is a wet-chemical synthesis technique for preparation of oxide gels, glasses, and ceramics at low temperature. It is based on control of hydrolysis and condensation of alkoxide precursors. As early as the mid-1800s, interest in the sol-gel processing of inorganic ceramics and
glass materials has begun with Ebelman and Graham’s studies on silica gel (Fudyna 1988). The investigator recognized that the product of hydrolysis of tetraethoxysilane (TEOS) under acidic conditions is SiO$_2$. In the 1950s and 1960s Roy and co-workers used sol-gel method to synthesize a variety of novel ceramic oxide composition with very high levels of chemical homogeneity, involving Si, Al, Zr, etc, which couldn’t be made using traditional ceramic powder methods (Tang et al 1998 and Dhiraj et al 2008). It is based on formation of a sol starting from a solution of precursors, the condensation of the sol into a gel, and finally the removal of the solvent.

A sol is defined as a colloidal suspension of solid particles in a liquid. The dispersed phase is so small, in the range of 1-1000 nm, in which the gravitational forces are negligible and interactions are dominated by short-range forces, such as vander Waals attraction and surface charges. The inertia of the dispersed phase is small enough that it exhibits Brownian motion.

A gel can be defined as a substance that contains a continuous solid skeleton enclosing a continuous liquid phase. A gel can also be described as a polymeric molecule with macroscopic dimensions so that it extends throughout the solution. The gel point is the time (or degree of reaction) at which the last bond is formed that completes this giant molecule. It is noteworthy about this method that the solid state can be reached at low temperature starting from a solution. This feature greatly expands the possibility to create new materials or to improve their properties. It becomes possible to synthesize materials under conditions that are not possible in the usual preparation of metal oxides (i.e. chemical vapor deposition) where high temperatures are required. It is possible to fabricate ceramics or glass materials in a variety of forms, such as ultra-fine powders, fibers, thin films, porous aerogel materials or monolithic bulky glasses and ceramics. An overview of sol-gel method as follows.
The sol-gel process, as the name implies, involves transition from a liquid ‘sol’ (colloidal solution) into a ‘gel’ phase (Wang et al, 2004). The sol-gel process uses inorganic metal salts or organic compounds such as metal alkoxides as precursors, and the whole process can be conducted at room temperature and ambient pressure. A colloidal suspension or a ‘sol’ is formed after a series of hydrolysis and condensation reaction of the precursors. Then the sol particles condense into a continuous liquid phase (gel). With further drying and heat treatment, the ‘gel’ is converted into dense ceramic or glass materials. Because water and alkoxides are immiscible, alcohol is commonly used as a co-solvent. Due to the presence of the co-solvent, the sol-gel precursor, alkoxides, mixes well. Hydrolysis with water to facilitate the hydrolysis.

\[
\text{- Si - OR + H - OH} \quad \xrightarrow{\text{Hydrolysis}} \quad \text{- Si-OH+ R-OH} \quad (1.1)
\]

During the hydrolysis reaction, the alkoxide groups (OR) are placed with hydroxyl group (OH) through the addition of water. Subsequent condensation reaction involving silanol group (Si-OH) produces siloxane bonds (Si-O-Si) with by-product of water (water condensation) or alcohol (alcohol condensation). As the number of siloxane group increases, they bridged with each other and a silica network is formed. Upon drying, the solvents that are trapped in the network are driven off. With further heat treatment at high temperature, the organic residue in the structure is taken out, the interconnected pores collapse and a densified glass or ceramics is formed. The sol-gel process of many molecular precursors is characterized by different sub-processes:

- Hydrolysis of the precursors
- Condensation
- Drying
- Sintering
Any of these phases has a big influence on the properties of the resulting material and the great number of variables involved makes the control of the whole process still very empirical. Therefore a detailed knowledge of the chemical mechanisms, which permits to control the properties of the final amorphous material at a molecular scale and to synthesize defined structures, is a great challenge.

**Hydrolysis:** The formation of the sol occurs from the hydrolysis reaction of the precursors in the solution, which are usually metal alkoxides because they react readily with water. The general formula for the alkoxide class is: \( M(OR)_n \), where the number of alkoxide groups \( n \) depends on the central atom \( M \). The compound \( \text{Si} \, (\text{OC}_4\text{H}_9)_4 \) (tetrabutoxysilane) also belongs to this class. This class of compounds is used because a hydroxyl ion becomes attached to the metal atom in the hydrolysis reaction:

\[
\begin{align*}
M(OR)_n + H_2O & \rightarrow HO.M(OR)_{n-1} + R.OH \\
(1.2)
\end{align*}
\]

The reaction involves a nucleophilic attack of the oxygen contained in water molecule to the central atom \( M \), followed by a proton transfer from \( H_2O \) to an alkoxy group -OR, and the exit of an alcohol molecule R-OH.

Often a catalyst is necessary because of the slow reaction rate of the hydrolysis process, as is the case when \( M = Si \). The catalyst can be both, an acid and a base. Acids serve to protonate negatively charged alkoxide groups and alkaline conditions produce strong nucleophiles via deprotonation of hydroxo ligands.

The hydrolysis reaction rate is influenced also by the kind of precursors chosen, because of the different steric hindrance of the alkyl groups. The bigger the alkyl group, the more crowded is the nucleus \( M \), and the slower the hydrolysis will be. Furthermore the longer the chain, the
weaker the inductive effects on the central atom, and the slower will be the substitution reaction.

A great role is also played by the solvent used, because of the difference in polarity, dipole moment and availability of labile protons that influence the rate of the hydrolysis and condensation reactions. Together with the hydrolysis reaction, in an alcoholic solution, two other reactions can occur: the reverse reaction, or reesterification, and the transesterification, in which an alcohol molecule displaces an alkoxide group to produce another alcohol molecule.

\[
M(OR)_n + R'OH \rightarrow M(OR)_{n-1}(OR') + ROH \tag{1.3}
\]

**Condensation:** The condensation process takes place as soon as some hydrolyzed precursor molecules are present in the solution, and it occurs at the same time as the hydrolysis, depending on the quantity of water and catalyst present in solution. With the existence of acid catalyst, weakly cross-linked polymer is formed and easily aggregate after drying yielding low-porosity microporous structure. On the contrary is used, discrete highly branched clusters are formed and lead to a mesoporous structure after condensation. The condensation reaction builds a metal-oxygen-metal bridge and can follow two different schemes:

**Alcoxolation (alcohol condensation):**

\[
M.OR + M.OH \rightarrow M.O.M + R.OH \tag{1.4}
\]

**Oxolation (water condensation):**

\[
M.OH + M.OH \rightarrow M.O.M + H.OH \tag{1.5}
\]
With the removal of the protonated species as either alcohol or water. This process leads to the formation first of oligomers and then of macromolecules, whose dimensions and characteristics depend on the reaction conditions used.

The way in which the inorganic polymer grows depends also on the functionality ‘f’ of the precursor, or on the number of oxygen bridges that can be bound to the central atom. Silicon has for example a functionality f = 4, but it can be decreased by chemical modification (i.e. β-diketones, carboxylic acids or other chelating ligands). When the functionality is more than 2, the chain will grow with cross links to build a three dimensional network.

**Drying:** The drying process is the first step from the gel to the final solid material, and it occurs with a contraction of the gel’s volume and a stiffening of its structure. Drying of gels can be divided into two stages a constant rate period and a falling rate period. During the constant rate period, mass transfer is limited by convection away from the gel surface, whereas during the falling rate period, mass transfer is limited by the permeability of the gel.

The evaporation of the liquid from the gel surface increases the vapor-solid interface. For this reason the liquid flows from the bulk of the gel to the surface, to cover the dried surface. Because of the evaporation the liquid cannot cover the whole surface without the creation of a meniscus on the pore surface. The capillary force exerted by the liquid causes the contraction of the solid phase, until the radius of the meniscus is equal to the radius of the pore. At this stage the shrinkage proceeds at a constant rate, and the contraction of the solid phase is equivalent to the volume of the evaporated liquid.
After this point the evaporation of the liquid continues moving the liquid-vapor interface towards the bulk of the solid phase leaving a dry solid. This contraction is irreversible, because of the further condensation of the unreacted hydroxyl or alkoxy groups that proceeds during the shrinkage process any time that two groups approach enough to react and form a new Si-O-Si bridge.

The drying of the gel produces anyway a pressure gradient in the liquid phase, which leads to differential shrinkage of the network. If the external part shrinks faster than the internal one, tensile stresses arise that tend to fracture the network. The formation of cracks is energetically favorable because at either side of the crack the material can contract more freely. To avoid this phenomenon, a slow evaporation rate of the solvent is required. The aging of the gel also reduces the risk of fractures, because it helps to strengthen the network, especially if it is still in presence of water and catalyst. During this process, further cross-links continuous, the gel shrinks as the covalent links replace non-bonded contacts and the pore sizes and pore wall strengths change with the evolution of the gel’s structure. The schematic representation of the sol-gel process is shown in Figures 1.2 and 1.3.

Figure 1.2   Different stages in the Sol-gel process
Figure 1.3 Effect of time on temperature during sol-gel process

1.7 ADVANTAGES AND LIMITATIONS OF SOL-GEL METHOD

1. Sol-gel method involves wet chemical synthesis of materials. So the composition of the materials can be tailored at molecular level. As a result, stochiometrical homogeneous control of the doping is easily achieved.

2. Since liquid precursors are used it is possible to cast the glass and ceramics in a range of shapes, such as thin film, fibers, and monoliths, etc, without the need of machining or melting.

3. The precursors, such as metal alkoxides, with very high purity are commercially available, which makes it easy to fabricate materials with high quality.

4. It is cost effective because the temperatures required in the process are low, close to room temperature, and no delicate vacuum system is needed.
Despite all the advantages, sol-gel method still has some limitations. Solvents, such as alcohol and water, are involved in the process, so it is not appropriate for fabrication which is very sensitive to solvents. Furthermore, stress induced cracks upon drying are not unusual and can’t be heated after densification. Very careful attentions are needed to avoid cracking. Despite of the disadvantages, sol-gel method is a very mild and flexible method to fabrication materials that posses properties not attainable by other methods. It inspires us to further investigate and modify the method to exploit its maximum value in application.

1.8 APPLICATION OF NANOMATERIALS

Nanotechnology is moving into the centre of world-wide public attention because of its broad range of applications which could dramatically impact both the scientific community and the commercial market place. Generally speaking, nanotechnology can be defined as the application of scientific and engineering principles to make and utilize very small things (Mu et al 2010). Nanotechnology applications have been applied across biomedical, optical, electronic, mechanical and chemical fields as well as in consumer goods such as foods and cosmetics. Nanotechnology is merging with information technology, biology and social sciences and is expected to reinvigorate discoveries and innovations in many areas of the economy. A complete list of the potential applications of nanomaterials is too vast and diverse. Few of these applications are described briefly as follows.

1.8.1 Chemical Applications

1.8.1.1 Catalysis

Catalysis is of vital importance in our society and constitutes a cornerstone of life from biological processes to large-scale production of bulk
chemicals. Nanomaterials having small size and large surface area exhibit unique catalytic properties. For example, gold is a poor catalyst in the bulk form whereas nanosized gold is not. Nanomaterial-based catalysts are usually heterogeneous catalyst. The extremely small size of the particles maximizes surface area exposed to the reactant, allowing more reactions to occur on the surface. However, thermal stability of these nanomaterials is limited by their critical sizes; the smaller the crystallite size, the lower thermal stability (Viswanathan 2009). The two types of catalyst that carry out chemical reactions with high rates and selectivity are (1) Enzymes (nature’s catalysts) and (2) Synthetic catalysts. There are three parameters, which are main key to determining the suitability of activity, selectivity and stability.

Zhong et al (2007) have synthesized three dimensional flowers like ceria micro/nanocomposite which is used as a support for gold nanoparticles to remove CO by catalytic oxidation. Similarly, Polshettiwar et al (2009) have studied on a number of metal oxides (Fe, Co, Mn, Cr, and Mo) three dimensional nanostructures which were observed to show a novel support for various catalytic organic transformations. Nanoferrites was functionalized and coated with Pd metal, which was catalyzing various C-C coupling and hydrogenation reactions with high yields. Positively-charged gold nanoparticles possess intrinsic peroxidase-like activity, and can catalyze oxidation of the peroxidase substrate 3, 3, 5, 5-tetramethylbenzidine (TMB) by H₂O₂ (Jv et al 2010).

1.8.1.2 Paints, pigments and coating

Nanomaterials are defined by its sizes of less than 100nm. Since a fairly long time they are part of the innovative materials for industry and research. In formulations of paints, coatings, inks and varnishes increases the use of nanomaterials rapidly. Color and gloss characteristics are numbered
among the decorative aspects; conductivity, microbial inactivation or antistatic properties are numbered to the functional aspects. By addition of nanoparticles, also the protective functions of paints and coatings, such as scratch resistance and UV stability can be improved. When changing the size of these materials, also the material properties are changing, such as the colour, the interaction with other substances and the chemical reactivity. This change in material properties results from a change in the electronic properties. Zinc phosphate nanomaterials is found to be the widest application in paints, since it provides excellent corrosion resistance and is non-toxic (Grzmil et al 2007). Mathiazhagan & Joseph (2011) have reviewed on nanomaterials used in a new prospective in organic coating. They have emphasized mainly on different types of coatings, pigments used in paint formulation and a special focus is set on the uses of nanomaterials/fillers in coating application.

1.8.2 Optical and Electronic Applications

Semiconductor nanomaterials possess unique and interesting optical properties and functionalities that find important applications in emerging technologies (Li & Zhang, 2009). In case of semiconductor materials, the reduction in particle size, results in increase in the band gap which results in shift of the absorption light towards the high-energy region. In addition, the band edge position of valence and the conduction bands are stabilized and destabilized respectively (Viswanathan 2009). This leads to an increase in the oxidation and reduction ability of the semiconductor. Certainly, the rate of recombination of photo excited electron-hole pair is also reduced greatly. Recently, Li et al (2010) have reviewed on nanocomposites composed of inorganic nanoparticles and the polymer matrix for optical applications. Polymer-inorganic nanocomposite are found to be
promising new lines of exploration which can show new bi-functional applications i.e. optoelectronic and magneto-optic.

1.8.3 Magnetic Applications

Magnetism is an intrinsic façade of existence of living creatures, from iron in blood to the capability of magneto tactic bacteria, birds and other creatures to navigate by the Earth’s magnetic field. Diverse applications in data storage, security/sensors to biomedical applications led to noteworthy advances in development of variety of multifunctional magnetic nanoparticles. Polymer inorganic nanocomposite is basically used in optical application, magnetic applications, mechanical applications, catalysis, electrochemical applications, electrical and thermal applications and biomedical applications (Li et al 2010). For magnetic applications, metal and metal alloys such as Fe or CoPt, oxides such as ferric oxide and ferrite are always used as inorganic nanofillers. Sharma et al (2011) have presented a review which recapitulates the development of state-of-the-art multifunctional magnetic nanoparticles and the foremost applications of these multifunctional magnetic nanoparticles in magnetic targeting, drug delivery, separation, and contrast agents in magnetic resonance imaging, hyperthermia and sensors.

Super-paramagnetic iron oxide nanoparticles with appropriate surface chemistry can be used for numerous in vitro applications such as MRI contrast enhancement tissue immunoassay, detoxification of biological fluids, hyperthermia, drug delivery, and cell separation (Laurent et al 2008). Liang et al (2010) have successfully fabricated free-standing graphene/Fe₃O₄ hybrid papers, which exhibit good flexibility, electrical conductivity, and mechanical strength, and also superparamagnetism. These hybrid papers can also show potential applications in fields such as magnetic controlling devices, data
storage, magnetic detection, electromagnetism shielding materials, electrochemical devices, batteries and so on.

1.8.4 Metal and Ceramics Applications

Metallic nanomaterials (nanoparticles, nanowires and nanorods) have gained a large interest in industry because of their unique physicochemical properties resulting from nanoconfinement effects. Abdullayev et al (2011) have reported on the selective formation of silver nanorods within the inner lumen of halloysites. Halloysite tube templates have a potential for scalable manufacturing of ceramic encapsulated metal nanorods for composite materials. In particular, ceramic with one dimensional nanostructure received increasing interest since it provides a good material system to investigate the dependence of electrical, optical, thermal and mechanical properties on dimensionality and size reduction (Lu et al 2009). For practical application of one-dimensional ceramic nanomaterials scalable materials production and convenient devices integration are extremely important (Wu et al 2012). An important class of fiber nanomaterials appeared encompassing simple, binary and ternary oxide ceramics.

Moreover, since the oxide ceramics are also biocompatible, novel electrospun fibrous materials have been synthesized for medical application (Starbova et al 2012). The fiber immobilization has been found very important for the development of various functional ceramic materials synthesis of many ferroelectric oxides ceramics of different structural families are reported by various group. For example, lead zirconate titanate ceramics, lead gadolinium zirconate (Panigrahi et al 2013). It is also observed that porous ceramics are widely used as filters, catalyst carriers, separation membrane and bio-ceramics. Isobe et al (2007) have synthesized porous alumina ceramics with unidirectional - oriented pores to study the gas
permeability and mechanical property. The gas permeability is higher than that of conventional sample; it is due to increasing porosity and pore size. Similarly, Kritikaki & Tsetsekou (2009) have fabricated porous alumina ceramics by sol-gel method. Thus, ceramics prepared by employing nanomaterials in powder form exhibits less uniform microstructure. Very recently, Fung & Wang (2013) have investigated on reinforcement of porous alumina by nickel aluminate spinel for its use as ceramic membrane.

1.8.5 Biological Applications

Nanomaterials have number of potential applications in medical and biological fields. From nanotechnology there is only one step to nanomedicine, which may be defined as the monitoring, repair, construction, and control of human biological systems at the molecular level, using engineered nanodevices and nanostructures. Nanomedicine is dominated by nanoparticulate drug delivery system because of their ability to cross biological barriers, accumulate at tumour sites and /or increase the solubility of drugs. Sahoo et al. (2007) have investigated on the present and future of nanotechnology in human health care. According to them applications of nanotechnology to medicine and physiology imply materials and devices designed to interact with the body at subcellular scales with a high degree of specificity. Recently, Marszal, (2011) has studied on the application of magnetic nanoparticles in pharmaceutical sciences. The use of magnetic nanoparticles as drug carriers in targeted therapy provides huge opportunities in cancer treatment. Similarly, Shao et al (2012) have reviewed on magnetic nanoparticles and micro NMR for diagnostic applications. They investigated that biosensing strategies using magnetic nanoparticles offer unique advantages over traditional detection methods.
Microorganisms such as bacteria, molds, and viruses are a big problem for human beings. Thus, novel antibiotics and antimicrobial agents have been synthesized and developed for preventing disease in public health settings and for antifouling treatment in the biomedical industries. Chae and co-workers, (2011) have synthesized electrospun nano fiber composite with functionalized silver nanoparticle on it. A mixture of PAN and β-cyclodextrin solution was used for synthesizing electrospun composite nanofiber. Here β-cyclodextrin acted as a stabilizing and reducing agent for the formation of silver nanoparticle. The antimicrobial activities of nanocomposite fibers containing silver nanoparticles (Ag/NFs) against *Escherichia coli* (*E. coli*) and *Staphylococcus epidermidis* (*S. epidermidis*) were evaluated by optical density testing. Silver is known for its antimicrobial properties and has been used in medical field for antimicrobial applications and are also used in water and air filtration to eliminate microorganisms (Sharma et al 2009).

Magnetic nanocomposite can be transported purposely to a certain location in the human body and may thus act as effective drug carriers. Combining magnetic iron oxide nanoparticle and silver nanoparticle shows a unique property (Prucek et al 2011). They have studied two types of magnetic nanocomposite exhibiting high antimicrobial activities—Ag@Fe$_3$O$_4$ and γ-Fe$_2$O$_3$@Ag. Both synthesized nanocomposites exhibited very significant antibacterial and antifungal activities against ten tested bacterial strains (minimum inhibition concentrations (MIC) from 15.6 mg/L to 125 mg/L) and four candida species (MIC from 1.9 mg/L to 31.3 mg/L).

1.8.6 Environmental Application

Presently, nano-environmental concerns are starting to be taken seriously around the globe. Direct applications of nanotechnology for environmental cleanup relate to the removal of some toxic elements or
compounds from the environment, through, the use of nanofiltration, nanoporous sorbents, and catalysis by filtering, separating, and destroying environmental contaminants. Vaseashtaa et al (2007) have investigated on nanostructures which are used in environmental pollution detection, monitoring and remediation. They have also presented the sorption studies using nanomaterials based sorbents that are effective in the removal of cadmium and arsenic from water streams. Pollution in water system impairs or destroys aquatic life, threatens human health and simply fouls the water such that recreational and aesthetic potential are lost. The waste water is not properly treated prior to discharge, and then highly toxic metal ions may leak into ground water. Conventional water treatment methods are such as activated charcoal, coagulation-flocculation, reverse osmosis, distillation, and adsorptive filtration through ion exchange resins.

Mauter & Elimelech (2008) have studied on environmental application of carbon based nanomaterials. Carbon-based nanomaterials have a broad range of environmental applications: sorbents, high-flux membranes, depth filters, antimicrobial agents, environmental sensors, renewable energy technologies and pollution prevention strategies.

1.9 REVIEW OF LITERATURE

Literature survey is the comprehensive and extensive examination of several research works done by many researchers on a selected field and the briefing of their findings. At the present day the attention of many researchers in science, technology and engineering has been drawn to the preparation and properties of nano particles. The important literature closely associated with the preparation and characterization of pure ZnO and (co)doped ZnO nanoparticles are surveyed. Furthermore, the applications of these materials have also focused in this section.
The Heyd–Scuseria–Ernzerhof (HSE) hybrid density functional was used to investigate the electronic structure and optical properties of (Zr–Al) codoped ZnO (Luo et al 2004). The calculated results show that the formation energy of (Zr–Al) codoped ZnO is low, indicating that it is the energetically favorable structure and the first absorption peak of optical absorption spectra for (Zr–Al) codoped ZnO has a red-shift compared with pure ZnO, which may lead to the improvement on the visible-light photocatalytic ability. The zinc and oxygen vacancies introduced by (Zr–Al) codoped ZnO have also been investigated. Through analysis the main absorption peaks of the imaginary part of the dielectric function on polarization vectors perpendicular or parallel to the Z axis, It is found that oxygen vacancy introduced by (Zr–Al) codoping can also improve the visible-light photocatalytic ability and zinc vacancy has weak effect to enhance the optical photocatalytic ability compared with (Zr–Al) codoped ZnO.

Nanocrystals of Na-doped and Na, Mg codoped ZnO thin films (Vettumperumal et al 2014) were prepared by sol–gel spin coating method on glass substrate at different annealing temperatures. The deposited films were characterized by X-ray diffraction (XRD), Micro Raman, photoluminescence (PL) and UV-Visible measurements. The codoped films had hexagonal wurtzite structure and there were no peaks belonging to Na and Mg or its oxides observed from XRD. Surface morphology of the films was scrutinized by scanning electron microscope (SEM) and atomic force microscope (AFM) showing wrinkle structures that appeared on the film surface. Elemental compositions of the films were analysed using energy dispersive X-ray (EDS) spectra.

The LO phonon modes were observed up to the fifth order and their enhancement was observed by the presence of Frohlich contribution. From μ-PL, the strong near band edge emission observed at 3.24 eV was blue shifted
due to the band filling of free carriers. Fundamental absorption edge was observed at 370 nm and the optical band gap was decreased with respect to ZnO. Reduction of Urbach energy among codopants is small indicating less disorder.

The electronic and optical properties of Al–Ga codoped ZnO thin films (Lee et al 2012) were investigated by post-annealing. The lowest resistivity of the Al–Ga codoped ZnO films was observed from the 450°C annealed sample. The Fermi-level shift of the Al–Ga codoped ZnO film was 0.6 eV from x-ray photoelectron spectroscopy, and the widening of optical-bandgap in the Al–Ga codoped ZnO film was 0.3 eV. The correlations of optical-bandgap with Fermi-level shift and conduction band filling were studied.

First-principle calculations have been performed to investigate the electronic and magnetic properties of (Mn, Fe) codoped ZnO (Cao et al 2014) within the generalized gradient approximation (GGA) and GGA+U schemes. The formation energy of five different configurations is investigated and the ground state is demonstrated to be ferromagnetic ordering. By applying the U correction, the band gap energy of pure ZnO is close to the experimental values, while the ferromagnetic ordering of the ground state remains unchanged. The ferromagnetic stabilization is mediated by double exchange mechanism. In addition, defects corresponding to Zn-vacancy and O-vacancy cannot enhance the ferromagnetism obviously. These results indicate that (Mn,Fe) codoped ZnO are promising magneto-electronic and spintronic materials.

In his previous research Cao et al (2013) the electronic structures and magnetic properties of Mn/Fe codoped ZnO nanowires systematically using the first-principles density functional theory. The calculated results of
formation energy indicate that the configuration of the lowest energy where Mn and Fe atoms form nearest neighbors on the outer cylindrical surface layer along the [0001] direction, will be determined. The magnetic coupling of 8 types of Mn/Fe codoped ZnO nanowires was investigated and ferromagnetic state was found in certain configurations. The mechanism is from the fierce hybridization between 3d of Mn and Fe with O 2p near the Fermi level. The relative energy difference for configuration VIII is 0.221 eV, which indicates that room temperature ferromagnetism could be obtained in such a system and Mn/Fe codoped ZnO nanowires are a promising nanoscale spintronic material.

Li and Al codoped ZnO (LAZO) thin films have been prepared by a sol–gel method and their structural and optical properties have been investigated by Nian et al (2010). The prepared LAZO films had an average transmittance of over 85% in the visible range. The UV absorption edge was red-shifted with Li-doping, whereas it was blue-shifted with Al-doping. A broad yellowish-white emission was observed from the LAZO films annealed above 600°C. The visible emission was enhanced with increasing annealing temperature and dopant concentration.

Li–Er codoped ZnO thin films have been prepared on Si(100) substrates by pulsed laser deposition (PLD) by Gu et al (2009). Both the as-grown and post-annealed films exhibit good crystalline quality with preferred c-axis orientation. After post-annealing at 850°C, the photoluminescence (PL) related to intra-4f shell of Er^{3+} can be clearly observed. The Li–Er codoped ZnO film shows higher intensity of PL around 1.54 μm than the Er monodoped ZnO film. The behaviour is attributed to the lowering of the symmetry of the crystal field around Er^{3+} ions by introducing Li^{+} into ZnO lattice, which is also confirmed by Raman scattering spectra.
Ruthenium (Ru = 0%, 1% and 2%) doped nano-crystalline zinc oxide (ZnO) nanorods were synthesized by using well-known sol gel technique. X-ray diffraction (XRD) results show that Ru (0%, 1% and 2%) doped ZnO nanorods crystallized in the wurtzite structure having space group C\textsubscript{3}v (P6\textsubscript{3}mc). Williamson and Hall plot reveal that in the nanoscale dimensions, incorporation of Ru induced the tensile strain in ZnO host matrix. Photoluminescence (PL) and Raman studies of Ru doped ZnO nanorods show the formation of singly ionized oxygen vacancies which may account for the observed room temperature ferromagnetism (RTFM) in 2% Ru doped ZnO. X-ray absorption spectroscopy (XAS) reveals that Ru replace the Zn atoms in the host lattice and maintain the crystal symmetry with slightly lattice distortion (Sanjeev Kumar et al 2013).

Pure and ruthenium (Ru) doped nano-crystalline zinc oxide (ZnO) powders were synthesized by using well-known citrate gel route (Navale et al 2009). Citric acid acts as a chelating agent and thus helps in the formation of nanoparticles. The detailed X-ray diffraction (XRD) studies using Hall equation reveal that in the nanoscale dimensions, incorporation of Ru modulates the lattice strain. It is interesting to note that on Ru doping, the compressive strain present in the undoped ZnO changes into tensile strain. They tested the response of these specimens individually for reducing gases like H\textsubscript{2}, liquefied petroleum gas (LPG), C\textsubscript{2}H\textsubscript{5}OH (ethanol), CO, acetone and oxidizing gases like NO\textsubscript{x} and Cl\textsubscript{2}. Undoped ZnO responses perceptibly to LPG while Ru doped sample highly senses ethanol vapors. This might be due to either change in composition on Ru doping or/and difference between basicity of LPG and C\textsubscript{2}H\textsubscript{5}OH vapors.

A series of Zn:Ru:Fe:LiNbO\textsubscript{3} crystals has been grown by Czochralski method (Fan et al 2011). Their infrared transmittance spectra and UV–vis absorption spectra were measured and discussed to investigate their
defect structure. The nonvolatile holographic recording of Zn:Ru:Fe:LiNbO$_3$ crystals was characterized by the two-photon fixed method. It is found that the recording time of Zn:Ru:Fe:LiNbO$_3$ crystals became shorter and nonvolatile diffraction efficiency increases with the increase of Zn doping concentration, especially doping with Zn approaches the so-called threshold. And the nonvolatility is best when the concentration of ZnO up to 5 mol%. The intrinsic and extrinsic defects were discussed to explain the nonvolatile holographic properties in the crystals.

Xu et al (2012) reported a series of LiNbO$_3$ crystals doped with various concentrations of ZnO and fixed concentrations of RuO$_2$ and Fe$_2$O$_3$ have been grown by the Czochralski method from the congruent melts. The type of charge carriers was determined by Kr$^+$ laser (476 nm) and He–Ne laser (633 nm). The results revealed that the holes were the dominant charge carriers at blue light irradiation. Dual-wavelength and two-color techniques were employed to investigate the nonvolatile holographic storage properties of Ru:Fe:LiNbO$_3$ and Zn doped Ru:Fe:LiNbO$_3$ crystals. The essential parameters of blue nonvolatile holographic storage in Zn:Ru:Fe:LiNbO$_3$ crystals were enhanced greatly with the increase of Zn concentration. This indicates that the damage resistant dopants Zn$^{2+}$ ions enhance the photorefractive properties at 476 nm wavelength instead of suppressing the photorefraction. The different mechanisms of blue photorefractive and nonvolatile holographic storage properties by dual wavelength recording in Zn:Ru:Fe:LiNbO$_3$ crystals were discussed.

The influence of the addition of a noble metal (Ru, Rh, Ir or Pd) on the catalytic performance of Co/ZnO was studied (Cai et al 2014) with respect to oxidative steam reforming of the bio-butanol raw mixture (butanol/acetone/ethanol = 6/3/1, mass ratio). Bimetallic catalysts, CoM/ZnO (M = Ru, Rh, Ir, Pd) had higher conversion values, decreased deactivation and
higher H₂ concentration in the outlet gas than monometallic Co/ZnO. However, significant differences were found in both raw mixture conversion and H₂ concentrations for the different CoM/ZnO, depending on M. CoRh/ZnO presented the best catalytic behaviour (65.1 mol% hydrogen in the outlet after 100 h of reaction at 500°C with 84% conversion). Characterization of catalysts post-reaction by Raman spectroscopy and TPO showed that less ordered and less abundant carbonaceous deposits were formed over bimetallic catalysts than over the monometallic one; CoRh/ZnO had the lowest amount of such coke.

Thin films of nanocrystalline Zn₁₋ₓRuₓO are deposited on ITO substrate by sol–gel (Sharma et al 2012). XRD and EDS analysis indicated dominant evolution of wurtzite ZnO with crystallite size in the range 26–43 nm. With no evidence of phase segregation, Ru insertion in the host lattice is probably indicated by distortion in lattice parameters and concomitant rise in microstrain and dislocation density. SEM images indicated homogenous and continuous growth of nanocrystallites. AFM images confirmed pillar like growth of crystallites along c-axis. Ru incorporation (1, 3, 5 and 7% at.) made film surface rougher, nevertheless roughness decreased with rise in Ru concentration. Ru incorporation at low concentrations significantly improved PEC response of films.

The selective hydrogenation of benzene to cyclohexene was studied over Ru–Cu/ZnO catalysts, which were prepared by deposition–precipitation, impregnation and co-precipitation methods. The influence of NaOH on the catalytic performance of catalysts prepared by these methods was discussed in detail. It was demonstrated that NaOH significantly enhanced the selectivity to cyclohexene over Ru–Cu/ZnO catalyst prepared by deposition–precipitation method. The properties of the catalysts were characterized by transmission electron spectroscopy (TEM), scanning electron microscopy
(SEM), X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and nitrogen adsorption–desorption techniques. The effects of ratio of Ru to Cu, concentration of NaOH and other reaction conditions including reaction temperature, hydrogen pressure, and reaction time on the reaction were studied. Using the preferable catalyst, the yield of cyclohexene reached a maximum of 49.4% with benzene conversion of 72.3% and selectivity to cyclohexene of 68.3% (Liu 2011).

The size effect of ZnO nanoparticles on catalytic activity of ZnO/MgO solids was studied in CO oxidation. Didenko et al (2011) have developed a simple method for preparing supported materials containing ZnO nanoparticles of a controllable size with the same chemical composition, structure, and shape. It is revealed that the turnover frequency of CO oxidation on ZnO nanoparticles of variable average radius (2.0–2.3 nm) shows bell-shaped dependence on ZnO nanoparticle size. A dependence of catalytic activity of ZnO nanoparticles on their electronic structure is found. This allows us to explain a maximum in the CO oxidation activity observed for ZnO nanoparticles with the size of about 2.2 nm within the framework of the quantum confinement effect.

The surface and catalytic properties of NiO and Co$_3$O$_4$ solids as being influenced by ZnO doping have been investigated by El-Shobaky & Ghozza (2004). The techniques employed were XRD, nitrogen adsorption at $-196^\circ$C, and catalytic oxidation of CO by O$_2$ at 150–250 $^\circ$C. The dopant concentration was varied between 2 and 8 wt.% ZnO, and the solids were subjected to heat treatment at 300, 500, and 700$^\circ$C. The results obtained revealed that ZnO treatment of NiO and Co$_3$O$_4$ followed by calcination at 300$^\circ$C resulted in a progressive decrease in their specific surface areas. This treatment brought about an increase in the crystallite size of NiO and Co$_3$O$_4$ phases. ZnO doping of Co$_3$O$_4$ conducted at 500 and 700$^\circ$C affected a
progressive increase in its BET surface areas. The catalytic activities towards carbon monoxide oxidation by oxygen expressed as reaction rate constant per unit surface area, catalytic activity, for NiO and Co$_3$O$_4$ precalcined at 300°C were found to increase by ZnO doping. On other hand, doping Co$_3$O$_4$ carried out at 500 and 700°C led to a measurable decrease in its specific catalytic activity. The doping process of the investigated solids did not modify the mechanism of the catalyzed reaction but changed the concentration of the catalytically active sites without changing their energetic nature.

A series of ZnO supported Ru–Ir bimetal catalysts were prepared and tested for vapor-phase selective hydrogenation of crotonaldehyde (Li et al 2013). The addition of Ir could effectively promote the catalytic performance, especially the catalyst stability. A Ru$_{0.5}$Ir/ZnO catalyst showed the highest activity (a conversion of 63.3%) and selectivity to crotyl alcohol (94.4%) after 30 h reaction. The enhanced stability was attributed to the modified electronic property of Ru by the formation of RuIr alloy as the X-ray photoelectron spectroscopy results showed charge transfer from Ru to Ir, as well as the weakened surface acidity in the Ru–Ir/ZnO catalyst as evidenced by NH$_3$ temperature-programmed desorption technique. Besides, the deactivation of the catalysts was due to the strong chemisorption of CO on the metal surface via decarbonylation reaction and deposition of organic compounds on the catalyst surface, which was characterized by CO poisoning experiment, CO temperature-programmed desorption and temperature-programmed oxidation methods.

Recent studies indicated the role of reactive oxygen species (ROS) toward antibacterial activity. Dutta et al (2012) reported ROS mediated membrane lipid oxidation of *Escherichia coli* treated with ZnO nanoparticles (NPs) as supported by detection and spectrophotometric measurement of malondialdehyde (MDA) by thiobarbituric acid-reactive species (TBARS)
assay. The antibacterial effects of ZnO NPs were studied by measuring the growth curve of *E. coli*, which showed concentration dependent bacteriostatic and bacteriocidal effects of ZnO NPs. The antibacterial effects were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Further, antibacterial effect of ZnO NPs was found to decrease by introducing histidine to the culture medium treated with ZnO NPs. The ROS scavenging action of histidine was confirmed by treating histidine to the batch of *Escherichia coli* + ZnO NPs at the end of the lag phase of the growth curve (Set-I) and during inoculation (Set-II). A moderate bacteriostatic effect (lag in the *E. coli* growth) was observed in Set-II batch while Set-I showed no bacteriostatic effect. From these evidences we confirmed that the antibacterial effect of bare as well as TG capped ZnO NPs were due to membrane lipid peroxidation caused by the ROS generated during ZnO NPs interaction in culture medium.

Zinc oxide nanoparticles are known to be one of the multifunctional inorganic nanoparticles with effective antibacterial activity. Gunalan et al (2012) attempted to determine the antimicrobial efficacy of green and chemical synthesized ZnO nanoparticle against various bacterial and fungal pathogens. Various microbiological tests were performed using varying concentrations of green and chemical ZnO NPs with sizes 40 and 25 nm respectively. Results prove that green ZnO nanoparticles show more enhanced biocidal activity against various pathogens when compared to chemical ZnO nanoparticles. Also effectiveness of nanoparticles increases with increasing particle dose, treatment time and synthesis method. In addition, the current study has clearly demonstrated that the particle size variation and surface area to volume ratio of green ZnO nanoparticle are responsible for significant higher antimicrobial activity.
ZnO nanoparticles have been synthesized (Sharma et al 2010) with and without the use of surfactants under different reaction conditions. The size of the ZnO nanoparticles varied in diameter (2 nm–28 nm) according to the reaction conditions employed. Promising particle size dependent antibacterial and antifungal activities of the ZnO nanoparticles have been observed. Transmission electron microscopy (TEM), X-ray diffraction (XRD) and Infrared spectroscopy (FTIR) techniques were used to characterize the particle size and morphology.

Investigations on treatment of ZnO nanoparticles on *Staphylococcus aureus* MTCC 737 strain was essentially made by using standard biochemical method (Roy et al 2013). The anti-microbial assay against *S. aureus*, and time kill assay revealed the anti-bacterial activity of ZnO nanoparticles. We have substantiated this property of ZnO nanoparticles and light depolarization property by using light scattering tool. Light scattering measurements were carried out for ZnO, *S. aureus*, and ZnO treated *S. aureus* as a function of scattering angle at 543.5 and 632.8 nm wavelengths. This was done in order to find the scattering profile of the consequent product after the action of ZnO nanoparticles on bacteria by means of light scattering tool. *S. aureus* treated with ZnO nanoparticles showed closer agreement of the scattering profiles at both the wavelengths, however, the scattering profiles of ZnO nanoparticles and untreated *S. aureus* significantly varied for the two different laser wavelengths. It was also observed that there was higher intensity of scattering from all *S. aureus* treated with ZnO particles compared to the untreated ones. In our work, we have studied ZnO nanoparticles and the possibility of observing its anti-bacterial activity by using light scattering tool.

Metal oxide nanoparticles represent a new class of important materials that are increasingly being developed (Stanković et al 2013) for use...
in research and health-related applications. Although the antibacterial activity and efficiency of bulk zinc oxide were investigated *in vitro*, the knowledge about the antibacterial activity of ZnO nanoparticles remains deficient. In their study, they have synthesized ZnO particles of different sizes and morphologies with the assistance of different types of surface stabilizing agents – polyvinyl pyrrolidone (PVP), polyvinyl alcohol (PVA) and poly (α,γ, l-glutamic acid) (PGA) – through a low-temperature hydrothermal procedure. The characterization of the prepared powders was performed using X-ray diffraction (XRD) method and field emission scanning electron microscopy (FESEM), as well as Malvern's Mastersizer instrument for particle size distribution. The specific surface area (SSA) of the ZnO powders was measured by standard Brunauer–Emmett–Teller (BET) technique.

The antibacterial behaviour of the synthesized ZnO particles was tested against gram-negative and gram-positive bacterial cultures, namely *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*), respectively. They compared the results of the antibacterial properties of the synthesized ZnO samples with those of the commercial ZnO powder. According to the obtained results, the highest microbial cell reduction rate was recorded for the synthesized ZnO powder consisting of nanospherical particles. In all of the examined samples, ZnO particles demonstrated a significant bacteriostatic activity.

A CdS–CdO–ZnO mixture annealed at different temperatures and loaded with Ru or Pt cocatalysts has been investigated (Navarro et al 2008) in the production of hydrogen from aqueous solutions containing SO$_3^{2-}$ + S$^2-$ as sacrificial reagents under visible light. The physicochemical characterization of the CdS–CdO–ZnO catalyst revealed significant changes in the crystalline structure and visible light absorption capacity as a result of thermal treatments. Catalytic activity was found to be strongly dependent on
physicochemical changes associated with thermal annealing. Hydrogen evolution over the CdS–CdO–ZnO catalyst was enhanced in the sample annealed at 773 K by the better contact between the CdS and CdO–ZnO phases, which improved physical charge separation. CdS–CdO–ZnO catalyst activity was significantly improved by the addition of Pt or Ru cocatalysts. Among the noble metals studied, activity promotion was higher for the sample loaded with Ru. The enhancement of activity associated with Ru loading is linked to a good interaction between Ru oxide particles and CdS, which reduces the possibility of electron–hole recombination, thus resulting in more efficient water splitting.

Ru doped anatase supported on silica (Sasirekha et al 2006) was prepared by solid-state dispersion method and examined for the photocatalytic reduction of carbon dioxide in aqueous medium at ambient conditions. To assist in interpreting the photocatalytic behaviour of Ru-TiO$_2$/SiO$_2$, reference systems consisting of Ru doped TiO$_2$ and TiO$_2$ supported on SiO$_2$ were also analyzed and the conditions were optimized. Ru/TiO$_2$ photocatalysts with metal loadings of 0.1, 0.3, 0.5 and 1.0 wt% were prepared by impregnation method and a series of TiO$_2$/SiO$_2$ catalysts with low TiO$_2$ (1, 3, 5 and 10 wt%) contents were prepared by solid-state dispersion method. The photocatalysts were characterized using X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscopy (TEM), UV–vis DRS, FT-IR and Raman spectroscopy. The results showed that TiO$_2$ particles with Ru ions have higher photocatalytic activity than undoped TiO$_2$ and the optimum Ru loading was found to be 0.5 wt%. Nevertheless, the yield increased notably when TiO$_2$ was supported on SiO$_2$. This strong enhancement suggests that in 10 wt% TiO$_2$/SiO$_2$ the efficiency of charge separation is strongly influenced through the presence of Ti-O-Si bridging bonds. On the contrary, Ru-TiO$_2$/SiO$_2$ has no significant improvement in activity over TiO$_2$/SiO$_2$ except that it shows nearly quadruple times higher
activity for the formation of methanol than Ru/TiO$_2$. The difference in the photocatalytic activity is related to its physico-chemical properties.

The energy levels and local structures of Eu$^{3+}$ incorporated in the lattice and surface sites of ZnO nanocrystals were investigated (Liu et al 2008) based on the high-resolution fluorescence spectra at 10 K. Radiative emissions from 5D1 were first observed for Eu$^{3+}$ at the lattice site of ZnO. It is shown that the site symmetry of Eu$^{3+}$ at the lattice site descends from C$_{3v}$ to C$_s$ or C$_1$, whereas Eu$^{3+}$ ions at the surface occupy more disordered sites of the lowest symmetry C$_1$. The luminescence decay of 5D$_0$ at the lattice site, showing a rise time and longer lifetime, behaves distinctly from that of the surface sites. Because of a small filling factor (52%) of nanoparticles, the 5D$_0$ lifetime of Eu$^{3+}$ is significantly affected by the surrounding medium, which can be well interpreted with the virtual-cavity model. The Judd–Ofelt intensity parameters of Eu$^{3+}$ in ZnO nanocrystals were determined, with Ω2, 4, 6 values of (9.59, 8.11, <0.25) and (21.51, 2.30, <0.25) in units of 10$^{-20}$ cm$^2$ for Eu$^{3+}$ at the surface and lattice sites, respectively. A defect-mediated energy transfer from the ZnO band gap to Eu$^{3+}$ was observed. The growth mechanism for the incorporation of Eu$^{3+}$ into the ZnO lattice was also revealed.

Panigrahy et al (2010) reported the optical and magnetic properties of Mn- and Co-doped ZnO nanorods fabricated via a simple one-step aqueous-based chemical method. Interestingly, SEM results reveal a uniform size distribution of the nanorods throughout the substrate. The UV emission band of doped ZnO nanorods reveals a red shift from 382 to 384.5 nm, indicating a band-edge bending due to the dopants. The defect-related band centered at 600 nm is suppressed (ID/IUV = 1− 0.35) considerably in doped nanorods, revealing the quenching of surface defects present in the nanostructures. XRD, XPS, Raman spectra, and EDS data demonstrate a
successful incorporation of TM dopants in ZnO nanorods. Localized SAED patterns taken using nanoprobe size reveals that the nanorods are single crystals, grown along the c-axis [0002] direction. A systematic evaluation of the enhancement in ferromagnetism ($M = 0.15 \times 10^{-2}$ to $1.3 \times 10^{-2}$ emu/g) is found in modified doped ZnO nanorods.

Free-standing ZnO nanocrystals simultaneously doped with Fe and Cu with varying Fe/Cu compositions have been synthesized using colloidal methods (Viswanatha et al 2012) with a mean size of $\approx$7.7 nm. Interestingly, while the Cu-doped ZnO nanocrystal remains diamagnetic and Fe-doped samples show antiferromagnetic interactions between Fe sites without any magnetic ordering down to the lowest temperature investigated, samples doped simultaneously with Fe and Cu show a qualitative departure in exhibiting ferromagnetic interactions, with suggestions of ferromagnetic order at low temperature. XAS measurements establish the presence of Fe$^{2+}$ and Fe$^{3+}$ ions, with the concentration of the trivalent species increasing in the presence of Cu doping, providing direct evidence of the Fe$^{2+}$ + Cu$^{2+}$ $\leftrightarrow$ Fe$^{3+}$ + Cu$^{+}$ redox couple being correlated with the ferromagnetic property. Using DFT, the unexpected ferromagnetic nature of these systems is explained in terms of a double exchange between Fe atoms, mediated by the Cu atom, in agreement with experimental observations.

Shin et al (2011) reported the design growth and characterization of quaternary Mg and Ga codoped ZnO (MGZO) thin films with transparent conductive characteristics deposited on glass substrates by RF magnetron sputtering. The effects of the Ga concentration (from 0 to 2 at %) on the structural, chemical, morphological, optical and electrical properties of MGZO thin films were investigated. X-ray diffraction study showed that all the MGZO thin films were grown as a polycrystalline hexagonal wurtzite phase with a c-axis preferred orientation and random in-plane orientation. The
2θ value of the (0002) peak of MGZO thin films decreased with increasing Ga concentration. X-ray photoelectron spectroscopy confirmed the Mg and Ga binding energy peaks from the MGZO thin films. The MGZO thin films had a smoother surface morphology. The optical study showed that the band gap energy of MGZO thin films systematically increased from 3.25 to 3.75 eV with increase Ga concentration. The electrical resistivity of the MGZO thin films was improved from $9.5 \times 10^{-2}$ to $6.89 \times 10^{-4}$ Ω cm with increasing Ga concentration.

Large channel length field effect transistors (FETs) based on Pt contacts to ferromagnetic Bi-Mn-codoped ZnO bicrystal nanobelts have been fabricated using dielectrophoresis and a focused ion beam (Xu et al 2007). Electrical transport studies show n-type behaviour of the ferromagnetic ZnO nanobelts. The current–voltage characteristics of the FETs exhibit Schottky barrier behaviour. The contact resistances and the Pt diffusion are responsible for the reduction of the conductance and the threshold shift. The reduction of the mobility can be attributed to the enhanced interface scattering at Pt electrodes/nanobelt contact regions after Pt deposition. The devices are also found to be strongly dependent on the channel length.

Infrared-to-visible upconversion emission intensities are investigated in Li$^+$ and Er$^{3+}$ codoped ZnO nanocrystals (Bai et al 2008). Li$^+$ ions doped in ZnO/Er$^{3+}$ nanocrystals can greatly enhance the upconversion emission intensity of Er$^{3+}$ ions. The extended X-ray absorption fine structure spectroscopy data show that both the Er–O bond length and coordination number of the Er–Er bond have been altered by introducing Li$^+$ ions in the ZnO/Er$^{3+}$ nanocrystals. The variation of Er–O bond length leads to the change in the local asymmetry around Er$^{3+}$ ions. Meanwhile, the greater coordination number of the Er–Er bond causes stronger interaction between neighboring Er$^{3+}$ ions and, hence, strengthens the reaction Er$^{3+}$ ($^4F_{7/2}$)
$\text{Er}^3+(4I_{11/2}) \rightarrow 2\text{Er}^3+(4F_{9/2})$. In this process, the $4F_{9/2}$ state is a metastable state that could be excited to the $2H_{9/2}$ state by absorbing one photon at high excitation power. Li$^+$ ions also can reduce the OH groups in specimen, which is the other reason for enhancing the upconversion emission intensities.

A series of supported Ru catalysts with achiral modifier triphenylphosphine (TPP) and chiral modifier (1R,2R)-1,2-diphenylethlenediamine [(1R,2R)-DPEN] were employed (Ye et al 2010) for the asymmetric hydrogenation of aromatic ketones. The textural and structural properties of the catalysts were characterized by X-ray diffraction, X-ray photoelectron spectroscopy, N$_2$ physisorption, transmission electron microscopy, CO$_2$ and NH$_3$ temperature-programmed desorptions, inductively coupled plasma atomic emission spectrometry, and ultraviolet–visible spectroscopy. Studies revealed that the enantiomeric excess (ee) followed this order according to the oxide supports used: MgO $> \gamma$-Al$_2$O$_3$ $> \text{CeO}_2$ $> \text{ZnO} > \text{SiO}_2$, which was correlated with their surface basicity. Moreover, the highest ee value and intrinsic activity for the asymmetric hydrogenation of acetophenone were attained over the catalyst with a mean Ru nanoparticle diameter of 4.4 nm, while those for the asymmetric hydrogenation of 1-acetonaphthone were obtained over a catalyst with 6.2 nm nanoparticle diameter. The catalyst system consisting of Ru/MgO, TPP, and (1R, 2R)-DPEN did not show a significant decrease in ee value after several recycles. The results indicate that there is a size matching effect between the Ru particles and the substrates, besides the acid/base influence of the oxide supports on the reaction (Ye et al 2010).