CHAPTER 1

Introduction to Nanostructured Semiconducting Oxides
1.1. Era of Nanomaterials

Beginning of 21st century has witnessed a tremendous upsurge of scientific activities in the field of nanoscience and nanotechnology. Scientists and technocrats are convinced that nanotechnology based on nanoscience is the technology of 21st century. Nanoscale science and technology presently encompasses almost all disciplines of science and engineering. The word ‘Nano’ originates from the Greek ‘nanos’ (or Latin ‘nanus’) means ‘dwarf’. Nanoscience is the study of atoms, molecules, and objects whose size is on the nanometer scale (1-50 nm). The diameter of the molecule is of the order of a nanometer. for comparison, a human hair is about 100,000 nanometers thick. However, it may be noted that nanomaterials are not really new. Michael Faraday synthesized stable gold colloidal particles of nanosize in 1857. His metallic gold particles are still in British museum in U.K. showing beautiful magenta-red color and not the lustrous golden yellow color.

Necessity being the mother of invention, by inventing appropriate materials and understanding the naturally available aviation system adopted from birds in the sky, man is now able to touch the sky. Hence for human being sky is not the limit and there is plenty of room at the bottom as said by Feynman in his famous talk [1]. Man has always challenged his knowledge and come up with new understandings. Mankind has been able to overcome all sort of limitations. He developed the communications and navigation systems, which take him or his instruments to distant places. He may not physically go everywhere but he has tried ingeniously to get some knowledge of our universe through the sophisticated gadgets developed by him. In an attempt of making lightweight and smaller and smaller electronic devices, scientists have reduced the size of materials to such an extent that it has reached nanometric dimensions.

Semiconductors and magnetic materials are the basis of most of the today’s technological devices. While semiconductors are used to develop microprocessors capable of processing information at high speed, magnetic materials are used for information storage due to their ability to maintain the magnetization in the fixed direction without power supply. Moore's Law describes an important trend in the history of computer hardware: that the number of transistors that can be inexpensively placed on an integrated
circuit is increasing exponentially, doubling approximately every two years. The observation was first made by Intel co-founder Gordon E. Moore in a 1965. Almost every measure of the capabilities of digital electronic devices is linked to Moore's Law: processing speed, memory capacity, even the resolution of digital cameras. All of these are improving at exponential rates as well. This has dramatically increased the usefulness of digital electronics in nearly every segment of the world economy. Moore's Law describes this driving force of technological and social change in the late 20th and early 21st centuries.

![Figure 1.1. Moore’s law](image)

However following this law the devices have reached now a lowest size of ~100 nm and the deviation from the Moore’s law has begun. It is now difficult to maintain the linearity what Moore had predicted. At nanolevel besides the surface effects, materials also have properties, which are size dependent. Therefore, nanodevices using active or passive nano components cannot be expected to behave like those of large (micrometers) sizes. Interestingly, this size dependent nature can be used to obtain some novel devices, which were not imagined earlier. For example single electron transistor (SET) is a completely new device due to unique properties of quantum dots. The magnetic spin valve, magnetic
tunnel junction (MTJ) using nanomaterials are some other high-speed devices, which are products of nanotechnology [2, 3].

Availability of new instruments, which can practically show the atom in direct space and is able to touch and move at nanoscale, has helped in fast growth of this exciting field of research. The continuous advances in the fabrication and characterization of structures at nanometer level are responsible for this fast growth. Invention of scanning tunneling microscopy (STM) in early 1980’s made it possible to practically see the atoms. Development of Atomic Force Microscopy (AFM) a few years later extended the capabilities and types of materials, which can be investigated. Since late 1980’s multiple similar techniques have evolved using Scanning Probe Microscopy type of instruments to control the properties at nanometer scale and study different properties. The other techniques e.g., electron microscopy, electron beam lithography, molecular beam epitaxy, focused ion beam have continue to evolve in order to match the requirements of development in the area of nanotechnology [4].

1.2. The Change of Properties in the Reduced Dimensions

Properties observed on a macroscopic scale generally change at nanometer scale when the effect of quantum confinement dominates the properties. As for the definition of nanostructures, a widely accepted one is that “nanostructure” represents a system or object with at least one dimension on the order of one hundred nanometers or less. Typical oxide nanostructures are of three types of dimensional categories: 0-dimension (quantum dots), 1-dimension (nanobelts and wires) and 2-dimension (tetrapods).

Now, in the reduced dimensions, the main reason for the evolution of novel properties could be understood by considering the electronic energy levels. In the reduced dimensions the electron energy levels cannot exist in any form. A quantum dot is by definition a system where the motion of electron is confined in all three spatial dimensions. Consequently, in a quantum dot crystal, the band gap is size dependent and can be altered to produce a range of energies between the VB and CB (also known as band gap engineering). Quantum mechanics dictates that the band gap of structures in reduced dimensions will always be larger in magnitude. More specifically, confining electrons to
small structures causes the continuous bulk bands to split-up into discrete levels for example quantum well states in a slab. Unlike quantum wells and quantum wires, quantum dots have only a finite number of atoms. The overall density of states in different system is depicted in Figure 1.2.

![Graphs showing density of states for different dimensions](image)

**Figure 1.2. Density of state for charge carriers for different dimensions [5]**

Two fundamental factors, both related to the size of the individual nanostructures, distinguish their behavior from the corresponding bulk material [6]. The first is the high dispersity (large surface to volume ratio) associated with the particles, with both the physical and chemical properties of the semiconductor being particularly sensitive to the surface structure. The second factor is the actual size of the particle, which can determine the electronic and physical properties of the material.

The mechanical, thermal, optical, magnetic and other properties of any type of the material are found to change when at least one of its dimensions is reduced below 50 nm. Nanoparticles are of great scientific interest as they effectively bridge between bulk materials and atomic or molecular structures. A bulk material should have constant
physical properties regardless of its size, but at the nano-scale this is often not the case. Size-dependent properties are observed such as quantum confinement in semiconductor particles, surface plasmon resonance in some metal particles and super-paramagnetism in magnetic materials [7].

Nanoparticles exhibit a number of special properties relative to bulk material. For example, the bending of bulk copper (wire, ribbon, etc.) occurs with movement of copper atoms/clusters at about the 50 nm scale. Copper nanoparticles smaller than 50 nm are considered super hard materials that do not exhibit the same malleability and ductility as bulk copper. The change in properties is not always desirable. Ferromagnetic materials smaller than 10 nm can switch their magnetisation direction using room temperature thermal energy, and therefore are not suitable for memory storage. Nanoparticles often have unexpected visible properties because they are small enough to confine their electrons and produce quantum effects. For example gold nanoparticles appear deep red to black in solution.

Nanoparticles have a very high surface area to volume ratio. This provides a tremendous driving force for diffusion, especially at elevated temperatures. Sintering can take place at lower temperatures, over shorter time scales than for larger particles. This theoretically does not affect the density of the final product though tendency of nanoparticles to agglomerate complicates matters.

A semiconductor like CdS, which is normally reddish in color, on bringing down its particle size to ~ 10 nm it still remains red however below about 6 nm a dramatic change in color occurs. At ~ 4 nm its color becomes orange while at 3 nm it turns yellow. Not only the physical appearance but also their other bulk property like melting point is reduced with reduced dimensions. Band gap increases with decrease in particle size. In case of GaAs energy gap \( E_g \) is almost double when its particles size decreases from 20 nm \( (E_g = 1.42 \text{ eV}) \) to 2 nm \( (E_g = 2.78 \text{ eV}) \) [8, 9].

Nano TiO\(_2\) is used for developing anti-UV, anti-bacterial and self-cleaning paints [10]. By learning about an individual molecule’s properties, one can put suitable molecules together as per the requirements to produce new materials with amazing characteristics. Most of these changes can be attributed to the following distinct origins:
(a) Quantum size effects: The electronic energy spectrum in small particles is quantised in to discrete levels with a level spacing (near the Fermi energy $E_F$) $\Delta = E_F / N^{2/3}$, where $N$ is the number of atoms. Quantum size effects appear when the particles are small enough for $\Delta$ to be comparable to characteristic energy parameters (thermal, electrical, magnetic, and optical) of the solid.

(b) Surface and interface effects: With decrease in the particle size, increased number of atoms lie near or on the surface and interface regions (e.g. for grain size of 100, 10 and 5 nm, the surface to volume ratio corresponds to about 1-3%, 15-30% and 30-60% respectively), making the effect of surface and interfacial electronic structure on material properties more and more important than the bulk.

As the size of nanostructures approaches the Bohr radius of exciton, both the band gap and photoluminescence are greatly affected by the quantum confinement effect (QCE) [11, 12]. In nanostructures, the carrier-state density is concentrated in discrete energy levels, which enables the enhancement of exciton oscillator strength and light emitting efficiency [13, 14].

1.3. Physical and Chemical Properties 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 $sp^3$ covalent bonding, but these materials also have a substantial ionic character. ZnO is II-VI compound semiconductor whose ionicity resides at the borderline between covalent and ionic semiconductor. It is mainly produced from the mineral called zincite. The crystal structures shared by ZnO are rocksalt ($B1$), zinc blende ($B3$) and wurtzite ($B4$) as schematically shown in Figure 1.3. At ambient conditions, the thermodynamically stable phase is wurtzite. 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.
The wurtzite structure has a hexagonal unit cell with two lattice parameters, a and c, in the ratio of \( \frac{c}{a} = \left( \frac{8}{3} \right)^{1/2} = 1.633 \) and belongs to the space group of \( \text{C}^4_{6v} \) or \( \text{P}6_{3}\overline{mc} \). Its physical and chemical properties are listed below.

**Table 1.1**

Properties of ZnO

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Properties</th>
<th>ZnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Molecular mass</td>
<td>81.389</td>
</tr>
<tr>
<td>2.</td>
<td>Specific gravity at 300 K (g/cm(^3))</td>
<td>5.642</td>
</tr>
<tr>
<td>3.</td>
<td>Point group</td>
<td>6mm (Wurtzite)</td>
</tr>
<tr>
<td>4.</td>
<td>Lattice constants (nm) at 300 K</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( a = 0.32495 )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( c = 0.52069 )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \frac{c}{a} = 1.602 )</td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>Melting point (°C)</td>
<td>1975</td>
</tr>
<tr>
<td>6.</td>
<td>Linear Expansion Coefficient (°C(^{-1}))</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( a_0 = 6.5 \times 10^{-6} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( c_0 = 3.0 \times 10^{-6} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Wurtzite structure</td>
<td></td>
</tr>
<tr>
<td>7.</td>
<td>Effective electron mass</td>
<td>0.28 ( m_0 )</td>
</tr>
<tr>
<td>8.</td>
<td>Effective hole mass</td>
<td>1.8 ( m_0 )</td>
</tr>
<tr>
<td>9.</td>
<td>Bandgap energy at 300 K, ( E_g ) (eV)</td>
<td>3.37, direct</td>
</tr>
<tr>
<td>10.</td>
<td>Exciton binding energy (meV)</td>
<td>60</td>
</tr>
<tr>
<td>11.</td>
<td>Specific heat (cal/gm)</td>
<td>0.125</td>
</tr>
<tr>
<td>12.</td>
<td>Thermal conductivity (W/cm(^2)°C)</td>
<td>0.6</td>
</tr>
<tr>
<td>13.</td>
<td>Dielectric constant ( \varepsilon(\infty) )</td>
<td>8.75</td>
</tr>
<tr>
<td>14.</td>
<td>Dielectric constant ( \varepsilon(x) )</td>
<td>3.75</td>
</tr>
</tbody>
</table>
There has been a great deal of interest in zinc oxide (ZnO) semiconductor materials lately, as seen from a surge of a relevant number of publications. The interest in ZnO is fueled and fanned by its prospects in optoelectronics applications owing to its direct wide band gap ($E_g \approx 3.3$ eV at 300 K). Some optoelectronic applications of ZnO overlap with that of GaN, another wide-gap semiconductor ($E_g \approx 3.4$ eV at 300 K) that is widely used for production of green, blue-ultraviolet, and white light-emitting devices (LED). However, ZnO has some advantages over GaN among which are availability of fairly high quality ZnO bulk crystals and a large exciton binding energy (60 meV). ZnO also has much simpler crystal-growth technology, resulting in a potentially lower cost for ZnO-based devices [15].

As a direct wide-band-gap material, ZnO is attracting a lot of attention for a variety of electronic and optoelectronic applications. Advantages associated with a large band gap include higher breakdown voltages, ability to sustain large electric fields, lower noise generation, and high temperature and high-power operation. Among the tetrahedrally bonded semiconductors, ZnO has the highest piezoelectric tensor or at least one comparable to that of GaN and AlN. This property makes it a technologically important material for many applications, which require a large electromechanical coupling [16].

1.4. Band Structure of ZnO

The wurtzite structure is the natural form of ZnO, shown in Figure 1.3 which has a hexagonal unit cell with two lattice parameters $a$, $c$ equal to 0.3249 and 0.52049 nm respectively belonging to space group $P6_3\overline{m}c$. Wurtzite structured ZnO is composed of two alternating which are tetrahedrally bonded to each other. Inevitably it is of a non-central symmetry, resulting in the existence of spontaneous polarization along its $c$ axis (Figure 1.4).
The band structure of ZnO (wurtzite) structure (Figure 1.5) has been defined by Rossler, using the Korringa-Kohn-Rostoker (KKR) method [15]. This is basically a variation iteration method to solve the Schrodinger equation in a periodic lattice yielding a compact scheme if the potential is spherically symmetric with in the inscribed spheres of the atomic polyhedra and constant in the space between them. The band structure of the lattice is calculated by (1) geometrical structure constants characteristic of the type of lattice and (2) the logarithmic derivatives, at the surface of the inscribed sphere of the s, p and d functions corresponding to \( V(r) \). The band structure of ZnO thus calculated exhibits a broad free-electron-like lowest CB, relatively wide (1.6 eV) Zn 3d levels lying closely below the upper VB states and p-antibonding CB states 17 eV above the valence band maxima. Experimentally determined maxima in the VB and CB are sketched in the Figure 1.5. The below band structure discussed for bulk ZnO can have very interesting changes due to size quantization. Recently, Wang and Dai et al. determined the loss function \( \text{Im}(-1/e\gamma) \) of the ZnO nanowires with selected diameters (~20, ~40, and ~60 nm) by removing the plural scattering from the corresponding electron energy-loss spectra (EELS) using a conventional Fourier-log deconvolution method [17,18].
Figure 1.5. KKR band structure for wurtzite ZnO [15, 19]

Several size-related features such as: surface-plasmon oscillation at about 11.5 eV, whose oscillator strength increases as the nanowire diameter decreases, a broadening of the bulk-plasmon peak with decrease in wire diameter, and a splitting of the O 2s state together with the red shift of the bulk plasmon in small-diameter ZnO nanowires with circular cross sections were identified. These were attributed to the increased scattering of the oscillating electrons by the wire surface when the surface to volume ratio increases and decrease in the relaxation time of the oscillating electrons leading to broadening of the bulk-plasmon peak. Such features have also been reported in nanocombs, nanorings, nanohelixes, nanosprings, nanobows, nanobelts, nanowires and nanocages of ZnO grown under different growth conditions using a solid-vapor phase thermal sublimation technique [20,21].

1.5. Semiconductor Nanoparticles

All the materials may be metals, semiconductors or insulators have size dependent physico-chemical properties below a certain critical size. This critical size is ~ 100 nm for most of the materials. In semiconductor this size is nothing but the size of the exciton. Understanding the concept of exciton and estimating its size for different semiconducting materials is the first step towards understanding the semiconductor nanoparticles.
In semiconductor or insulator, valence and conduction bands are separated by some finite energy gap characteristic of the material. When an electron from the valence band gets sufficient energy to overcome the energy gap, may be by thermal excitation or absorption of photon, and goes to conduction band, a hole is left behind. The bound electron hole pair so formed is a quasi particle called exciton. An exciton can move in the crystal whose center of mass motion is quantized. Different kinds of excitons are identified in variety of materials. When the electron-hole pair is tightly bound with the distance between them comparable to the lattice constant then it is called as a Frenkel exciton. At the other extreme, one may have an exciton with electron-hole separation much larger compared to the lattice constant. Such weakly bound electron-hole pair is called Mott-Wannier exciton.

The energy of such an exciton is slightly less than the energy gap ($E_g$) between valence and conduction band. The Hamiltonian for Mott-Wannier exciton is given as:

$$H = \frac{P_e^2}{2m_e} + \frac{P_h^2}{2m_h} - \frac{e^2}{\varepsilon |r_e - r_h|} \quad \text{..... Eqn. (1.1)}$$

Where $m_h$ and $m_e$ are the effective electron and hole mass respectively, $P_e$ and $P_h$ are the electron and hole momentum respectively and $\varepsilon$ is the dielectric constant of the semiconductor material. First two terms on the right hand side of equation (1) are the kinetic energies of electrons and holes respectively and the third is the coulomb energy of electron–hole attraction.

The Bohr radius of such an exciton is given as:

$$r_B = \frac{\hbar^2 \varepsilon}{e^2} \left[ \frac{1}{m_e} + \frac{1}{m_h} \right] \quad \text{..... Eqn. (1.2)}$$

It may be noted that the values of $r_B$ are of few orders on nanometers. Using equation (1) and assuming certain form of wave function and potential, it has been shown that excitonic energy can be expressed as:

$$\Delta E = \frac{\hbar^2 \pi^2}{2R^2} \left[ \frac{1}{m_e} + \frac{1}{m_h} \right] - 1.8 \frac{e^2}{\varepsilon R} + P.E \quad \text{..... Eqn. (1.3)}$$
Here $R$ is the radius of the cluster where an exciton would be created. The first term on right-hand side of the equation is localization energy of the electron and hole whereas second term is due to Coulomb energy between electrons and the hole. The third term is due to polarization of the cluster but is usually very small and size independent, hence neglected. The first two terms have sign opposite for each value of $R$. However, as the particle size decreases, the first term starts dominating and $\Delta E$ starts increasing rapidly. This would effectively mean that the energy gap in a semiconductor, which is characteristic of the material, would increase with the decreasing particle size or in other words one would obtain a size dependent energy gap [22, 23].

1.6. Methods for Synthesis of Nanostructured Materials

There are large numbers of techniques available for the synthesis of nanomaterials in various form like. colloids, clusters, powders, tubes, rods, wires, thin films, etc. The approach towards making of nanomaterials can be a ‘top-down’ or a ‘bottom-up’, mainly based on the breaking of large particles in to smaller ones or making the nanomaterials from the molecules. Nanotechnology being an interdisciplinary subject, therefore various physical, chemical, biological and hybrid techniques can be used to synthesize nanomaterials [24-28].

1.6.1. High-Energy Ball Milling:

It is one of the simplest and oldest techniques of making nanoparticles by mechanical milling of particles. This technique is widely adopted in most of the ceramic industries. Usually one or more containers are used at a time to make fine particles, as shown in Figure 1.6. Hardened steel or zirconia ($\text{ZrO}_2$) balls are put in containers along with powder of material of interest. The container closed with tight lids is rotated at high speeds for several hours at room temperature. Usually 2:1 mass ratio of balls to material is recommended for good results. In some cases inert liquids like propanol or ethanol are used for more homogenization of the contents.
Larger balls used for milling produce smaller grain size. The process may add some impurities from balls. The container is rotated at high speed along its own axis. Additionally it may rotate around some central axis and therefore it can be called as ‘planetary mill’. When the containers are rotating around the central axis, the material is forced to the walls and is pressed against the walls. While due to motion of the containers around their own axis, the material is forced to other region of the container. It is possible to grind the material to fine powder whose size can be quite uniform with the size between few nm to tens of microns [29]. This technique has been successfully used for the efficient production of ZnO nanowires by Glushenkov et al. [30].

The major limitation of this conventional technique is that it consumes more time. In addition to that contamination and strain due to defect formation is a major concern.

1.6.2. Chemical Vapor Deposition (CVD)

This method utilizes reactant in their vapor phase and is conventionally used to obtain coatings of a variety of materials viz. inorganic or organic materials. There are various forms of CVD like Metallo Organic CVD (MOCVD), Atomic Layer Epitaxy (APE), Vapor phase epitaxy (VPE), Plasma enhanced CVD (PECVD) etc. They differ in source gas, partial pressure, geometrical layout, temperature used etc. The CVD in general can be considered as a transport of reactant vapor or reactant gas towards the hot substrate where
the reactant decomposes into different products. The product then diffuses on the surface, undergoes some reaction at appropriate site, nucleate and grows in the form of desired film.

![Figure 1.7. Basic concept of CVD](image)

Vapors of desired materials are often transported through the mass flow controller into the reaction chamber using some carrier gas. In some cases the reactions may occur through aerosol formation in gas phase. There are various processes such as reduction of gas, chemical reaction between different source gases, oxidation or some disproportionate reaction by which the CVD can proceed. However it is preferable that the reaction occurs at the substrate rather than in the gas phase. Usually CVD is performed at higher temperatures using inert heating element as a catalysts or sometimes it is also performed at lower temperatures by using the highly reactive precursors. A typical concept of CVD is shown in the diagram above.

Cefe López et al. [31] made use of CVD to grow ZnO in synthetic opals. This method yielded large-area, high-quality ZnO–polystyrene (PS) composites and ZnO inverse opals with very precise control of degree of infiltration, which, in terms of thickness, means nanometer-thick layers. Kwang-Sik Kim and Hyoun Woo Kim have synthesized ZnO nanorods on bare Si substrate using metal organic chemical vapor deposition [32].
1.6.3. Molecular beam Epitaxy (MBE)

This technique is generally used to deposit elemental or compound quantum dots, quantum wells, quantum wires, etc. in a highly controlled manner. A schematic diagram is shown below in Figure 1.8. High degree of purity in materials is achievable using ultra high vacuum (better than $10^{-10}$ torr). Special sources of deposition known as Knudsen cell (K-cell) or diffusion cell are employed to obtain molecular beams of constituent elements. The rate of deposition is kept very low and the substrate temperature is rather high in order to achieve sufficient mobility of the elements on the substrate and layer growth to obtain nanostructures.

![Figure 1.8. Schematic diagram of MBE.](image)

ZnO layers were reported to be grown on (0001) GaN/sapphire substrates by molecular beam epitaxy (MBE) with the use of hydrogen peroxide as an oxidant by N. Izyumskaya [33]. Nitrogen dioxide was applied for molecular beam epitaxy of ZnO on (0001) sapphire substrates [34].

1.6.4. Wet Chemical Method

The different wet chemical methods employed to produce nanoparticles are coprecipitation, conventional alkoxide and citrate sol-gel process, sol-vothermal and combustion etc.
The synthesis of ZnO nanopowder with narrow particle size distribution via aqueous acetate citrate gelation method is discussed by D. Mondelaers et al. [35]. Tetrapod nano-ZnO was prepared based on a novel combustion method: melting-combustion method (MCM). Industrial pure zinc was melted and then ignited by the flame of acetylene and oxygen gas mixture at a proper ratio [36-38]. The combustion reaction has also been used to prepare ZnO and ZnO±Bi₂O₃ powders in an aqueous solution of zinc and bismuth nitrates in single step reaction [39]. Zinc oxide nanorods were successfully prepared by one-step solvothermal reaction of zinc acetate in alcohols [38].

The merits of these techniques are viz. high homogeneity, control of morphology, narrow particle size distribution, and low sintering temperature due to high reactivity which has attracted researchers for its use in the synthesis of nanomaterials. Sometimes even metastable phases can be stabilized at room temperature. The only limitation of these techniques is difficulty in getting large-scale production.

1.6.5. Vapor Phase Growth

This is commonly used to produce metallic as well as semiconducting nanowires. Starting with the simple evaporation technique in an appropriate atmosphere to produce elemental or binary nanostructures, this includes vapor-liquid-solid (VLS), vapor-solid (VS) and other processes as predicted by appropriate phase diagrams as a function of temperature and pressure.

1.6.5.1 Vapor-Liquid-Solid Growth

The growth of nanostructures via a gas phase reaction involving a VLS process has been extensively studied [39, 40]. Wagner et al. in 1960s proposed a mechanism for the growth of large single-crystalline whiskers via a gas phase reaction involving the so-called VLS process [41]. The anisotropic crystal growth is promoted by the presence of a liquid alloy-solid interface by this mechanism. This mechanism is widely accepted and applied to understand the growth of nanowires of many elements such as Si and Ge on suitable substrate as shown sequentially in Figure 1.9. In particular, when a substrate with a metal source is placed in a
Figure 1.9. Schematic representation of different stages involved during vapor-liquid-solid (VLS) growth [41].

During growth, the semiconductor material is provided by thermal evaporation of a powder target. The resulting vapor is transported to the substrate by the Ar flow, which also ensures the partial pressure of species, involved in the reaction.

The vapor dissolves in the metal particles and forms a eutectic. When the liquid particle becomes supersaturated, the crystalline nanowire starts to grow (tip growth). The liquid surface has a large accommodation coefficient and is therefore a preferred deposition site for incoming vapor. Because new vapor is continuously supplied, the nanowires will keep on growing in order to reach lengths exceeding even 100 μm. By controlling the nucleation and growth, it is possible to produce semiconductor nanowhiskers (e.g. InAs, GaAs) using organometallic vapor phase epitaxy [42]. By knowing the equilibrium phase diagram one can predict the catalyst materials and the growth condition for VLS approach. One of the advantages of the conventional metal-catalytic VLS growth is that the diameter and growth alignment of the nanowires can be readily controlled by using uniformly distributed metal seeds with well-designed sizes on the substrate. An important disadvantage is the use of flammable or toxic precursor gases.
such as SiH$_4$ or SiCl$_4$ and there are also environmental impacts for large-scale manufacturing.

1.6.5.2. Oxide Assisted Growth (OAG)

OAG have many advantages over well-established conventional VLS mechanism used for growth of Si and Ge nanowires [43]. Lee et al reported the synthesis of GaAs nanowires by the oxide-assisted laser ablation of a mixture of GaAs and Ga$_2$O$_3$ [44]. The nanowires have a thin oxide layer covering and a crystalline GaAs core with a [111] growth direction. In this oxide-assisted growth method, oxides, instead of metals play an important role in inducing the nucleation and growth of nanowires (Figure 1.10). The OAG technique not only allows a large-quantity production of nanowires with controllability, but also yields high-purity nanowires, free of metal impurities. The oxide-assisted 1D nanomaterials synthesis is complementary to and coexistent with the conventional-catalyst VLS approach.

The OAG approach can be a generic method capable of bulk production of nanostructures from host of materials other than Si including Ge nanowires, carbon nanotubes, silicon and SnO$_2$ nanoribbons, as well as Group III-V and II-VI compound semiconductor nanowires [45]. Interestingly, the OAG and metal catalytic VLS process can be co-existent, a fact that could be exploited for optimization of the nanowire growth by combining the complementary advantages of the two distinct methods.

However, both these processes vary in their growth mechanism, growth conditions, yield of the nanowires, abundant growth direction, diameters and finally in the chemical purity. Understandably, in the metal catalyst growth, the characteristics of the grown nanowires critically depend on the nature and size of metal catalyst used.
1.6.5.3 Vapor-Solid (VS) Method

In this process, vapors are first generated by evaporation, chemical reduction or gaseous reaction, which are subsequently transported and condensed onto a substrate. The VS method has been used to prepare oxide, metal whiskers with micrometer diameters. Using the VS method, synthesis of nanowires for oxides of Zn, Sn, In, Cd, Mg and Ga have been attempted [46,47]. Although, the VS growth process has demonstrated considerable flexibility in fabricating a wide range of nanosystems, it is difficult to control the nucleation i.e., the size control of the products. On the other hand, for growth of nanostructures by the VLS process, the key advantage is to generate nanosized catalyst clusters that define their size and direction of the growth.

1.6.6. Biological Methods

Large scale synthesis of commercially useful nanomaterials has been achieved by using microorganisms, biomimicking their role in nature. This method has been widely explored due to its potential as an attractive alternative to the conventional routes. Moreover this method is eco-friendly or so-called green synthesis route. Synthesis of nanomaterials using biological ingredients can be roughly divided into following three types [48]:

1. Use of microorganisms like fungi, yeasts (eukaryotes) or bacteria, actinomycetes (prokaryotes). Eukaryotes are higher organisms with proper nucleus in their cells and prokaryotes are lower organisms without any separate compartment for their DNA.
2. Use of plant extracts or enzymes.
3. Use of templates like DNA, membranes, viruses and diatoms.

By using spherobacterium Streptococcus thermophilus as a natural biotemplate, ZnO hollow spheres have been reported to be synthesized in a simple hydrothermal method based on the surface biofunctionality of the microorganism [49]. B.T.Su et al. has reported the use of cotton fibers as bio-template to successfully synthesize ZnO hollow fibers [50].

1.7. Applications of Nanostructures

Ability of materials to dramatically change their properties at nanoscale has opened up the possibility of making new devices, instruments, and consumer goods etc. to function in much better way than was possible earlier. Semiconducting oxides as an important series of materials candidates for optoelectronic devices and sensors have attracted considerable attention in scientific research and technological applications. Semiconducting metal oxides such as ZnO, SnO₂, TiO₂, WO₃, Fe₂O₃ and In₂O₃ have been found to be in various shapes and sizes. Some of the interesting discoveries reported by various research groups [1-2, 6, 51, 52]:

- Semiconductor nanocrystals (quantum dots) are used for dynamic angiography in capillaries hundreds of micrometers below the skin of living mice. It could be done to about twice the depth of conventional angiographic materials with one-fifth the irradiation power.
- Doped nanocrystals can enhance the quantum efficiency of light emission enormously leading to power saving.
- Nano-electro-mechanical sensors could detect and identify a single molecule of chemical warfare agent, which is an essential step towards realizing practical field sensors.
- Nanocomposite energetic materials for propellants and explosives are synthesized which have over twice the energy output of typical high explosives.
- Prototype data storage devices based on molecular electronics with data densities over 100 times that of today’s highest density commercial devices.
• It is demonstrated that iron nanoparticles can remove up to 96% of a major contaminant from ground water at an industrial site.

1.7.1. Applications of ZnO

Direct wide band gap ZnO semiconductor (n-type) has advantages in near UV emission and transparent conductivity, and possesses potential utilities for light-emitting/ detecting devices, transparent field effect transistors, solar cell windows, gas sensing devices and so on [53-55]. For example, ZnO surface supports strong chemisorption behavior of oxygen and sensitivity to UV light, which provide attractive applications to UV photodetector and optical devices [56-60]. It has extensive applications in light emitting diodes, field-effect transistors, flat panel displays, and so on [61-65]. Photoluminescence characteristics of semiconductor nanostructures have also been studied extensively [66-68]. Due to large exciton binding energy (60 meV) and the thermal energy at room temperature (26 meV), ZnO shows an efficient exciton emission at room temperature under low excitation energy. In ZnO, UV -band at 380 nm and green –yellow emission band at 520 nm mainly due to various point defects, either extrinsic [69], or intrinsic [70] are observed.

Nanostructures with flat ends can be exploited as optical resonant cavities to generate coherent light on the nanoscale. Huang et al. have demonstrated the room temperature UV lasing of ZnO nanowires [71]. The observed lasing action in these nanowire arrays without any fabricated mirror indicates that these single-crystalline faceted nanowires can, indeed, function as natural resonant cavities. This nanowire lasing has been further confirmed with the optical characterization of single ZnO nanowire by scanning near-field optical microscopy (SNOM).

ZnO nanostructures have negative electron affinity and the ease with which the morphology can be controlled makes them an appropriate alternative to carbon nanotubes and other solid-state devices for field emission microelectronic devices. Also diluted magnetic semiconductors (DMSs) are currently attracting immense interest in the merging field of spin based electronics or spintronics. The broad objective of this field is to control electron spins, in addition to charges so as to transmit information and provide new
functionality to semiconductor devices. The mechanistic study reveals that Co$^{2+}$ and Ni$^{2+}$ dopants inhibit nucleation and growth of ZnO nanocrystals [72].

Various chemical and physical processes, such as conventional sputter deposition technique [73], chemical vapor deposition (CVD) [74, 75], thermal evaporation [76-78], and hydrothermal processes [79, 80], can be used to synthesize nano- and microscaled ZnO crystals in various sizes and morphologies. Morphologies such as nanorods [81, 82], nanowires [83], nanotubes [84, 85], nanobridges and nanonails [86] have been obtained over past few years. Some novel morphologies, including tower [87, 88], star [89], dendrite [90] and flowerlike [91-94] have also been achieved via different chemical solution routes very recently. These complex structures are expected to have more potential applications in building functional electronic devices. Therefore development of morphological controllable synthesis of ZnO nano or microstructures is urgently important to answer the demand for exploring the potentials of ZnO.

1.8. Gas Sensors (GS) and Photoluminescence (PL) Reports

Since this thesis deals with gas sensing, literature survey in detail carried is given below. Chemical sensors and microanalytical systems constitute a paradigm for relevant, interdisciplinary endeavor in which some of the key limiting problems are remarkably fundamental in nature. A successful sensor-based system must respond with application-dependent sensitivity, selectivity, reversibility, speed, and longevity to a desired analyte, while consuming minimal power and volume, not to mention being manufacturable from inexpensive materials using economical batch methods. This over constrained problem can be solved only by an ingenious combination of the most fundamental interfacial chemistry, the basic physics of device platforms, clever engineering of the package and overall system, and an optimal use of mathematical techniques to produce from raw data, a meaningful response.

Among solid-state devices, semiconducting oxide sensors are one of the most promising conductometric chemical sensors, due to their smaller size, low price, compatibility with signal processing, minimum power consumption and modularity [95]. The sensing properties of these materials are based on reactions between semiconductor
surfaces and the analyte gas and these reactions produce changes in the semiconductor electrical properties. Although there are many possible kinds of surface fragmentation reactions, the more common interaction that leads to changes in the conductivity is the adsorption of analyte gases on its surface. The resistance of semiconducting thin films is strongly influenced by the presence of oxidizing or reducing gases. The molecules of the analyte gas can indeed interact with the surface of the semiconductor, which already has many oxygen species ($O_2$, $O_2^-$ and $O^-$) due to chemisorption. The charge exchange between adsorbed molecules and the analyte gas modifies the energy barrier ($eV$) for grain-to-grain current percolation and in turn, the electrical conductance of the layers. Accordingly, the conductance of the layer can be expressed by $G = G_0 \exp(-eV_s/kT)$ where $G_0$ is a constant. The interaction of an oxidizing (reducing) gas occurs with either the film surface or the oxygen coverage. It results in donating (capturing) electrons at the semiconductor surface, which leads to a positive (negative) conductance variation for an n-type semiconductor. In other words, for an n-type material like SnO$_2$, reducing gases (such as hydrogen, hydrocarbon, and ammonia) will cause a significant increase in conductivity. The opposite behavior occurs for a p-type semiconductor. In both cases, the variation of conductance, $\Delta G$, depends on gas concentration termed as (gas) in the given formula, $|\Delta G|/G = A[gas]^B$. where, $A$ and $B$ are constants determined by temperature, grain size, porosity and specifically on gas adsorption.

The effects of microstructure (which includes ratio of surface area to volume, grain size and pore size) have a strong influence on the sensing properties. Further, it has been established that with the decrease in the particle size down to nano regime, the sensitivity of the sensor material towards a particular gas gets enhanced [96]. The extremely high surface-to-volume ratio associated with these nanostructures makes their electrical properties significantly sensitive to the specific moieties adsorbed selectively on the surface. Further, they also offer the advantage of potentially drift free operation combined with smaller size, fast response and enhanced sensitivity. In addition a shorter response time (75 ms), low detection limit (2 ppm) and above all, room temperature detection is possible using these low dimensional structures.
As compared to other gas sensing semiconducting oxides such as WO₃, TiO₂, ZnO, In₂O₃, Fe₂O₃, and other mixed oxides, it is found that SnO₂ sensors are highly sensitive to reducing gases even at trace amounts. More significantly, the composition of SnO₂ can be tailored easily using different approaches for achieving high selectivity [96]. It is interesting to note here that the mobility of conduction electrons in SnO₂ and ZnO are quite high (160 and 200 cm²/V.s respectively) compared to that of other semiconducting oxides like In₂O₃ (100) and WO₃ (10 cm²/V.s). Further, hole mobility as low as 0.2 cm²/V.s has been reported in p-type oxide such as NiO, which is one of the reasons for its less utility as a p-type oxide. The same is also true for some of the other n-type semiconducting oxides such as TiO₂, which has only 0.4 cm²/V.s mobility of conduction electrons. Amongst ZnO and SnO₂ as gas sensing materials, both have their own merits and demerits. SnO₂ has proved, as a unique oxide sensor material due to its inherent physical and chemical properties. In this n-type material, the conductivity is very sensitive to the surface states in a temperature range between 300 and 700 K. At this temperature range, the redox reaction takes place on the surface of oxides. Besides, SnO₂ surface exhibits good adsorption/desorption phenomenon and surface reactivity, mainly due to the availability of free electrons in its CB and the presence of surface and bulk oxygen vacancies and active chemisorbed oxygen species. Further, it can be more easily processed in the bulk, thin film, and dispersed state of crystallite sizes of 5-20 nm. Nanosized powder has shown promising properties in sensor applications especially at low operating temperatures with enhanced sensitivity [97]. The availability of high surface area and stability of such structures demonstrates their usefulness to make improved and reliable gas sensors. There are a many reports [98-113] available on ZnO for its remarkable sensitivity to reducing gases in the literature. ZnO in thin and thick film configurations or porous bulk pellets and over a wide range of operating temperatures have been used. Pure zinc oxide or doped with aliovalent (may be donor or acceptor) element and sometimes supported with noble metals such as Au, Ag and Rh were also investigated for optimizing gas sensing properties. The important parameters for a very good gas sensor include its sensitivity, selectivity, stability, response and recovery time, low operating temperature amenable for large scale production and most importantly economical viability. Pristine zinc oxide nanowires prepared by thermal evaporation technique showed [98] good
sensitivity and fast response time towards ethanol vapors at an operating temperature ~ 240 C. Further ‘Au’ doping found to enhance sensitivity of these samples at this temperature.

Jiaqiang Xu et al. [102] prepared ZnO nanorods (diameter ~ 40-80 nm) by hydrothermal method which have excellent response time to ethanol and long term stability as compared to zinc oxide nanoparticles. The surfactant used for the synthesis of nanorods was CTAB. This result emphasizes the importance of morphology of these powders. The influence of humidity in the testing gas chamber for ZnO sensor in thick film form containing tetrapod shaped (or can be called Y-ZnO) particles [106] has also been investigated.

The PL property of ZnO had been extensively investigated all over the world [114-125]. Zinc oxide in single nanorod form as well as nanorod assemblies prepared by the solvothermal method [116] at 150 °C exhibits excellent UV (387 nm) emission. Three different solvents namely ethanol, hydrazine and ethylenediamine were employed in this procedure. According to Hui –Qui et al. [118] nanowires and nanorods were produced by thermal oxidation of Zn precursors under 5 Pa and at 400 °C. These samples show green emission which are related to oxygen vacancies. The needle shaped ZnO nanowires synthesized [119] without using any surfactant by thermal evaporation technique shows a sharp & strong UV emission in PL spectrum recorded at room temperature. The PL properties of ZnO were modified by the addition of polyaniline [124]. The authors attribute this change to surface modification of ZnO nanostructures by the presence of polyaniline

### 1.9. Objectives of Present Study

As the field of nano is growing, semiconductor oxides with various shapes and sizes are being produced depending on their synthesis methods. As the shape and size of the compound changes so does its properties more specifically the opto-electrical properties. In view of an active interest in the field of sensors based on nano-materials and more precisely ZnO, we have undertaken the present study of metal doped and undoped ZnO nanostructures with plan of exploring their gas sensing behavior. We are reporting the synthesis methods and the phsico-chemical characterization techniques such as DTA/TGA, XRD, BET, SEM, EDAX, TEM-HRTEM, PL, EPR and DRS that have been carried out.
These compounds are synthesized by using modified wet chemical routes. Al, Ru and Cu were incorporated in the nanostructures of ZnO, which has imparted novel morphologies with interesting gas sensing properties. Sn doping in ZnO was carried out using thermal evaporation method. The detailed studies of these compounds have presented in the following chapters. Short studies on field emission and PL have also been undertaken. The present thesis has been divided into seven chapters.

Chapter 1:
This chapter begins with general introduction of nanomaterials. The changes in physical and chemical properties accomplished with the reduced dimensions have been widely discussed in this chapter. Different synthesis methods adopted by various groups have also been discussed here which is one of the decisive parameter to control the morphology of the final product. At the end of the chapter a general applications of nanostructured semiconducting oxides and ZnO have been discussed in detail.

Chapter 2:
The principle, working and instrumentation of various characterization techniques utilized present work, viz. X-ray diffraction (XRD), Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). Transmission electron microscopy (TEM), High-resolution transmission electron microscopy (HRTEM), electron paramagnetic resonance (EPR), diffused reflectance spectroscopy (DRS), differential thermal and gravimetric analysis (DTA/TGA), photoluminescence (PL) etc. have been outlined in this chapter. Sample preparation as required for the different characterization techniques has also been discussed. This chapter also deals with the application-oriented characterizations based on the field emission and gas sensing studies in detail.

Chapter 3:
In this chapter gas sensing properties of Al doped ZnO synthesized using modified coprecipitation method has been discussed. The Al content was varied from 1 to 5 wt% and its structural and the gas sensing studies has been carried out with respect to the operating temperatures. All our experimental observations with different levels of Al
Chapter 1

Doping indicates 1 wt. % Al doping to be optimum concentration for high gas response with fast response and recovery times. Our study gives a strong evidence for the role of aluminum in the gas sensing behavior using less explored EPR and DRS characterization techniques to support the gas sensing results. The characterizations confirm that at low-operating temperatures, 5 wt. % Al:ZnO has maximum defects, which contribute towards gas sensing, while 1 wt. % Al:ZnO shows good sensing response only at higher temperatures. We have found that Fowler-Nordheim plots exhibit non-linear behavior and interestingly the non-linear character is found to be specimen dependent. We have also proposed a possible mechanism to explain the nonlinearity in field emission from semiconducting emitters.

Chapter 4:

This chapter deals with Ru doped ZnO synthesized using citrate gel method. The XRD analysis was used to study the strain calculations and texture coefficient in the ZnO after systematic addition of Ru. The TEM and HRTEM were used to observe the effect on their morphology. In addition to lattice strain calculations studied using Hall equation, the effective crystallite size obtained was also compared with that determined using Scherrer’s equation. We have also carried out the gas response study of pristine ZnO, which is highly sensitive towards liquefied petroleum gas (LPG) while Ru doped ZnO, is found to be highly selective towards ethanol (C₂H₅OH). It was interesting to note that the magnitude of sensing is also found to depend on Ru concentration.

Chapter 5:

This chapter is the study of Cu doped ZnO synthesized using hydrazine as a combustible agent. Various characterization techniques have been explored to perform the TEM, HRTEM, PL and gas sensing studies. The morphology of these powders is found to change from nano sphere to nano-rods by varying the ratio of zinc nitrate to hydrazine. In our investigations we found that hydrazine in addition to fuel is also acting as a surface directing agent. Their gas sensing study has also been carried out at various operating temperatures and is found to be good reducing gas sensor. The luminescent property of ZnO rods has been investigated extensively for their potential use as photoelectric material.
Chapter 6:
This chapter describes Sn doped and undoped ZnO synthesized using thermal evaporation and focuses on their gas sensing applications. ZnO and SnO$_2$ are well-known gas sensors. Incorporation of Sn in ZnO is also known to improve the electrical properties [18], hence we study the gas sensing properties of Sn-ZnO. The microstructure of these nanosized powders is studied in detail using techniques such as XRD, SEM-EDS. The PL studies have also been investigated for these samples.

Chapter 7:
Summary and conclusions of this work are given in this chapter. A thorough understanding of the sensing mechanism and their temperature dependent properties can help in fabrication of a device for commercial applications.
References


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