

CHAPTER I

INTRODUCTION

1.1. Nanoscience and Nanotechnology

Nanotechnology is an important initiative in science and technology in the 21st century. All mainstreaming aside, nanotechnology has become a dominant player in the scientific arena. This field explores materials and their properties when at least one dimension is in the range of one to one hundred nanometers in length, a size regime referred to as the nanoscale (Nalwa, H.S. (2002)). Materials at this scale may consist only of a few atoms or molecules clustered together. At the nanoscale, quantum confinement effects begin to dictate a material's properties dimensions (Nalwa, H.S. (2002)). Research in this field will likely provide some of the most exciting breakthroughs in technology. Nanotechnology has begun to seep into the national (and international) consciousness and awareness and is being spoken about as a revolutionizing technology that will change everything from basic building materials to computers to space travel.

Nanotechnology is the application of nanoscience to useful devices. Nanotechnology will likely provide some of the most exciting breakthroughs in technology. The ability to work with atoms at the nanoscale, on the molecular level, with atomically precise design, promises to open up a lot of areas of technological development. (Nalwa, H.S. (2002))

1.2. Nanomaterials

The current direction of nanotechnology research is the development, characterization, and functionalization of nanomaterials. Nanomaterial development represents a critical component in achieving the goals of nanotechnology.

Recently many investigations have been oriented to the study of the material at nano-scale. It has been discovered in recent years that many materials have extremely unique properties, when they are developed at a nanoscale. Many materials also configure themselves in different crystallographic structures not seen in bulk form of the

same material. Many of these properties are different regardless of whether it was formed from the bottom up or from the top down.

A nanostructure is reasonably defined as an object processing at least one critical dimension less than 100 nm in extent. Thus ultrafine microstructures having an average phase or grain size of the order of a nanometer are classified as nanostructured materials. Because of the small size of building blocks (particles, grains or phase) and high surface to volume ratio, these materials are expected to demonstrate unique mechanical, optical, electronic and magnetic properties. These materials also possess high strength, improved hardness, and ductility in normally brittle materials, wear resistance, erosion resistance, corrosion resistance and high chemical activity. Nanomaterials are much more formable than the conventional commercially available counterparts.

1.3. Classification of Nanostructure Materials

It was not until the development of electron microscopy that imaging materials at the nanoscale was possible. For successful imaging, a material must be at least as large as the wavelength that is being used to image it. For visible light, this is much larger than nanomaterials (400-700 nm).

Electron microscopes also allow for a proper classification of nanomaterials so that they can be discussed in an intelligible and useful manner. The main feature of nanomaterials is their small size in some dimensions, nanomaterials have come to be classified by the number of dimensions in which they are confined to the nanoscale. Depending upon whether nanostructure materials are single phased or multiphased polycrystals, they are classified as follows. The schematic diagram of different types of nanomaterials is shown in Figure 1.1

- (i) Zero dimensional atom clusters and cluster assemblies or quantum dots. Sol-gel process has been commonly used to generate clusters.
- (ii) One-dimensional or nanowires which has got immense applications. These are having layered or lamellar structure. Vapour deposition, sputtering techniques and electrodeposition techniques have been used to synthesize the one-dimensional

layered nanostructure materials. The magnitude of length and width are much greater than the thickness of the layered nanocrystals.

(iii) Two dimensional nanostructured materials with planar structure of thickness of the order of few nanometers with definite length and breadth. These will be filamentary in nature and length is substantially larger than the width or diameter.

(iv) The crystal size of which is of the order of a few (1 to 100 nm) nanometers equiaxed in nature and is termed as nanostructured crystallites or 3D (Three dimensional) nanostructure.

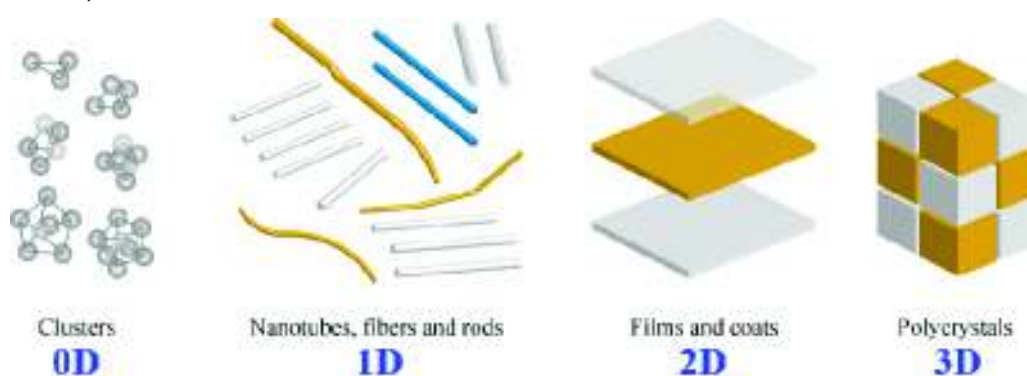


Figure 1.1: Schematic of the four types of nanocrystalline materials

As the dimensions of a material decrease in size, quantum confinement effects begin to occur; quantum confinement is when a material is on the order of or smaller than the exciton Bohr radius of its constituent compound (Bawendi *et al.*, 1992). This restricts each atom's movement, resulting in discrete energy levels and differences in material properties.

1.3.1. Zero-Dimensional Nanostructures

Quantum dots (QD) are semiconductors that have all three dimensions in the nanoscale and for this reason they are referred to as zero-dimensional structures. Quantum dots were first theorized in the 1970s and synthesized in the late 1980's. The nanostructures demonstrated a physical property phenomenon that had never been seen. Scientists could modify the luminescent and electronic properties by simply changing the size of the QD.

Quantum mechanics determines that only certain discrete energy levels are allowed within a single atom. If two identical atoms are held at large distances from each other electrons within each will have the exact same energy. As those two atoms are brought closer to one another, they interact, and no two electrons with the same spin can have the same energy. This governing principle is called the Pauli Exclusion Principle. When a large number of atoms are brought together to form a solid, the discrete allowed energy levels of the individual atoms becomes a continuous energy band. This band structure directly impacts electronic and optical properties. In bulk structures, these properties can only be altered by adding constituents to create defects, interstitials, or substitutions in the material. The impressive phenomenon in QDs is that the optical and electronic properties can be precisely tuned by changing the size of the dots in addition to adding dopants. The electronic and optical properties that were thought to be inherent to a material was transformed when the material was formed in a small enough (nanoscale) size. In QDs quantum confinement effects have a significant impact on the optical properties of the material. One popular quantum dot material is Cadmium Selenide (CdSe). Scientists at Bell Labs were some of the first to determine the direct relationship between quantum confinement in zero-dimensional cadmium selenide quantum dots and the induced higher energy shift in the electronic band structure (Alivisatos *et al.*, 1988, Brus *et al.*, 1984). Zinc sulfide plays an important role in quantum dot based nanosensors.

1.3.2. One-Dimensional Nanostructures

The wire- or rod-like shape of one-dimensional nanostructures has caused them to be the source of somewhat intensifying research of the past several years. In particular, their novel electrical and mechanical properties are the subject of intense research. The category of one-dimensional nanostructures consists of a wide variety of morphologies such as whiskers, nanowires, nanorods, fibers, nanotubules, nanocables, and nanotubes. Whiskers and nanorods are essentially shorter versions of fibers and nanowires. These one-dimensional structures have been studied for some time. One-dimensional structures with diameters ranging from several nanometers to several hundred microns have been referred to as whiskers and fibers in early literature, whereas nanowires and nanorods are more recent and refer to one-dimensional nanostructures whose width does not exceed 100 nanometers.

One-dimensional nanostructure of carbon nanotubes have been reported of being grown up to lengths of several centimeters (Zheng *et al.*, 2004)). The cross-sections of carbon nanotubes are only a few nanometers thick. Carbon nanotubes are made up of a hexagonal network of carbon atoms forming a crystalline graphite sheet. This sheet is “rolled up” to form a tubular structure. One important characteristic of the nanotube is the chirality, or the direction the nanotubes are rolled. There are three distinct types of nanotubes based on their chirality: chiral, armchair, and zig-zag. The chirality has a large impact on the physical properties (Odom *et al.*, 1998, Wilder *et al.*, 1998). Chirality is directly related to the electrical conductivity of carbon nanotubes. Armchair nanotubes have an electronic conduction closely resembling that of a metal (Wilder *et al.*, 1998). Such types of nanotubes are also called metallic nanotubes. Metallic one-dimensional nanotubes can have an electrical current density more than 1000 times stronger than metals like silver and copper. The zig-zag nanotubes have the electronic properties as a semiconductor.

The term “nanowire” is widely used to represent one-dimensional nanostructures that have a specific axial direction while their side surfaces are less well-defined (Westwater *et al.*, 1997, Zhang *et al.*, 2000). Typically, nanowires have a radius that is negligible in comparison to their length. A nanorod is typically much shorter in length than nanowires. Nanowires have been successfully synthesized out of a wide range of materials, including titanium oxide (Lei *et al.*, 2001), indium oxide (Liang *et al.*, 2001), indium-tin oxide (ITO) (Nguyen *et al.*, (2003), and aluminum (Ono *et al.*, 2003). Research in nanowires was dominated by silicon nanowires. One major benefit of silicon nanowires over carbon nanotubes is the electronic structure. Whereas nanotubes are either metallic or semiconducting depending on the chirality, silicon nanowires are always semiconducting, (Cui *et al.* 2001).

One of the more distinguishing features of nanowires is their very large length with respect to their width, making the sides essentially non-faceted. One of the more distinguishing features of nanorods is that their sides are faceted, but their length is comparable with their width. There is a type of one-dimensional nanostructure that combines the length of nanowires with the faceted structure of nanorods. This structure is the nanobelt. Nanobelts often referred to as nanoribbons, with two of their dimensions confined to the nanoscale, and the third dimension being relatively very long. (Pan *et al.*, 2001) first reported transparent semiconducting oxides of ZnO and

CdO synthesized in a belt-like manner in 2001. Nanobelts have also been synthesized in non-oxide semiconductors such as ZnS (Jiang *et al.*, 2003, Li *et al.*, 2003, Ma *et al.*, 2003), CdS (Dong *et al.*, 2003), CdSe (Ma *et al.*, 2004, & 2005), and ZnSe (Jiang *et al.*, 2004).

1.3.3. Two-Dimensional Nanostructures

Two-dimensional nanostructures have traditionally been studied and categorized as “thin films” because of their confinement to the nanoscale only in one dimension. They have been developed for use for a significant amount of time in fields as diverse as electronic devices and photovoltaic applications.

Two dimensional thin film nanostructures are good for highly efficient conversion of light to electrical power in photovoltaic cell devices due to their large surface area, on which photo-electro-chemical processes take place. A large amount of research has investigated synthesizing wide band gap semiconducting oxide materials such as ZnO and SnO₂ (Keis *et al.*, 2002, Chappel and Zaban 2002, Tennakone *et al.*, 2002, Chappel *et al.*, 2002, and Chen *et al.*, 2001). In addition, combination structures comprised of semiconducting oxide film and polymeric layers for solid-state solar cell devices have been examined to find the overall efficiency. So far, these devices have increased efficiency up to 5% for ZnO devices (Keis *et al.*, 2002), 1% for SnO₂ devices (Chappel and Zaban (2002), and up to 2% for hybrid devices (Huynh *et al.*, 1999).

1.3.4. Three-Dimensional Nanostructures

The most common method used to produce three dimensional nanocrystalline materials is to obtain an amorphous phase by rapidly solidifying the melt to appropriate composition and then by crystallising the glassy phase at a relatively low temperature. The gas condensation, mechanical alloying, chemical precipitation and spray conversion process techniques have been most commonly used to produce 3D equiaxed nanocrystallites.

1.4. Important Properties of Nanostructured Materials

The very small grain size nanostructured materials exhibit a variety of properties that are different and often considerably improved in comparison with those of conventional coarse – grained polycrystalline materials.

Some of them are

- i) Increased strength/hardness
- ii) Enhanced diffusivity
- iii) Enhanced ductility/toughness
- iv) Reduced density
- v) Reduced elastic modulus
- vi) Higher electrical resistivity
- vii) Increased specific heat
- viii) Higher thermal expansion coefficient
- ix) Lower thermal conductivity
- x) Super soft magnetic properties

Since nanostructured materials contain a very large fraction of atoms at the grain boundaries, the numerous interfaces provide a high density of short circuit diffusion paths. Consequently they exhibit an enhanced diffusivity in comparison to single crystals or coarse-grained polycrystalline materials with the same chemical composition. Another important consequence of the increased diffusivity is that sintering of the nanocrystalline powders can occur at temperatures lower than those required for sintering coarse-grained polycrystalline powders.

Recent experiments have showed that the electrical conductivities of nanocrystalline materials are greater than that of coarse – grained polycrystalline materials (Shikha Tiwari and Sanjay Tiwari 2006). This is due to the increased volume fraction of the atoms lying at the grain boundaries.

Specific heat of a nanocrystalline material is much greater than that of coarse-grained polycrystalline materials of the same composition. The specific heat of a material is closely related to its vibration and configurational entropy, which is significantly affected by the nearest neighbouring configurations. Thus an increase in specific heat of nanocrystalline materials has been attributed to the small crystal size, and consequent large interfacial component. The grain growth might have reduced the specific heat of nano-structured material.

By controlling the growth of nanostructure materials, mechanical, thermal, electrical, magnetic and other properties can be engineered. When particles become small enough to be nanoparticles, their mechanical properties change, and the way light and other electromagnetic radiation is affected by them changes (visible light wavelengths are on the order of a few hundred nanometers). Using nanoparticles in composite materials can enhance their strength, reduce weight, increase chemical and heat resistances and change their interaction with radiation.

Coatings made from nanoparticles can be usually tough or slippery, or exhibit unusual properties, such as changing colour when a current is applied or cleaning themselves when it rains. Although hard to quantify, it has been estimated that nanostructured materials and processes can be expected to have a market impact of over INR 50 x 10¹² (Rupees 50 trillion) by 2015.

1.5. Applications of Nanomaterials

Nanomaterials are materials that have one or more dimensions in the range of 1 to 100 nanometers. The reason that size matters is that the properties of materials can have some unexpected differences from their behavior in larger bulk forms that makes for new application opportunities. The two reasons for this change in behavior are an increased relative surface area (producing increased chemical reactivity) and the increasing dominance of quantum effects.

Various applications of nanomaterials in different fields are given in Figure 1.2.

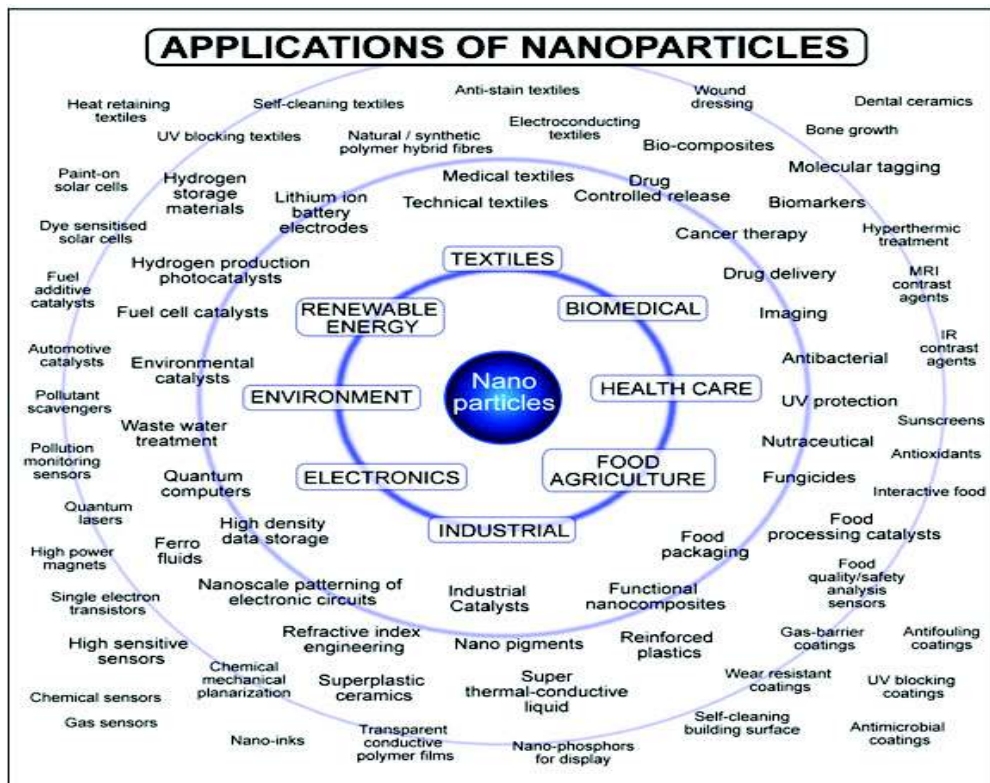


Figure 1.2: Application of Nanoparticles

Some existing applications of nanomaterials include:

- (i) Clay nanoparticles in packaging materials, where reduced porosity leads to less gas entering (e.g. less gas such as oxygen that spoils foods).
- (ii) Rolled graphite nanotubes used in coatings on car bumpers that better hold their shape in a crash;
- (iii) Carbon nanotubes which are sources of field- emitted electrons and create enhanced phosphorescence e.g. in “ jumbotron” lamps used at many athletic stadiums;
- (iv) Nanoparticles of zinc oxide in sunscreens are more efficient in absorbing UV than more traditional white titanium dioxide lotions and leaving the lotion smooth and transparent;
- (v) Textiles with nano coatings are dirt and crease resistant
- (vi) Nanoparticles used as antiseptics, for abrasives and in paints;
- (vii) Nano coatings on spectacle glasses make them scratchproof and crack resistant);

- (viii) Nanocoatings on tiles reduce slipping;
- (ix) Electrochromic or self- cleaning nanofilm coatings on windows, which in sunshine breaks down dirt and helps the water falling on it to carry the dirt away;
- (x) Nanofilms with non-stick properties used as anti- graffiti coatings for walls;
- (xi) Ceramic coatings for solar cells to improve scratch and erosion resistances;
- (xii) Glues containing nanoparticles with variable optical properties are used in optoelectronics (e.g. for coupling fibers to other optical components); and
- (xiii) Conductive nanofilms used in casings for electronic devices such as computers, to provide shielding against electromagnetic interference.

Applications under development, some of which are close to market, include:

- (i) “Smart” fabrics that can change their physical properties according to surrounding conditions, or even monitor vital signs;
- (ii) Drug delivery mechanisms including antibacterial and antiviral nanoparticles;
- (iii) Nanoceramics for more durable and better medical prosthetics;
- (iv) Improved catalysis for fuel production and
- (v) Nanoengineered membranes for energy efficient water purification.

Nanoparticles research is currently an area of intense scientific research, due to a wide variety of potential applications in biomedical, optical, and electronic fields. Processing, properties and cost issues are pushing down the particle sizes of powders used in a variety of industries. This feature allows the construction of a finely tunable and efficient semiconductor laser.

1.6. II-VI Compound Semiconductors

A compound semiconductor is a semiconductor compound composed of elements from two or more different groups of the periodic table. It has widely ranging physical properties. The physical properties which may vary include band gaps, crystal lattice structures, electron and hole mobilities, optical properties, thermal conductivities and so on.

For over a decade, II-VI semiconductors have attracted growing interest owing to their possible application in optoelectronics. There are generally recognized eight II-VI semiconductor materials. They are: ZnO, ZnS, ZnSe, ZnTe, CdO, CdS, CdSe, and CdTe. Mercury, the other group IIB metal, forms a liquid at standard temperature and pressure (STP) and therefore is not generally included in this list. Because of their uses in optoelectronic and semiconducting applications, II-VI semiconductors have recently been the focus of intense research in nanomaterials.

1.7. ZnO Semiconductor Thin Film

Zinc oxide is a wide band gap material that can crystallize in a cubic zinc blende or wurtzite structure with many promising properties for blue/ UV optoelectronics, transparent electronics, spintronic devices and sensor applications. Its research interest has waxed and waned as new perspective applications revive interest in the material, but the applications have been limited by the technology available at the time (Özgür *et al.*, 2005). ZnO-based materials have also been used in solar cells, chemical sensors, laser diodes, etc (Qifeng Zhang *et al.*, 2009, Fan *et al.*, 2004 and Sheng Chu *et al.*, 2008). ZnO thin films have been studied as the active channel material in thin film transistors development because of its exhibiting n-type semi conductive characteristic with band gap of 3.3eV and excellent thermal stability and can be well oriented crystalline on various substrates (Kathirvel *et al.*, 2009).

At present, the most widely publicized application for ZnO is an ITO replacement for displays and photovoltaic panels, where ZnO could lower costs of transparent conductors. In addition to its conductive nature, ZnO also can be used as a semiconductor for making inexpensive transistors for disposable electronics or even low-cost LEDs. ZnO is also finding applications in thin-film batteries, and ZnO's ability to be engineered into interesting nanostructures hints at new applications down the road. ZnO already is being tapped in spintronics.

1.7.1. Benefits of Zinc Oxide

As mentioned above, ZnO has several advantages over its competitors; it is inexpensive, relatively abundant, chemically stable, easy to prepare and non-toxic. One of the strongest market opportunities for ZnO is a cost-effective replacement for ITO, which costs (99.99 percent purity or higher) over \$700/kg. The cost of indium metal,

which as of this writing is over \$1,000/kg, accounts for a large share of the production costs. This compares to zinc, which is traded at less than \$1 on the London Metal Exchange, and although there is a cost associated with processing zinc metal into high purity zinc oxide powder, the overall cost is a fraction of the current cost of ITO. Additionally, its abundance and chemical stability has made ZnO a material of interest as a replacement for toxic, expensive GaAs transistors in the LED space.

Another benefit of ZnO is that it can be processed using various manufacturing process. This compares to ITO, which is typically sputtered and costly, wasteful process that causes interfacial damage. The sputtered layer is also adversely affected with each annealing, etching and drying stage causing brittleness and adhesion issues, all of which negatively impact the performance of the films. The ability to use chemical vapor deposition (CVD) or metal organic chemical vapor deposition (MOCVD) techniques is particularly attractive, resulting in better step coverage, higher deposition rates, improved composition grading and the elimination of interfacial damage. Less costly process methods add to the attractiveness of using ZnO for a variety of applications (Fan *et al.*, 2004, Kathirvel *et al.*, 2009).

1.7.2. Opportunities of Zinc Oxide as Semiconductor and Conductor

One of the benefits of ZnO is that it can be used as a conductor and a semiconductor. While NanoMarkets expects close to 70 percent of the applications in this report will favor ZnO as a conductor, the potential of ZnO as a semiconductor certainly is noteworthy. ZnO is a good conductor because of its environmental stability, low resistivity and high transparency, not to mention its low cost and abundance. The low cost naturally makes ZnO attractive as a semiconductor. As a semiconductor however, there are still technical issues in the ability to achieve repeatable, stable p-type film.

1.8. Properties of Zinc Oxide

In addition to cost savings, ZnO offers the following properties.

- High carrier mobility
- Transparency
- Wide band gap
- Low temperature process

The high carrier mobility is directly linked to transparency, which makes it fully possible for ZnO to compete with existing silicon materials. The wide band gap is important because it opens the possibility of creating Ultra Violet (UV) LEDs and white LEDs with superior color purity. Low temperature processing is preferred in some applications such as OLEDs. ZnO has direct band gap energy of 3.37 eV at room temperature, and exciton and biexciton energies of 60 meV and 15 meV, respectively. Epitaxy will likely further improve ZnO's exciton properties, which directly relates to the optical properties in photovoltaic's and displays.

Zinc oxides as transparent semiconductors are attracting interest mainly because there has been a sharp jump in the need for higher carrier mobility of transparent semiconductors. The carrier mobility determines transparent Tri fluoro toluene (TFT) characteristics. This is now exceeding the carrier mobility of materials such as low-temperature poly-Si (LTPS) and amorphous Si used in LCD panels.

1.9. Applications of ZnO

Most of the present applications of ZnO are as a conductive film. As research continues to refine the processes for manufacturing ZnO as a thin film it is becoming clear that this inexpensive abundant material may be suited for a number of applications. Without doubt, displays are the leading application where ZnO is being used as a replacement conductive material.

1.9.1. Applications of ZnO as a Conductor

Indium tin oxide has been the transparent conductor of choice for many display applications due to its combination of environmental stability, relatively low electrical resistivity and high transparency. However, ITO is far from the perfect solution to many transparent conductor needs driving the need for ITO substitutes. Due to the high cost of indium and ITO's reliance on sputtering, ZnO becomes an attractive replacement. Most proposals for metal oxide Transparent conducting oxides (TCOs) dispense with the indium altogether. Materials that have been considered for TCOs include variations on tin oxide or ZnO, especially the latter. ZnO-based materials that have been considered or used for TCOs include zinc oxide itself, Mg-doped zinc oxide (MZO), Al-doped ZnO (AZO), Ga-doped ZnO (GZO), Al-doped MZO (AMZO), gallium-doped ZnO

(AGO) and gallium-doped MZO (MMZO). Indium doped ZnO is also used, although this, of course, brings with it the high cost of indium. ZnO is inexpensive, relatively abundant, easy to prepare, and non-toxic. The use of ZnO and derivatives for TCOs does not impact the price of zinc in the way that the use of ITO impacts the price of indium because the use of ZnO as a TCO is an unimportant application from the perspective of the ZnO business as a whole. In addition, with the possible exception of Ga, most of the doping materials used with ZnO are also readily available. Finally, all the materials based on ZnO are thermally and chemically stable.

Photovoltaics and LEDs are both on high growth market trajectories and are becoming favorable applications for ZnO as a conductive coating. Several solar companies are basing their PV technology on copper indium gallium deselenide (CIGS). Characteristic to the CIGS process, all companies use molybdenum (Mo) as the back contact deposited by sputtering, and the majority use ZnO as the front contact deposited either by sputtering or CVD.

Another potential market for ZnO as a conductor is the thin-film battery market, which is growing steadily. Thin-film batteries are best suited where small power sources are needed and need to be manufactured in a variety of shapes and sizes to fit in obscure wasted space locations. ZnO is currently being successfully used as a printed conductive coating for thin film batteries. Other present day successful uses for ZnO as a conductive coating include EMI and RFI coatings and shielding.

1.9.2. Applications of ZnO as a Semiconductor and Other Applications

Some of the potential applications for ZnO as a conductor also lend themselves to ZnO as a semiconductor. These include photovoltaic's and LEDs, which could become favorable applications for ZnO as a semiconductor. However, there are technical difficulties still being worked out for ZnO. With regard to photovoltaic's, the band gap leaves little of the solar spectrum to be absorbed. Since the semiconductors are transparent to light with energy less than the band gap, they only absorb photons with energy greater than the band gap. ZnO has a bandgap of 3.37 eV leaving very little of the solar spectrum able to be absorbed.

ZnO presently struggles to fulfill the needs of the LED industry as an actual light emitter because of the need for stable repeatable p-type ZnO, but a number of

institutions appear to be close to solving this issue. This is a case of a clear market in need of a technological breakthrough. ZnO offers phosphor-free spectral coverage coupled with quantum efficiency approaching nearly 90 percent, making it an attractive replacement for traditional GaN LEDs.

ZnO is low cost TFTs for display backplanes. It is widely used in large-scale macro-electronics such as electronic paper, flexible/wearable electronics and in 3D imaging. Flexible transistors will be used primarily in active-matrix backplane electronics of displays in terms of low voltage driving ability.

Gas monitoring devices are in demand for a rapidly growing range of applications. Metal oxide based chemical sensors have been used extensively for the detection of toxic pollutant gases, combustible gases and organic vapors. The main advantages of chemical sensors are their low price, small size, high sensitivity and low power consumption. Semiconducting metal oxides SnO_2 and ZnO have been explored as gas sensing detectors. ZnO has demonstrated properties of unique nanostructures such as nanocombs, nanorings, nanohelices/nanosprings, nanobelts, nanowires and nanocages and properties for novel applications as sensors and biomedical transducers.

Other markets attracting the attention of ZnO are spintronics and smart textiles. Spintronics is a nascent field exploiting the spin of electrons rather than their charge. Investigations of cobalt-doped zinc oxide have shown promise in providing a diluted magnetic semiconductor. The smart textiles industry, also a nascent market, is experimenting with ZnO grown microarrays as part of flexible polyester filaments.

To summarize, ZnO is emerging as a promising material in a variety of electronics applications. The number of patent filings by academia and industry continues to grow, and it is hopeful that some of the technical challenges will be solved allowing ZnO to become ubiquitous in next-generation displays, solar panels and lighting.

1.10. Present Investigation

Recently many investigations have been oriented to the study of the material at nano-scale. Wurtzite ZnO is a direct wide bandgap (3.37 eV) semiconductor that is one

of the most important materials in photonics. This is because of its high transmittance in the visible range and its high index of refraction (about 2.0041) (Park and J. R. Schneider 1968). ZnO has been synthesized as nanowires, nanobelts, nanocombs, nanosprings, nanorings, nanocombs and most recently nanohelices (Hannes *et al.*, 2002, Chang Shi Lao *et al.*, 2005, Pan *et al.*, 2001, Kong *et al.*, 2003, Kong *et al.*, 2004, Gao *et al.*, 2005, Yan *et al.*, 2003 and Wang *et al.*, 2003). All of these are one-dimensional nanostructures. Recently, ZnO quantum dots have been doped with manganese without changing their crystal structure (Nick *et al.*, 2004). ZnO doped with manganese (Mn) exhibits attractive light-emitting properties with increased optically active sites for applications as efficient phosphors. All of these properties make ZnO an attractive candidate for use in modern devices and other advanced technologies.

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. ZnO is an II-VI compound semiconductor. The crystal structures shared by ZnO are wurtzite, zinc blende and rock salt. 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 rock salt. ZnO is not really a newly discovered material. Research on ZnO has continued many decades with interest following a roller coaster pattern. The semiconductor ZnO has gained substantial interest in the research community in part because of its large exciton binding energy (60meV) which could lead to lasing action based on exciton recombination above room temperature semiconductor field with studies of its lattice parameter dating back to 1935 by (Bunn *et al.*), detailed optical studies in 1954 by (Mollwo *et al.*) and its growth by chemical vapor transport in 1970 by (Galli and Coker *et al.*).

Kulkarni (2004) has reviewed the results reported on the doped II-VI compound semiconductor nanoparticles. It has been demonstrated that the PL yield can be greatly enhanced by forming a two-component nanocomposite (Vasa *et al.*, 2004). The nanocomposite (CdS-ZnO) films have very high Photo luminescence (PL) yield and enhanced coherence compared to individual nanoparticles of CdS and ZnO. A similar approach with ZnO and ZnO doped with Mn, Cu and Pb is expected to bring fruitful results.

After careful survey of literature ZnO and doped ZnO is studied for the present study. In view of the formidable challenges that lie in the synthesis of nanomaterials, for the first time, ZnO, ZnO:Mn²⁺, ZnO:Cu²⁺ and ZnO:Pb²⁺ nanoparticles (quantum dots) with different concentration of dopant mole percentage (2.5, 5.0, 7.5 and 10.0) has been prepared by using simple chemical bath deposition method and characterize the prepared samples.

X-ray diffraction spectra were recorded and analyzed. The reflections were indexed and lattice parameters were determined. Also the sizes of the samples were calculated by Debye-Scherrer and Voigt function methods. Energy dispersive X-ray absorption (EDAX) spectra were obtained to determine the chemical compositions.

Atomic force microscopic (AFM), Scanning electron microscopic (SEM) images and Transmission electron microscopic (TEM) images were taken for the prepared samples and analyzed.

UV-Vis spectra of all the prepared nanocrystals were also recorded using an UV spectrometer and analyzed.

PL spectra of all the 13 samples prepared in the present study were recorded using a luminescence spectrometer.

DC electrical conductivities were measured by using the four-probe method at various temperatures ranging from 30 to 150° C. Activation energies were determined for all the prepared samples.

Capacitances and dielectric loss tangents were measured using an LCR impedance analyzer at different frequencies ranging from 100 Hz to 1 MHz at various temperatures ranging from 30 to 150° C. Dielectric constants and AC electrical conductivities were determined.

The topic of research has already been introduced in this Chapter. Chapter 2 gives a review of various studies made on ZnO and ZnO doped with other metal impurities nanocrystals in the near past. Chapter 3 contains the details of materials used and various experimental and other methods followed in the present study. Results obtained in the present study are provided and discussed in Chapter 4. The present research work is summarized together with providing the conclusions and the scope for the future is in Chapter 5. The literature cited are listed in the 'References' section.