Chapter 1

General Introduction

1.1 Introduction

Nanoscience and Nanotechnology is emerging as a leading frontier of research and development in natural sciences, engineering and in high-tech industry of the present century. This field encompasses art and wisdom of the artificial nano-sized (one nanometer = one millionth of a millimeter) structures with atomic precision, their characterization, and their utilization for studying new phenomena of novel devices and systems beyond the conventional technologies. The field takes advantage of physical, chemical, and biological principles that are set by the nanometer size, often in a realistic and fundamental way.

Throughout the centuries, mankind has been searching for the useful materials and methods to nourish the quality of life. The various ages in history of mankind has been marked by the emergence of new materials and the technology based on these materials. The Stone age, Bronze age and Iron age marked key periods, when humans fashioned materials into new tools that vastly improved their lot. The contemporary technology has stimulated greater interest on searching for functional devices based on new materials. The most significant change in our way of life was probably brought about by the Industrial Revolution that began in Britain around the middle of the 18th century. This in turn was replaced by the information technology, marked by the unprecedented capabilities in the gathering and storage of information and heavily dependent on high speed electronic computers. However, the next revolution taking place along with information technology is nothing but the revolutionary, all encompassing field of nanoscience and nanotechnology [Nalwa et al., 2000; Balandin and Wang, 2006].

Nanoscience and Nanotechnology have been identified as the key to unlock a new generation of devices with dramatic properties and functionalities [Lee et al., 2009; Hao et al., 2009; Hod et al., 2006]. Nanotechnology is considered to be one of the most important future technologies involving several disciplines of science including
solid state physics, solid state chemistry, materials engineering, medical science and biotechnology [Nalwa et al., 2000]. Manipulating matter at the nanometer scale, using building blocks with dimensions in the nano-size range, makes it possible to create new materials with improved properties. Nanotechnology is an emerging field of research and development dedicated to increasing the control over material structures on nanometer size. Although study on materials in the nanometer scale can be traced back for centuries, the current interest in nanotechnology is driven by the ever shrinking size of devices in the semiconductor industry supported by the availability of techniques for characterization and manipulation at the nanometer level.

Presently, nanoscience and nanotechnology represents the most active discipline all around the world and is considered as the fastest growing technological revolution the human history has ever seen [Service, 2004]. The immense interest in the science of materials confined within the atomic scales stems from the fact that these nanomaterials exhibit fundamentally unique properties with great potential of bringing about revolutionary advancements of next-generation technologies in electronics, computing, optics, biotechnology, medicine, drug delivery, structural materials, automotives, aerospace, food and energy. Nanotechnology involves achieving the capability to manipulate matter in a desired fashion atom by atom. The possibilities of assembling materials atom by atom was first suggested as early as 1959 by Physics Nobel Laureate Richard Feynman in his speech at the California Institute of Technology where he stated “The principles of Physics as far as I can see do not speak against the possibility of maneuvering things atom by atom. I can hardly doubt that when we have some control of the arrangement of things on a small scale, we will get an enormously greater range of possible properties that substances have”.

1.2 Nanostructured materials

The prefix ‘nano’ comes from the Latin word ‘nanos’ meaning literally dwarf and, by extension, very small. A nanometer is one billionth ($10^{-9}$) of a meter. Ultrafine microstructures having a grain size of the order of a nanometer are classified as nanostructured materials [Gleiter, 1992; Gleiter, 1995]. Currently, any material that contains grain or clusters of size below 100 nm is considered to be nanostructured. The interest in these materials has been stimulated by the fact that, owing to the small size and the high surface-to-volume ratio, these materials are expected to demonstrate
unique mechanical, optical, electronic and magnetic properties compared to their bulk counterpart [Seigel, 1993; Gleiter, 1992].

1.3 Synthesis of nanostructured materials

There are numerous techniques used for the synthesis of nanostructured materials, which are generally divided into two main methods, top-down methods and bottom-up methods [Cao, 2004]. The techniques, considered as top-down nano-fabrication techniques, include photolithography, nano-molding, dip-pen lithography and nanofluidics [Cao, 2004]. However, the limits for the top-down methods are restricted by the miniaturization and precision manufacturing of semiconductor products at a smaller scale. Alternatively, in bottom-up approaches, nanostructured materials are fabricated from building blocks of atoms, molecules, clusters or nanoparticles in a controlled manner. Therefore, the idea of artificially creating materials using the bottom-up approaches is important for developing novel and multi-functional materials. For example, milling is a top-down method in making nanoparticles, whereas the colloidal dispersion is a good example of bottom-up approach in the synthesis of nanoparticles.

At present, there are lots of methods for producing nanostructures, and the commonest one is gas condensation method [Kimoto et al., 1963; Wada et al., 1969; Ohno, 1976]. In this method of fabrication, the metals under the condition of low pressure argon and nitrogen are heated. Upon vaporization, the metal will turn into smog and move upward along with the convection of the inert-gas to get close to a cooling tank (77K) that is filled with liquid nitrogen. During the process of getting close to the cooling tank, the original material vapour will firstly form into atomic cluster, and then into single nanoparticle and finally aggregate on the surface of the cooling tank. The nanopowder can be collected in powder form by scraping the surface of the tank.

1.4 Features of nanostructured materials

Nanostructured materials show distinct properties that make them different from conventional materials due to one or several of the following properties.

Size effects: In a bulk crystal, the electronic energy levels are continuous. However, the situation changes in the case of nanomaterials [Klimov, 2004]. When the size of a
material is smaller than the de Broglie wavelength, electrons and holes are spatially confined and discrete electronic energy level would be formed resulting in the change in energy spectra. This phenomenon is known as quantum size effect. In CdS nanocrystals, a blue shift in energy band gap of 1.54 eV is obtained for a particle with radius 1 nm. Blue shift in band gap is observed for many other semiconductors also because of the quantum confinement effects [Klimov, 2004].

**Large surface area-to-volume ratio:** One of the distinct features of nanostructured materials is that a considerable percentage of the atoms are linked with interfaces such as surfaces, grain boundaries or inter-phase boundaries [Nalwa, 2000]. If we consider any shape for the building blocks of the microstructure, the surface area-to-volume ratio increases with decrease in size.

**Boundary effects:** With decrease in average particle size, the characteristics of surface atoms have to be taken into consideration to describe the strange properties exhibited by materials with nanograin size. Simple calculations show that 70-80% of atoms will be associated with the interfacial regions when the grain size is reduced to 2-3 nm whereas in the case of bulk materials with grain sizes of the orders of micrometers, the number of atoms associated with the surface is 0.01% [Gleiter, 1992].

### 1.5 Classification of nanostructures

#### 1.5.1 Nanostructures in One Dimension

In thin films, electrons are free to move in two dimensions but are confined in one dimension. Nanostructured thin films and engineered surfaces have been developed and used for decades in fields such as electronic device manufacture and engineering. In the integrated-circuit industry, for example, many devices rely on thin films for their operation. Monolayers (layers that are one atom or molecule deep) are also routinely made and used in chemistry. The formation and properties of these layers are reasonably well understood from the atomic level upwards, even in quite complex layers. Advances are being made in the control of the composition and smoothness of surfaces.

Engineered surfaces with tailored properties such as large surface area are used routinely in a range of applications such as in fuel cells and catalysts. The large
surface area provided by nanoparticles, together with their ability to self assemble on a surface, could be of use in all of these applications.

1.5.2. Nanostructures in Two Dimensions

The term nanowire is widely used to represent one-dimensional nanostructures that have a specific axial direction. Nanowires represent two-dimensional confinement of electrons and holes. The category of one-dimensional nanostructures consists of a wide variety of morphologies. These include whiskers, nanowires, nanorods, fibers, nanotubules, nanocables, and nanotubes, among others. Nanowires and nanorods are one-dimensional nanostructures whose diameter does not exceed 100 nanometers.

Nanowires are ultra fine wires or linear arrays of dots, formed by self-assembly. They can be made from a wide range of materials. Semiconductor nanowires made of silicon, gallium nitride and indium phosphides have demonstrated remarkable optical, electronic and magnetic characteristics. Nanowires have potential applications in high-density data storage; either as magnetic read heads or as patterned storage media, and electronic and opto-electronic nanodevices. Recently nanowires have found applications in self powered devices called nanogenerators where the piezoelectronic property of the material is used to generate power [Wang et al., 2009].

Two dimensional nanomaterials such as tubes have generated considerable interest among the scientific community in recent years. In particular, their novel electrical and mechanical properties are the subject of intense research. Nanotubes are typically a few nanometers in diameters and several micrometres to centimetres long. Oxide-based nanotubes are being explored for their applications in photodetectors, energy storage and solar cells.

1.5.3. Nanostructures in Three Dimensions

Nanoparticles represent three dimensional confinement and are often defined as particles of less than 100 nm in diameter. We classify nanoparticles to be particles less than 100 nm in diameter that exhibit new or enhanced size-dependent properties compared with larger particles of the same material. Nanoparticles exist widely in the natural world: for example as the products of photochemical and volcanic activity, and created by plants and algae [Nalwa, 2000]. They have also been created for years as products of combustion and food cooking, and more recently from vehicle exhausts.
Nanoparticles are of interest because of the renewed properties (such as chemical reactivity and optical behaviour) that they exhibit compared with larger particles of the same materials. For example, titanium dioxide and zinc oxide become transparent at the nanoscale, and are able to absorb and reflect UV light, and have found application in sunscreens. The use of nanoparticles in sunscreens is one of the most common uses of nanotechnology in consumer industry. By replacing traditional forms of ZnO with nanoparticles of this material, manufacturers can reduce the visibility of the cream and they can be easily applied onto the skin. The large surface area of ZnO nanoparticles additionally provides potential use for increased UV absorption properties. However, achieving higher surface area by lowering the particle size limits its use in cosmetics since nanoparticles of too small a size might penetrate through the skin into the cells to damage them. Nanoparticles have a range of potential applications: in new cosmetics, textiles and sun screen lotions and in methods of targeted drug delivery where they could be used to deliver drugs to a specific site in the body. Nanoparticles can also be arranged into layers on surfaces, providing a large surface area and hence enhanced activity, relevant to a range of potential applications such as catalysts. When the characteristic dimension of the nanoparticles is sufficiently small and quantum effects are observed, quantum dots are the common term used to describe such nanoparticles. A quantum dot is a semiconductor nanostructure that confines the motion of electrons and holes in all three spatial directions.

1.6 Metal oxide nanostructured semiconductor thin films

The recent past has seen increased interest in the preparation and characterization of nanoporous, nanocrystalline semiconductor thin films. This interest in large part is as a result of the development of highly efficient regenerative nanoporous, nanocrystalline semiconductor electrodes. Further interest has been generated by the development of dye sensitized solar cells [Tan, 2006; Gratzel, 2001] and Nanogenerators [Wang, 2004; Wang, 2005; Wang, 2008].

A number of techniques have been developed and studied over the years to create thin films of nanoparticles that can lead to novel applications in the areas of catalysis, sensors and photonics. These include RF magnetron sputtering [Ghosh et al., 2010], vacuum thermal evaporation [Koshy and Khadar, 2011], sol-gel technique [Fan et al., 2006], and metal organic chemical vapour deposition [Nigro, 2005]. The
vacuum thermal evaporation is a common technique for making films. For depositing nanostructured films, the pressure and time of deposition are the crucial factors in vacuum thermal evaporation technique.

1.7 Significance of zinc oxide

The invention of the semiconductor transistor in 1947 by scientists at Bell Laboratories resulted in the development of the semiconductor industry at an incredible pace. Despite the first transistor being manufactured from germanium (Ge), silicon (Si) has come to a dominant position in the international semiconductor industry in fields such as communication, information technology and computing. The expansion in the Si based semiconductor industry is due to its exceptional material properties and compatibility with conventional processing. However, the performance of Si devices may be approaching their limit due to the material’s physical properties. At present a number of semiconductors are considered more suitable than Si for optical applications. Among many materials investigated, wide band gap semiconductors are of particular interest. ZnO has a very interesting and broad-ranging history in various applications. ZnO is and has been used extensively as a pigment in paints and enamel coatings and as an ingredient in cements, glass, tires, matches, white ink, photocopy flame retardant, cosmetics and dental cements with large scale production as reported by Klingshirn [2007]. These diverse applications rely on various properties of ZnO such as the white colour of the material, its chemical activity, UV absorption capability and bioactivity.

Apart from the above mentioned commercial usages, ZnO has attracted research attention for a long time for many applications in scientific and industrial fields. The first demonstration of the semiconducting properties of ZnO was performed in the 1920s [Jagadish, 2007]. Synthesis and characterization of ZnO has been reported since 1935 [Bunn, 1935]. Recent improvements in the growth of high quality, single crystalline ZnO, in bulk and thin film forms have renewed interest in ZnO. From about 1960s on, synthesis of ZnO thin films has been an attractive field because of the strong potential for applications such as sensors and catalyst. From 1940s it has been known that ZnO can be grown in various forms of nanostructures under variety of growth conditions [Fuller et al., 1944; Park et al., 1967]. In the last few decades, especially since the United States of America led the initiative of
nanotechnology, low dimensional ZnO material study became the leading edge in nanoscience and nanotechnology. At present, the interest in this material is at a peak. It is recognized as one of the most promising materials for applications related to optoelectronics in the blue and UV range due to its wide band gap, promising physical and optical properties [Osinky et al, 2004; Yan et al, 2001].

ZnO also shows good potential for applications in a diverse range of other areas, including spintronic devices [Tang et al., 1998], biomedical sciences [Nigro, 2005] and sensor applications [Ellmer, 2001; Chen, 2005]. It shows promise for space and nuclear applications [Look et al., 2001]. ZnO can also be used as a material for piezoelectric transducers [Zhang, 2006], varistors [Lin, 2006], phosphors [Heitsch, 2006] and transparent conducting films. For these later applications mostly polycrystalline material is suitable, however for light-emitting devices and other high-end electronic devices single crystal thin films or other high crystal quality morphologies are required. More recently extensive research on nanostructured ZnO has made this material even more attractive for various applications. The reduction in size introduces novel electrical, mechanical, chemical and optical properties, which are believed to be due to surface and quantum confinement effects in addition to major improvements in crystal quality for growth on lattice-mismatched substrates. Low dimensional nanostructures of ZnO may improve the efficiency and compactness of electronic and photonic devices including LEDs, optical waveguides and sensors. The structural, electrical, mechanical, chemical and optical properties of such devices have already been improved by the reduced size of ZnO nanostructures.

Zinc oxide (ZnO) is a wide band gap (3.4 eV), II-VI compound semiconductor and has a stable wurtzite structure with lattice spacing $a = 0.325$ nm and $c = 0.521$ nm [Tang et al, 1998]. It has aroused great interest for its unique properties and versatile applications in solar cells [Ellmer et al., 2001], ultraviolet (UV) light emitters [Nicoll et al., 1966; Bagnall et al., 1998; Bano et al., 2010; Klingshirn et al., 1975], piezoelectric devices [Chen et al., 2005] and gas sensors [Comini et al., 2002]. The high excitonic binding energy (~60 meV) makes it a potential candidate for light emission devices [Zhang et al., 2006]. ZnO has an effective electron mass of ~0.24 $m_e$ and exciton Bohr radius of ~1.8 nm.
The unique optoelectronic properties of zinc oxide and the low cost have attracted considerable interest over the last few years. The optical and electrical properties, high chemical and mechanical stability makes ZnO one of the most promising material for transparent conducting oxides (TCO). The availability of ZnO in nature makes it a low cost material than most of the currently used TCO's (SnO₂, ITO and TiO₂).

ZnO has three different crystal structures such as wurtzite, zinc blende and rocksalt as schematically shown in Fig. 1.1. At suitable conditions, the thermodynamically stable phase is wurtzite [Özgür et al., 2005]. The zinc-blende ZnO structure can be stabilized only by growth on cubic substrates, and the rocksalt, NaCl structure may be obtained at high pressures [Özgür et al., 2005]. Structurally, the wurtzite structured ZnO crystal is described as a number of alternating planes composed of four-fold coordinated O²⁻ and Zn²⁺ ions, stacked alternatively along the c-axis [Özgür et al., 2005; Meyer et al., 2003]. The wurtzite structure has a hexagonal unit cell with two lattice parameters, a and c, in the ratio of c/a=8/3 =1.633 and belongs to the space group of C64 or P63mc.

**Figure 1.1:** Representation of ZnO crystal structures: a) cubic rocksalt, b) cubic zinc blende and c) hexagonal wurtzite. The shaded gray and black spheres denote Zn and O atoms, respectively.
Table 1.1 Physical properties and values of ZnO Bulk.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constants (T = 300 K)</td>
<td>$a_0 = 0.32469 \text{ nm}$</td>
</tr>
<tr>
<td></td>
<td>$c_0 = 0.52069 \text{ nm}$</td>
</tr>
<tr>
<td>Density</td>
<td>5.606 g/cm³</td>
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<tr>
<td>Melting point</td>
<td>2248 K</td>
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<tr>
<td>Relative dielectric constant</td>
<td>8.66</td>
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<tr>
<td>Gap Energy</td>
<td>3.37 eV, direct</td>
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<tr>
<td>Exciton binding Energy</td>
<td>60 meV</td>
</tr>
<tr>
<td>Electron effective mass</td>
<td>0.24</td>
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</tbody>
</table>

1.8 One dimensional ZnO nanostructures- nanorods and nanowires

The science of nanomaterials has stimulated research interest in the growth of nanostructures and the investigation of their properties. Nanostructures of wide band gap semiconductor materials are of particular interest for their optoelectronic properties. ZnO, a wide band gap semiconducting oxide is a unique material with diverse properties and its properties can be tailored for semiconducting, piezoelectric and optoelectronic applications. In recent years, among all the other materials, the richest family of nanostructures has been reported for ZnO. These nanostructured materials have been extensively studied because of their potential applications in nanoelectronic devices, such as field-effect transistors [Martel, 1998], single-electron transistors [Kim et al, 2002], photodiodes [Shi et al., 2005], chemical sensors [Gratzel., 2001] and self powered nanogenerators [Wang et al., 2008]. Among these one dimensional semiconducting nanomaterials, there has been considerable attention focused on low-dimensional ZnO nanostructures on account of its many exciting properties including excellent chemical and thermal stability, transparency,
biocompatibility, and wide electrical conductivity range [Wang et al., 2009; Wang et al., 2008]. ZnO has the richest family of nanostructures, which exhibits the most splendid and abundant configurations of nanostructures that one material can form [Wang et al., 2004; Wang et al, 2005; Song et al, 2006; Heo et al., 2004]. ZnO has a wurtzite structure in which the Zn cation and O anions form a tetrahedral coordination. ZnO has two important characteristics: One is the presence of polar surfaces, such as $\text{Zn}^{2+}$ terminated (0001) and $\text{O}^{2-}$ terminate (0001). The interaction of the polar charges at the surface results in the growth of a wide range of unique nanostructures such as nanobelts, nanosprings, nanorings and nanohelicises [Wang et al., 2004; Wang et al., 2005; Song et al., 2006]. Single crystal ZnO nanorod is of particular interest due to its potential applications in emerging area of nanotechnology.

1.9 Present work

The aim of the present work was to synthesize undoped and copper doped nanostructured films of ZnO to characterize these samples and to study their properties. The nanostructured ZnO and copper doped nanostructured ZnO thin films were prepared by the thermal oxidation of respectively nanostructured Zn films and Zn films containing 4% of Cu deposited on glass substrates by vacuum deposition technique at a pressure higher than that used for vacuum coating of thin films. An inert gas (nitrogen) was used in the deposition chamber to maintain the desired pressure. The method of synthesis of the nanostructured films was similar to the gas evaporation technique. X-ray diffraction (XRD) and Transmission Electron Microscopy (TEM) were used for the structural characterization of the film samples. The surface features of the film samples were analyzed by Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM). X-ray photoelectron spectroscopy (XPS) was used to determine the oxidation states of the elements present in the sample. Micro-Raman and UV-Visible spectroscopy were used to further characterize the samples. Photoluminescence spectroscopy was used to study the near band edge emission as well as defect emissions by the nanostructured film samples. DC electrical resistivity measurements were used to study the mechanism of conduction of charge carriers in the nanostructured ZnO and copper doped nanostructured ZnO film samples. The Photocurrent measurements on the nanostructured ZnO films samples were also carried out.