Investigation of Electrical and Optical Properties of Novel ZnO Nano Structures

Islam Uddin

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Dedicated
to
My Parents
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Nano is a familiar prefix used everywhere these days as public interest in nano materials has grown rapidly. The last forty years people have seen a number of crucial technical developments in field. These developments have initiated changes in human life of an unprecedented kind. This period has simultaneously witnessed other landmark developments. The construction of point contact transistor in 1947 rapidly led to intensive research which ultimately led crystallized in the concept and subsequent realization of the information technology (IT) era. In the 1970’s, the information age per se started. We saw stepwise appearance of quartz optical fiber, III-V compound semiconductors and gallium arsenide (GaAs) lasers. During the evaluation of the information age, silicon (Si) occupied a dominant place in the commercial market, as it was used to fabricate the discrete devices and integrated circuits needs of for computing, data storage and communication.

Zinc oxide (ZnO) is a II–VI compound semiconductor with a wide direct band-gap of 3.3 eV and a hexagonal structure. ZnO is often used in the paint, paper, rubber, food and drug industries. It is also a promising material in nanotechnology applications, for example in nanoelectronics and nano-robotic technology. With its wide band-gap, high exciton binding energy and high breakdown strength, ZnO can be utilized for electronic and photonic devices, as well as for high-frequency applications. One-dimensional ZnO nanostructures have great potential applications in the fields of optoelectronic and sensor devices. Therefore, it is really important to realize the growth of ZnO nanostructures and investigate their properties. A physical vapor condensation method is used to synthesize the nanostructures of ZnO. These nanostructures are fabricated by resistive heating of Zn powder at a temperature of 400°C in the presence of oxygen and argon gases under a vacuum of order of 10^-6 mbar. The transmission electron microscope (TEM) images suggest that these nanostructures have some mixed morphology. They contain nanorods as well as nanoparticles. The typical diameter of these nanorods is in the range of 80-150 nm and the length is of the order of several micrometers, whereas the size of the nanoparticles vary from 50-80 nm. Temperature dependence of dc conductivity of these ZnO nanostructures is also studied in the temperature range (303-573K). It is found that the experimental data gives a good fit for thermally activated process. Therefore, it is suggested that thermally activated process is responsible for the transport in these nanostructures.

The main objective for this book to successfully synthesis of ZnO nanostructures with investigation of the electrical and optical properties in detail by the methods of Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM), Field Emission Scanning Electron Microscope (FESEM) etc. The entire book has been divided into six chapters, each of which is a self-contained unit in itself.

**Chapter 1** begins with some basic introduction to nanotechnology and provides a comprehensive introduction to ZnO nanostructures It also provides some historical background and a brief summary of some basic subject matter and definitions.
Chapter 2 presents an extensive review of the subject. This chapter provides some historical connection between the nanotechnology and ZnO nanostructures. It gives an access to most of the basic material on the structure, synthesis, general properties with electrical and optical properties production, growth mechanisms and applications of ZnO nanostructures. Many references are provided from which the reader can obtain more detailed information further.

Chapter 3 deals with techniques of synthesis and characterization of ZnO nanostructures begins with experimental details and the description of the method used to prepare the ZnO nanostructures. This includes synthesis of ZnO nanostructures by physical vapor deposition. It further provides the brief information about the characterization of ZnO nanostructures. Different characterization techniques like SEM, TEM and FESEM adopted for the characterization of ZnO nanostructures are duly incorporated in details and results are given in chapter 4, chapter 5 and chapter 6.

Chapter 4 presents results and discussion on the Electrical Transport Properties of ZnO nanostructures. The growth and characterization of ZnO nanostructures are also discussed along with their results.

Chapter 5 includes optical and electrical characterization of ZnO thin film. It presents results and discussion on the optical and electrical properties of ZnO thin film. The growth and characterization of ZnO nanostructures are also discussed along with their results.

Chapter 6 gives an overview of nanoparticles. It elaborates ways to produce ZnO nanoparticles with characterization including result and discussion.

Dr. Islam Uddin
**List of Symbols and Acronyms**

**Symbols:**

| Symbol | Description |
|--------|-------------|
| µm     | Micrometer  |
| A      | Ampere      |
| Ar     | Argon       |
| Cu     | Copper      |
| E      | Young’s Modulus |
| Fe     | Iron        |
| GHz    | Giga Hertz  |
| GPa    | Giga Pascal |
| H₂     | Hydrogen    |
| H₂O₂   | Hydrogen Peroxide |
| H₂SO₄  | Sulphuric Acid |
| He     | Helium      |
| K      | Kelvin      |
| Li     | Lithium     |
| mA     | Milli-ampere |
| MgO    | Magnesium Oxide |
| Mo     | Molybdenum  |
| NH₃    | Ammonia     |
| Ni     | Nickel      |
| nm     | Nanometer   |
| O₂     | Oxygen      |
| Pd     | Palladium   |
| Pt     | Platinum    |
| Si     | Silicon     |
| TPa    | Tera Pascal |
| V      | Volt        |
| V₅     | Group Velocity |
| W      | Watt        |
| W      | Wein        |
| °C     | Degree Celsius |
| κ      | Thermal Conductivity |
### List of Symbols and Acronyms

**Acronyms:**

| Abbreviation | Description                          |
|--------------|--------------------------------------|
| 0D           | Zero-Dimensional                     |
| 1D           | One-Dimensional                      |
| 2D           | Two-Dimensional                      |
| 3D           | Three-Dimensional                    |
| AC           | Alternating Current                  |
| APCVD        | Atmospheric Pressure Chemical Vapour Deposition |
| CVD          | Chemical Vapour Deposition           |
| DC           | Direct Current                       |
| FET          | Field-Effect Transistor              |
| HRTEM        | High Resolution Transmission Electron Microscopy |
| LPCVD        | Low Pressure Chemical Vapour Deposition |
| MFC          | Mass Flow Controller                 |
| MOCVD        | Metallo-Organic Chemical Vapour Deposition |
| MOSFET       | Metal-Oxide-Semiconductor Field Effect Transistor |
| MPCVD        | Microwave Plasma Chemical Vapour Deposition |
| MWNTs        | Multi-walled Carbon Nanotubes        |
| NT           | Nanotechnology                       |
| PECVD        | Plasma Enhanced Chemical Vapour Deposition |
| RF           | Radio Frequency                      |
| SEM          | Scanning Electron Microscopy         |
| STM          | Scanning Tunneling Microscopy        |
| SWNTs        | Single-walled Carbon Nanotubes       |
| TEM          | Transmission Electron Microscopy     |
| UHVCVD       | Ultra High Vacuum Chemical Vapour Deposition |
| VLS          | Vapour-Liquid-Solid                  |
| XRD          | X-Ray Diffraction                    |
Chapter 1: Introduction

1.1 Background

Nano is a familiar prefix used everywhere these days as public interest in nano materials has grown rapidly. The last forty years people have seen a number of crucial technical developments in field. These developments have initiated changes in human life of an unprecedented kind. This period has simultaneously witnessed other landmark developments. The construction of point contact transistor in 1947 rapidly led to intensive research which ultimately led crystallized in the concept and subsequent realization of the information technology (IT) era. In the 1970’s, the information age per se started. We saw step wise appearance of quartz optical fiber, III-V compound semiconductors and gallium arsenide (GaAs) lasers. During the evaluation of the information age, silicon (Si) occupied a dominant place in the commercial market, as it was used to fabricate the discrete devices and integrated circuits needs of for computing, data storage and communication. Zinc oxide (ZnO) is a II–VI compound semiconductor with a wide direct band-gap of 3.3 eV and a hexagonal structure. ZnO is often used in the paint, paper, rubber, food and drug industries. It is also a promising material in nanotechnology applications, for example in nano-electronics and nano-robotic technology. With its wide band-gap, high exciton binding energy and high breakdown strength, ZnO can be utilized for electronic and photonic devices, as well as for high-frequency applications. To produce such optoelectronic devices, control of electronic properties, such as the nature of conduction and carrier density, is required.

1.2 Moore’s Law

Since Si has an indirect band gap it is not suitable for optoelectronic devices such as light emitting diodes (LED) and laser diodes, GaAs with direct band gap is used instead. Hence the progress is often started by questing the famous Moore’s Law. It states that the number of transistors that can be placed on an integrated circuit is doubling every eighteen months, the increasing demands has been the driving force for the semiconductor industry ever since its beginning. Researchers are working hard to find ways to reduce the size of the transistors to squeeze more transistors inexpensively on the same die size. They have been able to keep up with the pace demand by Moore’s Law. As a result, the dimension of the transistor has shrunk to almost the minimum possible. Ultimately it is governed by underlying semiconductor physics. Scientists are therefore searching for viable alternatives in order keep pace with Moore’s Law and to make new progress possible.

Nanotechnology has recently become a focused research area and has the potential to become one of the key technologies of the new world. Nanotechnology involves the investigation and design of materials or devices close the atomic and molecular levels. One nanometer, a measure equal to one billionth of a meter, spans approximately 10 atoms and one may be able to rearrange matter with atomic precision to an intermediate size. Adopting one of the preceding definitions may however may
unduly restrictive. In a broad survey it is profitable to include anything and everything that has been described as nanotechnology. One may then evolve a framework for classifying and understanding the different types of nanotechnology.

1.3 The Short Scale Limits

In upcoming years, it may become possible to build any detailed object completely at the atomic level, consistent with the laws of physics and chemistry. It may well be that with new insights much of the existing brilliant predictive thought in chemistry and physics may become redundant. According to Richard Feynman, (a Nobel Laureate in 1959), small scale phenomenon may reveal a large number of extraordinary characteristics. In the 21st century, there is global surge in nanotechnology and science.

The two main consequences of miniaturizing a material are: 1) the surface area to volume ratio becomes large and 2) Quantum effects become important. In order to exploit nanotechnology to the full and extent, we must be able to accurately predict the characteristics and properties of materials at the atomic and molecular scale. The nano scale requires a new set of guiding theories and meta principles in order to understand describe and predict phenomenon. To frame such theories, one must investigate measure and build model at this scale. One may then accurately predict the relevant parameters. The present investigation, ZnO nanostructures have been synthesized, characterized and their optical and electrical properties studied.

1.4 ZnO nanostructures

The research interest in ZnO, (one of wide band gap semiconductors,) has increased in recent years. The first enthusiasts who started studies of the lattice parameter were M.L. Fuller in 1929 [1] and C.W. Bunn in 1935 [2]. During the last decade, the ZnO related research has received an increased impetus. The number of articles published on ZnO has steadily increased every year and in 2007, ZnO became the second most popular semiconductor material (after Si). This popularity, to a large extent, is due to the improvements in growth related techniques of single crystalline ZnO (in both epitaxial layers and bulk form). Another reason is emergence of novel electrical, mechanical, chemical and optical properties with reduction in size. They are largely believed to be the result of surface phenomena and quantum confinement effects. Study of one dimensional (1D) materials has become a frontier area in nano science and technology. Functionally ZnO is a versatile material. 1D ZnO nanostructures such as nanotubes [3], nanowires [4], nanorods [5], nanobelts [6], nanocables [7] and nanoribbons [8] have stimulated considerable interest leading to fundamental physics studies, and also to their potential applications in nanoelectronics, nanomechanics, and flat panel displays. Particularly, the optoelectronic device application of 1D ZnO nanostructure has become one of the major focal points in recent nanoscience researches [9-11]. The main advantages of ZnO are a wide band gap, large refractive indices over the infrared and visible ranges, its large exciton binding energy (60 meV) compared to GaN (25 meV), and the existence of well-developed bulk and epitaxial growth processes. For electronic applications, the attractiveness of ZnO lies in its high breakdown strength and high saturation velocity.
Chapter 1: Introduction

It is not surprising that Zinc oxide has received a vast amount of attention in the last few years. This material is both transparent and conductive with a wide variety of applications in both industry and research [Hartnagel et al, 1995]. An important aspect of these is the utilization of ZnO thin films for solar cell applications. Interesting aspects of ZnO include the anisotropy in crystal structure, a wide band gap the optical transparency in the visible range, it’s fairly high refractive index, and its large piezoelectric constant.

1.5 Applications

The applications of nanomaterials are based on the properties of these materials such as (i) peculiar physical properties of nano sized materials, (ii) the huge surface area and (iii) the small size that offers extra possibilities for manipulation and room for accommodating multiple functionalities. Since nanomaterials possess unique, beneficial chemical, physical, and mechanical properties, they can be used for a wide variety of applications. Due to the nanometer size, many of the mechanical properties of the nanomaterials are modified from the bulk materials including the hardness, elastic modulus, fracture toughness, scratch resistance and fatigue strength etc. ZnO is often used in paint, paper, rubber, food and drug industries. It is also a promising material in nanotechnology applications, for example in nano-electronics and nano-robotic technology. With its wide band-gap, high exciton binding energy and high breakdown strength, ZnO can be utilized for electronic and photonic devices, as well as for high-frequency applications. To produce such optoelectronic devices, control of electronic properties, (such as the nature and magnitude carrier density), is required. A few applications of ZnO are mentioned below.

ZnO nanostructures are used for sensing applications because of their high sensitivity to the chemical environment. Nanostructures have the advantage of a high surface area, and electronic processes are strongly influenced by surface processes. ZnO nanowires have demonstrated high sensitivity even at room temperature, whereas thin-film gas sensors often need to be operated at elevated temperatures. The sensing process is governed by oxygen vacancies on the surface that influence the electronic properties of ZnO. Upon oxidation, (via adsorption of molecules such as NO2 at vacancy sites that accept electrons), electrons are withdrawn and effectively depleted from the conduction band, leading to a reduction of conductivity. On the other hand, reducing molecules (such as those of H2) can react with surface-adsorbed oxygen, leaving behind an electron and a higher conductivity. The challenge is to sense certain gases selectively. A ZnO nanorods H2 sensor has now been developed [12]. The sensitivity of this sensor was improved by sputter deposition of Pd clusters on the ZnO rod surface. The addition of Pd appears to be effective in the catalytic dissociation of H2 into atomic hydrogen, increasing the sensitivity of the sensor device. The sensor detects hydrogen concentrations down to 10 ppm (in N2 at room temperature), whereas there is no response to O2. By exposing the sensor to air or O2, the conductance recovers up to 95% after 20 s. The same investigation has also shown H2 sensitivity for Pt-coated ZnO nanorods [13]. A different group used a thick film of ZnO nanoparticles for H2 sensing [14]. A sensitivity of 10-1000 ppm H2 was achieved for a Pt-impregnated, 3% Co-
doped ZnO nanoparticles film at a working temperature of 125°C or lower. O2, NO2, and NH3 oxidizing sensors in field–effect transistor geometry of single nanowires has also been demonstrated. The oxygen sensitivity is higher for smaller diameter nanowires and can be modulated by the gate voltage. Distortion of adsorbed NO2 molecules is observed when a large negative gate voltage is applied. This can be used as a method to store the sensor to its original level. An ethanol sensor with good sensitivity and fast response at 300°C has been demonstrated using Pt interdicting electrodes. Tetrapod-films prepared in a flow of humidified Ar show excellent performance in sensing ethanol with a short response time. A photo current gas sensor made of Ru-sensitized ZnO nano particles has been shown to be highly influenced by the gas molecules adsorbed on the surface. Presence of CO molecule increases the number of electrons on the surface of ZnO and, therefore, leads to an increase in photoconductivity. On the contrary, O2 can capture electrons directly on the surface and lower the concentration of charge carriers in the ZnO conduction band and, therefore, the photoconductivity. 

A glucose sensor based on ZnO nanorods has also been reported. The negatively charged glucose oxides (GOx) enzyme is immobilized on positively charged ZnO through electrostatic forces. At an applied potential of +0.8 V versus an Ag/AgCl reference electrode, the glucose biosensor shows a linear response from 0.01-3.45 mM and experiment limit of detection of 0.01 mM. The response time was less than 5 s.

Bao et al [14] have constructed a single nanowires light-emitting diode. They disperse ZnO nanowires on a Si substrate and then a poly (methyl methacrylate), or PMMA, thin film is spin-coated onto the substrate. The wire is imaged in a focus ion beam (FIB) system and a pattern for e-beam exposure of the PMMA is defined. The unexposed and partially exposed PMMA is removed and then a metallic contact is deposited onto the top surface of a single nanowires. In this way, the researchers are able to measure the current-voltage characteristics, photoluminescence, and electroluminescence of a single nanowires. Lee et al [15] have proposed the use of well-aligned single-crystalline nanowires to be used as sharp Atomic Force Microscopy (AFM) tips. They predict that ZnO nanowires are structurally compatible with AFM cantilevers under typical operating conditions and are promising candidates for high-aspect-ratio probes for AFM. Huang et al [16] have characterized the mechanical resonances of a single nanowire using an alternating electric field. They have monitored the flexural mode of the nanowires in situ in a Transmission Electron Microscope (TEM). With an elastic bending modulus of ~58 GPa and a damping time constant of ~14 ms for the resonance in vacuum, the investigators conclude that a single ZnO nano wire can be used as a nano resonator and a nanoscale cantilever.

Recently, ZnO has been used in dye-sensitized solar cells as an electrode material [17-20]. Investigations of nano porous dye-sensitized ZnO films have shown that ultrafast electron injection from the dye into the conduction band of the ZnO particles takes place [21-24] comparable to the time scale of electron injection into TiO2 layers, which has been the subject of investigation for a long time [25].

Semiconductors should have a wide band gap, high charge carrier mobility, and films fabricated from the material need to deliver a high surface area for efficient dye-sensitization and light harvesting, which
can only be achieved by a nanostructure film. Therefore, ZnO seems to be a promising material for this type of solar cell and has the advantage over other metal oxides of easy synthesis of controlled nanostructures. Dye-sensitized solar cells usually have an electrolyte (redox system) to regenerate the dye by electron donation to its ground state after excitation.

1.6 Zinc Oxide Synthesis Techniques

ZnO can be deposited by a variety of techniques such as physical vapor condensation method, radio frequency sputtering [Igasaki et al, 1991], direct current magnetron sputtering [Meng et al, 1995], spray pyrolysis [Song et al, 1994], and chemical vapor phase deposition [Manimi et al, 1997]. The material properties (i.e. optical and electrical properties) of the ZnO thin film is critically related to the specific growth technique employed and to the growth parameters used. There are many methods to synthesize ZnO but the method which is used mostly is vapor transport process. In this process Zn and Oxygen are transported and due to a reaction nanostructure ZnO is formed. The decomposition of ZnO is a very simple and direct method and it is applicable up to very high temperature ~1400 °C. The second method is to heat up Zn Powder under Oxygen flow. The temperature required for this method is smaller (around 500 °C to 700 °C). The vapor transport process is divided in two categories; Vapor Solid (VS) and Vapor Liquid Solid (VLS) process, depending upon the nano structure formed. ZnO nanostructures and nanobelts were synthesized by kong et al. In other vapor transport condensation process reported by Ren et al. nanostructures were grown. To achieve nanowires, nanostructures, and nanorods, Yao et al have reported a process in which Zn powder was mixed with graphite and heated to 1100 °C. The growth of nano tetrapod was found in catalyst free process. There was a report by Wat et al for the rapid heating of Zn pellet at 900 °C in the presence of ambient air. There is other method of synthesis (though vapor transport is dominant) such as electro deposition, solution gel, and polymer assisted growth. These methods operate at low temperature. A variety of methods exist for ZnO deposition and growth. For consolidation, methods have been categorized as either physical vapor deposition (PVD), chemical vapor deposition (CVD), or solution-based chemistry (SBC) [26].

1.7 Characterization Techniques

After the preparation of the samples, different characterization techniques were used to investigate their structure and optical properties. Scanning Electron Microscope (SEM) was used to get the morphology of the samples. An Atomic Force Microscope (AFM) was utilized to detect the morphology of pretreated substrates. The detailed information about the structure of the samples can be obtained from XRD measurement. The optical properties were investigated by UV spectrometer by absorption and transmission spectra.

1.7.1 Scanning Electron Microscope

The Scanning Electron Microscope (SEM) is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons
interact with the atoms to make the sample producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity. The types of signals produced by a SEM; include secondary electrons, back scattered electrons (BSE), characteristic x-rays, light (cathode luminescence), specimen current and transmitted electrons. These types of signal all require specialized detectors for their detection that are not usually all present on a single machine.

1.7.2 Transmission Electron Microscope (TEM)

Transmission Electron Microscope has been used traditionally as a tool for characterizing local atomic structures of material objects since the information obtained does not require the objects being periodic such as crystal. In the characterization of ZnO nanostructures, TEM is one of the most powerful instruments available due to its excellent imaging and analytical capabilities. TEM imaging allows both the imaging of relatively large areas and the precise measurement of nanostructures diameters. The TEM has a very high magnification and can give detailed information about the structure of even a single nanostructure. The nanostructures appear ‘transparent’ in the TEM pictures, which enables the measurement of both inner and outer diameter. It is also possible to determine the number of layers in a nanostructures tube wall and whether it contains any type of structural damage or irregularities. Another type of interesting observation permitted by the TEM is the shape and location of any residual catalyst that may be incorporated in the tube.

One disadvantage with the TEM is that it has to be manually calibrated by taking pictures of special calibration particles several times during each experimental session. The beads have a known size, which is used to compare and calculate the measurements of the particles in the sample. It can also be argued that the TEM is too powerful to generate a fair interpretation of a nanostructures sample. It is far too tempting to concentrate on details rather than on the general picture. Therefore, a SEM or an optical microscope is likely to give a more accurate overall view than a TEM, except when very short (<100 nm) nanostructures are present. The inner structure of the as prepared ZnO nanostructures synthesized by LPCVD was confirmed by TEM.

1.8 Optical properties of ZnO

In condensed matter physics a band gap, also called an energy gap or band gap, is an energy range in a solid where no electron states exist. It is the amount of energy required to free an outer shell electron from its orbit about the nucleus to a free state. The term "band gap" refers to the energy difference between the top of the valence band and the bottom of the conduction band; electrons are able to jump from one band to another. In order for an electron to jump from a valence band to a conduction band, it requires a specific minimum amount of energy for the transition. The required energy differs for different materials. Electrons can gain enough energy to jump to the conduction band by absorbing either a phonon or a photon. The band gap energy of semiconductors tends to decrease with increasing temperature. When temperature increases, the amplitude of atomic vibrations increased, leading to
larger inter atomic spacing. The interaction between the lattice phonons and the free electrons and holes will also affect the band gap to a smaller extent.

The optical properties of a semiconductor have their genesis in both intrinsic and extrinsic effects. Intrinsic optical transitions take place between the electrons in the conduction band and holes in the valence band, including excitonic effects due to the Coulomb interaction. Excitons are classified into free and bound excitons. In high quality samples with low impurity concentrations, the free excitons can also exhibit excited states, in addition to their ground-state transitions. Extrinsic properties are related to dopants/impurities or point defects and complexes, which usually create electronic states in the band gap, and therefore influence both optical absorption and emission processes. The electronic states of the bound excitons, which may be bound to neutral or charged donors and acceptors, depend strongly on the semiconductor material, in particular the band structure. For a shallow neutral donor bound exciton, for example, the two electrons in the bound exciton state are assumed to pair off into a two-electron state with zero spin. The additional hole is then weakly bound in the net hole-attractive Coulomb potential set up by this bound two-electron aggregate. Similarly, neutral shallow acceptor bound excitons are expected to have a two-hole state derived from the topmost valence band and one electron interaction. Other extrinsic transitions could be seen in optical spectra such as free-to-bound (electron acceptor) and bound-to-bound (donor-acceptor).

Optical properties and processes in ZnO as well as its refractive index were extensively studied many decades ago. The renewed interest in ZnO is fuelled and fanned by its prospects in optoelectronics applications owing to its direct wide band gap of 3.37 eV at room temperature with large exciton energy of 60 meV and efficient radioactive recombination. The strong exciton binding energy, which is much larger than that of GaN (25 meV), and the thermal energy at room temperature (25 meV) can ensure an efficient exciton emission at room temperature under low excitation energy. As a consequence, ZnO is recognized as a promising photonic material in the blue-UV region. Optical properties and processes in ZnO as well as its refractive index were extensively studied many decades ago. The renewed interest in ZnO is fuelled and fanned by its prospects in optoelectronics applications owing to its direct wide band gap of 3.37 eV at room temperature with large exciton energy of 60 meV and efficient radiative recombination. The strong exciton binding energy, which is much larger than that of GaN (25 meV), and the thermal energy at room temperature (25 meV) can ensure an efficient exciton emission at room temperature under low excitation energy. As a consequence, ZnO is recognized as a promising photonic material in the blue-UV region.

The optical properties of ZnO, such as photoluminescence, photoconductivity and absorption, reflectance the intrinsic direct band gap, a strongly-bound exciton state, and gap states due to point defects. A strong room temperature near band-edge UV photo luminescent peak at ~3.2 eV is attributed to an exciton state, as the excitation binding energy is of the order of 60 meV. Optical transitions in ZnO have been studied by a variety of experimental techniques such as optical absorption, transmission, reflection, photo reflection, spectroscopic ellipsometry, photoluminescence, cathode luminescence and calorimetric spectroscopy.
Electrical Properties of ZnO

Electrical conductivity is a measure of a material's ability to conduct an electric current. When an electrical potential difference is applied across a conductor its movable charges flow, giving rise to an electric current. Due to its physical properties (e.g., high excitonic binding energy, high saturation velocity, high piezoelectric constant) the wide-band-gap semiconductor ZnO is a very promising material for electronic and optoelectronic devices. Such devices include high power, high speed electronics, chemical sensors and blue or UV light emitters. However, most of these applications are currently hampered by the lack of control over the electrical conductivity. A conductor such as a metal has high conductivity and a low resistivity. An inductor like glass or a vacuum has low conductivity and a high resistivity. The conductivity of a semiconductor is generally intermediate, but varies widely under different conditions, such as exposure of the material to electric fields or specific frequencies of light, and, most important, with temperature and composition of the semiconductor material. The degree of doping in solid state semiconductors makes a large difference in conductivity. More doping leads to higher conductivity. The conductivity of a solution of water is highly dependent on its concentration of dissolved salts and sometimes other chemical species which tend to ionize in the solution. Electrical conductivity of water samples is used as an indicator of how salt-free, ion-free, or impurity-free the sample is; the purer the water, the lower the conductivity. Electrical conductivity is strongly dependent on temperature. In metals, electrical conductivity decreases with increasing temperature, whereas in semiconductors, electrical conductivity increases with increasing temperature. Over a limited temperature range, the electrical conductivity can be approximated as being directly proportional to temperature. In order to compare electrical conductivity measurements at different temperatures, they need to be standardized to a common temperature.

It is well known that there is a strong correlation between structural characteristics of the thin films and their electronic transport properties. On the other hand, a heat treatment of the films may modify these structural characteristics. Consequently, in situ measurement of some electrical properties such as the electrical resistivity of thin films during their heat treatment may offer very useful information about possible changes in the film structure determined by the heating process. Keeping in mind this assumption, the temperature dependence of the electrical resistivity, $\rho$, during heating of the Zn films was measured in the temperature range 290–660 K to emphasize the oxidation process. The degree of doping in solid state semiconductors makes a large difference in conductivity. Electrical conductivity is strongly dependent on temperature. In metals, electrical conductivity decreases with increasing temperature, whereas in semiconductors, electrical conductivity increases with increasing temperature. Over a limited temperature range, the electrical conductivity can be approximated as being directly proportional to temperature. (In order to compare electrical conductivity measurements at different temperatures, they need to be standardized to a common temperature). This dependence is often expressed as a slope in the conductivity vs temperature graph.
1.10 About this Book

The main objective for this book is to successfully synthesis of ZnO nanostructures with investigation of the electrical and optical properties in detail by the methods of Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM), Field Emission Scanning Electron Microscope (FESEM) etc. In this book, physical vapor deposition is used to grow ZnO nanostructures on glass substrates. One the other hand, the electrical and optical properties of ZnO nanostructures were investigated in detail. This book not only provides the effective way to synthesize, but also obtains some beneficial results in aspects of their optical properties and electrical optical properties with experimental foundation for much better and broader applications of ZnO nanostructures.

In the present work, the electrical conductivity and optical properties of ZnO nanostructures have been studied. For electrical measurements, we have measured conductivity in a certain temperature range. It is observed that the conductivity increases with the increase in temperature. There are several models available in the literature to explain this type of behavior. The optical properties of nano crystalline materials have been found to be exciting from both the scientific and technological point of view. The optical band gap of semiconductors and the optical transparency behavior of materials could be altered by controlling the grain and/or pore size in the nano crystalline state. For example, the band gap in CdSe semiconductor could be changed from 3.0 eV for clusters of 1.2/1.5 nm to 2.3 eV for cluster sizes of 3.0/3.5 nm due to quantum confinement effects; the bulk material has a band gap of 1.8 eV. The reduction of material dimensions has pronounced effect on the optical properties. The objectives of this investigation are synthesis, characterization, and study of optical & electrical properties of ZnO thin films. SEM was used to examine surface morphology, especially the influence of annealing. X-Ray Diffraction (XRD) was used to identify the crystal phases and lattice parameters. We have used inert gas condensation method. In this method, Zn is evaporated in the presence of oxygen and inert gas (Ar) and the resulting nanorods and nano particles of ZnO are collected on the Glass substrate. This Glass substrate is cooled with the help of liquid Nitrogen. After successful synthesis of these nanostructures, we have studied the electrical and optical properties of ZnO nanostructure. In electrical properties the temperature dependence of dc conductivity is studied to understand the conduction mechanism in these nanostructures. As for optical properties, the optical absorption is studied with the help of absorption spectra. We have calculated the optical band gap of these nanostructures. In the subsequent chapters the details of experimental procedure, literature review measurements of optical and electrical properties and conclusion will be presented.
Chapter 1: Introduction

1.11 References

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Chapter 2: ZnO Nanostructures-An Overview

2.1 Preliminaries

Zinc Oxide is found in nature as the mineral Zincite [1], ‘Zincum Oxydatum’ is the Latin name of Zinc Oxide and it is commonly used in homeopathic medicines. The chemical formula of Zinc oxide is ZnO. Zinc oxide is a type of material which exhibits semiconducting and piezoelectric dual properties (in its crystalline form). Zinc Oxide is a ‘direct band gap’ and wurtzite (hexagonal) type semiconductor; it has band gap energy of 3.37 eV at room temperature. It is insoluble in water but easily soluble in acids and alkalis. It is also thermo chromic i.e. it changes color when heated (from white to yellow) and regains the original color when cooled down. When Zinc Oxide comes in contact with air it forms, a nervous malady called metal fume fever. The ZnO nanostructure has many applications in optoelectronics, sensors, and transducers and in the biomedical field. ZnO nanobelts can also be used as nanosensors, nanocantilevers, field effect transistors and nanoresonators. The lack of centre of symmetry in wurtzite combined with large electrochemical coupling, results in strong piezoelectric and pyroelectric properties. Consequently, ZnO is used in mechanical actuators and piezoelectric sensors. Due to its wide band gap, it is suitable for short wavelength optoelectronic applications.

The chemical formula of Zinc oxide is ZnO. Zinc oxide is an important material for a variety of practical applications; therefore, it has been under intensive investigation since the 1950s [2]. It is used as a pigment in paints, filler for rubber goods, in coatings for paper, as safe food additives and drugs [3]. Zinc peroxide, ZnO2·1/2H2O, is used in antiseptic ointments. Zinc oxide is also a semiconductor with a direct band gap of ~3.3 eV (387 nm, deep violet/borderline UV) which make it a possible candidate as a white light source when combined with certain types of phosphors by comparison (current light sources consume more than 20% of world electricity) [4]. Such solid-state light sources offer huge advantages in energy efficiency. Because of the wide band gap, zinc oxide absorbs ultraviolet light; thus, it can be used in ointments, creams and lotions to protect against sunburn. However, in terms of future use, the major interest lays in semiconductor applications, due to the increasing need for near-ultra-violet optoelectronic devices. ZnO is a candidate for solid state ‘blue to UV optoelectronics’, including lasers. Its light sensitivity makes it a potential detector of radiation in the UV spectrum. Crystalline zinc oxide also exhibits the piezoelectric effect.

2.2 Research Directions

Research on the properties of bulk ZnO has been going on for quite a long time and it has found a number of uses within a variety of common products. On a day to day basis, most people probably come into contact with
it in sun screen and calamine lotion. The reason for its prominent use in sun screen goes back to the previously mentioned fact that it is transparent in visible spectrum and that it absorbs both UV A and UV B light. The more high-tech uses of ZnO have been in gas sensors and in the last couple of years blue LEDs. ZnO phosphors in the form of powders have in the past been the main focus of the scientific community. The ZnO phosphors usually appear as a strong green and efforts were to determine the origin of this color. A few reports would occasionally describe the appearance of other colors, such as red, which today are sometimes seen in nanostructures as well. From this point onwards research began into the creation and characterization of thin films. Many similar observations [3-10] were made as with the phosphors, such as green luminescence, but new observations were also made such as strong NBE emission. In fact, at low temperatures, a significant number of very fine and sharp peaks associated with bound excitons are usually present. There are various types of synthesis techniques that have been shown to create various nano sized morphologies. One of the earlier reports [6] of ZnO nanoparticles colloids shows a chemical reaction where Zn$^+$ and OH$^-$ precipitated from an alcoholic solution. In recent years either a hydrothermal or sol-gel method became two of the most popular. The downside to these techniques is that unless the particles’ surfaces are capped in a dielectric, the NBE emission will be significantly weaker than the defect emission. Since the particles created hydro thermally or through a sol-gel process must be dipped coated onto a substrate, a secondary process must then be used to do the capping. Various research groups [7] have also looked into the use of ion implantation for the creation of particles within a substrate. This is done by first implanting the substrate, usually SiO$_2$, with Zn ions and then a second time with O ions. After a subsequent annealing that varied from 300 to 700 °C, photoluminescence emissions near the band gap were found to be present. The growth process of the particles has been theorized to be a reverse Ostwald ripening. As the annealing temperature increases the intensity of the NBE emission increased.

One of the more important things to note is that even within the same synthesis procedure; there is a considerable variation in properties from batch to batch. There are a number of possible reasons for this, but usually the amount of oxygen in the environment is considered to be the culprit. Variations in other chemicals or impurities also play big roles. When it comes to the shapes of the particles, they can range from spherical, shells, rods, tetrahedrons, propellers, and many others. There have been reports that claim a link between the particle shape and spectra that is emitted, however looking across the literature as a whole, the connection between shape and properties appears to be unconvincing. Based on the wide variety of emissions seen within a given type of structures some other mechanism must be at work. Usually the NBE of as grown particles is rather weak and the defect emission, whether it is blue, green, yellow, orange, or red, is much stronger. One among the more interesting studies was from Shalish et al [8], who looked at nanorods of various sizes. They found that below a rod of radius 30 nm that the defect emission dominated the photoluminescence (PL) spectra, while above this size the NBE dominated. What they reasoned is that the defect emission is related to a recombination at the surface while the NBE emission is related to a recombination within the bulk of the material. This seems quite reasonable, since as the diameter of the rod becomes smaller, the ratio of the no. of atoms near the surface as compared to the bulk increases.
2.3 Basic Parameters

Zinc oxide (ZnO), an amorphous white or yellowish powder, has the molecular weight of 81.37, average atomic weight of 40.69 amu and an enthalpy of formation (298.15K) of 350.5 kJ/mol. Two main processes are employed for producing powdered zinc oxide. In the direct, or American, method of manufacture, zinc ores (or residues) are heated in air with coke or anthracite, and the resulting zinc vapour is subjected to controlled oxidation. In the indirect, or French, process, the zinc vapor to be oxidized is obtained by boiling zinc [9].

2.4 Structural, Electrical and Optical Properties of ZnO

ZnO normally forms in the hexagonal (Quartzite) crystal structure (6mm point group symmetry) with $a=3.25$ Å and $c=5.12$ Å. The Zn atoms are tetrahedral coordinated to four O atoms [6, 7] (Figure 2.1). The oxygen anions occupy the octahedral sites. The basic parameters of ZnO materials are presented in Table 2.1. As seen in Figure 2.2, the structure is non-centro symmetric, which gives rise to polarization and piezoelectric properties.

![Figure 2.1: Wurtzite (hexagonal) structure of ZnO [6, 7]](image1)

![Figure 2.2: Wurtzite (hexagonal) structure of ZnO](image2)
Chapter 2: ZnO Nanostructures - An Overview

Table 2.1: Properties of Wurtzite ZnO

| Property                          | Value                                                                 |
|----------------------------------|----------------------------------------------------------------------|
| Lattice parameters at 300K       | $a = 0.32495 \text{ nm}, c_0 = 0.52069 \text{ nm}$                |
| Density                          | 5.6803 g/cm$^3$                                                      |
| Melting point                    | 1975°C                                                               |
| Thermal conductivity             | 100 mW/cm.$^2$K at 300K                                             |
| Static dielectric constant       | 8.656                                                                |
| Refractive index                 | 2.008                                                                |
| Energy gap                       | 3.4 eV, direct                                                       |
| Intrinsic carrier concentration  | $< 10^6 \text{ cm}^{-3}$ (max n-type $> 10^{20} \text{ cm}^{-3}$ electrons; max p type $< 10^{17} \text{ cm}^{-3}$ holes) |
| Exciton binding energy           | 60 meV                                                               |
| Electron effective mass          | 0.24                                                                |
| Electron Hall mobility at 330K   | 200 cm$^2$/Vs                                                        |
| Hole effective mass              | 0.59                                                                |
| Hole Hall mobility at 300K       | 5-50 cm$^2$/Vs                                                       |

In the development of a crystalline morphology, the driving forces minimize the surface energy. Therefore, in near equilibrium conditions, a film grows with the crystallographic plane of the lowest free energy (i.e. the plane with the closest packing of atoms) parallel to the surface if no epitaxial exists between the film and substrate. ZnO tends to grow c axis oriented normal to the substrate with minimization of surface energy. ZnO is an II-
VI semiconductor which tends to intrinsically form as an n-type semiconductor material, in which the electrical conductivity is due to excess zinc, presumably interstitially within the lattice and in oxygen vacancies [9, 10]. Extrinsic defects such as hydrogen are more likely to be incorporated as shallow donors [10]. However, Studenkin et. al. [2] has reported that the effect of H incorporation increases the number of zinc rich defects and therefore n type conductivity. The defect chemistry for individually ionized Zn in vapor deposition can be written as follows [11]:

\[
\begin{align*}
\text{Zn(g)} & \rightarrow \text{Zn}_i & (2.1) \\
\text{Zn}_i & \rightarrow \text{Zn}_i^+ + e^- & (2.2) \\
\text{Zn(g)} + \frac{1}{2}\text{O}_2(g) & \rightarrow \text{ZnO(s)} & (2.3)
\end{align*}
\]

Therefore, the overall concentration of interstitial ions is determined by the vapor pressure (usually high for Zn) as indicated in equation (2.1). The extent of interstitial ionization is also a dependent of temperature. The mass-action equation for (2.2) is:

\[
K = \frac{[\text{Zn}_i^+][e^-]}{P_{\text{Zn}(g)}} = \frac{[e^-]^2}{P_{\text{Zn}(g)}}
\]

(2.4)

where KO2 is the equilibrium constant for the reaction (2.3). It can be seen from equation (2.5) that the charge carrier concentration is a dependent of the partial pressure of oxygen. A general expression for electrical conductivity \( \sigma \) and the concentration of conduction electrons \( n \) and holes \( p \) in an intrinsic semiconductor is the following:

\[
\sigma = n e \mu
\]

(2.6)

\[
n_i = p_i = A T^{3/2} \exp \left( \frac{-E_g}{2 k_B T} \right)
\]

(2.7)

where \( n_i \) or \( p_i \) is the number of conduction electrons or holes in unit volume, \( e \) is electronic charge, and \( \mu \) is the mobility of current carriers, \( A \) is a constant, \( E_g \) is the energy gap, and \( k_B \) is the Boltzmann constant. Generally speaking there would appear to be five possible conduction mechanisms including: ionic conduction; space-charge-flow; tunneling and internal field emission; Schottky emission and impurity conduction [12]. There are few reports about the electrical conduction mechanism in ZnO. Hartmann et al [12] have showed that copper implantation of ZnO thin films deposited by sputtering decreases the resistivity, while oxygen annealing
increases the resistivity of the ZnO thin film due to electron trapping by the Cu 3d states of Cu$^{2+}$. It has been recognized that the presence of Al or Co has the effect of enhancing the electrical conductivity of ZnO thin films, whereas mono valent ions (Li, Na) usually hinder it [13]. The electron Hall mobility in ZnO single crystals is in the order of 200 cm$^2$/Vs at room temperature. Electron doping, in nominally undoped ZnO, has been attributed to Zn interstitials, oxygen vacancies or hydrogen. The optical properties of ZnO, such as photoluminescence, photoconductivity and absorption, reflect the fact that it has an intrinsic direct band gap, a strongly-bound exciton state, and gap states due to point defects [14]. A strong room temperature near band-edge UV photo luminescent peak at $\sim$3.2 eV is attributed to an exciton state, as the excitation binding energy is of the order of 60 meV [8].

2.5 Applications of ZnO

ZnO is often used in the paint, paper, rubber, food and drug industries. It is also a promising material in nanotechnology applications, for example in nano-electronics and nano-robotic technology. With its wide band-gap, high exciton binding energy and high breakdown strength, ZnO can be utilized for electronic and photonic devices, as well as for high-frequency applications (Figure 2.3).

![Applications of ZnO](image-url)
To produce such optoelectronic devices, control of electronic properties, such as the nature of conduction and carrier density, is required. A few examples of applications of ZnO are discussed below.

2.5.1 Sensors

ZnO nanostructures are used for sensing applications because of their high sensitivity to the chemical environment. Nanostructures have the advantage of a high surface area, and electronic processes in them are strongly influenced by surface processes. ZnO nanowires have demonstrated high sensitivity even at room temperature, whereas thin-film gas sensors often need to be operated at elevated temperatures. The sensing process is governed by oxygen vacancies on the surface that influence the electronic properties of ZnO. Upon oxidation, via adsorption of molecules such as NO\textsubscript{2} at vacancy sites that accept electrons, electrons are withdrawn and effectively depleted from the conduction band, leading to a reduction of conductivity. On the other hand, reducing molecules such as those of H\textsubscript{2} can react with surface-adsorbed oxygen, leaving behind an electron and a higher conductivity. The challenge is to sense certain gases selectively. A ZnO nanorods H\textsubscript{2} sensor has been developed [12]. The sensitivity of this sensor was improved by sputter deposition of Pd clusters on the ZnO rod surface. The addition of Pd appears to be effective in the catalytic dissociation of H\textsubscript{2} into atomic hydrogen, increasing the sensitivity of the sensor device. The sensor detects hydrogen concentrations down to 10 ppm in N\textsubscript{2} at room temperature, whereas there is no response to O\textsubscript{2}. By exposing the sensor to air or O\textsubscript{2}, the conductance recovers up to 95% after 20 s. The same group has also shown H\textsubscript{2} sensitivity for Pt-coated ZnO nanorods [13].

Other workers used a thick film of ZnO nanoparticles for H\textsubscript{2} sensing [14]. A sensitivity of 10-1000 ppm H\textsubscript{2} was achieved for a Pt-impregnated, 3% Co-doped ZnO nanoparticles film at a working temperature of 125°C or lower. O\textsubscript{2}, NO\textsubscript{2}, and NH\textsubscript{3} oxidizing sensors in field-effect transistor geometry of single nanowires has also been demonstrated. The oxygen sensitivity is higher for smaller diameter nanowires and can be modulated by the gate voltage. Desorption of adsorbed NO\textsubscript{2} molecules is observed when a large negative gate voltage is applied. This can be used as a method to refresh the sensor to its original level. An ethanol sensor with good sensitivity and fast response at 300°C has been demonstrated using Pt interdicting electrodes. Tetrapod-films prepared in a flow of humidified Ar show excellent performance in sensing ethanol with a short response time.

A photocurrent gas sensor made of Ru-sensitized ZnO nanoparticles has been shown to be highly influenced by the gas molecules adsorbed on the surface. A CO molecule increases the number of electrons on the surface and lower the concentration of charge carriers in the ZnO conduction band and, therefore, leads to an increase in photoconductivity. On the contrary, O\textsubscript{2} can capture electrons directly on the surface and lower the concentration of charge carriers in the ZnO conduction band and, therefore, the photoconductivity. A glucose sensor based on ZnO nanorods has also been reported. The negatively charged glucose oxidase (GOx) enzyme is immobilized on positively charged ZnO through electrostatic forces. At an applied potential of +0.8 V versus an Ag/AgCl reference electrode, the glucose biosensor shows a linear response from 0.01-3.45 mM and an experiment limit of detection of 0.01 mM. The response time has been found to be less than 5 s.
2.5.2 Light-emitting diodes and lasing

Bao et al [14] have constructed a single nano wire light-emitting diode. They disperse ZnO nano wires on a Si substrate and then a poly (methyl methacrylate), or PMMA, thin film is spin-coated onto the substrate. The wire is imaged in a focus ion beam (FIB) system and a pattern for e-beam exposure of the PMMA is defined. The unexposed and partially exposed PMMA is removed and then a metallic contact is deposited onto the top surface of a single nano wire. In this way, the researchers were able to measure the current-voltage characteristics, photoluminescence, and electroluminescence of a single nano wire.

2.5.3 Cantilevers

Lee et al [15] have proposed the use of well-aligned single-crystalline nano wires as sharp atomic force microscopy (AFM) tips. They predict that ZnO nano wires are structurally compatible with AFM cantilevers under typical conditions and are promising candidates for high-aspect-ratio probes for AFM. Huang et al [16] have characterized the mechanical resonances of a single nano wire using an alternating electric field. They have monitored the flexural mode of the nano wire in situ in a transmission electron microscope (TEM). With an elastic bending modulus of ~58 GPa and a damping time constant of ~14 ms for the resonance in vacuum, the authors conclude that a single ZnO nano wire can be used as a nano resonator and a nanoscale cantilever.

2.5.4 Solar cell

ZnO has also been used in dye-sensitized solar cells as an electrode material [17-20]. Investigations of nano porous dye-sensitized ZnO films have shown that ultrafast electron injection from the dye into the conduction band of the ZnO particles takes place [21-24] at a time scale comparable to that of electron injection into TiO2 layers; which has been the subject of investigation for a long time [25]. Semiconductors should have a wide band gap, high charge carrier mobility, and films fabricated from the material need to deliver a high surface area for efficient dye-sensitization and light harvesting, which can only be achieved by a nanostructure film. Therefore, ZnO seems to be a promising material for this type of solar cell and has the advantage over other metal oxides of easy synthesis of controlled nanostructures. Dye-sensitized solar cells usually have an electrolyte (redox system) to regenerate the dye by electron donation to its Ground state after action.

2.6 Current Developments in ZnO

2.6.1 n and p Type ZnO

For ZnO, n-type conductivity is common in the as grown material, or relatively easy to realize via excess Zn, or with Al, Ga, or In doping. Reports indicate that the resistivity of ZnO or Al doped ZnO thin films prepared by magnetron sputtering are in the range of $10^4$ to $10^5$ Ω cm [30, 31]. A common opinion is that Zn-rich defects such as zinc interstitials (Zn$_i$) and oxygen vacancies (V$_O$) are the main source of conductivity in as grown material. Thus, the conductivity of films can be determined by the degree of non-stoichiometry of ZnO. It has been found that many factors affect the electrical properties of ZnO thin films such as film thickness, grain and agglomerate size, grain boundary and impurity distribution, all of these are determined by the synthesis conditions. However, the effect of microstructure on the electrical properties of ZnO thin films and related
correlations has not been widely discussed in the literature. Without question, the most significant barrier to the widespread exploitation of ZnO related materials in electronic and photonic applications is the difficulty in carrier doping, particularly as it relates to achieve p-type material. With respect to p-type doping, ZnO displays significant resistance to the formation of shallow acceptor levels. The shallow level is shown in Figure 2.4, the band model of ZnO [32, 33]. The model consists of conduction band and valance band. The energy difference between them is the energy gap of ZnO, \( \sim 3.37 \) eV. The Fermi energy is the maximum energy level occupied by an electron at 0K.

![Figure 2.4: The band model of ZnO](image)

### 2.6.2 ZnO and Nanotechnology

Nanoscience and nanotechnology involve studying and working with matter on an ultra-small scale from sub nanometer to several hundred nanometers [48]. These nano size materials have properties that are often significantly different from their counterparts with “ordinary size”. Nanotechnology is the next phase of Moore’s Law. This law was predicted in 1965 that the dimension of a device would halve approximately every 18 months. By combining silicon innovations with other novel non-Si nanotechnologies, it is expected that Moore's Law will extend well into the next decade [49]. ZnO is a promising material for the realization and future of nanotechnology. With its wide band-gap (3.37eV), high excitonic binding energy and high breakdown strength, ZnO can be utilized for electronic and photonic devices, as well as for high-frequency applications. The availability of a native substrate and the potential for room temperature operations opens the door to ZnO applications including chemical sensors and subscale electronic circuits. As a source of unique properties, Zinc Oxide (ZnO) has been widely studied as a novel material for its practical and potential applications such as micro, nano-electronics and micro, nano-robotic (machining) technology [50]. Several synthesis methods of ZnO nanoparticles or nanocrystalline films, such as sputtering, pulsed laser deposition, epitaxial techniques and chemical routes have been developed. Mechanical attrition also appears to be a suitable method for obtaining semiconductor nanocrystals [51].
Recently, the preparation of basic one-dimensional nanostructures and their assembly in two-dimensional and three-dimensional ordered architectures have been a major challenge faced by the modern synthetic chemists and materials scientists [52]. Up to now, much effort has been devoted to the fabrication of well-defined ZnO 1D nanostructure such as nanowires (or nanorods) [53], nano belts nanoribbons [54], nanorings [55], nanocolumns [56], nanonails [57] and well-aligned ZnO nanorods and nanotubes arrays [58]. One-dimensional ZnO nanostructures such as nanowires and nanorods have been studied for optoelectronic nanodevice applications as a promising candidate for UV light-emitting diodes and laser diodes because of both their fundamental importance and the wide range of their potential applications in nanodevices. ZnO nano-wires have potential for applications in laser devices due to their desirable optical properties. Therefore, a detailed understanding of ZnO wires and the influence of impurities on their properties is important. ZnO nanorods can be grown or deposited on various substrates including Si [59]. Many groups have recently demonstrated the catalyst-driven growth of ZnO nanorods using MBE or vapor transport [60, 61]. The large surface area of nanorods makes them attractive for gas and chemical sensing, and the ability to control their nucleation sites makes them good candidates for micro-lasers or memory arrays. Nanorods and nano-wires will lead to the possibility of nano devices, such as nano-lasers or memory arrays [62]. A SEM micrograph of a single rod is shown in Figure 2.5 (a). In addition, ZnO nano-particles are equally interesting and can be grown and synthesized by different methods. These nano-particles are of great interest since they have many technological as well as medical applications.

Exchange-spring magnets are nano composites that are composed of magnetically hard and soft phases that interact by magnetic exchange coupling. Such systems are promising for advanced permanent magnetic applications [63]. The two-dimensional system of thin coatings has been studied widely. Three dimensional (3D) interconnected networks of ZnO nanowires and nanorods are synthesized by a high temperature solid–vapor deposition process [64]. The nanorods and nanowires have diameters of 20–100 nm and they grow along the c-axis. The thickness of the multilayer nano-network could be as thick as 30 µm. The sharp nanowires tips, the high degree of networking, and the high surface area of these unique nano networks make them a potential candidate for field emission, ultra-sensitive gas sensing, catalysts and filtering. Large-scale synthesis of ZnO nanowires has been achieved on Au-coated silicon substrates by physical evaporation of the mixture of ZnO, graphite powders and polycrystalline ZnO nanowires have been fabricated within the nano channels of porous alumina [65].

More recently, complex and oriented ZnO 3D structures, e.g. flower- and urchin-like assemblies [58], dandelion-like structures [66], hollow microspheres [67], polyhedral cages and shells [68], complex architecture [69], and hierarchical nanostructure [70], comb-like nanowire arrays, nanoneedle arrays [71], nanohelices (Figure 2.5 (b) [72]), and nanobows [73] have been successfully synthesized. For example, single crystalline ZnO nanohelices have been prepared by thermal evaporation of ZnO powder. The piezoelectric and semiconducting properties of ZnO suggest that the nanohelix could be a fundamental unit for investigating electromechanically coupled nanodevices by using the super lattice piezoelectric domains. The nanohelix is likely to have important applications in sensors, transducers, resonators, and photonics. The structural configurations of ZnO nano-objects could form the basis for fabricating nanoscale sensors, transducers, and resonators [72]. In this study
nano-ZnO and polymer composites have been made in a water solution. This is a novel method of producing these materials.

![TEM images of single-crystal ZnO nanorod (top) and showing cored (Zn1-xMgx) O nanorods (bottom) (b) SEM images of the left- and right-handed ZnO nanohelices [72]](image)

**Figure 2.5:** (a) TEM images of single-crystal ZnO nanorod (top) and showing cored (Zn1-xMgx) O nanorods (bottom) (b) SEM images of the left- and right-handed ZnO nanohelices [72]

### 2.6.3 Implantation Doping

Ion implantation is an important and controllable technique of introducing dopants into a semiconductor and creating high resistance regions for inter-device isolation. Dopants may become embedded in the solid and may occupy the interstitial positions, there by changing the chemical composition of the solid. Implantation doping is in its infancy in ZnO and there has been no clear demonstration of activation of an implanted donor or acceptor. Damage due to ion implantation may occur as a result of ionization as well displacement collisions, associated with diffusion processes and phase changes. The residual implantation damage remaining after annealing appears to have donor-like characteristics. To minimize this damage, it may be necessary to adopt techniques used for other compound semiconductors, such as elevated temperatures during the implantation step, to take advantage of so-called dynamic annealing in which vacancies and interstitials created by the nuclear stopping process are annihilated, before they can form stable complexes [72]. Ion implantation is used for introducing conduction carriers and optical isolation, dry etching, and ion slicing. A wide range of implant...
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conditions (implanted species, ion mass, dose \((10^{12-18} \text{ atoms cm}^{-2})\), and implant temperature) affects the formation of lattice interstitials, vacancies and planar defects in a crystal such as GaN and ZnO [74]. Ion implantation of potential p-type dopants and co-implantation studies are beginning to show promising results for producing p-type ZnO [75]. Miyakawa [76], Komatsu [36], Jeong [77] and Ip [78] have reported implantations of As, In, N, Ga and H in a ZnO crystal at room temperature. Hartmann and Puchert [27] reported Cu implantation of ZnO thin films. Kucheyev et al [79] have recently reported a systematic study of implant isolation in n-type ZnO epilayers grown on sapphire. Mn-implanted \((5 \times 10^{16} \text{ atoms cm}^{-2})\) ZnO nanorods samples show magnetization vs. magnetic field (H) behaviour at 300 K after a 700 °C, 5 min anneal (Figure 2.6). Hysteretic behaviour is clearly present. Possible explanations include ferromagnetism, superparamagnetism or spin-glass effects. The magnetization of Mn implanted, annealed nanorods was as much as 3 orders of magnitude lower than in the implanted, annealed samples, demonstrating that the transition metals are responsible for the observed magnetic properties [72].

There was no significant chemical effect noted for Cr, Fe or Ni implantation relative to O, indicating these elements do not introduce a large concentration of deep acceptors into ZnO.

![Magnetizations vs. field at 300 K for Mn-implanted ZnO nanorods](image)

**Figure 2.6:** Magnetizations vs. field at 300 K for Mn-implanted ZnO nanorods [72]

In transparent oxides, although the implantation is mainly applied to the fabrication of optical devices such as wave guides and fluorescent materials, the history of application to carrier control is rather new as an approach to the fabrication of p-type ZnO. In this study, the dopants, Al, Ag, Sn, Sb, and TiN, are selected for this investigation to determine if these species can improve the conductivity of ZnO thin films and impart p-type properties to ZnO.
2.7 Composites and ZnO

A composite material consists of a combination of materials which differ in composition or form, remain bonded together, and retain their identities and properties. Composites include: (1) fibrous (composed of fibres, and usually in a matrix), (2) laminar (layers of materials), (3) particulate (composed of particles or flakes, usually in a matrix), and (4) hybrid (combinations of any of the above) [80]. Laminar and particulate composites have been used in the ZnO composites such as ZnO thin films deposited on PEN, nano-ZnO particles and polyvinyl alcohol blends and Al, Ag, Sn, Sb and TiN implanted ZnO thin films. The ancient concept of composite materials was to combine different materials to produce a new material with performance unattainable by the individual constituents, e.g. adding straw to mud for building stronger mud walls. More recent examples are carbon black in rubber and fibre glass in resin etc. Epoxy resin composites are filled with nano-particulates using a KH-560 silence coupling agent to enhance the interfacial bonding between the inorganic reinforcing agent and the polymer matrix [81]. The incorporation of modifying Zn ions into "poly diene latex-silica" systems increases their mechanical characteristics due to an increase of the interaction between the organic and inorganic networks [82]. In nature, examples are a bound: cellulose fibres in lignin matrix (wood), collagen fibers in an appetite matrix (bone) etc. Today, given the most efficient design, of for example an aerospace structure, a boat or a motor, we can make a composite material that meets or exceeds the performance requirements because of its unique combination of properties. Most of the savings are in weight and cost. These are measured in terms of ratios such as stiffness/weight, strength/weight, etc. [83, 84].

2.7.1 Advanced Processing Methods

There are many deposition techniques for ZnO thin films. Thin film deposition technologies can be either purely physical, such as evaporative methods, or purely chemical, such as gas and liquid phase chemical processes. A considerable number of processes (that are based on glow discharges and reactive sputtering) however combine both physical and chemical reactions and can be categorized as physico-chemical methods. Thin films of ZnO can be grown by:

(a) Sol gel processing,
(b) Molecular beam epitaxial,
(c) Chemical vapor deposition,
(d) Magnetron sputtering,
(e) Pulsed laser deposition, and
(f) Spray pyrolysis on several different substrates [27, 28].

2.8 Zinc Oxide Synthesis Techniques

ZnO nanostructures are usually obtained via a vapor transport process. Depending on the synthesis condition variations in temperature, catalyst, and composition of source materials, a wide range of nanostructures has been obtained. Using a vapor-solid process, complex ZnO nanostructures such as nanohelixes, nanorings and nanobelts were synthesized by Kong et al. In this process, ZnO powder was decomposed into Zn2+ and O2- at 1400 °C then transported by Ar carrier gas to a low temperature zone (400 °C), and nanostructures were
formed on a collecting chip. In a similar vapor transport and condensation process reported by Ren et al [57], hierarchical ZnO nanostructures were grown by mixing ZnO, In$_2$O$_3$ and graphite powder and heated up to 820-870 °C. A simplified method to achieve nanowires, nanoribbons and nanorods was reported by Yao et al [18, 31] ZnO powder was mixed with graphite and heated to 1100°C then cooled down, nanostructures were found to form on the wall of the furnace. These synthesis methods utilize the vapor-solid (VS) mechanism, in which ZnO nanostructures are formed by condensing directly from vapor phase. Although diverse nanostructures can be obtained, this method provides less control on the geometry of ZnO nanostructures. Controlled growth of ZnO nanowires has been achieved by using various nanoparticles or nanoclusters as catalysts, such as Au. In these cases, ZnO and carbon powder are usually used as source material and a vapor-liquid-solid (VLS) growth mechanism governs the synthesis. In the VLS mechanism, the catalyst nanoparticles become liquid droplet under reaction temperature. The reactant Zn vapor generated by carbon thermal reduction of ZnO powder is transported to the catalyst nano-droplets and form Zn-catalyst alloy. In the meantime, ZnO forms as a result of the reaction between Zn and CO/CO$_2$. Upon supper saturation, ZnO nanowires grow from the droplets. Recently we have found that this synthesis process can be further simplified by directly heating pure Zn powder in low concentration oxygen environment (2%) using Au nanoparticles as catalysts.

A variety of methods exist for ZnO deposition and growth. For consolidation, methods have been categorized as either physical vapor deposition (PVD), chemical vapor deposition (CVD), or solution-based chemistry (SBC). Each respective method can be subdivided into the individual techniques that are summarized in Table 2.2 below [85]

**Table 2.2: Methodologies for ZnO deposition and growth**
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2.8.1 Physical Vapor Deposition

Physical vapor deposition (PVD) occurs when a material is physically released from a source and transferred to a substrate. The three most important technologies for ZnO deposition are thermal evaporation, sputtering, and pulsed laser deposition; each of which will be described below.

2.8.1.1 Thermal Evaporation

During thermal evaporation, the substrate, crucible, and source material are placed inside a vacuum chamber at room temperature. A vacuum is required to increase the vapor pressure during sublimation and often ranges between $10^{-2}$ & $10^{-9}$ Torr (ultra-high vacuum). Once the vacuum chamber has stabilized at the appropriate pressure, a heating source is used to heat the source material within the crucible to its vapor point. Upon evaporation, the material will re-deposit along the cooler surfaces of the vacuum chambers, as well as the collection substrate. Typical heating sources include electron-beam, radio-frequency (RF) inductive, and resistive heating. During electron-beam evaporation, an electron source is aimed at the source material causing localized heating. In comparison, RF induction uses an AC power supply to produce an alternating current through an induction coil. The alternating current generates a magnetic field within the coil. When the source material is placed inside the coil, the magnetic field induces eddy currents within the source material providing localized heat. Although higher frequencies equate to higher heat rates, lower frequencies are better suited for thicker samples. Finally, resistive heating provides heat by sending a high current source through a resistive coil, such as tungsten, and is a non-localized heat source and therefore commonly used for furnace applications. Although inductive RF and electron-beam sources have been limited to highly-oriented, thin-films of ZnO [86] resistive sources have produced thin-films, as well as a diversity of ZnO nanostructures with different shapes, sizes, and orientations [87, 88].

2.8.1.2 Sputtering

Sputtering is the removal of surface atoms via high energy ions. Sputtered films are typically polycrystalline and form at low temperatures with good adhesion properties. Common types of sputtering are focused ion-beam, direct current (DC), radio-frequency (RF), and magnetron. During focused ion-beam sputtering, gallium ions are accelerated through a vacuum towards a sample surface. Acceleration and focusing capabilities are provided by a series of capacitive plates and magnetic coils, respectively. In general, the focused beam of ions provides an exquisite tool for milling and cutting at the nanoscale and has been used within this work as a tool for building prototype nanobelts devices. In comparison, during DC sputtering, the substrate and source (target) material are placed inside a vacuum chamber. Upon evacuation of foreign gases, an inert gas, such as argon, is introduced into the chamber at low pressures. Then, a DC power supply is used to ionize the inert gas in order to produce charged plasma. The ions are accelerated towards the surface of the target, causing atoms of the source material to break off from the target and condense on all surfaces including the substrate. A limitation to DC sputtering is the high voltage required to sputter insulating materials due to the build-up of positive charge on the target material. To solve this problem, the DC power source should be replaced by an RF power source (RF sputtering). In addition, a strong magnetic field (magnetron sputtering) can be used to
concentrate the plasma near the target to increase the deposition rate. When applied to ZnO, sputtering has been limited to polycrystalline thin-films [89].

### 2.8.1.3 Pulsed Laser Deposition

During pulsed laser deposition (PLD), a laser beam is focused through a vacuum onto the surface of a target material. At sufficiently high flux densities and short pulse durations, the target material is rapidly heated to its evaporation temperature and forms a vapor plume. Unlike thermal evaporation, where the vapor composition is dependent on the vapor pressures of the elements within the source material, laser ablation produces a plume of material with similar stoichiometry to that of the target material. Once the vapor plume has been formed, it is collected onto a cooler substrate that promotes nucleation and growth of crystalline films. It is important to note that by using a single crystal substrate; epitaxial single-crystals can be grown that are equal in quality to molecular beam epitaxy. As applied to ZnO, fabrication of (0001) epitaxial films on cubic (111) substrates have been formed using pulsed laser deposition [90] as well as aligned ZnO nanorod [91, 92] and nanodot [93] arrays without the aid of a catalyst.

### 2.8.2 Chemical Vapor Deposition

During chemical vapor deposition (CVD), the substrate is placed inside a reaction vessel where the pressure and gas flow are controlled. Fundamentally, the process is a chemical reaction between source gases; the product of which condenses during the formation of a solid material within the reaction vessel. The most common CVD techniques used to deposit ZnO are thermal CVD, low pressure CVD (LPCVD), plasma-enhanced CVD (PECVD), metal-organic CVD (MOCVD), molecular beam epitaxy (MBE), and atomic layer deposition (ALD). For each of these methodologies, a vacuum chamber with gas flow control is required.

### 2.8.3 Solution-Based Chemistry

Solution-based chemistry (SBC) is the study of any chemical reaction that requires a liquid. As a generic method for synthesis, SBC has been vital to the production of a diversity of materials that are often difficult to make using PVD or CVD. Typically, solution-based methodologies provide materials with high yield and uniformity. However, a common drawback is an increased number of points, line, and planar defects when compared to their simpler physical counterparts. The most important and common techniques for ZnO synthesis are hydrothermal and sol-gel synthesis, both of which will be discussed below.

#### 2.8.3.1 Hydrothermal Synthesis

As defined, hydrothermal synthesis is a subset of solvothermal synthesis which involves water at elevated conditions. The basic principle is that small crystals will homogeneously nucleate and grow from solution, when subjected to high temperatures and pressures. During the nucleation and growth process, water is both a catalyst and occasionally a solid-state phase component. Under the extreme conditions of the synthesis vessel (autoclave or bomb), water often becomes supercritical, thereby increasing the dissolving power, diffusivity, and mass transport of the liquid by reducing its viscosity. In addition, the ability to tune the pressure of the vessel provides an avenue to tailor the density of the final product. When compared to other methodologies, hydrothermal
synthesis is environmentally benign, inexpensive, and allows for the reduction of free energies for various equilibrium. Materials that are made hydrothermally are generally high-quality, single crystals with a diversity of shapes and sizes. Although hydrothermal synthesis is an established synthesis route within the ceramics industry, it has recently been rekindled within the scientific community by synthesizing one-dimensional nanostructures, such as carbon nanotubes and oxide nanowires. As of recent, hydrothermal synthesis has been used to synthesize well-aligned ZnO nanorods on GaN substrates for optical applications [106].

2.8.3.2 Sol-Gel Synthesis

The sol-gel process, as the name implies, involves the evolution of inorganic networks through the formation of a colloidal suspension (sol) and gelation of the sol to form a network in a continuous liquid phase (gel). The precursors for synthesizing these colloids consist of a metal/metalloid surrounded by various reactive ligands. Metal alkoxides are most popular because they react readily with water. At the functional group level, three reactions are generally used to describe the sol-gel process: hydrolysis, alcohol condensation, and water condensation. However, the characteristics and properties of a particular sol-gel inorganic network are related to a number of factors that affect the rate of hydrolysis and condensation reactions, such as pH, temperature and time of reaction, reagent concentrations, catalyst nature and concentration, aging temperature and time, and drying. When applied to ZnO, nanocrystals [107] thin films [108] and nanorods [109] have been synthesized with preferred crystallographic orientations using the sol-gel method. The synthesis of ZnO nanostructures, fabrication and electrical characterization of ZnO nanobelt devices, and predictive modeling intended to guide future research.

2.9 Growth Mechanism

Crystal solidification occurs by one of two means. Either a vapor condenses into a liquid which then condenses into a solid, or the vapor bypasses the liquid state and transforms directly to the solid state. Primary barriers to solidification are heterogeneous nucleation and growth which can be reduced using precise control of the synthesis conditions. Among one-dimensional nanostructures, two mechanisms are used to explain nucleation and growth during physical vapor deposition. The first mechanism is vapor-solid (VS) growth and the second is vapor-liquid-solid (VLS) growth. However, for the thrust of this research, vapor-solid growth was used and therefore will be the only mechanism discussed below.

2.9.1 Vapor-Solid Growth

Vapor-solid growth of one-dimensional nanostructures is historically based on whisker formation. As defined, a whisker is a single-crystalline eruption from the surface of a deposited metal film. Typically, whiskers are 5 microns in diameter with lengths between 1 and 500 microns. The first observation of a whisker was made in 1946 by H.L. Cobb [113] during the evaluation of electrical component failure caused by the formation of cadmium whiskers. This work was independently confirmed by K.G. Compton et al [114] of Bell Laboratories in 1951 when observing similar phenomenon in electroplated cadmium (Cd), zinc (Zn), and tin (Sn), as well as growth in an aluminum (Al) casting alloy and on electroplated silver (Ag) exposed to hydrogen sulfide (H2S). Within this work, the authors speculated without conclusion that the whiskers are “not compounds but are
metallic filaments in the form of single crystals.” In 1952, Herring and Galt inferred that whiskers were single-crystals because of their mechanical properties [115]. Then in 1953, the first dislocation theory for whisker growth was proposed by Peach [116]. Within this theory, the terminal step of a screw dislocation provides an energy sink to promote physical deposition where the Burgers’ vector is parallel to the whisker’s growth direction. However, this theory was quickly overshadowed in 1954 when Koonce and Arnold of Bell Laboratories published their seminal work describing that whisker growth occurred by the continual addition of material to the base of a whisker rather than by addition of material to the tip of the whisker [117]. Resounding evidence was provided by a series of electron micrographs, taken over several weeks, showing that the whisker tip shape did not change over time even though the overall length of the whisker increased. To date, this observation is consistent with current findings. Although F.C. Frank [118] and J.D. Eshelby [119] in 1953, and then S. Amelinchx et al [120] in 1957, proposed dislocation theories describing root growth of whiskers, the lack of microscopy evidence confirming the existence of dislocations eventually lead to the abandonment of all dislocation theories [119]. In 1955, Sears [121] proposed that for sufficiently small vapor super saturation, growth could occur at the tip of the whisker rather than at its base. Within this model, atoms simultaneously condense at the tip, as well as the sidewalls of the whisker. Under the assumption that nucleation and growth only occur at the growth front, condensed atoms must either migrate to the tip of the whisker or absorb from its surface.

### 2.9.2 Whisker growth characterization

As a diffusion-limited growth process, Sears suggested that whisker growth was exponential when the whisker length was less than the mean migratory distance of the adsorbed atoms. In comparison, if the length of the whisker was greater than this mean distance, the growth rate would become linear since the atoms would arrive at the tip at a constant rate with dependency on the partial pressure of vapor within the atmosphere. More specifically, if \( h \) is the instantaneous length at time, \( t \), and \( h_0 \) is the length at \( t = 0 \), then the exponential growth is given by:

\[
h = h_0 \exp(n \sigma / g)
\]

where \( n \) is the number of atoms condensing onto the surface per unit area per second and \( g \) is a geometrical constant [122]. Expanding on Sears’ concept, Blakely and Jackson [122] in 1962 solved for the two-dimensional nucleation probability \( (P_n) \) on the surface of a whisker:

\[
P_n = B \exp[-\pi \sigma^2 / k T^2 \alpha 
\]

where \( B \) is a constant, \( \sigma \) is the energy of the solid nanowire, \( k \) is the Boltzmann constant, \( T \) is absolute temperature and \( \alpha \) is defined as a ratio between the actual vapor pressure \( p \), and the equilibrium vapor pressure \( p_0 \) at temperature \( T \).

Upon evaluation of Equation 2.9, lower surface energies correspond to greater two-dimensional nucleation probability. However, low energy surfaces also have smaller sticking coefficients when compared to their higher energy counterparts. As a consequence, adsorbed atoms will have a higher probability of desorption on these low-index surfaces. Balance between these two distinct effects is fundamental to the formation of the low-index crystal planes that commonly enclose whiskers and one-dimensional
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As a consequence of this research, whiskers, as well as one-dimensional nanostructures, are thought to be kinetically-driven, anisotropic, crystallization processes that are heavily dependent on super saturation [123]. Fortunately, the temperature and super saturation ratio are easily controlled parameters during synthesis. Higher temperature and larger super saturation ratios facilitate two-dimensional nucleation resulting in the formation of films. In comparison, lower temperatures and smaller super saturation ratios are preferred for the nucleation and growth of wire-like structures. To sum up, temperature and the ‘super saturation ratio’ are the two dominant factors relevant to VS growth.

2.9.3 Self-Catalysis

Although, qualitative intuitive understanding, more research is required to develop a predictive model for one-dimensional nanostructures. Based on the aforementioned criteria, the VS growth process can be considered ‘self-catalyzed’. As applied to ZnO, Dai et al [124] have developed a conceptual model to explain the VS growth of ZnO nanobelts. It is schematically shown in Figure 2.7, ZnO vapor molecules are released from the solid state at elevated temperatures and they then condense onto a substrate located in a cooler region of the furnace (Figure 2.7(A)). Upon arrival of additional molecules, a critical nucleus will develop (Figure 2.7(B)) and it will continue to grow with each adsorbed molecule (Figure 2.7(C)). Throughout this process, the local vapor super saturation remains constant, through pressure control within the furnace. As a consequence of the relatively high mobility of the molecules at the deposition temperature (~800ºC), molecules migrate to the high-energy growth front, in a series of steps (Figure 2.7(D)). The rough tip surface becomes an ‘energy sink’ for incoming vapor molecules resulting in the rapid formation of a ‘nanobelts’ (Figure 2.7(E)).

![Figure 2.7: A proposed growth mechanism for ZnO nanobelts through a VS process [124]](image)

Confirmation of the model depicted in Figure 2.7 is shown below in Figure 2.8, where the growth front of an individual ZnO nanobelt is rounded. The rounded surface indicates atomic-scale roughness through the presence of steps, ledges, and kinks. This high energy surface readily adsorbs ZnO vapor molecules and leads to the anisotropic growth of ZnO nanobelts. It is important to note that the TEM micrograph below is obtained in the absence of a catalyst and therefore the ZnO nanobelt is believed to be self-catalyzed.
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2.9.4 Conductivity

Magnetron sputtering is a popular technique to prepare thin films (Figure 2.9). Zinc oxide thin films were prepared by dc (direct current) and rf (radio frequency) magnetron sputtering on glass substrates. The reported resistivity of ZnO or Al doped ZnO thin films prepared by magnetron sputtering are in the range of $10^{-4}$ to $10^5$ cm [125,126]. Generally, Zn–rich defects such as zinc interstitials (Zn$_i$) and oxygen vacancies (V$_O$) are believed to be the main source of conductivity in as-grown ZnO samples [127,128]. The effects of several parameters like film thickness, grain and agglomerate size, grain boundaries and impurities on the electrical properties of ZnO thin films have been reported [129-132]. However, there are fewer reports addressing the relationships of microstructure on the optical and electrical properties of ZnO thin films. It has been found that ZnO films produced by dc sputtering have a high resistance, while the films produced using rf sputtering are significantly more conductive. While the conductive films have a compact nodular surface morphology, the resistive films have a relatively porous surface with columnar structures in cross section. Compared to the dc sputtered films, rf sputtered films have a microstructure with smaller d-spacing, lower internal stress, larger band gap energy and higher density.

The dependence of conductivity on the deposition technique and the resulting d-spacing, stress, density, band gap, film thickness and Al doping are discussed. Correlations between the electrical conductivity, microstructural parameters and optical properties of the films have been made. However, the relationship between the band gap and the conductivity of ZnO thin films is complex. A series of ZnO films were deposited by dc and rf magnetron sputtering using direct and reactive sputtering modes. Argon or argon-oxygen mixtures were used as the plasma-forming gas. Working pressure in the chamber was varied from 2 to 20 m Torr keeping the cathode-to-substrate distance 13 cm and deposition time 1-4 hrs. The sputtering targets were ZnO (99.9%) or Zn (99.99%), with an Al thin strip attached on the surface of the target for Al doping. Microscopic glass slides were used as substrates, which were in rotation during deposition. The principle of sputter deposition of ZnO thin films is shown in Figure 2.10. To initiate the process, a large negative potential is applied between target and the ground so that electrons are emitted from the target surface. The ejected electrons accelerate through

![Figure 2.8: A transmission electron microscopy image showing the growth front of a ZnO nanobelt](image)
they collide with gas atoms and ionize them. Positive ions are accelerated to the cathode. When they hit the target, different types of particles are emitted. There are of course neutral atoms that will eventually get to the substrate and build the film, but also negative ions, photons and secondary electrons. If the secondary electron yield is high enough, plasma will be created. ZnO thin films were deposited under various deposition conditions. The electrical resistivity of the films was measured by standard two-probe and four probe (Figure 2.11) techniques. Scanning electron microscopy (SEM, Philips XL-30S with Energy-dispersive X-ray (EDX) using analytical ZnO pellets as standard materials) and X-ray diffractometer (XRD, Bruker D8, Cu Ka) were used to characterize the microstructure of the films. SEM was used for thickness measurement of the films. Hall coefficients of the samples were measured at room temperature by an automated dc Hall measurement system using the technique devised by Van Der Pauw in the laboratory of National University of Singapore. A HP 8254 spectrophotometer was used for recording the optical transmission spectra of the samples in the 190 – 800 nm spectral range.

![Figure 2.9: Magnetron sputtering](image)

![Figure 2.10: Magnetron sputtering deposition principles](image)
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The XRD patterns of the ZnO films are shown in Figure 2.12. The patterns revealed only strong (002) and weak (004) peaks, indicating a strong preferred orientation perpendicular to the substrate. As the surface energy density of the (002) orientation is the lowest in a ZnO crystal, (002) orientation is favoured in the film [133]. In most of the samples, d_{002} values are higher than the standard d_{002} value for unstressed powder (0.26033 nm, ASTM [134] suggesting an elongation of unit cells along the c axis, and existence of compressive stresses along the plane of the films. From diffraction simulations using ‘Rietan 2000’ (Authors: F. Izumi and T. Ikeda), if strong preferred orientation to the C-axis is introduced into the calculation, only (00n) diffraction can be observed. To derive the stress σ film parallel to the film surface, the following formula can be used for a hexagonal lattice [135].

\[ \rho = \frac{V/L}{W^{n}t/L} \text{ (Ω cm)} \]

**Figure 2.11:** Four-probe technique for measuring conductivity

**Figure 2.12:** The XRD pattern of the film
2.10 Characterization Techniques

After the preparation of the samples, different characterization techniques were used to investigate their structure and optical properties. Scanning electron microscope (SEM) was used to get the morphology of the samples. An atomic force microscope (AFM) was utilized to detect the morphology of pre-treated substrates. The detailed information about the structure of the samples can be obtained from XRD measurement. The optical properties were investigated by micro photoluminescence (PL), micro-Raman scattering, and resonant Raman scattering (RRS) measurements. The surface effect versus the diameter of the ZnO nanorods were studied by means of time resolved photoluminescence (TRPL). Here we will briefly describe these techniques.

2.10.1 Scanning Electron Microscope

The scanning electron microscope (SEM) is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms to make the sample producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity. The types of signals produced by a SEM include secondary electrons, back scattered electrons (BSE), characteristic x-rays, light (cathode luminescence), specimen current and transmitted electrons. These types of signal all require specialized detectors for their detection that are not usually all present on a single machine. A scanning electron microscope employs the use of high-energy electrons, rather than photons, to image a surface. The sample must have a moderate electrical conductivity and be stable in a high vacuum environment. It allows direct studying of the surfaces of solid objects and greater depth of focus than the optical microscope. It can hence produce an image that is a good representation of the three-dimensional sample. By heating the metallic filament, a beam of electrons is produced at the top of the microscope. The electron beam traverses a vertical path through the column of the microscope first and then through the electromagnetic lenses that focuses and directs the beam down towards the sample. After hitting the sample, backscattered and secondary electrons are ejected from the sample. Detectors further collect the above emitted electrons and convert them into a signal that is sent to a viewing screen thereby producing an image. The ZnO nanostructure produced by PVD was characterized using SEM. The schematic image of SEM is illustrated in Figure 2.13 in order to show how it works.

![Schematic image of SEM](image-url)
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The SEM uses electrons instead of light to form an image. A beam of electrons is produced at the top of the microscope by heating of a metallic filament. The electron beam follows a vertical path through the column of the microscope. It makes its way through electromagnetic lenses which focus and direct the beam down towards the samples. Once it hits the sample, other electrons such as backscattered or secondary are ejected from the sample. Detectors collect the secondary or back scattered electrons and convert them to a signal that is sent to a viewing screen similar to the one in an ordinary television, producing an image. To characterize the as-grown ZnO nanostructures, a JEOL JSM-6301F scanning electron microscope was used in our experiments. The chamber pressure was about 10^{-6} mbar. The gun voltage is 15kV. A max resolution of about 10nm can be achieved. Figure 2.14 gives the typical SEM images of sample. The SEM gives information on the morphology of the surface of the sample, which implies that it is possible to determine if any growth has taken place. However, the images from the SEM are not a definitive proof that obtained nanostructures actually consists of ZnO. Even though the SEM produces 3D images they give no information regarding the exact atomic structure of the sample. The 3D images are easy to interpret, and they reveal topographic features of the sample. The SEM images allow us to examine the diameter, length, shape and density of the ZnO nanostructures.

![SEM image of ZnO nanorod arrays](image)

**Figure 2.14: Typical SEM images of ZnO nanorod arrays**

2.10.2 X-ray diffraction

X-rays are electromagnetic radiation of wavelength about 1 Å (10^{-10} m), which is about the same size as an atom. They occur in that portion of the electromagnetic spectrum between gamma-rays and the ultraviolet. The discovery of X-rays in 1895 enabled scientists to probe crystalline structure at the atomic level. When X-rays interact with a crystalline substance (phase), one gets a diffraction pattern. About 95% of all solid materials can be described as crystalline. Each crystalline solid has its unique characteristic X-ray diffraction (XRD) pattern which may be used as a "fingerprint" for its identification. Today about 50,000 inorganic and 25,000 organic single components, crystalline phases, and diffraction patterns have been collected and stored on magnetic or optical media as standards.
Figure 2.15: Reflection of x-rays from two planes of atoms in a solid

Figure 2.15 illustrates the reflection of x-rays from two planes of atoms in a solid. A crystal lattice is a regular three-dimensional distribution (cubic, rhombic, etc.) of atoms in space. These are arranged so that they form a series of parallel planes separated from one another by a distance d, which varies according to the nature of the material. For any crystal, planes exist in a number of different orientations each with its own specific d-spacing. When a monochromatic X-ray beam with wavelength lambda is projected onto a crystalline material at an angle theta, diffraction occurs only when the distance travelled by the rays reflected from successive planes differs by a complete number n of wavelengths, which leads to

Bragg's Law:

\[ n\lambda = 2d\sin(\theta) \]  

where \( n \) is an integer 1,2,3…(usually equal 1), \( \lambda \) is wavelength in angstroms (1.54 Å for copper), d is inter atomic spacing in angstroms, and \( \theta \) is the diffraction angle in degrees. By varying the angle theta, the Bragg's Law conditions are satisfied by different d-spacing in polycrystalline materials. Plotting the angular positions and intensities of the resultant diffracted peaks of radiation produces a pattern, which is characteristic of the sample. Where a mixture of different phases is present, the resultant diffractogram is formed by addition of the individual patterns. Based on the principle of X-ray diffraction, a wealth of structural, physical and chemical information about the material investigated can be obtained. XRD has been in use in two main areas, for the fingerprint characterization of crystalline materials and the determination of their structure. Once the material has been identified, X-ray crystallography may be used to determine its structure, i.e. how the atoms pack together in the crystalline state and what the inter atomic distance and angle are etc. X-ray diffraction is one of the most important characterization tools used in solid state chemistry and materials science.
One can determine the size and the shape of the unit cell for any compound most easily using the diffraction of x-rays. Figure 2.16 shows the typical XRD pattern of our sample. All the peaks of the XRD patterns can be indexed to ZnO with the hexagonal wurtzite structure. In comparison with the standard card of bulk ZnO with hexagonal structure (see Figure 2.17), no diffraction peaks of other impurities are detected, which testify that the substance deposited on the substrates only belongs to ZnO.

![Figure 2.16: Typical XRD pattern of ZnO nanostructures](Image)

**ZnO**

**Zinc Oxide**

Ref: Calculated from ICSD using 9QwYD+12++. (1997)

Ref: Garcia-Martinez, D et al., Solid State Ionics, 63, 442 (1993)

![Figure 2.17: Standard JCPDS card of bulk ZnO with hexagonal structure](Image)
2.10.3 Atomic force microscope

The atomic force microscope (AFM) is a very high-resolution type of scanning probe microscope, with demonstrated resolution of fractions of a nanometer, more than 1000 times better than the optical diffraction limit. Binnig, Quate and Gerber invented the first AFM in 1986. The AFM is one of the foremost tools for imaging, measuring and manipulating matter at the nanoscale. The term 'microscope' in the name is actually a misnomer because it implies looking, while in fact the information is gathered by "feeling" the surface with a mechanical probe. Piezoelectric elements that facilitate tiny but accurate and precise movements on (electronic) command enable the very precise scanning. Figure 2.18 illustrates the block diagram of AFM.

The AFM consists of a micro scale cantilever with a sharp tip (probe) at its end that is used to scan the specimen surface. The cantilever is typically silicon or silicon nitride with a tip radius of curvature on the order of nanometers. The AFM works by scanning a fine ceramic or semiconductor tip over a surface much the same way as a phonograph needle scans a record. When the tip is brought into proximity of a sample surface, Van der Waals forces between the tip and the sample lead to a deflection of the cantilever. The magnitude of the deflection is captured by a laser that reflects at an oblique angle from the very end of the cantilever. A plot of the laser deflection versus tip position on the sample surface provides the resolution of the hills and valleys that constitute the topography of the surface. The AFM can work with the tip touching the sample (contact mode), or the tip can tap across the surface (tapping mode) much like the cane of a blind person. Compared with SEM, AFM provides extraordinary topographic contrast direct height measurements and unobscured views of surface features. Figure 2.19 shows the 1µm×1µm AFM image of the pre-treated substrates. From this image, it can be seen that the dispersion of ZnO nanoparticles is relatively uniform in the comparison with the nuclei formed on the bare substrates, and the average diameter and height of ZnO nanoparticles on the substrates is about 20nm and 3.5nm respectively. In the comparison between the SEM images of ZnO nanorods and the AFM images of pre-treated Si substrates, the relationship between the sample and seed layer is able to be revealed.
Transmission Electron Microscope (TEM)

Transmission electron microscopy has been used traditionally as a tool for characterizing local atomic structures of material objects since the information obtained does not require the objects being periodic such as crystal. In the characterization of ZnO nanostructures, TEM is one of the most powerful instruments available due to its excellent imaging and analytical capabilities. TEM imaging allows both the imaging of relatively large areas and the precise measurement. The TEM has a very high magnification and can give detailed information about the structure of even a single nanostructure. The nanostructure appears ‘transparent’ in the TEM pictures, which enables its measurement more accurately. It is also possible to determine the number of layers in a nanostructure and whether it contains any type of structural damage or irregularities. Another type of interesting observation permitted by the TEM is the shape and location of any residual catalyst that may be incorporated in the nanostructure. One disadvantage with the TEM is that it has to be manually calibrated by taking pictures of special calibration particles several times during each experimental session. The beads have a known size, which is used to compare and calculate the measurements of the particles in the sample.

Field Emission Scanning Electron Microscope

A field-emission cathode in the electron gun of a scanning electron microscope provides narrower probing beams at low as well as high electron energy, resulting in both improved spatial resolution and minimized sample charging and damage. Under vacuum, electrons generated by a Field Emission Source are accelerated in a field gradient. The beam passes through electromagnetic lenses, focusing onto the specimen. As result of this bombardment different types of electrons are emitted from the specimen. A detector catches the secondary electrons and an image of the sample surface is constructed by comparing the intensity of these secondary electrons to the scanning primary electron beam. Finally, the image is displayed on a monitor. The high-resolution reached by FESEM allows the study of very small micro-structural details. FESEM produces clearer, less electro statically distorted images. By FESEM high quality, low voltage images are obtained with negligible
investigation of electrical and optical properties of novel ZnO nanostructures is presented. The main applications of these nanostructures are also included in this chapter. In the next chapter, the methodology of my experimental work will be presented.

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Chapter 3: Techniques of Synthesis & Characterization of ZnO Nanostructures

3.1 Introduction

Among physical vapor deposition techniques thermal evaporation (TE) is the one with the longest standing tradition. However, during the last 30 years of booming semiconductor industry which involves a great deal of thin film technology, deposition techniques like CVD (chemical vapor deposition) or sputtering which often offer unquestionable advantages have been developed to perfection and TE has largely been replaced in production lines. On the laboratory scale, due to their simplicity, techniques like PLD (pulsed laser deposition) or sputtering are much more promising to realize fast results. Consequently, when the new superconductors emerged only a handful of research groups like Berberich (1988), Terashima (1988), Kwo (1989), Prakash (1990), and Chew (1990) performed deposition trials based on TE. However, as time went by it became clear that the performance of the various deposition methods strongly depends on material issues as well as economic aspects. With progressive commercialization, cost effective volume production and reproducibility became the driving forces and the intrinsic advantages of TE turned on the scales.

3.2 Preparation of ZnO Thin Films

To study the electrical and optical properties of ZnO nanostructures, thin films are generally used. The properties of thin films of the material are different from those of the bulk due to the presence of several additional factors such as discontinuities, structural defects, grain growth and phase changes in thin films. These additional factors in thin films are induced due to various deposition parameters [1]. Non crystalline thin films of the materials can be prepared by using different methods. The methods used to deposit thin films may be divided into two main groups, physical and chemical. Some of the physical methods for thin films deposition are vacuum evaporation [2-5], electron-beam evaporation [6], flash-evaporation [7], RF sputtering [8] multi-source evaporation, ion-beam evaporation [9] laser-beam evaporation, diode or triode sputtering, resistive evaporation, reactive evaporation and exploding wire evaporation. Some chemical methods of thin films deposition are anode electrolytic deposition [10], chemical bath deposition [11], cathode electrolytic deposition [12], chemical vapour deposition and plasma-enhanced chemical vapour deposition [13, 14] In the present work, physical vapor condensation method has been used for the preparation of ZnO nanostructures thin film. In this method, the source material is Zn powder (99.999 % pure), which is evaporated in the presence of oxygen and argon gases present in the chamber. Initially, small quantity of Zn powder has been kept in a molybdenum boat and the chamber is evacuated to a vacuum of the order of $10^{-6}$ Torr. After attaining this vacuum, the gases (oxygen and argon) are purged in to the chamber. The pressure of these gases is kept fixed at 16 mbar and 4 mbar respectively. Evaporated material is deposited on LN2 cooled glass substrate. The nanoparticles of ZnO are deposited on the glass substrate and also collected in the powder form by scratching it from the substrate.
3.3 Depositon System

Figure 3.1 shows schematic diagram of evaporation chamber. It consists of substrate holder, heating source, vacuum pump. The vacuum system consists of a vacuum chamber which is of cylindrical form of diameter around 350 mm, made up of stainless steel and electro-polished for good vacuum performance. The cylinder is having a substrate-loading window of 150 mm diameter and can be used as view port.

![Schematic diagram of evaporation chamber](image)

**Figure 3.1: Schematic diagram of evaporation chamber**

The deposition chamber is mounted over the diffusion pump to maintain vacuum in the deposition chamber. The deposition chamber is cleaned with acetone prior to each deposition. It consists of two copper electrodes. The boat used to evaporate sample consists of an element having very high melting point viz. molybdenum. Molybdenum boat is connected between these two copper electrodes. The argon gas is introduced into the chamber through specially designed inlet tube having a jet of diameter 0.5 mm. This jet is kept adjacent to the evaporation boat pointing towards the glass substrates. The flow of argon gas is controlled by using a needle.
valve. The electrodes are connected to a high current, low voltage source to pass high current through the boat. By passing high current, the material present in the boat turned to its molten state and the vapours of the material are formed. These vapours come in contact with inert gas and form clusters. These clusters are transported to the substrates by convectional currents in argon gas. The substrates are kept directly above the boat at a height of 15 cm from the boat. Before every deposition, the vacuum chamber is evacuated to a vacuum of 10⁻⁶ mbar using the diffusion pump. The films are deposited on the glass substrate. We have used silicon (100) and quartz substrate for deposition of ZnO thin film. Quartz substrate is used for the optical studies of the grown nanostructures. Powder X-ray diffraction (XRD) is performed using a Philips X-ray diffractometer with Cu Kα (λ ¼ 1:54178 Å) radiation. The morphology and the microstructure of these nanostructures are studied using a Joel field emission scanning electron microscope (FESEM 7500f) and transmission electron microscope (TEM) performed at 100 kV. UV–VIS absorption spectrum is recorded using a V–570 Jasco UV–Vis double-beam spectrophotometer. The scanning wavelength range is 300–900 nm.

3.4 Experimental

Thin film of ZnO is deposited by physical vapour condensation method. In this method, the starting material is Zn powder (99.999 % pure), which is heated at a temperature of 400°C in presence of oxygen and argon gases in the chamber. Initially, small quantity of Zn powder has kept in a molybdenum boat and the chamber has been evacuated to a vacuum of the order of 10⁻⁶ Torr. After attaining this vacuum, the gases (oxygen and argon) are purged in to the chamber. The pressure of these gases is kept fixed at 16 mbar and 4 mbar respectively. The substrate is cooled with liquid nitrogen and this evaporated material is deposited on glass substrate pasted on this LN₂ cooled substrate. The nanoparticles of ZnO are deposited on the glass substrate and also collected in the powder form by scratching from the substrate. Powder X-ray diffraction (XRD) is performed using a Philips X-ray diffractometer with Cu Kα (λ ¼ 1:54178 Å) radiation. The morphology and the microstructure of these nanostructures are studied using a Joel field emission scanning electron microscope (FESEM 7500f) and TEM performed at 100 kV.

UV–VIS absorption spectrum is recorded using a V-570 Jasco UV–VIS double-beam spectrophotometer. The scanning wavelength range is 300–900 nm. In this experiment, we have successfully grown the ZnO nanostructures at low temperatures, keeping the gases (O₂ and Ar) flow fixed at 6 mbar and 4 mbar respectively. The characterization of semiconducting materials is essential for understanding of their structure, conduction mechanism and for their exploitation in electronic applications. In the present chapter, the various methods and instruments used for the growth and characterization of ZnO nanostructure are described in brief.

3.5 Characterization of ZnO Nanostructures

Electron microscopy takes advantage of the wave nature of rapidly moving electrons. Optical microscopes have their resolution limited by the diffraction of light to about 1000 diameters magnification of around 1,000,000 diameters, primarily because of spherical and chromatic aberrations. The analysis of the structural makeup of ZnO nanostructures is based upon various characterization techniques with the ability to resolve their structure at the nano-scale. Chief amongst these are the TEM, SEM, HRTEM and FESEM, each having their unique
applications. The ZnO thin films are characterized to know about their crystallinity, size, and structure, electrical and optical properties. X-ray diffraction (XRD) gives us good information about structure, size and strain in nanocrystalline materials. Conductivity measurement method is a valuable diagnostic tool for the material quality. It is used to determine the energy distribution of various species of gap states. Optical studies give us good information about band gap and optical transparency of the materials. We also calculated the optical band gap.

3.5.1 X-ray diffraction

X-ray diffraction is a method for identification and quantitative determination of the various crystalline forms of compounds present in powdered and films. In XRD, each atom becomes the source of scattered X-ray radiation. The scattered radiation from all the atoms of amorphous material will combine destructively as they fall on top of one another in the random manner. However, in the case of perfect crystal, the X-rays scatter without the loss of energy and constructive interference may occur. The films of the samples are characterized by using XRD method in the 2θ range from 10° to 70°. Figure 3.2 shows the block diagram of XRD.

X-rays are electromagnetic radiation of wavelength about 1 Å (10^{-10} m), which is about the same size as an atom. They occur in that portion of the electromagnetic spectrum between gamma-rays and the ultraviolet. The discovery of X-rays in 1895 enabled scientists to probe crystalline structure at the atomic level. When X-rays interact with a crystalline substance (phase), one gets a diffraction pattern. About 95% of all solid materials can be described as crystalline.

![Block diagram of X-ray diffraction set up used to study thin film](image)

**Figure 3.2: Block diagram of X-ray diffraction set up used to study thin film**

Each crystalline solid has its unique characteristic X-ray diffraction (XRD) pattern which may be used as a "fingerprint" for its identification. Today about 50,000 inorganic and 25,000 organic single components, crystalline phases, and diffraction patterns have been collected and stored on magnetic or optical media as standards.
XRD has been in use in two main areas, for the fingerprint characterization of crystalline materials and the determination of their structure. Once the material has been identified, X-ray crystallography may be used to determine its structure, i.e. how the atoms pack together in the crystalline state and what the interatomic distance and angle are etc. X-ray diffraction is one of the most important characterization tools used in solid state chemistry and materials science. We can determine the size and the shape of the unit cell for any compound most easily using the diffraction of x-rays (Figure 3.3).

### 3.5.2 Atomic force microscope

The atomic force microscope (AFM) is a very high-resolution type of scanning probe microscope, with demonstrated resolution of fractions of a nanometer, more than 1000 times better than the optical diffraction limit. Binnig, Quate and Gerber invented the first AFM in 1986. The AFM is one of the foremost tools for imaging, measuring and manipulating matter at the nanoscale. The term 'microscope' in the name is actually a misnomer because it implies looking, while in fact the information is gathered by "feeling" the surface with a mechanical probe. Piezoelectric elements that facilitate tiny but accurate and precise movements on (electronic) command enable the very precise scanning. Figure 3.4 illustrates the block diagram of AFM. The AFM consists of a micro scale cantilever with a sharp tip (probe) at its end that is used to scan the specimen surface. The cantilever is typically silicon or silicon nitride with a tip radius of the order of nanometers. The AFM works by scanning a fine ceramic or semiconductor tip over a surface much the same way as a phonograph needle scans a record. When the tip is brought into proximity of a sample surface, Van der Waals forces between the tip and the sample lead to a deflection of the cantilever.

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**Figure 3.3: Typical XRD pattern of ZnO nanostructures**

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Figure 3.4: Block Diagram of Atomic Force Microscope

The magnitude of the deflection is captured by a laser that reflects at an oblique angle from the very end of the cantilever. A plot of the laser deflection versus tip position on the sample surface provides the resolution of the hills and valleys that constitute the topography of the surface. The AFM can work with the tip touching the sample (contact mode), or the tip can tap across the surface (tapping mode) much like the cane of a blind person.

3.5.3 Transmission Electron Microscope (TEM)

Transmission electron microscopy has been used traditionally as a tool for characterizing local atomic structures of material objects since the information obtained does not require the objects being periodic such as crystal. In the characterization of ZnO nanostructures, TEM is one of the most powerful instruments available due to its excellent imaging and analytical capabilities. TEM imaging allows both the imaging of relatively large areas and the precise measurement of nanostructures diameters. TEM has a very high magnification and can give detailed information about the structure of even a single nanostructure. The nanostructures appear ‘transparent’ in the TEM pictures, which enables the measurement of both inner and outer diameter. It is also possible to determine the number of layers in a nanostructures tube wall, whether it contains any type of structural damage or irregularities. Another type of interesting observation permitted by the TEM is the shape and location of any residual catalyst that may be incorporated in the tube.
One disadvantage with the TEM is that it has to be manually calibrated by taking pictures of special calibration particles several times during each experimental session. The beads have a known size, which is used to compare and calculate the measurements of the particles in the sample. It can also be argued that the TEM is too powerful to generate a fair interpretation of a nanostructures sample. It is far too tempting to concentrate on details rather than on the general picture. Therefore, a SEM or an optical microscope is likely to give a more accurate overall view than a TEM, except when very short (<100 nm) tubes are present. The inner structure of the as-prepared ZnO nanostructures synthesized by LPCVD was confirmed by TEM.

3.5.4 Scanning Electron Microscope (SEM)

The first scanning electron microscope (SEM) debuted in 1938 (Von Ardenne) with the first commercial instruments around 1965. Its late development was due to the electronics involved in "scanning" the beam of electrons across the sample. SEM is a microscope that uses electrons rather than light to form an image. There are many advantages to using the SEM instead of a light microscope. The SEM has a large depth of field, which allows a large amount of the sample to be in focus at one time. The SEM also produces images of high resolution, which means that closely spaced features can be examined at a high magnification. Preparation of the samples is relatively easy since most SEM only require the sample to be conductive. The combination of higher magnification, larger depth of focus, greater resolution, and ease of sample observation makes the SEM one of the most heavily used instruments in research areas today. The ZnO nanostructures synthesized by LPCVD and ECR-CVD were characterized by SEM.

3.5.5 High Resolution Transmission Electron Microscope

Among various analytical techniques, High-resolution transmission electron microscopy (HRTEM) has played a important role in the discovery and characterization of ZnO nanostructures. It may be claimed that ZnO nanostructures might have not been discovered without using HRTEM. HRTEM has been widely and effectively used for analyzing crystal structures and lattice imperfections in various kinds of advanced materials on an atomic scale. HRTEM images closely depend not only on some optical factors in the imaging process by the electron lens, but also on the scattering process of the electron's incident on the crystal specimen. HRTEM (HRTEM, JOEL-264 JEM3011) confirmed the diameter and inner wall structure of the as-prepared ZnO nanostructures grown by LPCVD and ECR-CVD.

3.5.6 Field Emission Scanning Electron Microscope (FESEM)

A field-emission cathode in the electron gun of a scanning electron microscope provides narrower probing beams at low as well as high electron energy, resulting in both improved spatial resolution and minimized sample charging and damage. Under vacuum, electrons generated by a field emission source are accelerated in a field gradient. The beam passes through electromagnetic lenses, focusing onto the specimen. As result of this bombardment different types of electrons are emitted from the specimen. A detector catches the secondary electrons and an image of the sample surface is constructed by comparing the intensity of these secondary electrons to the scanning primary electron beam. Finally, the image is displayed on a monitor. The high-resolution reached by FESEM (~ 2 nm) allows the study of very small micro-structural details. FESEM
produces clearer, less electrostatically distorted images. By FESEM high quality, low voltage images are obtained with negligible electrical charging of samples. FESEM (FESEM JOEL 6500) measurements have been performed for nanostructures synthesized by LPCVD.

3.5.7 Fourier Transform (FT) Raman Spectroscopy

Raman Spectroscopy is a form of vibrational spectroscopy, much like infrared (IR) spectroscopy. It is a powerful, multifaceted technique with wide-ranging applications in carbon nanostructures studies. Raman spectroscopy and Raman spectra allow one to obtain important qualitative and quantitative data. Raman bands arise from a change in the polarizability. The G- D- and G'- bands allow one to examine the diameter and chirality (chiral angle) of carbon nanostructures [15]. This may allow one to characterize carbon nanostructures classified as metallic, semi-metallic or semiconducting [16]. It provides deep insight in the physical properties as well as the material quality. It is further used to confirm the graphitic structure of the ZnO nanostructures. Raman spectroscopy (BRUKER, RFS 100/S) was done to confirm the graphitic structure of as-prepared ZnO nanostructures synthesized by LPCVD.

3.6 Optical

Optical characterization of thin film has done by using J. Tauc's method used for materials having direct transition [17, 18]. The glass substrates are used as reference for optical studies. These are having high transparency in the required wavelength range. Figure 3.5 shows the transmission spectrum of substrate used for optical measurements. The transmission spectrum is recorded using computer-controlled Double Beam Scanning NIR/UV/VIS Spectrophotometer [Camspec M550].

![Figure 3.5: Transmission spectrum of glass used for optical studies](image-url)
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3.6.1 UV and IR spectrophotometers

Monochromator spectrophotometer is used to measure the transmission spectrum. Optical layout of monochromator spectrophotometer is shown in Figure 3.6. The light after passing through entrance slit and turning mirror is routed by collimator spherical mirror onto diffraction grating. Grating converts the parallel beam from each point of entrance slit into a fan of monochromatic parallel beams. Camera spherical mirror forms the monochromatic images of these images, when combined, form a spectrum of a certain wavelength range.

![Figure 3.6: Optical layout of monochromator spectrophotometer](image)

The light shutter shuts off the light passing through entrance slit. Diffraction grating is installed on a quadruple turret. The change of diffraction gratings is affected by turning the turret at an angle of 90° around a particular axis. Flip mirror is used for the detector port selection. When the flip mirror is in position F, the axial port is selected as an exit port. When the flip mirror is brought to position F', the lateral port is selected as an exit port.

M550 is a completely automated device which uses an internal controller to control the operation of gratings (changeover and rotation), output mirror, entrance/exit slits, filter wheel and shutter. A Si-detector is mounted after the exit slit. The transmittance of the glass substrate with and without film is recorded. The transmission spectra of the film are obtained after subtracting the transmittance of substrate as reference. After passing through the sample compartment, the monochromatic beams are converged and then converted into an electric signal by the detector. The intensities of the two transmitted beams are electronically compared. The electric signal provided from the detector is processed by a CPU and the computational result is displayed directly on the CPU or output to recorder.
3.6.2 Ultraviolet-visible spectroscopy

The spectrophotometers (Figure 3.7) are used in the UV and visible regions of the spectrum and some of these instruments also operate into the near-infrared region as well. Visible region 400-700 nm spectrophotometer is used extensively in colorimetric science. Ink manufacturers, printing companies, textiles vendors, and many more, need the data provided through colorimetric. They usually take readings at every 20 nanometers along the visible region and produce a spectral reflectance curve. These curves can be used to test a new batch of colorant to check if it makes a match to specifications. Traditional visual region spectrophotometers cannot detect if a colorant has fluorescence. This can make it impossible to manage color issues if one or more of the printing inks are fluorescent. Where a colorant contains fluorescence, a bi-spectral fluorescent spectrophotometer is used. There are two major setups for visual spectrum spectrophotometers, d/8 (spherical) and d/45. The names are due to the geometry of the light source, observer and interior of the measurement chamber. Scientists use this machine to measure the amount of compounds in a sample. If the compound is more concentrated more light will be absorbed by the sample; within small ranges, the Beer-Lambert law holds and the absorbance between samples vary with concentration linearly. Samples are usually prepared in cuvettes; depending on the region of interest, they may be constructed of glass, plastic, or quartz. If you pass white light through a coloured substance, some of the light gets absorbed. Some colourless substances also absorb light -but in the ultra-violet region. Since we can't see UV light, we don't notice this absorption. Different substances absorb different wavelengths of light, and this can be used to help to identify the substance, the presence of particular metal ions, for example, or of particular functional groups in organic compounds. The amount of absorption is also dependent on the concentration of the substance if it is in solution. Measurement of the amount of absorption can be used to find concentrations of very dilute solutions. An absorption spectrophotometer measures the way that the light absorbed by a compound varies across the UV and visible spectrum.

Figure 3.7: The Camspec M550 Double Beam Scanning UV/Vis Spectrophotometer
3.6.3 A simple double beam spectrophotometer

![Block diagram of simple double beam spectrophotometer](image)

Figure 3.8: Block diagram of simple double beam spectrophotometer

The colour-coding of the light beams through the spectrophotometer is not to show that some light is red or blue or green. The colours are simply to emphasize the two different paths that light can take through the device (Figure 3.8). Where the light is shown as a blue line, this is the path that it will always take. Where it is shown red or green, it will go either one way or the other - depending on how it strikes the rotating disc.

3.7 Electrical properties

Electrical conductivity is a measure of a material's ability to conduct an electric current. When an electrical potential difference is applied across a conductor, its movable charges flow giving rise to an electric current. A conductor such as a metal has high conductivity and a low resistivity. An insulator like glass or a vacuum has low conductivity and a high resistivity. The conductivity of a semiconductor is generally intermediate, but varies widely under different conditions, such as exposure of the material to electric fields or specific frequencies of light, and, most important, with temperature and composition of the semiconductor material. The degree of doping in solid state semiconductors makes a large difference in conductivity. More doping leads to higher conductivity. The conductivity of a solution of water is highly dependent on its concentration of dissolved salts and sometimes other chemical species which tend to ionize in the solution. Electrical conductivity of water samples is used as an indicator of how salt-free, ion-free, or impurity-free the sample is; the purer the water, the lower the conductivity. Electrical conductivity is strongly dependent on temperature. In metals, electrical conductivity decreases with increasing temperature, whereas in semiconductors, electrical conductivity increases with increasing temperature. Over a limited temperature range, the electrical conductivity can be approximated as being directly proportional to temperature. In order to compare electrical conductivity measurements at different temperatures, they need to be standardized to a common temperature. It is well known that there is a strong correlation between structural characteristics of the thin films and their electronic transport properties.
On the other hand, a heat treatment of the films may modify these structural characteristics [19, 20]. Consequently, in situ measurement of some electrical properties such as the electrical resistivity of thin films during their heat treatment may offer very useful information about possible changes in the film structure determined by the heating process [21]. Keeping in mind this assumption, the temperature dependence of the electrical resistivity $\rho$, during heating of the Zn films has been measured in the temperature range $290–660$ K to emphasize the oxidation process. It is known that between the electronic transport properties of polycrystalline semiconducting thin films [22, 23] and their structural characteristics there is a strong correlation. Particularly, both the values and the variation of the electrical conductivity of such films are in connection with their structure and its changes. On the other hand, thermal treatments of the respective films will modify their structural characteristics and consequently, their electrical properties. On this basis, the study of the temperature dependence of the electrical properties of thin films, may offer useful information about the possible changes of the structural characteristics of the films. Moreover, when this study is carried out in situ during successive heating and cooling cycles, such structural changes can be revealed [24–28]. In the case of transparent conducting oxides with applications in optoelectronics (as contact electrodes), the measurements of the electrical resistivity during many successive heating and cooling cycles may provide useful information on the thermal stability of the electrode and temperature limitations.

We consider that the main factor that determines these behaviors of the electrical conductivity is the oxidation process that continues to take place during electrical measurements. Namely, due to the considerable interaction at higher temperature between the remaining Zn amount and atmospheric oxygen, a sharp decrease of the oxygen vacancies which act as shallow donors [29, 30] takes place. The loss of the free charges being irreversible, the electrical conductivity will decrease continuously until the complete oxidation of ZnO films. Also, the evaporation of interstitial Zn atoms due to the higher vapour pressure of zinc [31] can reduce the carrier concentration and hence the electrical conductivity [32] certainly, the structural changes during ZnO film annealing can also influence the carrier mobility, $m$, hence the electrical conductivity. But this influence is less pronounced in comparison with that of changes in the stoichiometry of ZnO films [33–37]. On the other hand, the non-linear dependence of the oxygen diffusion rate on the concentration gradient, time and temperature [38] can play an important role in the variation of the electrical conductivity and their irreversibility during the annealing process has been revealed. This behavior is attributed mainly to the oxidation of remaining Zn amount in the films due to the higher heating temperature during electrical measurements. This assumption is sustained by the strong c-axis orientated polycrystalline structures received for both typical two ZnO films after electrical measurements. To study the conduction mechanism in my ZnO films, conductivity measurements are performed at different temperatures for the films prepared by physical vapor deposition method. The calculated conductivity is found to follow the Arrhenius equation:

$$\sigma = \sigma_0 \exp \left( -\frac{E_a}{kT} \right)$$

(3.1)

where, $\sigma_0$ is a constant, $E_a$ is the activation energy of the electron transport in the conduction band, $k$ is the Boltzmann constant and $T$ is the absolute temperature.
The present measurements are found to be of the same nature in the ZnO thin film deposited in different temperature. Good Ohmic contacts are necessary for any electrical measurement. In the present work, predeposited silver electrodes are used for various electrical measurements. Electrodes thick silver electrodes are used for good electrical contacts. The electrodes are deposited using a mask with breadth equal to the side of the substrate and is tied in between so that a gap is left for the deposition of thin ZnO thin film between the electrodes. Thin ZnO thin film of the required samples are deposited on to the electrode gap (using a mask that exposes only the electrode gap of the substrates) by passing low voltage and high current through the Molybdenum boat containing the material. These ZnO thin films of the alloys are used to make the necessary electrical measurements. Figure 3.9 (i) show the silver electrodes, along with the thin film deposited on glass substrate, used for electrical measurements (Figure 3.9- ii). Here $L$ is the length (electrode gap), $B$ is the breadth and $T$ is the thickness of the thin film so that the area of cross-section for current is $A = B \times T$.

![Diagram](image.png)

(i)

**Figure 3.9:** (i) Pre-deposited silver electrodes with thin film on glass substrate

![Diagram](image.png)

(ii)

**Figure 3.9:** (ii) Setup for electrical measurements
3.7.1 Design of Sample Holder

To carry out the various electrical measurements on the ZnO thin film including both the dc and photoconductivity measurements at low and high temperature, we used a specially designed metallic (stainless steel) sample holder. The detailed diagram of the sample holder is shown in the Figure 3.10. Stainless steel is used to take care of the surface currents and unwanted disturbances in the measurements of small currents [of the order of pico amperes (pA)]. It also helps to provide proper shielding to the thin film samples for accurate current measurements during various experimental observations. At low and high temperatures, stainless steel is highly durable and corrosion-free.

![Diagram of Sample Holder](image)

**Figure 3.10:** Setup for electrical measurements
The sample holder is fitted with a Chromel-Alumel thermocouple using Teflon feed through. During different measurements, this thermocouple gives the exact temperature reading to which the thin film is subjected. The junction of thermocouple is placed on copper block over another glass substrate very near to the thin film so that the chances of error in temperature measurement are very rare. A small circular glass window is installed in the sample holder directly in front of the space at which the film is placed on the copper block. The other end of this copper block is in direct contact with liquid nitrogen. By this arrangement, the temperature gradient is very small between the copper block and the liquid nitrogen filled in the sample holder. The light is shown through a glass window to carry out the photoconductivity measurements on the thin films. To cut off the IR part of light, water in a transparent glass cell is kept in front of the glass window while taking various photoconductivity measurements. The copper block from lower side is fitted with two heaters. These heaters are used to anneal the thin ZnO thin film of various samples and to study their behaviour with rise in temperature. These heaters are connected to a variac using Teflon feed through from outside the sample holder to vary the rate of heating. The rate is monitored through display of the digital panel meter which is connected to the thermocouple. The leakage current in the feed through (BNC connectors) is below the measuring limit (10-12A) of the picoammeter used.

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Chapter 4: Electrical Transport Properties

In recent years, semi conducting nanostructures especially one-dimensional nanostructures have drawn a lot of attention due to their potential applications in nano devices. These 1D nanostructures have been found interesting due to their unique optical and electronic properties. Their importance as the building blocks for interconnects of transistors and junctions between metals and semiconductors, and tips of emitters has been recognized. A lot of reports on the whiskers and wires of III-V semiconducting nanostructures as well as the nanostructures of oxide semiconductors are available in the literature. Among the oxide semiconductor nanostructures studied so far, the nanostructures of ZnO have been the focal point of research. ZnO is an n-type material with a wide band gap of 3.3 eV. It emits short wavelength light and shows piezoelectric properties. It is also transparent to visible light and electrically conductive with the dopants such as Al, Ga, In, Sn etc. There are some reports on the fabrication of optical and electronic devices of ZnO nanostructures, also available in the literature. [1-4]. Zinc oxide is the semi-conducting material having wide band gap and high transparency. It is also stable for chemical as well as thermal fluctuations. Generally, optical transparent oxides tend to be electrical insulators by virtue of their large optical band gap \( E_g = 3.1 \) eV, but ZnO is has high transparency and conductivity matching the value for FTO, SnO\(_2\) films Its transparency and conductivity make it a promising candidate for optoelectronic applications like energy windows, liquid crystal displays, solar cells, gas sensors, ultrasonic oscillators, transducers, etc. As is well known there is a strong correlation between structural characteristics of thin films and their electronic transport properties. A heat treatment of the films may modify these structural characteristics [5, 6]. Consequently, in situ measurement of some electrical properties such as the electrical resistivity of thin films during their heat treatment may offer very useful information about possible changes in the film structure determined by the heating process [7]. Keeping in view, the important properties of ZnO nanostructure, we report the electrical transport properties of ZnO nanostructures. Keeping in mind the fact that electrical resistivity has temperature dependence, the ZnO films were investigated in the temperature range 303–573 K.

4.1 Experimental

ZnO nanostructures are fabricated using physical vapour condensation method. In this method, Zn powder (99.999 % pure) has been evaporated in the presence of oxygen and argon gases at a particular partial pressure. Initially, a small quantity of Zn powder has been kept in a molybdenum boat and the chamber has evacuated to a vacuum of the order of \( 10^{-6} \) Torr. After attaining this vacuum, the gases (oxygen and argon) are purged into the chamber. The pressure of these gases is kept fixed at 5 Torr and 1 Torr respectively. The evaporated material is deposited on LN\(_2\) cooled glass substrate. The nanostructures of ZnO are deposited on the glass substrate and also collected in the powder form by scratching from the substrate. Powder X-ray diffraction
(XRD) is performed on a Philips X-ray diffractometer with Cu Kα (λ = 1.54178 Å) radiation. The morphology and the microstructure of these nanostructures are studied using a transmission electron microscope (TEM) at 100 kV. For electrical measurements, we have used a four-probe set-up. The contacts are made using silver paste then and an electrometer (Keithley 6517A) is used to measure the current at different temperature, keeping the voltage fixed at 1.5 Volts.

4.2 Results and discussion

4.2.1 Structural studies

The transmission electron microscope (TEM) images of these nanostructures are shown in Figure 4.1. It is observed from the TEM image that nanostructures contain nanorods and nanoparticles of ZnO. The typical diameter of these nanorods is in the range of 80 to 150 nm and the length is of order of several hundreds of nanometers. Some nanoparticles and nanorods of very small diameter can also be seen, but it seems that these nanostructures contain a lot of impurities and defects.

![TEM images of the grown nanostructures](image)

**Figure 4.1: TEM images of the grown nanostructures**
4.2.2 XRD Studies

The crystallinity and phase identification of ZnO nano structures grown have ascertained by X-ray diffraction (XRD) and result is shown in figure 4.2. As can be seen, sharp diffraction peaks corresponding to wurtzite (hexagonal) structure of ZnO have been observed. The obtained diffraction peaks in all spectra correspond to the single crystallinity with wurtzite hexagonal phase for the grown ZnO nano structures as shown in figure 4.2.

![X-ray diffraction pattern of the grown film](image)

**Figure 4.2: X-ray diffraction pattern of the grown film**

4.2.3 Electrical Transport Studies

The dc conductivity of semiconductor at temperature $T$ is given by

$$\sigma_{dc} = \sigma_0 \exp \left( \frac{E}{kT} \right)$$

(4.1)

where $\sigma_0$ is pre exponential factor, $E$ is activation energy for the generation process and $k$ is Boltzmann constant. We may write

$$\ln \sigma_{dc} = \ln \sigma_0 - \left( \frac{E}{kT} \right)$$

(4.2)

or

$$\ln \sigma_{dc} = -\left( \frac{E}{1000k} \right) \left( \frac{1000}{T} \right) + \ln \sigma_0$$

(4.3)

When we plot a graph between $\ln \sigma_{dc}$ & $1000/T$, a straight line is obtained having slope $(E/1000K)$ and intercept $\ln \sigma_0$ is given in Figure 4.3. Thus, the activation energy can be calculated by using the slope of a straight line.
The dc electrical conductivities of the sample in dark, in the range of temperature from 303-573K were measured. The temperature dependence of the dark conductivity is shown in figure 4.3. The plot of ln $\sigma_{dc}$ against $1000/T$ is a straight line indicating that conduction is through thermal activation process [8]. The resistivity of ZnO has been determined from current voltage curve measured for different temperatures. For all studies a linear dependence typical of ohm’s behavior has been observed (the conductivity as a function of the temperature). The conductivity is directly proportional to temperature. Curve exhibits a minimum of conductivity at room temperature [9]. The conductivity increases with increase in the temperature and the increase in the conductivity by a factor of 10 in comparisons to the previous estimated values are given in table 4.1. The electrical conductivity changes in ZnO and other n type semiconductor under photo reduction in subsequent exposure in oxidizing gas atmosphere are in general explained by the formation and annihilation of oxygen vacancies at the metal oxide surface [10, 11].

![Figure 4.3: Plot of ln $\sigma$ vs 1000/T](image)

**Table 4.1: Variation of conductivity with temperature**

| Temperature(T) K | 312 | 357 | 416 | 455 | 500 | 555 |
|------------------|-----|-----|-----|-----|-----|-----|
| Conductivity( $\sigma$ ) | $2.52 \times 10^{-18}$ | $2.52 \times 10^{-16}$ | $2.38 \times 10^{-14}$ | $2.45 \times 10^{-13}$ | $2.33 \times 10^{-12}$ | $2.23 \times 10^{-11}$ |

### 4.3 Conclusion

ZnO nanosstructures are fabricated using physical vapour condensation method. Powder X-ray diffraction (XRD) is performed on a Philips X-ray diffractometer. The morphology and the microstructure of these nanostructures are studied using a transmission electron microscope (TEM) performed at 100 kV. For electrical measurements, we have used a four-probe set-up. The conductivity increases with increase in temperature.
Chapter 4: Electrical Transport Properties

4.4 References

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Chapter 5: Optical & Electrical Characterization

As is well known the transparent conducting oxides (TCOs) have applications in the fields of electrical devices and displays [1–3]. For these applications, the TCOs should have two important properties i.e. good electrical conduction and transmittance in visible region. Indium tin oxide (ITO) is the popular choice as TCO material due to its high electrical conductivity and greater optical transmittance. However due to its scarcity, high product cost, and environmental pollution problems associated with of ITO, the workers are trying to look for alternative of ITO. Among other TCO materials, ZnO and SnO₂ are good choices [4, 5]. ZnO is a promising alternative to ITO, because it is non-toxic, inexpensive, highly abundant, especially stable in hydrogen plasma, and undergoes crystallization at low decomposition temperature [6]. There are many characteristics of ZnO that makes it suitable for efficient utilization in various novel devices. ZnO is an n-type semiconductor with a wide band gap of 3.37 eV with large exciton binding energy (60 meV) [7].

Recent research shows that ZnO nanomaterials are promising piezoelectric nano generators. This fact has trigged a wide range of subsequent research in searching for new synthetic methods to synthesize ZnO nanomaterials [2]. Among the various ZnO nanostructures, ZnO nanoparticles are the most frequently studied [3], due to their relevance in fundamental study and also because their applications in the field of solar energy conversion, photo catalysis, light-emitting materials [4], transparent UV protection films and chemical sensors [5]. Until now, a variety of techniques have been employed for the synthesis of ZnO nanoparticles, such as metal organic chemical vapour deposition (MOCVD), spray pyrolysis, ion beam assisted deposition, laser-ablation, sputter deposition, template assisted growth and chemical vapor deposition [6–13]. Although the ZnO nanoparticles fabricated using the above methods have a high-purity and high-crystalline structure, but the growth temperature is too high to make them compatible with low-temperature endurance substrates such as glass. Therefore, we need to look for a low-temperature, large-scale, and simple synthetic process for the synthesis of ZnO nanoparticles, which can subsequently be used for nanoscale devices. In this chapter, we present the successful synthesis of ZnO nanoparticles on glass substrate using a simple physical vapor condensation method at a temperature as low as 400°C. The optical and electrical properties of this film containing ZnO nanoparticles were also studied in the wavelength of 300-900 nm and temperature range of 450-300K respectively.

5.1 Experimental

Thin film of ZnO is deposited by physical vapour condensation method. In this method, the starting material is Zn powder (99.999 % pure), which is heated at a temperature of 400°C in presence of oxygen and argon gases in the chamber. Initially a small quantity of Zn powder was kept in a molybdenum boat and the chamber was evacuated to a vacuum of the order of 10⁻⁶ Torr. After attaining this vacuum, the gases (oxygen and argon) are purged in to the chamber. The pressure of these gases is kept fixed at 16 mbar and 4 mbar respectively. The substrate is cooled with liquid nitrogen and this evaporated material is deposited on glass substrate pasted on
the LN$_2$ cooled substrate. The nanoparticles of ZnO are deposited on the glass substrate and also collected in the powder form by scratching from the substrate. Powder X-ray diffraction (XRD) is performed using a Philips X-ray diffractometer with Cu K$_\alpha$ (λ = 1.54178 Å) radiation. The morphology and the microstructure of these nanostructures are studied using a Joel field emission scanning electron microscope (FESEM 7500f) and transmission electron microscope (TEM) at 100 kV. UV–VIS absorption spectrum is recorded using a V-570 Jasco UV–Vis double-beam spectrophotometer. The scanning wavelength range is 300–900 nm. In this investigation, we have successfully grown the ZnO nanoparticles at low temperatures, keeping the gases (O$_2$ and Ar) flow fixed at 6 mbar and 4 mbar respectively.

![Figure 5.1: (a) FESEM image of ZnO nanoparticles](image)

![Figure 5.1: (b) FESEM image of ZnO nanoparticles](image)

![Figure 5.2: (a) TEM image of ZnO nanoparticles](image)

![Figure 5.2: (b) TEM image of ZnO nanoparticles](image)

5.2 Results and discussion

The field emission scanning electron microscope (FESEM) images of the thin film of ZnO are presented in Figures 5.1 (a) & (b). FESEM images reveal the typical morphologies of the grown ZnO nanoparticles. These nanoparticles look like clusters of two or more particles. The size of these nano clusters varies from 30-80 nm. It is observed from the TEM image (Figures 5.2 (a) & (b)) that the typical diameter of these nanoparticles obtained is in the range of 5 to 20 nm. The typical X-ray diffraction (XRD) pattern of these nanoparticles is
presented in Figure 5.3. The XRD spectrum shows that the deposition in the presence of oxygen leads to the formation of ZnO nanoparticles on the glass substrate. In the process used, the source material is heated at 400°C in the presence of oxygen. During this oxidation process, the starting material (Zn) is converted into ZnO film with a polycrystalline structure. The peaks at 36.6° and at 32° are associated with ZnO (101) and ZnO (100) crystallographic plane.

Figure 5.3: XRD pattern of ZnO thin film

The XRD spectrum very clearly demonstrates that the film deposited in oxygen atmosphere has a dominant (101) orientation. A peak associated with Zn is also observed at 57°. These peaks match with JCPDS data (JCPDS 36-1451). We have employed a V-570 Jasco UV–Vis double-beam spectrophotometer for recording the optical absorption of the ZnO film. The scanning wavelength range is 300–900 nm. The absorption is measured in terms of optical density. Thin film of ZnO deposited glass substrate and reference (glass) is kept inside the appropriate film holder. The optical absorption is measured as a function of incidence wavelength. The absorption coefficient (α) is calculated using the following relation;

\[ \alpha = \frac{OD}{t} \]  \hspace{1cm} (5.1)

where OD is the optical density measured at a given film thickness (t).

Figure 5.4 shows the variation of the absorption coefficient (α) as a function of incident photon energy (hv) for ZnO film. The value of absorption coefficient increases exponentially with the increase in photon energy. In both crystalline and amorphous materials, the exponential dependence of absorption coefficient on energy may arise from the random fluctuations of internal fields associated with the structural disorder/intrinsic defects.
such as zinc interstitials and oxygen vacancies [14] The dependence of optical absorption coefficient on photon energy may arise from electronic transitions between localized states.

Figure 5.4: Optical absorption (α) Vs wavelength of ZnO thin film in the wavelength range of (400-900 nm)

The density of these states falls off exponentially with energy. This behavior is consistent with the theory of Tauc [14] The absorption coefficient near fundamental absorption edge is exponentially dependent on the incident photon energy and obeys the empirical Urbach relation,

\[ \ln \alpha \text{ varies as a function of } h\nu. \]

Urbach energy can be calculated by the following relation [15],

\[ a = a_o \exp \left( \frac{h\nu - E_I}{E_U} \right) \]  \hspace{1cm} (5.2)

where \( E_I \) and \( \alpha_o \) are constants and \( E_U \) is the Urbach energy which refers to the width of the exponential absorption edge. Figure 5.5 shows the variation of \( \ln \alpha \) vs. photon energy for the films. The \( E_U \) value was calculated from Urbach plots using the relationship

\[ E_u = \left[ \frac{d(\ln \alpha)}{d(h\nu)} \right]^{-1} \]  \hspace{1cm} (5.3)

The value of Urbach energy \( (E_U) \) is also calculated using the slope of the plot \( \ln \alpha \) vs. photon energy and it is found to be 805.8 meV. This value of Urbach energy is comparable with that reported by other workers [19].

Figure 5.5: \( \ln \alpha \) Vs \( h\nu \) plot for ZnO thin film
In case of semiconductors, the fundamental absorption edge follows an exponential law. Above the exponential tail, the absorption coefficient has been reported [15] to obey the following equation:

\[(\alpha h \nu)^{1/n} = B(h \nu - E_g)\]  \hspace{1cm} (5.4)

where \(\nu\) is the frequency of the incident beam \((\omega=2\pi\nu)\), \(B\) is a constant, \(E_g\) is optical band gap, \(n\) is an exponent and it can have various values e.g. 1/2, 3/2, 2 and 3 depending on the nature of electronic transition responsible for the absorption. For allowed direct transition, \(n\) can have a value of either 1/2 or 3/2 and for forbidden indirect transition, \(n\) can have a value of either 2 or 3 [16]. Here, the direct and indirect transitions are optical transitions that occur in the crystalline semiconductors. It is well known that direct transition across the band gap is feasible between the valence and the conduction band edges in \(k\) space. In the transition process, the total energy and momentum of the electron–photon system must be conserved.

It is found that our experimental data recorded for ZnO film gives a best fit with \(n = 1/2\) using equation (4). This suggests that the absorption in ZnO film is due to direct transition. Therefore, the experimental data is replotted as \((\alpha h \nu)^2\) Vs photon energy \((h \nu)\) for direct transition. Figure 5.6 presents the variation of \((\alpha h \nu)^2\) with photon energy \((h \nu)\) for ZnO film. The value of direct optical band gap \((E_g)\) is calculated by measuring the intercept on the X-axis. The calculated value of \(E_g\) for the present ZnO sample is 3.54 eV. This value is comparable with the results of various workers for other ZnO nanostructures reported in the literature [17-18].

![Figure 5.6: \((\alpha h \nu)^{1/2}\) Vs \(h \nu\) for ZnO thin film in the wavelength range of (400-900 nm)](image-url)
Electrical conductivity in thin film of ZnO can proceed through a variety of mechanisms. Intrinsic defects in ZnO are notorious for their electrical activity, and along with extrinsic impurities, can give rise to impurity conduction phenomena and band conduction, near and above room temperature. In addition, the grain boundaries act as charge-carrier traps, leading to band bending and potential barriers all around the grains, thus affecting the electrical conductivity of this film [20]. This process may be taken into consideration for explaining the electrical conduction mechanism in the sample.

Temperature dependence of dc conductivity for the temperature range (450-300K) is presented in Figure 5.7. The dc conductivity varies exponentially with the temperature. For the present sample of ZnO thin film, the conductivity as a function of temperature shows Arrhenius behavior. The plot of lnσ Vs 1000/T for the temperature range of (450-300K) is presented in Figure 5.8. It is observed that the plot of lnσ Vs 1000/T is a straight line, which suggests that the conduction in this system is through thermally activated process. The conductivity can therefore be expressed by the usual relation

\[ \sigma = \sigma_0 \exp(-\Delta E/k_B T) \]  

where \(\Delta E\) is the activation energy and \(k_B\) is Boltzmann constant. The value of \(E\) calculated using the slope of Figure 5.8, is found to be 0.35 eV. As mentioned before, the present sample is grown in oxygen environment. In such a situation, the carriers are likely to originate in intrinsic defects such as zinc interstitials and oxygen vacancies. These defects are generally recognized as the source of n-type conductivity commonly observed in ZnO nanostructures grown in oxygen rich environment, producing defect levels that lie below the conduction band [21]. Therefore, the present sample exhibits n-type semiconducting behavior originating from native defects, mainly of Zn interstitials or oxygen vacancies.
5.3 Conclusion

From the above studies, it is concluded that the thin film of ZnO contains nanoparticles with the diameter varying from 5-20nm. The XRD spectrum shows the peaks at 36.6° and at 32° which are close to the characteristic peak of ZnO. In case of optical properties, the absorption mechanism is due to direct transition and the value of the optical band gap is found to be 3.54 eV. It has been observed that the absorption coefficient increases exponentially with the increase in photon energy. The value of Urbach energy ($E_U$) is also calculated using the slope of the plot $\ln \alpha$ vs. photon energy and is found to be 805.8 meV. Electrical conduction mechanism is successfully explained with thermally activated transport for the temperature range of 450-300K. For thermally activated process, the calculated value of activation energy is 0.35 eV. The present sample exhibits $n$-type semiconducting behavior originating from native defects, mainly of Zn interstitials or oxygen vacancies.

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Chapter 6: Synthesis of ZnO Nanoparticles

ZnO is a versatile material with an energy gap of 3.37 eV at room temperature. It has been used considerably for its catalytic, electrical, opto-electronic and photochemical properties and applications in transparent electronics, ultraviolet (UV) light emitters, piezoelectric devices, chemical sensors and spin electronics (Nakada et al., 2004; Lee et al., 2005). ZnO is being used as an active channel in invisible thin film transistors, which have achieved much higher field effect mobility than amorphous silicon TFTs (Hossain et al., 2004). These transistors can be widely used for display application. Surface acoustic wave filters using ZnO films have already been used for video and radio frequency circuits. Piezoelectric ZnO thin films have been fabricated into ultrasonic transducers arrays operating at 100 MHz (Ito et al., 1995). On the basis of these remarkable physical properties with the motivation of device miniaturisation, efforts have been focused on the synthesis, characterisation and device applications of ZnO nanostructures such as nanoparticles, nanowires, nanotubes and nanotetrapods. Due to its potential application in nanodevices, ZnO nanostructures, such as nanoparticles, nanorods, nanowires and nanoribbons, have attracted great deal of attention (Taton, 2003). The functional and structural applications of ZnO depend on the peculiar physical properties of exotic nanostructures. Tetrapods shaped whisker shows vibration insulation, microwave absorption, antibacterial effect and antistatic effect (Zhou et al., 2003). Xu and Sun (2003) reported the synthesis of needle-like morphology near the tip, such as nanopins of ZnO for field emitter cathode of high emission efficiency; the nanowires with high aspect ratio has been demonstrated to be good sensors (Wan et al., 2004). In addition, the investigation on ZnO nanostructures helps us to understand the fundamental growth process for the development of novel nanodevices. Different synthesis methods, such as vapour phase transport (VTP) [7,8] metal-organic vapour-phase epitaxy (MOVPE) and CVD [9], dip coating [10], hydrothermal route [11] and electrochemical deposition [12] aqueous thermal decomposition [13] have been reported to fabricate various ZnO nanostructures, such as nanoparticles, nanowires, nanorods, nanoribbon, nanosheet, nanotetrapod, nanobelt, nanodisk, nanowall, nanocage, etc. In the present work, the fabrication and characterisation of ZnO nanoparticles using physical vapour condensation method is reported.

6.1 Experimental

ZnO nanoparticles are synthesised by the physical vapour condensation method. In this method, 99.999% pure zinc pallets used as source material are heated in the presence of oxygen mixed with argon. It is one of the important methods for producing oxide nanostructures at low temperatures. There are some reports on the synthesis of nanomaterials using this method available in the literature [14,15]. Nanostructures synthesised from the metal or alloy using vapour condensation method in the oxygen atmosphere contain some intrinsic defects such as interstitial metallic atom or oxygen vacancies in the oxide nanostructures. These defects have an important effect on the characteristics of the oxide nanostructures. Argon is used as an inert gas in the chamber and its role is to offer the frequent collisions to the atoms of the evaporated materials, which results in the reduction of energy of the evaporated atoms. In this method, the material is typically vaporised into a low-density gas (inert gas) and the vapours move from the hot source to the liquid nitrogen cooled substrate. This
liquid nitrogen cooled substrate is used to enhance the deposition efficiency. The nanoparticles of ZnO are deposited on the substrate and collected in the powder form by scratching from the substrate. For this growth of ZnO nanoparticles, the gas pressure of oxygen and argon is maintained at 5 mbar and 1 mbar respectively. The source material is kept in a molybdenum boat placed at a suitable distance from the substrate. A high vacuum of the order of 10−6 mbar is maintained in the chamber with the help of diffusion pump attached with the rotary pump. The source material is heated at around 400 C in the presence of these gases to synthesise these ZnO nanoparticles. Powder X-ray diffraction (XRD) is performed using a Philips X-ray diffractometer with Cu Ka (λ = 1.54178 Å) radiation. The microstructure of these nanoparticles is studied using a transmission electron microscopy (TEM) operated at 100 kV. The UV-VIS absorption spectra is recorded using a V-570 Jasco UV-VIS double-beam spectrophotometer. The scanning wavelength range is 200 nm to 800 nm. In this experiment, we have successfully grown the ZnO nanoparticles at low temperatures, keeping the gases (O2 and Ar) flow fixed at 5 mbar and 1 mbar respectively.

6.2 Results and discussion

The TEM images of these nanoparticles are presented in Figures 6.1 to 6.4 TEM images reveal the typical morphologies of as-grown ZnO nanoparticles.

![TEM Image of ZnO nanoparticle](image1)

![TEM Image of ZnO nanoparticle](image2)

![TEM image of ZnO nanoparticle](image3)

![TEM image of ZnO nanoparticle](image4)
It is observed from these images that the size of these nanoparticles obtained is in the range of 40 nm to 100 nm, but it seems that these nanoparticles contain some impurities and defects. The typical XRD result of these nanoparticles is presented in Figure 6.5. XRD characterization shows that the deposition in the presence of oxygen led to the formation of ZnO nanoparticles. In our process, the source material is heated at 400°C in the presence of oxygen. During this oxidation process the starting material (Zn) is converted into ZnO with a polycrystalline structure. A sharp peak at 36.87° associated with ZnO (101) crystallographic plane is observed. Normally, the diffraction peaks corresponding to (100), (002), (101), (102) and (110) planes are an indication of ZnO with a hexagonal wurtzite structure. These peaks are clearly identified with JCPDS data (JCPDS 36-1451). The intensity of any of these peaks may be higher depending on the preparation conditions of the materials. In our case, the intensity of (101) peak is higher, which clearly demonstrate that the film deposited in oxygen atmosphere has a dominant (101) orientation [16], showing the presence of oxygen vacancies in the so formed ZnO nanoparticles. When the temperature of the melt exceeds its boiling point during resistive heating of the source material i.e. Zn, the smoke consisting of a large amount of embryos above the melt breaks out and spreads out.

![XRD spectra of as grown ZnO nanoparticles](image)

**Figure 6.5: XRD spectra of as grown ZnO nanoparticles**

An intensive mixing occurs at the interface between the smoke and the mixture gas ambience driven by the convection and then oxidation reaction takes place on the surface of these embryos near the interface. For these embryos, (101) is a preferred growth direction as (101) planes have a high surface energy and preferably absorbs the oxygen atoms for the embryos. The oxidising reaction usually takes place on this coarse prism
surface and forms four protrusions. These protrusions continue to grow by capturing more atoms and finally form the nanoparticles to minimise their interface energy. The growth mechanism of these ZnO nanoparticles in the inert gas condensation process includes nucleation, particle growth, particles coagulation and coalescence. The processing condition decides the role played by any of these mechanisms on the characteristics of as grown nanoparticles. The process involves the effusion of atoms from the source material and these atoms will rapidly lose their energy by colliding with gas atoms. As the collision mean free path is very short, the nucleation process is performed homogenously in the vapour phase. The nucleation begins abruptly and proceeds at a very high rate as the difference between the evaporation temperature and the gas phase is very high. For example, an under cooling of 400 K at the evaporation temperature of 1297 K results in a supersaturation value of the order of 105. According to Yang et al. (2002), the nucleation process is considered negligible when supersaturation exceeds 106. An under cooling of the order of few hundred degrees leads to the formation of nanoparticles as the critical diameter of embryonic particles and the nucleation energy barrier are extremely low. These particles serve as sink for additional vapour and quickly reduce the supersaturation, which results in the quenching of additional nucleation. If the supersaturation is limited, the rate of particle formation would be reduced, leading to lower initial number concentrations. The nucleuses can then grow to larger size as additional material is deposited on the surfaces of the growing particles. The distribution of the nanoparticle size must be narrow as reported by Okuyama et al. [17] and Flagan and Lunden [18] as the relative range of particle sizes will decrease during growth. In the present system, narrow particle size distribution was not obtained. Therefore, the supersaturation and thus nucleation are very high. In this case, the particle growth had to be performed due to Brownian coagulation, i.e., the collision of nucleuses resulted in particle growth. The present growth mechanism involves the vapourisation of material into allowed density gas by resistive heating and the vapours migrate from the hot source to liquid nitrogen cooled substrate. The decrease in the evaporation temperature leads to a far more rapid decrease in the equilibrium vapour pressure and correspondingly high supersaturation (Granqvist and Buhrman, 1976). At high supersaturation, the vapours rapidly nucleate, forming very large numbers of extremely small particles. The articles then grow by Brownian coagulation (Snickta et al., 2007). Figure 6.6 shows the room temperature absorption spectra of as-grown ZnO nanoparticles.

![Absorption Spectra](image)

**Figure 6.6:** UV visible spectra of as grown ZnO nanoparticles
The absorption spectra have a very narrow peak near the band edge in the exciton absorption region (at about 381 nm) and red-shifted relative to the bulk exciton absorption (373 nm). From the absorption spectra, one can see that there is absorption almost in the whole violet and visible region. The band edge absorption begins with the wavelength at ~800 nm suggesting that more absorption states or defect energy bands exist in this sample, which agrees well with the discussion on the formation mechanism of these nanoparticles. Moreover, the broad peak at 373 nm may be associated with the presence of oxygen in as grown ZnO nanoparticles (Nan et al., 2005). This broad peak is accounted for the conversion of Zn into ZnO, which corresponds well with the XRD data. The UV-VIS absorption spectra of these nanoparticles also show a typical behaviour between 400 nm and 500 nm. This may be attributed to oxygen vacancies/defect levels in the band gap, which have an important effect on the characteristics of these zinc oxide nanoparticles. Due to the excellent optical properties, these nanoparticles grown at low temperatures are quite interesting for device applications.

6.3 Conclusions

These nanoparticles of ZnO are grown at a low temperature of 400 C using a simple technique. These nanoparticles are almost spherical in shape and the size varies from 40 nm to 100 nm. The XRD spectra shows a broad peak at 36.87, which confirms the growth of ZnO nanoparticles. From the absorption spectra, a broad peak at 373 nm is accountable for the conversion of Zn into ZnO, which agrees fairly with the XRD result. The growth mechanism of these nanoparticles involves the vaporisation of material into a low-density gas by resistive heating and the vapours migrate from the hot source to liquid nitrogen cooled substrate. The decrease in the evaporation temperature leads to rapid decrease in the equilibrium vapour pressure and correspondingly high supersaturation. At high supersaturation, the vapours rapidly nucleate, forming very large numbers of small particles. These small particles then grow by Brownian coagulation.

6.4 References

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