CHAPTER - II

DIFFERENT SYNTHESIS TECHNIQUES AND CHARACTERIZATION STUDIES

2.1 INTRODUCTION

Many techniques have been employed to deposit and grow a variety of ZnO nanostructures. They can be broadly classified into three main categories: physical vapor deposition (PVD), chemical vapor deposition (CVD) and solution based chemistry (SBC). Each method can be subdivided into different individual techniques as given shown in Table 2.1 (Hughes 2006; Ansari et al., 2010).

<table>
<thead>
<tr>
<th>General Techniques</th>
<th>Sub-techniques</th>
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</table>
| Physical Vapour Deposition (PVD) | Thermal evaporation  
Electron beam-PVD  
Sputtering Deposition  
Cathodic Arc Deposition  
Pulsed laser ablation deposition  
Molecular beam epitaxy (MBE) |
| Chemical Vapour Deposition | Thermal CVD  
Low pressure CVD  
Plasma enhanced CVD  
Metal-organic CVD |
| Solution Based Chemistry (SBC) or Wet Chemistry | Hydrothermal synthesis  
Polyol-mediated synthesis  
Sol-gel synthesis  
Template-assisted synthesis |
Gas phase synthesis methods (PVD and CVD) are applied in a gaseous environment in a closed chamber and have been widely used to prepare ZnO nanostructures. However, due to the complex processes, sophisticated equipment and high temperatures, they can hardly be used for large-scale production in commercial applications (Yin et al., 2010). In recent years, solution based chemical methods have attracted more and more attention and have already been commonly used to grow ZnO nanostructures with high yield and uniformity at relatively low temperature.

2.2 PHYSICAL VAPOR DEPOSITION

Physical vapor deposition (PVD) is a variety of vacuum deposition and is a general term used to describe any of a variety of methods to deposit thin films by the condensation of a vaporized form of the material onto surface of various substrates. The coating method involves purely physical processes, such as high temperature vacuum evaporation or plasma sputter bombardment rather than involving a chemical reaction at the surface to be coated as in chemical vapor deposition. Various PVD methods for the deposition or synthesis of zinc oxide thin films or nanostructured materials include thermal evaporation, electron beam PVD, sputtering (magnetron and RF sputtering), cathodic arc deposition and pulsed laser ablation deposition etc. These deposition methods for the fabrication of zinc oxide are discussed in brief as follows.

2.2.1 Thermal Evaporation

In thermal evaporation the material to be deposited is heated to a high vapour pressure by electrically resistive heating in "low" vacuum. Various type of zinc oxide nanostructures are synthesized by thermal evaporation technique. It is a simple process in
which condensed or powder phase of source material is vaporized at elevating temperature and then the resultant vapor phase condenses at certain conditions (temperature, pressure, atmosphere, substrate etc.) to form the desired product. There are several processing parameters, such as temperature, pressure, carrier gas (including gas species and its flow rate), substrate and evaporation time period that can be controlled and need to be selected properly before or during the thermal evaporation. The source temperature selection mainly depends on volatility of the source material. Usually, it is slightly lower than the melting point of the source material. The pressure is determined according to the evaporation rate or vapor pressure of source material. The substrate temperature usually drops with increasing distance from the position of source material. The local temperature determines the type of the product to be received. It is also noted that the thermal evaporation process is very sensitive to the concentration of oxygen in the growth system. Oxygen influences not only the volatility of the source material and the stoichiometry of the vapour phase, but also the formation of product. The most common method to synthesize ZnO nanostructures utilizes a vapor transport process. In such a process, Zn and oxygen or oxygen mixture vapour are transported and react with each other, forming ZnO nanostructures. There are several ways to generate Zn and oxygen vapour. Decomposition of ZnO is a direct and simple method, however, it is limited to a very high temperatures (~1200 - 1400 °C) (Dai R. Z. et al., 2003). Another direct method is to heat up Zn powder under oxygen flow (Yao et al., 2002). This method facilitates relative low growth temperature (500 - 900 °C), but the ratio between the Zn vapour pressure and oxygen pressure needs to be carefully controlled in order to obtain
desired ZnO nanostructures. It has been observed that the change of this ratio contributes to a large variation on the morphology of nanostructures.

The indirect methods to provide Zn vapour include metal-organic vapor phase epitaxy, in which organometallic Zn compound, diethyl-zinc for example, is used under appropriate oxygen or N₂O flow (Park and Yi 2004). In the widely used carbothermal method, ZnO powder is mixed with graphite powder as source material (Yao et al., 2002). At about 800 - 1100 °C, graphite reduces ZnO to form Zn and CO/CO₂ vapors. Zn and CO/CO₂ later react and result in ZnO nanocrystals. In this method the existence of graphite significantly lowers the decomposition temperature of ZnO.

2.2.2 Electron Beam PVD

In electron beam PVD the material to be deposited is heated to a high vapour pressure by electron bombardment in "high" vacuum of the order of 10⁻⁶-10⁻⁹ torr. Polycrystalline zinc oxide pellet or zinc metal are used as target for the electron beam bombardment and deposition of nanostructured thin film on the substrate. Electron beam energy, distance between target and substrate, substrate temperature and orientation, order of vacuum are some key parameters to control the morphology of zinc oxide nanostructures by electron beam evaporation method. Usually O₂ gas at low pressure of the order of 10⁻⁵ torr is introduced in the deposition chamber. Electronic as well as target material collision with O₂ ionize it and improve the crystallinity and stochiometry of zinc oxide thin film. The growth rate of the film is of the order of 3-5 Å/s depending on the key parameters used. Asmar et al., (2006), have deposited zinc oxide nanostructured thin film using electron beam evaporation. They employed polycrystalline ZnO target placed
in the deposition chamber with $10^{-6}$ torr pressure, 5 keV energy of electron beam, 12 cm separation between the target and substrate, Si (100) substrate at 500 °C temperature and $8\times10^{-5}$ torr oxygen pressure. In another report Qiu et al., (2005), have fabricated well aligned ZnO nanocolumns on Si (100) wafers using electron beam evaporation.

### 2.2.3 Sputter Deposition

In sputter deposition technique a glow plasma discharge (usually localized around the "target" by a magnet) bombards the material sputtering some away as a vapour. Saw et al., (2008), have fabricated ZnO thin film of 1 µm thickness on sapphire (0001) substrate using sputtering of a pure sintered ZnO bulk target in argon atmosphere using a 200 W direct current magnetron source. After sputtering, the film was annealed at 80 °C temperature in nitrogen atmosphere for 2 hours. Tetrapod like nanostructures of zinc oxide are grown after the annealing of as synthesized ZnO thin film. Metallic zinc was used as magnetron target for the fabrication of ZnO thin film on the soda lime glass substrate by Kim et al., (2009). Single crystalline ZnO nanobelts are synthesized by Choopun et al., (2005), using radio frequency (RF) sputtering. In a typical experimental procedure, ZnO polycrystalline target placed in the Nanostructured ZnO thin films are grown on p-type Si (100) substrate using RF sputtering by Kim K. S. et al., (2003). Deposition chamber with $1\times10^{-5}$ torr vacuum is subjected to 300 W of RF power for 60 minutes to deposit ZnO thin film on the copper substrate at room temperature.

### 2.2.4 Cathodic Arc Deposition (or) Arc-PVD

It is a physical vapour deposition technique in which an electric arc is used to vaporize material from a cathode target (Zn for the fabrication of ZnO). The vapourized
material then condenses on a substrate, forming a thin film. The technique can be used to deposit a metallic, ceramic and composite film. The arc evaporation process begins with the striking of a high current, low voltage arc on the surface of a cathode (known as the target) that gives rise to a small (usually few µm wide), highly energetic emitting area known as a cathode spot. The localized temperature at the cathode spot is extremely high (around 15000 °C), which results in a high velocity (10 km/s) jet of vapourized cathode material, leaving a crater behind on the cathode surface. The cathode spot is only active for a short period of time and then it self-extinguishes and re-ignites in a new area close to the previous crater. This behavior causes the apparent motion of the arc. Since the arc is basically a current carrying conductor it can be influenced by the application of an electromagnetic field, which in practice is used to rapidly move the arc over the entire surface of the target, so that the total surface is eroded over time. The arc has an extremely high power density resulting in a high level of ionization (30-100%), multiply charged ions, neutral particles, clusters and macroparticles (droplets). If a reactive gas is introduced during the evaporation process, dissociation, ionization and excitation can occur during interaction with the ion flux and a compound film will be deposited.

2.2.5 Pulsed Laser Ablation Deposition

High energy laser is used to vaporize or ablated depending on laser irradiance zinc/zinc oxide bulk target in O₂ or/and inert gas at particular pressure. Vaporized materials get deposit on seeded/unseeded, crystalline/non crystalline substrate placed perpendicular to the direction of plume flow at particular distance from the target substrate. Laser irradiance, laser wavelength, pressure inside the chamber, ratio of
oxygen with inert gas, distance of substrate from target, substrate temperature, nature and orientation of substrate are some key parameters to control morphology of laser produced zinc oxide thin films or nanostructures.

2.2.6 Molecular Beam Epitaxy (MBE)

MBE is a widely used thin film deposition technique involving the reaction of one or more thermal beams of atoms or molecules with a crystalline surface in an ultrahigh vacuum of the order of $10^{-8}$ Pa (Steiner 2004). MBE allows delicate control of atomic level deposition and dopant species. Gas phase MBE has been used to grow ZnO nanorods and nanowires (Heo et al., 2002). During MBE depositions, site-selective catalyst driven growth is also possible. The ability to synthesize nanorods at arbitrary locations at moderate temperatures is possible and makes this technique excellent for nano-device integration. During this process the background base pressure should be low and well controlled. For ZnO growth, an oxygen/ozone mixture is required as oxidising source. This requirement for ozone makes the system expensive to operate, in addition to the high costs associated with the ultra-high vacuum (UHV) operation.

2.3 CHEMICAL VAPOUR DEPOSITION

Chemical-vapour deposition (CVD) technology is particularly interesting not only because it gives rise to high-quality films but also because it is applicable to large-scale production. This technique is widely used in the fabrication of epitaxial films toward various GaN-based optoelectronic devices and similar trend might be expected for future applications of ZnO. There are several modifications of this method depending on precursors used. In the CVD method, ZnO deposition occurs as a result of chemical
reactions of vapor-phase precursors on the substrate, which are delivered into the growth zone by the carrier gas. The reactions take place in a reactor where a necessary temperature profile is created in the gas flow direction.

### 2.3.1 Thermal CVD

Thermal CVD is widely used because the system construction and process are relatively simple. The schematic diagram of a horizontal CVD system is shown in Fig. 2.1. In synthesizing ZnO nanostructures using horizontal thermal CVD, ZnO powder mixed with carbon powder is normally used as source material and the ZnO nanostructures are formed via carbothermal reduction under Ar or Ar+O₂ flow conditions (Zhao et al., 2005). If the ZnO nanostructures are synthesized using thermal CVD, the temperature, the reactor pressure and the gas ambient are very important factors affecting the morphologies and the properties of the synthesized nanostructures (Park et al., 2005). Because the temperature and the partial pressures of the reactive vapors are different depending on the positions of the substrates in the reactor, the position of the substrates has a significant effect on the morphologies and the properties of the synthesized nanostructures. In most cases of thermal CVD, the substrates are placed on the alumina boat with the source powders or on some position next to the alumina boat in the reactor tube. From the viewpoints of substrate types, Si and Al₂O₃ are mostly used as substrates for the synthesis of ZnO nanostructures.
2.3.2 Low Pressure CVD

Low pressure chemical vapour deposition (LPCVD) is a process used in the manufacturing of the deposition of thin films on semiconductors usually ranging from a few nanometers to many micrometers. LPCVD is used to deposit a wide range of possible film compositions with good conformal step coverage. These films include a variety of materials including polysilicon for gate contacts, thick oxides used for isolation, doped oxides for global planarization, nitrides and other dielectrics. LPCVD is similar to other types of CVD in that it is a process where a gaseous species reacts on a solid surface or wafer and the reaction that occurs produces a solid phase material. Each and every CVD process has the same four steps that must happen. First, the reacting gaseous species must be transported to the surface. Second, the gaseous species must absorb into the surface of the wafer. Third, the heterogeneous surface reaction produces reaction products (Stoffel et al., 1996). Finally the gaseous reactants need to be removed from the surface. In the LPCVD ZnO deposition process, the deposition occurs as a result of chemical reactions of vapor phase precursors on a hot substrate.

The schematic diagram of a typical LPCVD system is shown in Fig. 2.2. The LPCVD system has a quartz tube placed in a spiral heater that starts with tube pressure at
very low pressure around 0.1 Pa. The tube is then heated to the desired temperature and the gaseous species ("working gas") is allowed into the tube at the pressure predetermined between 10-1000 Pa. This working gas consists of dilution gas and the reactive gas that will react with the substrate and create a solid phase material on the substrate. After the working gas enters the tube it spreads out around the hot substrates that are already in the tube at the same temperature. The substrate temperature is extremely important and influences what reactions take place. This working gas reacts with the substrates and forms the solid phase material and the excess material is pumped out of the tube.

![Fig. 2.2. Schematic diagram of a typical LPCVD system](image)

2.3.3 Plasma Enhanced CVD

A schematic of the plasma source is shown in Fig. 2.3 (Barankin et al., 2007). It consist of two perforated aluminum electrodes, 33 mm in diameter, separated by a gap 1.6 mm wide (Atomflo™ - 250D from Surfx Technologies). The electrodes were perforated to allow helium and either carbon dioxide or oxygen to flow through them. The upper electrode was connected to an RF power supply at 13.56 MHz, while the lower
electrode was grounded. A third aluminum plate was installed beneath the lower electrode. It contained a network of channels and holes that mixed the metal organic precursors with the plasma afterglow. Located 4 mm further downstream was a rotating sample stage with integrated heating system.

The plasma was fed with 30 L/min. of ultrahigh purity helium (99.999%) and 44 cm$^3$/min of either medical grade carbon dioxide (99.8%) or ultrahigh purity oxygen (99.999%). Diethylzinc (DEZn) and trimethylaluminum were stored in stainless steel bubblers that were placed in baths maintained at 26.0 °C and 16.7 °C, respectively. The bubbler pressures were fixed at 1160 torr and 1100 torr, respectively, using pressure controllers with Baratron sensors. The helium was further purified by pure-gas monotorr purifier to reduce the oxygen concentration below 1 ppb before entering the flow system. A dilution flow rate of 5.5 L/min. was added to the precursor delivery lines downstream of the bubblers to improve the mixing in the showerhead. The substrates used were Corning 1737 glass coupons, 3.8 x 3.8 cm$^2$, or silicon (1 0 0) wafers, 10 cm in diameter. The films were deposited by PECVD using the procedure given below. Thermal CVD differed from PECVD only in that the plasma was extinguished prior to the introduction of the precursors. The substrate was washed in de-ionized water and acetone, dried with compressed air and baked in a fume hood at 300 °C for 5 min. before being placed on the sample holder. The chamber was evacuated to a pressure of 30 mtorr, and then pressurized with helium to 800 torr. After heating the substrate to the growth temperature while spinning at 150 rpm, a glow discharge was struck with 75 W of RF power. After 4 min. of operation the carbon dioxide or oxygen flow was introduced. Then deposition
was initiated by feeding 47 to 165 cm$^3$/min of helium to the diethylzinc bubbler and 1.3 cm$^3$/min. of helium to the trimethylaluminum bubbler. The corresponding partial pressures were 20–70 mtorr of diethylzinc and 0.2 mtorr of trimethylaluminum. At the end of the deposition time, the precursor flow was switched to a vent line and after one additional minute, the dilution flow was switched off and the plasma extinguished.

2.3.4 Metal-Organic CVD

Amongst all the CVD techniques MOCVD is considered as one of the superior technique for epitaxial films (Ozgur et al., 2005). Recently MOCVD has made great a progress in the field of ZnO growth. MOCVD is one of the most important preparation methods from practical point of view because of its high step coverage, high deposition rate by laying down multiple layers of atoms with incredible precision and large area uniformity of the film quality. Due to excellent conformality of deposited films,
elimination of pinhole type defects, low particle count, the absence of radiation process induced damage, has made MOCVD more beneficial and useful for the growth of ZnO epitaxial layers. Due to a lot of demands in different applications, MOCVD growth of ZnO can be divided in two distinct periods. During the first period, roughly from 1964 to 1998, the films were dedicated to such applications like solar cell transparent electrodes, piezoelectric devices or surface acoustic wave (SAW) filters. In this period the “epitaxy” quality was not as essential as it became after 1998. After 1998 due to the hope of p-type doping, ZnO layers were used as photonic and optoelectronic devices.

Premature reaction between the Zn metal-organic compounds and the oxidants, leading to the deposition of particular upstream from the susceptor has been the main problem to solve. In order to solve this key issue, less reactive Zn metalorganic in combination with various oxidants, along some adducts have been used. Separate inlets to inject the metalorganic compound and the oxidant have been used to get rid of the problem of pre-reaction. Various carrier gases, different geometries, horizontal or vertical reactors, high speed rotation have been used, as well. The main criteria of the selection of precursors depend on their cost, safety, purity, availability, the key problem of premature reactions and the growth rate of the layers.

2.4. SOLUTION BASED CHEMISTRY (OR) WET CHEMISTRY

2.4.1 Hydrothermal Synthesis

Hydrothermal synthesis can be defined as a synthesis method for growing crystals from an aqueous solution at high temperature under high vapour pressure. Since no sophisticated equipment is required and crystalline material can be created directly from
the solution, hydrothermal synthesis provides a simple and effective option for large-scale production of ZnO nanocrystals. Compared to other growth methods, hydrothermal synthesis has several advantages such as low cost, high yield, rapid growth rates and environmental friendliness (Aneesh et al., 2007). The size and shape of the obtained ZnO particle can be easily controlled by adjusting the reaction temperature, reaction time, reactant concentrations or molar ratio of precursors. For example, a controlled synthesis of flower-like and rod-like ZnO particles has been realized by hydrothermal method at 120 °C. The well-defined morphologies were obtained by simply tuning the ratio of sodium hydroxide to zinc acetate in narrow range (Zhang et al., 2007). Well-faceted hexagonal ZnO nanorods have been synthesized at relatively low temperature (90 °C) without any catalyst or templates. The experiments have shown that the diameter of the ZnO nanorods decreased with prolonging the reaction time (Yang Y. H. et al., 2009).

2.4.2 Polyol-Mediated Synthesis

Polyol-method synthesis has turned out to be well suited for the preparation of spherical oxide particles of 30-200 nm (Feldmann et al., 2001a). This method is based on heating suitable metal salts and a defined amount of water in a multivalent and high-boiling alcohol, such as ethylene glycol, diethylene glycol or polyethylene glycol. The alcohol itself can act as a stabilizer and therefore, it can limit the growth of particles and prohibit the particles agglomeration. Due to high reaction temperature which can be applied (> 150 °C), highly crystalline oxides are often produced (Feldmann et al., 2003). This technique is comparably easy to perform and has been applied to prepare a variety of materials including sulfides (Feldmann et al., 2001b), phosphates and elemental metals
(Wiley et al., 2005; Sun et al., 2003; Xiong et al., 2005). Feldmann et al., (2003) have applied this method to prepare nanoscale functional materials, such as colour pigments, transparent conducting oxides and catalytically active oxides. The reactants mixture was heated to 180 °C - 240 °C for 2-12 hours. The average particles diameter can be adjusted by tuning the reaction temperature and time, the concentration of metal precursor and the amount of water.

2.4.3 Sol-Gel Synthesis

The sol-gel process involves the evolution of inorganic networks through the formations of a colloidal suspension (sol) and gelation of the sol to form a network in a continuous liquid phase (gel). With further processes, it is possible to produce powders, films, fibers and monoliths. The sol-gel process normally consists of the hydrolysis and condensation of a precursor.

The sol-gel routes to prepare visible luminescent ZnO nanoparticle colloids were invented in the 1980s and were investigated intensively in the 1990s (Xiong, 2010). The most popular way is to hydrolyze zinc acetate in ethanol and produce ZnO nanoparticles with typical green-yellow emission at 500 nm - 550 nm. However, the prepared ZnO colloids are very unstable. They can grow and precipitate from the mother-liquor at room temperature. Meulenkamp (1998) has prepared ZnO nanoparticles with diameters from 2 nm to 7 nm by sol-gel synthesis. It is found that aging of particles is governed by temperature, water content and the presence of reaction products. Water and acetate can induce considerably accelerated particle growth.
Solochemical (SC) processing is a sol-gel technique used for the production of zinc oxide nanopowder. This method involves preparation of a solution containing zinc complex and subsequent decomposition of the complex into the zinc oxide nanopowder. Another name for this method is two-stage solochemical (TSSC) method. TSSC method can also be used for production of other oxides such as Mn$_2$O$_3$ and NiO. Pouring of a limpid chemical (containing zinc complex) onto a second chemical leads to the formation of a nanoscale powder. The solochemically formed nanopowder can further be doped with other oxides. The product can be nanocomposite. Nanocomposite particles are usually used as varistores with nanostructure morphology. Due to simplicity, versatility and low cost of solochemical method, this process is extremely viable for industrial production of zinc oxide (Vaezi et al., 2007).

In the present work granular ZnO nanostructures were synthesized with an average diameter of 24 nm using sol-gel method for applications in solar cells. (Sornalatha and Murugakoothan, 2013).

2.4.4 Template-Assisted Synthesis

Recently, there is increasing interest in the template-assisted method because it has been used to synthesize various nanotubes composed of many types of materials, such as silica (Mitchell et al., 2002; Gao et al., 2011), metal oxides (Son et al., 2005), polymers (Jayaraman et al., 2005) and biological macromolecules (Hou et al., 2005). An important characteristic of template synthesis method is the ability to control the dimensions of nanotubes obtained. For example, the outside diameters of nanotubes can be well determined by the diameters of pores in template and the lengths can be well determined.
by the thickness of template. However, up to now, the template-assisted method is still difficult to control the inside diameters of nanotubes (Chen et al., 2005; Siwy et al., 2005). For some applications, precise controlling of the inside diameters is absolutely essential (Hou et al., 2004). It is also highly difficult to realize the design and synthesis of multi-walled nanotubes by the template-assisted method.

Recently, the multi-walled nanotubes have attracted much interest because of their special properties (Gu et al., 2010; Kim et al., 2008). Based on the above considerations, here we set up a novel ZnO nanorod array template-assisted electrodeposition method for the design and synthesis of single- and multi-walled nanotube arrays (NTAs) because this method enables excellent control of NTAs. Here single-walled polypyrrole (PPy) NTAs and triple-walled MnO$_2$/PPy/MnO$_2$ NTAs as examples, were successfully synthesized.
and as electrodes they exhibited superior supercapacitive performance with excellent long-term cycle stability and high energy and power densities. The synthetic pathway to single-walled nanotubes proposed by Wang et al., (2013), is illustrated in Fig. 2.4(a). In this study, ZnO nanorod arrays (NRAs) attached on conductive substrate are firstly synthesized and utilized as templates, and then the electropolymerization of polypyrrole (PPy) is carried out on the surfaces of ZnO NRAs to form ZnO/PPy coreshell NRAs. Finally, PPy NTAs are fabricated by etching ZnO from ZnO/PPy core-shell NRAs. This method has the advantages of controlling the outside and inside diameters of nanotubes by adjusting the wall thickness and diameters of ZnO nanorod precursors as shown in Fig. 2.4(b) and (c).

2.5 CHARACTERIZATION STUDIES

2.5.1 X-Ray Diffraction (XRD)

The interatomic distance in solids is approximately one angstrom (Å) and the energy corresponds to this distance can be calculated as, \( E = \frac{hc}{\lambda} \); \( E \approx 12 \times 10^3 \text{ eV} \) (for \( \lambda = 1 \text{ Å} \)). If the structure of the solid is to be probed by electromagnetic waves then these waves should have energy at least equal to the interatomic distance energies. X-rays have approximately same energy (keV) as the interatomic distance energies of solids. X-ray diffraction (XRD) is the most common characterization technique to investigate the composition, quality, lattice parameters, orientation, defects, stress and strain in semiconductor materials. After the discovery of X-rays in 1895, a new way was possible to probe the crystalline materials at the atomic scale. In 1913 W.H and W.L. Bragg found that the X-rays gave characteristic patterns after reflection from crystalline materials. The
schematic diagram of Bragg reflection from crystalline planes having interplane distance 
d is shown in Fig. 2.5. The incident and reflected x-rays from the two planes are also  
shown in this figure.

Fig 2.5. Schematic diagram of Bragg reflection from crystalline lattice planes having  
interplane distance “d” between two lattice planes

Bragg concluded that the path difference between the two X-rays diffracted from  
two consecutive lattice planes is $2d \sin \theta$ and it leads to Bragg’s law, which states that the  
condition for diffraction of X-rays for a crystalline material is:

$$n\lambda = 2d \sin \theta$$

Here $\theta$ is the angle of incidence and $\lambda$ is the wavelength of the X-rays, $n$ is an  
integer and it is the order of reflection and $d$ is the distance between the lattice planes.

The X-ray diffractometer 3003 (Seifert, Germany) used in our work is shown in  
Fig. 2.6. It consists of three basic elements: an X-ray tube, a sample holder and an X-ray  
detector. X-rays are generated in a cathode ray tube by heating a filament to produce  
electrons, accelerating the electrons toward a target by applying a voltage and  
bombarding the target material with electrons. These X-rays are collimated and directed  
onto the sample. As the sample and detector are rotated, the intensities of the reflected X-
rays are recorded, processed and the signals are converted to a count rate which is then output to a device, such as a printer or computer monitor.

The schematic diagram of an X-ray diffractometer is shown in Fig. 2.7. The Geometry of the X-ray diffractometer is such that the sample rotates in the path of the collimated X-ray beam at an angle $\Theta$ while the X-ray detector is mounted on an arm to collect the diffracted X-rays, rotates at an angle of $2\Theta$.

By using X-ray diffractometer we can find the crystalline structure of powder samples. The powder samples were finely grinded in agate mortar and then put on in sample holder. The crystallinity and phase purity of the products were analyzed using XRD with Cu-K\textalpha radiation ($\lambda = 1.5406$ Å) operating at 20 kV; 15 mA, at a scanning rate of 5°/min. in the 2$\theta$ range of 20° – 70°.
The identification of samples were assisted by Philips X’Pert High score Computer Software (search-match program) on the database of JCPDS software and we can determine the mean crystallite size of the sample using Debye Scherrer's equation,

\[ D = \frac{K \lambda}{\beta \cos \Theta} \]

where

“D” is mean crystallite size of the sample

“\( \lambda \)” is the wavelength of Cu-K\( \alpha \) radiation = 1.5406 Å

“\( \beta \)” is the full width at half maximum (FWHM)

“\( \Theta \)” is the bragg diffraction angle

“\( K \)” is a constant = 0.89

2.5.2 Scanning Electron Microscopy (SEM)

Scanning electron microscopy is a versatile technique that delivers a rich variety of information on specimen properties, such as composition, topology and crystallography. During SEM inspection a beam of accelerated electrons that is emitted
from a tungsten gun is focused into a fine probe, scanned across the surface of the specimen with the help of scanning coils as shown in the schematic diagram of SEM, Fig. 2.8. These bombarding electrons, is referred to as primary electrons. Each point on the specimen that is struck by the accelerated electrons emits signal in the form of electromagnetic radiation. Selected portions of this radiation, usually secondary (SE) and/or backscattered electrons (BSE), are collected by a detector and the resulting signal is amplified analyzed and translated into the SEM image. Depending on the instrumental aperture and resolution, the maximum magnification for a SEM can be as large as one million times, thus allowing the observation of atomic clusters and nanostructures.

Fig. 2.8. Schematic diagram of SEM
In our experiments, the morphology of the as-grown ZnO nanostructures was studied using a JEOL JSM-6335F scanning electron microscope, shown in Fig. 2.9. The powder samples were dispersed in absolute ethanol using an ultrasonic bath. The dispersed sample was dropped on the conductive gold tape which is attached to the SEM stub. The stub was then coated with gold particle in order to increase conductivity under argon atmosphere by plasma sputtering. The chamber pressure is about $10^{-6}$ mbar. The gun voltage is 15 kV. A max resolution of about 10 nm can be achieved.

A typical SEM image of our sample is shown in Fig. 2.10. The SEM gives information on the surface morphology of the sample. 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.

2.5.3 Transmission Electron Microscopy (TEM)

The transmission electron microscope (TEM) forms an image by accelerating a beam of electrons that pass through the specimen. The schematic diagram of TEM is shown in Fig. 2.11. In TEM, electrons are accelerated to 100 keV or higher (up to 1 MeV), projected onto a thin specimen (less than 200 nm) by means of the condenser lens system and penetrate the sample thickness either undeflected or deflected. An image is formed from the interaction of the electrons transmitted through the specimen. The image is magnified and focused onto an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a CCD camera.
The greatest advantages that TEM offers are the high magnification ranging from 50 to $10^6$ and its ability to provide both image and diffraction information from a single sample. The scattering processes experienced by electrons during their passage through the specimen determine the kind of information obtained. Elastic scattering involves no energy loss and gives rise to diffraction patterns. Inelastic interactions between primary electrons and sample electrons at heterogeneities, such as grain boundaries, dislocations, second phase particles, defects, density variations etc., cause complex absorption and
scattering effects, leading to a spatial variation in the intensity of the transmitted electrons. In TEM one can switch between imaging the sample and viewing its diffraction pattern by changing the strength of the intermediate lens.

In addition to the capability of structural characterization and chemical analyses, TEM also has been explored for other applications in nanotechnology. Examples include the determination of melting points of nanocrystals, in which, an electron beam is used to heat up the nanocrystals and the melting points are determined by the disappearance of electron diffraction. Another example is the measurement of mechanical and electrical
properties of individual nanowires and nanotubes. This technique allows a one-to-one correlation between the structure and properties of the nanowires.

In this work, TEM investigations were carried out using TEM, FEI-Technai Sprit transmission electron microscope, shown in Fig. 2.12, with an accelerating voltage of 200 kV. The TEM samples were deposited on thin amorphous carbon films supported by copper grid from ultrasonically processed absolute ethanol solution of the sample.

2.5.4 FTIR Spectroscopy

Fourier Transform Infrared (FTIR) spectroscopy is a technique used to determine qualitative and quantitative features of IR-active molecules in organic or inorganic solid, liquid or gas samples. It is a rapid and relatively inexpensive method for the analysis of solids that are crystalline, microcrystalline, amorphous or films. Samples are analyzed on the scale of microns to the scale of kilometers and new advances make sample preparation, where needed, relatively straightforward. The term Fourier Transform Infrared Spectroscopy refers to a fairly recent development in the manner in which the data is collected and converted from an interference pattern to a spectrum. Today's FTIR instruments are computerized which makes them faster and more sensitive than the older dispersive instruments.

FTIR is perhaps the most powerful tool for identifying types of chemical bonds (functional groups). The wavelength of light absorbed is characteristic of the chemical bond as can be seen in the IR annotated spectrum. By interpreting the infrared absorption spectrum, the chemical bonds in a molecule can be determined. FTIR spectra of pure compounds are generally so unique that they are like a molecular "finger print". While
organic compounds have very rich, detailed spectra, inorganic compounds are usually much simpler. For most common materials, the spectrum of an unknown can be identified by comparison to a library of known compounds. Less common materials can be identified if IR is combined with nuclear magnetic resonance, mass spectrometry, emission spectroscopy, X-ray diffraction and/or other techniques.

Fig. 2.13. Block diagram of a FTIR spectrometer

A common FTIR spectrometer consists of a source, interferometer, sample compartment, detector, amplifier, A/D convertor and a computer. The block diagram of an FTIR spectrometer is shown in Fig. 2.13. The source generates radiation which passes the sample through the interferometer and reaches the detector. Then the signal is amplified and converted to digital signal by the amplifier and analog-to-digital converter,
respectively. Eventually, the signal is transferred to a computer in which Fourier transform is carried out.

This FTIR instrument (Perkin Elmer Spectrum One Fourier Transform Infrared spectrometer) used for the functional group analysis of our samples is shown in Fig. 2.14. It has an auto image microscope attachment including both triglycine sulphate (TGS) and mercury cadmium telluride (MCT) detectors.

![Fig. 2.14. Perkin Elmer Spectrum One FTIR](image)

### 2.5.5. UV-vis Diffuse Reflectance/Absorption Spectroscopy

UV-vis Diffuse Reflectance Spectroscopy (DRS) is a powerful technique to identify and characterize the metal ion coordination. It is a non destructive technique that uses the interaction of light, absorption and scattering, to produce a characteristic reflectance spectrum, providing information about the structure and composition of the
medium. It also provides the information regarding the band gap of the materials, especially the semiconducting metal oxides.

![Diffuse reflection](image1)

Fig. 2.15. (a) Diffuse reflection by a sample (b) Optical arrangement for diffuse reflection

The diffuse reflection by a powder sample and the optical arrangement for diffuse reflection is shown in Fig. 2.15(a) and (b). The diffuse reflectance spectra of our samples were recorded using a LAMBDA 650 UV-vis Spectrophotometer - Perkin Elmer, shown in Fig. 2.16, equipped with a diffuse reflectance accessory in the wavelength range of 800-200 nm. The band gap energy of the sample was estimated from the differential plots obtained from the UV-vis diffuse reflectance spectra.

![Spectrophotometer](image2)

Fig. 2.16. LAMBDA 650 UV-vis Spectrophotometer (Perkin Elmer)
2.5.6 Photoluminescence Spectroscopy

Photoluminescence (PL) is the spontaneous emission of light from a material under optical excitation. PL measurement is a kind of powerful and nondestructive technique, which has been carried out on most of semiconductors. In this technique the semiconductor under investigation is excited optically and then the PL spectrum of the spontaneous emission from radiative recombination in the semiconductor band gap is obtained. The excitation energy and intensity can be chosen to probe different excitation types and also different parts of the sample.

![Fig. 2.17. Typical experimental set-up for PL measurements](image_url)

A schematic diagram of the PL setup used in this research work is shown in Fig. 2.17. PL investigations can be used to characterize a variety of materials parameters. Features of the emission spectrum can be used to determine band gap, identify surface, interface and impurity levels and recombination process in the semiconductor materials. Under pulsed excitation, PL intensity transients yield life times of excited states. In
addition, thermally activated processes of non-radiative recombination cause changes of PL and can be investigated. In this research work, PL measurements were performed at room temperature using laser lines with a wavelength of 266 nm from a diode laser pumped resonant frequency doubling unit (MBD266) as an excitation source using LS55 Fluorescence Spectrometer, 230 V - Perkin Elmer shown in Fig. 2.18.

Fig. 2.18. LS55 Fluorescence Spectrometer (Perkin Elmer)

2.6 CONCLUSION

There has been great development in synthesis and characterization of ZnO nanostructures. The literature survey provided in this report shows that with more research, production of nano ZnO devices are not far from reality. The tools used to characterize ZnO nanostructures have been well understood and utilized to understand
the versatile properties of novel ZnO nanostructures. Still, there are challenges to grow nanostructures of uniform diameter and morphology. As research progresses further in this field of work, new applications will emerge which will demand mass production of novel ZnO nanostructures.