CHAPTER 1

OVERVIEW ON ZINC OXIDE NANOSTRUCTURES
AND THIN FILMS

1.1 INTRODUCTION

II-VI compounds have always been an interesting classification of semiconductors. For over a decade, II-VI semiconductors have attracted growing interest owing to their possible applications in opto-electronics. The wide band gap II-VI semiconductors are efficient emitters in the blue to ultraviolet (UV) spectral range and are likely candidates to replace materials like GaN in light emitting laser diodes. Despite some similarities, each of the II-VI semiconductors demonstrates their own unique and novel physical properties. These compounds mostly crystallize in the cubic (zinc blende) or hexagonal (wurtzite) structure.

Semiconductors are normally classified according to the type of band gap as direct or indirect semiconductors. The band gap has a major influence on the properties like optical absorption, electrical conductivity and index of refraction of the material. The direct band gap semiconductors are found to be advantageous over indirect band gap semiconductors, as they do not require phonons to satisfy wave vector conservation. Most of the II-VI compounds are found to exist as direct band gap semiconductors and have been dominating the optical field for short wavelength applications. They are
used in various applications such as ultraviolet light emitting diodes (UVLEDs) (Hosono et al 2002, Sekiguchi and Koizumi 2002) and ultraviolet photodetector (Park et al 2003, Law and Thong 2006) and so on. A common characteristics that all II-VI semiconductors share is the ability to form into the wurtzite crystal structure.

Table 1.1  Comparison of the properties of ZnO with other wide gap semiconductors

<table>
<thead>
<tr>
<th>Material</th>
<th>Structure</th>
<th>Lattice constant</th>
<th>Band gap</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>a (Å)</td>
<td>c (Å)</td>
</tr>
<tr>
<td>ZnO</td>
<td>Wurtzite</td>
<td>3.250</td>
<td>5.206</td>
</tr>
<tr>
<td>GaN</td>
<td>Wurtzite</td>
<td>3.189</td>
<td>5.185</td>
</tr>
<tr>
<td>6H – SiC</td>
<td>Wurtzite</td>
<td>3.081</td>
<td>15.12</td>
</tr>
</tbody>
</table>

Zinc oxide (ZnO) is also one of the II-VI compounds with some exceptional and comparable properties to their III-V counterparts. In Table 1.1, the properties of ZnO are compared with other wide band gap semiconductors. ZnO has a unique position among semiconducting oxides due to its piezoelectric and transparent conductive properties. It has a high electrical conductivity and optical transmittance in the visible region. These properties make it an ideal candidate for applications like transparent conducting electrodes in flat panel displays and window layers in solar cells (Ginley and Bright 2000, Pei et al 2001, Hong et al 2004). The band gap of ZnO is 3.44 eV at low temperatures and 3.37 eV at room temperature possessing applications in optoelectronics in the blue/UV region, including light-emitting diodes, laser diodes and photodetectors. The free-exciton
binding energy for ZnO is 60 meV, compared with, 25 meV for GaN. This large exciton binding energy indicates that efficient excitonic emission in ZnO can persist at room temperature and higher. Since the oscillator strength of excitons is typically much larger than that of direct electron–hole transitions in direct band gap semiconductors, the large exciton binding energy makes ZnO a promising material for optical devices that are based on excitonic effects. The low symmetry of the wurtzite crystal structure combined with a large electromechanical coupling in ZnO gives rise to strong piezoelectric and pyroelectric properties. Due to a strong luminescence in the green–white region of the spectrum, ZnO is also a suitable material for phosphor applications in vacuum fluorescent displays and field emission displays. High thermal conductivity property makes ZnO useful as an additive (e.g. ZnO is added to rubber in order to increase the thermal conductivity of tires). High thermal conductivity translates into high efficiency of heat removal during device operation. The most attractive feature of ZnO as a semiconductor is that large area single crystals are available. Hence epitaxial growth of ZnO thin films can be realized on ZnO single crystal substrates. ZnO thin films can be etched with acidic, alkaline as well as mixture solutions. This possibility of low-temperature chemical etching adds great flexibility in the processing, designing and integration of electronic and optoelectronic devices. Radiation hardness is important for applications at high altitude or in space. It has been observed that ZnO exhibits exceptionally high radiation hardness, even greater than that of GaN (Tuomisto et al 2005, Look et al 1999).

ZnO has three crystal forms: the hexagonal wurtzite, the cubic zinc blende and the cubic rock salt, which is rarely observed. The wurtzite structure is most commonly used as it has the highest stability under normal
working conditions. At ambient conditions, the thermodynamically stable phase is wurtzite. The zinc blende ZnO structure can be stabilized only by growth on cubic substrates, and the rock salt NaCl structure may be obtained at relatively high pressures. Table 1.2 shows a compilation of physical parameters for ZnO.

**Table 1.2 Properties of Wurtzite ZnO**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice parameters at 300 K</td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>0.325 nm</td>
</tr>
<tr>
<td>c</td>
<td>0.5206 nm</td>
</tr>
<tr>
<td>a/c 1.602 (Ideal hexagonal structure shows 1.633)</td>
<td>u 0.345</td>
</tr>
<tr>
<td>Density</td>
<td>5.606 g/cm³</td>
</tr>
<tr>
<td>Stable phase at 300 K</td>
<td>Wurtzite</td>
</tr>
<tr>
<td>Melting point</td>
<td>1975 ºC</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>0.6, 1-1.2</td>
</tr>
<tr>
<td>Linear expansion coefficient (/°C)</td>
<td></td>
</tr>
<tr>
<td>( a_o ): ( 6.5 \times 10^{-6} )</td>
<td></td>
</tr>
<tr>
<td>( C_o ): ( 3.0 \times 10^{-6} )</td>
<td></td>
</tr>
<tr>
<td>Static dielectric constant</td>
<td>8.656</td>
</tr>
<tr>
<td>Refractive Index</td>
<td>2.008, 2.029</td>
</tr>
<tr>
<td>Energy gap</td>
<td>3.4 eV, direct</td>
</tr>
<tr>
<td>Intrinsic carrier concentration</td>
<td>(&lt; 10^6 \text{ cm}^{-3} ) (max n-type doping ( &gt;10^{20} \text{ cm}^{-3} ) electrons; max p-type doping (&lt; 10^{17} \text{ cm}^{-3} ) holes)</td>
</tr>
<tr>
<td>Exciton binding Energy</td>
<td>60 meV</td>
</tr>
<tr>
<td>Electron Hall mobility at 300 K for low n-type conductivity</td>
<td>200 cm²/Vs</td>
</tr>
<tr>
<td>Hole effective mass*</td>
<td>0.59</td>
</tr>
<tr>
<td>Hole Hall mobility at 300 K for low p-type conductivity*</td>
<td>5-50 cm²/Vs</td>
</tr>
</tbody>
</table>
1.2 CRYSTAL STRUCTURE

Zinc oxide (ZnO) is a well-known wide band gap semiconductor (3.37 eV at room temperature), which has a wurtzite structure with a lattice parameter \(a = 0.325\) nm and \(c = 0.5206\) nm (Özgür et al 2005). The wurtzite structure has an ABAB hexagonal close packing (HCP) structure. The structure of ZnO consists of alternating planes composed of \(\text{O}^{2-}\) and \(\text{Zn}^{2+}\) ions, which are tetrahedrally coordinated and stacked along the c-axis on an alternate basis (Figure 1.1.). The \(\text{Zn}^{2+}\) and \(\text{O}^{2-}\) ions create a normal dipole moment and instant polarization, which results in a diversification of surface energy.

The tetrahedral coordination in ZnO results in non-centro symmetric structure and consequently results in piezoelectricity and pyroelectricity in ZnO. Another important characteristics of ZnO is its polar surfaces. The most common polar surface is the basal plane. Extensive surface reconstructions are means of obtaining a stable structure but ZnO ± (0001) are exceptions. In addition to the inherent polarity of ZnO crystal, the tetrahedral coordination of this compound is also a common indicator of sp\(^3\) covalent bonding. However, the Zn-O bond also possesses a very strong ionic character, and thus ZnO lies on the borderline between being classified as a covalent and ionic compound.
Figure 1.1  (a) Schematic representation of a wurtzite ZnO structure having lattice constant \( a \) in the basal plane and \( c \) along the basal direction. (b) Tetrahedral coordination
1.3 **ZnO NANOSTRUCTURES**

Recently, nanostructures have attracted increasing interest because of their enhanced physical and chemical properties in the nanoscale regime. “Nanostructure” is a material of interest, represents a system or object with at least one of its dimensions approximately one hundred nanometer or less. For example, nanorods have one dimensions in the nanoscale, i.e. the diameter of the nanorods is between 1 and 100 nm and its length can be very large. In the case of spherical particle, it has all three dimensions between 1 and 100 nm. The nanostructures can be classified into three categories,

i) 0-dimensional (0D) (e.g. quantum dots and nanoparticles)

ii) 1-dimensional (1D) (e.g. nanorod, nanowire, nanobelt and nanoneedle)

iii) 2-dimensional (2D) (e.g. ultra-thin films)

Synthesis and understanding the growth aspects of these nanostructures are important to effectively make nanoscale devices. During the last decade, growth of one dimensional (1D) ZnO nanostructures such as wires, rods and tubes have become the focus of intensive research owing to their unique applications in mesoscale physics and fabrication of nanoscale devices (Huang et al 2001, Li et al 2001, Yao et al 2002). The ability to precisely control or tune their dimensions, chemical composition, surface properties, phase purity and crystal structure have become more and more important for the utilization of 1D nanostructures in a broad range of areas. ZnO nanorods are being displayed due to their novel properties and potential applications. ZnO nanorods are attractive components for nanometre scale electronic and photonic device applications because of their unique chemical and physical properties. ZnO nanorods have been synthesized by various methods such as the chemical vapour deposition and condensation process,
template-based growth method, and wet chemical synthesis. Recently, a wide variety of nanodevices including ultraviolet lasers (Choy et al 2003), sensors (Fan and Lu 2005), field effect transistors (Goldberger et al 2005), and light emitting device arrays (Park and Yi 2004) have been fabricated using ZnO nanorods. Generally, two categories of synthesis and fabrication techniques are in use. Top-down and Bottom-up. Attrition or milling is a typical top-down method in making nanoparticles, whereas the colloidal dispersion is a good example of bottom-up approach in the synthesis of nanoparticles. The ‘top-down’ approach, utilizing the lithography and precision engineered tools like cutting, etching, grinding etc to fabricate nanoscale objects out of bulk materials. In ‘bottom-up’ approach, where materials and devices are built from molecular components which assemble themselves chemically using principles of molecular recognition. Bottom up approach refers to the build up of a material from the bottom, i.e. atom by atom, molecule by molecule or cluster by cluster. The schematic of the top down and bottom up approaches are shown in Figure 1.2.

Figure 1.2 Schematic of the top down and bottom up approaches
In the bottom-up category, several approaches have been well established, which includes an extensively explored vapor phase deposition method, including chemical vapor deposition (CVD) and physical vapor deposition (PVD), and solution based techniques.

1.4 SYNTHESIS OF 1D ZINC OXIDE NANOSTRUCTURES

1.4.1 Aqueous solution synthesis

Aqueous solution synthesis is widely used for the preparation of oxide nanostructures and ceramic materials at low temperature. This method consists of heating an aqueous solution of metal salts or complexes at moderated temperatures below 100°C (Wahab et al 2007). Therefore, such technique does not require high-pressure containers and is also entirely recyclable, safe and environment friendly because only water is used as a solvent. Such a process avoids the safety hazards or organic solvents and their eventual evaporation and potential toxicity. The morphology of the resulting nanostructures can be tuned by changing parameters such as temperature, precursor concentrations and pH. More importantly, doping during the aqueous chemical growth is very simple and typically involves mixing the precursors in an appropriate ratio. In addition because no organic solvents or surfactants are present, the purity of the materials is substantially improved. The residual salts are easily washed out by water due to their high solubility. In most cases no additional heat or chemical treatment is necessary, which represents a significant improvement compared with surfactant-, template-, or membrane based synthesis methods. Until recently, there has been a great interest to synthesize and develop rare earth doped nanostructures from the chemical methods, given that direct chemical approaches are generally compatible with large-scale production, and the resulting colloidal suspensions are ready for application in self-assembly strategies that have become a mainstay of nanotechnology.
1.4.2 Sol-gel Method

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.

Sol-gel method is a versatile method useful for preparing metal oxides. Stoichiometric and homogeneous control of the doping is easily achieved. Since liquid precursors are used, it is possible to cast the glass and ceramics in a range of shapes, such as thin film, fibers, and monoliths, etc, without the need for machining or melting. The precursors such as metal alkoxides, with very high purity make it easy to fabricate materials with high quality and cost effective and the temperature required in the process is low and no delicate vacuum system is needed. Despite its advantages, sol-gel method still has some limitations. Sol-gel technique is not widely used in industries due to weak bonding, low wear-resistance, high permeability and difficulty in controlling the porosity. Figure 1.3 shows the flow chart of the materials derived from sol-gel method.
1.4.3 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 acts both as 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 equilibria.

Materials prepared 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.

1.4.4 Template directed growth

Nanostructures growth can be realized by using template-directed methods, in which a periodic structured template (for example an anodic alumina membrane or a polymeric membrane) is exploited to lead the growth of the material. Pores of these templates can be filled by using other techniques such as thermal evaporation, PLD or electro deposition. After the deposition of materials, the templates can be effectively etched out leaving the nanostructures. For example nanodots have been deposited by PLD using an anodic alumina membrane. Nanorods have been obtained by evaporation on a gold membrane. This template directed approach can be employed to synthesis nanostructures of complex materials, which are otherwise difficult to be synthesised by other common methods. Other solution-based methods used to synthesize ZnO nanostructures are, like electrochemical methods, sonochemical synthesis and microwave-assisted synthesis. In addition to these, several less popular techniques and combination of these techniques have been employed for the growth of nanostructures.
1.4.5 Sonochemical Synthesis

Sonochemistry is chemistry assisted/enhanced by ultrasound. The chemical effects of ultrasound arise from acoustic cavitation: the formation, growth and implosive collapse of bubbles in liquid. This means that chemical reactions that take place under more conventional conditions are accelerated, or even yield totally different products. The reason for this can be due to either physical or chemical effects of cavitation. The physical effects can enhance the reactivity of a catalyst by enlarging the surface area, or accelerate a reaction by proper mixing of reagents. Chemical effects of ultrasound enhance reaction rates because of the formation of highly reactive radical species formed during cavitation. Cavitation in a liquid occurs due to the stresses induced in the liquid by passing of a sound wave through the liquid. Sound waves comprise of longitudinal waves that consists of compression and decompression/rarefaction cycles as they passes through the medium. If the pressure during the decompression cycle is low enough, the liquid can be turn apart to leave small bubbles. These cavitation bubbles are at the heart of sonochemistry systems. These bubbles are subjected to the stresses induced by the sound waves. This causes the bubbles to grow during a decompression phase, and contract or even implose during a compression phase.

These bubbles are filled with vapour and gas and can produce radicals during such an implosion. The implosive collapse of the bubble generates localized hot spots through adiabatic compression or shock wave formation within the gas phase of the collapsing bubble. Cavitation bubble collapse is a remarkable phenomenon induced through out the liquid by the power of sound. In aqueous systems at an ultrasonic frequency of 20 kHz each cavitation bubble collapse acts as a localized hotspot generating transient temperatures of about 5000 K and in excess of 1800 atmospheric pressures. These extreme conditions attained during bubble collapse have been exploited to prepare nanoparticles of metals, metal carbides, metal oxides, and metal sulphides.
1.4.6 Electrochemical Deposition

In electrodeposition, thin film is deposited by the flow of electric current using an electrolytic cell, which consists of a positively charged electrode (anode), a negatively charged electrode (cathode) and the electrolyte solution. A number of metal and metal alloys, semiconductor systems have been successfully electroplated from both aqueous solutions. By this technique, films can be deposited from very thin films to very thick coatings (electroforming), which find widespread applications in industries.

1.5 DOPING IN ZnO

ZnO is an important material for its multi-functional properties (semiconducting, magnetic, piezoelectric etc.) for electronic and optoelectronic devices. One of the key requirements for many of these applications is the doping of ZnO with various elements for enhancing and controlling its electrical and optical properties. As-grown ZnO is an n-type semiconductor and its n-type conductivity can be controlled by growing it in an oxygen deficient atmosphere or by doping it with group III elements like Al, Ga, or In (Goyal et al 1993). ZnO based dilute magnetic semiconductors doped with transition metals (Co, Mn) have been predicted theoretically to be good candidates for room temperature ferromagnetism and large magnetization (Dietl et al 2000, Sato and Katayama-Yoshida 2001, Ueda et al 2001). Besides these dopants, by doping with luminescent centers such as rare-earth metal ions, the emission properties of ZnO can be tailored toward selected wavelengths in the visible region, which is of interest for a variety of applications including multi-color emission in light emitting devices (Panatarani et al 2004, Lima et al 2002, Abdullah et al 2003).
1.5.1 Doping of Rare-Earth (RE) Ions in ZnO

Rare-earth ions play an important role in much of modern optical technology as the active constituents of materials. Rare-earth ions also play a critical role in energy-efficient luminescent materials, such as phosphors for fluorescent lamps, cathode ray tubes (CRT's), and plasma displays. The lanthanides form a special group of elements, which are characterized by an incompletely filled 4f shell. Typically trivalent rare earth elements have very stable emissions, due to the 4f electrons, which are deeply buried and hence well shielded from the outer shells.

Rare earths are characterized by a unique structure of partially filled 4f shell that is shielded from external fields by $5s^2$ and $5p^6$ electrons. The energy levels of the elements in this series are therefore largely insensitive to the environment in which they are placed. When incorporated in crystalline or amorphous hosts, the rare earths exist as 3+, or occasionally 2+, ions. The 3+ ions all exhibit intense narrow band intra-4f luminescence in a wide variety of hosts, and shielding provided by the $5s^2$ and $5p^6$ electrons means that rare earth radiative transitions in solid hosts resembling those of the free ions and electron-phonon coupling is weak.

As a result of the shielding of the 4f electrons, the positions of rare earth electronic levels are much more influenced by spin orbit interactions than by the applied crystal field. The intra-4f transitions are parity forbidden and are made partially allowed by crystal field interaction mixing opposite parity wave functions. Light emission due to radiative transitions in the partly occupied 4f shell of rare earth ions, which are found in the form of many narrow bands throughout the visible and near infra-red spectra, form the basis of a great number of applications, such as solid state lasers and phosphors.
Trivalent rare earth doped semiconductors such as GaN:RE and Si:Er are technologically important materials in optoelectronic devices and have received great research interest (Andreev et al 2006), in which an efficient energy transfer from semiconductor host to RE$^{3+}$ ions is essential for most of the potential applications. By careful selection of the appropriate ion, intense, sharp emission can be obtained across much of the visible region and into the near-infrared. And the emission peak positions are known to be stable, and almost host independent. For these practical advantages, rare earths have been widely utilized in optical applications such as solid lasers and phosphor in color television.

The doping of RE$^{3+}$ into ZnO lattice remains challenging (Bhargava et al 2002) and could be attributed to major issues. The first one is the low saturated concentration of rare earth ion in ZnO lattice due to the large differences in ionic size and charge between RE$^{3+}$ and Zn$^{2+}$. The second difficulty is the inappropriate energy level position of rare earth ions relative to the valence band and conduction band of ZnO host. Dorenbos and van der Kolk (2006) observed that the charge transfer level of RE$^{3+}$ in ZnO is equal or higher than the bottom of conduction band of ZnO, which leads to the absence of efficient ZnO RE$^{3+}$ energy transfer.

A high dispersion of rare-earth species has to be obtained to prevent concentration quenching, which is highly detrimental for the luminescent properties. Besides the rare-earth content and distribution, a further important issue for the development of optoelectronic devices is the production of nanocrystalline host semiconductor matrices with tailored features. In particular, the size-dependent optical properties and high grain boundary content in nanosystems might be responsible for higher device efficiency since it is believed that the rare-earth active luminescence centers are localized at the grain boundaries (Ronfard-Haret 2003). Hence, the light-emitting properties of pure and doped ZnO nanocrystalline films are critically dependent on the defect concentration; the nature, amount, and distribution of dopants; and the degree
of crystallinity. For these reasons, the synthesis conditions can strongly influence the luminescence properties of such systems.

### 1.6 Zinc Oxide Thin Films

Numerous materials have been prepared in the form of thin films over a century because of their potential technical value and scientific curiosity in their properties and the applications to modern technology. The preparation techniques can be divided into two types called physical process and chemical process. The physical process includes the pulsed laser deposition, physical vapour deposition, molecular beam epitaxy and sputtering. Schematic chart representing various methods employed in the synthesis of ZnO thin films and nanostructures are shown in Figure 1.4.

![Figure 1.4 Schematic chart representing various methods employed in the synthesis of ZnO thin films and nanostructures](image-url)
The gas-phase methods are chemical vapour deposition (CVD) (Bryant 1997; Ghoshtagore 1978) and atomic layer epitaxy (ALE) (Suntola 1992), while spray pyrolysis (Chamberlin and Skarman 1966), sol-gel (Brinker et al 1990), spin-(Chen et al 1993) and dip-coating (Brinker et al 1991) methods employ precursor solutions. Owing to their simplicity and inexpensiveness, chemical techniques have been used extensively for the preparation of thin films.

1.7 PREPARATION OF ZINC OXIDE THIN FILMS

ZnO thin films can be prepared on several substrates by many techniques, such as vacuum evaporation, sputtering, chemical vapor deposition (CVD), sol-gel, pulsed laser deposition and spray pyrolysis. The chemical spray pyrolysis has attracted several research groups because of its simplicity, efficient, inexpensive technique, and can be used effectively for the deposition of large area thin films.

1.7.1 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 $10^{-2}$ and $10^{-9}$ Torr (ultra high vacuum). Once the vacuum chamber gets 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 chamber, 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. 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.

1.7.2 Activated reactive evaporation

In this process, evaporated metal reacts with the gases such as oxygen, nitrogen or other gases in the presence of plasma and deposit as compound films. Both the metal vapors and reactive gases are ionized, increasing the reactivity of the species and promotes the compound formation. Resistively heated boat or e-beam has been widely employed for evaporation of the materials. Different plasma sources such RF and DC are employed for the generation of gas plasma. In addition to electric field, transverse magnetic field can be applied to effectively extend the lifetimes of the plasma species. Recently, growth of ZnO nanostructures has been realized at room temperature using ARE technique. This methods has been widely used to deposit oxides (ZnO, Al$_2$O$_3$, TiO$_2$), nitrides (TiN, HfN), carbides (TiC, ZrC), transparent conducting oxides (TCO) and other dielectric films for optical, electrical and hard coating applications.
1.7.3 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), RF and magnetron. During the 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 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 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.

1.7.4 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-crystal layers can be grown that are equal in quality to molecular beam epitaxy.

### 1.7.5 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).

### 1.7.6 Thermal and Low Pressure Chemical Vapor Deposition

During thermal and low-pressure chemical vapor deposition (LPCVD), pressures range between $10^{-3}$ Torr (thermal CVD) and 0.1 Torr (LPCVD) where the reactions occur in excess of 900ºC between supplied gases. The processes are typically performed simultaneously on both sides of the substrate and produce layers with excellent uniformity and characteristics. Although LPCVD is commonly used for depositing thermal oxides within the semiconductor industry, it is limited by its high temperatures and slow deposition rates. However, the method has recently been revitalized through the synthesis of carbon nanotubes, silicon nanowires, and well-aligned ZnO nanorods.
1.7.7  **Metal Organic Chemical Vapor Deposition (MOCVD)**

In MOCVD, epitaxial layer grows via the chemical reaction of the constituent chemical species at or near the heated substrates. One of the major advantages of MOCVD is the possibility of precise control of the gas precursors for growth and doping. It has been used to grow on relatively large areas and is commonly used in industry. The growth takes place in the gas phase at moderate pressures, and has become the preferred technique for the growth of devices and the dominant process for the manufacture of laser diodes (LDs), solar cells and LEDs. ZnO films have been grown on a wide range of substrates including Al₂O₃, Si, GaAs, GaN and ZnO by MOCVD.

1.7.8  **Plasma Enhanced Chemical Vapor Deposition (PECVD)**

The Plasma Enhanced Chemical Vapor Deposition (PECVD) is a process used to deposit thin films from a gas state to solid state on a substrate. In PECVD process, glow discharge plasma was sustained within the chamber, where simultaneous vapor phase chemical reaction and film deposition occurs. Usually the chemical reactions are involved after creating the plasma of the gases. In PECVD process, glow discharge plasma is excited by an RF frequency or DC discharge between two electrodes, the space between the electrodes is filled by the reacting gases. In PECVD, plasma is used in order to enhance the chemical reaction rates of the precursors. PECVD process is widely employed to deposit silicon nitride films for the passivation and encapsulation of completely fabricated microelectronic devices.

1.7.9  **Molecular Beam Epitaxy**

Molecular Beam Epitaxy (MBE) is an epitaxial growth technique, which provides thin films of extraordinary quality. MBE is a sophisticated,
finely controlled technique for growing single-crystal epitaxial films in a high vacuum ($10^{-11}$ torr). The films are formed on single-crystal substrates by slowly evaporating the elemental or molecular constituents of the film from separate Knudsen effusion source cells (deep crucibles in furnaces with cooled shrouds) onto substrates held at a temperature appropriate for chemical reaction, epitaxy and re-evaporation of excess reactants. The furnaces produce atomic or molecular beams of relatively small diameter, which are directed at the heated substrate. Fast shutters are interposed between the sources and the substrates and by controlling these shutters, superlattices can be grown with precisely controlled uniformity, lattice match, composition, dopant concentrations, thickness and interfaces down to the level of atomic layers. MBE has been employed to grow ZnO thin films. This technique has the major limitations of extremely limited product throughput, the complex operation of the process and equipment, and the necessity for expensive equipment.

### 1.7.10 Spin Coating Technique

The spin coating process involves, dispense of an excessive amount of sol onto a stationary or slowly spinning substrate. The sol is deposited through a nozzle at the center of the substrate. An excessive amount of sol is used to prevent the discontinuities coating at the edge. In the spin up stage, substrate is accelerated to the final spin speed. As rotational forces increase, the sol is pulled upward and a wave front is formed. But at the substrate edge fairly uniform layer is formed due to the centrifugal force.

The spin off stage is the spin coating stage, where the excess solvent is flung off the substrate surface as it rotates at speeds between 2000 and 8000 RPMs. The sol is being thinned primarily by centrifugal forces until enough solvent is removed to increase viscosity to a level, where flow ceases. The spin off stage takes place for approximately 10 seconds after spin up.
Evaporation is the complex process by which a portion of the excess solvent is absorbed into the atmosphere. If significant evaporation occurs prematurely, a solid layer forms on the fluid surface, which impedes the evaporation of solvent trapped under this layer and, when subjected to the centrifugal forces of the spinning substrate, causes coating defects. The spin coating process can be divided into the four stages as shown in Figure 1.5. The deposition, spin up, and spin off stages occur sequentially while the evaporation stage occurs throughout the process.

Figure 1.5 Four Stages of the Spin Coating Process
Spin coating has many advantages like controlling the film thicknesses by changing the spin speed, or switching to a different viscosity photoresist and ability to get progressively more uniform, and if the film becomes completely uniform during the coating process, it will remain so for the duration of the process.

Spin coating have few disadvantages like large substrates cannot be spun at a sufficiently high rate in order to allow the film to thin and dry in a timely manner resulting in decreased throughput. Typical spin coating processes utilize only 2-5 % of the material dispensed onto the substrate, while the remaining 95-98 % is flung off into the coating bowl and disposed.

1.7.11 Spray Pyrolysis

Spray pyrolysis has been used to deposit dense films, porous films, and for powder production. Even multilayered films can be easily prepared using this versatile technique. Unlike many other film deposition techniques, spray pyrolysis represents a very simple and relatively cost-effective processing method.

It offers an extremely easy technique for preparing films of any composition. Spray pyrolysis does not require high-quality substrates or chemicals. Typical spray pyrolysis equipment consists of an atomizer, precursor solution, substrate heater, and temperature controller. Figure 1.6 shows the schematic diagram of home made spray pyrolysis system. In spray pyrolysis technique, the properties of the films depend upon the substrate temperature and precursor solution. Thin-film deposition using spray pyrolysis can be divided into three main steps: atomization of the precursor solution, transportation of the resultant aerosol, and decomposition of the precursor on the substrate (Perednis and Gauckler 2005). In spray pyrolysis, the key issue is to understand the basic atomization process of the atomization
device in use. Depending upon the application of the films one can choose the atomizer. Air blast, ultrasonic, and electrostatic atomizers are normally used in spray pyrolysis technique.

During aerosol transport, it is important that as many droplets as possible are transported to the substrate without forming powder or salt particles. Sears and Michael et al (1988) investigated the mechanism of SnO$_2$ film growth. The influence of forces, which determine both the trajectory of the droplets and evaporation were examined and a film growth model was proposed and gravitational, electric, thermophoretic and Stokes forces were also taken into account. Hsuan-Fu Yu and Wen-Haur Liao et al (1998) developed a model describing the evaporation of solution droplets before the formation of a solid crust. In this model the transfer of mass, momentum, temperature outside and around the droplet as well as effects of precursor precipitation were taken into account.

![Figure 1.6 Schematic diagram of homemade spray pyrolysis equipment](image)
Lenggoro et al. (2000) investigated the powder production by spray pyrolysis using a temperature-graded laminar flow aerosol reactor and calculated the evaporation rate and the change of the precursor concentration within the droplets. The predicted numerical simulation results were in good agreement with the experimental results. Finally during the decomposition of the precursor, many processes occur simultaneously when a droplet hits the surface of the substrate: evaporation of residual solvent, spreading of the droplet, and salt decomposition. Many models exist for the decomposition of a precursor and many authors suggest that chemical vapour deposition based process gives high quality films by spray pyrolysis.

Figure 1.7 shows the deposition of the precursor with increasing substrate temperature (Perednis and Gauckler 2005). In the lowest temperature regime (process A), the droplet splashes onto the substrate and decomposes. At higher temperatures (process B) the solvent evaporates completely during the flight of the droplet and dry precipitate hits the substrate, where decomposition occurs.

Figure 1.7 Description of the deposition processes initiated with increasing substrate temperature
At even higher temperatures (process C) the solvent also evaporates before the droplet reaches the substrate. Then the solid precipitate melts and vaporizes without decomposition and the vapour diffuses to the substrate to undergo a CVD process. At the highest temperatures (process D) the precursor vaporizes before it reaches the substrate, and consequently the solid particles are formed after the chemical reaction in the vapour phase. Spray pyrolysis is a versatile and effective technique to deposit metal oxide films. The most important parameter is the substrate temperature and if the substrate temperature is higher, then the films are very rough and more porous. If the temperature is too low, the films will be cracked. Also, the substrate temperature influences the crystallinity, texture, and other physical properties of the deposited films. Another important spray parameter is the precursor solution and it affects the morphology and the properties of the deposited films. In addition, the film morphology and properties can be drastically changed by using various additives in the precursor solution (Perednis and Gauckler 2005).

1.8 SCOPE OF THE THESIS

Considering the importance of luminescent materials in interdisciplinary materials science and future optoelectronics applications, the present thesis is focused on the synthesis and property studies of pure and rare earth doped ZnO nanorods and thin films. ZnO with a wide band gap (3.3 eV) at room temperature has potential use in low-voltage luminescence in flat panel display applications. It has attracted increasing interest in fabricating ZnO nanostructures with designed morphology and properties while the desired optical and electrical properties could be achieved by doping ZnO
with various elements. One dimensional ZnO nanostructures prepared through chemical routes without involving catalysts or templates provides promising option for the large-scale production of well dispersed materials. With this motivation, undoped and Pr doped ZnO nanorods were prepared by a simple aqueous solution route and their structural and optical properties have been studied. Doping ZnO with RE ions, such as Sm and Dy, allows a better absorption of photons in the red region and thus enlarge the absorption spectra. In the present investigation Sm and Dy doped ZnO thin films have been prepared by cost effective spray pyrolysis technique. Their structural, surface morphology and optical properties have been investigated. The results reveal that ZnO with rare earth dopants possess promising properties useful for luminescence applications.