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Experimental Techniques

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3.1 Introduction

Chapter I deal with the review of zinc oxide and definition of the problem. It also explains the major applications of Zinc Oxide. The theoretical background required is discussed in chapter II. Zinc oxide has taken a prominent part in revolutionary development of the various fields of science and technology, including the diverse fields of electronics, optics, space science, aircraft science, defense and other industries [1, 2, 3, 4, and 5]. Applications of thin films range from micrometer dots in microelectronics to the coatings of several square meters on window glasses. Hence, thin film physics and technology is a keystone in modern applied physics. It is the prime need of this informative, global society, to develop technology at nanoscale level which is also a fascinating research.

In view of this aspect in the present investigation an attempt has been made to fabricate thin films of zinc oxide by using the recently assembled in house developed spray Chemical Vapor Deposition (CVD) technique. This chapter also discusses the various characterization techniques used to characterize the thin films of metal oxides. This information is very essential when one has to use these oxides in many applications. Hence the chapter is divided into two sections. First section deals with different deposition techniques used for synthesis of thin films with an outline of the method used in current work for the fabrication of undoped and doped ZnO thin films. The various characterization techniques applied during synthesis has been described in this section. The latter section will focus on fabrication of undoped zinc oxide films and optimization of preparative parameter to get the better quality films of zinc oxide.

Section (A): Thin film Deposition and Characterization

3.2A Thin film Deposition Methods

Deposition of high quality, uniform thin films, so as to use in many electronic and optoelectronic and much other application is a sensitive issue. The present section deals with the different techniques used for fabrication of thin films. Thin films of metal oxides are deposited by many physical and chemical techniques and are shown in Fig. 3.1. According to the application of thin film, careful selection of technique is essential to control its different properties.
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3.2A.1 Physical Deposition Methods

These are based on the formation of vapor of the solid material which is deposited as thin film. The material in the solid form is either evaporated by heating (thermal evaporation) or sputtered by ions (sputtering). It is also possible to bombard the sample by an external ion source. It is a group of vacuum coating techniques used to deposit thin film. A physical deposition process consists of three steps viz. emission of the particles from a source, transport to the substrate and finally condensation on the substrate. Two technologies are often used in physical methods. They are, i) Thermal Evaporator: Material is heated to attain gaseous state. ii) Sputtering: The ejection of particles from a solid surface after exposure to the bombardment with heavy particles usually ions of sufficient energy.

3.2A.2 Chemical Deposition Methods:

The chemical methods are relatively economical and easier than the physical methods. In chemical synthesis methods; film deposition takes place in liquid or gaseous phase. But there is no single ideal method, to prepare thin films which will satisfy all the possible requirements. Every method has its own merits and demerits. Such as CVD leads good quality but requires high purity and precise control over the deposition parameters; sol-gel suffers from slow drying and
reheating steps, while pulsed laser deposition is only suitable for small areas. The reactive sputtering and evaporation need vacuum environment and are quite expensive for large scale production. Among all different chemical deposition methods two technologies often used are spray pyrolysis technique and Chemical Vapor Deposition technique (CVD). The comparison of these methods made and tabulated in Table 3.1.

Table 3.1 Comparison of different Deposition methods

<table>
<thead>
<tr>
<th>Parameters of Deposition</th>
<th>Physical Vapor Deposition Method</th>
<th>Chemical Vapor Deposition Method</th>
</tr>
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<tr>
<td></td>
<td>Evaporation</td>
<td>Sputtering</td>
</tr>
<tr>
<td>Mechanism of Deposition</td>
<td>Thermal Energy</td>
<td>Momentum Transfer</td>
</tr>
<tr>
<td>Deposition Rate</td>
<td>High up to 7.5 x 10^5 A^0/min.</td>
<td>Low except for pure metals</td>
</tr>
<tr>
<td>Deposition Species</td>
<td>Atoms and ions</td>
<td>Atoms and ions</td>
</tr>
<tr>
<td>Energy of Deposited species</td>
<td>Low 0.1-0.5 eV</td>
<td>can be high 1-100eV</td>
</tr>
<tr>
<td>Throwing Power</td>
<td>Poor</td>
<td>non uniform thickness</td>
</tr>
<tr>
<td>Scalable to wafer size</td>
<td>up to large</td>
<td>up to large</td>
</tr>
</tbody>
</table>

Apart from all these methods the chemical spray pyrolysis technique is one of the major chemical techniques applied to deposit variety of materials in the form of thin films, owing to its simplicity, as well as its good productivity [6, 7, 8, 9, 10 and 11]. This method has the potential in the deposition of metal oxide thin film, gas tight coatings at conventionally low temperatures. It is a simple and low cost technique for ceramic thin film deposition at nm-size. The process equipment is rather simple. The method is robust and when properly controlled, it yields oxide films of high quality at rather low costs. It does not require high quality substrates or chemicals. The method has been employed for the deposition of dense films, porous films, and for powder production. Even multi-layered films can be easily prepared using this versatile technique. Spray pyrolysis has been used for several
decades in the glass industry [8] and in solar cell production to deposit electrically conducting electrode.

As the substrates are heated, the formation of the oxide layers from precursor solutions occurs directly on the substrate surface by pyrolysis and very homogeneous layers with good adhering on the substrates can be expected. The cation composition of the deposited layers is determined solely by the composition of the precursor solution only. Spray pyrolysis is a processing technique to prepare dense and porous oxide films, ceramic coatings, and powders. Unlike many other film deposition techniques, spray pyrolysis represents a very simple and relatively cost-effective method, especially regarding equipment cost.

In conventional spray pyrolysis, deposition involves spraying an aerosol of a liquid precursor onto a hot surface, where its pyrolytic decomposition takes place and metal oxide is formed. The optimization of different preparative parameters is the basic requirement of this technique. Here, the various parameters like air pressure, deposition rate, spray rate, cooling rate, substrate temperature, distance between nozzles to substrate, must be optimized. The film properties are sensitive to their structure and also to many other parameters including thickness, morphology etc. Typical spray pyrolysis equipment consists of an atomizer, precursor solution, substrate heater, and temperature controller.

In recent years an emphasis has been made on development of the variety of atomization techniques. The different atomizers usually used in spray pyrolysis technique and there characteristics are mentioned in Table 3.2. The atomizers like pressure, air blast or nebulizer (the liquid is exposed to a stream of air)[12], ultrasonic (ultrasonic frequencies produce the short wavelengths necessary for fine atomization) [13] and electrostatic (the liquid is exposed to a high electric field) [14] are used in spray pyrolysis technique. This is the most critical parameter as it enables control over the size of the droplets and their distribution over the preheated substrates. The enhancement in deposition efficiency and improvement in quality of the thin films can be achieved with these atomization techniques. However, in the present research work an innovative effort were made to modify the conventional spray pyrolysis technique in to Spray CVD (Chemical Vapor Deposition) technique by retaining all the advantages of the conventional spray pyrolysis system [15].
Table 3.2 Characteristics of Atomizer commonly used for SPT

<table>
<thead>
<tr>
<th>Atomizer</th>
<th>Droplet Size (µm)</th>
<th>Atomizer Rate (cm²/min.)</th>
<th>Droplet Velocity (m/sec.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure</td>
<td>10-100</td>
<td>3 – no limit</td>
<td>5 – 20</td>
</tr>
<tr>
<td>Nebulizer</td>
<td>0.1 - 2</td>
<td>0.5 – 5</td>
<td>0.2 -0.4</td>
</tr>
<tr>
<td>Ultrasonic</td>
<td>1 -100</td>
<td>less than 2</td>
<td>0.2 -0.4</td>
</tr>
<tr>
<td>Electrostatic</td>
<td>0.1 - 10</td>
<td></td>
<td></td>
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</tbody>
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In routine spray pyrolysis system substrate temperature is the key parameter at which pyrolytically decomposition of aerosol droplets takes place. This temperature dependence decomposition of droplets can be analyzed by three main routes.

1) Low substrate temperature:- Sprayed aerosol droplets directly arrive at substrate to form liquid films.

2) High substrate temperature:- In this case without decomposition of droplets direct precipitation due to solvent evaporation takes place. It results into powder like deposits.

3) Adequately high temperature:- It is associated with chemical vapor deposition (CVD) mechanism. In this, sufficient amount of heat is supplied to particles so that precursor becomes volatile through total solvent evaporation and gives rise to heterogeneous solid-vapor phase reaction which eventually results into thin solid film. Thus the substrate surface temperature is the most critical parameter as it influences films roughness, cracking, crystallinity.

The conventional spray pyrolysis techniques require high substrate temperature to deposit thin films as well as to promote crystalline growth of material. It limits the type of substrate that can be used. Hence in the present work, spray CVD system is employed to deposit thin film in crystalline form at low substrate temperature. In the present setup, thermal decomposition of precursor species to form the film constituents and waste products take place in the reaction chamber. With air flow the mass transports towards the preheated substrate where the adsorption of the atomic film takes place. Finally, the nucleation and growth mechanism of surface diffused and migrated film constituents takes place. Hence,
this method is the amalgamation of chemical vapor deposition and conventional spray pyrolysis technique.

The initial experiments were designed to investigate whether thin polycrystalline binary semiconductor oxide thin films like ZnO can be fabricated with this system. We report our observations regarding the effect of core temperature, substrate temperature, and precursor properties like concentration variation, the optimization of distance between nozzle and substrate, and the installation of a proper furnace for heating the reaction chamber. Using the above instrument, the films of SnO$_2$, ZnO and ZnO with some dopant were prepared by Shewale et al. and results obtained were reported [15]. This method is convenient for preparing pinhole free, homogenous, smoother thin films with the required thickness.

3.3A Spray CVD Technique

“It is the aerosol process, which atomizes the solution, thermally decomposes the atomized droplets in reaction chamber and offers nucleation and island growth to produce solid phase at a substrate.”

3.3A.1 Principal of Technique

1. In the newly fabricated, homemade Spray CVD system the spray nozzle is kept facing in upward direction instead of facing downward as in conventional spray pyrolysis system.
2. It allows only atomized droplets to reach in the reaction chamber and resists the large size droplets.
3. These droplets undergo thermal decomposition in the reaction chamber.
4. With the help of air currents, vapors of thermally evaporated solute are pushed upwards.
5. The preheated substrate offers initial nucleation growth and grain growth to produce solid phase of single crystallite or clusters of crystallites.

3.3A.2 Spray CVD Set Up

Spray CVD technique consists of a thermally stimulated chemical reaction between clusters of atomized aerosol droplets of different chemical species. It involves spraying of a solution, usually non-aqueous, containing soluble salts of the desired
compound, followed by thermal decomposition in the reaction chamber, and finally nucleation growth, followed by grain growth and crystal growth onto preheated substrates. Every sprayed droplet reaching into the hot reaction chamber undergoes pyrolytic decomposition and forms a single crystalline or cluster of crystallites as a product and pushed to the preheated substrate. The other volatile byproducts have been escaped in the vapor phase. The preheated substrates provided thermal energy for the nucleation growth and subsequent recombination of the constituent species, followed by crystallization of the clusters of crystallites and thereby resulting into the coherent film. The atomization of the spray solution into a spray of fine droplets also depends on the geometry of the spraying nozzle and pressure of a carrier gas.

![Fig. 3.2 Schematic Set up of Spray CVD technique](image)

The properties of thin films depend upon the anion to cation ratio, spray rate, core (reaction chamber) temperature, substrate temperature, ambient atmosphere, carrier gas, droplet size and also on the cooling rate after deposition. The film thickness depends on the distance between the nozzle and substrate,
solution concentration, quantity of solution, core (reaction chamber) and substrate temperature. The film formations rely on the process of droplet landing into the reaction chamber and solvent evaporation, which are related to droplet size and its momentum. An ideal deposition condition is when the droplets totally decompose in the reaction chamber just as the solvent is completely removed. The schematic diagram of the spray pyrolysis technique is shown in figure 3.2. It consists of mainly a) Reaction chamber, b) spray nozzle mounted on a fixed wooden block, c) liquid level monitor, d) substrate heater (hot plate) with temperature controllers e) gas regulator valve and f) air tight chamber with an exhaust, g) PID temperature controllers.

1. Spray nozzle: The atomization of aerosol particles of solute with the help of air as carrier gas is obtained using specially design glass nozzle that provided a narrow conical spray. It was constructed from a bore of capillary having very small diameter ≈ 0.1mm which consists of the inner solution tube surrounded by the gas tube through which carrier gas flows. With the application of pressure of the carrier gas (air), a vacuum is created at the tip of the nozzle and the solution is automatically sucked and the spray starts. The efficiency of deposition went through a maximum for the optimized distance between substrate and nozzle. The effect of distance of nozzle on the efficiency varies from nozzle to nozzle because the divergences of the conical spray changes. Consequently, each spray tip must be calibrated.

2. Liquid level monitor - The spray rate at a fixed pressure is depend on the height of the solution column, measured with reference to the tip of the nozzle and the arrangement for the change in height of the solution, forms liquid level monitor. The spray rate can be altered by varying the air pressure and solution height (not shown).

3. Reaction Chamber - It is a cylindrical furnace which is fixed on an MS stand. Chromel-alumel thermocouple was used to measure the temperature of the core which is fixed at the centre of the chamber. PID temperature controller is used to control the reaction chamber temperature with an accuracy of ±5 K.

4. Hot plate - The iron disc with 20cm diameter and 7 mm thickness was supported on the electric heater (2000 W). Chromel-alumel thermocouple was used to measure the temperature of the substrates and is fixed at the centre of the iron
disc. The temperature of the hot plate was monitored by PID temperature controller. The substrate heater is placed at the top of the cylindrical furnace.

5. **Gas regulator valve** - The gas regulator valve is used to control the pressure of the carrier gas flowing through the gas tube of the spray nozzle. Gas flow meter was used to regulate the flow of carrier gas.

6. **Air tight chamber** - The system is enclosed in an air-tight chamber provided with an exhaust to remove the gases and vapors produced during the spray pyrolysis process. In between outlet tube and outlet of chamber the air blower is fitted to exhaust the gases evolved during thermal decomposition.

### 3.3A.3 Optimized parameters

#### a) Core temperature

The core temperature i.e. the reaction chamber temperature should be optimum so that the sprayed solution aerosols could undergo decomposition process. For core temperature less than the optimum value, the aerosol droplets directly arrive at the substrate as a result decomposition of solute does not takes place and these liquid molecules will cause semi-solid deposits with non adherent thin film due to lack of thermal energy. On the other hand, if the core temperature is higher than its optimum value (for optimum air pressure—or optimum nozzle–substrate distance), the decomposition as well as oxidation reaction takes place in the reaction chamber itself resulting to deposit inhomogeneous oxide particles or clusters on substrates without adherence. Thus the core temperature is recommended to set at the decomposition temperature of the relevant precursor salt.

#### b) Atomizing air pressure

The optimized air pressure determines the size of the droplets which is the prime important parameter in the synthesis of thin film. The optimum air pressure is required to form the uniform films of different compound semiconductors.

#### c) Nozzle to substrate distance

The nozzle to substrate distance is important parameter to obtain good quality films. The change in distance changes the deposition rate of the films. Many times because of the short distance in complete decomposition may take place. To avoid this minimum distance is necessary between nozzle and substrate. For very large
distance deposition may not take place. The optimum distance should be kept to obtain the good results.

d) Substrate temperature

The substrate temperature is the key parameter in the thin film deposition. During the synthesis of ZnO thin film by spray CVD technique our main goal is to deposit film at low substrate temperature so as to provide the cost effective technique and can be used in multilayer deposition. The substrate temperature provides nucleation growth in the growth mechanism of thin film. It can affect structural, morphological, opto-electronic properties of the films. The optimum temperature is required to obtain the films with good conductivity and transparency.

3.3A.4 Growth Mechanism

Various steps to involve in growth of the films in advanced spray pyrolysis technique in Fig. 3.3.

1. **Aerosol formation** - Precursor solution is converted into aerosols by spray nozzle
2. **Evaporation** – The solvent evaporation from the surface takes place when it enters in the reaction chamber. The process is followed by diffusion of solvent vapor away from the droplet, change in droplet temperature, then the solute diffuse toward the centre of the droplet and resulting into the reduction in size.

![Fig. 3.3 Droplet Evolution](image-url)
3. **Precipitation and drying** - It involves surface precipitation of solute. If the solute concentration at the center of the drop is less than the equilibrium saturation of the solute at the droplet temperature, then precipitation occurs only in that part of the drop where the concentration is higher than the equilibrium saturation, i.e., surface precipitation.

4. **Thermal Decomposition** - The pyrolysis of the precipitate occurs in the core of the reactor furnace. When the solid-vapor reaches the preheated substrate (kept at comparatively low temperature) nucleation and growth of thin films on the substrate surface takes place. Finally, growth of the nuclei leads to the formation of continuous thin layer of films.

### 3.3A. 5. Limitations

As compared to the conventional spray pyrolysis technique, the reaction chamber has been additionally introduced in the spray CVD set up; where the pyrolytic reaction takes place. During synthesis of thin film, controlling core temperature is tricky job for exothermic solvents like alcohols which will increase the temperature above set value. Hence individual expertise is needed to minimize this difficulty. In this novel spray CVD technique the pyrolytic reaction takes place in the reaction chamber whereas the substrate provides the nucleation growth mechanism. As a result the chemical wastage could be the troublesome case. However, such limitations can be immensely motivating for the further research.

### 3.4A Thin film Characterization Techniques

The fundamentals of growth of thin film and properties of the films can be well understood from their characterizations. Before using the films in applications, one has to characterize the films to obtain the important information of its use in different application. In this section the characterization techniques such as Thickness measurement, X-ray diffraction, field emission scanning electron microscope (FESEM), Atomic force microscope (AFM), electrical resistivity, optical spectroscopy, etc. have been described with relevant principles and working. The gas sensing performance of the undoped and doped ZnO films was tested using a homemade gas sensor assembly and it is explain here.
3.4A.1 Thickness Measurement

Thickness measurements provide the growth rate of deposit. The thickness of the film is the most significant parameter that affects the properties of the thin film. There are various direct and indirect measurement techniques for thickness measurement. Recently, the technique of profilometer is used to measure a surface's profile, in order to quantify its roughness. It was a device similar to a phonograph that measures a surface.

Surface Profilometers are used to measure surface profiles, roughness, waviness, and other parameters. There are two basic surface profilometer technologies: contact and non-contact. Contact or stylus-based Surface Profilometers measure surface texture by dragging a sharp, pointed tool across the surface. Height variations of the tip are recorded and then used to form a texture profile. Roughness and waviness are also calculated from the surface profile data. Non-contact surface profilometers measure the surface texture by optically scanning a surface with a light or laser. Optical or light-based instruments may also use triangulation or interferometry to measure or capture a surface profile. Although most surface profilometer provide only a two-dimensional (2D) or line file, some instruments can provide three-dimensional (3D) or areal topography measurements.

**Contact Profilometers**

![Fig. 3.4 Diagram of basic surface profilometer](image-url)
A diamond stylus is moved vertically in contact with a sample and then moved laterally across the sample for a specified distance with the specified contact force. A profilometer can measure small surface variations in vertical stylus displacement as a function of position. A typical profilometer can measure small vertical features ranging in height from 10 nm to 1 mm. The height position of the diamond stylus generates an analog signal which is converted into a digital signal; which is stored, analyzed and displayed. The radius of diamond stylus ranges from 20 nm to 25 μm, and the horizontal resolution is controlled by the scan speed and data signal sampling rate.

**Non-contact Profilometers**

Profilometer is a measuring instrument used to measure surface's profile, in order to quantify its roughness. Vertical resolution is usually in the nanometer level. An optical profilometer is a non-contact method for providing much of the same information as a stylus based profilometer. There are many different techniques which are currently being employed, such as laser triangulation (triangulation sensor), confocal microscopy (used for profiling of very small objects), low coherence interferometer and digital holography.

### 3.4A.2 X-Ray Diffraction

![Fig. 3.5 Schematics of X-ray diffractometer](image-url)
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X-ray diffraction (XRD) is a powerful technique used extensively for analyzing the structural properties of solid materials [16, 17]. Figure 3.5 illustrates the basic configuration of a diffraction system. In this mode of operation, the primary beam from the target of the x-ray tube emerges from the machine through a collimator and strikes the sample, which diffracts it in a characteristic manner. The diffraction pattern is measured with photographic film or a radiation counter.

Structure identification, determination of lattice parameters and grain size are based on the of the X-ray diffraction pattern. Improved detection methods of X-ray, the availability of commercial mono-chromator and intense micro focus of X-ray sources have made X-ray diffraction method applicable to films as thin as 100 Å [18]. This technique employs a chromator to provide a diffracted beam, which is further diffracted from the film surface oscillating about the mean diffraction position. The X-ray diffraction technique based on monochromatic radiation is more important because the spacing of the planes (d-spacing) can be deduced from the observed diffraction angles. The phenomenon of X-ray diffraction can be considered as reflection of X-rays from the crystallographic planes of the material and is governed by the Bragg’s equation [19-21].

\[ 2d \sin \theta = n\lambda \]  \hspace{1cm} \text{ (3.1)}

where ‘d’ is lattice spacing, ‘\( \lambda \)’ is the wavelength of the monochromatic source, ‘n’ is the order of diffraction and ‘\( \theta \)’ is diffraction angle. The ‘d’ values are calculated using above relation for known values of \( \theta, \lambda \) and n. The X-ray diffraction data thus obtained is compared with American Standard for Testing of Materials (ASTM) or Joint Committee Powder Diffraction Standards (JCPDS) powder diffraction data to identify the unknown material. The sample used may be powder, single crystal or thin film. The crystallite size of the deposits is estimated from the full width at half maximum (FWHM) of the most intense diffraction line by Scherer’s equation as follows,

\[ D = \frac{K\lambda}{\beta \cos \theta} \]  \hspace{1cm} \text{ (3.2)}

D is grain size, \( \lambda \) is wavelength of X-rays, \( \beta \) is full width of half maxima of the peak (FWHM) in radians, \( \theta \) is Bragg’s angle and K is constant. Value of K varies from 0.89 to 1.39, but for most cases it is closer to one. However, this technique is not useful
for identification of individuals of multilayer's or percentage of doping material and does not give any idea about surface morphology.

3.4A.3. Scanning Electron Microscopy (SEM)

All electron beam instruments are built around an electron column, which produces a stable electron beam, controls beam current, beam size and beam shape, and raster's the beam. Most of the principles of an electron beam column can be understood by thinking of the electrons as rays of light and the electron optical components as simply their optical counterparts. It is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. This beam of electrons interacts with electrons in the sample, producing various signals that can be detected and that contain information about the sample’s surface topography and composition.

Fig.3.6 Interaction signals evolved during interaction of electron beam

In scanning electron microscopy, (SEM) an electron beam is scanned across the sample's surface. When electrons strike the sample, a variety of signals are generated, and it is the detection of specific signals which produces an image or a
sample's elemental composition. The three signals which provide the greatest amount of information in SEM are the secondary electrons, backscattered electrons, and X-rays. In a typical SEM, an electron beam is thermionically emitted from an electron gun fitted with a tungsten filament cathode. Tungsten is normally used in thermionic electron guns because it has the highest melting point and lowest vapor pressure of all metals, thereby allowing it to be heated for electron emission, and because of its low cost. Other types of electron emitters include lanthanum hexaboride (LaB6) cathodes, which can be used in a standard tungsten filament SEM if the vacuum system is upgraded and field emission guns (FEG), which may be of the cold-cathode type using tungsten single crystal emitters or the thermally assisted Schottky type, using emitters of zirconium oxide.

**Fig. 3.7 Schematic Diagram of Scanning Electron Microscope (SEM)**

The electron beam, which typically has an energy ranging from 0.2 keV to 40 keV, is focused by one or two condenser lenses to a spot about 0.4 nm to 5 nm in diameter. The beam passes through pairs of scanning coils or pairs of deflector plates in the electron column, typically in the final lens, which deflect the beam in the x and y
axes so that it scans in a raster fashion over a rectangular area of the sample surface. When the primary electron beam interacts with the sample, the electrons lose energy by repeated random scattering and absorption within the specimen. The energy exchange between the electron beam and the sample results in the reflection of high-energy electrons by elastic scattering, emission of secondary electrons by inelastic scattering and the emission of electromagnetic radiation, each of which can be detected by specialized detectors. The beam current absorbed by the specimen can also be detected and used to create images of the distribution of specimen current. Electronic amplifiers of various types are used to amplify the signals, which are displayed as variations in brightness on a computer monitor [22].

The detectors count the number of secondary electrons produced at its spot, on the surface as the electron beam is scanned over specimen surface. Simultaneously the spot of CRT is also scanned as the brightness of the spot is modulated by the amplified current from the detector. The overall effect is to produce a topographic image of the surface on the CRT screen.

**3.4A.4. Field emission Scanning Electron Microscopy (FESEM)**

![Fig. 3.8 Schematic Diagram of Field Emission Gun](image)

The field emission tip is made up of a sharply etched piece of mono-crystalline tungsten. A field is applied to the tip causing electrons to tunnel out of the tip and accelerates down the column. Fig. 3.8 is a basic diagram of the electron gun assembly in a field emission system. In addition to the usual accelerating voltage
anode \( (V_0) \), second voltage anode has been placed in close proximity to the Field Emission tip. The desired accelerating voltage is obtained by adjusting \( V_0 \) to accelerate or decelerate electrons emitted at the extraction voltage \( V_1 \). It is the ultimate combination of these two anode potentials which sets the final electron speed down the optical column.

![Fig. 3.9 Schematic Diagram of FESEM](image)

The ratio of these values automatically can be set with computer. In field emission gun, emitters are either of Cold-cathode type, usually made of single crystal tungsten sharpened to a tip radius of about 100 nm, or of the Schottky type, in which thermionic emission is enhanced by barrier lowering in the presence of a high electric field. There are several benefits to cold field emission and few detractors. Cold Cathode Field Emission microscopy provides higher resolution, higher beam density (brightness), and longer tip life than Thermal Tungsten wire SEMs and thermally assisted “Schottky” field emitters. The following Table 3.3 highlights those parameters responsible for the Cold Cathode Field Emission’s higher performance at lower accelerating voltages. The field emission tip is made up of a sharply etched piece of mono-crystalline tungsten. A field is applied to the tip causing electrons to tunnel out of the tip and accelerates down the column.

**Table 3.3 Parameters for Cold Cathode Field Emission**

<table>
<thead>
<tr>
<th></th>
<th>Source Diameter</th>
<th>Energy spread</th>
<th>Brightness</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Thermal Tungsten</strong></td>
<td>50-100 (KA)</td>
<td>&lt;2.0</td>
<td>1x</td>
</tr>
<tr>
<td><strong>Cold Cathode Field Emission</strong></td>
<td>30-50 (A)</td>
<td>0.2</td>
<td>1,000 x</td>
</tr>
</tbody>
</table>
3.4A.5 Atomic Force Microscopy (AFM)

It is recent technique for the investigation of the topography of conducting and non-conducting materials and can provide spatial resolution in nanometer range as well as atomic resolution under certain boundary conditions. The additional advantage is that the images obtained are digital. A key of AFM is its micrographic force sensor or cantilever. One or more beams of silicon or silicon nitride of length 100 to 500 µm and about 0.5 to 5 µm thick usually form the cantilever. At the end of the cantilever, a sharp tip is mounted which is used to sense a force between the sample and tip, for continuous or intermittent contact with the sample and raster-scanned over the surface. Fine motion piezoelectric scanner is used to generate images and force measurements. A piezoelectric scanner is a device that moves by a microscopic amount when a voltage is applied across its electrodes. A piezoelectric scanner for AFM’s can translates in three dimensions (x, y and z axes) and come in different sizes to allow maximum scan ranges of 0.5 to 125 µm in the x, y and several microns in the vertical (z) axis. A well-built scanner can generate stable motion on the scale below 1 Å. By scanning the AFM cantilever over a surface (or scanning a sample under the cantilever) and recording the deflection of the cantilever, local height of the sample is measured. The measured cantilever deflection allows a computer to generate a map or surface topography. Three-dimensional topographical maps of the surface are then constructed by plotting the local sample height verses horizontal probe tip position. Other imaging techniques are also used including measuring the change in amplitude or phase of an oscillating cantilever, using tapping mode. This tapping mode is useful to study the surface morphology of thin films. The three main classes of interaction are contact mode, tapping mode, & non-contact mode.

Non Contact Mode

In this mode, the probe operates in the attractive force region and the tip-sample interaction is minimized. The use of non-contact mode allowed scanning without influencing the shape of the sample by the tip sample forces. In most cases, the cantilever of choice for this mode is the one having high spring constant of 100 N/m so that it does not stick to the sample surface at small amplitudes. The tips mainly used for this mode are silicon probes.
Contact Mode:-

![Block diagram of atomic force microscope](image)

It is the most common mode of operation. In the so-called contact-AFM mode, the tip makes soft “physical contact” with the surface of the sample.

**Tapping Mode (intermittent contact Mode)**

In tapping mode-AFM the cantilever is oscillating close to its resonance frequency and an electronic feedback loop ensures that the oscillation amplitude remains constant, such that a constant tip-sample interaction is maintained during scanning.

**3.4A. 6 Optical Absorption Studies**

The equilibrium situation in semiconductor can be disturbed by generation of carriers due to optical absorption. Optical photon incident on any material may be reflected, transmitted or absorbed. The phenomena of absorption in a material is altogether considered to be due to (1) inner shell electron, (2) valance band electron, (3) free carriers including holes as well as electrons, and (4) electron bound to localized impurity centers or defects of some type. The absorption by the second type of electron is of great importance in study of fundamental properties of semiconductors. In an ideal semiconductor, at absolute zero temperature the valance band would be completely full of electrons, so that electron could not be
excited to higher energy state from the valence band. Absorption of quanta of sufficient energy tends to transfer of electrons from valence band to conduction band. For crystalline materials, the transition of electrons from valance band to conduction band can be grouped into direct and indirect process. In direct inter-band optical transitions, the wave vector $K$ for elements remains unchanged in E-K space; here momentum also does not change, while in indirect inter-band transition the wave vector $K$ for electrons changes in the E-K space.

Fig. 3.11 Transmission and Reflection of light by a single film

Thus, vertical transitions are important when the valance and conduction band extreme are located at the same point in the Brilliouin zone. For indirect transition, the band extreme differ in their positions E-K space. It is possible to differentiate the nature of optical transition as direct allowed or direct forbidden by using classical relation $[23]$. 

$$\alpha = \alpha_0 (\hbar \nu - E_g)^n / \hbar \nu$$

where $\alpha_0$ is constant, $E_g$ is the separation between bottom of the conduction band and top of the valance band, ‘$\hbar \nu$’ is the photon energy, ‘$n$’ is constant. For allowed direct transition $n = \frac{1}{2}$ and allowed indirect transition $n = 2$. Hence for direct allowed transition the above equation becomes,

$$(\alpha \hbar \nu)^2 = \alpha_0 (\hbar \nu - E_g)$$ ................................................................. (3.3)

The optical band gap values were determined by the plot of $(\alpha \hbar \nu)^2$ against $\hbar \nu$. If it is linear, then the transition is direct allowed. The optical band gap values were determined $(E_g)$ by extrapolating the linear portion of the curve to the energy axis
at \( \alpha = 0 \). Though the optical band gap, nature of transition, transmission etc. are obtained easily from optical absorption, the reflectance, \( R \) is assumed to be zero and the equation depends on only classical approach. The effect of different deposition parameters on the band gap and optical constants (refractive index, extinction coefficient, and dielectric constants) of these films has been investigated and the deposition parameters significantly change the optical constants. In order to calculate the refractive index of the films, we recorded the reflectance spectra of the films. We have calculated the refractive index values of the films using the above equation [3.9]. As shown in Fig. 3.9, a beam of light incident on the Zinc oxide thin film of thickness ‘\( d \)’. The beam gets partly reflected (R), transmitted (T) and absorbed (A). The reflectance ‘R’ is calculated from the relation [28],

\[
A + R + T = 1 \quad \text{or} \quad R = 1 - (A + T) \quad \text{(3.4)}
\]

The absorption coefficient (\( \alpha \)) can be calculated from the observed absorbance data. Using Beer and Lambert's formula [29] given by,

\[
\alpha = 2.303 \frac{(A/d)}{d} \quad \text{(3.5)}
\]

The photon energy, \( E \), is given by [28] with ‘\( h \)’ is Planck’s constant and ‘\( \nu \)’ is the frequency of photon, \( c' \) is speed of light and ‘\( \lambda \)’ is the wavelength.

\[
E = h\nu \quad \text{(3.6)}
\]

\[
E = \frac{hc}{\lambda} \quad \text{(3.7)}
\]

Substitutes for constants in above equation (3.7) give

\[
E = \frac{12400}{\lambda} \ \text{(eV)} \quad \text{(3.8)}
\]

For semiconductors \( \{K^2 << n^2\} \), there exists a relationship for ‘\( R \)’ and ‘\( n \)’ [30]

\[
R = \frac{(n+1)^2}{(n-1)^2} \quad \text{(3.9)}
\]

Where ‘\( R \)’ is reflectance and ‘\( n \)’ is refractive index. There exists a relationship between extinction coefficient ‘\( k \)’ and absorption coefficient ‘\( \alpha \)’ given by,

\[
K = \frac{\alpha \lambda}{4\pi} \quad \text{(3.10)}
\]

Since the particle diameter is two to three hundredth the wavelength of visible light the particles transmit the visible light without absorbing. The refractive index of zinc oxide (1.9) is small as a result it hardly scatters light, thereby making it colorless and enhancing the transparency. In particular extinction coefficient reduces to zero for very transparent thin films. The result suggests that the prepared thin films have excellent optical transparency in visible regions.
3.4A.7. Photoluminescence (PL) spectroscopy

Photoluminescence (abbreviated as PL) is a process in which a substance absorbs photons (electromagnetic radiation) and then re-radiates photons. Hence by absorbing photons it jumps into the higher excited state and then return to a lower energy state accompanied by the emission of a photon. As the excitation is due to the photon, due to which luminescence is observed, hence it is called as photoluminescence. The period between absorption and emission is typically extremely short, in the order of nanoseconds. Under special circumstances, however, this period can be extended into minutes or hours [24]. Photoluminescence spectroscopy is a contactless, non-destructive method of probing the electronic structure of materials specifically, light is directed onto a sample, where it is absorbed and imparts excess energy into the material in a process called “photo excitation”. One way this excess energy can be dissipated by the sample is through the emission of light, or luminescence. In case of the photo excitation this luminescence is called photoluminescence. The intensity and the spectral content of this photoluminescence is a direct measure of the various important material properties. Photoluminescence spectra can be recorded with an experimental arrangement as shown in the Fig. 3.12.

![Photoluminescence measurement setup](image)

Fig. 3.12 Photoluminescence measurement setup
The sample is mounted in a variable temperature cryostat and is illuminated with a laser or bright lamp (like xenon lamp) with photon energy greater than $E_g$. If a liquid helium cryostat is used, sample temperatures from 2K upward are easily obtained. The luminescence is emitted at lower frequencies and in all directions. A portion is collected with a lens and focused onto the entrance slit of a spectrometer. The spectrum is recorded by scanning the spectrometer and measuring the intensity at each wavelength with a sensitive detector such as a photomultiplier tube. Alternatively, the whole spectrum is recorded at once using an array of detectors such as a charge-coupled device.

3.4A. 8 Transport properties

3.4A.8a) Two Probe Resistivity Measurement

The Experimental setup for two probe resistivity measurement is shown in Fig.3.13.

![Fig. 3.13 Two Probe Electrical Resistivity measurement unit.](image)

1-Sample holder, 2-Mica Sheet, 3-Thin film, 4- Thermocouple, 5- Heater, 6-Copper wire.

The two probe method is simple, easy to use and useful for high resistive thin films. In this method, constant voltage ‘$V$’ is applied between two-fixed probes separated by distance of ‘$d$’ and current passing thorough a sample of known dimensions (cross section area $A$) is measured with an appropriate current meter. For uniform sample the resistivity is given by,
\[ \rho = \frac{A}{I} \times \frac{V}{d} \] \hspace{1cm} (3.11)

In case of semiconducting thin films, resistivity decreases with increase in temperature. The dependence of resistivity on temperature is expressed by the following equation.

\[ \rho = \rho_0 \exp \left( - \frac{E_a}{kT} \right) \] \hspace{1cm} (3.12)

symbols have their usual meaning. From the slope, \( \log \rho \) vs. \((1000/T)\) plot activation energy of the semiconducting material can be estimated.

**3.4A.8b) Vander Pauw-Hall configuration measurement**

The standard Vander Pauw technique [28] is used to determine the Hall parameters. From the Hall Effect measurement one can determine the type of change carrier concentration, Mobility of the change carriers and hall coefficient of the film. This can be used for the low resistivity materials. The experimental setup for measurement is as shown in Fig. 3.14.

![Fig. 3.14 Circuit setup for Vander Pauw-Hall effect measurement.](image)

The Hall Voltage \( V_H \) for different samples for applied current \( I_B \) be determined by using the formula,

\[ R_H = \frac{(V_H d)}{I_B} \times 10^8 \text{ cm}^3/\text{Coulomb} \] \hspace{1cm} (3.13)

The carrier concentration for different samples was calculated by using following equation.
Chapter Three  Experimental Techniques

\[ n = \frac{1}{R_{1}\rho} \text{ cm}^3 \]  

(3.14)

By measuring the values of \( n \) and substituting value of \( \rho \), the carrier mobility \( \mu \) can be calculated by using the following relation.

\[ \mu = \frac{1}{n\rho} \text{ cm}^2/\text{V-s} \]  

(3.15)

3.5A Gas Sensing Measurement Assembly

The gas sensing unit assembly is design and fabricated in the laboratory to test harmful and hazardous gases is as shown in Fig. 3.15.

![Fig. 3.15 Schematic diagram of the Gas sensor unit](image)

It consists of hot plate which is enclosed in airtight stainless still housing. It’s volume is 250cc. The gas is injected into the vessel through a septum having provision of a rubber gasket at lower end of SS housing. The pair of spring-enabled pressure contacts made up to the film under test. A “Rigol DM3062 model” digital multimeter/ data acquisition system connected to the external leads of the films for resistance measurements with and without exposing to the gas. The heater temperature was monitored and controlled using PID temperature controller unit.

The films are placed on the heater block and its resistance was monitored with computer interfaced “Rigol Digital Multimeter”. Then the sensitivity of thin
film for varying operating temperature in the range 298-673K was measured; at a different gas concentration depending on their nature and response. Once the optimum operating temperature was determined, further characterization was made by using the same setup.

The desired gas concentration in parts per million (ppm) was obtained by taking a measured quantity of the gas from a canister, containing pressurized gas (~20 kg/cm²) at 1000 ppm concentration, by means of a syringe, and introducing it into an airtight SS housing having a volume of 250 cc. The gas was injected through a septum in the housing. The “unit” ppm being a volume ratio, 1 ppm of a given gas therefore occupies a volume of $2.5 \times 10^{-4}$ cc in 250 cc housing. Therefore, the volume of gas required to be taken in a syringe from a canister containing the gas at 1000 ppm such that it gives rise to 1 ppm of gas concentration in a 250 cc housing is $(2.5 \times 10^{-4} \times 10^6 \text{ cc}) / (1000) = 0.25 \text{ cc}$. Other gas concentrations employed in our gas sensing studies were thus obtained proportionally.

**Response and recovery measurements**

The response time of film to a particular gas is measured by introducing the gas of known concentration into the housing and recording the resistance using Rigol digital multimeter as a function of time till its steady state value is reached. To record the recovery time, the solid state casing is opened and the films are allowed to expose to the atmosphere and the subsequent film recovery on gas removal is recorded. It is characterized by the resistance reaching its base value. The response and recovery characteristics of films exposed to different gas concentrations are thus studied by plotting their resistance as a function of time.

### 3.6. Section (B)

**Synthesis of ZnO thin film by Spray CVD technique**

**3.6B Preparation of ZnO film**

Synthesis of undoped ZnO thin films has been successfully done by using spray CVD technique. For proper analysis of decomposition temperature of selected precursor investigation on differential thermal analysis was carried out by using SDT-2960 analyzer. The preparative parameters were optimized in order to get
transparent and good quality conductive oxide material. The high optical transmittance and low electrical resistivity are key elements for good TCO films.

3.6B.1 Substrate Cleaning

In the deposition of undoped ZnO thin films, substrate cleaning plays an important role. It is the prime and essential need for making uniform, crack free and homogeneous deposition over the substrate. The contaminated surface provides non uniform nucleation growth which results into different orientation. Effective surface cleaning treatment should be chosen depending on the type of the substrate used for deposition. In the present work glass micro slides supplied by ‘Blue Star’ with dimensions 75 mm × 25 mm × 1.35 mm have been used as the substrates. The following procedure has been adopted for cleaning the substrates:

1. Initially, glass slides were washed with detergent and distilled water,
2. These substrates were boiled in concentrated chromic acid (0.5 M) and kept in it for half an hour.
3. The substrates were washed with double distilled water,
4. The substrates were ultrasonically cleaned for 30 min,
5. Then, the substrates were exposed to the methanol vapors for 5 minutes and were used for deposition.

3.6B.2 TGA-DTA analysis

Referring the TG-DTA analysis was performed before synthesis of ZnO thin film. From the analysis it was observed that the decomposition temperatures was 330°C. The rapid decay in TGA curve takes place at 330°C with total weight loss was 60.15%. These consequents weight losses are attributed to the decay leading to the decomposition of acetate groups.

3.6B.3 Experimental details

ZnO thin film were prepared by spraying 200ml non-aqueous solution of high purity Zinc Acetate [Zn (CH₃COO)₂ · 2H₂O] (Thomas Baker, India) in methanol with 0.075M concentration. The solution was sprayed through a specially designed glass nozzle onto the ultrasonically cleaned glass substrates. The distance between spray nozzle and glass substrate is kept 36cm fixed for total length of experiment. The optimized spray rate of ~6 ml min⁻¹ is regulated by using compressed air at a
pressure of 10 LPM. The different preparative parameters such as solution quantity, concentration, and spray rate were optimized in order to obtain low resistive and highly transparent undoped ZnO thin films. In the first stage of the work, an effect of variation of reaction chamber temperature (core temperature) was studied. The reaction chamber temperature was varied from 300°C to 360°C with step of 30°C by keeping substrate temperature constant (220°C). In the next stage; effects of variation substrate temperature from 190°C to 250°C with step of 30°C was studied by keeping core temperature constant at 330°C. Throughout the experimentation, the both the substrate and core temperature were controlled using electronic temperature controllers. Hazardous gases evolved during the thermal decomposition were expelled out by using exhaust fans.

3.6B.4 Characterization Techniques

The structural investigations on ZnO thin films were carried out using a Bruker AXS X-ray diffractometer (German make Bruker axs D-8 Advance Model) with Cu–Kα (λ = 1.54 Å) as radiation source operating at 40 kV and 30 mA. The diffraction angle ‘2θ’ was varied from 20° to100° with a step of 0.02°/min. The films thickness and roughness was measured by surface profilometer (model Ambios XP-1). The films surface morphology was studied with the Field emission scanning electron micrographs (FESEM) with 50,000X magnification. The transmission spectrum (normal incidence) measurements were made at room temperature in the spectral range of 290–1100 nm using a UV–VIS spectrophotometer (Shimatzu1800model). Measurements of room temperature transport properties like resistivity (ρ), conductivity (σ), sheet resistance (Rs), carrier concentration (n), and mobility( μ) were carried out by the Van der Pauw technique and Hall effect set up, supplied by Scientific Equipments, Rookie, India. Colloidal silver paste was used for ohmic contacts. Photoluminescence spectra of the samples were recorded with a spectrofluorimeter (JASCO, model–F.P.-750, Japan) using a 260nm line of an ultraviolet lamp as an excitation source. The three dimensional morphology of the growth was examined by using atomic force microscopy (AFM), Nanoscope instruments, USA in contact mode, with V shape silicon nitride cantilever of length 100μm and spring constant 0.58N/m.
3.6B.5 Results and Discussion

Non-aqueous solution of 0.075M Zinc Acetate sprayed over the preheated substrates through the specially designed glass nozzle having bore of diameter 0.01cm. When aerosol droplets arrive in the reaction chamber pyrolytic decomposition of droplets takes place. Particles of the final product (i.e. of ZnO) are pushed upward by the atomized air and reach to the preheated substrates. The substrate heater offers initial nucleation centers on to the pre heated substrates for growth of films and provides average kinetic energy for the even distribution of the particles. After the initial nucleation process at the respective substrate temperature, the grains may tend to form large clusters. This process is stopped or slowed down when particles move them to the thermally stable sites on the films to form an even distribution of the deposits. Thus, deposition occurs in two steps, namely requisite chemical pyrolysis and nucleation growth. The low substrate temperature and solid–vapor phase growth overcome probable films cracking and hazy ripples (as observed in some as-deposited sprayed films) and lead to a homogeneous coating. It was observed that, at the suitable atomizing air pressure and nozzle–substrates spacing (about 38cm), only critical-sized sprayed particles will reach the substrates and the residual particles will be drawn back by micro gravity at the core of the reaction chamber, and result in large-area crack-free deposits on the substrate. The possible chemical reaction of ZnO film formation from zinc acetate solution as follows,

\[ \text{Zn(CH}_3\text{COO)}_2 \cdot 2\text{H}_2\text{O} + 2 \text{ CH}_3\text{OH} \rightarrow \text{ZnO} + 2\text{(CH}_3\text{COCH}_3) + 3\text{H}_2\uparrow + \text{O}_2\uparrow \]

The films deposited onto the amorphous glass substrates were mirror smooth, uniform and well adherent to the substrate.

3.6B.6 Core Temperature variation:-

The goal of the chapter is to optimize the preparative parameters to obtain good quality Zinc oxide thin film by newly fabricated spray CVD technique. The first stage of optimization in synthesis of the ZnO thin films was to study the dependence of the properties of the films with variation in the core temperature. To achieve the same set of undoped ZnO thin films were deposited at different core temperatures in the range of 300°C to 330°C with the step of 30°C on glass substrate.
3.6B.6a) X ray diffraction studies

X-ray diffraction pattern is helpful in studying synthesis of different morphologies of ZnO with the crystallite size, structure and phase formation. The X-ray diffraction patterns for the as deposited ZnO films at different core temperatures are shown in Fig. 3.16. It shows that the structural properties of the ZnO films largely depend on core temperature. It can be observed from Fig. 3.16 that zinc oxide films are polycrystalline and have a hexagonal close-packed structure. The reflection corresponding to the plane (002) is found to be more intense; which evidenced that the films crystallites are preferentially oriented along with c-axis normal to substrate surface. Similar texturing of the films has also been observed by other [25]. Other well defined diffraction planes of ZnO, observed clearly are (100), and (101) along with weak peaks (102), (110), (103), (200) and (112). The observed d values are in good agreement with the standard values reported in the PDF for ZnO (JCPDS card file no: 80-0075, \(a = 3.24982\) and \(c = 5.20661\) Å) indicates the polycrystalline wurzite structure of ZnO is confirmed. It is evident from this figure that structural properties of the ZnO films are strongly depend on core temperature. The films deposited at 3300C core temperature exhibits highly oriented films as compared to the other core temperatures. No traces of acetate group are present in XRD indicates the complete decomposition of initial ingredients.

The average crystallite size calculated using Debye Scherrer relation (3.4) and tabulated in Table 3.4. It is observed that crystallite size changes from 18nm to 22nm. It is seen that the average crystallite size increases with increase in core temperature, the crystallites of highest average size ~22 nm are obtained at 3300C core temperature; while for the higher core temperature the crystallite size decreases slightly. The amount of the defects in the as deposited film was resolved by evaluating the dislocation density (\(\delta\)). It was calculated using following formula with the simple approach of Williamson and Smallman, & is mentioned in Table 3.4. The smaller value of dislocation densities and larger grains is the indication of the better crystallization which is observed for 3300C core temperature.

\[
\delta = \frac{1}{D^2}
\]
The texture coefficient \( T_c \) represents the texture of the particular plane, deviation of which from unity implies the preferred growth. The different \( T_c(hkl) \) values have been calculated from the X-ray data using the well-known formula

\[
T_c(hkl) = \frac{I(hkl)/I_o(hkl)}{(1/N) \sum I(hkl)/I_o(hkl)} \quad \text{.......................... (3.17)}
\]

where \( I(hkl) \) is the measured relative intensity of a plane \( (hkl) \), \( I_o(hkl) \) is the standard intensity of the plane \( (hkl) \) taken from the JCPDS data, \( N \) is the number of diffraction peaks. The variations of \( T_c \) calculated for the (002) diffraction peak of wurtzite ZnO, are shown in Table 3.4. A sample with randomly oriented crystallite presents \( T_c(hkl) =1 \), while the larger \( T_c \) indicates good orientation of the film along that \( (hkl) \) direction.
### Table 3.4 Variation of structural parameters with core temperature

<table>
<thead>
<tr>
<th>Core Temperature (°C)</th>
<th>Crystallite Size (nm)</th>
<th>Dislocation Density (m⁻²)</th>
<th>Texture Coeff.</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>20</td>
<td>2.5 x 10¹⁵</td>
<td>1.2764</td>
</tr>
<tr>
<td>330</td>
<td>28</td>
<td>1.3 x 10¹⁵</td>
<td>2.9934</td>
</tr>
<tr>
<td>360</td>
<td>22</td>
<td>2.1 x 10¹⁵</td>
<td>1.9612</td>
</tr>
</tbody>
</table>

### 3.6B.6b) Field Emission Scanning Electron Micrograph (FESEM)

Fig. 3.18 FESEM micrographs of ZnO films for varying core temperatures

The field emission scanning electron micrograph corresponding to the different core temperature is as shown in Fig 3.18. It illustrates the interesting morphology of ZnO thin film with increase in core temperature. From FESEM it is observed that there is no cracks large scan area of all samples. The films surface exhibits granular, polycrystalline morphology. The film prepared at 330°C shows most compact surface supporting the maximum intensity observed for the (002) plane in XRD studies. The formation of various pyramidal shapes particles are clearly seen from all the micrograph. However the size of the particles changes with core
temperature. It is seen that with at 330°C core temperature the particles are clearly visible and size of the grains is maximum.

3.6B.6c) Atomic Force Micrograph (AFM) Study

![AFM micrograph](image_url)

**Figure 3.19 AFM micrograph of a typical undoped ZnO at 330°C**

Fig. 3.19 depicts a typical micrograph at reaction chamber temperature 330°C. Here the scanning area of the AFM image in Fig. 4.6 is 3×3×2 μm. The films are uniform, dense and well packed between particles. It shows well covered surfaces with pyramidal shaped grains structure. The bright area in the 2D micrographs is the overgrown clusters. The apparent size of the grains from the surface images is higher than the values calculated from the XRD measurements, indicating that these grains are probably an aggregation of crystallites.

![Thickness & Roughness variation](image_url)

**Fig. 3.20 Thickness & Roughness variation**
A quantitative method to examine the surface morphology and structure is obtained by analyzing the surface roughness using AFM. The variation of surface roughness with core temperature is shown in Fig. 3.20. It shows that, due to the pyramidal shaped grains, the surface roughness of thin film increases and which is found to be greater than 300nm for the sample prepared at 330°C. The surface thickness is also recorded using XP-1 surface profiler which shows maximum thickness at 330°C and its behavior is as shown in the Fig. 3.20.

3.6B.6d) Electrical Resistivity Measurement

![Graph showing variation of ln(\(\rho\)) with \((1000/T)\) for ZnO thin film.](image)

Fig. 3.21 Variation of ln(\(\rho\)) with \((1000/T)\) for ZnO thin film.

The electrical resistivity measurement was carried out by using standard two probe techniques. The resistivity was measured by varying temperature from 60°C to 300°C for samples prepared at various core temperatures. For the electrical conductivity measurements both faces of the thin films were coated with
conducting silver pest to obtained the ohmic contacts to the films. A Chromel-Alumel thermocouple was employed to measure the temperature. Ohmic behavior of the contacts are confirmed by checking the current (I)–voltage (V) characteristic across the contacts which show a linear dependence of current on applied voltage.

A plot of \( \ln(\sigma) \) versus 1000/T for the advanced sprayed ZnO film deposited at different core temperatures is shown in Fig. 3.21. It shows the semiconducting behavior of the ZnO thin film. The room temperature resistivity was found to be of the order of \( 10^{-2} \, \Omega\cdot\text{cm} \) for the sample prepared at \( 330^\circ\text{C} \) core temperature. The observed high resistivity may be due to nanocrystalline nature of the films and may also be attributed to the oxygen chemisorptions at grain boundaries; since air was used as carrier gas for deposition and the decomposition reaction takes place in the ambient core of the reaction chamber.

Activation energy is the amount of thermal energy required to release an electron from trap level to the conduction band (CB). These trap levels are the levels are located few eV below the CB in the forbidden region and are nothing but the crystal defects. The activation energy values are determined from the slope of the graphs and are found between 0.08 to 0.27 eV. These activation energies may be related with the inter-crystalline barrier height separating the ZnO grains from each other and different oxygen vacancies. For polycrystalline TCO’s with lower carrier density (less than \( 10^{26} \)), the resistivity is mostly due to the grain boundary electron trapping [29, 30]. Correlation was found between the resistivity and X-ray diffraction studies. The resistivity measurement shows that it is minimum for the sample prepared at \( 330^\circ\text{C} \); it indicates that it is minimum for the film with good crystallite size.

### 3.6B.6e) Optical Properties

The optical transmission variation with wavelength for the ZnO thin films synthesized by spray CVD system on corning glass substrates is as shown in Fig. 3.22. The maximum visible average transmission was found to be 90% for core temperature \( 360^\circ\text{C} \). This observed highest transmission at \( 360^\circ\text{C} \) may be due to observed decrease (Fig. 3.20) in film thickness at that core temperature. At optimized core temperature (\( 330^\circ\text{C} \)) the films show 83% average transparency.
These transmittance curves with interference fringe pattern between the wave fronts generated at interfaces (air and substrate) are clearly seen. This reveals the smooth reflecting surfaces of the film and there was not much scattering/absorption loss at the surface suggesting that it has uniform distribution of film thickness i.e. films are more homogeneous.

Fig. 3.22 Optical transmission spectra of ZnO thin films for core temperature variation

At lower temperatures, i.e. at 300°C, relatively lower transmission is due to reduction in homogeneity of the films, due to insufficient thermal energy. This may be responsible for increasing in scattering of light. Fig. 3.23 shows the optical absorption spectrum vs. wavelength. The graph reveals that the absorption in ZnO thin film is low; less than 0.1% of absorption occurs in the visible region. However, at band edge absorption sudden increase in absorption is found. The absorption coefficient 'α' of the films was determined from absorbance measurements. In order to investigate the effect of the core temperature on the absorption of ZnO films, the recorded absorption spectra was employed to determination the optical energy gap $E_g$. Assuming a direct transition between the edges of the valence and the conduction band, the variation of the absorption coefficient $\alpha$ with the photon energy $h\nu$ can be given by the Tauc’s equation (3.3).
Figure 3.23 Optical Absorbance spectra of ZnO thin films

Figure 3.24 shows the plot of \((\alpha h \nu)^2\) vs. \(h \nu\) for undoped ZnO thin films synthesized by spray CVD technique. It has been observed that the plot is linear over a wide range of photon energies indicating a direct type of transitions. The intercepts (extrapolations) of these plots (straight lines) on the energy axis gives the energy band gaps energy and it is found to be vary from 3.22eV to 3.27eV. 

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It reveals minimum optical band gap value for optimized 330°C temperature indicating better crystallinity. These observed values of optical band gap are in good agreement with the reported value [31].

3.6B.7 Substrate Temperature Variation

The films of zinc oxide are prepared by varying substrate temperature are found to be uniform and are good adherent to the substrate. The crystallographic, electrical and optical properties of these films were studied. The results are discussed in the following sections.

3.6B.7a) X ray diffraction studies

![XRD patterns of ZnO thin films with substrate temperatures](image)

**Fig. 3.25 XRD patterns of ZnO thin films with substrate temperatures**

The crystal structure and orientation of the ZnO thin films were investigated by X-ray diffraction (XRD) patterns. The XRD spectra for ZnO thin films prepared at various substrate temperatures are shown in Fig. 3.25. It shows three well-defined
peaks, identified corresponding to (100), (002), and (101) diffraction planes of ZnO, along with less intense peaks (102), (110), (103), (200), (112) indicates the polycrystalline wurzite structure of ZnO. These values are in good agreement with those reported in the PDF of ZnO (JCPDS card file no: 80-0075). All the samples show enhanced intensities for the peak corresponding to (002) plane, which indicate the preferential orientation along the c-axis [8]. Assuming a homogeneous growth across crystallites, the size of crystalline can be estimated from the full width half maximum (FWHM) values of diffraction peaks. An average crystallite size could be obtained for the films using the well known Debye-Scherrer formula for crystallite size broadening of diffraction peaks. The dislocation density $\delta$ represents the defects in the film and is determined by using the equation (3.6) and texture coefficient are determined by using equation (3.7). These values are listed in Table 3.6. The $T_c(hkl)\approx 1$ indicates that the films are with a randomly oriented crystallite similar to the JCPDS reference, while values higher than 1 indicate the abundance of grains along (002) direction. Values $0<T_c(002)<1$ indicate the lack of grains oriented in that direction. As $T_c$ for plane (002) is high as compare to other planes is the indication of preferential growth of the crystallites in the direction perpendicular to c-axis i.e. along (002) plane for all samples.

**Table 3.6 Variation of structural parameters with Substrate temperature**

<table>
<thead>
<tr>
<th>Substrate Temperature ($^0C$)</th>
<th>Crystallite Size (nm)</th>
<th>Dislocation Density ($m^{-2}$)</th>
<th>Texture Coeff.</th>
</tr>
</thead>
<tbody>
<tr>
<td>190</td>
<td>22</td>
<td>$2.1 \times 10^{15}$</td>
<td>1.9764</td>
</tr>
<tr>
<td>220</td>
<td>28</td>
<td>$1.3 \times 10^{15}$</td>
<td>2.993</td>
</tr>
<tr>
<td>250</td>
<td>23</td>
<td>$1.9 \times 10^{15}$</td>
<td>2.2612</td>
</tr>
</tbody>
</table>

However, it is observed that, for films prepared at $220^0C$ substrate temperature texture coefficient is high and it shows the high preferential orientation along c-axis for the films prepared at $220^0C$ substrate temperature. The crystallite size for undoped ZnO thin film is calculated by using the method described in previous section and values are tabulated in Table 3.6. The marginal rise in grain size is found at $220^0C$ substrate temperature. The substrate temperature $220^0C$, provides optimal surface energy to occupy lowest energy sites growth along (002) plane.
This optimized temperature is attributed to the increased surface mobility and resultant grain growth [26].

3.6B.7b) Morphological Characterization

Fig. 3.26  Surface Morphology of ZnO thin films for varying substrate temp.

Fig. 3.26 (a-c) shows the plain view FE-SEM micrographs of ZnO films prepared at various substrate temperature temperatures. Film surface is rough and irregular for all films prepared at various substrate temperatures. However, no cracks are observed on large scan area for all samples. The films surface exhibits granular, polycrystalline morphology. This may be assigned to the incomplete crystallization due to insufficient thermal energy. The more irregular growth is observed at low and high substrate temperature and slight regular growth is observed at 220° substrate temperature. The film prepared this shows most compact surface supporting the (002) intensity maxima observed in XRD studies.

3.6B.7c) Topographical Characterization

Figure 3.27 and 3.28 shows typical 2D and 3D topography of the typical sample(for 220°C substrate temperatures) of pure ZnO thin films synthesized by spray CVD technique. The 2D topography shows the development of dense,
triangular pyramidal shaped crystallite with some over grown particles. It supports the results observed by FESEM micrographs. It shows pure ZnO is composed of large grain size and is almost uniform over the surface which results in to large crystals suggesting high crystallinity of the film as confirmed by XRD analysis. Thus the synthesis conditions can correlate with the grain size and crystallinity of films. The 3D topography of the typical sample shows large height of triangular shaped pyramids which confirms vertically aligned growth of crystal structure (along c-axis perpendicular to substrate) as observed with X ray diffraction technique.

![Figure 3.27 (2D) Topography for a typical 220°C substrate temperature](image)

![Figure 3.28 (3D) Topography for a typical 220°C substrate temperature](image)

The shape of grains causes to increase the roughness (~380nm) as compared with other samples. The triangular shape causes to increase the light scattering properties of films which is essential for transparent electrodes in solar cell applications.
All these topographical results give us possibility to improve the gas sensing properties for gas sensor applications also. Thus the films roughness (RMS), grain size and dimensions were found to correlate with the synthesis of applied deposition technique. The surface thickness and roughness is also recorded using XP-1 surface profiler for all samples. Its behavior is as shown in following Fig. 3.29.

![Graph showing variation of Thickness and Roughness with substrate temperature.](image)

**Fig. 3.29 Variation of Thickness and Roughness with substrate temperature**

### 3.6B.7d) Electrical Resistivity

The dependence of the electrical resistivity on temperature can be explained by the well-known exponential law. A plot of \( \ln(\rho) \) versus 1000/T for the ZnO film deposited at different substrate temperatures are shown in Fig. 3.30. It clearly shows the semiconducting behavior of the ZnO thin film. In the low temperature region of conduction, the conductivity increases due to increase in mobility of charge carriers. Thus in this region, a small thermal energies are quite sufficient for the activation of charge carriers to take part in the conduction process. The increases in conductivity in high temperature region may be due to desorption of adsorbed oxygen molecules from the surface of thin film; hence potential barrier at grain boundaries decreases which causes the electrons to cross grain boundaries. It also affects to increase donor densities due to thermal excitation. The activation energy in two temperature zone can be calculated by using equation (3.19) and are mentioned in Table 3.7. It shows that the activation energy in the low temperature region is always less than the energy in the high temperature region this is because material transfers from semiconducting behavior to metallic behavior with increase
in temperature [24]. Thus the high value of activation energy is mainly determined by the intrinsic defects and hence is called as intrinsic conduction [24, 25]. The activation energy in both the region is low for the highly oriented and large crystallites size sample prepared at 220°C substrate temperature.

![Graph showing variation of In (σ) Vs 1000/T with substrate temperature](image)

**Fig. 3.30 Variation of ln (σ) Vs 1000/T with substrate temperature**

<table>
<thead>
<tr>
<th>Substrate temp of sample (°C)</th>
<th>Low temp region 60-150°C (eV)</th>
<th>High temp region 150-300°C (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>190</td>
<td>0.025</td>
<td>0.73</td>
</tr>
<tr>
<td>220</td>
<td>0.02</td>
<td>0.63</td>
</tr>
<tr>
<td>250</td>
<td>0.03</td>
<td>0.70</td>
</tr>
</tbody>
</table>

**Table 3.7 Activation Energy of ZnO**
3.6B.7e) Optical Absorption Studies

The room temperature transmittance spectrum of ZnO thin films grown at various substrate temperatures is measured in the wavelength range of 350nm to 1000nm and is shown in Fig. 3.31. The interference phenomena between the wave fronts generated at interfaces (air and substrate) shows the excellent homogeneity and optically smooth surfaces at interface. These films exhibited good transparency in the visible and infrared region which is higher than 83% with a sharp fundamental absorption edge. It reveals that the increased crystallinity with increase in substrate temperature may affect transparency of thin films.

Figure 3.31: Transmittance spectra of the crystalline ZnO thin film

Figure 3.32: Variation of optical absorptions with wavelength
Figure 3.32 shows absorption spectra for the crystalline ZnO thin film, prepared at various substrate temperatures. The spectra reveal that the deposited film has low absorbance in the visible and near infrared regions while the absorbance is high in the UV region. It indicates that the absorbance is high for photons of energy greater than the band gap while beyond the gap edge the absorbance is very small and the transmittance is high. It shows that the films synthesized above 220°C are of low impurities and have few lattice defects. Also, the interference fringes pattern emphasizes the surface with large crystallite size.

**Fig. 3.33 Plot of \((\alpha h\nu)^2\) vs. \(h\nu\) for ZnO thin films**

The recorded optical absorption data was further used to evaluate the band gap energy. Figure 3.33 shows the variation of \((\alpha h\nu)^2\) with respect to incident photon energy \(h\nu\). The optical band gap of the films is determined by applying the Tauc model and the Davis and Mott model in the high absorbance region as calculated by equation (3.11). The band gap is thus determined by extrapolating a linear portion of the plot to the energy axis at \(h\nu = 0\). It shows red shift of band gap with increase in temperature. The change in band gap may be attributed to change in crystallinity. The similar behavior of band gap with increased crystallinity was also reported by [31].
3.6B.7f) Photoluminescence Spectra

The Photoluminescence measurements was carried out at room temperature with an excitation wavelength of 325 nm to examine the luminescence spectra of undoped ZnO thin film fabricated at various substrate temperatures. Its dependence on substrate temperatures is as shown in Fig. 3.34. It shows a strong peak at 375 nm (3.26 eV) which corresponds to the near band edge emission of ZnO. It is attributed to the near band edge emission from the recombination of free excitons through exciton-exciton collision process [32]. The broad and intense PL band is associated with the electron transition from the level of interstitial Zn to the valence band [32, 33]. It is also observed that the near band edge UV emission is enhanced at substrate temperature 220°C and on the other hand for lower and upper temperature it is suppressed. The narrower and higher energy near band edge emission UV peak indicate that the undoped ZnO thin films synthesized by spray CVD technique exhibits higher crystalline quality for substrate temperature.
220°C and the results are analogous with the results reported by XRD, FESEM, and AFM morphology. Similar behavior crystalline quality was also reported by Jun-Liang Zhao et al. [34]. In addition, a weak blue green emission peak is present at the wavelength 470nm. It corresponds to the electron transition from the level of interstitial Zn (Zni) to the Zinc vacancy (VZn).
Chapter Three  Experimental Techniques

References