CHAPTER 2

DEPOSITION METHODS AND CHARACTERIZATION TECHNIQUES

2.1 INTRODUCTION

The preparation methods of polycrystalline thin films may be divided into two types such as chemical and physical methods. In this chapter deposition and characterization techniques used for present investigation are discussed. Chemical bath deposition, photochemical deposition and Thermal evaporation methods were used to deposit the polycrystalline thin films for the present investigation. The characterization studies of the deposited materials are very important to understand the physical properties.

The X-ray diffraction studies were used to find the structural properties of the films. The optical properties of the films were analysed using UV-Visible spectrophotometer, Raman and Photoluminescence spectrometer. High Resolution Scanning Electron Microscopy (HRSEM) and Atomic force Microscopy (AFM) were employed to evaluate the surface nature of the grown films. The standard van der Pauw technique was used to measure the electrical properties such as electrical resistivity, carrier concentration, conductivity and Hall mobility of the deposited films. The thickness of the deposited films was measured with the help of stylus profilometer.
2.2 CHEMICAL METHODS

The chemical methods generally adopted for thin film deposition are given below:

(i) Chemical bath deposition
(ii) Photochemical deposition
(iii) Electrodeposition
(iv) Spin coating
(v) Spray pyrolysis
(vi) Chemical vapour deposition (CVD)
(vii) Metal organic chemical vapour deposition (MOCVD)
(viii) Plasma enhanced chemical vapour deposition (PECVD)

2.2.1 Chemical Bath Deposition

Chemical Bath Deposition is a convenient and low cost technique for producing large area thin film for semiconducting materials, used to deposit on the conducting and non-conducting substrates (insulators, semiconductors and metals). The chemical bath deposition method was used to deposit the polycrystalline semiconducting thin films of II-VI and IV-VI compounds etc. (Herrero et al 2000, Roberts and Baines 1958, Kale and Lokhande 2005, Weixin Zhang et al 2000 and Brajesh K. Rai et al 1997) for photovoltaic applications. The deposition by chemical bath method is frequently carried out in an aqueous solution containing specific chemicals and ions. The basic principles underlying the chemical bath deposition of semiconductor thin films have been presented in the review articles (Lokhande 1991 and Mane and Lokhande 2000).
In the chemical bath deposition process, the precipitation of compound semiconductor is controlled through the use of suitable complexing agents and the amount of ions. EDTA was used as a complexing agent for the release of metal ions, to control the release of sulphide, selenide ions in the bath during the thin film deposition (Lin Xu et al 2011). The deposition of the thin film takes place through the condensation of the metal and sulphide/selenide ions on this initial layer (Mane and Lokhande 2000). However, CBD technology has a lack mainly in aspects such as chemical kinetics and growth mechanisms, which have an important relevance in order to improve the quality of the materials and processes.

The experimental setup of presently used chemical bath deposition unit is shown in Figure 2.1. The experimental setup was established in our laboratory, for the present investigation, which consists of dimmerstat attached with temperature controller to maintain constant temperature, via temperature sensor. In this technique the substrate has been kept stationary and the solution has been stirred well with magnetic stirrer and the oil bath was used to heat the chemical bath to get a desired temperature. The process generally operates under ambient conditions and has the potential to replace expensive energy. In chemical bath deposition, the chalcogenide film forms when the substrate is immersed into the solution, generally alkaline solutions. The solution contains metal ions and an appropriate source of chalcogenide ions and complexing agent. The chalcogenide anion is usually generated by the decomposition or hydrolysis of an organic or inorganic precursor. The deposition of sulphide and selenide thin films was attempted using chemical bath deposition method on the glass substrates with dimension of 70 mm × 25 mm × 2 mm by the decomposition of sodium selenosulphate (for selenide), thiourea (for sulphide) in an alkaline media of aqueous solution.
2.2.1.1 Mechanism of CBD technique

The formation of the solid phase from the solution involves nucleation and particle growth. For any precipitate, there is some minimum number of the ions or molecules required to produce the stable phase in contact with a solution is called nucleus. The formation of nucleation is necessary for precipitate formation. The concept of nucleation in solution is that the clusters of molecules formed undergo rapid decomposition and particles combine to grow up to a certain thickness of the film. Depending upon the deposition conditions such as bath temperature, stirring rate, pH of
the solution, concentration etc. The film growth can take place by ion-by-ion condensation of materials by adsorption of colloidal particles from the solution on the substrate surface. In this chemical bath deposition the heterogeneous reaction occurs on the surface of the substrate and homogenous reaction is formed in the solution and also the materials deposit on the wall of the reaction vessel.

The soluble salt AB, when placed in water a saturated solution containing A and B ions in contact with undissolved solid AB is obtained and an equilibrium established between the solid phase and in the solution as

\[ AB(S) \rightleftharpoons A^+ + B^- \]  

(2.1)

Applying law of mass action, chemical reaction is directly proportional to the molecular concentrations of the reacting substances

\[ K = \frac{C_A^+ C_B^-}{C_{AB}} \]  

(2.2)

where \( C_A^+ \), \( C_B^- \) and \( C_{AB} \) are concentrations of \( A^+ \), \( B^- \) and AB in the solution respectively. The concentration of pure solid is a constant number i.e; \( C_{AB}(S) = a \text{ constant} = K' \)

\[ K = \frac{C_A^+ C_B^-}{K'} \quad \text{or} \quad KK' = C_A^+ C_B^- \]  

(2.3)

Since K and \( K' \) are constants, the products KK' is also constant, say \( K_S \) therefore Equation (2.1) becomes
The constant $K_S$ is called solubility product (SP) and $C_A^+C_B^-$ is called ionic product (IP). When the solution is saturated the ionic product is equal to the solubility product. When the ionic product exceeds the solubility product that is $IP/SP=S>1$ the solution is supersaturated (S degree of supersaturation) precipitation occurs and ions combine on the substrate and in the solution to form nuclei (Mane and Lokhande 2000).

For the deposition of CdSe thin film, sodium selenosulphate by hydrolysis in alkaline solution releases selenium ions. Sodium selenosulphate can be synthesized by dissolving selenium metal in the sodium sulphate solution, which can be used as a selenium ion source for CBD. In the present work, CdSe thin films were deposited on the glass substrates using chemical bath deposition technique involving the reaction of $Cd^{2+}$ with $Se^{2-}$ in the bath. In order to optimize conditions for deposition of CdSe films, the cadmium salt and sodium selenosulphate solutions were mixed in various ratios. Experiments were carried out with different compositions to get the good quality thin films. It is noted that the growth is highly dependent on temperature, pH and concentration of complexing agent. In this technique reaction kinetics, effects of various preparative parameters and the role of complexing agents are the very important parameters for the formation of films. The details of the synthesis procedure are mentioned in the respective chapters.

### 2.2.2 Photochemical Deposition

Over the last ten years, there has been a huge interest in the photochemical deposition of all types of materials on various substrates. The
photochemical deposition technique was invented by Goto et al (1997). Ichimura et al (1999) have deposited the semiconducting thin films for solar cell applications by photochemical method. The photographic view of photochemical deposition technique used for the present investigation is shown in Figure 2.2.

The experimental setup consists of super high pressure mercury lamp purchased from USHIO Company of Japan, 250W light about 100 mW/cm². A motorised magnetic stirrer was used to maintain the homogeneous mixture of the solution and also used spherical converging lens to focus the light at particular area. A diameter of the illuminated region was about ~1 cm. The detailed reaction kinetics on the deposition of thin films using PCD are explained in the fifth chapter.

The present investigation is made on the deposition of PbS semiconducting thin films by photochemical deposition techniques. The films were obtained by illumination of UV light in the depositing solution at a particular area on the substrate. The photochemical process involves the absorption of photons which generate the photoexcited electrons (e⁻). The photoexcited electrons may diffuse the metal ions and form the compound, followed by interfacial electron transfer to adsorbed acceptor molecules and ions. The sulphide compounds were deposited by various researchers using this technique as reported in the literature (Ichimura et al 1999, Gunasekaran et al 2003, Ichimura et al 2002, Ichimura et al 2004, Marandi et al 2005 and Podder et al 2005) and selenide based compounds were also deposited using this technique (Ichimura et al 2002a and Wen-Bo Zhao et al 2003). The ternary compounds were deposited using PCD (Moriya et al 2005 and Podder et al 2005a).
2.2.2.1 Process involved in PCD

Photochemical reaction takes place under the ultraviolet rays with $\lambda = 200\text{-}360$ nm. This technique uses photons from an ultraviolet or visible light source, which breaks the chemical bonds and induces the solubility and activation of molecules that lead to the rapid growth of thin films. The role of light is to produce more active sites on the surface of the solid specimen (for a heterogeneous system) during photoexcitation (Niyazi et al 2008, Mary D. Archer and Arthur J Nozik 2008). In photochemical process light is absorbed
and the photoexcited ions are adsorbed on the surface of the substrate, the following processes take place:

(i) The photochemical reaction occurs at surface of the substrate when light is absorbed by the reagent that leads to the generation of electrons (e\(^-\)) and holes (h\(^+\))

(ii) Adsorption of reagents on the sites of the substrate

(iii) Desorption of absorbed molecules to maintain the equilibrium constant (adsorption/desorption)

(iv) Photoexcitation of adsorbed molecules to form an excited state of electrons

(v) Chemical reactions regenerate the product

2.2.2.2 Mechanism of photochemical deposition

Let us consider a stable liquid mixture composed of two species A and B in solution. It is assumed that species A can be activated by light source at a suitable wavelength and that activated A (denoted A* in the following) reacts with species B to irreversibly generate the product C and the by-product D. This two step reaction scheme is illustrated as follows,

\[ A + h\nu \xrightleftharpoons[k_\uparrow]{k_\downarrow} A^* \]  \hspace{1cm} (2.5)

\[ A^* + v_B B \xrightarrow{k_{A^*B}} C + v_D D \]  \hspace{1cm} (2.6)

where k_\uparrow, k_\downarrow, k_{A^*B} are the different reaction rates, and v_B and v_D are stoichiometric coefficients.
2.2.3 Electrochemical Deposition

In electrochemical deposition, the 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. A number of metal and metal alloys, semiconductor systems have been successfully electroplated from aqueous solutions. By this technique, films can be deposited from very thin films to very thick coating (electroforming), which find widespread applications in industries (Milan Paunovic and Mordechay Schlesinger 2006).

2.2.4 Spin Coating

Spin coating is a technique used to deposit the thin films on the surface of the substrate. Spin coating is a procedure in which the centrifugal force is used to deposit the materials on the flat surface of the substrate. Spin coating involves spreading a liquid or a suspension dispensed onto the center of a rotating substrate. The liquid is dispensed by a pipette onto a substrate rotating at a constant angular speed. The spinning speed of the substrate is generally controlled to get a good quality thin film with the desired thickness. In this technique spin speed, spin time, surface tensions are the factors that affect the thickness of the spin coated film and it has some advantages to other dip coating technique. Another advantage of spin coating is the ability of the film to get progressively more uniform (Stanley Middleman 1998).

2.2.5 Spray Pyrolysis

Spray pyrolysis has been used to deposit semiconducting thin films and multilayered thin films can be easily prepared using this versatile technique. Spray pyrolysis is an extremely easy technique for preparing films
of any composition. Compared to other chemical techniques spray pyrolysis is one of the very simple and relatively cost effective processing method for thin film deposition.

Typical spray pyrolysis setup consists of a spray gun, precursor solution, substrate heater and temperature controller. In spray pyrolysis, the properties of the films depend upon the substrate temperature and precursor solution. Depending upon the application the nanocrystalline semiconducting thin films, metal oxides, ceramic, polymer thin films can be deposited using the spray gun (Bhavana Godbole et al 2009).

2.2.6 Chemical Vapour Deposition

During Chemical Vapour 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 (Hitchman and Jensen 1993 and Carlsson 1994). The most common CVD techniques used to deposit thin films are thermal CVD, low pressure CVD (LPCVD), plasma-enhanced CVD (PECVD), atomic layer deposition (ALD).

2.2.7 Metal Organic Chemical Vapour Deposition (MOCVD)

In MOCVD, epitaxial layer grows via the chemical reaction of the constituent chemical species at 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) (Yasuo Ohba et al 2007), solar cells (Hiroshi Uda et al 2003 and Sudharsanana and Rohatgi 1991) and LEDs (Cockyane and Wright 1984).

### 2.2.8 Plasma Enhanced Chemical Vapour Deposition (PECVD)

The plasma enhanced chemical vapour 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 vapour 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 Radio Frequency (RF) or Direct Current (DC) discharge between two electrodes, the space between which 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 (Sherman 1994).

### 2.3 PHYSICAL METHODS

The physical methods for thin film deposition are given below

(i) Thermal evaporation
(ii) Electron beam evaporation
(iii) Molecular Beam Epitaxy (MBE)
(iv) Pulsed Laser Deposition
(v) Sputtering
2.3.1 Thermal Evaporation

Thermal evaporation deals with the evaporation of the source materials in a vacuum chamber and condensing the evaporated particles on a substrate. This process is conventionally called vacuum deposition. A thermal evaporator uses an electric resistance heater to melt the material and raise its vapour pressure to a useful range. On heating the material in vacuum, sublimation takes place, the atoms are transported and get deposited on the cleaned substrates at desired temperature. During thermal evaporation, the substrate, crucible and source materials are placed inside the vacuum chamber at room temperature and also at different substrate temperatures to deposit thin films. This is done in a high vacuum, both to allow the vapour to reach the substrate without reacting in the chamber and reduce the incorporation of impurities. The schematic diagram of thermal evaporation unit is presented in Figure 2.3.

![Figure 2.3 Schematic diagram of thermal evaporation unit](image)
Thermal evaporation is the simplest way of depositing materials onto the substrate. Once the vacuum chamber gets stabilized at the appropriate pressure the heating source is used to heat the source material within the crucible to its vapour point. Upon evaporation, the material will re-deposit along the cooler surfaces of the vacuum chambers, as well as deposit on the surface of the substrate. The presently used experimental setup of Hind High Vac thermal evaporation coating unit, is shown in Figure 2.4. Thermal evaporation deposition process was widely used for the deposition of compound semiconducting materials (Barlow et al 1998 and Donald M. Mattox 1998).

Figure 2.4 Experimental setup of presently used thermal evaporation unit
In the present work the synthesized CdSe, PbSe and PbS were used to deposit thin films at a vacuum $10^{-5}$ Torr using Hind High Vac Coating unit at various substrate temperatures (RT, 150, 250, 350 and 450°C). The substrate heater was designed and fabricated with suitable substrate holder and placed horizontally inside the chamber. The distance between the substrate and source was optimized before deposition with many trail experiments to get good quality thin films and it is found to be 17 cm. The chamber was evacuated to $10^{-5}$ Torr using both rotary and diffusion pumps. The evaporant material in the pellet form is deposited using a molybdenum boat. The heater (molybdenum boat) which is connected to the evaporation source was switched on when the vacuum chamber attained $10^{-5}$ Torr. The low tension (LT) supply for evaporation source is obtained from a 230 V input transformer by means of parallel or series connections in the secondary side of the transformer. The molybdenum boat heats (200 amps) the source materials and the material got evaporated and deposited on the substrate.

### 2.3.1.1 Optimization

(i) Purity of the film depends on the purity of the source material and the quality of the vacuum.

(ii) Thickness of the film varies due to the geometry of the chamber.

(iii) Distance between the substrate and source materials should be varied

### 2.3.2 Electron Beam Evaporation

This is a typical physical process that is performed in a vacuum chamber. A high DC voltage is applied through the tungsten filament the stream of electrons excites the solid and turns it into vapor, which travels to
the substrate. As they reach the surface, they condense and form a thin film coating. This technique is based on the heat produced by the bombardment of high energy electron beam on the material to be deposited. The schematic of the electron beam evaporation is shown in Figure 2.5.

The electron beam is generated by an electron gun, which uses the thermionic emission of electrons produced by an incandescent filament (cathode). Emitted electrons are accelerated towards an anode by a high difference of potential (kilovolts). The crucible itself or a near perforated disc can act as the anode. A magnetic field is often applied to bend the electron trajectory, allowing the electron gun to be positioned below the evaporation line. As electrons can be focused, it is possible to obtain a much localized heating on the material to evaporate, with a high density of evaporation power. This allows controlling the evaporation rate from low to very high values and best of all, the chance of depositing materials with high melting point (W, Ta, C, etc.). Cooling the crucible avoids contamination problems from heating and degasification.

![Figure 2.5 Schematic of electron beam evaporation experimental setup](image-url)
2.3.3 Molecular Beam Epitaxy

Molecular Beam Epitaxy (MBE) is a new development in evaporation process and facilitates the deposition of high quality thin films by slow evaporation of material from Knudsen effusion cells; the deposition process is controlled very accurately by a computerized system (Vossen and Kern 1980). MBE is very expensive technique of depositing and is certainly not suitable for mass depositions. MBE is a single crystal film growth technique which provides thin films of extraordinary good quality. MBE essentially involves highly controlled evaporation of the source material in an ultra high vacuum (10^{-10} Torr) system. The reaction of one or more evaporated beams of atoms with the single crystalline substrates yields the desired epitaxial film. MBE has been employed to grow semiconducting thin films (Robin F. Farrow 1996).

2.3.4 Pulsed Laser Deposition

Pulsed Laser deposition (PLD) technique with many names was first used by Howard M. Smith and Turner in (1965) to deposit thin films in a vacuum chamber using a pulsed ruby laser. PLD is an improved thermal process used for the deposition of alloy thin films with a controlled chemical composition. During pulsed laser deposition, a laser beam is focused through a quartz window onto the surface of a target material. Laser power density is increased by a use of quartz lens. At sufficiently high flux densities and short pulse durations, the target material is rapidly heated to its evaporation temperature and forms a vapour plume. Unlike thermal evaporation, where the vapour composition is dependent on the vapour pressures of the elements within the source material, laser ablation produces a plume of material with similar stoichiometric to that of the target material. Once the vapour plume has been formed, it is collected onto a cooler substrate that promotes

2.3.5 Sputtering

The most basic and well known process is sputtering. The ejection of surface atoms from an electrode surface by momentum transfer from bombarding ions to surface atoms. Sputtered films are typically polycrystalline and form at low temperatures with good adhesion. Common types of sputtering are focused ion-beam, direct current (DC), RF and magnetron. During focused ion-beam sputtering, gallium ions are accelerated through a vacuum towards a sample surface. Acceleration and focusing capabilities are provided by a series of capacitive plates and magnetic coils, respectively. In comparison, during DC sputtering, the substrate and source (target) material are placed inside a vacuum chamber. 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 (Rossnagel 2002).

2.4 SYNTHESIS OF II-VI AND IV-VI COMPOUNDS - METHODS

II-VI and IV-VI compounds, which are more ionic compared to other compounds. Recently, there has been a great interest to synthesize
II-VI and IV-VI compounds by adding different complexing agents to get the nanoparticles through the chemical methods. Various techniques are used to synthesis the nanocrystalline materials via chemical route.

2.4.1 **Aqueous Solution Synthesis**

Aqueous solution synthesis is widely used for the preparation of oxide, sulphide, selenide and telluride nanostructure materials at low temperature. This method consists of heating an aqueous solution of metal salts at moderate temperatures below 100°C. Therefore, such technique is safe and eco-friendly because only water is used as solvent. This process avoids the safety hazards or organic solvents and does not require high-pressure containers. The morphology of the resulting nanostructures can be tuned by changing the parameters such as temperature, time, precursor concentrations and pH. In this technique doping is an important one, the chemical route method is a very simple to mix the precursors in an appropriate ratio. In addition of dopants the purity of the materials is substantially improved by adopting this simple chemical route method. Cadmium sulphide (CdS), Cadmium selenide and lead sulphide (PbS), lead selenide (PbSe) and copper selenide (CuSe) were synthesized. The residual salts are easily washed out by water due to their high solubility.

2.4.2 **Hydrothermal Method**

Hydrothermal synthesis is a subset of solvothermal synthesis which involves water at elevated conditions. The hydrothermal technology was used for the preparation of nanomaterials for various technological applications. The basic principle is that small crystals will homogeneously nucleate and grow from aqueous solution when subjected to high temperatures and pressures. One significant advantage of hydrothermal method is the relatively
low reaction temperature, which is typically less than 200°C. The chemical reactions taking place in a closed system in the presence of solvent, whether it is aqueous or non-aqueous.

The process of hydrothermal method can be divided into four steps, involving dissolution of growth species, diffusion through the solution, chemical reactions between different precursors and finally deposition of materials resulting in the formation of nanostructures (Byrappa 1991 and Vayssieres 2003). The major mechanism responsible for this method is dissolution-condensation growth. Compared to other methodologies, hydrothermal synthesis is an inexpensive, variety of nanostructures, such as metal oxides (Vayssieres 2003), sulphides (Byrappa and Masahiro Yoshimura 2001) etc., have been reported by this method. Different morphologies of nanostructures can be obtained by hydrothermal method using different procedures (Aleksandra B. Djurisic et al 2007).

2.4.3 Sonochemical Synthesis

The chemical effects of ultrasound arise from acoustic cavitations the formation, growth and implosive collapse of bubbles in liquid. This means that chemical reactions take place under more conventional conditions yield different products. The reason for this can be due to either physical or chemical effects. 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. In this the stresses induced in the liquid by passing of a sound wave through the liquid. Sound waves comprises of longitudinal waves that consists of compression and decompression cycles as they pass through the medium. These extreme
conditions attained during bubble collapse have been exploited to prepare nanoparticles (Arul Dhas and Gedanken 1998 and Li B et al 2001).

2.5 CHARACTERIZATION TECHNIQUES

In recent years, synthesis, deposition, characterization and application of the semiconductor nanocrystalline thin films have importance in the field of solar cells, IR detectors and optoelectronic devices. There are number of experimental techniques used to characterize the properties of the deposited materials such as structural (XRD), morphological (SEM and AFM), energy dispersive X-ray spectroscopy (EDX), optical (UV-Visible, photoluminescence and Raman) and Electrical (Hall Effect) measurements.

2.5.1 Structural Analysis

The analysis of crystal structure is of great importance in the description of materials; such an analysis is typically performed by employing X-ray diffraction techniques (Other techniques include electron diffraction method and neutron diffraction method). The basic information that can be obtained from such diffraction patterns is the $d_{hkl}$ spacing the crystal lattice type, lattice parameters and crystalline phases present in materials, the structural properties of these phases and atomic arrangements of crystalline materials. In general, two interacting waves interfere constructively if they are in phase, i.e., in step, whereas the waves interfere destructively, i.e., cancel each other out, if they are out of phase, this is called diffraction.

In XRD, the electron beam strikes a metal target and X-rays are generated. The X-rays is incident on a specimen in an angle $\theta$. If the specimen is crystalline and the distances between the atoms are of the same magnitude as the wavelength of the X-rays, diffraction will occur. The diffraction
condition is illustrated in Figure 2.6, which demonstrates that the path difference between X-ray waves, which are specularly reflected from two adjoining (parallel) planes, is $2d\sin\theta$. The intensity of diffracted X-rays is measured as a function of the diffraction angle $2\theta$ and the orientation of specimen. This diffraction pattern is used to determine the crystalline phases and structural properties of the specimen according to Bragg’s law.

$$2d\sin\theta = n\lambda$$  \hspace{1cm} (2.6)

where $n$ (called the order of the corresponding reflection) is an integer $\lambda$ is the wavelength of X-rays, $d$ is the atomic spacing and $\theta$ is characteristic angle (Richard Brundle 1992). If the wavelength is known (depends on the type of x-ray tube used) and the angle can be measured (with a camera or diffractometer), the interplanar distance can be calculated from the Bragg equation, so the reciprocal lattice of the crystal can be directly mapped (René Guinebretière 2007).

![Figure 2.6 The Bragg reflections from lattice plane separated by $d$ spacing](image)
2.5.2 Optical Characterization

2.5.2.1 Thickness Measurement

Thickness plays an important role in the properties of thin films. The results obtained can be reproduced only when the film thickness and the deposition parameters are kept constant. The film thickness was determined by employing weight gain method, optical interference technique and stylus profilometry.

The initial estimation of thickness was done using the conventional gravimetric method. In this method, the weight of the substrates before \( (W_1) \) and after deposition \( (W_2) \) was used to find out the weight of the film deposited \( (W_3) \) by the given relation \( W_3 = (W_2-W_1) \). Thus knowing the weight of the material coated on the area and the film density \( (\rho_d) \), the thickness \( (t) \) of the film can be obtained by the Equation 2.7.

\[
t = \frac{W_3}{A\rho_d}
\]  
(2.7)

The thickness of the layers deposited onto the glass plates was calculated from the optical interference maxima \( (\lambda_1, \lambda_2) \) appearing in the transmission spectra of the films and the refractive index \( (n) \) of the film material according to the formula Equation 2.8.

\[
t = \frac{\lambda_1\lambda_2}{2n(\lambda_1-\lambda_2)}
\]  
(2.8)

The optically and gravimetrically measured thickness was consequently verified by the stylus profilometry technique.
2.5.2.2 UV-Visible spectroscopy techniques

Ultraviolet-Visible (UV-Visible) absorption spectroscopy is the measurement of light when it is passed through the sample. The principle of UV-Visible spectroscopy is based on the ability of molecule to absorb ultraviolet and visible light. The absorption of light corresponds to the excitation of outer electrons in the molecule. The absorption can be measured at a single wavelength or on spectral extended range. Ultraviolet and visible spectroscopy are enough energetic to excite outer electrons to high energy level and it is very useful for quantity measurement. The Beer-Lambert Law is used to measure the absorbance at various wavelengths.

Absorption and transmittance spectra of deposited thin film samples were recorded using SHIMADZU UV-Visible spectrophotometer. The light generated from a Xenon flash lamp is passed through the monochromator which splits the beam into different wavelengths out of the continuous spectrum. The intensity ‘\(I_0\)’ measured by the fraction of beam using beam splitter. The transmitted intensity ‘\(I\)’ of the light beam is measured at photodetector and the absorbance is calculated by the following Equation 2.9. The schematic representation of the UV-Visible spectrophotometer is shown in Figure 2.7.

\[
A = \log \frac{I_0}{I} \tag{2.9}
\]
2.5.2.3 Photoluminescence

Photoluminescence (PL) is a commonly used characterization technique for materials analysis. In Photoluminescence, absorption of light results in a transition from the ground state to an excited state of an atom or molecule; then the system undergoes a non radiative internal relaxation and the excited electron moves to a more stable excited level; after a characteristic lifetime in the excited state, the electronic system will return to the ground state. The energy is released in the form of light and this emitted light is detected as photoluminescence. From the Photoluminescence spectrum, the spectral dependence of its intensity can provide information about the properties of the material, the time dependence of the emission can provide information about energy level coupling and lifetimes (Richard Brundle 1992). The presence of defects in the materials can also be estimated by the
PL emission involving defect level transitions, so the quality of materials can be determined.

2.5.2.4 Raman spectroscopy

Raman spectroscopy is based on the Raman effect, an inelastic scattering process that was discovered by the Indian physicist Raman in 1928. The basic principle of this technique is that a monochromatic beam of light is focused onto the sample and the energy shifted fraction of the scattered light is detected. Raman scattering is used to investigate the vibrational energy levels of molecules (Raman and Krishnan 1928). It can immediately provide useful information about the structure and identification of solid, liquid and gaseous substances. The technique is non-contact and non-destructive. Raman scattering is different from infrared absorption, these two techniques provide complementary information about the material.

In Raman scattering, a photon is scattered by the molecular system. Most photons are elastically scattered (Rayleigh scattering) and have the same wavelength as the absorbing photon. But in Raman scattering, the energies of the incident and scattered photons are different because the inelastic scattering of photons by molecules. The energy of the scattered radiation is less than the incident radiation for the Stokes line and for the anti-Stokes line. This increase or decrease in energy is related to the vibrational energy spacing in the ground electronic state of the molecule, so the wavelength of the Stokes and anti-Stokes lines are direct measurements of the vibrational energies of the molecule.

Since the Raman scattering is not very efficient, a high power excitation source is needed. Raman scattering combined with a conventional optical microscope opens up the possibility of Raman micro structural
investigations. The experimental setup used for the present investigation comprises a He-Ne excitation source at the wavelength of 632.8 nm and Argon 488 nm coupled with a Labram2HR800 micro Raman spectrometer. The incident laser was focused to a spot size of 2 µm and power of the laser was 2 mW with high stability confocal Microscope for Micro Raman 10X, 50X, 100X objective lens. The spectral resolution is of the order of 1 cm⁻¹ and it is shown in Figure 2.8.

![Figure 2.8 Raman spectrometer presently used for analysis at UGC-DAE CSR Indore](image)

**2.5.3 Surface Analysis**

Surface morphology is an important property, to understand growth surface of the deposited layers and surface roughness of the thin film. Scanning electron microscopy and atomic force microscopy studies clearly demonstrate an idea about the surface of the thin films.
2.5.3.1 Scanning Electron Microscope

Scanning Electron Microscopy (SEM) can provide a highly magnified image of the surface and the composition information of surface regions of the materials (Richard Brundle et al 1992). The resolution of scanning electron microscope can approach a few nanometers and the very high magnifications. In scanning electron microscope, electron beam is accelerated by an electron gun at low voltage of 1-20 kV and is scanned on the specimen surface. As the electron beam strikes the surface, a large number of signals are generated from the surface in the form of electrons or photons. These signals emitted from the specimen are collected by detectors to form images and the images are displayed on a cathode ray tube screen.

In scanning electron microscope one can get the three types of images such as, secondary electron images, backscattered electron images and elemental X-ray maps. Secondary electrons (SE) are considered to be the electrons resulted from inelastic scattering with atomic electrons and with the energy less than 50 eV; Backscattered electrons (BSE) are considered to be the electrons resulted from elastic scattering with the atomic nucleus and with the energy greater than 50 eV. The backscattering will likely occur in a material of higher atomic number, so the contrast caused by elemental differences can be built up (Richard Brundle et al 1992). After the primary electron beam collides with an atom in the specimen and ejects a core electron from the atom, the excited atom then decays to its ground state and emit either a characteristic X-ray photon or an Auger electron (Richard Brundle et al 1992). The schematic diagram of the scanning electron microscope is shown in Figure 2.9.

In this present study the HRSEM, FEI Quanta 200F model with a greater resolution, is used to observe and analyse surface of the films.
Energy Dispersive X-ray Spectroscopy (EDX) can provide information about element present in the materials. All elements in the periodic table above beryllium (Z = 4) can be detected by EDX and the practical minimum detection limit (MDL) for elements with atomic numbers greater than Z = 11 is about 0.1% weight.

In EDX, the electron beam incident on the specimen creates secondary electrons and leaves thousands of holes in the electron shells. Electrons from outer shells will drop into the inner shells and lose some energy in the form of X-rays at the same time (Figure 2.10). The X-rays emitted from the sample atoms are characteristic in energy and wavelength too, not only the element of the parent atom, but which shells lose electrons
and which shells replaced them. Essentially, each element has characteristic X-ray line(s), so the elemental composition of a sample can be identified by a non-destructive technique. EDX can also quantify the peak intensity of each element in the sample is compared to the peak intensity obtained from a reference standard measuring under same conditions (Richard Brundle et al 1992).

![Figure 2.10 Principle of energy dispersive X-ray spectroscopy](image)

2.5.3.3 Atomic Force Microscopy

The working principle of Atomic Force Microscope (AFM) is very simple. The atomic force microscopy was used to scan the surface of the sample using a cantilever with a sharp tip near the sample surface. The cantilever is typically silicon or silicon nitride with a tip radius of curvature of the order of nano meters. Atomic force microscope operates by measuring attractive or repulsive forces between a tip and the sample surface. In its contact mode (repulsive) atomic force microscope was used to measure the local sample height. In its non-contact mode (attractive) atomic force microscope derives topographic images; the tip does not touch the sample.
The tip is fixed at a constant distance from the surface. As the tip raster scans in two dimensions (XY), a piezo-electric sensor moves in the Z direction to maintain a constant deflection using a feedback loop. Depending on the difference in the deflection value, a voltage is applied to the piezo-electric sensor to move the sample up or down to maintain the constant deflection. The voltage applied to the piezo-electric sensor plotted against the tip movement gives the true height variations on the sample surface. This provides a three-dimensional image of the sample topography. The deflection of the tip is detected by a light sensitive detector sensing displacement of laser beam reflecting off the back of the cantilever. Various forces such as van der Waals, electrostatic, capillary, adhesive and double layer can act between the tip and the sample (Victor et al. 2010). The schematic diagram of the atomic force microscopy is shown in Figure 2.11.

![Schematic diagram of the atomic force microscopy](image)

**Figure 2.11** Schematic diagram of the atomic force microscopy
2.5.4 Electrical Properties

Electrical properties such as resistivity, carrier concentration and Hall mobility were estimated from Hall measurements in van der Pauw configuration at room temperature.

2.5.4.1 van der Pauw configuration

The van der Pauw method involves applying a current and measuring the voltage using four small contacts on the circumference of a flat, arbitrarily shaped sample of uniform thickness (van der Pauw 1958). This method is particularly useful for measuring very small samples because geometric spacing of the contacts is unimportant. Effect due to the size of a sample, which is the approximate probe spacing, is irrelevant. Using this method, the resistivity can be derived from a total of eight measurements that are made around the periphery of the sample with the configurations shown in Figure 2.12.

Figure 2.12 Symmetric contacts in van der Pauw configuration
The gold spring probes were placed at the corners of the sample symmetrically as shown in Figure 2.12. A constant current of 1µA and 1nA was supplied to the sample. The sample was subjected to uniform magnetic field of 0.57 Tesla. A known current was passed through the electrodes of the samples and voltage across the other two electrodes was measured. The polarity was reversed for each measurement and the voltage was measured. Once all the voltage measurements are taken, two values of resistivity, $\rho_A$ and $\rho_B$ are derived as follows,

\[
\rho_A = \frac{\pi}{\ln 2} f_A \frac{(V_1 - V_2 + V_3 - V_4)}{4I}
\]  \hspace{1cm} (2.10)

\[
\rho_B = \frac{\pi}{\ln 2} f_B \frac{(V_5 - V_6 + V_7 - V_8)}{4I}
\]  \hspace{1cm} (2.11)

where, $\rho_A$ and $\rho_B$ are resistivities in Ω-cm, $t_s$ is the sample thickness in µm, $V_1$-$V_8$ represents the voltages measured by the voltmeter, $I$ is the current passed through the sample in amperes, $f_A$ and $f_B$ are geometrical factors based on sample symmetry. Once $\rho_A$ and $\rho_B$ are known, the average resistivity ($\rho_{AVG}$) can be determined as follows:

\[
\rho_{AVG} = \frac{\rho_A + \rho_B}{2}
\]  \hspace{1cm} (2.12)

The Hall signal is measured between two ends while the current is passing through the other two ends. Hall mobility ($\mu$) is given by the ratio

\[
\mu = \frac{\Delta R}{BR_{sh}} \times 10^8
\]  \hspace{1cm} (2.13)
where, $\Delta R$ is the change in resistance due to magnetic field (B) which was applied to measure Hall voltages and $R_{sh}$ is sheet resistance of the material. Carrier concentration is determined using the relation

$$\rho = \frac{1}{en\mu}$$  \hspace{2cm} (2.14)

The Hall coefficient $R_H$ is given by,

$$R_H = \rho \times \mu$$  \hspace{2cm} (2.15)

The type of carriers can be understood from the sign of the $R_H$ and thus the type of conductivity can be identified. The negative value of $R_H$ corresponds to the flow of electrons (n-type) and positive value corresponds to the flow of holes (p-type) (Schroder Dieter 1998).

In the work ECOPIA Hall Effect measurement system was used to study the Electrical properties such as resistivity, carrier concentration and Hall mobility and conductivity of the deposited thin films. The experimental setup of Hall Effect is shown in Figure 2.13.

![Figure 2.13 Presently used Hall effect instrument experimental setup](image)