Chapter 2

Experimental Details

2.1 Spray pyrolysis experimental setup

Spray pyrolysis is a chemical method which is based on the Pyrolytic decomposition of the precursor spray solution on the hot substrate. It is a simple and inexpensive technique for the preparation of uniform coatings over large areas. The spray pyrolysis method has several advantages such as reproducibility, uniformity, deposition parameters such as spray rate, spray time and spray interval can be easily controlled. Doping can be conveniently done by simply dissolving the dopants in the spray solution in the required quantity. The spray pyrolysis method was first described by Chamberlin and Skarman in 1966 for preparing CdS and certain other sulfide and selenide films [1]. Spray pyrolysis involves a thermally stimulated chemical reaction between fine droplets of different chemical species. In this technique of film preparation, a solution (usually aqueous) containing soluble salts of the constituent atoms of the compound is sprayed onto a heated substrate in the form of fine droplets by a nozzle sprayer with help of a carrier gas. Upon reaching the hot surface, these droplets undergo pyrolytic decomposition to form a film on the substrate surface. The hot substrate provides the thermal energy for the decomposition and subsequent recombination. Repeated cycles of spray pyrolysis can produce films with desired thickness. Quality of the thin films deposited by spray pyrolysis method depends upon several deposition parameters such as the substrate temperature, distance between the spray nozzle and the substrate, spray angle, spray rate, spray time and spray interval.
A schematic diagram of the spray pyrolysis experimental setup [2] utilized for the deposition of thin films in our laboratory is shown in Fig. 2.1. The unit consists of a spray gun, hot plate connected to a temperature controller through a chromel-alumel thermocouple and a compressor. The spray gun is a coaxial assembly of Pyrex glass tube and a capillary tube having inner diameter of \( \sim 1 \text{ mm} \) and outer diameter of 6.5 mm respectively. It consists of inner capillary tube for the inlet of solution and outer tube for passing carrier gas. Corning glass was used as substrate and was placed on the hot plate. Substrate temperature was maintained constant with the help of temperature controller, which is connected through a chromel-alumel thermocouple fixed at the centre of the hotplate. Carrier gas flow through the spray gun was controlled by a regulator. Precursor spray solution was taken in a glass beaker and connected to the capillary tube of the spray gun. Pressure of carrier gas was maintained at \( \sim 6.5\times10^4 \) N/m\(^2\), spray time (3s) and spray interval (45s) were kept constant. Precursor solution was pulverized by means of carrier gas and the solution reaches the hot substrate, pyrolytic decomposition takes place and continuation of this process leads to formation of thin film. Finally the substrate heater was switched off and the films were allowed to reach room temperature naturally. The spray setup was placed in a closed chamber with exhaust fan arrangement.
2.2 Electron beam evaporation technique

Physical vapor deposition (PVD) involves the generation of a vapor flux and its subsequent condensation in the form of a thin film on a substrate in a vacuum chamber. The term PVD encompasses several techniques, including thermal, electron-beam evaporation, sputtering, and laser ablation. The major differences between all of these PVD techniques are in the way that the vapor flux is generated from a target made of a specific material. Heating of metals by bombardment with electrons in X-ray generators was known to scientists for quite some time, but it was first put to use for melting of refractory metals by M von pirani [3] in 1907. Electron-beam evaporation uses high-energy electron beams, typically accelerated with voltages from about 5 to 20 kV, to bombard the target material or materials that are placed in a crucible. Crucibles of copper have been widely used for many years, although crucibles of boron nitride, graphite, nickel, and tungsten are also used, depending on the target materials. This evaporation technique can vaporize most pure metals, including those with high melting points.

The basic principle of the electron beam evaporation technique is that a stream of electrons is accelerated through fields of typically 5–10 kV and focused onto the surface of the material for evaporation. The electrons lose their energy very rapidly upon striking the surface and the material is evaporated. That is, the surface is directly heated by impinging electrons. Direct heating allows the evaporation of materials from water-cooled crucibles. This allows the preparation of high-purity films because crucible materials or their reaction products are practically excluded from evaporation. Figure 2.2 shows a schematic diagram of the electron beam evaporation unit. The deposition chamber must be evacuated to a pressure of at least $7.5 \times 10^{-5}$ Torr to allow passage of electrons from the electron gun to the material to be evaporated. Electron beams are generated by thermionic emission, field electron emission, or the anodic arc method. The generated electron beam, accelerated to a high kinetic energy, is directed toward the evaporation material. Upon striking the evaporation material, the electrons will lose their energy very rapidly. The kinetic energy of the electrons is converted into other forms of energy through interactions with the evaporation material. The thermal energy produced heats up the evaporation material causing it to melt or sublimate. When temperature and vacuum levels are sufficiently high, vapor will result from the
melt or solid. The resulting vapour is deposited as thin film on the substrate. In our laboratory thin films were deposited by employing 12” Hind High Vacuum coating unit (model – 12A4D) fitted with electron beam power supply (model-EBG-PS-3K).

Fig. 2.2 Schematic diagram of electron beam evaporation experimental set-up

2.3 Thermal annealing in vacuum

Thin film prepared by electron beam evaporation method was annealed in vacuum to improve the structural, morphological, optical and electrical properties. The prepared films were placed on a substrate heater and desired vacuum (∼5 × 10⁻⁵ mbar) was achieved by means of rotary and diffusion pumps. The temperature of the substrate heater was controlled by a digital temperature controller connected through a thermocouple. The required temperature was set in the digital temperature controller. After reaching the desired temperature the films were allowed to anneal for the required time (30 min or 1h). The substrate heater was switched off immediately and allowed to cool to room temperature. The samples were removed from the vacuum chamber and used for further studies.

2.4 Reflux method

Reflux refers to an experimental method that involves heating a reaction mixture to the boiling point temperature of the reaction solvent and inducing the solvent to recondense back into the reaction flask using a condenser. Refluxing a reaction mixture is a simple and efficient way to maintain a constant reaction temperature. The advantage of this technique is that it can be left for a long period of time without the need to add more solvent or fear of the reaction vessel boiling dry as
any vapour is immediately condensed back into the reaction flask. In addition as a given solvent will always boil at a certain temperature, it is sure that the reaction will proceed at the same temperature and the temperature can be controlled by selecting a solvent of an appropriate boiling point. By using the simple reflux method copper selenide and copper bismuth sulfide powder was synthesised and used for the deposition of thin films by electron beam evaporation method. The experimental setup consists of a magnetic stirrer with hot plate, oil bath, round bottom flask and condenser. The reaction mixture is taken in the round bottom flask and is placed on the oil bath. The condenser is fitted to the round bottom flask. The reaction mixture is allowed to boil and refluxed for the required time. The product obtained was washed with double distilled water and ethanol for several times and dried in the oven.

2.5 X-ray diffraction

X-ray diffraction (XRD) study is noncontact and non-destructive characterization technique, which makes it ideal for in situ studies. X-ray Diffraction is a powerful technique used to uniquely identify the crystalline phases present in materials and to measure the structural properties such as preferred orientation of polycrystalline material, lattice parameters, crystallite size, defects, stresses, etc. In XRD, a collimated beam of X-rays, with a wavelength typically ranging from 0.7 to 2 Å, is incident on a specimen and is diffracted by the crystalline phases in the specimen according to Bragg’s law. Bragg’s law defines the conditions for obtaining X-ray diffraction from a crystalline material: $n\lambda = 2ds\sin\theta$ where $n$ is a small integer giving the order of diffraction analogous to a ruled grating; $\lambda$ is the wavelength of the characteristic line of X-ray from the X-ray tube and is usually the Cu $K_\alpha$ doublet with $Cu \; K_{\alpha} = 0.1540562 \; nm$; $d$ is the distance (nm) between a set of parallel lattice planes; and $\theta$ is the angle between the incident collimated X-ray beam and an atomic lattice plane in the crystal. The intensity of the diffracted X-rays are measured as a function of the diffraction angle $2\theta$ and the specimen’s orientation. This diffraction pattern is used to identify the specimen’s crystalline phases and to measure its structural properties.
The lattice spacing \( d \) of the prepared films was calculated from the Bragg’s equation

\[
d = \frac{n\lambda}{2 \sin \theta}
\]  

(2.1)

The crystallite size \( D \) of the deposited films was calculated using Scherrer’s relation [4]

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

(2.2)

Where, ‘\( K \)’ is the shape factor

‘\( \theta \)’ is the Bragg’s angle,

‘\( \lambda \)’ is the wavelength of X-rays used

‘\( \beta \)’ is the full width at half maximum of the respective XRD peak (in radian).

The dislocation density \( (\delta) \) was determined using the relation [5]

\[
\delta = \frac{n}{D^2}
\]  

(2.3)

where ‘\( n \)’ is a factor, which equals unity giving minimum dislocation density.

The microstrain \( (\varepsilon) \) was evaluated from

\[
\varepsilon = \frac{(\beta \cos \theta)}{4}
\]  

(2.4)

2.6 X-Ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is also known as electron spectroscopy for chemical analysis (ESCA). XPS was developed as a surface analysis technique to measure the elemental composition, chemical stoichiometry, chemical state and electronic state of the elements that exist in a material. Simple identification can be achieved by recording low resolution spectra, often called survey scans, over a broad binding energy range. All elements except hydrogen and helium can be identified and quantified. Beyond simple identification, acquisition of high resolution spectra in binding energy region of interest followed by peak fitting can provide information concerning the chemical (oxidation) state or environment for these atoms. XPS is based on the photoelectric effect in which the binding energy of a core level electron is overcome by the energy \( (h\nu) \) of an impinging soft X-ray photon and the core-level electron is excited and ejected from the analyte. The kinetic energies of the ejected photoelectrons are measured by an electron spectrometer and are plotted. Photoelectrons free of inelastic collision are only from the top of the material (1 to 10
nm). Thus XPS is a surface – sensitive method for chemical analysis. The surface of a sample is irradiated with photons of characteristic energy. These photons directly interact with core electrons of the sample atoms. As a result, ionized states are created and a photoelectron is emitted with a kinetic energy given approximately by the difference between the photon energy and the binding energy. The measured photoelectron spectrum is therefore a direct indication of the binding energies of the different atomic electron levels and is often directly calibrated in eV of binding energy.

The XPS instrument consists of a X-ray source, electron lens, hemispherical energy analyser, electron detector and system controller. X-ray photoelectron spectroscopy is performed in ultrahigh vacuum typically $10^{-9}-10^{-11}$ torr. The X-ray source used in XPS must produce beams energetic enough to overcome the binding energies of core electrons. Mg K\( \alpha \) and Al K\( \alpha \) are the most commonly used X-ray photon sources. X-rays generated from the X-ray source is incident on the sample. Photoelectrons are produced as the incident X-rays strike the sample surface. The photoelectrons are then directed into the energy analyzer through electron lens, where they are sorted according to their respective energies. The most common types of electron energy analyzers for XPS are the cylindrical mirror analyzer (CMA) and the concentric hemispherical analyzer (CHA). The number of electrons per energy interval is then transduced to a current by an electron detector. The photo current is subsequently converted and processed into a spectrum by electronics.

### 2.7 Scanning electron microscope

Scanning electron microscope (SEM) is one of the most versatile instruments available for the examination and analysis of microstructure morphology and chemical composition characterizations. This technique images and analyses a specimen by scanning an accelerated electron beam, followed by selectively collecting and recording secondary electrons, backscattered electrons, and other signals arising from the beam and specimen interactions. SEM permits the observation and characterization of materials at micro to nano – scale. The resolution of the SEM can approach a few nm and it can operate at magnifications that are easily adjusted from about 10x – 300,000x. Image formation in the SEM is dependent on the acquisition of signals (secondary electrons, backscattered electron, auger electrons, and characteristic X-rays) produced
from the electron beam and specimen interactions. When primary beam of electron strikes the sample surface causing the ionization of specimen atoms, loosely bound electrons may be emitted and these are referred to as secondary electrons. As they have low energy, typically an average of around 3-5 eV, they can only escape from a region within a few nanometers of the material surface. So secondary electrons accurately mark the position of the beam and give topographic information with good resolution. Secondary electrons are used principally for the visualization of surface texture and roughness. The topographical image is dependent on how many of the secondary electrons actually reach the detector. A secondary electron signal can resolve surface structures down to the order of 10 nm or better.

Scanning electron microscope consists of an electron gun, condenser lens, the objective lens and the scanning or deflection coils. The electron gun is on the top of the column, produces the electrons and accelerates them to an energy level of 0.1 – 30 keV. The diameter of electron beam produced by the electron gun is too large. So electromagnetic lenses and apertures are used to focus and define the electron beam and to form a small focused electron spot (1-100 nm) on the specimen. In order to form an image the probe spot must be moved from place to place by a scanning system. Scanning coils are used to deflect the electron beam so that it can scan on the specimen surface along x or y – axis. Complex interactions occur when the electron beam in an SEM impinges on the specimen surface and excites various signals from SEM observation. The magnitude of these signals was recorded with suitable detectors. The detected signal is also processed and projected on the CRT screen or camera.

2.8 Energy Dispersive X-ray Spectroscopy

The energy dispersive X-ray spectroscopy (EDS) is one of the powerful techniques to analyze the elements or chemical composition of the sample based on energies of X-rays emitted by the atoms of elements in the sample. It can be employed to detect elements with atomic number greater than carbon without any ambiguity. EDS systems are attachments to Electron Microscopy instruments (Scanning Electron Microscopy (SEM) or Transmission Electron Microscopy (TEM)) instruments where the imaging capability of the microscope identifies the specimen of interest. The data generated by EDX analysis consist of spectra showing peaks corresponding to the
elements making up the true composition of the sample being analysed. Elemental mapping of a sample and image analysis are also possible to analyze the elemental distribution in a sample surface.

The electron beam is projected onto the sample, followed by diversion of the characteristic X-rays toward Si detector, which is connected to preamplifier and linear amplifier then computer. When the electron beam impinges on the sample, the X-rays eject from the sample, which are diverted toward the detector in which the electron-hole pairs are created. Then they are converted into charge pulses having special amplitude and width by applying bias to the detector. Finally, the preamplifier converts charge or electric pulse into voltage pulse. The converted signals are further amplified by the linear amplifier and processed to the computer.

2.9 Elemental Mapping

An element map is an image depicts the spatial distribution of elements in a sample. One can use either an EDS or WDS system to produce an element map. X-ray intensities are measured while the beam is rastered over a specified area of the sample. The resulting image is a brightness intensity map showing points of high concentration, and low concentration of a specific element. SEM is paired with an EDS system to provide in situ elemental mapping during imaging.

2.10 Atomic Force Microscopy

The atomic force microscope (AFM) provides quantitative topographic images of surfaces. Also referred to as a surface force microscope or a scanning force microscope (SFM), it uses a sharp tip scanned over the specimen to sense surface forces. The cantilever of the AFM has a sharp, force – sensing tip at its end, and it interacts with the surface. As the interaction force between the cantilever tip and the surface varies, deflections are produced in the cantilever. These deflections may be measured, and used to compile a topographic image of the surface. The AFM is based upon force measurement, there is no longer any need for the sample to be an electrical conductor. This is the reason that AFM has attracted such widespread interest. The useful magnification range is from x 10^3 to greater than x 10^7. Atomic resolution, of the order of 0.1 – 0.2 nm, has been achieved on smooth surfaces.
**Contact mode**

In the contact-mode AFM, also known as repulsive mode, the tip is mechanically contacted with the sample surface at an applied force. This applied force can be evaluated from the force-distance curve, measured when the tip is brought to and then retracted from the sample surface. A soft cantilever (spring constant 0.01-1 N/m) is usually used in contact AFM. The cantilever is so soft that it can be pulled onto the surface due to high attractive force between them. After a mechanical contact between the tip and sample, there is a repulsive force between them. This repulsive force is usually used as the feedback parameter by maintaining a constant force through the adjustment of sample height while the tip is scanning the surface to obtain AFM images. In the most common scheme, a laser beam bounces off the back of the cantilever onto a position sensitive photodetector. As the cantilever bends, the position of the laser beam on the detector shifts. The position sensitive photodetector itself can measure displacements of light as small as 10 Å. The ratio of the path length between the cantilever and detector to the length of the cantilever itself produces a mechanical amplification. As a result, the system can detect sub-angstrom vertical movement of the cantilever tip. Once the AFM has detected the cantilever, it can generate the topographic data set.

**Non-contact mode**

In non-contact mode, the cantilever is vibrated near the surface of a sample. Spacing between the tip and the sample for non-contact AFM is of the order of tens to hundreds of angstrom. A non-contact mode is desirable because it provides a means for measuring sample topography with little or no contact between tip and sample. The system vibrates a stiff cantilever near its resonant frequency (100 – 400 kHz). The change in the resonant frequency or vibrational amplitude as the tip approached the sample is then detected. Since the force between the tip and sample in a non-contact AFM is low, it is more difficult to measure than the force in contact mode, which can be several orders of magnitude greater.

**Tapping mode**

Tapping mode is similar to non-contact mode except the vibrating cantilever tip is brought closer to the sample so that at the bottom of its travel it just touches the
sample. Tapping mode is less likely to damage the sample than contact mode because it eliminates lateral forces between the tip and the sample. Furthermore, in comparison with non-contact mode, tapping mode can image larger scan sizes that can include greater variations in sample topography.

### 2.11 UV-Vis spectrophotometer

In a double-beam instrument, the primary light beam is split and directed along two paths which traverse alternately the reference and measurement cuvette, which are approximately 10-15 cm apart. Thus, after both beams have been refocused, light of varying intensity falls onto the detector and generates an alternating – voltage signal. This principal forms the basis of recording spectrophotometers.

The experimental set up in principle is very simple. A high intensity lamp (deuterium or tungsten lamp) gives radiation from UV to NIR region. A monochromator (gratings or prisms) selects different wavelengths, which fall on the sample. Depending upon its properties, the sample reflects or absorbs certain wavelengths and transmits the rest. The transmitted (or reflected) intensity at different wavelengths are detected by a photodetector and given as an input to a recorder or computer. When the monochromator signals corresponding to selected wavelengths falling on the samples are the signals for X-axis and photodetector signal for Y-axis, gives the absorption plots.

**Optical absorption coefficient and energy band gap**

The optical absorption measurements are extremely important in evaluating the optical properties of the thin films. The dependence of absorption coefficient ($\alpha$) on the photon energy ($h\nu$) gives the information regarding the type of optical transition occurred between the valence band and conduction band of the sample. The optical absorption coefficient in the absorption region was determined using the relation [6]

$$\alpha = \frac{1}{t} \ln \frac{1}{T}$$

(2.5)
where the $T$ is the transmittance and $t$ is the thickness of the film. The energy absorbed by the sample for direct/indirect optical transitions from the incident photon energy ($h\nu$) is calculated using the relation [7,8]

$$\alpha h\nu = A(h\nu-E_g)^x$$  \hspace{1cm} (2.6)

where $A$ is a constant, $E_g$ is the energy gap, $h\nu$ is the incident photon energy and $x$ is a constant. The value of $x$ depends upon the type of transition that occurs between the parabolic band of the sample. The value of $x$ is 1/2 for direct allowed transition, 3/2 for direct forbidden transition, 2 for indirect allowed transition and 3 for indirect forbidden transition. The optical energy gap of the sample is determined by extrapolating the linear portion of the $(\alpha h\nu)$ versus $(h\nu)$ plot onto the energy axis.

### 2.12 Resistivity and Hall measurement

The van der Pauw method [9] involves applying a current and measuring voltage using four small contacts on the periphery of a flat, arbitrarily shaped sample of uniform thickness. This method is particularly useful for measuring very small samples because geometric spacing of the contacts is unimportant. Effects due to a sample’s size, which is the approximate probe spacing, are irrelevant.

![Fig.2.3 Van der Pauw Resistivity measurement.](image)

**Resistivity derivation**

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 Fig. 1.3. Once all the voltage measurements are taken, two values of resistivity, $\rho_A$ and $\rho_B$, are derived as follows:

$$\rho_A = \left[ \frac{\pi}{\ln 2} \times [f_A t] \times \frac{V_1 - V_2 + V_3 - V_4}{4I} \right]$$

$$\rho_B = \left[ \frac{\pi}{\ln 2} \times [f_B t] \times \frac{V_5 - V_6 + V_7 - V_8}{4I} \right]$$

(2.7)

(2.8)

where, $\rho_A$ and $\rho_B$ are volume resistivities (ohm-cm);
- $t$ is the sample thickness (cm);
- $V_1$ through $V_8$ represent the measured voltages;
- $I$ is the current through the sample (amperes);
- $f_A$ and $f_B$ are geometrical factors based on sample symmetry ($f_A = f_B = 1$ for perfect symmetry). The average resistivity ($\rho_{AVG}$) is simply $(\rho_A + \rho_B) / 2$.

**Hall Voltage Measurements**

Hall effect measurements are important to semiconductor material characterization, because from the Hall voltage the carrier density, mobility, and conductivity type can be derived [10]. With an applied magnetic field, the Hall voltage can be measured using the configurations shown in Fig. 1.4.

![Hall voltage measurement configuration](image)

**Fig. 2.4** Hall voltage measurement configuration.

**Procedure**

With a positive magnetic field of known flux $B$, applied to the sample, a current is sourced and voltages measured between the sample terminals as follows:

- Constant current is applied between terminals 1 and 3; voltage drop ($V_{24+}$) is measured between terminals 2 and 4.
- Reverse the current and measure the voltage drop ($V_{42-}$).
• Apply current between terminals 2 and 4; measure the voltage drop \((V_{13^+})\) between terminals 1 and 3.
• Reverse the current and measure voltage drop \((V_{31^+})\).
• Reverse the magnetic field, \(B\), and repeat the procedure, measuring the four voltage drops \((V_{24^-}), (V_{42^-}), (V_{13^-}),\) and \((V_{31^-})\).

**Calculations**

From the eight Hall voltage measurements, the average Hall coefficient can be calculated as follows:

\[
R_{HC} = \frac{t(V_{4^{-2^+}} - V_{2^{-4^+}} + V_{2^{-4^-}} - V_{4^{-2^-}})}{BI}
\]

(2.9)

\[
R_{HD} = \frac{t(V_{3^{-1^+}} - V_{1^{-3^+}} + V_{1^{-3^-}} - V_{1^{-3^-}})}{BI}
\]

(2.10)

where,

- \(R_{HC}\) and \(R_{HD}\) are Hall coefficients in \(\text{cm}^3/\text{C}\);
- \(t\) is the sample thickness in cm;
- \(V\) represents the voltages measured by the voltmeter;
- \(I\) is the current through the sample in amperes;
- \(B\) is the magnetic flux in \(\text{V} \cdot \text{S}/\text{cm}^2\) (1 \(\text{V} \cdot \text{S}/\text{cm}^2\) = 108 gauss)

Once \(R_{HC}\) and \(R_{HD}\) have been determined, the average Hall coefficient \((R_{HAVG})\) can be calculated as \((R_{HC} + R_{HD}) / 2\). From the resistivity \((\rho_{AVG})\) and Hall coefficient \((R_{HAVG})\), the mobility \((\mu_H)\) can be calculated:

\[
\mu_H = \frac{|R_{HAVG}|}{\rho_{AVG}}
\]

(2.11)

the carrier concentration \((n)\) in the sample can be calculated from the relation

\[
n = \frac{1}{\rho_{AVG} e \mu_H}
\]

(2.12)
References