CHAPTER II
DEPOSITION AND CHARACTERIZATION TECHNIQUES

2.1 Introduction:

The industrial importance of coatings and synthesis of new novel materials have given rise to remarkable increase of inventive thin film processes. Generally any thin film synthesis process follows two step mechanisms via: 1) the source material is converted into the micro level species (atomic or ionic) from solid or liquid, and 2) the atomic or ionic species are transported to the substrate and allowed to condense on the substrate surface in the form of solid film [1].

Depending on how the atomic or ionic level species are created for the condensation process, the deposition techniques are classed into, physical and chemical methods. Several physical and chemical thin film deposition techniques were employed such as pulsed laser deposition, Sputtering, Spray Pyrolysis, Inert Gas condensation, Chemical vapor deposition, Hydrothermal synthesis, Sol-gel technique, Wet-chemical Process, Chemical Bath Deposition [2-9 ].

2.2. Chemical Bath Deposition:

The technique of Chemical Bath Deposition is simple, very economic, less instrumentation, non-vacuum easy to operate and needs small space. It is suitable for any type of substrates [10]. It can be used for large area deposition with low wastage of chemicals. The thickness of the film can be controlled by pH, temperature and reagent
concentration. The first report of CBD was in 1884 [11] for the preparation of PbS. Today different types of chalcogenide (CdS, CdTe, MnS) and chalcopyrite materials (e.g. CulnS$_2$ and CulnSe$_2$) have been prepared using this method [12-16].

Several kinds of Chemical Bath Deposition (CBD) techniques are available today. In the present work very simple CBD equipment was employed and was presented in figure 2.1. It consists of a reaction bath is a beaker containing the solution of experimental reagents of the deposition. Previously cleaned glass substrates were immersed in vertical position in it. The reaction bath was kept in constant temperature bath. The temperature of the bath was controlled by temperature controller thermocouple. Temperature of chemical bath was constantly measures by thermometer externally. It is to be specifically noted that the deposition is usually processed at atmospheric pressure and at relatively low temperature.

2.2.1 Principle of CBD:

The principle of CBD is based on the principle of solubility product and ionic product. Therefore it is essential to brief knowledge of solubility and ionic product.

Solubility product

The solubility product is attributed mostly to sparingly soluble salts. It is defined as the solubility product of a sparingly soluble salt forming a saturated solution in water is given by the product of the concentrations of the ions raised to a power number ions occur in the
equation representing the dissociation of the solute [17]. The solubility product of general salt $A_x B_y$ was represented by the equation

$$A_x B_y = xA^{y+} + yB^{x-} \quad (2.1)$$

$$K_{sp} = [A^{y+}]^x [B^{x-}]^y \quad (2.2)$$

Where $x$ is the concentration of $Ay^+$ ions and $y$ is the concentration of $Bx^-$ ions.

The solubility product simply defined as the product of the equilibrium concentrations in Mol/Litre of its constituent ions in the saturated solutions at a given temperature, with concentration of its coefficient in the balanced equilibrium equation.

**Ionic Product**

The ionic product is represented in same way as solubility product before reach the condition of super saturation.

The chemical bath Deposition works on the principal that the product of concentration of the salt ions present in a solution (ionic product) exceeds the solubility product of the salt at a given temperature.

In this technique, super saturation is important in the reaction bath. At a given temperature when ionic product of reactants is greater than solubility product, precipitation occurs. If the ionic product is less than the solubility product, then the solid phase produced will dissolve back to the solution there is no any net precipitation.

This is the basic principle of any chemical deposition process. This deposition technique is mostly used for precipitation of metal
chalcogenide thin films. This will happen only if the ionic product of the impurity species is greater than its solubility product. However chances of this are rare, as the impurity concentrations will be usually less than 2% [18-19].

2.2.2. Process of thin film deposition:

There are three different possibilities for the process of thin film deposition in CBD technique.
1. Ion-by-ion process in which nucleation initiate and the ions condense on the substrate to form the film.

2. Cluster-by-cluster processes in which colloidal particles that are formed in the solution as a result of homogenous reaction gets adsorbed at the substrate surface. The interaction of both these processes leading to the formation of films.

3. Heterogeneous and homogeneous nucleation: Heterogeneous nucleation is a result of reaction occurring at the surface of the substrate while homogeneous nucleation is a result of reaction occurring within the bulk of the solution.

2.2.3. Mathematical model for Chemical Bath Deposition growth:

P. K. Nair et al. has put forth mathematical model of growing semiconductor in thin film form via chemical bath deposition [20]. Development of this model was based on the experimental growth curve of thin films of different materials grown in this method. The following are the general features occur in chemical bath deposition growth process as:

1: The nucleation or incubation period, in which the various chemical equilibrium are formed in the bath and an initial monolayer of the metal chalcogenides is formed on the substrate.

2: The initial monolayer of the metal chalcogenides formed on the substrate acts as a nucleation for the condensation of the metal ions and chalcogenides ions resulting in the film growth. This is known as growth phase.
3: The growth rate at a certain time depends on the bath parameters and finally reaches a terminal phase at which the film stops to grow.

4: A decrease in the time of the induction period with increase in temperature and in concentration of ions in the bath.

5: The suitable temperature-concentration combination to obtain maximum film thickness for a given time of deposition. In this method, the metal ions are complexes with legends and based on their instability constant they will gradually dissociate releasing free metal ions. This forms the main rate determining step. Thus the first order reaction rate kinetics is applied to the dynamics involved in chemical bath deposition process.

\[ \frac{dC}{dt} = -KC_t \]  \hspace{1cm} (2.3)

Where \( C_t \) is the unreacted metal ion concentration at time \( t \) resulting from an initial concentration \( C_i \).

\[ C_t = C_i \left( e^{-kt} \right) \]  \hspace{1cm} (2.4)

and \[ k = A e^{-Ea/RT} \]  \hspace{1cm} (2.5)

Where
1. \( A \) = Arrhenius constant.
2. \( Ea \) = activation energy.
3. \( R \) = gas constant
4. \( T \) = temperature.

The used up concentration \( C_{Ut} \) of the metal ions can be expressed with the help of Avrami equation
Depending on the theory developed with this idea and the concepts of geometric factor and induction factor, the growth curve for CdS thin film was obtained. They are found to be in good agreement with the experimental curve. The other important experimental observations that were reaffirmed through this model include,[21-24]

2.3 Characterization techniques:

There are several types of characterization techniques used for characterizing different types of thin films. These are film thickness, Absorption spectrophotometer (UV-VIS), X-Ray diffraction (XRD), Scanning electron Microscope (SEM)/EDAX and dc Electrical transport characterization.

2.3.1 Film Thickness Characterization:

Film thickness of the deposited thin films has been estimated by using simple weight and difference method. Initially weight of substrates was noted by using high precision analytical balance before deposition. Then weight of the substrate was noted after the film deposition. Difference of weight has been estimated. Using the relation given in equation (2.7) which was used in the previous work [25] thickness of deposited films was estimated:

\[ t = \frac{m}{A \rho} \]  

(2.7)

where:

\( m \) = mass of the deposited material on the substrate,  
\( A \) = area of the film and \( \rho \) is the density of the material in the bulk form.
2.3.2 Structural characterization:

X-ray diffraction is a capable technique commonly used for investigation of crystal structure, grain size and lattice constants. The structural characterization was carried out by recording the x-ray diffraction (XRD) of the samples. XRD data was obtained using miniflex-II x-ray diffractometer with Cu-K radiation (\(\lambda=1.5418\ \text{\AA}\)).

The analysis of diffraction of X-ray from atomic planes is useful for investigation of structure of chemical combination of the elements involved in specific symmetry. Compared with ordinary chemical analysis the X-ray diffraction method is very advantageous since it is usually much faster, requires only very small quantity of sample and is non-destructive [26-27].

The Bragg’s law is the basic principle used for structural analysis of the material. When plane monochromatic X-ray incident upon the atomic arrangement in the crystal lattice, each atom acts as a source of scattering.

The plans in the lattice are responsible for reflection of X-ray. At certain angles of diffraction the intensity will be higher if the path difference between two reflected waves is an integral multiple of \(\lambda\). The Bragg’s condition for reflection of X-ray from atomic planes is given by the relation 2.8,

\[
2d\sin \theta = n\lambda \quad (2.8)
\]
Where \( n \) is the order of diffraction, \( \lambda \) is the wavelength of the x-rays, \( d \) is the spacing between consecutive parallel planes and \( \theta \) is the Bragg’s angle \([28]\).

X-ray diffraction studies give detailed information about the crystal structure, orientation, average crystalline size and stress in the films.

Experimentally obtained diffraction data of the sample are compared with the standard powder diffraction (JCPDS) files published by the inorganic crystal structure database (ICSD) to investigate the type of structure. The grain size of the film can be calculated using the Scherer’s formula \((2.9)\) \([26]\),

\[
D = \frac{(0.94) \lambda}{\beta \cos \theta} \quad (2.9)
\]

where, \( \lambda \) is the wavelength of the x-ray and \( \beta \) is the full width at half maximum intensity in radians. In the estimation of crystalline size, the peaks become broader due to the effects of small crystallite sizes, and thus an analysis of the peak broadening can be used to determine the crystallite size in the nanoscale range. The lattice constants \( a \), \( b \) and \( c \) have been estimated by using relation \((2.10)\).

\[
\frac{1}{d} = \left[ \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) \right]^{\frac{l^2}{c^2}} \quad (2.10)
\]
2.3.3 Scanning Electron Microscopy (SEM):

The surface morphology of deposited samples has been investigated by using Scanning electron microscopy (SEM) technique. It involves interaction of electrons with electrons in atoms in the sample. In this technique the beam electrons can be focused on sample with micron size and micron sized areas has been analyzed. When an electron strikes the atom, different kinds of interaction taking place was shown in figure 2.2. A well-focused mono-energetic electron beam is incident on a sample giving various types of electron and photon signals.

1. Backscattered electrons
2. secondary electrons
3. Auger electrons or X-ray photons produced by primary electrons with sufficient energy.

Backscattered and secondary electrons are particularly involved in the SEM scan as their intensity variation dependence number of atoms in the sample. These electron interaction carries information about the sample. It reflects on the scan image of the sample [29].

2.3.4 Compositional analysis:

The composition of various elements in the deposited thin films was studied using the analysis technique like energy dispersive x-ray and inductively coupled plasma.
2.3.5 Energy Dispersive X-Ray (EDX) Analysis:

EDX (Energy Dispersive analysis by X-ray Measurement), have been used for compositional study. It is sometimes referred to as EDAX. It is a technique used for identifying the different kinds of elements in the composition of the specimen. The EDAX analysis is an integrated aspect of a scanning electron microscope (SEM), and cannot operate on its own without the latter [30-31].
The electrons are strike on the specimen in the SEM tube. The bombarding electrons collide with the sample atoms and characteristics X-ray are emitted. The atoms of particular element emit the X-ray of particular wavelength and energy. The emitted X-ray is then analyzed and the constituents in the sample are qualitatively investigated. Furthermore, the atom of every element releases x-rays of unique energy. Thus, by measuring the emitted x-ray energy, the identity of the atom from which the x-ray was emitted can be established.

The EDAX spectrum is a plot of intensity of x-ray v/s energy of the emitted x-ray. An EDAX spectrum normally displays peaks corresponding to the energy levels. Each peak corresponds to particular element in the sample. The intensity of the peak corresponds to the atomic percentage of the elements in the composition. Thus the composition of the sample and its atomic percentage of the particular element can be obtained from the EDAX spectrum.

2.3.6 Optical Absorption Studies:

Low absorption and higher transmittance exhibited by solar cell window layer materials that extend over wide range of electromagnetic spectrum is the main condition exhibit by window layer materials used in the fabrication of solar cell photovoltaic devices. Thus the characterization of the thin film using spectrophotometer is very important which helps to determine that whether material deposited in thin film form is useful for solar cell application.

UV- visible spectrophotometer is able to record the absorption spectra in the range of 190 nm and extending up to 1100nm. For getting
the radiations in the wide range of electromagnetic spectrum two sources of radiations have been employed in the spectrometer.

UV source (Deuterium lamp) and visible source (tungsten halogen lamp) are used. Deuterium lamp is used to emit radiations in the range of 190 to 326 nm wavelengths and tungsten halogen lamp is used to get the radiation in the range of 326 to 1100 nm wavelengths. Two sources together cover wide range of electromagnetic spectrum for 190 to 1100 nm.

Therefore UV-Visible Spectrophotometer (Systronic 2201) was employed for absorption study of deposited CdS and Cd1-xMnxS thin films as shown in figure 2.3. In the absorption process incident photon energy is divided in to three parts as: 1) reflected 2) transmitted 3) absorbed.

The absorption process in a material is considered to be due to 1) inner shell electrons 2) valence band electrons 3) free carriers including holes as well as electrons and 4) electrons bound to defects of some type. In case of semiconductors, the second type absorption of electrons is very useful. At absolute Zero of the temperature the valance band is completely filled and conduction band is completely empty and does not contribute conductivity.

When a photon of light is absorbed by the semiconductor able to excite the electron and transfer it form valance to conduction bands. The conservation of energy and momentum must be satisfied in optical absorption process. In the semiconductor thin film absorption is significant in ultraviolet region of the spectrum the absorption edge
shifted in low wavelength region. This leads to increase in optical band gap of semiconductor chalcogenised.

Basically there are two types of optical transitions direct and indirect can occur at the fundamental edge of the crystalline semiconductor. Both the transitions involve the interaction of an electromagnetic wave with an electron in the valence band. However, in indirect transition photon interacts with lattice vibration simultaneously. This causes the change in wave vector of the electron. The change momentum gives raise the phonon.

In the direct band gap semiconductor the transition of electron is vertical from the valence band to the conduction band and the momentum as well as energy of the electrons both are conserved as presented in figures 2.4.

Hence a wave vector k for electron remains unchanged in E-K space. Absorption coefficient $\alpha$ for direct transition is given by the relation (2.11) [32-33].

![Uv-Visible Spectrophotometer](Image)
\[ \alpha = \frac{A}{h\nu} \cdot (h\nu - E_g)^n \]  

\text{where}

1. \( E_g \) = optical band gap energy

2. \( h\nu \) = energy of incident,

3. \( n = 1/2 \) (allowed direct transitions)

4. \( n = 3/2 \) (forbidden transitions)

5. \( A \) = constant depending upon the transition probability for direct transition.

6. \( n = 2 \) (allowed indirect transition)

Thus if the plot of \((\alpha h\nu)^2\) against \(h\nu\) is linear then the transition is direct allowed. The band gap energy \( E_g \) is determined by extrapolating the linear portion of the curve to the energy axis at zero absorption that is at absorption edge.

The direct and indirect optical transitions was presented in Figure 2.4 (a, b) where interband transition takes place between different \( k \)-states. Since these must satisfy the momentum conservation laws.
The only way such a transition can take place is through emitting or absorbing of a phonon with wave vector q as;

\[ K' \pm q = k + K \]  \hspace{2cm} (2.12)

The transition defined by equation (2.12) is termed indirect transition. The indirect transition is represented as in equation (2.13).

\[ \alpha = \frac{A}{h\nu} (h\nu - E_g)^n \]  \hspace{2cm} (2.13)

Where,

\( E_g = E_{g'} \pm E_p \), \( E_g \) is indirect band gap energy and \( E_p \) is the phonon energy [34].
2.3.7 Electrical resistivity measurements:

Numerous investigations have been made on the electrical properties of thin film materials to understand the conduction phenomena [35-37]. Researchers were doing a systematic study on the effect of various parameters such as nature of substrate, substrate temperature, film thickness, doping and its concentration etc. [37-38] on the electrical properties of thin films. The contact methods are most widely used for the measurement of resistivity; there are two types of contact methods 1) two-point probe and 2) four point probe. The two-point probe method is simple, easy to use and useful for high resistive thin films.

High temperature dc electrical conductivity measurement was carried out by using two probes, electrical conductivity equipment. It is presented in figure 2.5. It consists of PID controller connected to the furnace. A sample holder and a dc power supply which is used to apply bias potential across the piece of sample. The current measurement was carried out at the interval of 10 °C by digital picoameter. All the accessories are purchased from scientific equipment, private LTD Roorki.

Initially the thin film sample is mounted on the sample holder consisting of two probes for making contact. In between the probes and sample a silver foil was used for better contact. The mounted substrate holder was kept in the furnace. The temperature of furnace was set by set knob on the PID controller up to 200 °C. After the temperature of the sample reached to 200 °C Set knobs is placed on wait. The current
due to charge carrier through the sample was measured at the interval of 10 °C decrease in temperature.

In this method, constant voltage ‘V’ is applied between two-fixed positions of probes separated by distance ‘l’ and current passing thorough a sample of known dimensions (cross section area A) is measured with an appropriate picoameter. For uniform sample the resistivity is given by,

$$\rho = \frac{A}{l} \times \left( \frac{V}{I} \right) = \frac{1}{\sigma} \quad (2.15)$$

where \( \sigma \) is the electrical conductivity of the film sample.

In case of semiconducting thin films, resistivity decreases with increase in temperature. The thermal activation energy ‘Ea’ are calculated by using resistivity equation (2.15) \[38-41\],

$$\rho = \rho_0 \exp \left( -\frac{Ea}{k.T} \right) \quad (2.15)$$

where, symbols have their usual meaning. The slope of log \( \rho \) vs (1000/T) is used to estimate the activation energy. The resistivity measurement of material gives information of room temperature resistivity, activation energy.

### 2.3.8 Thermoelectric power (TEP) measurements:

If metal electrodes placed in contact to the two ends of a semiconductor and if one junction is maintained at higher temperature than that of the other, an emf is induced between the two electrodes.
In a semiconductor, if the charge carriers are predominantly electrons, the cold junction becomes negatively charged and if the charge carriers are positive holes, the cold junction becomes positively charged. Thus from the sign of the thermoelectric voltage, it is possible to determine whether a given specimen exhibits n-type or p-type electrical conductivity.

The ratio of thermoelectric power to thermally generated voltage to the temperature difference across the piece of the semiconductor which gives the information about the type of carriers.

The Fig. 2.6 shows the experimental set up for thermoelectric power measurement. It consists of heating plate and arrangement made manually for cold end having a cavity inside.
The cotton wounded on the ice was kept in the cavity to provide the lower temperature of the cold junction. The film of size 10 Sq. mm. on glass substrates was used. Digital micro voltmeter (DMV 001) was used for TEP measurement. Commercial thermocouple was used for controlling the temperature of hot junction. Silver paste was used for making perfect holmic contacts [42-43].
REFERENCES:


