3.1 Introduction

In the modern technology, there has been a lot of interest in semiconductor materials, because their physical and chemical properties change rapidly with particle size. These materials are attracting considerable interest due to their fundamental electronic and optical properties. The chemical and physical photo-electrochemical properties of such materials are mainly depending upon methodology used for the preparation of the thin film. The characteristics of thin film materials are different from the bulk materials which specially depend upon the thickness. It is necessary to select the proper techniques for the deposition of semiconducting materials in thin film form. Similarly, it is seen that the photoelectronic and other properties of thin films of I-III-VI group of compounds, are highly structure sensitive which in turn severally influence the device performance. Therefore, it is essential to characterize the semiconductor material through its diverse properties prior to its use as a photoelectrode in the photoelectrochemical cells [1-5]. This chapter deals with experimental chemical bath deposition technique, various characterization techniques of the thin film material and photoelectrochemical cell properties.

3.2 The chemical bath deposition system

The chemical bath deposition (CBD) process uses a controlled chemical reaction to effect the deposition of a thin film by precipitation. In a typical experiment, substrates are immersed in an alkaline solution containing the chalcogenide source, and the metal ion. A chelating agent is also added to control the hydrolysis of the metal ion. The process is based on the slow release of chalcogenide ions into an alkaline solution in which the metal ions, in particular the free metal ion concentration, is controlled by the formation of complex species. The method is simple, economically viable and capable of generating alloys without use of
sophisticated instrumentation and process control. The technique has been used extensively to grow CuSe thin films. There exists a numerous literature [6]. Recently we have successfully used the modified CBD for deposition of CuSe, CuInSe$_2$ and In$_2$Se$_3$ [7, 8]. In the present work, a modified 35°c temperature CBD technique is adopted to synthesize CuInSe$_2$ thin films. A schematic diagram displaying the system constructed is shown in Fig. 3.1. The experimental setup consists of ice bath, reaction vessel, a substrate holder and motor.

3.2.1 A dust proof chamber

A plywood dust proof, clean chamber of the dimension 2.5 x 0.9 x 0.15 m was designed and fabricated. It provides the clean and contaminantless environment for the deposition of materials. Inside the chamber, hallow pipe outlet at the top of the chamber is fitted with an exhaust fan. This assembly helps to remove the gases evolved during the thin film deposition.

3.2.2 Ice Bath

A metallic container containing crushed ice was used as ice bath. The container was insulated with a thermocol in order to present the thermal loss to surrounding. A thermometer was used to measure the temperature of the bath.

3.2.3 Oil Bath

A metallic container containing paraffin oil was used as a bath. A thermometer was used to measure the temperature of the oil bath.

3.2.4 Reaction Vessel

A 100 ml capacity borosil make glass beaker was used as a reaction container. The beaker was fitted in ice bath by means of a suitable ring stand. Individual solutions were kept in ice bath to attain
uniform constant temperature \(5^\circ\text{C}\) and then mixed. After that, beaker was kept outside the ice bath to attain the room temperature \(27^\circ\text{C}\).

3.2.5 Substrate Holder

The glass and steel substrates were mounted on specially designed ‘substrate holder’ and are rotated with certain speed in the reaction bath at a suitable temperature. A substrate holder is a circular disc; made up of bakelite material having thickness around 10 mm and the diameter less than the diameter of beaker so that the substrates attached to the substrate holder can move freely in the reaction mixture present in a beaker. The disc has four slots to fix glass/steel substrates with the help of screw in such a fashion that each of the substrate was exactly at right angle to other as shown in Fig.3.2. A substrate holder was fitted to a synchronous universal motor so that the substrate can be rotated in reaction mixture. The desired speed was maintained with the help of a regulator. Thus, a continuous and proper bulk churning of the solution was made possible which helped in depositing uniform films with better orientation of the crystallites. The motor was kept mounted on a drilling machine stand. The stand was modified in such a way that height of the motor can be properly adjusted. In our experiments we adjusted the position of the motor so as to dip more than 80% portion of the substrates into the solution.
1. Reaction container
2. Substrate holder
3. Temperature controlling assembly with sensor indicator
4. Speed controller
5. Rotating motor

Fig. 3.1: Schematic diagram of chemical bath deposition system for thin film formation
Fig. 3.2: Cross-section view of thin film substrate holder
3.2.6 Substrate Cleaning

Substrate cleaning is important in getting the uniform and adherent deposits. Therefore cleaning of substrate surface is essential. All the glass substrates were boiled in concentrated chromic acid bath for about 30 min and then boiled and washed several times with double distilled water in order to remove the oxidized and adsorbed materials on the surface. The films were then degreased by washing with acetone followed by several washes using distilled water. They were further dipped in a detergent solution and washed with double distilled water. All the substrates were kept dipped in an air tight container containing double distilled water for long time before use [9]. The stainless steel substrates were first degreased with a detergent solution and then polished by using emery cloth and used. The cleaning of stainless steel plates was done just before deposition.

3.3 Synthesis of Thin Film Material

Many methods are in existence for the deposition of thin films. The choice of a particular method depends upon various factors such as material to be deposited, nature of the support material, required film thickness, structure and therefore the quality of thin film etc. Among the various methods, chemical bath deposition method is most widely used for deposition of I-VI, III-VI and pseudo-binary I-III-VI group compounds. The formation and properties of the film deposited are sensitive functions of the cleanliness of the substrate material.

3.3.1 Nature of Substrate

For depositing the films, amorphous glass micro slides of the size 75 x 25 x 2 mm (Golden Glass Industries Delhi – 95) and polished stainless steel strips of suitable thickness (1 mm) were used as a substrate. The film deposited on the amorphous glass substrates were used to study XRD, SEM, AFM, AAS, optical and electrical properties
of the films. The films deposited on stainless were used for photoelectrochemical study.

3.3.2 Preparation of the solutions

All the chemicals used for the depositions were of AR grade. All the solutions were prepared in double distilled water. The chemicals used were

i) Copper Sulphate, S.D. Fines Chemical Ltd., Boisar, Mumbai.

ii) Indium Trichloride, E – Merck Ltd., India.


iv) Potassium Hydroxide Flakes, Qualigens Fine Chemicals, Glaxo Ltd., India.


vii) Anhydrous Sodium Sulphite, Qualigens Fine Chemicals, Glaxo Ltd., India.


ix) Lithium Chloride S.D. Fine Chemical Ltd., Mumbai.

3.3.3 Sodium Selenosulphate Preparation

Sodium selenosulphate, a moderately stable source of selenium ion was prepared by refluxing grey selenium powder (5g) and anhydrous sodium sulphite (15g) in 200 ml distilled water on water bath for 9 hrs. At 90°C [10]. The resulting solution was filtered through filter paper and stored in an airtight container. The solution when kept in contact with air for long time, a red modification of selenium is precipitated. The molarity of the resulting solution is 0.25 m slight excess of the
sodium sulphite was added during preparation to prevent the possible oxidation of metal ions.

3.3.4 Deposition of the CuSe, In$_2$Se$_3$ and CuInSe$_2$ thin materials

Non conducting glass micro slides and stainless steel plates of desired dimensions were used for deposition of the samples. The experimental procedure for the deposition of thin film sample is described below.

The deposition of CuInSe$_2$ thin films were made from a reactive solution obtained by mixing 5ml (0.2M) copper sulphate, 5 ml (0.2M) indium trichloride, 2.5 ml (1M) tartaric acid, 10mL (2%) hydrazine hydrate and 20 ml (0.25M) sodium selenosulphate and finally diluted to 80 ml by adding double distilled water. The beaker containing the reactive solution was kept at the room temperature. The pH of the resulting solution was found to be 10.±0.05. Four cleaned glass substrates were positioned vertically on a specially designed substrate holder and rotated in a reactive solution with a speed of 50±2 rpm. The temperature of the solution was then allowed to rise slowly to 308 K. The substrates were subsequently removed from the beaker after 2 h of deposition. The films thus deposited were washed with distilled water, dried in air and preserved in the desiccator.

Lithium chloride was used as source of dopant in the CuInSe$_2$ thin films. The sample was deposited by following closely the above procedure. Lithium chloride in mol% was added directly into the reaction mixture. The conditions were the same as mentioned above.

The rate of deposition of CuSe films mainly depends upon supersaturation, pH, and temperature of bath and composition of the reactive species. Initially, at 278 K, reaction mixture can be prepared by mixing copper sulphate, ammonia and sodium selenosulphate. It was noted that a clear solution (i.e. homogeneous system) at 278 K is formed and no film or precipitate formation could be observed even though the
solution was kept for a long time. This is because the metal ions are in a stable complexed state $[\text{Cu (NH}_3\text{)}_4]^{2+}$ and ionic product of Cu$^{+2}$ and Se$^{-2}$ ions does not exceed the solubility product. The release of metal ions by the complexing species is the thermally activated process by means of which a soluble species of respective ions in reaction mixture can be generated [11]. The dissociation of sodium selenosulphate and complexed copper ion was achieved in an alkaline medium by increasing temperature. The increase in temperature results in dissociation of complexes as well as sodium selenosulphate thus, releasing Cu$^{+2}$ and Se$^{-2}$ ions which get incorporated as an alloy in the form of a thin film. The kinetics of growth of the film can be understood from the following reactions:

$$\text{Cu}^{+2} + 4\text{NH}_3 \rightarrow \text{Cu(NH}_3\text{)}_4^{+2}$$

$$\text{Na}_2\text{SeSO}_3 + 2\text{OH}^- \rightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} + \text{Se}^{-2}$$

$$\text{Cu (NH}_3\text{)}_4^{+2} + \text{Se}^{-2} \rightarrow \text{CuSe} + 4\text{NH}_3$$

All the films were homogeneous, well adherent to the substrate and found to be dark red in color.

The deposition of In$_2$Se$_3$ thin films was made in a reactive solution obtained by mixing 10 ml (0.2M) indium trichloride, 2.5 ml (1M) tartaric acid, 10 ml (10%) hydrazine hydrate and 15 ml (0.25M) sodium selenosulphate. The total volume of the reactive mixture was made unto 100 ml by adding double distilled water. The beaker containing the reactive solution was transferred to ice bath at 278 K temperature. The pH of the resulting solution was found to be 11.80±0.05. To obtain the film, four glass substrates were positioned vertically on a specially designed substrate holder and rotated in a reactive solution with a speed of 55±2 rpm. The temperature of the solution was then allowed to rise slowly to 293K. The substrates were subsequently removed from the beaker after 120 min (2h) of deposition. The films obtained were washed with distilled water, dried in air, kept in desiccator.
Chapter III

3.4 Various Characterisation Techniques of Thin Film Material

Thin films properties are mainly dependant on the preparatory technique. Therefore, it is necessary to characterize films before they are used in any device. In this section, various characterization techniques are described in brief.

3.4.1 Films Thickness Measurement

The thickness of a thin film is an important parameter since it determines the properties of the materials. The thickness of the film was measured by employing well known gravimetric method, called weight difference density consideration technique. The method is most convenient and is based on the measurement of the mass of material from known area of the film. By knowing density \( d \) in gram/cm\(^3\), mass \( m \) in gram of the sample from known area \( A \) of the film in cm\(^2\), the layer thickness \( t \) can be calculated by using the equation.

\[
t = \frac{m}{A \cdot d}.
\]

The density of CuSe, In\(_2\)Se\(_3\) and CuInSe\(_2\) were taken as 6.12 g/cm\(^3\), 8.15 g/cm\(^3\) and 5.75 g/cm\(^3\) respectively. In order to get accurate results, films having larger area were used. The weight of the film was determined by using electronic microbalance of accuracy of ± 0.1 mg.

3.4.2 X-ray Diffraction Properties (XRD)

The crystallographic analysis of the thin film samples were made by using x-ray diffraction technique. A Phillips PW-1710 x-ray diffractometer (XRD) with CuK\(\alpha1\) line (\(\lambda = 1.54056 \, \text{Å}\)) and CrK\(\alpha1\) (\(\lambda = 2.28960 \, \text{Å}\)) was used for this purpose. The range of \(2\theta\) was varied between 10\(^0\)-80\(^0\). The x-ray tube was operated at 20 kV, 20 mA with a scanning speed of 0.25 Sec. per step. For comparative purpose, the standard JCPDS data were also used. The indexing of spectra as well as lattice parameters of the samples was examined using the powdmult program.
3.4.3 Morphological Properties

a) Scanning Electron Microscopy (SEM)

The scanning electron microscopy is used to study the surface morphology of thin films. The surface morphology of the semiconductor electrode plays a vital role in the performance of PEC cell; therefore it was essential to analyze the surface morphology analysis. The surface of thin film samples was observed through scanning electron microscope (SEM), Stereoscan 250 MK-III (Cambridge Instrument Ltd. U.K.). The accelerating voltage was kept at 20 kV. The SEM micrographs of different samples were obtained at the same magnification so as to have comparative study.

b) Atomic Force Microscopy

Atomic Force Microscopy (AFM) is a form of scanning probe microscopy (SPM) where a small probe is scanned across the sample to obtain information about the sample’s surface. The information gathered from the probe’s interaction with the surface can be as simple as physical topography or as diverse as measurements of the material’s physical, magnetic, or chemical properties. These data are collected as the probe is scanned in a raster pattern across the sample to form a map of the measured property relative to the X-Y position. Thus, the AFM microscopic image shows the variation in the measured property, e.g. height or magnetic domains, over the area imaged (Fig 3.3).

The AFM probe has a very sharp tip, often less than 100 Å diameter, at the end of a small cantilever beam. The probe is attached to a piezoelectric scanner tube, which scans the probe across a selected area of the sample surface. Interatomic forces between the probe tip and the sample surface cause the cantilever to deflect as the sample’s surface topography (or other properties) changes. A laser light reflected from the back of the cantilever measures the deflection of the cantilever.
Fig. 3.3 Schematic of AFM

Fig 3.4. AFM Unit
This information is fed back to a computer, which generates a map of topography and or other properties of interest. Areas about 100 µm square to less than 100 nm square can be imaged.

(1) Contact Mode AFM
The AFM probe is scanned at a constant force between the probe and the sample surface to obtain a 3D topographical map. When the probe cantilever is deflected by topographical changes, the scanner adjusts the probe position to restore the original cantilever deflection. The scanner position information is used to create a topographical image. Lateral resolution of less than 1 nm and height resolution of less than 1 Å can be obtained.

(2) Intermittent - Contact (Tapping Mode) AFM
In this mode, the probe cantilever is oscillated at or near its resonant frequency. The oscillating probe tip is then scanned at a height where it barely touches or “taps” the sample surface. The system monitors the probe position and vibrational amplitude to obtain topographical and other property information. Accurate topographical information can be obtained even for very fragile surfaces. Optimum resolution is about 50 Å lateral and less than 1 Å height. Images for phase detection mode, magnetic domains, and local electric fields are also obtained in this mode.

In the present investigation AFM measurements were carried out using a scanning probe microscope (SPM-Solver P47, NT-MDT, Russia) in contact mode. Rectangular cantilevers of silicon nitride (length 200 µm and width 40 µm) having a force constant of 3N/m were employed for the measurement. Roughness of the films was obtained using the software provided with the AFM. The instrument is shown in Fig. 3.4.
3.4.4 Atomic Absorption Spectroscopy (AAS)

Atomic absorption spectroscopy (AAS) was used for compositional analysis of the thin film samples. The thin film material was dissolved in concentrated AR grade HNO$_3$. This solution was used for quantitative analysis by Perkin Elmer (USA) 3030 atomic absorption spectrometer following a standard method. The instrument was calibrated to zero absorbance for aqueous solution. The selenium is precipitated as free metal in acidic medium, [12] and hence determined gravimetrically. The results were confirmed by an energy dispersive X-ray spectroscopy using Kelvex (7000-77) spectrophotometer. All the samples were coated with gold in an automatic sputter-coating unit. The accelerating voltage was 20 kV.

3.4.5 Optical Absorption Measurement

The optical absorption measurements were made in the wavelength range 400-800 nm by using a Hitachi-330 (Japan), double beam spectrophotometer at room temperature. Placing an identical, uncoated glass substrate in the reference beam made a substrate absorption correction. The optical absorption was measured as a function of wavelength. The spectra were used to determine the absorption coefficient, energy band gap and the type of transition.

3.4.6 Electrical transport properties

a) Electrical Conductivity Measurements

To determine the dark ‘dc’ electric conductivity of the sample in 300-525 K temperature range, a two probe contact method was adopted in our laboratory, as shown in Fig 3.5. A regulate power supply (Aplab-make) was employed to pass the current through samples. The current flowing through the circuit was measured by sensitive nanometer. A
calibrated chromel alumel thermocouple (24 gauge size) was used to sense the working temperature as shown in Fig 3.6.

b) Thermoelectric Power Measurements

A thermoelectric power set up as shown in Fig. 3.7 was fabricated in our laboratory and used to measure thermoelectric power. The conditions under which thermoelectric power is measured are maximum temperature difference and minimum contact resistance as proposed by Bauerie et.al. [13-17]. Two brass plates of suitable size were used as a sample holder cum heater. They were grooved from the lower side to site the electric heater (75 watts). The size of the film sample used for studying TEP was 2.5 x 0.5 cm. A chromel-Alumel thermocouple was fitted at the centre of the block. Silver paste and silver strips were used for press contacts and ohmic contact purpose respectively. The whole assembly was housed in a Bakelite box to prevent any thermal loss. Thermovoltage was measured by a digital millivoltmeter. (Mero.Make), and differential voltage was measured by Aplab make millivoltmeter. A Schematic of electrical circuitry is shown in Fig. 3.8.
1: Electrical Heaters
2: Brass plates
3: Mica sheet
4: Thin film samples
5: Thermocouple
6: Asbestos Sheet
7: Shield

Fig.3.5: Design and Experimental setup for conductivity measurement
1: ‘dc’ power supply
2: Ammeter
3: Ohmic contact grid
4: Thin film
5: Silver paste
6: Heated surface (Brass plate)
7: Thermocouple
8: To potentiometer

Fig.3.6: Circuit diagram for thermal conductivity measurement
1: Electrical Heaters
2, 6: Brass plates
3: Mica sheet
4: Thin film sample
5: Differential Thermocouple
7: Asbestos Sheet
8: Shield

Fig. 3.7: Design and Experimental setup for Thermoelectric Power measurement
3.5 Photoelectrical Cell Properties

The numerous research papers report [18-23] on the photoelectrical (PEC) behavior of polycrystalline material, which include different deposition techniques, various substrates different surface treatments and electrolytes. There are few reports available on the film stability of the crystalline structure of CuSe, In$_2$Se$_3$ and CuInSe$_2$ [7, 8, 24]. The stability of films is an important parameter which requires detailed investigation.

3.5.1 Electrical Contact

The nature of contacts between a photoconductor and an electric contact was tested for both types of polarities. A better ohmic contact was needed for optimum device performance. In our case, the films were obtained on stainless steel / FTO coated films, and the nature of contact was evaluated from current-voltage measurements. A regulated dc power supply was used to provide a voltage across the contact and a current flowing through it was measured by a sensitive digital multimeter.

3.5.2 Design of Photoelectrochemical cell

PEC cell consists of H-shaped glass tube. One of the arms of the tube was made from hard glass having diameter of size 2.7 cm and length 7 cm. and other is ordinary test tube of inner diameter 1.5 cm. This H-shaped glass container was fitted in a copper pot. A window having the dimension of 2 cm. x 1.5 cm. was made available for irradiation of the photoelectrode. The cell can be represented as nCuInSe$_2$ / NaOH (1M)/C$_{\text{graphite}}$. Counter electrode was constructed by using a graphite rod sensitized in a medium containing concentrated CoS solution for 24 hours. A rubber cork was used to make the cell air tight and to support both the counter and photoelectrode. The active area of the size 1 X 1 cm$^2$ was exposed to light. The remaining part of the
film was masked by the use of common epoxy resin. The schematic diagram of the photoelectrochemical cell constructed and used in our laboratory is shown in Fig. 3.9.

Fig. 3.8: Circuit diagram for Thermoelectric Power measurement

1: Microvoltmeter  
2: Contact grid  
3: Silver paste contact  
4: Thin film sample  
5: Hot block of brass  
6: Cold block of brass  
7: Differential thermocouple  
8: To potentiometer
L: Light
A: Anode
P.E.: Photoelectrode
C.E.: Counter Electrode
S.E.: Standard Calomel Electrode
S: Stirrer
W: Water
H: ‘H’ shaped cell
E: Electrolyte

Fig. 3.9: A schematic diagram of Photoelectrochemical cell
3.5.3. **Electrical Properties of Photoelectrochemical Cell**

The electrical properties of PEC cell provide the information regarding the nature of the junction formed between photoelectrode and electrolyte and the charge transfer process across the electrode/electrolyte interface. The properties have been studied through the measurements of current-voltage characteristics in the dark, under illumination and power output curves.

Following electrical properties of PEC Cells are studied.

1) **Current Voltage Characteristics in dark and in light**

In PEC cell the current voltage characteristics, conventional two electrode cell geometry was used. The voltage applied to the junction was varied by a helical potentiometer (10 turn, 10 KW) and recorded with a digital voltmeter. A Hewlett Packard 6.5 digital multimeter was used to measure the current flowing at the junction. A schematic diagram of the circuit is shown in Fig. 3.10. A 500 W tungsten filament lamp was employed to illuminate the cell. To avoid the heating of the cell, a water filter was imposed between the cell and the lamp.

2) **Capacitance – Voltage Characteristics in dark**

To determine the C-V characteristics of PEC cell in dark, the capacitance voltage measurements in reverse biased condition were carried out using a three electrode configuration consisting photoelectrode, counter electrode and a saturated calomel electrode as a reference electrode. The potential across the junction (Vs. SCE) was varied by a helical, wire wound potentiometer and measured by an Alpha make capacitance meter at a super imposed frequency of 1 KHZ. A Schematic of electrical circuitry used is shown in Fig.3.11.
3) Barrier Height Determination

The barrier height for a cell configuration was determined by noting the temperature dependent reverse saturation current of the photoelectrochemical cell. The reverse saturation current was noted in the temperature range starting from 363 K to room temperature.

4) Power output Characteristics

The power output characteristics of the PEC cell have been obtained at a constant illumination of 30 mW/cm². To illuminate the cell, a 500 W tungsten filament lamp was used. Water filter was placed between the cell and the lamp to avoid the heating of the cell. The illumination intensity was measured on digital lux-meter (Meco-make).
Fig. 3.10: Circuit Diagram for measuring Current-Voltage of various PEC cell

1: Light Energy
2: Electrolyte
3: Photoelectrode
4: Potentiometer
5: Counter electrode
3.5.4 Optical Properties of the Photoelectrochemical Cell

a) Photo Response

The photo response of the PEC cell was obtained by measuring the short circuit current (Isc) and open circuit voltage (V_{oc}) at various illumination intensities. The illumination intensity was measured on digital lux-meter (Meco make).
b) Spectral Response

The spectral response of PEC cell was recorded by using a photo spectrometer. The range of wavelength used was from 400 nm to 900 nm. The short circuit current was recorded with a Hewlett – packard, 6.5 digit multimeter at different wavelengths.
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