CHAPTER – III

Experimentation and Preparation of Thin Films

3.1 Introduction

The thin film technology based on the II-VI group family of compound semiconductors, namely Cadmium telluride (CdTe), Zinc telluride (ZnTe) and Mercury telluride (HgTe) has been the focus of great interest for applications in optoelectronics including solar energy conversions [1-2]. The solar energy is converted into electrical energy by using solid state (photovoltaic) semiconductor device (solar cells). These solar cells are manufactured from highly pure and perfectly crystalline materials and the p-n junctions are obtained by using sophisticated technology. These requirements make the cell very costly, which does not permit their wide application in near-future energetic. During the last decade much work has been done on photo-electrochemical (PEC) system [3] in search of suitable liquid junction photovoltaic solar cells. One of the advantages is that the photo-electrochemical cell offers a good electrical contact for solar energy applications. That is formed as soon as the semiconductor electrode is immersed in the electrolyte. Another one is that, with a proper choice of redox couple in the electrolyte, the Fermi level in the electrolyte can be controlled and thus the barrier height can be adjusted to the desired level. A good contact formed at the electrode / electrolyte interface makes it feasible to use the cheap polycrystalline materials. Thus, photo electrochemical (PEC) solar cells can in principle be much cheaper than the traditional solid state cells. The future prospects of photo electrochemical solar energy conversion method depend on how completely its potential advantage can be realized in practice. Secondly, the photo electrochemical method is convenient in that one of its versions - photo electrolysis enables light energy to be directly converted into chemical energy of the photo electrochemical reaction products and thus
permits the energy storage problem to be solved along with proper energy conversion.

In recent years, thin film semiconducting materials have gained much importance in today’s technology because of their wide variety of applications in physical and chemical properties which changes rapidly with particle size. The thin films can be a single component or multi component, mixed, alloyed, multilayered on suitable substrate. The physical, chemical and photo electrochemical properties of such materials are mainly dependent upon methodology used for preparation of the thin film. Hence it is essential to evolve the proper technique to be adopted for the deposition and measurement of their parameters. The basic steps involved in the thin film deposition techniques are a) Creation of thin film material to be deposited in atomic, molecular, particulate or ionic form at specific rate. b) Transport of material that created towards the substrate. c) Deposition of film by nucleation and growth process.

The characteristics of thin film material are different from the bulk materials which specially depend upon thickness. Several techniques have been developed for deposition of the desired thin films [4, 6]. In this chapter, we summarize the experimental techniques used to prepare thin film materials, their characterization, fabrication of PEC cells and measurements of its various properties. This chapter also includes the essential theoretical background and details of the charge transfer involved in processes occurring in the photo-electrochemical cells.

3.2 Thin Film Technology

Thin film deposition techniques are mainly classified into two groups;

a) Chemical method

b) Physical method
Physical methods are further classified into vapor deposition and sputtering. While the various chemical deposition methods are spray pyrolysis, electrodeposition, screen painting, chemical vapor deposition, sol-gel, anodization, chemical bath deposition etc. Chemical deposition techniques are the most important tools for deposition of thin films owing to their versatility in depositing a large number of elements and components at various temperatures.

3.3 Requirements For Preparation of Thin Film

3.3.1 The Chemical Bath Deposition System

Chemical bath deposition method is also called as solution growth, controlled or arrested precipitation, electroless deposition technique etc. This method is economically feasible, very simple, convenient and capable of generating alloys without use of sophisticated instrumentation and process control [7-8]. A chemical bath deposition technique, used for deposition of most of the II-VI group metal chalcogenides and other semiconductor materials, is proved to be better than other costly methods [9-17].

The advantages of chemical bath deposition methods are as follows; [18-19]

1) This method is applicable for large area deposition.

2) This method is simple and does not require any sophisticated instrumentation.

3) Electrical conductivity of the substrate materials is not an important criterion.

4) In this method stoichiometry can be easily maintained

5) The deposition can takes place even at low temperature.

6) The intimate contact between substrate and reacting solution can
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gives pin hole free and uniform deposition.

7) The process is slow that provides better orientation of crystallites with improved grain structure.

8) It involves the use of dilute solutions of the basic ingredients which offers minimum toxicity and occupational hazards, since the vapour phase of the reactants are avoided.

In this present work a modified chemical bath deposition method is used for the formation of Zn$_{1.4}$Hg$_2$Te semiconducting thin film materials. A schematic diagram displaying the system constructed is shown in Fig. 3.1. The experimental set up consists of a dust proof chamber, thermostatic bath, a reaction vessel, a substrate holder, a motor and speed controller.

3.3.2 A Dust Proof Chamber

To obtain a film free from any contamination a deposition system is housed in a wooden dust proof chamber of the dimension 2.5 x 0.9 x 0.15m. It provides a clean environment for the deposition of materials. This chamber is equipped with a hollow pipe outlet at the top fitted with an exhaust fan to remove the gases evolved during the deposition.

3.3.3 Thermostatic Bath

A metallic container containing paraffin oil immersed with a glass coated heating coil which is specially designed for heating a thermostatic bath. The whole container was insulated with a thermocol from surrounding. A thermometer was used to measure the temperature of the paraffin oil bath.

3.3.4 A Reaction Vessel

A Borosil make glass beaker of 250 ml capacity was used as a reaction vessel. The beaker was fitted in a thermostatic bath. Individual solutions were first mixed at room temperature and then the reaction
mixture was allowed to heat with constant stirring up to desired temperature.

3.4. Design and Fabrication

A substrate holder is a Bakelite circular disc. The disc has four slots to fix glass/steel substrates with the help of screw in such a way that each of the substrate is exactly $90^\circ$ to the next as shown in Fig. 3.2

![Chemical Bath Deposition System](image)

1. Reaction container/Thermostatic bath
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: A thin film substrate holder

The thickness of the substrate holder is approximately 10 mm. The diameter of this circular disc is kept less than the diameter of the beaker, so that the substrate holder can move easily in the reaction bath. The glass/steel substrates were mounted on this specially designed “substrate holder” and are rotated with certain speed in the reaction bath at a suitable temperature. The desired speed was maintained with the help of a regulator. Thus the continuous and proper churning of the solution in the reactive bath was made possible which helps in the deposition of the uniform films with a better orientation of the crystallites. The motor holding the substrate holder was kept mounted on an adjustable drilling machine stand, so that the height of the substrate can be properly adjusted. About 80% of the portion of the substrates was kept dipped into reaction vessel.
3.5 Preparation of Thin Films

The formation and the properties of the film deposited are sensitive functions of the cleanliness of the substrate material, the purity of the basic ingredients, the various deposition conditions set and proper methodology adopted. The various processing used in our study for thin film deposition are discussed below.

3.5.1 The Substrates

The substrates used for depositing the films were amorphous glass micro slides of the size 75 x 25 x 2 mm (supplied by Blue Star Co. Mumbai) and polished good quality stainless steel strips of suitable thickness (2mm). The film deposited on the amorphous glass substrates were used to study properties of the films while the films deposited on stainless steel were used for photo electrochemical study.

3.5.2 Substrate Cleaning

The cleaning of substrate surface is very essential as cleaning plays very important role in getting the uniform and adherent thin film deposit. To remove all the oxidized and absorbed materials on the surface, the glass substrates were boiled in concentrated chromic acid bath for about 30-40 minutes and then washed with several times with double distilled water. All the substrates were kept dipped in an air tight container containing double distilled water for long time before use [20]. The stainless steel substrates were first degreased with a detergent solution and then polished using emery cloth and a polishing paper of zero number. The cleaning of stainless steel plates was done just before deposition.

3.5.3 Preparation of the Solution

The chemicals used were all of AR grade. All the solutions were prepared in double distilled water and kept in air tight borosil glass bottles. The different chemicals used were zinc nitrate (Zn(NO$_3$)$_2$, mercuric nitrate
Hg(NO₃)₂, Liquid ammonia, Tellurium powder (Te) and Anhydrous sodium sulphite (Na₂SO₃)

3.5.4 Preparation of Anionic Precursor

For deposition of zinc and mercury chalcogenides, a metastable source of Tellurium ion in -2 oxidation state was used. A sodium telluro sulphate (an anionic precursor) was prepared by dissolving 10 gm (excess) finely powered grey tellurium metal in 200 ml solution of sodium sulphite (0.25 M) solution by refluxing at 90°C temperature for 9 hours. The metastable sodium telluro sulphate was formed in hot condition only. Solution was then filtered through filter paper and stored in an air tight container. The tellurium metal gets added to sulphur of sodium sulphite to produce telluro sulphate. The normality of the resulting solution is 0.25 N. A little excess of the sodium sulphite taken during preparation helps to prevent the possible oxidation. In colder condition, atmospheric air oxidize tellurium ion to metallic tellurium as the reduction potential of Te is low (E_red = - 1.143 V), therefore anionic precursor solution was kept in an air tight container throughout at 318 K before use.

3.5.5 Preparation of Cationic Precursor

A cationic precursor solutions were prepared by mixing mercuric nitrate (0.25M, 10-x ml) zinc nitrate (0.25M, x ml) (where x varies 0 to 10 ml and represents compositional of parameters in Zn₁ₓHgₓTe) with complexing agent ammonia (25% v/v, 40 ml) with vigorous stirring.

3.5.6 Deposition of Zn₁ₓHgₓTe Thin film Materials

The deposition of Zn₁ₓHgₓTe (0.1 ≤ x ≥ 0.9) thin films have been achieved by decomposition of sodium telluro sulphate in an ammonical medium containing Zn²⁺ and Hg²⁺ ions from their respectively salts. A solution containing mixture of these salts allows the formation of thin films with alloyed or mixed compositions. A series of Zn₁ₓHgₓTe thin films with composition parameter x between 0 and 1 were obtained on glass and
stainless steel substrates. 10 ml of (0.25M) zinc nitrate /mercury nitrate or mixtures of both (as per composition parameter x) were taken in a 250 ml beaker. To this cationic precursor, 1 ml of hydrazine hydrate and about 40 ml of 25% NH₃ solution were added with stirring and the final volume was made to 180 ml by adding distilled water. The pH of the resulting reaction mixture was measured using pH-meter. This beaker was transferred to a bath whose initial temperature is 313K. The specially designed holder holding two cleaned glass slides were rotated vertically in the bath solution slowly (45±5 rpm). The temperature of bath was then increased gradually to 343K (within half hour). At this temperature, 10 ml anionic precursor (kept at 343K temp.) was gradually added at the junction of the wall of beaker and bath solution via an external syringe. After a deposition time of 180 minutes, the glass slides coated with films were removed from bath washed with hot distilled water and dried in dark desiccator under anhydrous calcium chloride [21-23].

3.6 The Thin Film Characterization

The properties of thin film material mainly depend on the techniques used for preparation of thin film. Therefore it is necessary to characterize it before its use in any device. In this section, various characterization techniques are discussed in brief.

3.6.1 X-ray diffraction

The crystalline nature and structure of all samples were examined by a x-ray diffraction technique. A Philips PW 1710, x-ray diffractometer (with Cu kα line, λ = 1.54056 Å) was used to study the crystallographic parameters. The range of 2θ angle variation was from 10° to 80°. The X-ray tube was operated at 20 kV, 20mA with a scanning speed of 0.25 sec per steps. The X-ray diffractograms were further analyzed to determine the crystal structure, lattice parameters, crystal orientation and particle (grain) size. The standard ASTM data were used for comparative purpose.
3.6.2 Thickness Measurement

The thickness of a thin film is an important parameter because most of the properties depend upon it. There are various methods to determine thickness of the thin film, the most appropriate and convenient method is gravimetric method, called weight difference density consideration technique. The method is based on the measurement of the mass of material from known area of the film. The layer thickness (t) can be calculated by using the equation, which is related to the mass (m) in grams, area ‘A’ of the film in cm² and Density ‘d’ in g/cm³ by,

\[ t = \frac{md}{A} \]  \hspace{1cm} ...(3.1)

The weight of the film was determined by using electronic microbalance of accuracy of ± 0.1 mg. The density of Zn₁₋ₓHgxTe thin films was calculated by considering actual proportion of the Zn and Hg in the films. In order to get accurate results the films having larger area were used.

3.6.3 Optical Absorption Measurements

The optical absorption spectra were used to evaluate the absorption co-efficient (\(\alpha\)), energy band gap (Eg) and the type of optical transition. The optical absorption measurements (OD) were measured as a function of wavelengths (\(\lambda\)). The optical absorption measurements were made in the wavelength range 350-2100 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.

3.6.4 Scanning Electron Microscopy (SEM)

As the surface morphology of the semiconductor electrode plays an important role in the performance of the Photo electrochemical cell, it is very essential to examine the surface structure. The surface morphology of
all thin film samples deposited on glass substrate were studied by a Scanning Electron Microscope (SEM). A stereoscan 250 M.K. (III) (Cambridge Instrument Ltd, U.K.) was used, the accelerating voltage was kept at 20 kV. The Au coating of thickness 100Å by an automatic sputtering unit was done before taking photograph. The SEM micrographs were obtained at the same magnification so that a comparative study can be made.

3.6.5 Electrical Transport Properties

The electrical transport properties play very important role in deciding the quality of a semiconductor devices. It involves measurements of electrical conductivity and thermoelectric properties. The nature of the conduction mechanism, activation energy of an electrical conduction, carrier density etc, were determined from these observations.

a) Electrical Conductivity Measurements

The dc electrical conductivity of the film samples were measured by employing a two probe method. A conductivity measurement set up has been designed and fabricated in our laboratory is shown in Fig. 3.3.a. In conductivity measurements set up, two brass plates grooved at a centre were sandwiched together with a strip heating elements (100 watt) by means of screws. The sample holder of dimensions 2.5 x 0.5 x 0.2 cm along with a film of size 2.0 x 0.5 cm and silver connector strip for electrical contact was fitted on upper brass plate at the centre by means of a screw (as shown). A mica sheet was used to insulate brass plate and the films. A cover was put on the assembly to prevent the thermal loss. A silver paint was applied to all the samples for ohmic contact purpose. A regulated dc power supply (Aplab make) was used to pass the current through the samples. The potential drop across the sample was measured by a digital multimeter (Meco-Model 9A) and a current flowing through a circular was measured by a sensitive nanometer. A calibrated Chromel-
Alumel thermocouple (24 gauge size) was used to sense the working temperature. The other end of couple was kept in ice bath. The range of working temperature was from 300K to 500K. A schematic of electrical conductivity circuit is shown in Fig 3.3 b.

b) Thermoelectric Power (TEP) Measurements

To measure thermoelectric power, a thermoelectric power set up was fabricated and is as shown in fig. 3.4 a. To fabricate the set up, two brass plates of suitable size were used as a sample holder cum heater. They were grooved from the lower side to fit the electric heaters (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. A silver strips and silver paste were used for press contacts and ohmic contact purpose respectively. Thermo-voltage was measured by a digital microvoltmeter (Meco make), mean temperature was recorded on digital milli volmeter (Meco make), and differential voltage was measured on Aplab make millivoltmeter. The conditions under which thermoelectric power is measured are maximum temperature difference and minimum contact resistance as proposed by Bauerie et al [24]. A schematic of electric circuit is shown in Fig. 3.4 b.

3.7 Construction and Characterization of Photoelectrochemical Cell

3.7.1 The Nature of Electrical Contacts

The nature of electrical contacts between a photoconductor and a substrate was tested for both types of polarities. A better ohmic contact was needed for optimum device performance. Here, the films were obtained on stainless strips 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 multi meter.
1: Electrical Heaters
2: Brass plates
3: Mica sheet
4: Thin film samples
5: Thermocouple
6: Asbestos Sheet
7: Shield

Fig.3.3 a) : 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.3.3 b) : 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.3.4 a) : Design and Experimental setup 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

Fig.3.4 b) : Circuit diagram for Thermoelectric Power Measurement
3.7.2 Construction of a Photoelectrochemical Cell

A photoelectrochemical cell was fabricated in our laboratory as shown in Fig. 3.5. and used to measure electrical and optical properties of thin film materials. It consists of H-shaped glass tube in which two test tubes are connected to each other by a small glass tubing horizontally. One of the glass test tubes was made from hard glass having diameter of size 2.7 cm and length 7 cm and the other is ordinary test tube of inner diameter 1.5 cm and length 7 cm. This ‘H’ shaped glass container was fitted in a copper pot of a suitable size. A window having the dimension of 2 cm x 1.5 cm was made available for illumination of the photoelectrode. The cell can be represented as;

\[ \text{n-ZnHgTe} \rightarrow \text{NaOH(1M)},0.1\text{M}, [\text{Fe(CN)}_6]^{3+},0.1\text{M} [\text{Fe(CN)}_6]^{4+} \text{ C}_{\text{(gasp)}} \]

Counter electrode can be constructed by using a graphite rod (C) sensitized in a medium containing concentrated CoS solution for 24 hours. The distance of 0.3 cm. was kept between a photodeffractode and a counter electrode. A rubber cork was used to air tighten the cell and to support both the counter electrode and photodeffractode. The active area of the size 1 x 1 cm² was exposed to light. The other part of the film was masked by using common epoxy resin.

3.7.3 Electrical Properties of Photoelectrochemical Cell

The electrical properties of a photoelectrochemical cell provide the information about the nature of the junction formed between photodeffractode and electrolyte and the charge transfer process across the electrode / electrolyte interface. These properties have been studied through the measurements of current-voltage characteristics in the dark, under illumination and power output curves.
a) The Current Voltage Characteristics in Dark and Light

A schematic of the cell geometry along with circuitry used is shown in Fig. 3.6 a. For the current-voltage characteristics, a conventional two electrode cell geometry was used. The applied voltage to the junction was varied by a helical potentiometer (10 turn, 1kΩ) and was recorded with a digital voltmeter. The current flowing through the junction was measured by a Hewlett-Packard, 6.5 digit multimeter. To illuminate the cell a 500 watt tungsten filament was employed. A water filter was imposed between the cell and the lamp to avoid the heating of cell.

b) Capacitance-voltage Characteristics in Dark

A schematic of electrical circuitry used in shown in Fig. 3.6 b. The capacitance-voltage measurements in reverse biased condition were carried out using a three electrode system consisting of 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 Aplab-make capacitance meter at a super imposed frequency of 1 kHz.
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.3.5: A schematic diagram of Photoelectrochemical cell
1: Light Energy
2: Electrolyte
3: Photoelectrode
4: Potentiometer
5: Counter electrode

Fig. 3.6 a) : Circuit Diagram for measuring Current-Voltage of various PEC cell
c) The Barrier Height Determination

A barrier height of a cell was determined by noting the temperature dependant reverse saturation current of a photoelectrochemical cell at different temperature starting from 363K to a room temperature.

d) Power Output Curves

The power output curve has been obtained for a given photoelectrochemical cell at a constant illumination of 30mW/cm². To irradiate the cell, a tungsten filament lamp (500 Watt) as light source was employed. A water filter was imposed between a lamp and a cell to avoid heating effect. The illumination intensity was measured on Meco make Digital Lux meter.
3.7.4 Optical properties of Photoelectrochemical Cell

i) Photo Response

The photo-responses of all the cell structures were obtained by measuring the short circuit \( (I_{sc}) \) and open circuit voltage \( (V_{oc}) \) at different illumination intensity. The illumination intensity was measured with a Meco make digital Lux meter.
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