

<u>CHAPTER-III</u>

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Deposition of Semiconducting Films and Their

Characterisation Suitable for Heterojunctions

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3.1 Introduction

Number of methods have been employed for the deposition of polycrystalline thin films. The choice of the deposition method depends on the film properties required, on the type of other device fabrication and processing technique employed. For convenience, the deposition methods can be divided into vacuum and non-vacuum methods. The non vacuum method includes spray pyrolysis, liquid-gas interface, chemical bath deposition, sintering, electrolyte deposition etc. Out of these, chemical bath deposition technique is relatively less expensive, simple and convenient, in which variety of substrates like metal, semiconductor and insulator can be used.¹⁻⁵ Film deposition by this method is a slow process which allows better crystallinity than other methods.

In this chapter experimental arrangement of chemical bath deposition technique, for the deposition of CdS and PbS films and fabrication of CdS/PbS heterojunction is described in detail.

3.2 Preparation of FTO

SnO₂ coated glass substrate with more than 80% transmission were prepared in our laboratory by spray pyrolysis technique. The details of the spray pyrolysis method is described else where⁶ and is beyond the scop of this thesis.

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100 ml 2<u>M</u>-SnCl₄ solution doped with 20 wt % fluorine was prepared in double distilled water. 5 ml of this solution was added to 20 ml isopropyl alcohol. The final solution was sprayed through a fine spray nozzle with a spray rate of 6 cm³/min. The temperature of deposition was 550° C.

3.3 <u>Controlled Precipitation Chemical Bath Deposition</u> Technique

The Fig. 3.1 shows the experimental set up necessary for the deposition of CdS-PbS films. Essentially, it consists of dust proof chamber, constant temperature unit, solution container and substrate holder.

3.3.1 Dust Proof Chamber :

In a view to obtain the films free from contamination by dust particles, a metallic dust proof and clean chamber of dimension (1.1 x 0.8 x 1) meter was designed and constructed. An outlet at the top of the chamber is fitted to an exhaust fan via a hallow pipe to remove the gases evolved during the film deposition.

3.3.2 Constant temperature unit :

Constant temperature unit is used to deposit the films at desired temperature. It consists of a cylindrical oil pot of 20 cms in height and 18 cms in diameter fitted in a sequare wooden box. The thermal losses from the pot are minimised by

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Fig. 3.1 - Photograph of controlled precipitation chemical bath deposition technique. 1) A.C. gear motor, 2) Substrate holder, 3) Reaction container, 4) Paraffin oil bath, 5) Electric heater. 6) Oil stirring (Remi) motor, 7) Thermometer, 8) Temperature controller, 9) Arrangement for thiourea addition, 10) Drilling machine stand and 11) Handle for fixing the position of A.C. gear motor.

insulating the pot. A 1000 watt electric heater was used to heat the parafin oil and a synchronors. Remi motor was used for continuouss stirring of the oil to maintain the uniform temperature of the oil bath. A relay circuit with a mercury contact thermometer (Jumbo, Germany Make) was employed to control the oil temperature within + 1°C.

3.3.3 <u>Solution Container</u> :

A 250 ml corning beaker in which appropriate amount of solutions of cadmium sulphate or lead acetate and ammonia were taken. The solution container was heated with a parafin oil bath. The desired quantity of thiourea solution was added within a predetermined time of deposition in the reaction mixture by specially designed and fabricated cylindrical corning glass tube.⁷

3.3.4 Substrate cleaning :

One of the most important precaution taken before the deposition of CdS film is the careful cleaning of the substrate as the sticking coefficient of the films to the substrate is a function of cleanliness of the substrate. Following was the procedure adopted for cleaning the substrates. The FTO glass substrates, (72 x 10 x 1) mm, were boiled in the chromic acid for 5 minutes and washed with double distilled water. Again they were dipped in "teepol", detergent solution and

washed several times with double distilled water and then with ultresonic cleaner. All the substrates were kept immerced in double distilled water before use.

3.3.5 Preparation of the solutions :

All the solutions were prepared in freshly prepared double distilled, deionized water. The chemicals used for the preparation of CdS films were listed below.

- i) A.R. grade cadmium sulphate supplied by Reanal, Budapest (Hungery)
- ii) G.R. grade thiourea supplied by Chemo=FineChemicals, Bombay (India)
- iii) G.R.grade Ammonia solution (about 25%)supplied by Sarabhai M.Chemicals (India)
- iv) L.R. grade. Lead Acetate supplied by Sarabhai M. Chemicals (India).

3.3.6 Deposition of CdS films :

20 ml l <u>M</u> Cadmium Sulphate solution was taken in a solution container (beaker of capacity 250 ml) and a sufficient amount of liquor ammonia (14 N) was added with continuous stirring till the just redissolution of complex compound [$Cd(OH)_2$] occured. The pH of the mixture was adjusted in between 10.5 to 11.0 The reaction mixture was immediately placed in an oil bath whose temperature was controlled to 90° C. The substrates attached to the substrate holder were kept rotating with a controlled speed of 75 r.p.m. in the reaction mixture. 1 <u>M</u> thiourea solution was added as described in (3.3.3). After half an hour, the substrates were removed and washed several times with double distilled water. These films were preserved in a dark desiccator and were used for further study.

3.3.7 Deposition of PbS Films :

The CdS films so deposited on the substrates were taken out of the reaction vessel, washed several times with double distilled water, dried and then heated in vacuum for one hour at 200° C in a furnace. Area was defined with a coal tar to avoid the shortening effect. Exactly similar procedure was adopted for the preparation of PbS films. CdS films deposited on FTO glass substrates have been used as a substrate for the deposition of PbS films. Initial ingradients used were Lead acetate and Thiourea. Deposition temperature was kept at 40° C. PbS films thus deposited on CdS were washed with double distilled water and dried. Electrical contact to PbS films was made with help of silver paste. The CdS-PbS heterojunction thus formed, was used for further study.

3.4 Post Preparative Treatment

Freshly prepared CdS films were annealed in Hindhivac vacuum pumping system (Model VS-4). The vacuum achieved was of the order of 10^{-3} torr with the help of Rotary pump. The films were annealed in vacuum at 220° C for one hour. These annealed films were preserved in a dark desiccator and were used for further study.

3.5 Characterisation of the Films

The photovoltaic properties of a PEC cell depends mainly on the properties of the photoelectrode. The change in the properties of photoelectrode changes the electrical and optical properties of a PEC cell. To obtain acceptable output power from PEC cell, it is necessary to characterise the photoelectrode in the thin film form. The experimental details of some of the properties of the photoelectrodes are described.

3.5.1 Microstructure :

The surface of the semiconductor photoelectrode has considerable influence on the characterisation of the

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solar cell. Microstructure study provides the information about the crystal structure of the material. The CdS thin films are used for microstructure study. The microstructure was observed for both as prepared and vacuum annealed CdS films with an optical microscope (Carl, Zeiss Leitz Microscope) with amplification 160 times to original one.

The crystal structure of as prepared and vacuum annealed CdS film is shown in fig. 3.2(a) and (b). From the micrographs, it can be observed that as prepared films are uniform and smooth; having relatively smaller grain size. Absence of white particles is observed on the surface of as prepared CdS film, whereas the microstructure of vacuum annealed CdS film show that surface of film is not smooth as compared to as prepared CdS film, white particles are also present on the surface of vacuum annealed CdS film.

3.5.2 Optical Absorption :

This study provides the information of the type of the transition and the band gap energy of the material.

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(ь)

Fig. 3.2 : Microstructure for,

- a) as prepared CdS and
- b) vacuum annealed GdS films.

The CdS thin films (having thickness 0.15 μ m were cut into size (2.5 x 1 cm) are used for the optical absorption study. The optical density (α t) was measured as a function of wavelength (λ) with a monochromator (Spectrometer, Hitachi 330) for both as prepared and vacuum annealed CdS films in the wavelength range 3500 A^o to 6600 A^o.

In an ideal semiconductor, at absolute zero temperature, the valence band would be completely full of electrons. Absorption of sufficient energetic guanta tends to transfer of electrons from valence band to conduction The transition of electrons from valence band to band. conduction band can be grouped into direct and indirect process. In direct transitions, the wave vector k, for electrons remains unchanged in the E-k space hence the momentum also does not change. While in indirect transitions, the wave vector k for electrons, changes in E-k space. Fig. 3.3(a) & (b) shows direct and indirect transitions between valence and conduction band. The forbidden gap Eg is found to be different for different semiconductors. For the same semiconductor Eg is found to change with temperature, pressure, impurity, magnetic and electric field.^{8,9} The band gap energy is also found to alter with the composition of alloyed semiconductor. 10,11

51 b



The optical absorption coefficient (α) is defined as relative decrease of the intensity per unit distance in the propogation direction of the light wave. This absorption coefficient is related to intensity of transmitted light by the Lambert's equation

$$I = I_{0} \exp(-\alpha d)$$
 ... (3.1)

where d is distance travelled by light wave to change its intensity from I₀ to I. The optical density for as prepared and vacuum annealed CdS film is recorded in the wavelength range 3500 A⁰ to 6600 A⁰. The variation of optical absorption coefficient α versus wavelength, λ (nm) is shown in fig. 3.4. At higher wavelengths there occurs steep fall, which corresponds to absorption in band gap region.

It is possible to differentiate direct and indirect transitions by the dependence of α on the photon energy h_{ν} . For direct transition the dependence of α on h_{ν} is given by¹¹

 $(n\alpha h\nu)\alpha (h\nu - Eg)^{1/2}$ for allowed transition

 $(n\alpha h\nu)\alpha (h\nu - Eg)^{3/2}$ for forbidden transition.

For indirect transition the dependence of α on $h\nu$ is given by¹¹.

(α)α	(hv	-	Eg) ²	for	allowed d	irect t	ransition		
(α)α	(hv	-	Eg) ³	for	forbidden	direct	transition	at	k=0



Fig.3.4 Plot of coefficient of absorption (\checkmark) versus wavelength (λ) for as prepared and vacuum annealed CdS film,

Hence plot of $(\alpha h\nu)^2$ as a function of $h\nu$ should give a straight line intercepting the energy axis at Eq. If transitions are direct and allowed. While $(\alpha h\nu)^{2/3}$ against $h\nu$ gives a straight line intercepting energy axis at Eg; if the transitions are direct and forbidden. Similarly plot of $(\alpha)^{1/2}$ against $h\nu$ should give st line intercepting energy axis at Eq for indirect transitions.

Fig. 3.5 shows the plots of $(\alpha h\nu)^2$ versus h ν for as prepared and vacuum annealed CdS films respectively. The linear nature of the plots supports the facts that the transitions are direct and allowed. Extrapolation of graph gives the band gap energies (Eg) as 2.24 eV and 2.32 eV for as prepared and vacuum annealed CdS films respectively.

The value of absorption coefficient (α) of these films is found to be of the order of 10^4 to 10^5 cm⁻¹ which is generally case for direct transitions. The films show higher absorption on shorter wavelength side and presence of absorption edge. It has been shown by many authors^{12,13} that absorption edge coefficient for the direct band gap semiconductors are generally large, of the order of 10^{+4} cm⁻¹.

3.5.3 Resistivity Measurements :

The resistivity of the as prepared and vacuum annealed films were measured with the help of experimental set up, schematic diagram of which is shown in fig. 3.6. The two



Fig. 3.5 Variation of $(\ll h\nu)^2$ as a function of $h\nu$ for as prepared and vacuum annealed CdS film.



brass plates of same size (10x5x0.5)cm are grewed at the center to fix the heating element (Toni 60 W). Two heating elements were fixed parallel in order to achieve the uniform temperature in we required area. The sample holder was at the top of the upper plate. The films of size 2.5x0.5 cm on FTO glass substrates were used. Press contacts were made to the films with copper strips. Silver paint was used to get good contact. The mica sheet was placed on the brass plate to avoid the contact between the film and plate. Thermal radiations are avoided by using the cover with asbestos sheet.

Temperature was measured with Chromel-Alumel thermocouple (24 gauge) which was fixed at the centre of the sample. The regulated power supply was used for passing the current through the films. The potential drop across the film was measured with the help of digital multimeter (Pla-DM-14-B) and current through the film was measured with Aplab FET nanoammeter (TFM-13). In the resistivity measurement with the resistance of as prepared and vacuum annealed films are measured at different temperature in range (323 K - 473 K).

The resistivity was measured as a function of temperature. The diagramic representation of log vith reciprocal of temperature is shown in the fig. 3.7 for as prepared and vacuum annealed CdS films. It is observed that the



resistivity decreases for vacuum annealed CdS film. Nature of the curve is linear and slope gives the activation energy. Activation energies for both samples, as prepared and vacuum annealed were calculated and it comes out to be 0.571 and 0.325 respectively. It is found that the activation energy of vacuum annealed CdS film is less than that of as prepared film. This may be due to removal of extended states, present in the forbidden gap of CdS film. The resistivity decreases with increase in temperature for both as prepared and vacuum annealed CdS films, indicating thereby the semiconducting nature of the films.

Vacuum annealed CdS film shows decrease in resistivity presumably owing to the effect of oxygen adsorption and desorption respectively which is a result similar to that reported by Chen-Lo-Wu and Richard H. Bube.¹⁴

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