CHAPTER-III

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CHEMICAL DEPOSITON PROCESS AND DEPOSITION OF CdS AND CdS:Sb THIN FILMS

3.1 Introduction.

The details of theoretical aspects and various processes involved in both thin films and electrochemical photovoltaic cells are described in Chapter-II. It is our prime aim to prepare an efficient material for the conversion of optical energy into an electrical, therefore development of an efficient experimental process for the preparation of the material is the need. Further characterisation of the material is also of the key importance. In this chapter a description is made of the design and fabrication of a chemical deposition system. (Section 3.2). The features by which the chemical deposition process overrides the other conventional deposition processes are outlined in section 3.3. The possible growth mechanism for the preparation of CdS thin films is given in section 3.4 whereas the exact preparation procedure both for CdS and CdS:Sb thin films is described in section 3.5.

3.2 Design, Fabrication, and Development of a Chemical Deposition System.

Being one of the pioneer workers of the Thin Film Research Laboratory, a gradual development of a chemical deposition process was undertaken in view to optimise the different parameters and mechanical adjustments. The photograph showing the minimum requirements of the experimental set up necessary for the deposition of CdS and CdS:Sb films is shown in fig.3.1.Essentilly it consists of a

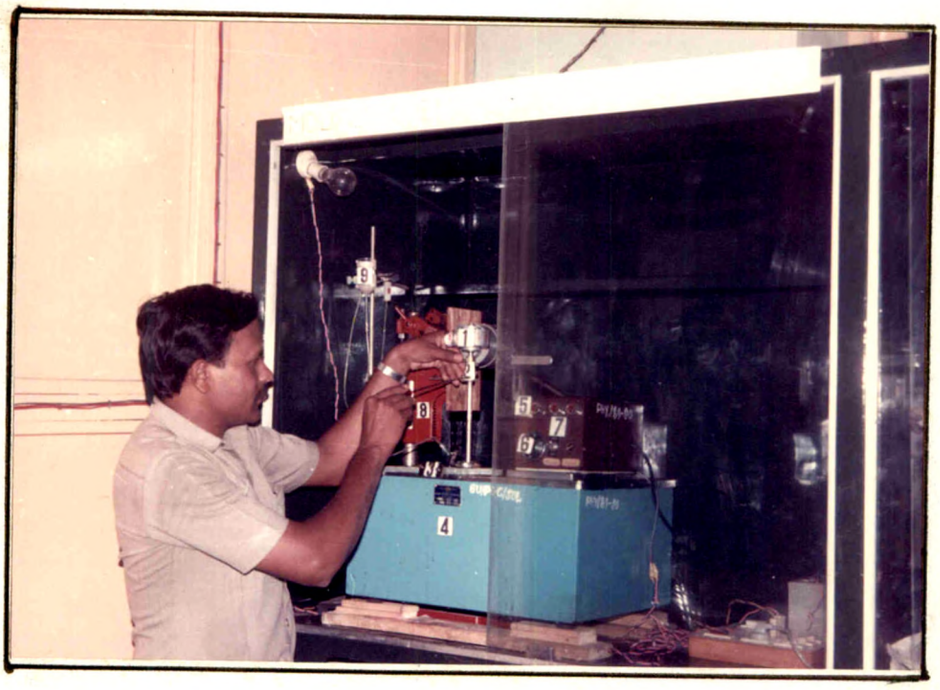

Fig.3.1 Photograph showing the essentials of Modified Chemical Deposition System.

1. Constant speed AC gear moter.
2. Substrate holder.
3. Reaction container.
4. Paraffin oil trough.
5. Electric heater.
6. Temperature controlling assembly with sensor.
7. Oil stirring moter.
8. Drilling machine stand, and
9. Thiourea addition.

dust proof chamber,an oil trough,and constant temperature assembly, reaction vessel and substrate holder.

3.2.1 Dust proof chamber :

A metallic dust proof, clean chamber of the dimensions 1.8 x 0.8 x 1 meter was designed and fabricated in order to avoid contamination of the samples by dust particles, humidity, natural gases etc. An outlet at the top of the chamber is fitted to a exhaust fan via a hollow pipe to remove the gases evolved during the film deposition.

3.2.2 An oil trough and constant temperature assembly:

A leak proof stainless steel oil trough of the dimensions 21 x 16 x 10 inch with 27 litre in capacity, supplied by Modern Industrial Corporation, Bombay, was used in order to achieve the required temperature. In order to minimise thermal losses from the trough, a glass wool was interposed between the inner stainless steel and outer metallic walls. A 2000 W electric heater was used to heat the parafin oil within an accuracy of $\pm$ 0.5° C. A synchronous universal motor was used for continuous churning of the oil to maintain the constant and uniform temperature throughout the oil trough.

3.2.3 Reaction Vessel :

It was a 250 ml borosil glass beaker to which appropriate amounts of solutions of codmium sulphate, and ammonia, were mixed. The mixture was heated to a suitable

temperature using an oil trough. The continous addition of thiourea was done by a specially fabricated cylindrical corning glass tube open at one end and at the other end a 0.1 cm capillary was sealed to which a medical saline controlling tube was attached. A required quantity of thiourea solution was added within a predetermined time of deposition. The whole assembly was fixed to a reaction vessel stand attached to an oil trough as shown in fig 3.2.

3.2.4 Substrate holder :

The chemically deposited CdS films in respect of their quality are dependent on the geometry of the substrate holder. Hence a substrate holder as shown in fig. 3.3 was designed and fabricated in our laboratory. It consists of a circular bakelite disc of 5 cm in diameter and 1.2 cm thick. The disc was slotted to fix the substrates in such a way that each slot is exactly perpendicular to the other (i.e. the slots were cut into the holder making 30°, 120°, 210° and 300° angles with respective diameters of the holder). As every substrate is perpendicular to the other, a proper and continuous bulk churning of the solution in reaction vessel, in all possible directions was made possible. The stem of the substrate holder can be fitted to a universal constant speed A.C. gear motor via a bushing arrangement fabricated in our laboratory. The motor was permanently fitted to a drilling machine stand. The drilling machine stand was modified in such a fashion that we can adjust any constant position of the motor. For the

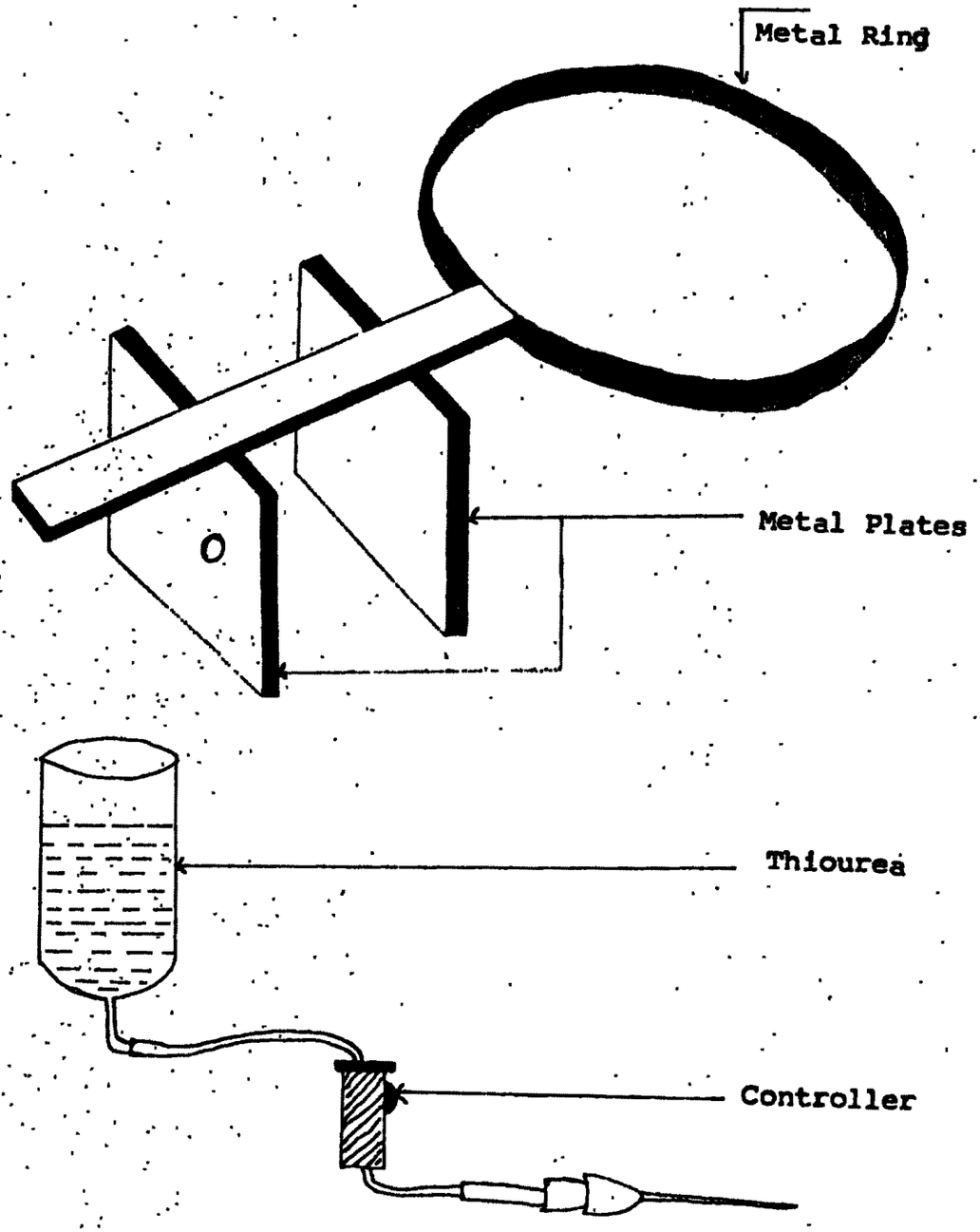

Fig.3.2 Arrangements for addition of thiourea and position of reaction container.

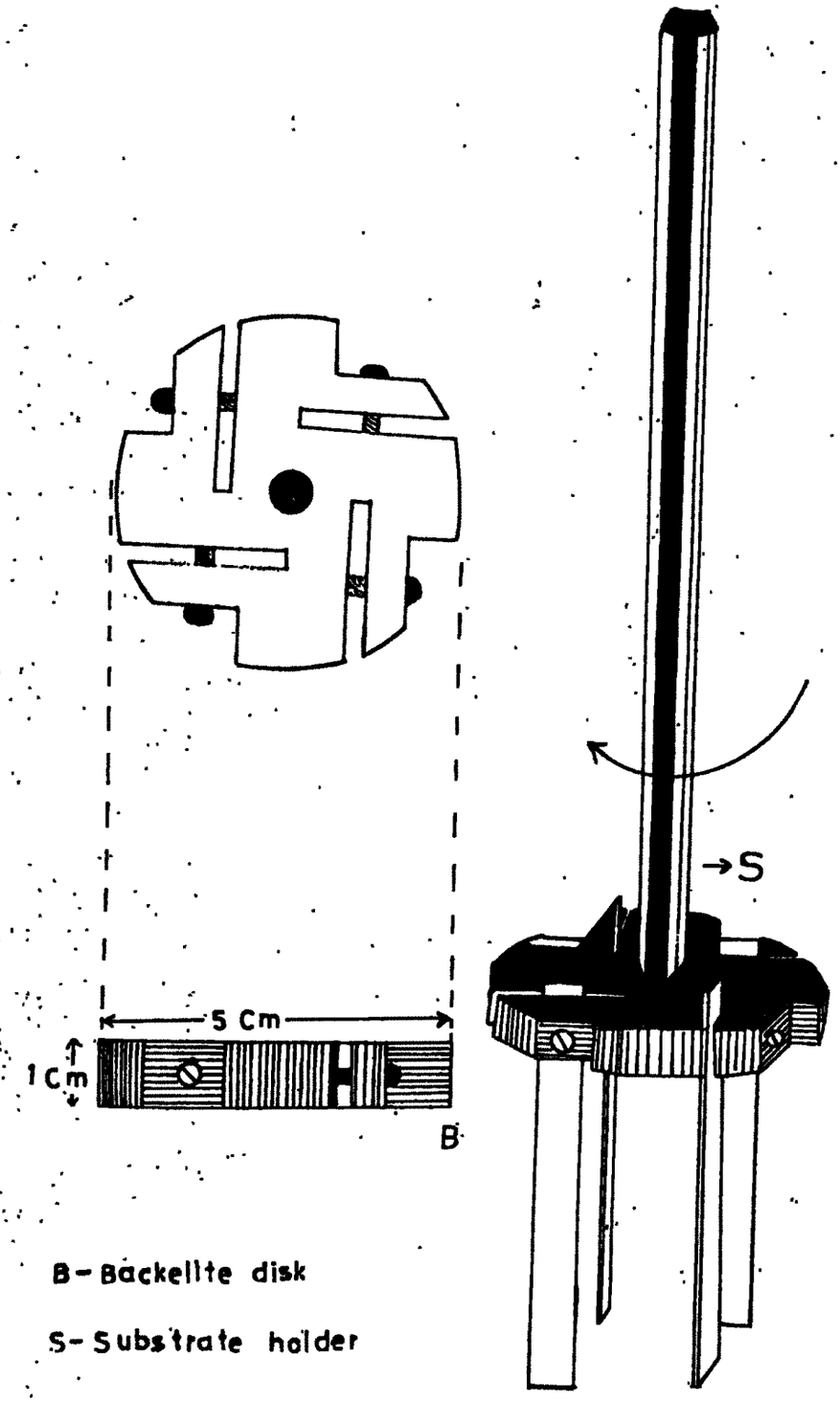

Fig-3-3 Design of the substrate holder

experimental purpose we adjusted the position of the motor so as to dip more than 2/3 portion of the substrates into the reaction vessel. The care was taken from touching any of the substrates to the walls of the reaction container which may cause serious damages of scratches to the samples and breaking of the reaction container.

3.3 Advantagaes of a Chemical Deposition Process.

A discussion in brief is made of the design and fabrication considerations of a chemical deposition process and is given section 3.2. In this article the superiority of chemical deposition process is discussed. [43, 46].

i) The method does not require sophisticated instrumentation like vaccum system and other expensive equipments. It can be carried out in a glass beaker only. An oil bath and stirrer are the equipments needed and hence power consumption is also negligible. Further it is cheap due to very small quantity of the active materials.

ii) The method is ideally suited for large area deposition it can be done by using large volume vessels.

iii) A large number of substrates can be coated in a single run with a proper design. The design includes only positioning of the substrates along the wall of the reaction container.

iv) Electrical conductivity of the substrates is not a hard and fast requirement. Hence any insoluble surface

to which the solution has free access will be suitable substrate for deposition.

v) The deposition is at low temerature and avoids oxidation or corrosion of the metallic substrates. Further,the low temperature allows a differential crackfree deposits.

vi) The method yields pinhole free, uniform deposits as the solution from which the films are deposited always remains in touch with the substrates.

vii) Stoichiometric deposits can easily be obtained since the basic building blocks are ions instead of atoms.

viii) Doping of foreign impurity can easily be achieved.

ix) The process of film growth is slow which facilitates better orientation of crystallites with improved grain structure.

x) A provision for vigourous stirring of reaction solution is not needed. The substrate holder is designed such that substrates attached to it churn well the bulk of the mixture and each time the surface of the deposit is exposed to new building blocks of Cd^{2+} and S^{2-}.

xi) Compound films such as sulphides and selenides of Cd, Pb,Zn,and Hg and their alloys can be easily deposited.

xii) The important and cheap advantage of this method is that it is possible to deposit films on non-accessible surface i.e.inside of glass tubes etc., where they will be protected from physical damages.

The detailed procedure for the deposition of CdS thin

films followed during the work is summarised in section 3.5 of this chapter.

3.4 Growth Mechanism of CdS Thin Films :

Cadmium sulphide thin films are generally prepared by controlled precipitation from a solution containing the cadmium complex and an organic sulphur bearing compounds such as thiourea added at a slow rate to have controlled and slow precipitation of CdS [43,44].

The growth of CdS from aqueous solutions of cadmium sulphate and thiourea in an alkaline medium is first suggested by Lundin and the various steps involved are

i) Formation of complex compounds as,

$$CdSO_4 + 4\ NH_3 \longrightarrow [Cd(NH_3)_4]\ SO_4,$$

ii) Diffusion of the complex ion, OH^- and thiourea to the catalytic surface of CdS,

iii) Catalytic CdS dissociates thiourea as,

$$(NH_2)_2 - C = S + OH^- \longrightarrow CH_2N_2 + H_2O + SH^-,$$

iv) Formation of bivalent sulphide ion,

$$SH^- + OH^- \longrightarrow H_2O + S^{--},$$

v) Formation of CdS,

$$Cd(NH_3)_2 + S^{--} \longrightarrow CdS + 2NH_3 \uparrow.$$

It is known that the nucleation of precipitate at some local inhomogenity occurs when ionic product exceeds the solubility product. Growth of these nuclei by the addition of more ions from solution results in the formation of stable nuclei of the size greater than the critical size.

Further, growth upto particle size of 10μm results in formation of colloidal dispersion. These primary colloids as a result of adsorption starts nucleation forming thin, adherent, and specularly reflecting films indicating the cluster by cluster film growth. Kaur et al [89] showed that the film growth is by atomistic or "ion by ion" rather than cluster by cluster, supported by the fact that CdS film is a mixture of hexagonal and cubic phases, whereas the precipitate is always a cubic. Further they pointed out that the cluster by cluster growth results in loose and powdery films with only cubic structure.

The quantity of ammonia alters the quality of CdS films. If the ammonia solution is insufficient to redissolve completely the white precipitate of $Cd(OH)_2$, thin, adherent, and specularly reflecting films are obtained. This can be explained as [89] : when the substrates are dipped in the reaction mixture, a layer of $Cd(OH)_2$ on it stimulates the decomposition of thiourea. The S^{--} ions thus formed are adsorbed by this layer resulting in CdS film formation. Further, the growth takes place by addition of more and more Cd^{2+} and S^{2-} ions. Stirring of the solution increases the rate of arrival of Cd^{2+} and S^{2-} ions on the substrate and also speeds up the rate of coagulation of colloidal particles in solution. This results in precipitation of collodial CdS particles which now cannot be adsorbed on the substrate leaving the chance for "ion by ion" film growth.

If the ammonia is just sufficient to redissolve the precipitate, non-reflecting, thick, and less adhesive films are obtained. When solution is stirred, the colloidal solution becomes unstable due to enhanced coagulation forming large number of CdS particles which can not be adsorbed to start the nucleation. During the stirring substrate surface is bombarded with large number of Cd^{2+} and S^{2-} ions. This coupled with the fact that a hydrophillic surface preferentially adsorbs OH^- ions from an alkaline solution resulting in formation of $Cd(OH)_2$ in the solution due to high ammonia concentration. These $Cd(OH)_2$ nuclei acts as a nucleation centres for CdS to grow "ion by ion" and coalesce to form a continuous CdS film.

3.5 Deposition of CdS and CdS:Sb Thin Films :

A variety of techniques are available for the preparation of thin films. The selection of a deposition method is an important task and is dependent on the various factors like material to be deposited, nature of the substrates, required film thickness, structure, and quality of the films and application of the films etc. Among the most widely used methods for the depositon of CdS films such as vacuum evaporation, sintering, sputtering, sprary pyrolysis, chemical deposition process, the later is relatively less expensive, simple, and provides a convenient way in which a variety of substrates like metals semiconductors, and insulators can be used [89,90-93]. Film deposition by this method is a slow process which allows for

better stoichiometry and crystallinity compared to other methods. Impurity doping can easily be done by the addition of a proper volume of the required concentration of the desired dopant directly into the solution container.

3.5.1. Preparation of the substrates :

The substrates used in the various stages of this work were amorphous glasses (microslides) and good quality stainless steel. Especially, stainless steel substrates were used while studying photoelectrochemical properties. Film properties were studied on amorphous glass substrates.

a) Preparation of the glass substrates :

The amorphous glass substrates of approximately 100% transmission were procurred from Blue Star, Bombay (size 72 x 25 x 1mm.). These are cut finely by means of a diamond point into the substrates of the size 72 mm x 9mm x 1 mm and were utilised for the deposition and further studies.

b) Preparation of stainless steel substrates:

A stainless steel sheat of a suitable guage (24) was cut into the strips of the size 75 x 9 x 1mm and were used as a substrate. The substrates were polished to a mirror grade by using an emery cloth and a polishing paper (0-paper).

3.5.2. Substrate cleaning :

The key precaution taken before the deposition of CdS

and CdS:Sb films is the careful cleaning of the substrates procurred as above. As the stickness of the film layer has a direct bearing on cleanliness of the substrate, following was the procedure adopted while cleaning the substrates. The glass substrates were boiled in chromic acid for about 20 minutes and washed with double distilled water. They were further dipped in a medium concentrated teepol detergent solution and washed several times with double distilled water and then with ultrasonic cleaner. All the substrates were kept immersed in double distilled water before use. In a similar fashion, stainless steel strips were first degreased by washing with mild teepol solution and then polished (mirror smooth) on a sylvate emery cloth. Further procedure was similar to glass substrates except the use of chromic acid.

5.5.3. Preparation of the solutions :

All the solution, used for the preparation of CdS and CdS:Sb films, were prepared in a fresh double distilled water. Following were the chemicals used: i) A.R. grade cadmium sulphate supplied by Reanol, Budapest : (Hungery). ii) A.R. grade thiourea supplied by Chemo Fine Chemicals, Bombay (India), iii) A.R. grade antimony trichloride (, Fluka Made (Hungery), iv) L.R. grade ammonia supplied by B.D.H. Glaxo Laboratories (India).

3.5.4. Deposition of CdS and CdS:Sb thin films :

Thin layers of CdS and CdS:Sb were prepared in an alkaline medium by a modified chemical deposition process [29,45]. The substrates used were non conducting glass microslides and stainless steel strips of the size mentioned earlier . The detailed procedure is as follows : a 20 ml 1M CdSO4 solution was taken in a 250 ml beaker to which an appropriate 14 N aqueous ammonia solution was added drop by drop with continuous stirring until it redissolved the white precipitate of cadmium hydroxide. The pH of the reaction mixture was adjusted to 8 - 9. The temperature of the reaction mixture was then raised to 85° C. by means of an oil trough whose temperature was controlled to 95° C. The substrates mounted on a specially designed substrate holder were kept rotating with a constant speed of 75 rpm in the reaction vessel containing complex compound. 1 M thiourea solution was added at the rate of 0.7 ml/minute with a special but separate arrangement as discussed earlier. The period of depositon was 45 min. The films were detached from the system and washed with double distilled water and 2% hot ammonium nitrate. To obtain CdS:Sb samples an appropriate $SbCl_3$ solution was added in the reaction vessel. The films were dried and preserved in a dark desiccator.