CHAPTER III - DEPOSITION OF n-CdSe FILMS AND CONSTRUCTION OF SEMICONDUCTOR SEPTUM SOLAR CELLS

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3.1 INTRODUCTION

The semiconductor photoelectrode is the heart of photoelectrochemical (PEC) cells. Various techniques are used for deposition of n-CdSe films and construction of semiconductor septum solar cells. In this chapter we report on preparation of large area photoelectrode and construction details of semiconductor septum solar cells for hydrogen production and generation of electricity.

The photoelectrode used in the semicondcutor septum cell should satisfy the following requirements [1].

1) $h\nu > Eg$ the energy of the incident light should be greater than the band gap of the semiconductor.
2) It should be stable in the electrolyte and should not decompose during illumination.
3) The absorption coefficient α of semiconductor must posses large values.
4) The thickness of the bulk of the semiconductor must be optimum to absorb all the incident radiations.
5) Charge carriers in the material should have high mobility and life time.
6) Recombination states must be minimum cost of the material, manufacturing process and efficiency should be acceptable.

Cadmium selenide has shown great promise as

semiconductor material for photoelectrochemical conversion, because of its near ideal direct band gap (1.7 eV). We have selected d.c. electrodeposition technique to deposit n-CdSe films. The details of preparation of n-CdSe films are given in this chapter.

3.2 SURVEY OF DEPOSITION OF n-CdSe FILMS

The photo-electrochemical properties of semiconductor electrodes have been subject for many studies, strongly stimulated by the prospect to use photoelectrochemical system for the solar energy conversion [2-4].

It is also interesting to note from various results [5] that the efficiency of device depends upon the material and its method of preparation. The materials should be prepared by a method which can give high efficiency.

The choice of the perticular method depends upon several factors like material to be deposited, nature of the substrate, required film thickness, structure of the film, application of the film etc. Scientists have prepared n-CdSe polycrystalline films with different techniques as follows.

a) EVAPORATION AND CO-EVAPORATION

Films of n-CdSe on ceramic substrate have been prepared using evaporation technique by Sharma and co-workers [6]. The films were prepared with evaporation of

n-CdSe as well as by co-evaporation of Cd or Se. In both cases materials were evaporated from tungstan boats with a background pressure 10^{-6} torr. The thin films of n-CdSe with thickness of 0.5 to 2 μm were deposited on pure titanium substrates [7,8].

b) CHEMICAL BATH DEPOSITION

The reaction was utilized between complexed cadmium ions $Cd(NH_3)^{2+}$ and selenide ions by Boudreau et al [9]. Thin film formation proceeds simultaneously with the precipitation of the n-CdSe. Pawar and Lokhande [10] also prepared films by chemical bath deposition techniques.

c) SPRAY PYROLYSIS

The polycrystalline n-CdSe films were prepared by taking 0.05 M aqueous solution of selenourea [NH_2-CSe-NH_2] and 0.05 aqueous solution of cadmium chloride as the starting solution by Mangolhara et al [11]. The solutions were mixed throughly and sprayed on to titanium substrates heated at temperature ranging from 200°C to 300°C.

d) ELECTRODEPOSITION

Recently, electrodeposition technique has been employed in the production of thin film semiconductors to use in the solar cells as well as solar selective coatings. The electrodepostion technique has many advantages over other physical and chemical deposition techniques like, it

is quite simple, low cost technique for preparation of semiconducting films for solid state and liquid junction solar cells. Cathodic electrodeposition of thin n-CdSe films from an aqueous solution of selenous acid has been studied by a number of workers [12].

e) PALLETS SINTERING

A powder of n-CdSe was pressed into pallets, which were sintered in air at 1000°C. A conversion efficiency in the polysulphide redox system 5.1% was reported [13].

3.3 ELECTRODEPOSITION

Electrodeposition is an attractive method for preparation of thin films, the main advantage being the easy control of growth rate through electrical quantities. This method has been successfully employed for thin films of elemental, binary and ternary semiconductors and also offers many intrinsically attractive features of thin film, heterojunction solar cells [14].

Apart from single crystal, pressure sintered polycrystalline disc, Chandra and Panday [15] have obtained n-CdSe films on metal substrates by electrodeposition from an acidic solution containing $CdSO_4$ and SeO_2. Pawar and Lokhande et al [16] have prepared n-CdSe films using cathodic electrodeposition technique. The films were heat treated in air at different temperatures.

There is another method of electrodeposition i.e. anodic electrodeposition Miller [17] used anodic electrodeposition to prepare a thin film of CdS, an alkaline electrolyte containing S^2 was electrolysed using a cadmium rod as anode and platinum rod as counter electrode (cathode).

In contrast to anodic electrodeposition, the cathodic electrodeposition is not limited in thickness. This method is superior to other quantities to prepare thin films of n-CdSe for photoelectrochemical purposes [18-22]. The advantages of this methcd are as follows.

1) It is isothermal process.
2) This method controles film thickness and composition.
3) The ability to form films on large sheet or non planer surfaces.

By considering number of applications of this method, we have selected cathodic electrodeposition technique for preparation of n-type CdSe semiconductor.

The cathodic electrodeposition is simple and easy technique than any other methods.

3.4 EXPERIMENTAL

3.4.1 ELECTRODEPOSITION CELL

The electrodeposition cell used for electrodeposition of n-CdSe film of large area is as shown in Fig.3.1. It consists of,

a) Backlite holder

b) Solution container

c) Counter electrode

d) Substrate

e) Saturated calomel electrode (SCE)

a) Backlite Holder

It is disc type in shape having thickness 1 cm and diameter 12 cm. It consists of three slots one for substrate, second for counter electrode and third for SCE, with attachment of screws to hold them. The distance between counter electrode and substrate was 1 cm.

b) Solution Counter

It was the glass cell cylinderical in shape of capacity 1000 cc.

c) Counter Electrodes

While depositing the n-CdSe films two types of counter electrodes were used.

i. Graphite plate of size 9 X 14 cm^2

ii. Stainless steel plate of size 9 X 14 cm^2

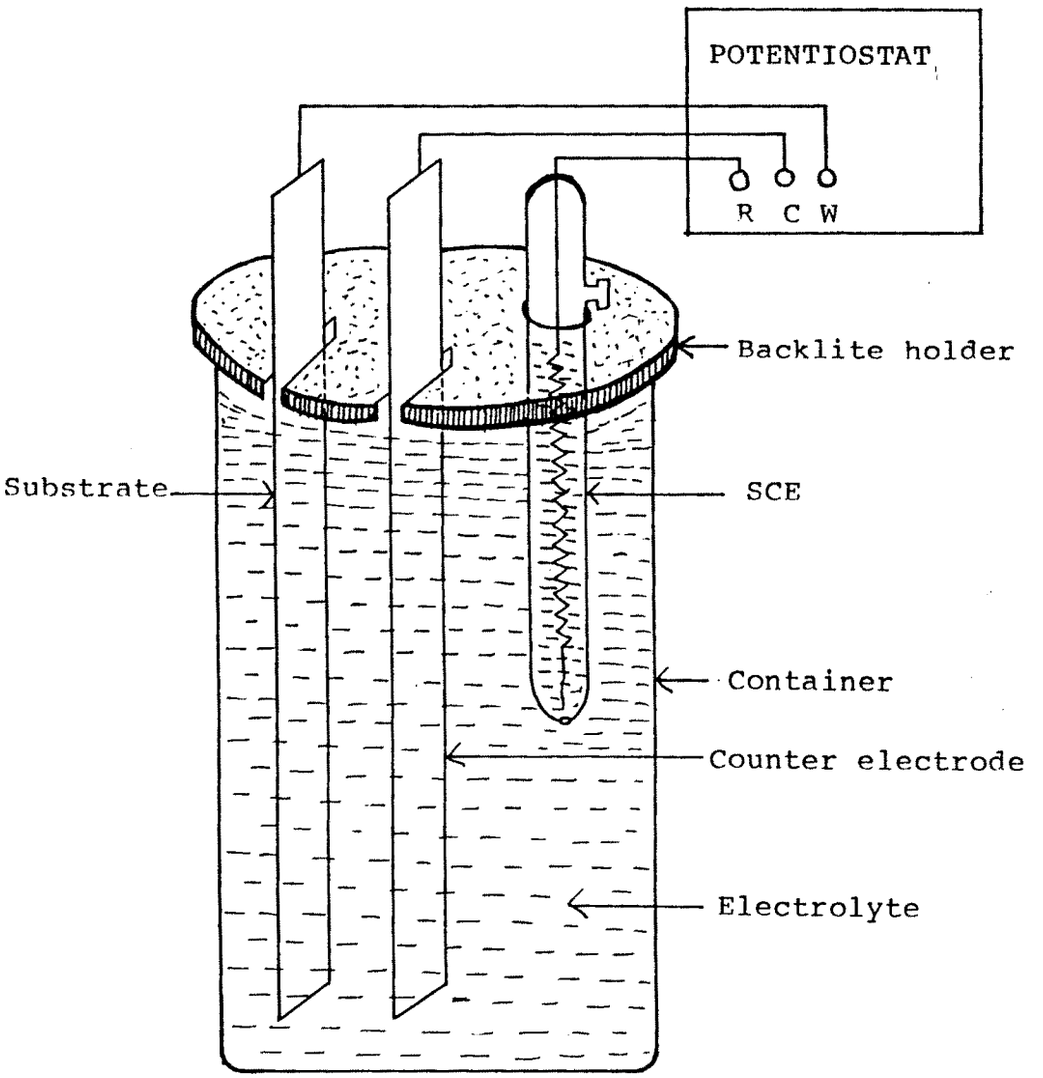


Fig.3.1. Schematic diagram of electrodeposition cell

It is found that stainless steel plates are more suitable than graphite. The n-CdSe films were sticky and uniform when stainless steel plates were used as counter electrodes.

d) Substrates

Commerciably available stainless-steel (A_1S_1-302 type) was used as substrates was 9 X 14 cm^2. The size of is substrate was 9X14 cm^2.

3.4.2 SUBSTRATE CLEANING

Substrates cleaning for thin film deposition is one of the most important factor for obtaining the reproducibility of the properties. It also affects the adherence, smoothness, brightness and uniformity of the film. The technique to be adopted for cleaning depends upon the nature of the substrates. For cleaning of stainless steel substrates, following procedure is adopted.

The stainless steel substrates were polished by using carborandom powder and washed with flowing water for 5 minutes. After washing some drops of acetone were put on substrate and by using cotton, dust particles were removed from the surface.

Drying of substrate was done in the vapour of isopropyl alcohol. For this purpose few drops of alcohol

were added in stainless-steel box containing stand for keeping substrates of size 9 X 14 cm^2.

In electrodeposition technique, it is very essential to have very clean substrates. Such types of substrates were preserved in box free from moisture, dust etc.

3.4.3 SOLUTION PREPARAITON

The solution of $CdSO_4$, $8H_2O$ and SeO_2 of same concentration 10 mM were prepared by using doubled distilled water. Weights for solution preparation were taken by using micro-balance.

Just prepared solution is not suitable for deposition of n-CdSe films. The solution prepared 12 hours before electrodeposition was found suitable to get sticky and uniform films.

3.4.4 ELECTRODEPOSITION OF LARGE AREA n-CdSe FILMS

The films of n-CdSe were deposited under d.c. potentio-static condition using potentio-stat model 362 (EG and G). Three electrode system was employed and potentials were measured w.r. to saturated calomel electrode (SCE). The electrolysis was accomplished potentio-statically by using 1000 cc cell. Three electrodes of the electrolytic cell working electrode (cathode, reference electrode [saturated

calomel electrode] and counter electrode [stainless steel]) were connected directly to the scanning potentiostat with the help of clips provided. The back side of stainlesssteel substrate was covered with insulating tape to avoid two sides deposition. All depositions were carried out under unstirred condition and at the ambient temperature 300°K.

The cathodic polarization curves for electrodeposition of n-CdSe films were studied with a potentiostat galvanostat model (362 EG and G) and x-y-t recorder. The photograph of experimental set up of electrodeposition is as shown in Fig.3.2. Cathodic polarization curve to determine deposition potential is as shown in Fig.3.3. The deposition potential -0.65V Vs SCE was kept constant for electrodeposition of large area n-CdSe films. The pH of the solution while depositing n-CdSe films on stainless steel substrate was 2 to 3. The current density varies with time as shown in Fig.3.4. Deposition of thin films of n-CdSe is described as following.

$$SeO_2 + H_2O \rightleftharpoons H_2SeO_3 \quad \ldots\ldots 1$$

$$H_2SeO_3 + 4H^+ + 4e \longrightarrow Se + 3H_2O \quad \ldots\ldots 2$$

$$Cd^{+2} + 2e \longrightarrow Cd \quad \ldots\ldots 3$$

$$Cd(S) + Se(S) \rightleftharpoons CdSe \quad \ldots\ldots 4$$

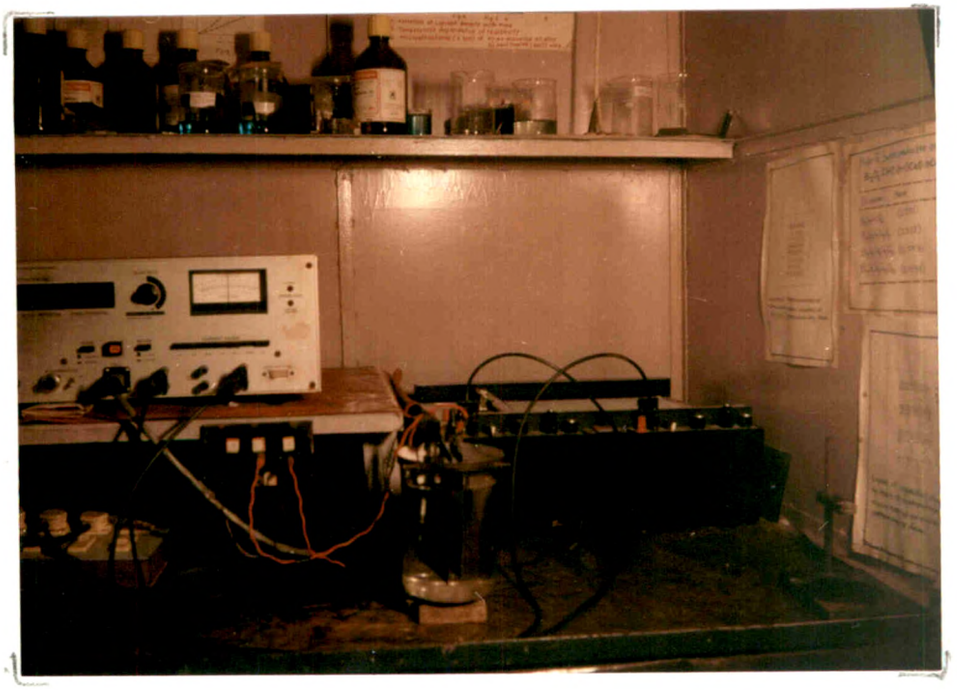


Fig.3.2. Photograph of experimental set up of electrodeposition

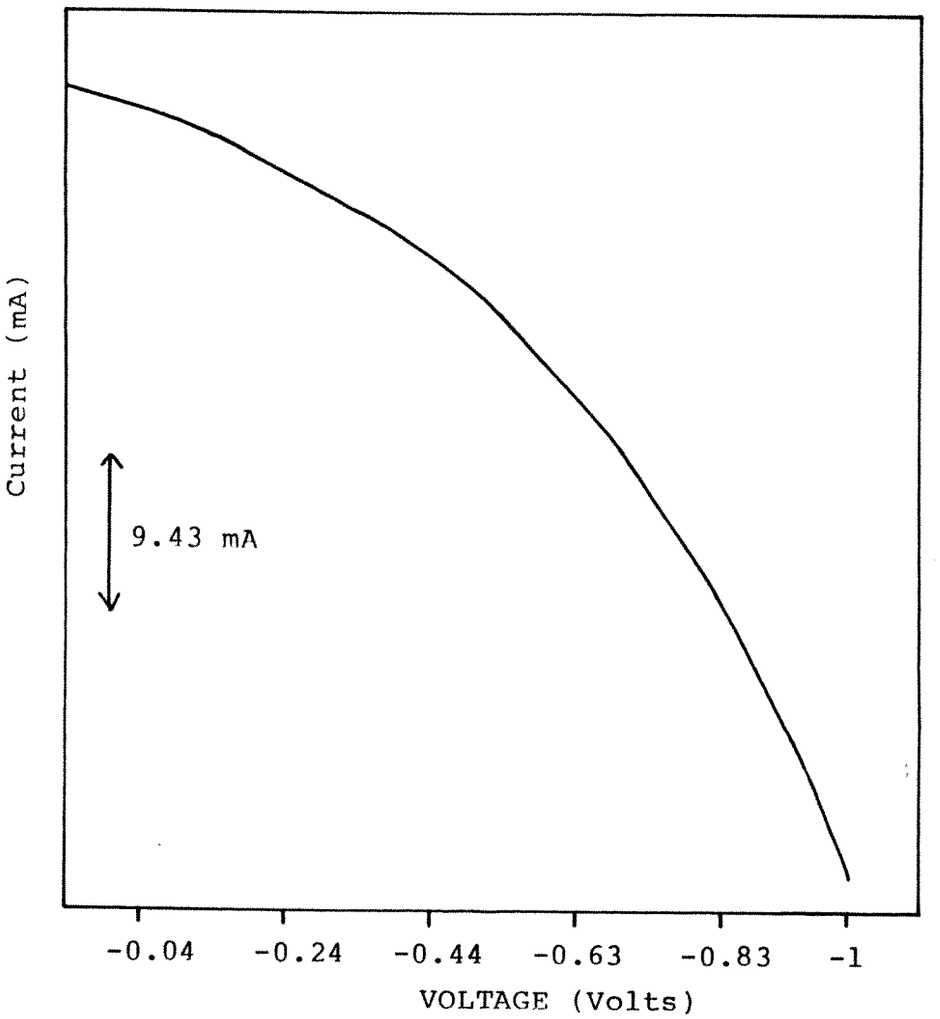


Fig.3.3. Cathode polarisation curve for CdSe deposition.

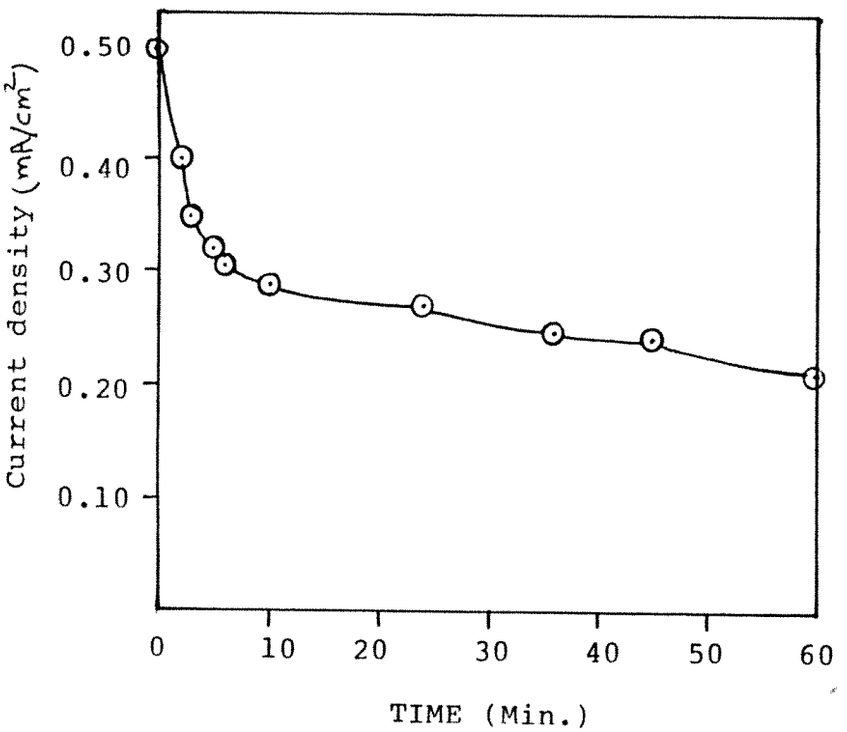


Fig.3.4. Variation of current density with time during deposition of CdSe film

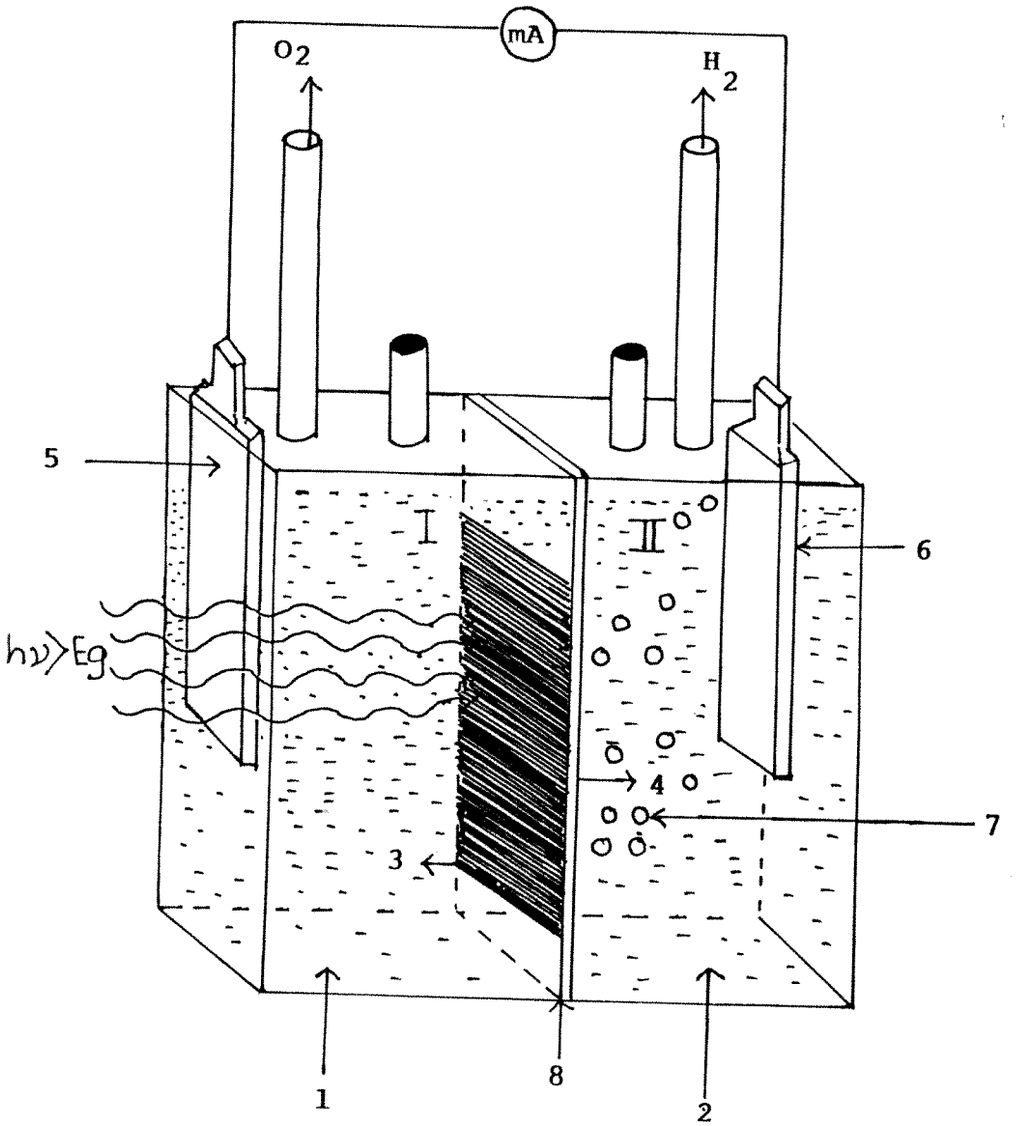
photosensitivity of thin films of n-CdSe electrode depends on the composition of the electrolytic solution, used for its preparation. All the chemicals used were of reagent grade. For deposition time 60 minutes, at deposition potential -0.65 V vs SCE sticky, uniform and thick films were electrodeposited.

3.4.5 CONSTRUCTION OF SEMICONDUCTOR SEPTUM SOLAR CELLS FOR HYDROGEN PRODUCTION

In semiconductor septum solar cells, different approaches have been carried out where semiconductor electrode acts as photoanode as well as separator of two aqueous compartments. The idea for construction of such type of redox cell was derived from pigmented bilayer lipid membrane [23-26] studies. It is easy to construct, simple to operate and appears to be a practical approach to the photochemical conversion and storage of solar energy.

In present investigation attempt has been made to construct SC-SEP cells for study of hydrogen production. Seven semiconductor septum cells were constructed for hydrogen production study and one SC-SEP cell was constructed for charging and discharging characteristics study.

The complete SC-SEP cell for hydrogen production is as shown in Fig.3.5. The cell consists of two compart-



1) Polysulphide 2) Artificial sea water, 3) n-CdSe film,
4) St. steel substrate, 5) Graphite electrode, 6) Lead electrode,
7) H_2 bubble, 8) SC-SEP.

Fig.3.5. Schematic diagram of SC-SEP cell for hydrogen production.

ments made up of transparent plastic boxes. The n-CdSe/ stainless steel septum electrode of area about 45 cm^2 was fixed between two compartments using Araldite pastes made by Hindustan CIBA ENERGY, Bombay. The metallic electrodes c, Pb were used as contact electrodes. The size of each electrode was 8 X 1.8 X 1.4 cm^3. A piece of glass was fitted on front side of the first compartment to illuminate the film. Graphite electrode was fixed in light facing compartment and lead electrode was fixed as contact electrode in dark compartment. In both compartments small glass tubes were fitted, which were used as outlets for O_2 and H_2.

The light facing compartment was filled with polysulphide/ferro-ferricynide + 1MKOH and dark compartment was filled with artificial sea water. The configuration of the cell for hydrogen production is as follows.

Graphite|3S|n-CdSe|Stainless-steel|Artificial sea water|Pb

The tungstan halogen lamp (500 watt) was used to illuminate n-CdSe septum electrode. The water filter was interposed between the cell and light source to avoid excessive heating. Digital multimeter was used for current measurements. The photograph of SC-SEP cells used in our study is as shown in Fig.3.6.

Fig.3.6. Photograph of SC-SEP cells.

3.4.6 SC-SEP CELL FOR STUDY OF CHARGING AND DISCHARGING CHARACTERISTICS

The construction of semicondcutor septum cell for study of charging and discharging characteristics is as shown in Fig.3.7. It consists of two compartments made up of plastic boxes with 10 cm X 8 cm area cut on their sides. The n-CdSe septum electrode was fixed between two compartments. The counter electrodes in both compartments were graphite plates of area about 108 cm^2.

The first compartment facing to the light was filled with 1 M 500 ml polysulphide (Na_2-S-NaOH). The other dark compartment was filled with redox couple like 1 M $FeCl_3$. A water filter was interposed between the cell and light source to avoid excessive heating. The configuration of cell for study of charging and discharging characteristics is,

Graphite|Na_2S-S-NaOH|n-CdSe|stainless steel|1M$FeCl_3$|Graphite

3.5 RESULTS AND DISCUSSION

3.5.1 VARIATION OF CURRENT DENSITY WITH TIME

The electrodeposition of n-CdSe film was performed by using same power supply at different current densities. Fig.3.4 shows the variation of cathodic current density with deposition time of n-CdSe alloyed films at potential -0.65 V vs SCE which was decided by using polarization curve. From

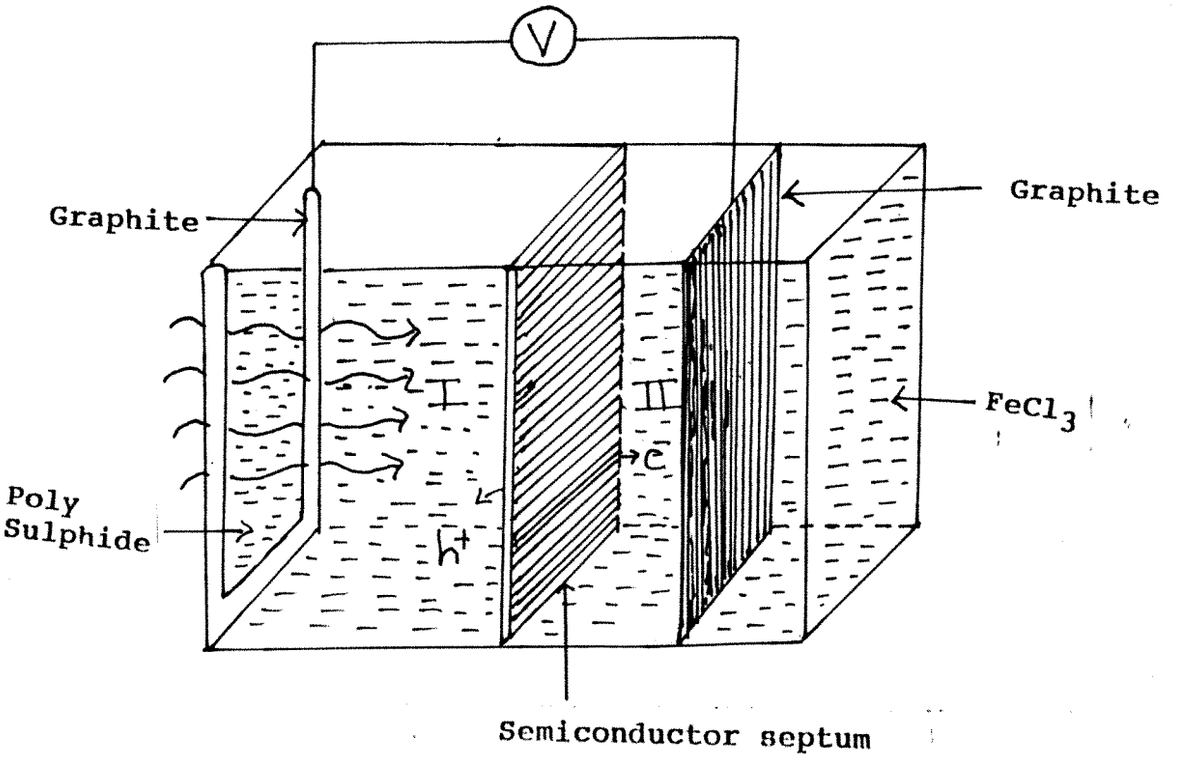


Fig.3.7. SC-SEP cell for charging and discharging studies.

the Fig.3.4 it is seen that initially deposition current density drastically decreases and then slowly decreases with time. Deposition area of the film was 90 cm^2 on substrate of size 9 X 14 cm^2.

3.5.2 EFFECT OF COUNTER ELECTRODE ON DEPOSITION

When stainless steel was used as counter electrode, instead of graphite then it was observed that the n-CdSe films were sticky and uniform as compared with films obtained by using graphite, as counter electrode. These films also showed greater PEC effect.

3.5.3 PERIOD OF DEPOSITION SOLUTION

When fresh solution was used just after preparation of solution, then it was observed that the films were not good. When solution was used after about 12 hours, for deposition then it was observed that the films were good and showed more photoelectrochemical effect.

3.5.4 THICKNESS OF n-CdSe FILM

The film thickness is an important parameter in the study of the film properties. Thickness is defined as the distance perpendicular to the surface from a point on the boundary surface, through the film to the other boundary surface. If boundary surfaces are rough or non parallel, then thickness is not well defined. The photoelectrochemical

properties of PEC cells depend on thickness of the film [27-29].

Usually a definate thickness of semiconductor is required for protection to itself. The thickness of the film was measured by weighing method using the relation.

$$\text{thickness } t = \frac{m}{A\rho}$$

where, A = Area of film

ρ = density of material of bulk

At the deposition period of 60 minutes, the thickness of n-CdSe film was about 1.79 μm.

3.5.5 EFFECT OF ANNEALING ON n-CdSe FILMS

Annealing of n-CdSe film was carried out at temperature 370°C for 30 minutes. It was seen that after annealing n-CdSe film showed better photoelectrochemical effect. The stability of films in polysulphide solution was found better after annealing at 370°C.

3.5.6 MICROGRAPHS

The photograph of set up for microstructural studies is as shown in Fig.3.8. Micrographs of n-CdSe films of two different deposition potentials are as shown in Fig.3.9. The deposited areas were 90 cm^2. It is observed from the micrographs that the n-CdSe films deposited at

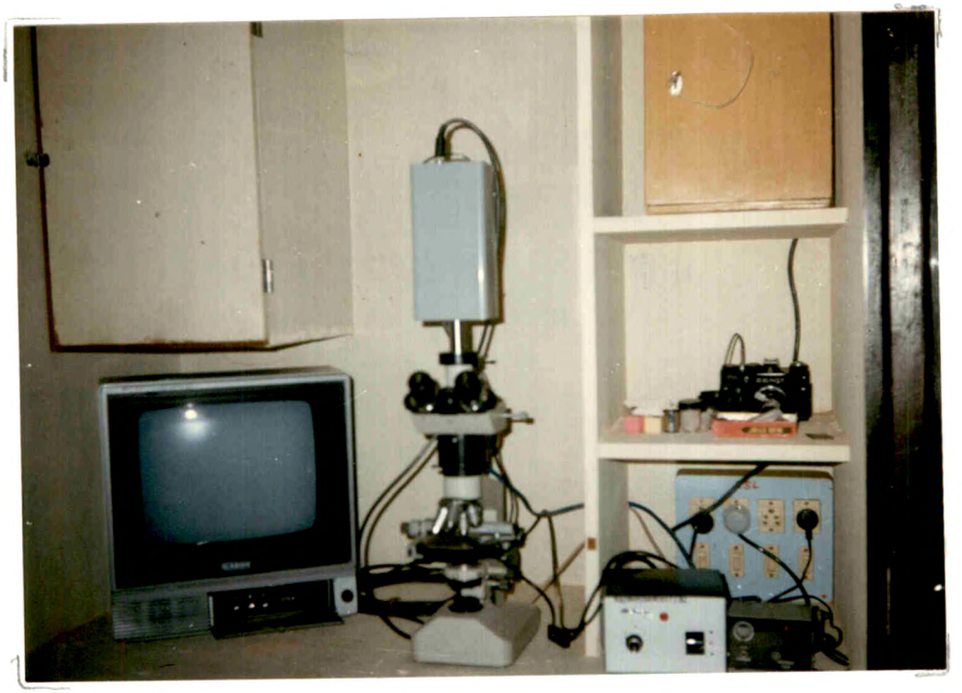
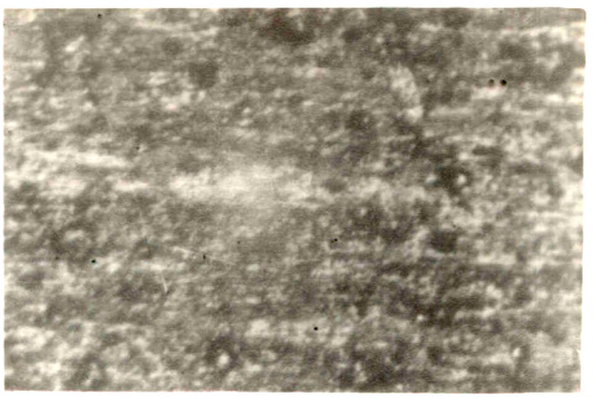
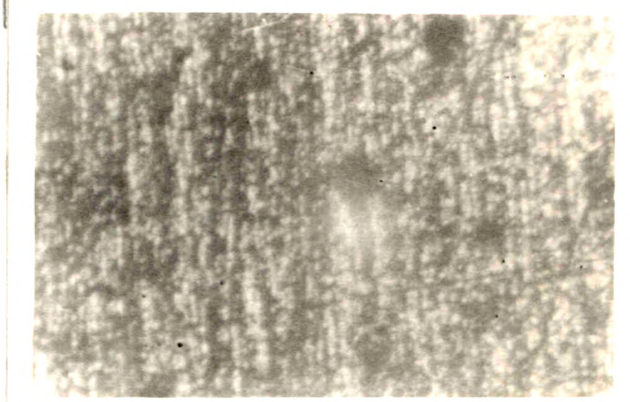


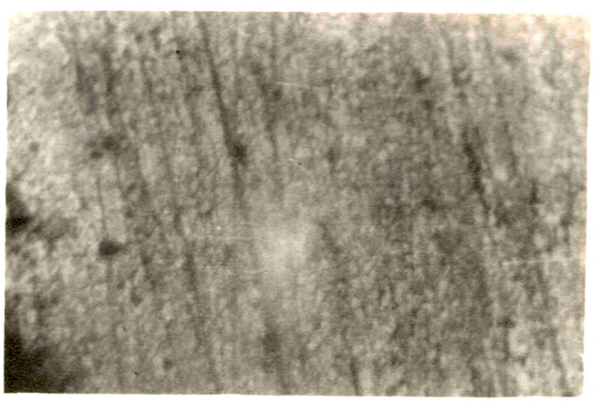
Fig.3.8. Photograph showing set up for microstructure studies.



n-CdSe film deposited at -0.65 V vs SCE

After annealing n-CdSe film deposited at 0.65 V vs SCE





n-CdSe film deposited at -0.55 V vs SCE

Fig.3.9. Micrograph of electrodeposited n-CdSe films.

-0.65 V vs SCE are uniform/dense and packed arrangement of grains than films deposited at -0.55 V vs SCE. More improved structure was obtained for the annealed films.

3.5.7 X-RAY DIFFRACTION

The XRD pattern of n-CdSe film was recorded by using X-ray diffraction model Phillips PW-1710. The XRD diffraction pattern for the n-CdSe film deposited at -0.65 V vs SCE is as shown in Fig.3.10. The presence of sharp peaks shows that the n-CdSe film is polycrystalline in nature comparisation of observed d-values with standard d values from ASTM data (30) are listed in Table 3.1. The observed d-values are well matched with standard d-values of hexagonal structure of n-CdSe film. Hence structure of the material is hexagonal.

The lattice parameter a= 4.297 Å and c = 7.2819 Å were calculated using the formula for hexagonal structure,

$$\frac{1}{d^2} = \frac{4}{3}\left[\frac{h^2 + hk + k^2}{a^2}\right] + \frac{l^2}{c^2}$$

3.6 CONCLUSIONS

The mirror polished stainless steel substrats are suitable to electrodeposit n-CdSe films. Substrate cleaning affect the adherence, smoothness, brightness and uniformity of films. Cadmium selenide films of area 90 cm^2 were electrodeposited at potential -0.65 V vs SCE. The deposition

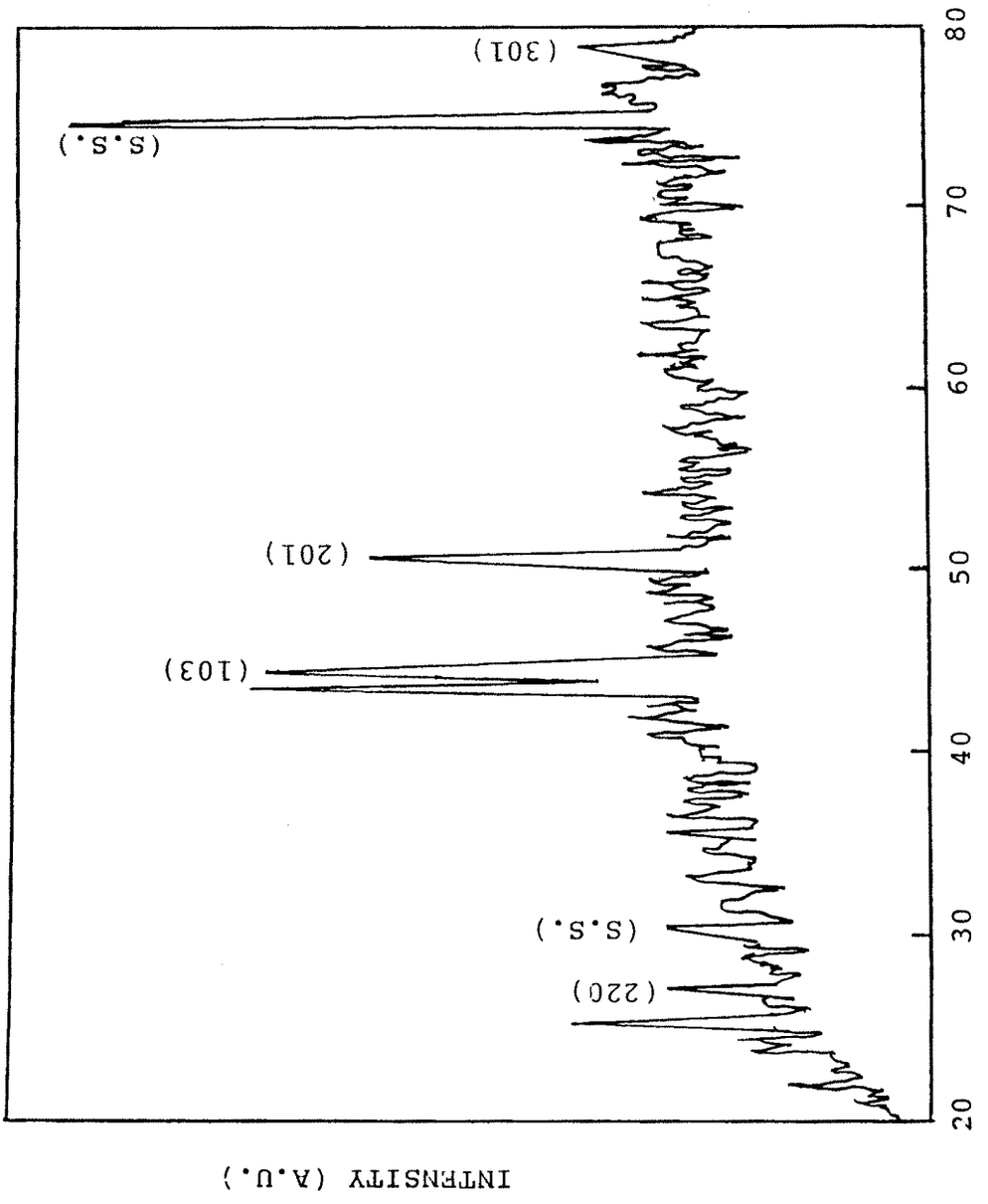


Fig.3.10. XRD pattern of CdSe film electrodeposited at -0.65 V (vs SCE).

Table 3.1

XRD data of electrodeposited n-CdSe film with lattice parameters (structure hexagonal)

d-values observed	d-values from ASTM data	hkl	I/I_{max}
3.2612	3.149	220	10.08
2.0257	1.980	103	42.35
1.7922	1.800	201	42.35
1.2147	1.221	301	13.91

potential was determined from polarization curve. These electrodeposited films in bath (10 mM $CdSO_4$, $8H_2O$ + 10 mM SeO_2) at potential -0.65 V vs SCE for 60 minutes deposition were sticky and uniform. The solution prepared before 12 Hrs for electrodeposition of films was more suitable than just prepared solution to get better films.

It was observed that films electrodeposited by using stainless steel as counter electrode are more sticky and uniform than by using graphite electrode. The thickness of the electrodeposited films was 1.79 μm.

It was found that annealed films were more stable and showed more PEC effect. Micrograph shows that films electrodeposited at potential -0.65 V vs SCE are dense, uniform and packed arrangement of grains. Annealed films showed more improved structure. The presence of sharp peaks in XRD diffraction pattern shows, the n-CdSe film is polycrystalline in nature. The observed 'd' values are well matched with standard d values (from ASTM data) of hexagonal structure of n-CdSe film.

Annealed, large area n-CdSe films are suitable in fabrication of semiconductor septum solar cells. In semiconductor septum solar cells, different approaches have been carried out, where (n-CdSe) semiconductor electrode acts as photoanode as well as separator of two aqueous compartments.

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