CHAPTER III

CADMIUM SELENIUM FILM PHOTOELECTROCHEMICAL SOLAR CELLS
Cadmium selenide is a promising material for Solar Cells because its band gap of 1.7 eV favourably matches the solar spectrum. It also lies well within the range of optimum band gap requirement of 1.4 eV for electrochemical photovoltaic Solar Cells. Till now, photoelectrochemical Solar Cells (PESC) having cadmium selenide as photoelectrode used CdSe either in the form of single crystals or polycrystalline films (Ellis et al, 1976; Hodes et al, 1976; Miller et al, 1977; Heller et al, 1977; Manassen et al, 1977; Gerrard and Owen, 1977; Heller et al, 1978; Chandra and Pandey, 1980; Chandra et al, 1980). For large scale production, CdSe in the film form is an obvious choice. In the present work a simple electrocodeposition method for obtaining CdSe film has been used as discussed in Chapter I.

Earlier attempts (Hodes et al, 1976) using this method, and the subsequent PESCs developed, suffered from the following drawbacks:

(i) the reproducibility was found to be poor,

(ii) good quality CdSe films could only be obtained on titanium substrates which being a costly metal can not compete as commercially exploitable alternative for solar energy conversion. The earlier attempts to obtain CdSe films on stainless steel substrates met with little success (Hodes, 1977; private communication),
(iii) invariably all PESC used platinum as counter electrode which is again a high cost material.

The present work was undertaken (i) to find optimum conditions of electrolysis for good quality, reproducible cadmium selenide film - PESCs using titanium substrates, (ii) to find conditions such that electrocodeposition technique could give CdSe films on stainless steel substrates also and subsequently to yield a good quality reproducible PESC, (iii) to investigate the possibility of getting CdSe films on graphite substrates, (iv) to demonstrate the feasibility of using graphite as a counter electrode in place of platinum in the cell using CdSe films on stainless steel substrate. Thus, a low cost cell with stainless steel as substrate for CdSe along with graphite as counterelectrode is described.

3.1 EXPERIMENTAL

3.1.1 Preparation of CdSe Film

The key to the formation of a PESC is a semiconductor electrode. In the present case, it is CdSe film deposited on titanium, stainless steel or graphite substrate. The experimental arrangement is described in Section 1.3 of Chapter 1. The electrocodeposition was carried out at different electrolysis temperatures (26° to 70°C), current densities (0.8 to 3 mA/cm²) and different SeO₂ concentrations (5 to 20 mg/50 ml) in an aqueous solution containing CdSO₄
The electrolysis conditions have a dominant effect on the quality of the film (and hence PESC). The results are discussed later in this chapter.

3.1.2 Fabrication of PESC

A typical photoelectrochemical cell is shown in Figure (3.1). They were obtained by dipping CdSe films (≈40 μm) deposited on different substrates in an electrolyte consisting of 1 mole NaOH, 1 mole Na₂S and 1 mole S. Thus, the electrolyte chosen contained sulfide-polysulfide redox couple. Choosing S²⁻/S₂⁻ as redox couple is known to facilitate the stabilisation of CdSe electrode (Ellis et al, 1976a; Gerischer, 1977, 1978). The counter electrode chosen was either platinum or graphite. Graphite counter electrode was prepared by dipping a graphite plate in an aqueous 1 mole solution of cobaltous nitrate which seems to improve the performance of graphite electrode. Dipping the cobalt nitrate impregnated graphite counter electrode in an electrolyte containing S²⁻/S₂⁻ ions results in the formation of CoS in the pores of graphite. Cobalt sulfide has been reported to act as electrocatalyst for the reduction of sulfur (Hodes et al, 1977).

The following cell configurations were prepared:

CELL I  Ti/CdSe//electrolyte//Pt (counter electrode)

CELL II  Steel/CdSe//electrolyte//Pt (counter electrode)
A typical CdSe photoelectrochemical Solar Cell.
CELL III  Steel/CdSe//electrolyte//C (counter electrode)
CELL IV  Graphite/CdSe//electrolyte//Pt (counter electrode)

3.1.3  J-V Characteristics of Solar Cells

A 300 W tungsten lamp was used for illumination. The illumination level was measured with a "Suryamapi" reading in mW. The distance between the bulb and the photoelectrode was adjusted such that an illumination level of 100 mW/cm² (=1 Sun) could be achieved, on the surface of the photoelectrode. The current-voltage characteristics were measured by varying an external resistance \( R_e \). Digital multimeter (Philips Model) was used to record the current and cell voltage.

3.2  RESULTS AND DISCUSSIONS

The general principle of PESC has already been discussed in Chapter II. Figure (3.2) shows the relative positions of the conduction band edge \( (E_C) \), valence band edge \( (E_V) \), decomposition potential \( (pE_D) \); Fermi level \( (nE_F) \) of the semiconductor along with the Fermi levels of the redox species \( (E_{F,\text{redox}}) \) and metal counter electrode \( (mE_F) \) for the specific photoelectrochemical Solar Cell using n-CdSe film. The broadening of the energy levels of reduced species \( (S^{2-}) \) and the oxidised species \( (S^2_2) \) is also shown by a distribution curve. The flow of photogenerated holes and electrons is represented by arrows. The electrostatic
Fig. 3.2. Relative energy positions in a metal/CdSe film/electrolyte/metal photoelectrochemical Solar Cell and current flow under illumination.
potential in the space charge layer is such that the holes move towards the semiconductor/electrolyte interface, where they can participate in the oxidation reaction with the sulfide ions. The remaining photogenerated electron moves in the semiconductor bulk. Thus a current flow results in the external circuit. At the metal counter electrode, reduction of the polysulfide ions by electrons takes place completing the overall reaction which is expressed as:

(i) At the semiconductor electrode:

\[ 2S^{2-} + 2h^+ \rightarrow S_2^{2-} \]

the overlapping of the valence band edge with the energy distribution curve of the sulfide ion facilitates such a charge transfer reaction.

(ii) At the metal counter electrode:

\[ S_2^{2-} + 2e^- \rightarrow 2S^{2-} \]

the redox potential of the reaction is -0.48 V with respect to normal Hydrogen electrode (NHE).

According to this model, the cadmium selenide photoelectrode and the metal counter electrode do not participate in the chemical reaction. However, the thermodynamical considerations (Gerischer and Gobberrecht, 1978) reveal that cadmium selenide may participate in the following decomposition reaction induced by photogenerated holes:
CdSe + 2 H⁺ → Cd²⁺ + Se

The decomposition potential of cadmium selenide is (-0.45 V) with respect to NHE in 1 molar S²⁻/S₂⁻ solution. Since the redox potential of the hole transfer reaction (-0.48 V) is very near to the decomposition potential of CdSe, the semiconductor CdSe may decompose with cadmium and selenium going into solution. Addition of sulfur, however, checks this decomposition reaction because of the formation of sulfide polysulfide ions. The reaction can be written as:

Cd²⁺ + S²⁻ → CdS

which amounts to locking Cd²⁺ ions into position. Thus, dipping CdSe film in the sulfide/polysulfide solution results in the conversion of a first few layers of CdSe into CdS. Further decomposition is stopped because the kinetics of the charge transfer reaction over-ride the decomposition reaction.

Formation of CdS onto CdSe will, however, result in the lowering of efficiency of the Solar Cells because of high band gap of CdS and higher degree of lattice mismatch between CdSe and CdS.

The results on various CdSe film PESC's are described below.
3.2.1 CELL I: Ti/CdSe/electrolyte/Pt

(a) Effect of electrolyte concentrations during CdSe formation

Figure (3.3) gives the current-voltage plots of the photoelectrochemical Solar Cells formed with CdSe film on titanium substrate. The results for five CdSe films obtained at different SeO₂ concentrations have been plotted. It is obvious that the cell performance depends strongly on the concentration of SeO₂ during electrolysis. Figure (3.4) shows it more vividly where the open circuit cell voltage (OCV), the short circuit current density (j_sc) and the maximum derivable power P_max have been plotted as a function of SeO₂ concentration.

It is obvious that the best PESC was obtained when CdSe film was electrodeposited using SeO₂ concentration \( \sim 5 \text{ mg/50 ml} \). A typical PESC formed with such a film gave \( \text{OCV} = 300 \text{ mV} \) and \( j_{\text{sc}} = 2.36 \text{ ma/cm}^2 \).

Films prepared at lower concentrations between \( \sim 2 \text{ mg} \) and \( 5 \text{ mg/50 ml} \) were greyish black in appearance. As the concentration of SeO₂ was increased the films became more and more brownish. The increased brownish hue on CdSe film may be due to increased stoichiometric proportion of Se in cadmium selenide. This is supported by the fact that the electrolysis current density during film formation decreased gradually for higher SeO₂ concentrations because of the
Fig. 3.3. j-V characteristics of Ti/CdSe PESC cells for five SeO₂ concentrations of 2 mg, 6 mg, 10 mg, 15 mg and 20 mg per 50 ml.
Fig. 3.4. Variation of open circuit voltage, short circuit current density and maximum derivable power as a function of SeO₂ concentration for Ti/CdSe PESC.
formation of insulating Se layer on CdSe. Films prepared at concentrations \(> 10 \text{ mg/50 ml}\) exhibited rapid deterioration in OCV values when dipped into the electrolyte containing sulfide/polysulfide couple and on illumination. Very high SeO\(_2\) concentrations \(> 20 \text{ mg/50 ml}\) did not yield stable CdSe films.

Panicker et al (1978) have studied another cathodically deposited chalcogenide film, e.g., CdTe. Their results also show that the quality of CdTe film is strongly dependent on the concentration of TeO\(_2\). Panicker et al. have calculated the free energy changes involved in various steps of electrodeposition. As discussed in Chapter I, the electrodeposition of CdTe (or CdSe) is mediated via HTeO\(_2^+\) (or HSeO\(_2^+\)) ions. The free energies involved require Cd\(^{++}\) ions to deposit only after Te\(^{++}\) (or Se\(^{++}\)) has been deposited. Therefore, the deposition of CdTe (or CdSe) is mostly dependent on the rate of Te (or Se) deposition, and hence it should be proportional to TeO\(_2\) (or SeO\(_2\)) concentration.

(b) **Effect of electrolysis current density during CdSe formation**

CdSe films prepared at different electrolysis current densities with SeO\(_2\) concentration of 5 mg/50 ml did not show any appreciable change in their performance in FESCs. The results are summarised in Table (3.1).
Table 3.1. The open circuit voltage and short circuit current obtained from various CdSe/Ti PESCs prepared at different electrolysis current densities at electrolysis temperature 27°C. The concentration of SeO₂ fixed at 5 mg/50 ml of water.

<table>
<thead>
<tr>
<th>Cell parameter</th>
<th>Electrolysis current densities (ma/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6.7</td>
</tr>
<tr>
<td>OCV (mV)</td>
<td>250±20</td>
</tr>
<tr>
<td>( \dot{j}_{\text{sc}} ) (ma/cm²)</td>
<td>2.50±0.2</td>
</tr>
</tbody>
</table>
(c) **Effect of electrolyte temperature during CdSe formation**

Electrolyte temperature (30-50°C) during CdSe film deposition on titanium substrates was also found to have negligible effect on PESC performance using these CdSe films.

3.2.2 **CELL II: Steel/CdSe/Electrolyte/Pt**

(a) **Effect of SeO₂ concentration during CdSe formation**

The current voltage characteristics of PESCs obtained from cadmium selenide films on stainless steel substrate electrodeposited at room temperature and different SeO₂ concentrations are shown in Figure (3.5). These results are qualitatively similar to those of titanium substrate discussed above. Films formed at SeO₂ concentration between 5 and 10 mg/50 ml gave better performance. The OCV, j_sc and P_max values for five different SeO₂ concentrations are plotted as a function of SeO₂ concentration in Figure (3.6). The concentration of SeO₂ > 15 mg/50 ml generally gave unstable films which dissolved in sulfide/polysulfide solution.

(b) **Effect of electrolysis current density**

The effect of electrolysis current density during film formation was also investigated and the results are tabulated in Table (3.2). It is clear that a different deposition current density has negligible effect on the performance of PESCs formed with the corresponding CdSe films.
Fig. 3.5.  j-V characteristics of PESC's using steel/CdSe films deposited at five SeO₂ concentrations.  2 mg;  5 mg;  10 mg;  15 mg and  20 mg per 80 ml.
Fig. 3.6. Variation of open circuit voltage, short circuit current and maximum derivable power as a function of SeO₂ concentration for steel/CdSe PECs.
Table 3.2. The open circuit voltage and short circuit current obtained by various CdSe/steel PECs prepared at different electrolysis current densities at temperature 27°C. The concentration of SeO₂ fixed at 5 mg/50 ml of water.

<table>
<thead>
<tr>
<th>Cell parameter</th>
<th>Electrolysis current density (mA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3</td>
</tr>
<tr>
<td>OCV (mV)</td>
<td>215±20</td>
</tr>
<tr>
<td>JSC (mA/cm²)</td>
<td>1.8±0.6</td>
</tr>
</tbody>
</table>
(c) **Effect of electrolysis temperature**

The temperature of the electrolyte during electrodeposition was found to have a significant effect on the properties of CdSe films. The experiments were conducted with films deposited at different electrolysis temperatures at SeO₂ concentration = 5 mg/50 ml and current density 3 ma/cm². The OCV, \( j_{sc} \) and \( P_{max} \) values for PESCs using these CdSe films as a function of electrolysis temperature are plotted in Figure (3.7). These results are an average of a large number of cells prepared at each temperature. Generally CdSe films were obtained with good adhesion, reproducibility and showing good performance in its PESC when they were electrodeposited at 32-40°C.

Figure (3.8) gives the plot of current and power output against cell voltage for a typical CdSe/steel PESC prepared at an electrolysis temperature of 32.5°C. This cell gave OCV = 260 mV, \( j_{sc} = 4.0 \, \text{ma/cm}^2 \) and \( P_{max} = 0.3 \, \text{mW/cm}^2 \) under illumination from a 300 W tungsten lamp (≈ 100 mW/cm²). This typically represents the best CdSe/steel PESC which compares favourably well with the best CdSe/Ti PESC.

3.2.3 **CELL III: Steel/CdSe/Electrolyte/C**

There is a need to replace platinum counter electrode because:

(i) It is not economically feasible in a Solar Cell to use Pt as counter electrode.
Fig. 3.8. J-V and power characteristics of a typical steel/CdSe/electrolyte/Pt PESC for 100 mW/cm² illumination for a tungsten lamp.
(ii) In any practical Solar Cell the counter electrode should not only be inert but also have low overpotential for redox reactions. In the present case since the competing reactions are the reduction-oxidation of polysulfide and sulfide ions, the counter electrode should possess low overpotential for this reaction. Since graphite with electrocatalyst, has been known to possess these properties (Hodes et al, 1977a). PECs using CdSe/steel photoelectrode and graphite counter electrode were studied.

The result for CELL III are given in Figure (3.9a). This cell gave OCV = 310 mV; $j_{sc} = 3.6 \text{ ma/cm}^2$; $P_{max} = 0.42 \text{ mW/cm}^2$ for 100 mW/cm$^2$ illumination from a tungsten lamp.

3.2.4 CELL IV: C/CdSe//Electrolyte//Pt

The current-voltage characteristic of a typical photoelectrochemical Solar Cell using CdSe film on graphite substrate is shown in Figure (3.9b). This cell gave OCV = 200 mV; $j_{sc} = 0.9 \text{ ma/cm}^2$ and $P_{max} = 0.06 \text{ mW/cm}^2$. Obviously this is a poor cell configuration.

Figures (3.10) and (3.11) respectively give the j-V and power output characteristics for all the four cell configuration.

Table (3.3) compares the efficiency and fill factor. It is clear that the best results are obtained with configuration steel/CdSe//electrolyte//C. Astonishingly, this is the lowest cost cell also.
Fig. 3.9. j-V and power characteristics of (a) steel/CdSe/electrolyte/C and (b) C/CdSe/electrolyte/Pt PESC.
**Fig. 3.10.** Comparison of j-V characteristics of four typical PESCs.
Fig. 3.11. Power characteristics of four typical PESCes.

CELL I : Ti/CdSe/electrolyte/Pt
CELL II : Steel/CdSe/electrolyte/Pt
CELL III : Steel/CdSe/electrolyte/C
CELL IV : C/CdSe/electrolyte/Pt
Table 3.3. Comparison of efficiency and fill factor of CELL I, CELL II, CELL III and CELL IV.

<table>
<thead>
<tr>
<th>Cell configuration</th>
<th>Percentage efficiency</th>
<th>Fill factor $F$</th>
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</thead>
<tbody>
<tr>
<td>$Ti/CdSe//electrolyte//Pt$</td>
<td>0.23</td>
<td>0.32</td>
</tr>
<tr>
<td>$Steel/CdSe//electrolyte//Pt$</td>
<td>0.3</td>
<td>0.29</td>
</tr>
<tr>
<td>$Steel/CdSe//electrolyte/C$</td>
<td>0.42</td>
<td>0.38</td>
</tr>
<tr>
<td>$C/CdSe//electrolyte//Pt$</td>
<td>0.06</td>
<td>$0.33 \times 10^{-3}$</td>
</tr>
</tbody>
</table>
3.3 STRUCTURAL CHARACTERISATION OF CdSe FILM FROM ELECTRON DIFFRACTION STUDIES

The electron diffraction studies of electrodeposited CdSe films were undertaken to ascertain their structure. A Philips EM 200 was used for the purpose. Standard gold pattern was taken to calculate the camera constant.

The camera constant of the electron microscope is given by

\[ 2L \lambda = \frac{2R_{\text{gold}} x a}{\sqrt{N}} \]

where \( 2R_{\text{gold}} \) are the diameters of various rings obtained in the powder pattern of gold; \( N = (h^2+k^2+l^2) \) with \((h,k,l)\) giving the indices of the diffracting planes corresponding to a given ring diameter; 'a' is the lattice parameter of gold.

The d-values of the diffraction rings (or spots) for a given specimen can be calculated as

\[ d = \frac{\text{camera constant}}{2R} \]

where \( 2R \) is the diameter of a ring (or the distance between two opposite diffraction spots in case of single crystalline pattern).

Figure (2.13a) gives the standard gold diffraction pattern taken under conditions identical to those used for
Fig. 3.12. (a) Electron diffraction pattern of gold used for calculation of camera constant, (b) Electron diffraction pattern of electrocodeposited CdSe film.
obtaining diffraction patterns of CdSe.

The 2Rgold, values of the first three rings (measured by a Bosch and Lamp eyepiece (X12) with an accuracy of \( \pm 0.05 \text{ cm} \)); the corresponding hkl values and the camera constant calculated from these are listed in Table (3.4). The average value of 2\( \lambda \)L is taken as 11.83 \( \AA \).

A typical diffraction pattern obtained for CdSe film is shown in Figure (3.12b). The electron diffraction pattern obtained show that the CdSe films are polycrystalline in nature.

Cadmium selenide is known to occur in three crystalline phases, viz., hexagonal close pack (hcp-wurtzite type) with a = 4.29 \( \AA \), c = 7.01 or c = 84.3 \( \AA \) or f.c.c. (NaCl type a = 5.49 \( \AA \) or ZnS type a = 6.05 \( \AA \). The diffraction pattern corresponds to that of hcp-structure. The calculated 2R and d-values for the observed diffraction pattern are given in Table (3.5) along with the standard d-values of CdSe (hcp) showing a reasonably good agreement.

3.4 CONCLUSIONS

The electrodeposition method can be used to obtain good quality and reproducible CdSe films under optimised conditions. The most important controlling factor is SeO\(_2\) concentration which should be between 5-10 mg/50 ml. The electrolyte temperature between 22-40\(^\circ\)C was found to be the
Table 3.4. The $2\theta_{\text{gold}}$ values and calculated camera constant of the electron microscope.

<table>
<thead>
<tr>
<th>Ring No.</th>
<th>$2\theta$ (^\circ)</th>
<th>hkl</th>
<th>$N = \sqrt{h^2+k^2+l^2}$</th>
<th>$2\lambda,^\circ$</th>
<th>Average $2\lambda,^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( A )</td>
<td></td>
<td></td>
<td>(( \text{A.cm} ))</td>
<td>(( \text{A.cm} ))</td>
</tr>
<tr>
<td>1</td>
<td>5.0</td>
<td>111</td>
<td>1.732</td>
<td>11.77</td>
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</tr>
<tr>
<td>2</td>
<td>5.8</td>
<td>200</td>
<td>2.0</td>
<td>11.82</td>
<td>11.83</td>
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<td>3</td>
<td>8.25</td>
<td>220</td>
<td>2.828</td>
<td>11.89</td>
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</table>
Table 3.5. Observed 2θ and d-values from the electron diffraction pattern of CdSe films and their comparison with the standard d-values for a h.c.p. CdSe powder pattern.

<table>
<thead>
<tr>
<th>Observed values</th>
<th>Standard values</th>
</tr>
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<tbody>
<tr>
<td>2θ</td>
<td>d**</td>
</tr>
<tr>
<td>Å</td>
<td>Å</td>
</tr>
<tr>
<td>3.2</td>
<td>3.69</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>4.1</td>
<td>2.88</td>
</tr>
<tr>
<td>5.55</td>
<td>2.14</td>
</tr>
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<td>5.9</td>
<td>2.00</td>
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<td>6.1</td>
<td>1.93</td>
</tr>
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<td>6.45</td>
<td>1.83</td>
</tr>
<tr>
<td>6.95</td>
<td>1.69</td>
</tr>
<tr>
<td>7.4</td>
<td>1.59</td>
</tr>
<tr>
<td>8.1</td>
<td>1.46</td>
</tr>
</tbody>
</table>

** Accuracy ±0.05 Å
best for steel substrate while for titanium small temperature changes had no effect.

The electron diffraction studies show that the CdSe films are polycrystalline with a h.c.p. structure.

The PESCes prepared from CdSe/steel films compare favourably well with CdSe/Ti-PESC.

The replacement of platinum counter electrode by graphite results in an improved cell performance due to low electrode overpotential. The use of steel and graphite in place of titanium and platinum facilitates considerable cost reduction and efficiency improvement in PESCes.