Chapter IV

Results on Cadmium Selenide

4.1 Introduction

High purity cadmium selenide powder is not being manufactured in our country at present. Photo grade powder is imported from standard chemical vendors. In this laboratory, a method to prepare the cadmium selenide powder of requisite purity has been developed. This material is generally prepared by bubbling purified hydrogen selenide through a cadmium salt solution under near neutral or faintly alkaline condition (pH – 6.5 to 8.0). Hydrogen selenide is generated in a fair state of purity by the hydrolysis of aluminium selenide. Aluminium selenide is prepared by igniting a mixture of pure aluminium powder and selenium powder with a magnesium ribbon, the reaction spreading throughout the mass (after degreasing both the powders with trichloroethylene). However, during hydrolysis, pollution of the atmosphere is large and in spite of the precautions taken, the hydrolysis cannot be controlled to proceed in a smooth manner. The practical difficulties encountered and the hazardous nature of free hydrogen selenide gas makes the process undesirable for routine preparation.

Selenourea, like its sulphur analog, is a good source to supply selenide ions in solution under suitable conditions. Thus insoluble selenide ions in solution can be prepared by chemical precipitation [165]. The process is simple and besides precipitates of selenides of cadmium, thallium and silver, smooth adherent mirrory layers can be deposited. However, the high cost of selenourea comes in the way for adopting this method to large scale preparation of selenide
powders. As the objective was to develop a method for preparing the selenide powder on a large scale, when required, an alternative process which does not involve the direct use of hazardous hydrogen selenide and further which does not employ such a costly imported raw material like selenourea has been developed. Selenium dissolves in hot aqueous solution of alkali sulphite \([166]\) giving selenosulphate, analogous to sulphur forming alkali thiosulphate \([167,168]\). Selenium in selenosulphate is more easily parted as \(\text{Se}^{2-}\) ion than sulphur in thiosulphate. However, this selenosulphate is stable only under high alkaline conditions \((\text{pH} = 10)\). As the \(\text{pH}\) is lowered gradually, \(\text{pH}\) of 5.5 and below, selenium is thrown out in the red form. The reactions involved may broadly be represented as:

\[
\text{Se} + \text{SO}_3^{2-} \rightarrow \text{SeSO}_3^{2-}
\]

\[
\text{Cd}^{2+} + 2\text{OH}^- + \text{SeSO}_3^{2-} \rightarrow \text{CdSe} + \text{SO}_4^{2-} + \text{H}_2\text{O}
\]

Traces of selenium are likely to be present which have to be removed by washing with hot solution of alkali sulphite. Studies on the kinetics of this precipitation reaction have been reported \([169]\). Cadmium to selenium ratio has been varied over a limited range \(\text{between 0.5 and 1.25}\) and it has been observed that, a ratio of unity is good.

### 4.2 Preparation of CdSe powder

High purity cadmium selenide powder has been prepared by the reaction of aqueous solutions of cadmium acetate with sodium seleno sulphate under optimum conditions of \(\text{pH} = 10\), obtained by the addition of ammonium hydroxide. Normally selenium dissolves in hot aqueous solutions of alkali metal sulphites
yielding alkali selenosulphate or selenosulphites. Selenosulphate is stable under high alkaline conditions (pH=10). As the pH is decreased gradually below 5.5, selenium is precipitated out. This selenium reacts with the cadmium ions to yield cadmium selenide.

About 30g of pure selenium powder was washed with distilled water and degreased with trichloroethylene or acetone. 235g of sodium sulphite was added and heated upto 95°C allowed to remain for 20 hours. The solution was filtered till it was ensured that no more selenium separated out. The solution was allowed to age for 20 hours. 34g of cadmium acetate was dissolved in 250 ml of triple distilled water. This solution was kept in a 3 litre pyrex round bottomed flask fitted with ground joints. 100ml of ammonia was added to obtain a clear solution. 250ml of selenosulphate solution was mixed with 30 ml of ammonia and added to the cadmium ammonia complex in the flask and slowly refluxed over an electric heating mantle. The solution was initially yellow which slowly turned to orange red with tiny crystals of CdSe floating on the surface of the solution along the sides of the flask. The remaining seleno sulphate solution was added and refluxing continued for 4 hours when the precipitate turned into shiny black colour. The precipitate was kept for 20 hours and then filtered through a Whatmann filter paper using a Buchner funnel with vacuum suction arrangement. Thus obtained precipitate was thoroughly mixed with hot solution of sodium sulphite to remove any trace of selenium. Washing with distilled water was continued till the filtrate was free from sulphite. To remove traces of cadmium oxide, the precipitate was washed with hot acetic acid solution (70°C). Further
washing with distilled water was continued till the pH of the filtrate was found to be neutral. Purified Ethanol was employed for final washing to remove moisture. The precipitate was dried in a vacuum oven. Thus prepared CdSe powder has been annealed at 300°C in argon atmosphere for 20 minutes. This ensured the complete removal of excess selenium. The powders were stored in a vacuum desiccator.

4.3 Atomic Absorption Spectroscopy (AAS)

AAS was used for the trace elemental analysis of the prepared CdSe powders. Also, commercially available imported powder (Kochlight) has been analysed for comparison. The determination of the concentration of metallic elements in CdSe powders was carried out. For the purpose of analysis, 10 mg of CdSe powder was dissolved either in 15 ml of HNO₃ or 20 ml of HCl and 5 ml of HNO₃. The presence of impurities such as calcium, potassium, sodium, thallium, zinc, lead, cobalt and arsenic were screened and is given in Table-4.1.

Table - 4.1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Impurity content in ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ti</td>
</tr>
<tr>
<td>CdSe (Prepared)</td>
<td>18</td>
</tr>
<tr>
<td>CdSe (Kochlight)</td>
<td>16</td>
</tr>
</tbody>
</table>
4.4 X-ray Analysis of the Powder

X-ray diffractograms (XRD) of the as-prepared and annealed CdSe powders are shown in Fig.4.1, for the sake of comparison, XRD pattern of the Koch light CdSe powder is also shown in Fig.4.2. The fig.4.1a exhibits all reflections corresponding to single phase hexagonal CdSe. The prominent peaks are observed at 2θ = 23.9°, 25.4°, 27.08°, 35.1°, 41.8°, 45.78° and 49.6° having reflections (100), (002), (101), (102), (110), (103) and (112) respectively. Apart from these reflections, two more peaks at 2θ = 55.6° and 61.22° are also observed. These reflections correspond to elemental selenium. XRD pattern corresponding to the powder annealed at 300°C in argon atmosphere is shown in Fig.4.1b. The peak corresponding to elemental selenium is absent and all the other peaks observed in Fig.4.1a are present. This is due to the vapourisation of selenium during annealing.

The XRD patterns of the annealed and as obtained commercial imported powder are shown in Fig.4.2a and 4.2b. Prominent peaks corresponding to hexagonal CdSe with (100), (002), (101), (102), (110), (103) and (112) reflections are observed in both the cases.

4.5 Preparation of CdSe films

CdSe films were prepared on steatite and titanium substrates using screen-printing technique described in Chapter III. The substrates were fixed to a porcelain tile. The affixed substrates were cleaned with cotton wool dipped in acetone. The paste formed with the CdSe powder and ethylene glycol was applied with a doctor's blade to the polyurethane squeegee and pulled on the
Fig 4.1 - X-ray diffraction pattern of CdSe powder synthesized in the laboratory
a) as-prepared
b) after heat treatment at 300°C in argon
Fig 4.2- X-ray diffraction pattern of commercial Kochlight CdSe powder
a) as-prepared
b) after heat treatment at 300°C in argon
screen, once in unidirection, thus getting layers of uniform thickness and finish. At a time 20 – 30 substrates could be coated. These layers were dried in vacuum at 120°C. The thickness of the coated layers after drying was around 15 micrometers and after sintering it was around 12 micrometers. These layers were sintered at different temperatures in the range 450 - 550°C in argon atmosphere for 20 minutes.

4.6 X-ray diffraction studies

XRD patterns of the films annealed in argon atmosphere at different temperatures are shown in Fig.4.3. The prominent peaks corresponding to (100), (002), (101), (110), (103) and (112) are observed in all cases. It is observed that as the annealing temperature increases the intensity of the peaks also increase due to improved crystallinity. The lattice constants 'a' and 'c' calculated using the XRD data are 4.304Å and 7.044 Å, which are in close agreement with the ASTM data. The crystallite size calculated using the Debye Scherrer equation is found to increase with increase of annealing temperature. Table.4.2 indicates the crystallite size for the films post annealed at different temperatures in the range 450 - 550°C.

4.7 EDAX measurements

EDAX measurements were made on the samples annealed at different temperatures. The chemical composition for the films annealed at 475°C is Cd(64.1%) and Se(35.9%). For the films annealed at 550°C (Fig.4.4), the composition was Cd (65.3%) and Se (34.7%).
Fig 4.3- X-ray diffraction pattern of screen-printed CdSe thin films heated at different temperatures
a) 450°C
b) 500°C
c) 525°C
d) 550°C
Fig 4.4 - EDAX spectrum of CdSe films annealed at 550°C in argon
Table- 4.2
Crystallite size of CdSe films

<table>
<thead>
<tr>
<th>Annealing Temperature (°C)</th>
<th>Crystallite size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>450</td>
<td>2.0</td>
</tr>
<tr>
<td>475</td>
<td>3.5</td>
</tr>
<tr>
<td>500</td>
<td>4.7</td>
</tr>
<tr>
<td>525</td>
<td>5.3</td>
</tr>
<tr>
<td>550</td>
<td>6.0</td>
</tr>
</tbody>
</table>

4.8 XPS studies

The XPS spectra of the CdSe films annealed at different temperatures are shown in Fig.4.5a and Fig.4.5b for the binding energies of the Cd (3d_{5/2} and 3d_{3/2}) and Se (3d_{5/2} and 3d_{3/2}) level. After annealing the area under the selenium binding energy curves decrease indicating a small amount of loss of selenium upon evaporation from the sample due to heat treatment. As shown in the fig.4.5a, the peak energy levels associated with Cd (3d_{5/2} and 3d_{3/2}) appeared at 405 and 411.7 eV respectively, which are in good agreement with the literature [170]. These findings are characteristic of the Cd in CdSe and are in good agreement with the literature [170]. Fig.4.5b shows the binding energies of the Se (3d_{5/2} and 3d_{3/2}) levels at 53.9 and 59.2 eV respectively. The selenium binding energies shift to lower energies after annealing due to loss of selenium by evaporation. There is no evidence of shifting of the energy levels to higher binding.
Fig 4.5- XPS spectra of Cd and Se in CdSe films annealed at
A) 500°C
B) 550°C in argon for
a) Cd
b) Se
energies corresponding to SeO\textsubscript{2} formation [170]. Depth profiling studies were made on the films heat-treated at 550°C, by ion etching at the rate of 10 nm/minutes. Fig.4.6 shows a uniform distribution of Cd and Se throughout the thickness.

Atomic concentration measurements made on the heat-treated samples yielded an apparent Cd/Se ratio of 1.681, this calculation is based on the consideration of area sensitivity factors for Cd and Se respectively and agreed well with the composition estimated from EDAX measurements.

4.9 Optical studies

Fig.4.7 shows the diffuse reflectance spectra of the CdSe films annealed at 550°C. The energy gap obtained from the wavelength at which onset of maximum absorption is obtained corresponds to 1.67 eV. This value is similar to the value obtained on thin film CdSe [171-173].

4.10 Scanning electron microscopy

The CdSe films heat-treated at 450°C and 550°C indicate an increase of the grain size (Fig.4.8) as the temperature of heat treatment increases. The surface of the films become uniform and the grain size increases from 1.8 – 6.0 μm. These values are nearly the same as that obtained from XRD.

4.11 Electrical Properties

The resistivity (ρ) of the films was calculated by using the equation 5. The influence of annealing temperature on the resistivity of the films is depicted in Fig.4.9. The magnitude of the resistivity varies from 0.2 – 30 ohm cm as the annealing temperature increases from 450 - 550°C.
Fig 4.6- Depth profile of Cd and Se in CdSe films annealed at 550°C in argon
Fig 4.7- Diffuse reflectance spectra of CdSe film heat-treated at 550°C in argon atmosphere.
Fig. 4.8(a) – Scanning electron micrograph of CdSe films heat-treated at 450°C

Fig. 4.8(b) - Scanning electron micrograph of CdSe films heat-treated at 550°C
Fig 4.9- Dependence of Resistivity of CdSe films on temperature of heat-treatment.
Fig. 4.10 shows the variation of Hall mobility ($\mu_H$) of all the films with annealing temperature. The Hall mobility was determined by using the equation 7. It is observed from the figure that the mobility decreases as the annealing temperature increases. The magnitude of the mobility decreases from 10.5 – 1.5 cm$^2$/V.sec as the annealing temperature increases.

Fig. 4.11 shows the variation of carrier concentration (N) calculated using equation 8 with annealing temperature. It is evident from the figure that the value of 'N' decreases as the annealing temperature increases. The carrier concentration varies from $1.25 \times 10^{18}$ cm$^{-3}$ to $2.1 \times 10^{17}$ cm$^{-3}$.

The result that the resistivity increases with increase of annealing temperature may be due to the change in film stoichiometry (excess cadmium or selenium vacancy, which are electron donor sites that provide the additional carriers and decrease the resistivity). Also CdSe dissociates during annealing by evaporation modifying the ratio of Cd/Se. Further, during annealing oxygen fills the Se vacancies in CdSe and as these donor sites are eliminated, the free carrier concentration is reduced. Invariably, the absorbed oxygen offsets the decrease in resistivity due to the excess carriers provided by the excess cadmium obtained on heat treatment resulting in a net increase of resistivity.

The grain boundaries between the crystallites dominate the electrical properties of the polycrystalline thin film semiconductors [174]. Traps at the grain boundaries are responsible for the potential barrier that limit carrier mobility.
Fig 4.10- Dependence of mobility of CdSe films on temperature of heat-treatment.
Fig 4.11- Dependence of carrier density of CdSe films on temperature of heat-treatment.
4.12 Photoconductivity studies

Fig.4.12 shows the variation of photosensitivity of the films with intensity of illumination for the cells prepared by using the powder synthesized in the laboratory. The photosensitivity was calculated using the equation 13.

It is observed from the figure, that as the intensity of illumination increases, the corresponding photosensitivity also increases. Of all the annealing temperatures, the cells prepared with the films annealed at 550°C exhibited maximum photosensitivity. The dependence of photosensitivity on light intensity at room temperature can be described in terms of the oxygen absorption effects at high annealing temperature. The thermal release of oxygen from the surface is the possible mechanism, which is always dominant for cells annealed in argon containing ppm of oxygen and hence both the photo and dark conductivity are increased [175]. The increase in photosensitivity may be due to the creation of opposite type of carriers in the n-type CdSe, as oxygen acts here as an acceptor impurity [176]. Similar behaviour has also been observed in CdSe photocells [177]. It was reported [178] that CdSe films annealed at a lower temperature contained larger electron concentrations because of a slight excess of Cd, and the carrier concentration has not changed appreciably on illumination to exhibit photoconductivity. Since the films annealed at 550°C exhibited maximum photosensitivity, further studies were made only on these films.

4.13 Effect of Doping

Fig.4.13 represents the plots of illumination intensity versus photosensitivity for all the cells doped with 0.001, 0.003, 0.005, 0.007, 0.009 and
Fig 4.12- Dependence of Photosensitivity on illumination intensity for undoped CdSe films heated at different temperatures:

- a) 450°C
- b) 500°C
- c) 525°C
- d) 550°C
Fig 4.13- Dependence of Photosensitivity on illumination intensity for CdSe films doped with different concentrations of copper

a) 0.001 M  
b) 0.003 M  
c) 0.005 M  
d) 0.007 M  
e) 0.009 M  
f) 0.011 M
0.011 M of copper. Similar to the undoped cells, the photosensitivity increases as 
the intensity of illumination increases. The magnitude of the photosensitivity is 
increased by two orders when compared to the undoped cells. Also, it is 
observed from the figure, as the copper concentration increases for a particular 
intensity and for a particular annealing temperature, the corresponding 
photosensitivity increases and it reaches a maximum when the copper 
concentration is 0.007 M and then decreases. Hence further studies were made 
only on the films with this doping concentration.

The incorporation of copper impurity in the CdSe films decreased the dark 
conductivity. Due to the dual nature of Cu impurities, the holes and electrons may 
recombine with the majority carriers under illumination thereby increasing the 
photosensitivity of the cell. In fact, studies of copper diffusion in CdS and CdSe 
[149,179] have shown that copper can act both as an acceptor and as a donor 
depending on whether it occupies substitution of interstitial sites in the lattice. 
The acceptor dominant behaviour copper arises when the number of copper ions 
on Cadmium substitutional sites is larger than the number of atoms in the 
interstitial positions. It is clear from the results observed here that in the II-VI 
semiconductor compounds, copper is associated with photoconductivity 
sensitizing centers.

Copper (Cu+) centers are situated at 0.6eV above the valence band as 
reported by Tyurn et al [148]. The maximum photosensitivity is observed for the 
doping concentration of 0.007 M which corresponds to 441 ppm of copper. AAS 
analysis of the copper concentration corresponding to this particular doping
revealed the presence of 405 ppm of copper. This particular concentration corresponds to a acceptor to donor ratio around unity. For other concentrations of copper doping this ratio varies and hence photosensitivity decreases. The acceptor dominant behaviour of copper arises when the number of copper ions on cadmium substitutional sites is larger than the number of atoms in the interstitial positions. Thus to fix the acceptor and donor concentrations as required above, the total donor concentration must be determined and, a distinction between electrically active impurities and crystal defects as a function of processing variables must be made.

4.14 Effect of Aging

Fig.4.14 exhibits the variation of photosensitivity of both undoped and doped cells with time. The encapsulated cells which were kept upto 220 days indicated a constant value of photosensitivity for both undoped and doped cells. After keeping the cells for 250 days, the value of the photosensitivity decreased. This behaviour may be due to effect of atmospheric oxygen introducing acceptor states in CdSe, since the cells are unencapsulated. For the doped cells, both oxygen and copper introduce acceptor levels in CdSe, which in turn decreases the photosensitivity after keeping the cells for 220 days.

4.15 Spectral distribution of photoconductivity

The spectral distribution of photoconductivity of the cells doped with different concentrations of copper (0.003, 0.005, 0.007 and 0.009 M) is shown in Fig.4.15. It is evident from the figure that for all the four concentrations of copper doping, the photocurrent (I_{ph}, normalized) of the cell increases as the wavelength
Fig 4.14-Variation of Photosensitivity of CdSe films with time
a) Undoped
b) Copper doped (0.007 M)
Fig 4.15- Spectral distribution of photocurrent of copper doped CdSe films
a) 0.003 M
b) 0.005 M
c) 0.007 M
d) 0.009 M
of incident light increases and the photocurrent reaches a maximum for \(\lambda = 0.8\mu m\). Above this particular wavelength, the photocurrent starts to decrease and a minimum is reached at \(\lambda = 1.0\mu m\).

The long wavelength response extends upto 1.1 and 1.15\(\mu m\) for the doping concentration of 0.007 and 0.009M of CuCl\(_2\) respectively. From the figures it is also evident that the impurity excitation dominates the spectrum. Similar results were observed by Sarma [180]. Generally pure CdSe has a peak photo response at \(\lambda = 0.72\mu m\). This response is essentially caused by intrinsic excitation. Lattice defects which may be present in the crystal introduce levels in the forbidden gap, which requires less energy than excitation across the band gap. Consequently in crystals with such defects, the peak response shifts to longer wavelengths. Such longer wavelength (in this case 0.8\(\mu m\)) response might also be attributed to the presence of incorporated impurities like chloride or copper or the combined effects of copper and chloride centers [149]. The presence of adsorbed oxygen on the annealed CdSe films also contributes to the high peak value (0.8 \(\mu m\)). The long wavelength tail of the response for the doped cells may be due to the excitation of electrons directly from the sensitizing centers (copper levels) [150].

The sharp decrease in the photocurrent at shorter wavelengths may be partly associated with the corresponding decrease in the lamp response, but this would not have been sufficient, on its own, to account for the observed behaviour. However this could result from the interaction of the class - II (i.e., the Cu level) center located in the upper half of the band gap with a class - I center.
located near the middle of the band gap \((\sigma_p/\sigma_n - 1)\). When scanning from the long to short wavelengths, an initial increase in the photocurrent due to the promotion of electrons from the class-II center to the conduction band has been observed. At this stage, the class-I center would be saturated with electrons and therefore would not participate in any recombination process. However, when the energy of illumination exceeds the energy difference between the class-II center and the valence band, holes will be released to the valence band from the class-II center. These will be captured by the class-I center, effectively switching on a fast recombination route. This reduces the lifetime of electrons in the conduction band and hence the photoconductivity gain.

4.16 Photocurrent- Illumination characteristics

Fig.4.16 shows the variation in the photocurrent with illumination for both the undoped and doped cells. As discussed earlier, the high photosensitivity associated with CdSe arises due to the presence of compensated acceptors, which act as sensitizing centers. As the excitation intensity is increased, these centers become more active and the photosensitivity sharply increases at some region of excitation. It is observed from the figure, that upto 5000 lux, the photocurrent varies linearly with illumination, becoming super-linear above this intensity. But for the doped cells, linearity is observed upto 4000 lux and above this intensity super linearity is observed. The super linearity arises from the conversion of hole traps into recombination centers when the hole quasi Fermi level moves towards the valence band with an increase in light intensity. These recombination centers, which have higher capture cross sections for the holes.
Fig 4.16-Variation of photocurrent with illumination intensity for CdSe films
a) Undoped
b) Doped with copper (0.007 M)
than electrons, in conjunction with another set of recombination centers with equal capture cross sections for both the carriers, decrease the lifetime of the holes thereby increasing the lifetime of the electrons. While the hole traps are being converted into recombination centers, the electron lifetime is continuously increasing and the photocurrent varies super linearly with increasing light intensity [152]. The transition from linearity to super linearity occurs when the hole demarcation level is at the level of the recombination centers with equal capturing cross section. Similar results were observed in sprayed [151], vacuum evaporated [153] and single crystal CdSe [154]. The super linearity in CdSe occurs only when the Fermi level varies between 0.3 and 0.6 eV from the conduction band. Also it is reported [155] that the small time constants of highly photosensitive films have been attributed to the super linearity of CdSe at higher intensity of illumination.

4.17 I-V characteristics

The conduction mechanism in semiconductors can be understood by analyzing the current-voltage plots. For single carrier injection at low voltages, the plot is generally a straight line showing the validity of Ohm’s law. However, at higher voltages, some deviation is expected. The I-V characteristics of both undoped and doped films are shown in Fig.4.17 and Fig.4.18 respectively. The dark current ($I_D$) and photocurrent were of the order of $10^{-6}$ and $10^{-3}$A respectively. When compared with undoped films, the dark current for doped films was very less but photocurrent was very large. From the figures, it is understood that the plots follow a relation of the form $I \propto V^0$. In the dark, both,
Fig 4.17- Plots of current Vs applied voltage for Undoped CdSe films
a) photocurrent
b) dark current
Fig 4.18- Plots of current Vs applied voltage for copper doped (0.007 M) CdSe films
a) photocurrent
b) dark current
the undoped and doped films exhibit linear characteristics up to the applied bias of 280V. But on illumination, the plots exhibit a linear characteristic up to the applied bias of 240V. Beyond this particular voltage, the current increases sharply. This explained by noting that the current transport in the semiconductor is controlled by space charge and the current is said to be space charge limited.

The linear behaviour observed up to 240 V is attributed to the filling up of a discrete set of traps lying below or at the Fermi level. Further it is observed that for a small increase in voltage after the critical voltage ($V_{TFL}$) voltage at trap filled level is 240 V, the current shoots up. This could be explained by arguing that the traps are directly filled by the charge carriers up to $V_{TFL}$. When the voltage reaches $V_{TFL}$, all the traps are filled and further increase in voltage causes a rapid increase in current. Lampert et al [155] have shown that $V_{TFL}$ is related to the trap density $N_t$ by the relation, $N_t = 1.1 \times 10^6 \times \varepsilon \times V_{TFL}/l^2$, where $l$ is the film thickness and $\varepsilon$ is the relative dielectric constant of the material. The trap density for both the undoped and doped films was found to be of the order of $10^{17}$ cm$^{-3}$. Similar observations have been noticed by Murali et al [156], Rooz et al [157] for electrodeposited CdSe films. Also Smith et al [158] observed similar results in the case of CdS single crystals. At sufficiently high voltages, above 240 V, the current is no longer linear and shoots up very sharply. This is consistent with the argument that the behaviour is either Ohmic or space charge limited depending on whether the volume generated carrier density or the injected carrier density predominates. The sudden increase in voltage causes the sharp increase of
current to very high values. This implies that the increase in voltage forces a corresponding increase of charge in the conduction band.

4.18 Photoelectrochemical Measurements

Photoelectrochemical (PEC) cells were prepared using the films deposited on titanium substrates heat-treated at different temperatures. The films were lacquered with polystyrene in order to prevent the metal substrate portions from being exposed to the redox electrolyte. These films were used as the working electrode. The electrolyte was 1 M polysulphide. This electrolyte was chosen as it is well known that CdS electrode has reasonable stability and yield respectable outputs ion polysulphide. The light source used for illumination was an ORIEL 250 W tungsten halogen lamp. A water filter was introduced between the light source and the PEC cell to cut off the IR portion. The intensity of illumination was measured with a CEL suryamapi, whose readings are directly calibrated in mW cm\(^{-2}\). The intensity of illumination was varied changing the distance between the source and the cell. The power output characteristics of the cells were measured by connecting the resistance box and an ammeter in series, the voltage output was measured across the load resistance. The photocurrent as well as dark current was measured with a HIL digital multimeter. The output voltage was measured by a HIL digital multimeter.

The CdSe photoelectrodes were dipped in the electrolyte and allowed to attain equilibrium under dark conditions for about 10 minutes. The dark current and dark voltage values were noted. The cells were then illuminated by the light source and the current and voltage were measured for each setting of the
resistance box. The photocurrent and photo voltage were calculated as the difference between the current and voltage under illumination and the dark current and dark voltage respectively.

The power output characteristics of the PEC cells made using the photoelectrodes heat-treated at different temperatures is shown in Fig.4.19. From the figure, it is observed that the PEC output parameters, viz., open circuit voltage and short circuit current were found to increase for the electrodes heat-treated up to a temperature of 500°C. Photoelectrodes heat-treated at temperatures greater than this value exhibited lower open circuit voltage and short circuit current due to the reduction in thickness of the films as well as the slight change in stoichiometry, hence further studies were made only on the films heat-treated at 500°C.

The power output characteristics of the electrodes heat-treated at 500°C were studied at different intensities of illumination in the range 20 – 100 mWcm². It was observed that both \( V_{oc} \) and \( J_{sc} \) increased with increase of intensity (Fig.4.20). \( V_{oc} \) increased from 0.2V to 0.6V as the intensity increased from 20 – 100 mW cm². Beyond 80 mW cm² illumination, \( V_{oc} \) was found to saturate as is commonly observed in the case of photovoltaic cells and PEC cells, \( J_{sc} \) is found to increase with intensity of illumination.

It is observed that the \( J_{sc} \) increases from 4.0 mA cm² to 15.0 mA cm² as the intensity increased from 20 – 100 mW cm². A plot of \( \ln J_{sc} \) vs \( V_{oc} \) (Fig.4.21) yielded a straight line. Extrapolation of the line to the y-axis yields a \( J_0 \) value of
Fig 4.19- I-V characteristics of CdSe films heat-treated at different temperatures
a) 450°C
b) 475°C
c) 500°C
d) 525°C
e) 550°C
Fig 4.20- I-V characteristics of CdSe films heat-treated at 500°C in argon for different intensities of illumination

a) 20 mW cm$^{-2}$
b) 40 mW cm$^{-2}$
c) 80 mW cm$^{-2}$
d) 100 mW cm$^{-2}$
Fig 4.21- Plot of $\ln J_{sc}$ Vs $V_{oc}$ for CdSe films heat-treated at 500°C in argon
9.1 x 10^{-8} \text{ A cm}^{-2}, the ideality factor (n) was calculated from the slope of the straight line and it was found to be 1.85.

The effect of photo etching on the PEC performance was studied by shorting the photoelectrode and the graphite counter electrode under an illumination of 100 mW cm\(^{-2}\) in 1:100 HCl for different durations in the range 0–100s.

Both photocurrent and photovoltage are found to increase up to 80s photo etch, beyond which they begin to decrease (Fig.4.22). Photo etching leads to selective attack of surface states not accessible to chemical etchants. It is observed that during photo etching, the open circuit voltage and short circuit current increase from 0.5 V to 0.60 V and from 13.2 mA cm\(^{-2}\) to 16 mA cm\(^{-2}\) respectively for an intensity of 80 mW cm\(^{-2}\). The decrease in the voltage and current beyond 80s photo etching can be attributed to increase in surface area due to prolonged photoetching [160]. The power output characteristics (Fig.4.23) after 80s photo etching indicates a \(V_{oc}\) of 0.60V, \(J_{sc}\) of 16 mA cm\(^{-2}\), \(ff\) of 0.58 and \(\eta\) of 6.75% for 80 mW cm\(^{-2}\) illumination. The photovoltaic parameters of the electrodes with and without photo etching are shown in Table.4.3. The efficiency of the photoelectrodes are higher than the earlier reports [181].

Mott-Schottky plots (1/C\(^2\) vs V) were studied using 1M Na\(_2\)SO\(_4\) as the blocking electrolyte and a EG&G PARC impedance analyzer model 6310. The CdSe films heat-treated at different temperatures were used as working electrode, graphite was used as counter electrode and SCE was used as the reference electrode. The frequency was fixed at 1 kHz and the bias voltage was
Fig 4.22- Variation of $J_{sc}$ and $V_{oc}$ of CdSe films heat-treated at 500°C in argon for different durations of photoetching.
Fig 4.23- I-V characteristics of CdSe films heat-treated at 500°C in argon after photoetching
Table. 4.3
Photovoltaic parameters of CdSe photoelectrodes
(Intensity – 80 mW cm⁻²)

<table>
<thead>
<tr>
<th>Temp of heat treatment (°C)</th>
<th>( V_{oc} ) (V)</th>
<th>( J_{sc} ) (mA cm⁻²)</th>
<th>( ff )</th>
<th>( \eta ) (%)</th>
<th>( R_s ) (( \Omega ))</th>
<th>( R_{sh} ) (k( \Omega ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>450</td>
<td>0.351</td>
<td>7.2</td>
<td>0.491</td>
<td>1.52</td>
<td>33.2</td>
<td>2.55</td>
</tr>
<tr>
<td>475</td>
<td>0.375</td>
<td>9.2</td>
<td>0.650</td>
<td>2.64</td>
<td>16.2</td>
<td>2.58</td>
</tr>
<tr>
<td>500</td>
<td>0.500</td>
<td>13.6</td>
<td>0.545</td>
<td>4.39</td>
<td>5.0</td>
<td>1.59</td>
</tr>
<tr>
<td>525</td>
<td>0.476</td>
<td>11.0</td>
<td>0.500</td>
<td>3.90</td>
<td>10.6</td>
<td>2.00</td>
</tr>
<tr>
<td>550</td>
<td>0.440</td>
<td>11.9</td>
<td>0.504</td>
<td>3.54</td>
<td>12.6</td>
<td>1.60</td>
</tr>
<tr>
<td></td>
<td>0.600</td>
<td>16.0</td>
<td>0.580</td>
<td>6.75</td>
<td>5.0</td>
<td>2.59</td>
</tr>
<tr>
<td>(After photoetch)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

varied in the range –0.8 to +0.4V vs SCE, the value of C was estimated from the imaginary part of the impedance using the equation,

\[
C = \frac{1}{2\pi \cdot f \cdot Z}
\]

Fig.4.24 exhibits the Mott-Schottky plots for the films heat-treated at different temperatures in the range 450 - 550°C. The nature of the plot indicates n-type behaviour. Extrapolation of the plot to the voltage axis yields a \( V_{fb} \) of -1.2V(SCE). The value of carrier density from the slope of the plot yields a value
Fig 4.24-Mott-Schottky plot of CdSe electrode heat-treated at different temperatures in argon
a) 450°C
b) 500°C
c) 550°C
around $3.8 \times 10^{17}$ cm$^3$. This value agrees well with the carrier density obtained from Hall measurements.

Spectral response measurements were carried out on the photoelectrodes by using photo physics monochromator and a 250 W tungsten halogen lamp, 1 M polysulphide as electrolyte, graphite as counter electrode and the photoelectrode as the working electrode. The wavelength was varied in the range 400 – 900 nm and the photocurrent was noted at each wavelength.

The photocurrent value were used for the calculation of the quantum efficiency ($\phi$) using the well known equation [164],

$$\phi = 1240 \frac{J_{sc}}{\lambda \cdot P_{in}}$$

Where, $J_{sc}$ is the photocurrent, $\lambda$ is the wavelength of illumination, $P_{in}$ is the power of the light incident on the photoelectrode. Plot of $\phi$ vs $\lambda$ for the CdSe electrode heat-treated at 500°C is shown in Fig.4.25. The value of $\phi_{max}$ occurs at 0.72 $\mu$m corresponding to the band gap of 1.69 eV. This value matches well with the band gap value of 1.67 eV estimated from optical absorption measurements.
Fig 4.25-Variation of quantum efficiency with wavelength for CdSe electrode
heat-treated at 500°C in argon