Chapter - V

RESULTS ON CdSe$_x$ Te$_{1-x}$ FILMS
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5.1 Introduction

There is a recent spur for synthesizing and characterizing II-VI semiconducting materials by virtue of their proven potential capabilities in a variety of electronic and opto-electronic devices. It is worth mentioning that cadmium telluride and selenide have an important place in this respect and it is already documented and established that CdTe and CdSe form a solid solution throughout the entire composition range, the addition of CdTe to CdSe has resulted in very interesting properties related to photoelectrochemistry and opto-electronics.

5.2 Deposition of films

CdSe$_x$Te$_{1-x}$ films of 2.5 μm thickness were deposited on titanium and conducting glass substrates by the brush plating technique. Pretreatment of the Ti substrate was found to be an essential step to obtain very good adhesion. The titanium substrates were first degreased with trichloroethylene, then etched for 30s in a solution containing equal volumes of 2: 1 HNO$_3$ and 1:1 HCl and finally treated for 30s in 10 % by volume of NaOH. The plating bath consisted of 0.25M CdSO$_4$, 0.01 M SeO$_2$ and 0.01 M TeO$_2$. 3 ml of CdSO$_4$ solution was taken, the volume of SeO$_2$ and TeO$_2$ were suitably adjusted to obtain different compositions of CdSe$_x$Te$_{1-x}$ films (Table 5.1). For obtaining films of composition x = 0.5, 1.5 ml each of SeO$_2$ and 0.01 M TeO$_2$ were taken. The films were characterized for their structural, optical, electrical, morphological and photoelectrochemical properties.
### TABLE 5.1
Concentration of precursors taken for brush plating of CdSe$_x$Te$_{1-x}$ films
Concentration of CdSO$_4$ - 0.5M

<table>
<thead>
<tr>
<th>Concentration of SeO$_2$ (mM)</th>
<th>Concentration of TeO$_2$ (mM)</th>
</tr>
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<tbody>
<tr>
<td>0</td>
<td>50</td>
</tr>
<tr>
<td>5</td>
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</tr>
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<td>45</td>
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<td>50</td>
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</table>
5.3 Structural Characterization

The XRD patterns of the films of different composition are shown in the Fig.5.1 – 5.9. The peaks corresponding to (100), (002), (101), (102), (110), (103), (112), and (203) reflections were observed. Moreover, the intensity of the (100) peak was found to increase with increase of deposition temperature. The peaks were observed to shift to higher $2\theta$ values as the ‘x’ value increased from 0 to 1. All the samples exhibited hexagonal structure and the lattice parameters ‘a’ and ‘c’ were calculated using the standard relation,

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

‘a’ and ‘c’ values for CdSe and CdTe were taken from the ASTM data. The variation of lattice constants of cadmium selenide telluride solid solutions with composition is shown in Fig.5.10. A linear variation of the lattice constants with composition indicates that Vegard’s law is obeyed [136]. Generally the alloy structures depend on the composition and method of preparation. Conventional method of preparation like hot wall evaporation resulted in CdSeTe with mixture of cubic and hexagonal phases and conversion of cubic to hexagonal phase required an additional heat-treatment step. By this technique only hexagonal phase was obtained for all compositions in a single step.

5.4 EDAX Measurements

Composition analysis was done by EDAX study (Fig.5.11 – Fig.5.15) and the composition of the films is indicated in the Table 5.2. From the table, it is clear that the EDAX analysis data are almost similar to the theoretical composition expected from the starting materials. The data corresponding to CdL$_{\alpha}$, SeL$_{\alpha}$ and TeL$_{\alpha}$ lines were used for estimating the composition.
Fig. 5.1- XRD patterns of CdSe$_{0.1}$Te$_{0.9}$ films deposited at different deposition temperatures (a) 30 ºC (b) 50ºC (c) 80ºC
Fig. 5.2- XRD patterns of CdSe\textsubscript{0.2}Te\textsubscript{0.8} films deposited at different deposition temperatures (a) 30 °C (b) 50°C (c) 80°C
Fig. 5.3- XRD patterns of CdSe$_{0.3}$Te$_{0.7}$ films deposited at different deposition temperatures (a) 30°C (b) 50°C (c) 80°C
Fig. 5.4- XRD patterns of CdSe$_{0.4}$Te$_{0.6}$ films deposited at different deposition temperatures (a) 30 °C (b) 50°C (c) 80°C
Fig. 5.5- XRD patterns of CdSe$_{0.5}$Te$_{0.5}$ films deposited at different deposition temperatures (a) 30 °C (b) 50 °C (c) 80 °C
Fig. 5.6- XRD patterns of CdSe$_{0.6}$Te$_{0.4}$ films deposited at different deposition temperatures (a) 30 °C (b) 50°C (c) 80°C
Fig. 5.7 - XRD patterns of CdSe$_{0.7}$Te$_{0.3}$ films deposited at different deposition temperatures (a) 30 °C (b) 50°C (c) 80°C
Fig. 5.8- XRD patterns of CdSe$_{0.8}$Te$_{0.2}$ films deposited at different deposition temperatures (a) 30 °C (b) 50 °C (c) 80 °C
Fig. 5.9 - XRD patterns of CdSe$_{0.9}$Te$_{0.1}$ films deposited at different deposition temperatures (a) 30 °C (b) 50 °C (c) 80 °C
Fig. 5.10 – Variation of lattice parameters with composition.
Fig. 5.11 – EDAX spectrum of CdSe$_{0.1}$Te$_{0.9}$ films deposited at 80°C
Fig. 5.12 – EDAX spectrum of CdSe$_{0.3}$Te$_{0.7}$ films deposited at 80°C
Fig.5.13 – EDAX spectrum of CdSe$_{0.5}$Te$_{0.5}$ films deposited at 80°C
Fig. 5.14 – EDAX spectrum of CdSe$_{0.7}$Te$_{0.2}$ films deposited at 80°C
Fig. 5.15 – EDAX spectrum of CdSe$_{0.9}$Te$_{0.1}$ films deposited at 80°C
**TABLE 5.2**

Composition of CdSe$_x$Te$_{1-x}$ films

<table>
<thead>
<tr>
<th>Starting Composition</th>
<th>EDAX values</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdSe$<em>{0.83}$Te$</em>{0.07}$</td>
<td>CdSe$<em>{0.94}$Te$</em>{0.06}$</td>
</tr>
<tr>
<td>CdSe$<em>{0.86}$Te$</em>{0.14}$</td>
<td>CdSe$<em>{0.85}$Te$</em>{0.15}$</td>
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<tr>
<td>CdSe$<em>{0.65}$Te$</em>{0.35}$</td>
<td>CdSe$<em>{0.66}$Te$</em>{0.34}$</td>
</tr>
<tr>
<td>CdSe$<em>{0.48}$Te$</em>{0.52}$</td>
<td>CdSe$<em>{0.49}$Te$</em>{0.51}$</td>
</tr>
<tr>
<td>CdSe$<em>{0.34}$Te$</em>{0.66}$</td>
<td>CdSe$<em>{0.36}$Te$</em>{0.64}$</td>
</tr>
<tr>
<td>CdSe$<em>{0.31}$Te$</em>{0.69}$</td>
<td>CdSe$<em>{0.30}$Te$</em>{0.70}$</td>
</tr>
</tbody>
</table>
5.5 Optical absorption studies

Optical absorbance of the films was measured using the films deposited on conducting glass substrates. Fig. 5.16 shows the absorbance spectra of the films of different composition deposited at 80˚C. The bandgap of the films were estimated from the Tauc’s plot (Fig. 5.17). The variation of band gap with composition is shown in Fig. 5.18.

5.6 XPS Studies

Fig. 5.19 – 5.27 show the XPS spectra of Cd(3d$_{5/2}$ and 3d$_{3/2}$) and Se(3d$_{5/2}$ and 3d$_{3/2}$) and Te(3d$_{5/2}$ and 3d$_{3/2}$) levels for the films of different composition. As observed from the figures, the Cd(3d$_{5/2}$ and 3d$_{3/2}$) appeared at 405.0 and 411.7 eV respectively; the Se(3d$_{5/2}$ and 3d$_{3/2}$) appeared at 53.9 and 59.2 eV respectively, and the Te(3d$_{5/2}$ and 3d$_{3/2}$) appeared at 576.2 eV and 586.1 eV respectively. Atomic concentration measurements were made on the films of different composition selecting suitable sensitivity factors for Cd, Te and Se. It was observed that these concentrations agreed well with the concentration values estimated from EDAX measurements. Further, as the ‘x’ value increased, the area under the peak for Se (3d$_{5/2}$) also increased and the area under the Te(3d$_{5/2}$) decreased.

5.7 Electrical Properties

Hall measurements were made on the films adopting the procedure reported earlier [108]. In this method, the CdSeTe layers of different composition are mechanically transferred from the conducting substrate onto a non-conductive epoxy resin without the formation of cracks [109, 110].
Fig. 5.16- Optical absorbance spectra of CdSe$_x$Te$_{1-x}$ films deposited at 80°C
(a) x = 0.9 (b) x = 0.8 (c) x = 0.7 (d) x = 0.6 (e) x = 0.5 (f) x = 0.4 (g) x = 0.3
(h) x = 0.2 (i) x = 0.1
Fig. 5.17 - Tauc's plot CdSe$_x$Te$_{1-x}$ films deposited at 80°C

(a) $x = 0.9$ (b) $x = 0.8$ (c) $x = 0.7$ (d) $x = 0.6$ (e) $x = 0.5$ (f) $x = 0.4$ (g) $x = 0.3$

(h) $x = 0.2$ (i) $x = 0.1$
Fig.5.18 - Variation of Band gap with Composition
Fig.5.19 – XPS spectra of CdSe$_{0.1}$Te$_{0.9}$ films deposited at 80°C
Fig. 5.20 – XPS spectra of CdSe$_{0.2}$Te$_{0.8}$ films deposited at 80°C
Fig. 5.21 – XPS spectra of CdSe$_{0.3}$Te$_{0.7}$ films deposited at 80°C
Fig.5.22 – XPS spectra of CdSe$_{0.4}$Te$_{0.6}$ films deposited at 80°C
Fig. 5.23 – XPS spectra of CdSe<sub>0.5</sub>Te<sub>0.5</sub> films deposited at 80°C
Fig. 5.24 – XPS spectra of CdSe$_{0.6}$Te$_{0.4}$ films deposited at 80°C
Fig. 5.25 – XPS spectra of CdSe$_{0.7}$Te$_{0.3}$ films deposited at 80°C
Fig. 5.26 – XPS spectra of CdSe$_{0.8}$Te$_{0.2}$ films deposited at 80°C
Fig. 5.27 – XPS spectra of CdSe$_{0.9}$Te$_{0.1}$ films deposited at 80°C
The electrical properties of the CdSeTe layers were examined at room temperature by resistivity and Hall measurements using Van der Pauw method. The resistivity ($\rho$) of CdSe$_x$Te$_{1-x}$ films was calculated using the equation 5. The influence of composition on the resistivity of the films is depicted in Fig.5.28. Only the results on the films annealed at 550°C are presented, since they have exhibited maximum photoconductivity. The magnitude of the resistivity varies from 2.10 ohm cm to 31.0 ohm cm as the ‘x’ value increases from 0 to 1. The increase in resistance may be associated with increase in tellurium/selenium vacancies (due to increase of depth of donor level associated with the tellurium/selenium vacancy).

Fig.5.29 shows the variation of Hall mobility with composition. The Hall mobility was determined by using the equation 6. It was observed from the figure that the Hall mobility decreases as the composition increases; this may be associated with the scattering at the chalcogen vacancies.

Fig.5.30 shows the variation of carrier concentration calculated using equation 8, with composition. It is evident from the figure that the carrier concentration decreases as the composition of the films shifts towards CdSe side. The carrier concentration is found to increase from $2 \times 10^{17}$ cm$^{-3}$ – $1.4 \times 10^{18}$ cm$^{-3}$ as ‘x’ value increases from 0 to 1.

5.8 Photoconductivity studies

Photoconductivity studies were made on the films transferred to non-conducting epoxy after doping/heat treatment. In order to obtain very high photosensitivity, the sintering temperature was varied in the range of
Fig. 5.28– Variation of resistivity with composition for CdSe$_x$Te$_{1-x}$ films.
Fig. 5.29 – Variation of mobility with composition for CdSe$_x$Te$_{1-x}$ films
Fig. 5.30 – Variation of carrier concentration with composition for CdSe$_x$Te$_{1-x}$ films
500 - 600°C. It was observed that post heat treatment temperature had a profound influence on the sensitivity and stability of the photoconductive cells.

It is observed that as the post heat treatment temperature increases, the photosensitivity also increases. Higher heat treatment temperatures lead to rapid decrease in light resistance, while at low temperature, instability of the cell is observed. Appropriate temperature is necessary to control the diffusion rates of impurities and mobile defects so that optimum sensitivity and reasonable stability are obtained, besides useful light resistance. It is observed that a post heat treatment temperature of 550°C results in high photosensitivity as well as low light resistance. The results of photosensitivity of the films of different compositions are shown in Fig.5.31a – 5.31e.

Duration of post heat treatment has a significant role to play in the process of obtaining useful photoconductive cells. This time has been varied from 10 – 30 minutes. As the post heat treatment time is gradually increased, significant lowering of light resistance is observed while practically no pronounced increase in dark resistance takes place. For 15 minutes heat treatment, the dark resistance slightly increases while the light resistance attains a minimum. The fall in light resistance with heat treatment time, may also be attributed to the removal of grain boundaries due to optimum recrystallization. Longer heat treatment time may result in partial evaporation of the film with consequent increase in the dark as well as the light resistance. In other words, heat treatment time, when other parameters are fixed, decides the optimum transport of dopants, besides removal of grain boundaries.
Fig. 5.31 – Variation of photosensitivity with illumination for CdSe$_x$Te$_{1-x}$ films of different composition (a) $x = 0.2$ (b) $x = 0.4$ (c) $x = 0.6$ (d) $x = 0.8$ (e) $x = 0.9$
5.9 Effect of doping

To study the effect of copper on the photoconductive properties, copper concentration was varied in the range 100 – 500 ppm, keeping other parameters constant. The density of copper states introduced at the forbidden gap decides the photoconductive properties as the copper levels are the sensitizing centers in cadmium chalcogenides. Since it has been reported [122] that cadmium selenide shows a more sensitive behaviour to copper concentration than does cadmium telluride, it is felt that a study of the behaviour of copper in these solid solutions would be interesting. Hence, variation of copper content is studied for all the compositions. In all these studies no donors are deliberately added to the compositions. The maximum rate of change of dark current with acceptor concentration in single crystals [137] of cadmium sulphide occurs when the acceptor and donor concentrations are equal. It is assumed that the change in copper concentration causes no other changes, like vacancy concentration, in the material and that a constant fraction of the added copper enters the lattice as an electrically active species. The first assumption is probably valid [138]. However, a Cu$^+$ to Cu$^{2+}$ equilibrium probably exists and further that the equilibrium may be assumed to be constant for identical processing conditions. The properties of the resulting photoconductors are strongly dependent on copper concentration. As the copper concentration is increased, the dark resistance starts rising rapidly. At 400 ppm copper, the rate of increase of dark resistance is maximum and the light resistance
reaches a minimum. Further increase in copper concentration, raises both
dark as well as light resistances and the usefulness of the photocell
decreases, as the light resistance starts increasing although the
photosensitivity remains more or less constant. As the selenium concentration
increases, the rate of change of dark resistivity occurs at 300 ppm copper
instead of at 400 ppm due to the structural defects like cation vacancies which
are acting as compensated acceptors [139]. The lower activation energy of
the copper centers in CdSe might play some role, these copper centres being
more active as sensitizing centers in CdSe rich lattice [140]. The results are
shown in Fig.5.32 for films of different composition doped with 400 ppm
copper.

A discussion on the role of copper in CdSe type photoconductors
requires an understanding of the basic sensitization mechanism. Unsensitized
CdSe or CdTe is an insulator and has a considerable density of Type I
centers. They aid fast recombination of photogenerated carriers with the result
no appreciable sensitivity is observed.

When donor levels are incorporated, both dark and light resistances
fall, as more free carriers are now available.

The variation of photocurrent with excitation intensity in cadmium
sulphide type photoconductors is interesting and is of fundamental importance
in the operation of these photo resistors in devices. As discussed earlier, the
large photosensitivity associated with these materials arises due to the
presence of compensated acceptors, which act as sensitizing centers. As the
excitation intensity is increased at a fixed temperature, these centers become
Fig. 5.32 – Variation of photosensitivity with illumination for CdSe$_x$Te$_{1-x}$ films doped with 400 ppm copper

(a) $x = 0.2$ (b) $x = 0.4$ (c) $x = 0.6$ (d) $x = 0.8$ (e) $x = 0.9$
more active and photosensitivity sharply rises at some region of excitation. As the temperature is increased under a given excitation intensity, sensitivity is reported to fall [141].

5.10 Spectral distribution of photoconductivity

The spectral distributions of sensitivity of the cells of different composition are shown in Fig.5.33 and Fig.5.34. Pure cadmium telluride crystals have a peak response at 850 nm, while pure CdSe has a peak response at 720 nm [142]. This response is essentially caused by intrinsic excitation. Lattice defects, which may be present in the crystals, introduce levels in the forbidden gap, which require less energy than excitation across the band gap. Consequently, in crystals with such defects, the peak response may also be attributed to the presence of incorporated impurities like chloride or copper or the combined effects of copper and chloride centers [143]. Further, there is a tendency for sintered layers to have more response in the red and infrared due to copper to chloride ion ratio being more at the surface than in the bulk [144]. This may arise due to higher ratio of copper to chloride type centers at the surface of the sintered layer, than in the bulk, owing to the lower chloride concentration existing at the surface. Accompanying this increase is the relative number of copper type centers with respect to chloride type centers, there will be a darkening in the body colour of the surface. This body colour shift results in a more efficient absorption of longer wavelength, which combined with the greater effectiveness of activation due to higher copper center concentration.
Fig. 5.33 - Spectral response of CdSe$_x$Te$_{1-x}$ films of different composition. 

Composition:
- (a) $x = 0.1$
- (b) $x = 0.2$
- (c) $x = 0.3$
- (d) $x = 0.4$
- (e) $x = 0.5$
Fig. 5.34 – Spectral response of $\text{CdSe}_x\text{Te}_{1-x}$ films of different composition (a) $x = 0.7$ (b) $x = 0.8$ (c) $x = 0.9$
The darkening of the body colour associated with increasing copper concentration at the surface primarily may introduce the possibility of affecting the position of the spectral response peak by a simple filtering action that is, modifying the composition of the activating radiation reaching the portion of the layer involved in photoconduction. The presence of chemisorbed oxygen, on the films in particular, which act as an acceptor may also contribute to such shifts [145].

It is clear from the graphs that the wavelength of peak response and also the edge gets progressively shifted to longer wavelengths as the telluride content is increased. The linear increase in the wavelength of peak response is due to the solid solution formation with progressively increasing cadmium telluride content. Similar observations have been reported earlier [146].

The broad spectral response of these sintered layers can be made use of in device fabrication, where composite illumination over a range happens to be the activating source.

5.11 Aging Studies

The variation of photosensitivity of the undoped and doped cells of different composition with time was studied. The unencapsulated cells which are kept up to 275 days indicated a constant value of photosensitivity for both the doped and undoped cells. After keeping the cells for 275 days, the photosensitivity decreased. This behaviour may be due to the effect of atmospheric oxygen introducing acceptor levels, since the cells are
unencapsulated. For the doped cells, both copper and oxygen introduce acceptor levels, causing a decrease of photosensitivity beyond 275 days.

5.12 I-V Characteristics

The conduction mechanism in semiconductors can be understood by analyzing current voltage plots (I-V 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. As a representative case the I-V characteristics of CdSe$_{0.5}$Te$_{0.5}$ films both undoped and doped are shown in Fig.5.35 and Fig.5.36 respectively. In all the plots, a relation of the type $V \propto I^n$ is followed. The plots are linear upto 240 V, beyond which non linear behaviour is observed. The plots can be explained in a fashion similar to that for CdSe cells.

5.13 AC photoconductivity studies

AC photoconductivity studies were made on the films of different composition transferred to the epoxy using a chopper of frequency of 90 Hz.

The AC photosensitivity of the films was calculated using the relation,

$$\%S = (\Delta R_c / R_c) \times 100 = \left( E - \frac{\Delta V}{V_1} (E - V_2) \right) \times 100$$

where $\Delta R_c$ is the change in resistance, $R_c$ is the dark resistance, $E$ is the applied bias, $V_1$ is the load voltage under dark conditions and $V_2$ is the load voltage on illumination.

$$V_2 = (V_1 + \Delta V), \Delta V$$

is the signal voltage

The AC photosensitivity values are indicated in Table.5.3.
Fig. 5.35 – I-V characteristics of CdSe$_{0.5}$ Te$_{1-0.5}$ film
Fig. 5.36 – I-V characteristics of CdSe$_{0.5}$Te$_{0.5}$ films doped with 400 ppm copper
### TABLE 5.3
AC photosensitivity of films of different composition

Applied bias = 120V  
Intensity = 5000 lx

<table>
<thead>
<tr>
<th>Composition</th>
<th>$S = \Delta R_c / R_c$ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdSe$<em>{0.1}$Te$</em>{0.9}$</td>
<td>26.00</td>
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<tr>
<td>CdSe$<em>{0.33}$Te$</em>{0.67}$</td>
<td>35.55</td>
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<tr>
<td>CdSe$<em>{0.52}$Te$</em>{0.48}$</td>
<td>47.87</td>
</tr>
<tr>
<td>CdSe$<em>{0.72}$Te$</em>{0.28}$</td>
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</tr>
<tr>
<td>CdSe$<em>{0.85}$Te$</em>{0.15}$</td>
<td>95.64</td>
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</tbody>
</table>
5.14 Morphological studies

Fig. 5.37 shows the AFM images (1 x 1µm) of the CdSe$_x$Te$_{1-x}$ films of different composition deposited at 80°C. These images show that the grain size of the films increase as the x value increases from 0.1 to 0.9. Investigation of the AFM images demonstrates that for low ‘x’ values, the grain sizes are small (Fig. 5.37(a)). By increasing the concentration of Se, these small grains gradually combine and make bigger grains (Fig. 5.37(b)). When the Se concentration was increased further, the grains become bigger (Fig. 5.37(c) and (d)). The roughness of the films also increases from 50 to 150Å with Se concentration.

5.15 Photoelectrochemical measurements

Photoelectrochemical (PEC) cells were prepared using the films of different composition deposited on titanium substrates. The films were lacquered with polystyrene in order to stop off the metal substrate portion from being exposed to the redox electrolyte. These films were used as the working electrode. The electrolyte was 1 M 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 mWcm$^{-2}$. The photocurrent and photovoltage were measured by HIL digital multimeters.
Fig. 5.37 – Atomic force micrographs of CdSe$_x$Te$_{1-x}$ films of different composition deposited at 80°C (a) $x = 0.2$ (b) $x = 0.4$ (c) $x = 0.6$ (d) $x = 0.8$
The CdSe\textsubscript{x}Te\textsubscript{1-x} electrodes of different composition were dipped in the electrolyte and allowed to attain equilibrium under dark conditions for about 10 min. The dark current and 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 photovoltage were calculated as the difference between the current and voltage under illumination and the dark current and voltage respectively.

The power output characteristics were obtained for the PEC cells using the photoelectrodes of different composition and heat treated at different temperatures. Fig.5.38 – Fig.5.46 show the load characteristics of the electrodes of different composition heat treated at different temperatures. It was observed that the PEC output was high for electrodes heated at 525°C irrespective of composition. Photoelectrodes heat treated beyond 525°C exhibited lower \( V_{oc} \) and \( J_{sc} \) values due to the change in concentration of tellurium and selenium vacancies as well as reduction in thickness. Amongst the electrodes of different compositions, it was observed that the overall output started to increase as the selenium content increased in the material. Electrodes with the composition CdSe\textsubscript{0.6} Te\textsubscript{0.4} exhibited the maximum PEC output; hence, further studies were made on the films of this composition. The load characteristics for the films of this composition are shown in Fig.5.47. This value is lower than the reported value of 0.75 V for electrodes prepared by sintering mixture of CdTe and CdSe [147], but the \( J_{sc} \) value for this composition is higher. The value of \( J_{sc} \) is higher than that reported earlier for
Fig.5.38 – Load characteristics of CdSe_{0.1}Te_{0.9} films heat treated in argon at different temperatures (a) 450°C (b) 500°C (c) 525°C (d) 550°C.
Fig. 5.39 – Load characteristics of CdSe$_{0.2}$Te$_{0.8}$ films heat treated in argon atmosphere at different temperatures:
(a) 450°C, (b) 500°C, (c) 525°C, (d) 550°C
Fig. 5.40 - Load characteristics of CdSe$_{0.3}$Te$_{0.7}$ films heat treated in argon atmosphere at different temperatures (a) 450°C (b) 500°C (c) 525°C (d) 550°C
Fig.5.41 - Load characteristics of CdSe$_{0.4}$Te$_{0.6}$ films heat treated in argon atmosphere at different temperatures
(a) 450°C (b) 500°C (c) 525°C (d) 550°C
Fig. 5.42 - Load characteristics of CdSe$_{0.5}$Te$_{0.5}$ films heat treated in argon atmosphere at different temperatures
(a) 450°C (b) 500°C (c) 525°C (d) 550°C
Fig. 5.43 - Load characteristics of CdSe$_{0.6}$Te$_{0.4}$ films heat treated in argon atmosphere at different temperatures

(a) 450°C (b) 500°C (c) 525°C (d) 550°C
Fig. 5.44 - Load characteristics of CdSe$_{0.7}$Te$_{0.3}$ films heat treated in argon atmosphere at different temperatures:
(a) 450°C (b) 500°C (c) 525°C (d) 550°C
Fig. 5.45 - Load characteristics of CdSe$_{0.8}$Te$_{0.2}$ films heat treated in argon atmosphere at different temperatures
(a) 450°C (b) 500°C (c) 525°C (d) 550°C
Fig. 5.46 - Load characteristics of CdSe$_{0.9}$ Te$_{0.1}$ films heat treated in argon atmosphere at different temperatures (a) 450°C (b) 500°C (c) 525°C (d) 550°C
Fig. 5.47 - Load characteristics of CdSe$_{0.6}$Te$_{0.4}$ films heat treated in argon atmosphere at 525°C and at different intensities

- (a) 20 mW cm$^{-2}$
- (b) 40 mW cm$^{-2}$
- (c) 60 mW cm$^{-2}$
- (d) 80 mW cm$^{-2}$
- (e) 100 mW cm$^{-2}$
the brush plated electrode [46]. At intensity values beyond 80 mWcm$^{-2}$, $V_{oc}$ was found to saturate as is commonly observed for photovoltaic and PEC cells, $J_{sc}$ was found to increase with increase in intensity of illumination. Since the electrode of composition CdSe$_{0.6}$Te$_{0.4}$ showed maximum voltage output, further studies were made on the electrodes of this composition. A plot of ln$J_{sc}$ versus $V_{oc}$ (Fig.5.48) yielded a straight line. Extrapolation of the line to the $y$-axis yields a $J_0$ value of $10^{-7}$ A cm$^{-2}$, the ideality factor was calculated from the slope of the straight line and it was found to be 1.88. The effect of photoetching on the PEC performance was studied by shorting the CdSe$_{0.6}$Te$_{0.4}$ 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 – 100 s. Both the photocurrent and photovoltage are found to increase up to 80s photoetch, beyond which they begin to decrease (Fig.5.49). Photoetching leads to selective attack of surface defects not accessible to chemical etchants. It is observed that during photoetching the $V_{oc}$ increased from 0.675 V to 0.72 V and $J_{sc}$ increased from 12.5 mA cm$^{-2}$ to 14.5 mA cm$^{-2}$. The decrease in photocurrent and photovoltage beyond 80s photoetching can be attributed to separation of grain boundaries due to prolonged photoetching [130]. The power output characteristics (Fig.5.50) after 80s photoetching indicates a $V_{oc}$ of 0.72 V, $J_{sc}$ of 14.5 mA cm$^{-2}$, ff of 0.72, $\eta$ of 7.81% for 80 mWcm$^{-2}$ illumination. The photovoltaic parameters of the electrodes of different composition are shown in Table 5.4. The short circuit current density and efficiency of the photoelectrodes are nearly equal to the earlier reports.
Fig. 5.48 – \( \ln J_{sc} \) versus \( V_{oc} \) plot for \( \text{CdSe}_{0.6}\text{Te}_{0.4} \) films heat treated in argon atmosphere at 525°C.
Fig. 5.49 – Effect of photoetching time on open circuit voltage and short circuit current density for Cd$\text{Se}_{0.6}\text{Te}_{0.4}$ films heat treated in argon atmosphere at 525°C.
Fig. 5.50 – Load characteristics of CdSe$_{0.6}$Te$_{0.4}$ films heat treated in argon atmosphere at 525°C after photoetching.
TABLE 5.4
Photovoltaic parameters of CdSe$_x$Te$_{1-x}$ electrodes
(Intensity of illumination : 80 mW cm$^{-2}$)

<table>
<thead>
<tr>
<th>Comp</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>$x = 0.1$</td>
<td>0.47</td>
<td>4.0</td>
<td>0.60</td>
<td>1.42</td>
<td>30</td>
<td>1.50</td>
</tr>
<tr>
<td>$x = 0.2$</td>
<td>0.48</td>
<td>5.0</td>
<td>0.48</td>
<td>1.43</td>
<td>25</td>
<td>1.50</td>
</tr>
<tr>
<td>$x = 0.3$</td>
<td>0.50</td>
<td>6.3</td>
<td>0.49</td>
<td>2.07</td>
<td>22</td>
<td>1.50</td>
</tr>
<tr>
<td>$x = 0.4$</td>
<td>0.51</td>
<td>7.9</td>
<td>0.62</td>
<td>2.65</td>
<td>18</td>
<td>1.5</td>
</tr>
<tr>
<td>$x = 0.5$</td>
<td>0.51</td>
<td>9.0</td>
<td>0.65</td>
<td>3.75</td>
<td>15</td>
<td>1.80</td>
</tr>
<tr>
<td>$x = 0.6$</td>
<td>0.69</td>
<td>12.3</td>
<td>0.66</td>
<td>7.05</td>
<td>12</td>
<td>2.25</td>
</tr>
<tr>
<td>$x = 0.7$</td>
<td>0.63</td>
<td>11.3</td>
<td>0.68</td>
<td>7.00</td>
<td>14</td>
<td>2.10</td>
</tr>
<tr>
<td>$x = 0.8$</td>
<td>0.58</td>
<td>10.5</td>
<td>0.58</td>
<td>5.64</td>
<td>15</td>
<td>1.80</td>
</tr>
<tr>
<td>$x = 0.9$</td>
<td>0.52</td>
<td>9.0</td>
<td>0.54</td>
<td>3.18</td>
<td>18</td>
<td>2.00</td>
</tr>
<tr>
<td>$x = 0.6$ (After photoetch)</td>
<td>0.73</td>
<td>14.4</td>
<td>0.63</td>
<td>8.25</td>
<td>9</td>
<td>2.50</td>
</tr>
</tbody>
</table>
Mott Schottky plots were studied using 1M Na$_2$SO$_4$ as the blocking electrolyte and a EG&G PARC impedance analyzer model 6310. The CdSe$_x$Te$_{1-x}$ films of different compositions were used as the working electrode and SCE was used as the reference electrode. The frequency was fixed at 1 kHz and the bias voltage was varied in the range –0.8 to +0.4 V (SCE), the value of C was estimated from the imaginary part of the impedance using the relation,

$$C = \frac{1}{2\pi fZ}$$

Fig.5.51 exhibits the Mott Schottky plots for the films of different composition and heat treated at 525°C. The nature of the plot indicates n-type behaviour. Extrapolation of the plots to the voltage axis yields $V_{fb}$ values in the range -1.1 to -1.2 V(SCE). The value of $N_D$ estimated from the slope of the plots yields value in the range of $10^{17}$ cm$^{-3}$. These values are in agreement with the carrier density values obtained from Hall measurements. Amongst the electrodes, the electrodes with composition CdSe$_{0.6}$Te$_{0.4}$ exhibited maximum $V_{fb}$, hence the higher open circuit voltage for the above electrode.

Spectral response measurements were carried out on the photoelectrodes using a photophysics monochromator and a 250 W tungsten halogen lamp, 1M polysulphide was used as the electrolyte, graphite as counter electrode and the photoelectrodes as working electrodes. The wavelength was varied in the range 400 – 900 nm and the photocurrent was noted at each wavelength.
Fig. 5.51 – Mott Schottky plot for CdSe$_x$Te$_{1-x}$ films for different composition heat treated in argon atmosphere at 525°C

(a) CdSe$_{0.2}$Te$_{0.8}$ (b) CdSe$_{0.4}$Te$_{0.6}$ (c) CdSe$_{0.6}$Te$_{0.4}$

(d) CdSe$_{0.8}$Te$_{0.2}$ (e) CdSe$_{0.9}$Te$_{0.1}$
Plot of $J_{ph}$ vs $\lambda$ for the CdSe$_x$Te$_{1-x}$ electrodes of different composition, heat treated at 525°C is shown in Fig.5.52 – Fig.5.55. The value of $J_{ph(max)}$ occurs at the wavelength value corresponding to the band gap of each composition. The values match very well with the band gap values obtained from the optical absorption measurements.

As in the case of CdTe or CdSe, the electronic mechanism in CdSe$_x$Te$_{1-x}$ films are associated with the lattice Se and Te vacancies ($V_{Te}$ & $V_{Se}$), which are known to behave both as shallow donor centers and deep electron traps [148]. Tellurium and selenium vacancies are generated as a result of partial electrode evaporation during the annealing step. The higher the annealing temperature, the greater is the selenium and tellurium vacancy concentrations. The minority carrier diffusion length decreases due to the vacancies of tellurium and selenium behaving as recombination centers [148]. For an efficient control of the vacancy concentration, the annealing treatment has to be performed in an inert atmosphere (eg. He) contains a few ppm of oxygen in order to facilitate oxygen chemisorption. Chemisorbed oxygen behaves as an efficient electron acceptor [149] able to compensate the excess concentration of free electrons, which results in an efficient control of carrier density. This effect was evidenced, after annealing, when the electrode was heated in hydrogen atmosphere at 200°C. The oxygen is desorbed, electrons are freed and the carrier density increases.

The results on the photoelectrochemical investigation can be explained on the above basis. Higher values of the open circuit voltage were observed
Fig. 5.52 – Variation of $J_{ph}$ vs wavelength plots of CdSe$_x$Te$_{1-x}$ films deposited at 80°C (a) $x = 0.1$ (b) $x = 0.2$ (c) $x = 0.3$
Fig. 5.53 – Variation of $J_{ph}$ vs wavelength plots of CdSe$_x$Te$_{1-x}$ films deposited at 80°C (a) $x = 0.4$ (b) $x = 0.5$
Fig. 5.54 – Variation of $J_{\text{ph}}$ vs wavelength plots of $\text{CdSe}_x\text{Te}_{1-x}$ films deposited at 80°C (a) $x = 0.6$ (b) $x = 0.7$
Fig.5.55 – Variation of $J_{ph}$ vs wavelength plots of CdSe$_x$Te$_{1-x}$ films deposited at 80°C (a) $x = 0.8$ (b) $x = 0.9$
as the selenium concentration increases due to the larger value of the flat band potential. Maximum value of open circuit voltage was obtained for the composition \( \text{CdSe}_{0.8}\text{Te}_{0.2} \). As the selenium concentration increases, though the \( V_{oc} \) is less, the short circuit current is higher owing to the lower resistivity value compared to CdTe.

Large area \( \text{CdSe}_{0.6}\text{Te}_{0.4} \) photoelectrodes were deposited by the brush plating technique and the results of \( V_{oc} \) and \( J_{sc} \) under sunlight illumination is indicated for the photoelectrodes of different area in Table 5.5.
TABLE 5.5
Photo output of CdSe$_{0.6}$Te$_{0.4}$ photoelectrodes of different area under sunlight illumination (100 mW cm$^{-2}$)

<table>
<thead>
<tr>
<th>Area of photoelectrode(cm$^2$)</th>
<th>$V_{oc}$(mV)</th>
<th>$J_{sc}$(mA cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.69</td>
<td>12.3</td>
</tr>
<tr>
<td>5.0</td>
<td>0.65</td>
<td>7.0</td>
</tr>
<tr>
<td>10.0</td>
<td>0.67</td>
<td>5.0</td>
</tr>
<tr>
<td>25.0</td>
<td>0.63</td>
<td>4.5</td>
</tr>
<tr>
<td>50.0</td>
<td>0.67</td>
<td>4.0</td>
</tr>
<tr>
<td>100.0</td>
<td>0.68</td>
<td>3.0</td>
</tr>
</tbody>
</table>