CHAPTER VII
PHOTOCONDUCTION STUDIES

7.1 Introduction

CdSe_xTe_{1-x} thin films are used in many opto-electronic device applications especially for solar cells due to their special characteristics. Photoconductivity measurements on CdSe_xTe_{1-x} thin films provide useful information on electronic properties, which are essential for device applications. When a semiconductor is illuminated with light of an appropriate wavelength, often an increase in its conductivity is observed and this phenomenon is known as photoconductivity. The effect of illumination is to increase the number of mobile charge carriers in the substance. Photoconductivity includes several successive and simultaneous mechanisms such as optical absorption, hot carrier relaxation, charge carrier transport and recombination. Photoconductivity effects have obvious applications in the detection and measurement of light in the whole electromagnetic spectrum. The absorption of light in a semiconductor leads to

a) photoionization of the semiconductor atom. This is excitation of valence electrons to conduction band
b) photoionization of impurity atoms. This leads to the transition of an electron from donor level to conduction band or from valence band to acceptor level and
c) excitation of electrons from valence band to imperfection level.

The phenomenon of photoconductivity has been described in detail by many workers [1-5]. Cd(Se,Te) alloy layers have been electroplated onto titanium substrates by Hodes et al[6]. They have reported that analysis of photocurrent in the long-wavelength cut-off region yielded a direct band gap of 1.39 eV (about 890 nm). By studying the dependence of photo current on wavelength or energy (hv), Mirovsky et al[7] have determined the band gap of electroplated CdSe₀.65Te₀.35 electrodes. They have observed a band gap of 1.46 eV.

Belyaev et al[8] have studied the photoconductive properties of CdSeₓTe₁₋ₓ crystals and have reported that for weak fields (< 100 V) the photocurrent is proportional to applied voltage. They have measured the photoresistivity as 10⁴ - 10⁶ Ω cm. Ermolovich et al[9] have studied the composition dependence of the spectral position of photoconductivity maximum in CdSeₓTe₁₋ₓ films prepared by vacuum evaporation. The
photoconductivity maximum corresponds to the band gap of the material and it has been observed that the band gap exhibited a minimum corresponding to a composition of \( x = 0.6 \).

Photosensitive sintered films of \( \text{CdSe}_x \text{Te}_{1-x} \) solid solutions have been prepared by Budyonnaya et al[10]. They have reported that the spectral distribution of photocurrent exhibits a peak corresponding to the band gap. The obtained band gap has been found to vary non-linearly with composition exhibiting a minimum for the composition of \( x = 0.3 \). They have observed that films with a CdSe base show higher photoconductivity values than those with a CdTe base. At \( x = 0.3 \), they found a sharp transition from the high photosensitivity values typical of CdSe to the low values of CdTe. Relative photoconductivity approaching \( 10^6 \) for an illumination of 550 Lx has been reported for \( \text{CdSe}_{0.9} \text{Te}_{0.1} \) layers grown from compacted plates of CdSe-CdTe-Cr_2O_3 powders by Kabassanova et al[11].

CdTe-CdSe films have been prepared using a quasi-closed space arrangement by Izakson et al[12]. They have reported that the region of spectral sensitivity of the deposited layers extends from 400 to 950 nm with the position in the maximum ranging from 720 to 860 nm. They have also
observed that the studies revealed that the forbidden band contains numerous energy levels, the complex distribution of which varies very markedly with the solid solution composition.

CdSe$_x$Te$_{1-x}$ films have been prepared using electrodeposition technique by Ravichandran et al.[13]. They have observed the photocurrent to increase with applied voltage. The spectral dependence of photocurrent exhibited a maximum at 745 nm, 825 nm and 860 nm for tellurium concentration of 0.2, 0.3 and 0.4 respectively. The photoconductive properties of CdSe$_x$Te$_{1-x}$ films prepared by spraying an aqueous suspension of mixtures onto ceramic substrates have been studied by Ermolovich et al.[14]. They have reported that the photoconductivity spectra showed one intrinsic peak corresponding to the band-to-band transition. The position of the peak has been found to vary non-monotonically with composition.

Hodes [15] has reported that in CdSe$_{0.65}$Te$_{0.35}$ thin films prepared by slurry painting method, the observed photocurrent has been much greater than in CdSe. CdSe$_x$Te$_{1-x}$ thin films of different compositions have been prepared by Murali[16] using brush plating technique. It has been observed
that out of all the compositions CdSe$_{0.7}$Te$_{0.3}$ films were the ones which exhibited maximum photoactivity.

The survey of the reported work on photoconductive studies reveals that only limited work has been done on the photoconduction characteristics of CdSe$_x$Te$_{1-x}$ thin films. Hence in the present investigation a detailed study on the photoconduction characteristics of hot wall deposited CdSe$_x$Te$_{1-x}$ films has been carried out.

7.2 Theory

The observation of any photoconduction phenomenon requires the presence of at least one type of mobile charge carrier. If the energy of the incident photon is higher than the band gap then each photon absorbed by the material will excite an electron to the conduction band producing a hole in the valence band and thereby increasing the conductivity of the material. Holes and electrons will eventually recombine but the time spent between release and recombination depends upon the trapping centres. The conductivity due to photons can be written as

\[ \sigma = q \mu n \]  

(7.1)
where $q$ is the electronic charge, $\mu$ the mobility and $n$ the carrier concentration. The photoconductivity or variation of conductivity upon light irradiation has the general form

$$\Delta \sigma = q(\mu \Delta n + n \Delta \mu)$$

(7.2)

The photoconductivity may arise due to change in carrier concentration and/or carrier mobility\([1,4,5]\). These changes result from the generation of electronic excited states in the semiconductor by the absorption of light energy. Either these excited states represent the excess carrier concentration $\Delta n$ or they indicate a mobility variation $\Delta \mu$. The excited states have a finite lifetime and their energy is lost through the different processes of relaxation and recombination.

The process involved in photoconductivity is quite complex\([1]\) due to the presence of innumerable defects such as vacancies, dislocations, grain boundaries etc., in the material which may act as trapping or recombination centers of the carriers. These imperfections present in the solid play a dominant role in photoconduction. Energetically, traps are localized positive potential centres for electrons and negative potential centres for holes. As a result there will be localized discrete energy levels i.e., traps in the band gap in the vicinity of the conduction and valence bands respectively. When an
electron (or a hole) falls into a trap it spends some finite time there and is no longer free to move. The probability of its release to the nearest conduction (or valence) band by thermal energy depends on the energy level of the trap as well as energy of the carrier and the temperature. The traps can capture both electrons and holes and the charges may recombine terminating their free lifetime i.e., the time they are free to contribute to the conductivity of the material. Such traps are called recombination centres. Both the types of centres affect the density of free carriers and their lifetime and consequently the photoconductivity of the material. Generally centres with energy level nearer to one of the band edges are likely to act as a trap rather than a recombination centre.

The phenomenon of photoconductivity in semiconductors can be explained using two models: (i) recombination model and (ii) barrier model[17].

7.2.1 Recombination model

The concept of hole or electron trap is important in the recombination theory of photoconductivity because of the presence of impurities and other
lattice imperfections having energies in the energy gap. Only at high carrier densities and therefore at high intensities of illumination does the direct recombination process compete with trapping. The photoconductivity in equilibrium will be determined by a balance between the processes which create charge carriers and those by which they disappear. The generation process by which carriers are produced include

a) generation of hole – electron pairs by thermal and radiant energy
b) creation of free electron by thermal or radiant energy leaving a trapped hole behind
c) creation of a free hole by thermal or radiant energy, leaving a trapped electron behind
d) release of a trapped electron and
e) thermal release of a trapped hole.

The recombination processes by which carriers disappear include

a) direct recombination of a free electron and free hole
b) trapping of a free hole
c) recombination of a free electron and a trapped hole and
d) recombination of a free hole and a trapped electron.
7.2.2 Barrier model

This model applies to polycrystalline semiconductor, which possesses a high surface state density. It is assumed that illumination produces little or no change in density of charge carriers but the effective mobility of such charge carriers is increased. It is also assumed that a large number of surface states are produced along the crystalline boundaries due to the oxidation of these boundaries. These surface states capture electron from the interior of the single crystalline domains and produce space charge barriers. Illumination reduces the number of electrons in the surface states and thereby lowers the barrier height between domains, which may then be observed as an increase in conductivity.

The dynamics of photogeneration of carriers is well understood in terms of transitions taking place between the electronic states[18]. The various electronic transitions that take place when a semiconductor absorbs a photon leading to photoconduction are shown in figure 7.1[19]. In this, the process 1 shows the production of electron-hole pair in the conduction and valence band respectively due to absorption of high photon energy. Process 2 shows the absorption of photon at localized imperfection site producing a free electron and also a hole. The hole being bound to the neighbouring
Figure 7.1. Schematic diagram illustrating different types of electronic transitions due to photon absorption.

- holes, - or — traps, ◦ electron, ○ excited states
defect centre. Process 3 shows the absorption of photons due to which an electron from valence band is raised to unoccupied impurity level. The hole is created in the valence band. Processes 4 and 4' represent the capture of hole by a trap centre. Processes 5 and 5' represent the capture of electron in a trap centre and its thermal excitation to conduction band. Processes 6 and 7 indicate the capture of the electron and hole respectively in the recombination centres. Process 8 represents the combination of free electron directly with a free hole. Process 9 indicates the capture of an electron by an excitation centre containing a hole. Process 10 shows a hole captured by an excited centre containing an electron. Both the processes 9 and 10 may be radiative.

As the photo current is proportional to the number of carriers available for conduction we can write, $I_{\text{ph}} \propto \exp\left(-\frac{E_g}{kT}\right)$. For trap free cases the photoconductivity will be proportional to light intensity $L$. In the presence of traps $I_{\text{ph}}$ will not be a linear function of $L$, but will be modified as $I_{\text{ph}} \propto L^z$, where the magnitude of $z$ can vary from 0.5 to 1 [20].
7.2.3 Photosensitivity

Photosensitivity is the ratio of increase in conductivity of the material in the presence of light to the conductivity in darkness and is given by the relation

\[
\text{Photosensitivity} = \frac{\Delta \sigma}{\sigma} = \frac{I_L - I_d}{I_d} \tag{7.3}
\]

where \( I_L \) and \( I_d \) represent the current under illumination and in the dark respectively. Any transition that creates additional free carriers effectively increases the free lifetime increasing the photosensitivity of the material. Imperfections which act as trapping centres will enhance photosensitivity whereas the recombination centres on the other hand decrease the photosensitivity.

7.2.4 Spectral response

When the photoconductivity is measured as a function of wavelength a maximum response is usually found at a particular wavelength. For shorter wavelength the absorption coefficient is much higher and only the surface regions are excited where defect states give shorter lifetime and
hence drop in the photosensitivity. At higher wavelength the radiation is partially absorbed giving rise to less photocurrent than the maximum. The presence of the defect centres extends the spectral response to longer wavelengths due to direct excitation of carriers from defect levels. Generally photocurrent spectra show peaks near the absorption edge which are related to the energy band gap[21].

### 7.3 Experiment

Hot wall deposited CdSe$_x$Te$_{1-x}$ films were illuminated by tungsten lamp (230 V, 150 W Philips). The intensity of illumination was measured using a suryamapi (CEL, India). The intensity of light was varied by changing the distance between the film and the light source. The spectral response of CdSe$_x$Te$_{1-x}$ films have been studied by allowing the radiation to pass through a series of interference filters in the wavelength range 650 – 1200 nm. The current was measured using optical power meter [70310, Oriel Instruments, USA].

### 7.4 Results and discussion

The dependence of photocurrent on light intensity in CdSe$_x$Te$_{1-x}$ thin films of different compositions and thicknesses are shown in figures 7.2 to
Figure 7.2. Variation of photocurrent with light intensity of CdSe$_{0.15}$Te$_{0.85}$ thin films
7.6. It is observed from the plots that the photocurrent increases with light intensity for all the deposited films. The photocurrent is also found to increase with increase in film thickness. The increase in photocurrent with light intensity is due to the increase in the concentration of majority charge carriers with light intensity. This is due to the presence of impurity centres in the photoconductor. These impurity centers act as recombination centers for minority carriers thereby enhancing the lifetime of majority charge carriers. The dependence of photo current on light intensity is power functional and indicates the presence of energy levels with complex distribution in the forbidden band. A similar behaviour has been reported in CdSe$_x$Te$_{1-x}$ thin films by earlier workers[12,13].

The spectral response of photocurrent in CdSe$_x$Te$_{1-x}$ thin films are shown in figures 7.7 to 7.11. The photocurrent is found to increase with increase in wavelength of the incident photons, reach a maximum and then decreases as shown in the plots. The maximum observed in the photocurrent spectral response curve corresponds to the absorption edge, which is related to the energy gap of the material. This is in accordance with the observations made by Rose[21] about spectral response curves. The spectral distribution of the photocurrent has been found to exhibit a peak corresponding to the band
Figure 7.3 Variation of photocurrent with light intensity of CdSe$_{0.4}$Te$_{0.6}$ thin films
Figure 7.4 Variation of photocurrent with light intensity of CdSe$_{0.6}$Te$_{0.4}$ thin films
Figure 7.5. Variation of photocurrent with light intensity of CdSe$_{0.7}$Te$_{0.3}$ thin films
Figure 7.6. Variation of photocurrent with light intensity of CdSe$_{0.85}$Te$_{0.15}$ thin films
Figure 7.7. Spectral response characteristics of photocurrent of CdSe$_{0.15}$Te$_{0.85}$ thin films
Figure 7.8. Spectral response characteristics of photocurrent of CdSe$_{0.4}$Te$_{0.6}$ thin films.
Figure 7.9. Spectral response characteristics of photocurrent of CdSe$_{0.6}$Te$_{0.4}$ thin films
Figure 7.10. Spectral response characteristics of photocurrent of CdSe$_{0.7}$Te$_{0.3}$ thin films
Figure 7.11. Spectral response characteristics of photocurrent of CdSe_{0.85}Te_{0.15} thin films
The variation of photocurrent with composition is as shown in figure 7.12. The band gap values have been calculated using the peak position and the obtained values are as shown in Table 7.1. The band gap is found to vary nonlinearly with composition with a minimum value occurring for a composition of \( x = 0.4 \). These are in agreement with the results obtained for CdSe\(_x\)Te\(_{1-x}\) films by Budyonnaya et al[10], Izakson et al[12], Ravichandran et al[13] and Ermolovich et al[14].

The observed low value of photocurrent in the short wavelength range may be due to the high absorption coefficient and only surface regions are excited where defect states give shorter lifetime.

In the long wavelength region, the radiation is partially observed giving rise to less photocurrent than the maximum, the presence of defect centers extends the spectral response to long wavelength region due to direct excitation of carriers from defect levels. The sharpness of the peak in the response curve is found to be dependent on film thickness. If the photoconductor is very thin, no sharp maximum is observed in the response curve and this can be attributed to the fact that all the photo excited carriers recombine by surface recombination kinetics. Figures 7.13 to 7.17 shows the
Figure 7.12. Variation of photocurrent with composition in CdSe$_x$Te$_{1-x}$ thin films
### Table 7.1 Band gap values of CdSe\(_x\)Te\(_{1-x}\) films

<table>
<thead>
<tr>
<th>Composition</th>
<th>Band gap (eV)</th>
</tr>
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<tbody>
<tr>
<td>CdTe</td>
<td>1.55</td>
</tr>
<tr>
<td>CdSe(<em>{0.15})Te(</em>{0.85})</td>
<td>1.46</td>
</tr>
<tr>
<td>CdSe(<em>{0.4})Te(</em>{0.6})</td>
<td>1.38</td>
</tr>
<tr>
<td>CdSe(<em>{0.6})Te(</em>{0.4})</td>
<td>1.46</td>
</tr>
<tr>
<td>CdSe(<em>{0.7})Te(</em>{0.3})</td>
<td>1.55</td>
</tr>
<tr>
<td>CdSe(<em>{0.85})Te(</em>{0.15})</td>
<td>1.65</td>
</tr>
<tr>
<td>CdSe</td>
<td>1.77</td>
</tr>
</tbody>
</table>
Figure 7.13. Variation of photosensitivity with light intensity of CdSe$_{0.15}$Te$_{0.85}$ thin films
Figure 7.14. Variation of photosensitivity with light intensity of CdSe$_{0.4}$Te$_{0.6}$ thin films.
Figure 7.15. Variation of photosensitivity with light intensity of CdSe$_{0.6}$Te$_{0.4}$ thin films.
Figure 7.16. Variation of photosensitivity with light intensity of CdSe$_{0.7}$Te$_{0.3}$ thin films
Figure 7.17. Variation of photosensitivity with light intensity of CdSe$_{0.85}$Te$_{0.15}$ thin films
variation of photosensitivity with the intensity of light in CdSe$_x$Te$_{1-x}$ films. The photosensitivity is found to increase with increase in light intensity. Thicker films are found to exhibit greater photosensitivity.
References


