Chapter V

Results on Cadmium Sulpho Selenide

5.1. Introduction

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

5.2. Preparation of CdS$_x$Se$_{1-x}$ Powder

CdS$_x$Se$_{1-x}$ powders were prepared by the reaction of aqueous solutions of cadmium acetate, sodium seleno sulphate and thiourea under optimum conditions of pH ~10, obtained by the addition of ammonium hydroxide.

40 g of cadmium acetate was dissolved in 200 ml of triple distilled water, 25 g of thiourea was dissolved in 250 ml of triple distilled water by gentle heating, seleno sulphate solution was prepared by dissolving 30 g of selenium in a sodium sulphite solution (prepared by dissolving 235 g of sodium sulphite in 500 ml triple distilled water). The cadmium acetate solution was taken in a three litre flask fitted with grounded joints, and 150 ml of fresh ammonia was added when a clear solution of cadmium ammonia complex was obtained. To this clear solution different quantities of selenosulphate and thiourea solutions were taken in 100 ml
of ammonia and added to the complex and refluxed on a heating mantle provided with facility for magnetically stirring the contents for a few hours. 30 ml of ammonia was added at intervals of 30 minutes. The colour of the precipitate changed from orange colour to shiny bright black colour as the composition of the powder changed from sulphur rich to selenium rich side. The precipitate was kept for about 15 hours and filtered through a Whatman 42 filter paper using Buchner funnel with vacuum suction arrangement. The powders were then washed with hot sodium sulphite to remove traces of selenium, and washed with hot acetic acid to remove traces of cadmium oxide. Further washing was continued until the pH of the filtrate was found to be neutral. Purified ethanol was employed for final washing to remove moisture. The powders were dried in vacuum oven. The powders were then annealed at 300°C in argon atmosphere for 30 minutes to remove any traces of excess selenium. The powders were then stored in vacuum desiccators.

5.3. Structural Characterization

The XRD patterns of the powders of different compositions are shown in Fig.5.1 to Fig.5.9. The peaks corresponding to (100), (002), (101), (102), (110), (103) and (112) reflections were observed in all cases. The peaks were observed to shift to higher 2θ 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,

\[
\frac{1}{d^2} = \frac{4}{3} \left[ \frac{h^2 + hk + k^2}{a^2} \right] + \frac{l^2}{c^2}
\]
Fig 5.1-X-ray diffraction pattern of Cd$_{0.4}$Se$_{0.9}$ film
Fig 5.2- X-ray diffraction pattern of Cd$_{0.2}$Se$_{0.8}$ film
Fig 5.3- X-ray diffraction pattern of CdS$_{0.3}$Se$_{0.7}$ film
Fig 5.4- X-ray diffraction pattern of Cd$_{0.4}$Se$_{0.6}$ film
Fig 5.5-X-ray diffraction pattern of Cd$_{0.5}$Se$_{0.5}$ film
Fig 5.6- X-ray diffraction pattern of CdS_{0.6}Se_{0.4} film
Fig 5.7 - X-ray diffraction pattern of CdS$_{0.7}$Se$_{0.3}$ film
Fig 5.8- X-ray diffraction pattern of Cd$_{0.8}$Se$_{0.2}$ film
Fig 5.9- X-ray diffraction pattern of CdS$_{0.9}$Se$_{0.1}$ film
‘a’ and ‘c’ values for CdSe and CdS are taken from the ASTM data. The variation of lattice constants of cadmium sulpho selenide solid solutions with composition is shown in Table 5.1. A linear variation of the lattice constants with composition indicates that Vegard’s law is obeyed [182]. Similar variation has been observed for sintered pellets [183], flash evaporated layers [184], single crystals [185] and sprayed layers [186].

**Table 5.1**

<table>
<thead>
<tr>
<th>Composition</th>
<th>Lattice Constants</th>
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<tbody>
<tr>
<td></td>
<td>a (Å)</td>
</tr>
<tr>
<td>0</td>
<td>4.304</td>
</tr>
<tr>
<td>0.1</td>
<td>4.292</td>
</tr>
<tr>
<td>0.2</td>
<td>4.281</td>
</tr>
<tr>
<td>0.3</td>
<td>4.262</td>
</tr>
<tr>
<td>0.4</td>
<td>4.244</td>
</tr>
<tr>
<td>0.5</td>
<td>4.228</td>
</tr>
<tr>
<td>0.6</td>
<td>4.211</td>
</tr>
<tr>
<td>0.7</td>
<td>4.198</td>
</tr>
<tr>
<td>0.8</td>
<td>4.188</td>
</tr>
<tr>
<td>0.9</td>
<td>4.165</td>
</tr>
<tr>
<td>1.0</td>
<td>4.147</td>
</tr>
</tbody>
</table>

The c/a ratio in all the cases is around 1.634 which is in close agreement with the theoretical value obtained from the relation that the axial ratio in a regular hexagonal system is \( \frac{2\sqrt{2}}{\sqrt{3}} \), that is 1.633 [187].
5.4 EDAX Measurements

Composition analysis was done by EDAX study and the composition of the powders is indicated in the Table 5.2.

Table 5.2

Composition of CdS\textsubscript{x}Se\textsubscript{1-x} Powders

<table>
<thead>
<tr>
<th>Starting Composition</th>
<th>EDAX Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS\textsubscript{0.9}Se\textsubscript{0.1}</td>
<td>CdS\textsubscript{0.89}Se\textsubscript{0.11}</td>
</tr>
<tr>
<td>CdS\textsubscript{0.8}Se\textsubscript{0.2}</td>
<td>CdS\textsubscript{0.80}Se\textsubscript{0.20}</td>
</tr>
<tr>
<td>CdS\textsubscript{0.7}Se\textsubscript{0.3}</td>
<td>CdS\textsubscript{0.70}Se\textsubscript{0.30}</td>
</tr>
<tr>
<td>CdS\textsubscript{0.6}Se\textsubscript{0.4}</td>
<td>CdS\textsubscript{0.58}Se\textsubscript{0.42}</td>
</tr>
<tr>
<td>CdS\textsubscript{0.5}Se\textsubscript{0.5}</td>
<td>CdS\textsubscript{0.49}Se\textsubscript{0.51}</td>
</tr>
<tr>
<td>CdS\textsubscript{0.4}Se\textsubscript{0.6}</td>
<td>CdS\textsubscript{0.39}Se\textsubscript{0.61}</td>
</tr>
<tr>
<td>CdS\textsubscript{0.3}Se\textsubscript{0.7}</td>
<td>CdS\textsubscript{0.28}Se\textsubscript{0.72}</td>
</tr>
<tr>
<td>CdS\textsubscript{0.2}Se\textsubscript{0.8}</td>
<td>CdS\textsubscript{0.19}Se\textsubscript{0.81}</td>
</tr>
<tr>
<td>CdS\textsubscript{0.1}Se\textsubscript{0.9}</td>
<td>CdS\textsubscript{0.09}Se\textsubscript{0.91}</td>
</tr>
</tbody>
</table>

From the table, it is clear that the EDAX analysis data (Fig.5.10 – Fig. 5.12) are almost similar to the theoretical composition expected from the starting materials. The data corresponding to CdL\textalpha, SeK\textalpha and SK\textalpha lines were used for estimating the composition.
Fig 5.10 – EDAX spectrum of CdS$_x$Se$_{1-x}$ film ($x = 0.1 - 0.3$)
Fig 5.11 - EDAX spectrum of CdS$_x$Se$_{1-x}$ film ($x = 0.4 - 0.6$)
Fig 5.12 - EDAX spectrum of CdS$_x$Se$_{1-x}$ film (x = 0.7 - 0.9)
5.5. Density Measurements

The density of the powders of different compositions was determined by specific gravity method. Dioxane was used as the liquid for this determination. Experimentally estimated density values of the synthesized powder with varying composition were in close agreement with the theoretically calculated values (Table 5.3).

**Table 5.3.**
Density versus composition

<table>
<thead>
<tr>
<th>Composition</th>
<th>Density values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Theoretical</td>
</tr>
<tr>
<td>CdS&lt;sub&gt;0.9&lt;/sub&gt;Se&lt;sub&gt;0.1&lt;/sub&gt;</td>
<td>4.894</td>
</tr>
<tr>
<td>CdS&lt;sub&gt;0.8&lt;/sub&gt;Se&lt;sub&gt;0.2&lt;/sub&gt;</td>
<td>5.004</td>
</tr>
<tr>
<td>CdS&lt;sub&gt;0.7&lt;/sub&gt;Se&lt;sub&gt;0.3&lt;/sub&gt;</td>
<td>5.096</td>
</tr>
<tr>
<td>CdS&lt;sub&gt;0.6&lt;/sub&gt;Se&lt;sub&gt;0.4&lt;/sub&gt;</td>
<td>5.188</td>
</tr>
<tr>
<td>CdS&lt;sub&gt;0.5&lt;/sub&gt;Se&lt;sub&gt;0.5&lt;/sub&gt;</td>
<td>5.280</td>
</tr>
<tr>
<td>CdS&lt;sub&gt;0.4&lt;/sub&gt;Se&lt;sub&gt;0.6&lt;/sub&gt;</td>
<td>5.372</td>
</tr>
<tr>
<td>CdS&lt;sub&gt;0.3&lt;/sub&gt;Se&lt;sub&gt;0.7&lt;/sub&gt;</td>
<td>5.464</td>
</tr>
<tr>
<td>CdS&lt;sub&gt;0.2&lt;/sub&gt;Se&lt;sub&gt;0.8&lt;/sub&gt;</td>
<td>5.556</td>
</tr>
<tr>
<td>CdS&lt;sub&gt;0.1&lt;/sub&gt;Se&lt;sub&gt;0.9&lt;/sub&gt;</td>
<td>5.648</td>
</tr>
</tbody>
</table>
5.6. Preparation of CdS_xSe_{1-x} Films

The powders were screen printed on steatite and titanium substrates and sintered under usual conditions. For photoconductivity measurements, the films were sintered in air and for photoelectrochemical measurements, the films on titanium substrates were sintered in argon atmosphere. Films of the mixed system were prepared by adding 10% of cadmium chloride and after thoroughly grinding in an agate mortar in the presence of iso-propanol. The mixture was made into a paste by adding propylene carbonate. The paste was then screen printed on to steatite and titanium substrates. The printed films were dried in air at 120°C for a few hours. They were then sintered in argon/air atmosphere at different temperatures in the range 500 - 600°C for about 30 minutes. Copper doping was achieved by adding requisite amount of cupric chloride to the slurry containing cadmium chloride along with the cadmium sulpho selenide powder. The thickness of the films after sintering was around 10 μm (by gravimetry).

5.7. Structural Characterization

X-ray diffraction studies were made on the films screen printed on titanium substrates. The films exhibited identical XRD patterns similar to the powder used as starting material to prepare the films, except the peaks were sharper than the powder patterns. Hence, the patterns are not shown separately.

5.8. Optical Characteristics

Diffuse reflectance measurements were made on the films of different composition and the wavelength at which onset of maximum absorption takes place is found to shift towards the red region as the selenium content in the films
increased (Fig.5.13 – Fig.5.21). The variation of band gap with composition is shown in Fig.5.22. The band gap increases from 1.68 eV to 2.41 eV as the value of ‘x’ increases.

5.9. Scanning Electron Microscopy

Surface morphology of the films was determined for the films of different composition heat-treated at 550°C are shown in Fig.5.23. The grain size is observed to increase from 1.0 µm to 10 µm as the sulphur concentration in the films increase.

5.10. XPS Studies

Fig.5.24 to Fig.5.32 show the XPS spectra of Cd (3d_{5/2} and 3d_{3/2}) and Se (3d_{5/2} and 3d_{3/2}) and S (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 S (3d_{5/2} and 3d_{3/2}) appeared at 163.2 eV and 168.0 eV respectively. Atomic concentration measurements were made on the films of different composition selecting suitable sensitivity factors for Cd, S 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 S (3d_{5/2}) also increased and the area under the Se (3d_{5/2}) decreased. The values of binding energies obtained for the Cd, S and Se levels are in very good agreement with that reported in the literature [188]. To determine the distribution of the concentration of Cd, S and Se throughout the
Fig 5.13- Diffuse reflectance spectrum of CdS$_{0.8}$Se$_{0.2}$ film
Fig 5.14- Diffuse reflectance spectrum of Cd$_{0.8}$Se$_{0.2}$ film
Fig 5.15- Diffuse reflectance spectrum of CdS$_{0.7}$Se$_{0.3}$ film
Fig 5.16- Diffuse reflectance spectrum of CdS$_{0.6}$Se$_{0.4}$ film
Fig 5.17 - Diffuse reflectance spectrum of Cd$\text{S}_{0.5}$Se$_{0.5}$ film
Fig 5.18- Diffuse reflectance spectrum of CdS$_{0.4}$Se$_{0.6}$ film
Fig 5.19- Diffuse reflectance spectrum of Cd$_{0.3}$Se$_{0.7}$ film
Fig 5.20- Diffuse reflectance spectrum of CdS$_{0.2}$Se$_{0.8}$ film
Fig 5.21- Diffuse reflectance spectrum of Cd$_{0.1}$Se$_{0.9}$ film
Fig 5.22- Variation of band gap of CdS$_x$Se$_{1-x}$ films with composition
Fig. 5.23(a) - Scanning electron micrograph of CdS$_{0.1}$Se$_{0.9}$ films heat-treated at 550°C

Fig. 5.23(b) - Scanning electron micrograph of CdS$_{0.2}$Se$_{0.8}$ films heat-treated at 550°C
Fig. 5.23(c) - Scanning electron micrograph of Cd$_{0.3}$Se$_{0.7}$ films heat-treated at 550°C

Fig. 5.23(d) - Scanning electron micrograph of Cd$_{0.4}$Se$_{0.6}$ films heat-treated at 550°C
Fig. 5.23(e) - Scanning electron micrograph of CdS$_{0.5}$Se$_{0.5}$ films heat-treated at 550°C

Fig. 5.23(f) - Scanning electron micrograph of CdS$_{0.6}$Se$_{0.4}$ films heat-treated at 550°C
Fig. 5.23(g) - Scanning electron micrograph of CdS$_{0.7}$Se$_{0.3}$ films heat-treated at 550°C

Fig. 5.23(h) - Scanning electron micrograph of CdS$_{0.8}$Se$_{0.2}$ films heat-treated at 550°C
Fig 5.24- XPS spectra of CdS0.1Se0.9 film
Fig 5.25- XPS spectra of Cd$_{0.2}$Se$_{0.8}$ film
Fig 5.26 - XPS spectra of Cd$_{0.3}$Se$_{0.7}$ film
Fig 5.27- XPS spectra of CdS$_{0.4}$Se$_{0.6}$ film
Fig 5.28 - XPS spectra of Cd$_{0.5}$Se$_{0.5}$ film
Fig 5.29- XPS spectra of CdS$_{0.6}$Se$_{0.4}$ film
Fig 5.30- XPS spectra of CdS$_{0.7}$Se$_{0.3}$ film
Fig 5.31- XPS spectra of CdS$_{0.8}$Se$_{0.2}$ film
Fig 5.32- XPS spectra of CdS$_{0.9}$Se$_{0.1}$ film
entire thickness, depth profiling studies were made at the rate of 10 nm/min. The depth profiling of the films show a uniform distribution of the starting composition.

5.11. Electrical Properties

The resistivity ($\rho$) of CdS$_x$Se$_{1-x}$ films was calculated by using the equation 5. The influence of composition on the resistivity of the films is depicted in Fig.5.33. The results on the films annealed at 550°C are only presented, since they have exhibited maximum photoconductivity. The magnitude of the resistivity varies from 30 ohm cm to 480 ohm cm as the 'x' value increases from 0 to 1. The increase in conductance may be associated with increase in sulphur/selenium vacancies (due to decrease of depth of donor level associated with the sulphur/selenium vacancy) [189].

Fig.5.34 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 increases as the composition increases and this might be associated with the scattering at the chalcogen vacancies. Fig.5.35 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 CdS side. The carrier concentration is found to decrease from $2.4 \times 10^{17}$ cm$^{-3}$ to $1.3 \times 10^{17}$ cm$^{-3}$ as 'x' value increases from 0 to 1.

5.12. Photoconductivity Studies

In order to obtain very high photosensitivity, the sintering temperature was varied in the range of 500 - 600°C. It was observed that sintering temperature
Fig 5.33- Dependence of resistivity with composition for CdS$_x$Se$_{1-x}$ films
Fig 5.34- Dependence of mobility with composition for CdS$_x$Se$_{1-x}$ films
Fig 5.35- Dependence of carrier density with composition for CdS$_x$Se$_{1-x}$ films
had a profound influence on the sensitivity and stability of the photoconductive cells. The results of the effects of sintering temperature on sensitivity are shown in Fig.5.36.

It is observed from the figures that as the sintering temperature increases, the photosensitivity also increases. Higher sintering temperatures lead to rapid decrease in light resistance, while at low temperature, incomplete sintering is observed which subsequently leads to instability of the cells. 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 sintering temperature of 550°C results in high photosensitivity as well as low light resistance.

Sintering time has a significant role to play in the process of obtaining useful photoconductive cells. Photosensitivity was calculated for various sintering time and the results are shown in Fig.5.37. As the sintering time is gradually increased, significant lowering of light resistance is observed while practically no pronounced increase in dark resistance takes place. For 15 minutes sintering, the dark resistance slightly increases while the light resistance attains a minimum. As sintering goes on, more sensitization centers get incorporated. While donor incorporation (Chloride) seems to have been accomplished mostly during prefiring, as indicated by the dark and light resistance behaviour. The fall in light resistance with sintering time, may also be attributed to the removal of grain boundaries due to optimum recrystallization. Longer sintering time may result in partial evaporation of the chloride with
Fig 5.36- Variation of Photosensitivity with sintering temperature for CdS$_x$Se$_{1-x}$ films
a) $x = 0.2$

b) $x = 0.4$

c) $x = 0.6$

d) $x = 0.8$
Fig 5.37 - Variation of Photosensitivity with sintering time for CdS$_x$Se$_{1-x}$ films

a) $x = 0.2$

b) $x = 0.4$

c) $x = 0.6$

d) $x = 0.8$
consequent increase in the dark as well as the light resistance. In other words, sintering time, when other parameters are fixed, decides the optimum transport of dopants, besides removal of grain boundaries.

To study the effect of copper on the photoconductive properties, copper concentration was varied in the range 100 – 600 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 [149] that cadmium selenide shows a more sensitive behaviour to copper concentration than does cadmium sulphide, it is felt that a study of the behaviour of copper in these solid solutions will be interesting. Hence, variation of copper content is studied for all the compositions and this variation is shown for CdS$_{0.5}$Se$_{0.5}$ films (Fig.5.38).

In all these studies, no donors are deliberately added to the compositions. The chloride used for fluxing action, does enter the lattice as donor and selenium/sulphur vacancies also manifest as donors [190]. The maximum rate of change of dark current with acceptor concentration in single crystals [191] 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 [192]. However, a Cu$^+$ to Cu$^{2+}$ equilibrium probably exists and further that the equilibrium may be assumed constant for identical processing conditions. The properties of the resulting photoconductors are
Fig 5.38 - Variation of Photosensitivity with copper doping for CdS$_x$Se$_{1-x}$ films

a) $x = 0.2$

b) $x = 0.4$

c) $x = 0.6$

d) $x = 0.8$
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 [193]. 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 [148].

A discussion on the role of copper in CdS type photoconductors requires an understanding of the basic sensitization mechanism. Unsensitized CdS or CdSe is an insulator and has a considerable density of Type-I centers (Fig.5.39a). They aid fast recombination of photo generated 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. Donors may be halide ions, which substitute the sulphide or selenide in the lattice, freezing an electron for conduction. Gallium or Indium substituted in the lattice, supplying an electron for conduction. Donor levels may also arise out of non-stoichiometry of the material itself, as metal excess or chalcogen deficit, each anion vacancy adding two
Fig 5.39-Energy level representation of the sensitizing process
electrons towards conduction. These donor levels are near the conduction band (~ 0.03 eV) and are ionized at room temperature (Fig. 5.39b).

Even though the incorporation of donors brings down the resistivity, the photosensitivity is still not high. High photosensitivity in most of II-VI compounds is associated with the presence of compensated acceptors, which have an effective negative charge with respect to the rest of the crystal, such as a Cu\(^+\) in the place of Cd\(^{2+}\) or a cation vacancy. The effect of incorporation of these compensated acceptors (II levels) is shown in Fig. 5.39c. The presence of II centres has sensitizing effect. This comes along in the following way: (a) holes captured by II centres have a longer life there before recombination than holes captured by I centres, because of the small cross-section of II centres containing holes for capturing free electrons, (b) the II centres become occupied principally by holes, if the concentration of I and II centres is much larger than the density of free carriers. This means that the electrons initially in II centres are effectively transferred to the I centres, (c) the lifetime of a free electron is increased because it now faces mainly centres with a small capture cross-section and only few centres with a large capture cross-section. If the concentration of I and II centres is not much larger than the density of free carriers, the incorporation of II centres provides effectively only additional recombination centres and no sensitization results [193].

The variation of photocurrent with excitation intensity in cadmium sulphide type photoconductors is interesting and is of fundamental importance in the operation of these photoresistors 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 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 [194].

Fig.5.40 depicts the variation of photocurrent with illumination at room temperature for CdS$_x$Se$_{1-x}$ cells. An examination of the graphs reveals that as the selenide content is increased, the behaviour of the photocurrent with excitation intensity changes progressively towards the behaviour of cadmium selenide. Thus for cells with 'x' values less than 0.3, the super-linear behaviour is not observed under all experimental conditions. Further, the photocurrent at saturation decreases progressively as the selenide content is increased.

The spectral distribution of sensitivity of the cells of different composition is shown in Fig.5.41. Pure cadmium sulphide crystals have a peak response at 520 nm, while pure CdSe has a peak response at 720 nm [195]. This response is essentially caused by intrinsic excitation. Lattice defects that may be present in the crystal, introduces levels in the forbidden gap that 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 [196]. 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.
Fig 5.40 - Variation of photocurrent with intensity for CdS$_x$Se$_{1-x}$ films

a) $x = 0.2$

b) $x = 0.4$

c) $x = 0.6$

d) $x = 0.8$
Fig 5.41 – Action spectra for CdS$_x$Se$_{1-x}$ films of different compositions

a) $x = 0.8$
b) $x = 0.4$
c) $x = 0.2$
d) $x = 1.0$
e) $x = 0.0$
than in the bulk [197]. 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 deepening 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.

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, which is modifying the composition of the activating radiation reaching the portion of the layer involved in photoconduction. The presence of chemisorbed oxygen, on the sintered layers in particular, which act as an acceptor may also contribute to such shifts [198].

It is clear from the graphs that the wavelength of peak response as also the edge gets progressively shifted to longer wavelengths as the selenide content is increased. Fig.5.42 gives a plot of the wavelengths of peak response with composition of the CdS\textsubscript{x}Se\textsubscript{1-x} photoconductive cells. The linear increase in the wavelength of peak response is due to the solid solution formation with progressively increasing cadmium selenide content. Similar observations have been reported earlier [199].
Fig 5.42 – Plot of wavelength of peak response with composition
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.

5.13. Aging Studies

Fig.5.43 exhibits the variation of photosensitivity of the undoped and doped cells of the composition CdS\textsubscript{0.5}Se\textsubscript{0.5} with time as an illustration. All the cells behaved in a similar fashion. The unencapsulated cells, which are kept upto 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 250 days.


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. The I-V characteristics of both undoped and doped films of composition CdS\textsubscript{0.5}Se\textsubscript{0.5} are shown in Fig.5.44 and Fig.5.45 respectively. In all the plots, a relation of the type $V \propto I^n$ is followed. The plots are linear upto 240V, beyond which non-linear behaviour is observed. The plots can be explained in a fashion similar to that for CdSe cells.
Fig 5.43 - Variation of Photosensitivity of CdS$_x$Se$_{1-x}$ films, with time

a) undoped
b) copper doped
Fig 5.44 – Plots of photocurrent Vs applied voltage for CdS$_x$Se$_{1-x}$ films

a) $x = 0.2$
b) $x = 0.4$
c) $x = 0.6$
d) $x = 0.8$
Fig 5.45 – Plots of photocurrent Vs applied voltage for copper doped CdS$_{0.5}$Se$_{0.5}$ film
a) 100 ppm
b) 200 ppm
c) 400 ppm
d) 500 ppm
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 prevent 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 photo voltage were measured by HIL digital multimeter.

The CdS\(_x\)Se\(_{1-x}\) electrodes of different composition 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 were obtained for the PEC cells made using the photo electrodes of different composition and heat-treated at different temperatures. It was observed that the PEC output was maximum for electrodes heated at 550°C irrespective of composition and hence the load characteristics were obtained for different intensities for these electrodes heat-treated at 550°C.
Fig. 5.46 – Fig. 5.54. Photoelectrodes heat-treated beyond 550°C exhibited lower \( V_{oc} \) and \( J_{sc} \) values due to change in concentration of sulphur 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 \( \text{CdS}_{0.8}\text{Se}_{0.1} \) exhibited the maximum \( V_{oc} \) of 0.675V for 80 mW cm\(^{-2}\) illumination. This value is lower than the reported value of 0.70V for electrodes prepared by sintering mixture of CdS and CdSe [200], but the \( J_{sc} \) value for this composition is higher. The value of \( J_{sc} \) is higher than that reported for the electrodeposited electrode [201]. At intensity values beyond 80 mW cm\(^{-2}\), \( V_{oc} \) 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. It was observed that \( J_{sc} \) increases from 2.65 mA cm\(^{-2}\) to 6.25 mA cm\(^{-2}\) as the intensity of illumination increased from 20 to 100 mW cm\(^{-2}\). Since the electrode of composition, \( \text{CdS}_{0.8}\text{Se}_{0.1} \) showed maximum voltage output, further studies were made on the electrodes of this composition. A plot of \( \ln J_{sc} \) versus \( V_{oc} \) (Fig. 5.55) yielded a straight line. Extrapolation of the line to the \( \ln J_{sc} \) 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 2.20. 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 the photocurrent and photo voltage are found to increase upto 80s photo etch, beyond which they begin to decrease (Fig. 5.56).
Fig 5.46 – I-V characteristics of CdS$_{0.1}$Se$_{0.9}$ electrodes 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$^{-2}$
Fig 5.47 - I-V characteristics of CdS_{0.2}Se_{0.8} electrodes 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\(^{-2}\)
Fig 5.48 – I-V characteristics of CdS\textsubscript{0.3}Se\textsubscript{0.7} electrodes at different intensities

a) 20 mW cm\textsuperscript{-2}
b) 40 mW cm\textsuperscript{-2}
c) 60 mW cm\textsuperscript{-2}
d) 80 mW cm\textsuperscript{-2}
e) 100 mW cm\textsuperscript{-2}
Fig 5.49 – I-V characteristics of CdS$_{0.4}$Se$_{0.6}$ electrodes 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$^{-2}$
Fig 5.50 – I-V characteristics of CdS\textsubscript{0.5}Se\textsubscript{0.5} electrodes at different intensities

\begin{itemize}
  \item a) 20 mW cm\textsuperscript{-2}
  \item b) 40 mW cm\textsuperscript{-2}
  \item c) 60 mW cm\textsuperscript{-2}
  \item d) 80 mW cm\textsuperscript{-2}
  \item e) 100 mW cm\textsuperscript{-2}
\end{itemize}
Fig 5.51 – I-V characteristics of CdS$_{0.6}$Se$_{0.4}$ electrodes 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$^{-2}$
Fig 5.52 – I-V characteristics of CdS$_{0.7}$Se$_{0.3}$ electrodes 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$^{-2}$
Fig 5.53 – I-V characteristics of CdS_{0.8}Se_{0.2} electrodes 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\(^{-2}\)
Fig 5.54 – I-V characteristics of CdS$_{0.9}$Se$_{0.1}$ electrodes 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$^{-2}$
Fig 5.55 – Plot of $\ln J_{sc}$ Vs $V_{oc}$ of CdS$_{0.9}$Se$_{0.1}$ electrode
Fig 5.56 - Variation of CdS_{0.9}Se_{0.1} electrode for different durations of photoetching
etching leads to selective attack of surface defects not accessible to chemical etchants. It is observed that during photo etching the $V_{oc}$ increased from 0.675 V to 0.81 V and $J_{sc}$ increased from 6.25 mA cm$^{-2}$ to 10.00 mA cm$^{-2}$. The decrease in photocurrent and photo voltage beyond 80s photo etching can be attributed to increase in surface area due to prolonged photo etching[160]. The power output characteristics (Fig.5.57) after 80s photo etching indicates a $V_{oc}$ of 0.81 V, $J_{sc}$ of 10.00 mA cm$^{-2}$, ff of 0.65, $\eta$ of 5.06% for 80 mW cm$^{-2}$ illumination. The photovoltaic parameters of the electrodes of different composition are shown in Table 5.4.

**Table-5.4**

Photovoltaic parameters of CdS$_x$Se$_{1-x}$ electrodes

(Intensity of illumination : 80 mW cm$^{-2}$)

<table>
<thead>
<tr>
<th>Composition</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>ff</th>
<th>$\eta$ (%)</th>
<th>$R_s$ (Ω)</th>
<th>$R_{sh}$ (kΩ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>x = 0.1</td>
<td>0.53</td>
<td>12.5</td>
<td>0.65</td>
<td>5.38</td>
<td>10</td>
<td>1.50</td>
</tr>
<tr>
<td>x = 0.2</td>
<td>0.52</td>
<td>11.8</td>
<td>0.54</td>
<td>4.14</td>
<td>9</td>
<td>1.50</td>
</tr>
<tr>
<td>x = 0.3</td>
<td>0.515</td>
<td>11.0</td>
<td>0.60</td>
<td>4.25</td>
<td>9</td>
<td>1.50</td>
</tr>
<tr>
<td>x = 0.4</td>
<td>0.51</td>
<td>10.8</td>
<td>0.59</td>
<td>4.00</td>
<td>8</td>
<td>1.50</td>
</tr>
<tr>
<td>x = 0.5</td>
<td>0.51</td>
<td>9.7</td>
<td>0.72</td>
<td>4.50</td>
<td>15</td>
<td>1.50</td>
</tr>
<tr>
<td>x = 0.6</td>
<td>0.53</td>
<td>8.2</td>
<td>0.72</td>
<td>3.75</td>
<td>12</td>
<td>1.80</td>
</tr>
<tr>
<td>x = 0.7</td>
<td>0.54</td>
<td>7.0</td>
<td>0.68</td>
<td>3.25</td>
<td>20</td>
<td>1.80</td>
</tr>
<tr>
<td>x = 0.8</td>
<td>0.58</td>
<td>5.8</td>
<td>0.59</td>
<td>2.52</td>
<td>18</td>
<td>1.80</td>
</tr>
<tr>
<td>x = 0.9</td>
<td>0.68</td>
<td>6.0</td>
<td>0.74</td>
<td>3.75</td>
<td>15</td>
<td>2.00</td>
</tr>
<tr>
<td>x = 0.9</td>
<td>0.82</td>
<td>10.0</td>
<td>0.61</td>
<td>6.25</td>
<td>12</td>
<td>2.50</td>
</tr>
<tr>
<td>(After photo etch)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Fig 5.57 – I-V characteristics of Cd$_{0.9}$Se$_{0.1}$ electrode after photoetching
The short circuit current density and efficiency of the photoelectrodes are higher than the earlier reports for the electrodes of composition CdS$_{0.9}$Se$_{0.1}$.

Mott-Schottky plots were studied using 1 M Na$_2$SO$_4$ as the blocking electrolyte and a EG&G PARC impedance analyzer model 6310. The CdS$_x$Se$_{1-x}$ 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,

$$C = \frac{1}{2\pi f Z}$$

Fig.5.58 exhibits the Mott-Schottky plots for the films of different composition and heat treated at 550°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 -1.21 to -1.30 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.

Spectral response measurements were carried out on the photoelectrodes by using a photo physics monochromator and a 250 W tungsten halogen lamp, 1 M 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.

The photocurrent values were used for the calculation of the quantum efficiency ($\phi$) using the well known relation [164],
Fig 5.58 – Mott-Schottky plots of Cd$_x$Se$_{1-x}$ electrodes

a) $x = 0.2$

b) $x = 0.4$

c) $x = 0.6$
\[ \phi = 1240 \frac{J_{sc}}{\lambda \cdot P_{in}} \]

where \( J_{sc} \) is the photocurrent, \( \lambda \) is the wavelength of illumination, \( P_{in} \) is the power of the light incident on the photoelectrodes. Plot of \( J_{ph} \) vs \( \lambda \) for the CdS\(_{0.9}\)Se\(_{0.1}\) electrodes heat treated at 550°C is shown in Fig.5.59(c). The value of \( \phi_{\text{max}} \) occurs at a wavelength value corresponding to the band gap 2.3 eV. The values match very well with the band gap values obtained from the optical absorption measurements. The plots of \( J_{ph} \) vs \( \lambda \) for the CdS\(_x\)Se\(_{1-x}\) electrodes of other compositions are shown in Fig.5.59–Fig.5.61. The photocurrent reaches maximum at different wavelengths depending upon the composition. The values of wavelengths at which photocurrent maximum agrees very well with the band gap values estimated from optical absorption measurements. The quantum efficiency (\( \phi \)) values estimated using the above equation is indicated in Table 5.5.

<table>
<thead>
<tr>
<th>Quantum efficiency values for CdS(<em>x)Se(</em>{1-x}) electrodes of different composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition (x)</td>
</tr>
<tr>
<td>Quantum Efficiency (( \phi ))</td>
</tr>
</tbody>
</table>

As in the case of CdS or CdSe, the electronic mechanism in CdS\(_x\)Se\(_{1-x}\) films are associated with the lattice Se and S vacancies, which are known to behave as both shallow donor centers and deep electron traps [202].
Fig 5.59—Variation of Photocurrent Density ($J_{ph}$) with wavelength for:

a) $\text{CdS}_{0.7}\text{Se}_{0.3}$

b) $\text{CdS}_{0.8}\text{Se}_{0.2}$

c) $\text{CdS}_{0.9}\text{Se}_{0.1}$
Fig 5.60-Variation of Photocurrent Density ($J_{ph}$) with wavelength for

a) Cd$_{0.4}$Se$_{0.6}$

b) Cd$_{0.5}$Se$_{0.5}$

c) Cd$_{0.6}$Se$_{0.4}$
Fig 5.61-Variation of Photocurrent Density ($J_{ph}$) with wavelength for
a) CdS$_{0.1}$Se$_{0.9}$
b) CdS$_{0.2}$Se$_{0.8}$
c) CdS$_{0.3}$Se$_{0.7}$
Sulphur and selenium vacancies are generated because of partial electrode evaporation during the annealing step. The higher the annealing temperature, the greater is the selenium and sulphur vacancy concentrations. The minority carrier diffusion length decreases due to the vacancies of sulphur and selenium behaving as recombination centers [203]. For an efficient control of the vacancy concentration, the annealing treatment has to be performed in an inert atmosphere (e.g., He) containing a few ppm of oxygen in order to facilitate oxygen chemisorption. Chemisorbed oxygen behaves as an efficient electron acceptor able to compensate the excess concentration of free electrons, which results in an efficient control of carrier density. This effect was evidenced when, after annealing, if 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 as the sulphur concentration increases due to the larger value of the flat band potential. Maximum value of open circuit voltage was obtained for the composition CdS_{0.9}Se_{0.1}. 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 CdS. The reduction in photocurrent for the sulphur rich ternaries may also be due to a slight absorption of light by the polysulphide electrolyte, as the band gap value shifts closer to polysulphide absorption.