# CHAPTER-4

ELECTRICAL AND OPTICAL PROPERTIES OF CdSe FILMS

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4.1 INTRODUCTION

The electrical properties of semiconductor thin films are profoundly influenced by minute quantities of structural and chemical imperfections, which in turn are controlled by the detailed preparation and growth conditions. Conversely, optical and electrical measurements can be used to characterize with great sensitivity the defect of structure of thin films. But the measurements by themselves usually revealed nothing of the quantitative nature of the defects. This can only be inferred by tracing their behavior through systematic variations in growth conditions, annealing effects or the gaseous environment.

The current transport properties of semiconductor thin films may be characterized by the resistivity, Hall mobility, type of conductivity and carrier concentration, etc. When the transport of carriers takes place through thin films, the carriers are subjected to considerable scattering by the grain boundary in addition to the normal bulk scattering. Polycrystalline films are made up of a large number of small single crystals. Except the size, the crystallite in polycrystalline films should be similar in characteristics to the large single crystals, but the nature of grain boundary is different. Thus the additional scattering due to the grain boundary densities will reduce the effective carrier mobility below that of bulk value. Hence the measurements of the electrical properties of films should yield results which represent the average contributions of the carriers in crystallites and the grain boundaries as well as averaging of the anisotropics in the randomly oriented grains.

A study of the dependence of the electrical parameters on the growth parameters is generally essential for the fabrication of semiconductor thin film devices. Keeping in view these points, the effect of the substrate temperature and
that of the film thickness on the electrical and optical characterizations of CdSe thin films are described in the present chapter.

4.2 EXPERIMENTAL

CdSe thin films were deposited on ultrasonically cleaned glass substrates at different substrate temperatures and thicknesses by thermal evaporation technique. The source material was fine powder of CdSe (Koch Light Laboratories-U.K.).

In order to study the effect of the substrate temperature on the electrical parameters such as resistivity, carrier mobility and carrier concentration and also optical band gap, the samples were prepared under identical conditions by keeping all other parameters viz. the source temperature about 1353K, rate of evaporation about 0.5nms⁻¹, residual pressure order of 2.66x10⁻⁵Pa during the deposition, the thickness about 100nm of the deposits etc. constant.

In order to study the effect of thickness of CdSe films on electrical parameters such as resistivity, carrier mobility, carrier concentration and activation energy at substrate temperature of 550K, the samples were fabricated under identical conditions by keeping all other parameters viz. source temperature about 1353K, deposition rate 0.5nms⁻¹ and residual pressure order of 2.66x10⁻⁵Pa during deposition, constant.

The thickness and deposition rate of films were measured with the quartz crystal digital thickness monitor. The substrate temperature was controlled by digital temperature controller. A digital high impedance electrometer(KEITHLEY-614) is used for all electrical measurements. All the electrical measurements were made in dark. The optical energy band gap of CdSe thin film was determined using the spectrophotometer(Systronics-105).

The resistivity of CdSe thin films was determined using VAN DER PAUW'S[21] method. To eliminate the electrode size errors, the resistivity measurements were made on four-leaf clover shape specimens as shown in Fig.
4.1(a). The specimens were fabricated by depositing the CdSe material through mica sheet masks.

Hall effect studies of CdSe thin films were made by using samples in the form of Hall bridge geometries as shown in Fig.4.1(b). The bridge geometry with width w = 0.1cm, length l = 0.4cm with l/w ratio = 4.0 was used, as shorting effect of Hall voltage is negligible only if this ratio exceeds 2.5. The CdSe film samples with Hall bridge geometries were obtained by depositing CdSe material on to glass substrates through mica sheet masks.

4.3 RESULTS AND DISCUSSION

4.3.1 METAL-SEMICONDUCTOR CONTACTS

To evaluate the electrical properties of a semiconductor material, a better understanding of the type of contacts made by different metals to the semiconductor and the effects of the contact material on it, if any, unless it is natural, is necessary. When a metal-semiconductor junction is formed, the type of contact obtained depends on the relative magnitudes of work function of the metals($\phi_m$) and that of the semiconductor material($\phi_s$) and is summarized in Table 4.1.

Table 4.1
Metal-semiconductor contacts

<table>
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<tr>
<th>Nature of contact</th>
<th>Ohmic</th>
<th>Rectifying</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal-n-type semiconductor</td>
<td>$\phi_m &lt; \phi_s$</td>
<td>$\phi_m &gt; \phi_s$</td>
</tr>
<tr>
<td>Metal-p-type semiconductor</td>
<td>$\phi_m &gt; \phi_s$</td>
<td>$\phi_m &lt; \phi_s$</td>
</tr>
</tbody>
</table>

Basically, an ohmic contact is a neutral contact, which offers negligible resistance to the flow of current through the semiconductor for either polarity of bias voltage and is characterized by symmetrical I-V characteristics. A rectifying contact on other hand is a blocking contact, which offers some high resistance to
Figure 4.1 Configuration of the samples used for measurement: (a) four-leaf clover shape for measurement of resistivity and (b) bridge shape used to measure Hall effect.
the flow of current through the semiconductor for either positive or negative bias voltage and characterized by asymmetrical I-V characteristics.

In the present study, six pair of contacts of Cr, In, Al, Ag, Cu and Au films on CdSe films grown at 373K were studied applying I-V characteristics. The metal contacts of approximate dimensions of 5x3mm and 500nm thick were vacuum deposited side by side on a single CdSe film using proper masking arrangement in order to make metal-semiconductor-metal coplanar structure. An inset of Figure 4.2 shows photograph of the top view of metal-semiconductor-metal structure for study of contact characteristics and I-V curves for different metal contacts on CdSe films at room temperature. The apparent resistance offered by these metal contacts increased in the following order Cr, In, Al, Ag, Cu and Au. It is observed that Cr, In, Al, Ag and Cu contacts exhibit good ohmic contacts, while Au contact exhibit good nonohmic. In the present investigation vacuum deposited indium films with silver-pasted were used for ohmic contacts.

4.3.2 EFFECT OF SUBSTRATE TEMPERATURE ON RESISTIVITY($\rho$), CARRIER MOBILITY($\mu$), AND CARRIER CONCENTRATION($n$) OF CdSe FILMS

Figure 4.3 shows the variation of electrical resistivity($\rho$), carrier mobility($\mu$) and carrier concentration($n$) as a function of substrate temperature($T_s$). It is observed that the film resistivity decreased with increase of substrate temperature and reached minimum value of 2.26x10$^{-4}$ ohm.cm at the substrate temperature 550K and again it increased at the substrate temperature above 550K. The decrease in resistivity may be explained using PETRITZ'S[22] barrier model. Because the crystallites do not grow sufficiently large at low temperatures, the intercrystalline barriers are wide, offering a high resistance to the motion of charge carriers, while at higher substrate temperatures large crystallite sizes are obtained which ultimately decrease the intercrystalline barriers. The charge carriers, therefore have to cross comparatively narrow intercrystalline barriers and this results in a decrease of
Figure 4.2 I-V characteristics of Metal-CdSe semiconductor contacts with inset photograph of the top view of metal-semiconductor-metal structure for study of contact phenomena.
resistivity. The resistivity of the films deposited at substrate temperature above 550K increased, this may be due to the deviation from stoichiometric composition of film. The variation of carrier concentration and mobility of CdSe films with substrate temperature is also shown in Figure 4.3.

The carrier mobility increases with increasing substrate temperature up to 550K. Above 550K substrate temperature the mobility drops which may be due to the saturation grain size and deviation from stoichiometric composition of films.

During evaporation CdSe dissociates into Cd and Se. At lower substrate temperature CdSe film deposit is more rich in cadmium, thereby increasing carrier concentration. At higher substrate temperature, it has been suggested that the ratio of the condensation coefficient of both Cd and Se is modified during nucleus growth and coalescence so that with increasing substrate temperature films of better stoichiometry (550K) are deposited. In addition, at elevated substrate temperatures, the depositing atoms of Cd and Se are more mobile on the substrate surface and as a result of this, the film has improved crystal structure. This explains the reduction in carrier concentration with increasing substrate temperature. However at very high substrate temperature the depositing atoms may have higher tendency of reevaporation. During Hall measurement, it has been observed that all films are n-type.

4.3.3 EFFECT OF THICKNESS ON RESISTIVITY ($\rho$) OF CdSe FILMS

Figure 4.4 shows the variation of electrical resistivity ($\rho$), carrier mobility ($\mu$) and carrier concentration ($n$) with different thickness of the CdSe films deposited at constant substrate temperature 550K. The resistivity decreases as the thickness increases up to 900nm. For the thickness up to 10nm, the film has an island structure and carrier transfer between the islands occurs by either field emission or field assisted thermionic emission. Beyond this thickness the film is essentially continuous but resistivity changes with thickness because of appreciable surface
Figure 4.3 Variation of resistivity ($\rho$), carrier mobility ($\mu$) and carrier concentration ($n$) of CdSe thin films with different substrate temperature ($T_s$) at constant thickness of 100nm.
Scattering effect. SONDHEIMER'S[23] theory qualitatively explains that the scattering of carriers at the surface of the film effectively reduces the mean free path of the carriers, so that the resistivity decreases with increasing thickness. But it is inadequate to offer quantitative explanation, because during the initial stages of growth of semiconducting films, it contain defects, voids, intercrystalline barriers and impurities, which also influence the resistivity. Beyond 800nm thickness the resistivity starts approaching that of bulk value since the surface scattering effects become negligible. It has also been observed that the resistivity of very thick film is higher than that of reported value in bulk CdSe crystal. This may be due to the surface unevenness of thin films, as reported by LUCAS[32]. Above 1000nm thickness the resistivity becomes nearly constant, which may be due to the saturation of grain size above 1000nm thickness.

4.3.4 EFFECT OF THICKNESS ON CARRIER MOBILITY(µ), AND CARRIER CONCENTRATION(n) OF CdSe FILMS

Hall mobility(µ) and carrier concentration(n) of CdSe films of different thicknesses have been measured at room temperature and are shown in Fig. 4.4. It has been observed that an increase in carrier concentration with decrease in thickness ultimately results in a decrease in mobility in the films. This may be explained as being due to the increase in grain size and imperfection of these films. It may be mentioned that Hall mobility in films drops with increase in carrier concentration more vigorously than in single crystals. This may be due to presence of scattering effect in the films, whose contribution increases with decrease in film thickness. Table 4.2 shows the estimated value of the grain size of CdSe films from the electron micrographs and calculated values of the mean free path for the collision of the carrier(l) using formula[33,34]
Figure 4.4 Variation in the resistivity ($\rho$), carrier mobility ($\mu$) and carrier concentration ($n$) of CdSe films with the different thicknesses.
\[ I = \frac{h}{2e} (3n/\pi) \mu_H \]                                                (4.1)

where \( h \) is Planck's constant and \( e \) is the charge of electron.

Table 4.2
Estimated values of the grain size and the mean free path of the carriers at different
thicknesses of CdSe films.

<table>
<thead>
<tr>
<th>Thickness (T nm)</th>
<th>Grain size (D nm)</th>
<th>Mean free path of the carriers (l nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>120</td>
<td>0.67</td>
</tr>
<tr>
<td>400</td>
<td>236</td>
<td>1.61</td>
</tr>
<tr>
<td>800</td>
<td>330</td>
<td>3.07</td>
</tr>
<tr>
<td>900</td>
<td>347</td>
<td>3.54</td>
</tr>
<tr>
<td>1000</td>
<td>352</td>
<td>3.92</td>
</tr>
</tbody>
</table>

It is observed from Table 4.2 that the increase in the thickness of the films increases the grain size, which leads to increase in the mean free path for the collision of the carriers. It is also observed that the mean free path of the carriers is shorter than the grain size. It is likely that the scattering of carriers in thicker film may be due to imperfection in film.

4.3.5 EFFECT OF THICKNESS ON ACTIVATION ENERGY(\( \Delta E \)) OF CdSe FILMS

The semiconductor behavior of the films is determined not only by the change in carrier concentration, generally dominant in the extremely low and high temperature region but also by their mobility normally effective in the intermediate temperature range where charge scattering due to lattice vibrations and charged impurity centers dominate.

The variation of resistance as a function of temperature is used to determine the activation energy(\( \Delta E \)). The variation of log\( \rho \) with inverse temperature(\( T \)) for polycrystalline CdSe thin films grown at substrate temperature of 550K having different thickness is shown in Fig. 4.5. The electrical measurements were made in
Figure 4.5 Plots of log $\rho$ versus $1/T$ for different thicknesses of CdSe films.
dark and in high vacuum. It is observed from Fig. 4.5 that each curve consists of two linear portions with a break at a certain change of structure or phase of the films deposited.

A sharp rise in resistivity with decrease of temperature in the high temperature region and a gradual but slow increase eventually to a constant nature in the low temperature is experienced. The activation energies ($\Delta E$) for two linear portions were calculated by equating the slope to $\Delta(\log \rho)/\Delta(T^{-1})$ and

$$
\frac{\Delta(\log \rho)}{\Delta(T^{-1})} = \frac{\Delta E}{2k \times 2.303}.
$$

where $k = \text{Boltzmann constant}$.

$$
\Delta E = \frac{\Delta(\log \rho)}{\Delta(T^{-1})} x 2k x 2.303.
$$

Table 4.3

<table>
<thead>
<tr>
<th>Thickness t (nm)</th>
<th>Intrinsic $\Delta E$ (eV)</th>
<th>Extrinsic $\Delta E$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.286</td>
<td>0.062</td>
</tr>
<tr>
<td>300</td>
<td>0.198</td>
<td>0.040</td>
</tr>
<tr>
<td>500</td>
<td>0.174</td>
<td>0.026</td>
</tr>
</tbody>
</table>

The results are tabulated in Table 4.3. It is observed from Table 4.3 that the values of activation energy in both regions gradually decrease with the increase in thickness. However, above the thickness of 500nm the variation in $\Delta E$ is not considerable.

The increase of $\Delta E$ with the decreasing thickness can be understood from the NEUGEBAUER theory[24,25] for the electrical conduction in thin films which in a modified form could be applied to semiconductor continuous film.
On decreasing the thickness of the film, the average dimension of island decreases, ultimately resulting in the increase of \( \Delta E \). As the film grows above 500nm total isolation of the grains become highly unlikely and hence variation in \( \Delta E \) was not considerable. Similar result was also reported by ROULT[35].

4.3.6 THE EFFECT OF ILLUMINATION ON ACTIVATION ENERGY (\( \Delta E \))

The plots of \( \log p \) versus \( T^{-1} \) for a typical films of 100nm thick and deposited at the substrate temperature of about 550K, under illuminations and in the dark are shown in Fig. 4.6. Table 4.4 shows the activation energies calculated by equating slope to \( \Delta(\log p)/\Delta(T^{-1}) \)

Table 4.4

<table>
<thead>
<tr>
<th>Temperature range</th>
<th>Activation energy ( \Delta E (\text{eV}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dark</td>
<td>3000 lux</td>
</tr>
<tr>
<td>Low range</td>
<td>0.062 0.036</td>
</tr>
<tr>
<td>High range</td>
<td>0.286 0.178</td>
</tr>
</tbody>
</table>

It is observed that the activation energy of the 100nm thick CdSe film in the low temperature region is lower than that in the high temperature region. It is also seen that on illumination of film the activation energies are reduced both in the low and high temperature ranges in comparison to those in dark.

According to PETRITZ[22] the change in conductivity(\( \Delta \sigma \)) due to illumination of sample could be caused by a change in the effective mobility \( \mu^* \) and \( \Delta \sigma \) is given by equation

\[
\Delta \sigma = q \mu^* \Delta \rho + q \rho \Delta \mu^* \]

\[ (4.3) \]

\( q \) = charge of electron, and
Figure 4.6 Temperature dependence of resistivity of CdSe film deposited at 550K in the dark and under illumination.
since \( \mu^* = \mu \exp (-q\phi/kT) \). \hspace{1cm} (4.4)

\[ \Delta \mu^* = (-q\mu/KT) \exp(-q\phi/kT) \Delta \phi. \]

where \( \phi \) is the intercrystalline barrier height and \( \Delta \phi \) is the change in intercrystalline barrier height produced by light. Although the effect of illumination is to free additional carriers and to produce increased conductivity, it also reduces the height of the potential barrier between the crystallites composing the films and hence the activation energy is reduced under illumination.

4.3.7. EFFECT OF SUBSTRATE TEMPERATURE ON THE SPECTRAL RESPONSE OF CdSe FILMS

The variation of photoresponse as a function of wavelength of the incident radiation measured at room temperature for four different films deposited at 373K, 473K, 550K and 623K is shown in Fig. 4.7. It is observed that the photoresponse of CdSe films strongly depends on the substrate temperature. The dark resistivity and photoresponse were always greater for films deposited at higher substrates temperature upto 550K. This may be due to the fact that photogeneration of carriers is assisted[4,8] by the attainment of improved crystalline structure and stoichiometric with increase in substrate temperature as revealed by TEM and EDAX(Chapter-3, section-3.2) studies. It is observed from Fig. 4.7 that the photoresponse of CdSe films deposited at the substrate temperature 623K is lower than that of film deposited at 550K. This may be due to the fact that these film have been non stoichiometric (Chapter-3, section-3.3.1) and have higher resistivity. It is also observed that there is a broad peak in the photoresponse near about 705nm as indicated in Fig. 4.7 which shifts towards higher wavelength for films deposited at higher substrate temperatures indicating that the centers of photoresponse are intimately connected with the microstructure of the films[36].
Figure 4.7 Plots of photoresponse of CdSe films with incident wavelength ($\lambda$) deposited at four different substrate temperature: (a) 373K, (b) 473K, (c) 550K, (d) 623K.
4.3.8 STUDY OF OPTICAL ABSORPTION OF CdSe FILMS

The study of the interband absorption spectrum near the threshold of its rapid increase (near the absorption edge) can obviously provide information on the structure of the electron's energy spectrum near the top edge of the valence band and the bottom edge of the conduction band; this information is of essential importance for the determination of the semiconductor properties. Therefore, the measurement of the absorption coefficient constitutes the most important means of determining the band structures of semiconductors. In order to verify the nature of the transition energy gap, one should examine the dependence of the absorption coefficient $\alpha$ on the photon energy, which is given by

$$\alpha h\nu = A (h\nu - E_g)^{n/2}$$ ................................. (4.6)

where $h\nu$ is the energy of incident photon, $A$ is a constant which depends on the material and the nature of transition, $E_g$ represents the band gap energy and $n=1$ for direct and $n=4$ for indirect transitions.

Figure 4.8 shows plot of $(\alpha h\nu)^2$ versus photon energy $h\nu$ for 100nm thick CdSe films deposited at about 550K substrate temperatures. The intercepts of these straight line plot on the energy axis at $(\alpha h\nu)^2 = 0$ gives the value of energy bandgap of CdSe film. It is found to be 1.75 eV. As it satisfy $n=1$ in relationship of equation (4.6), it indicates that the CdSe film is direct band gap semiconductor.

The band gap of CdSe film was reported between 1.65 eV to 1.74 eV at room temperature by several researchers[26-30]. KAITHLA et al.[30] and GUPTA et al.[31] have reported a band gap of 1.74 eV, 1.75 eV respectively at room temperature. Only direct transition is obtained in the film. THUTUPALLI et. al.[27] have also reported that no indirect transition takes place in CdSe and ZnSe films.
Figure 4.8 Plot of \((ahv)^2\) vs \(hv\) for CdSe thin films deposited at substrate temperature 550K.
4.4 CONCLUSIONS

1. The metal-semiconductor contact study reveals that chromium and indium metals provide good ohmic, while, gold metal provides non-ohmic contact to the CdSe film.

2. The variation in the electrical resistivity, carrier mobility, carrier concentration and photoresponse of CdSe films with different substrate temperature can be explained on the basis of the stoichiometric composition and the variation in the crystallite size. The CdSe films deposited at substrate temperature of 550K have minimum electrical resistivity, maximum carrier concentration and maximum photoresponse.

3. The resistivity of CdSe film decreases with increase of thickness upto about 1000nm on account of increase of mean free path of carriers.

4. The decrease of the activation energy with increase in thickness may be explained by the NEUGEBAUER[24] theory.

5. The decrease of activation energy $\Delta E$ with illumination can be explained with the help of PETRITZ theory.

6. The optical energy band gap of CdSe films is found to be 1.75eV at 550K substrate temperature, which is in good agreement with value reported by other researcher.

Thus, the change in the electrical and optical properties of CdSe films with varying growth parameters (viz. substrate temperature and thickness etc.) can be attributed mainly to the change of the structural perfection.
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