CHAPTER IV

RESULTS ON CdS FILMS

4.1 INTRODUCTION

CdS is one of the most promising materials for solar cell applications mainly as the window material. There are many deposition techniques used to prepare CdS layers such as vacuum evaporation, electrodeposition, sputtering, epitaxial deposition, spray pyrolysis and chemical bath deposition. In this chapter, results obtained on brush plated CdS films are reported.

4.2 DEPOSITION OF CdS FILMS

CdS films were prepared on conducting glass and titanium substrates using selective/brush plating technique described in Chapter III. The precursors used for the deposition of CdS were 0.5M CdSO₄, 0.2 M sodium thiosulphate and triply distilled water to make up the solution to 10 ml. The films were deposited at a current density of 80 mA cm⁻² and at different temperatures in the range 30 - 80°C. The deposition current density was fixed based on our earlier experience with brush plated films. It took 20 minutes to deposit a film of thickness 5.0 microns (thickness estimated by gravimetry). These layers were heat treated at different temperatures in the range 450 - 550°C in argon atmosphere for 20 minutes.
4.3 X-RAY DIFFRACTION STUDIES

X-ray diffraction (XRD) patterns of cadmium sulphide films deposited at different temperatures is shown in Fig.4.1. The films exhibit polycrystalline nature with peaks corresponding to the cubic phase. The intensity of the peaks increased with deposition temperature. The XRD patterns of the films post heat-treated at different temperatures in the range 450 - 550°C are shown in Fig.4.2. Peaks corresponding to the hexagonal phase were observed. As the heat treatment temperature increases, the crystallinity of the films also increased as evidenced by the sharpness of the XRD peaks. Peaks corresponding to (100), (002), (101), (110), (103) and (112) reflections were observed. The lattice parameters calculated from the XRD data are $a = 4.145\text{Å}$ and $c = 6.752\text{ Å}$. These values are found to be in close agreement with the ASTM data. The crystallite size calculated using the Debye-Scherrer’s equation is indicated in Table.4.1.
Fig. 4.1 - XRD patterns of CdS films deposited at different deposition temperatures (a) 80°C (b) 50°C
Fig. 4.2 - XRD patterns of CdS films annealed in argon atmosphere at different temperatures (a) 450°C (b) 500°C (c) 525°C (d) 550°C.
Table 4.1
Crystallite size of CdS films

<table>
<thead>
<tr>
<th>Annealing Temperature (°C)</th>
<th>Crystallite Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>450</td>
<td>50</td>
</tr>
<tr>
<td>475</td>
<td>70</td>
</tr>
<tr>
<td>500</td>
<td>85</td>
</tr>
<tr>
<td>525</td>
<td>100</td>
</tr>
<tr>
<td>550</td>
<td>117</td>
</tr>
</tbody>
</table>

4.4 EDAX MEASUREMENTS

EDAX studies indicated the composition of the films annealed at 475°C to be Cd (60.1%) and S (39.9%). For the films annealed at 550°C, the concentration varied slightly and it was Cd (62.2%) and S (37.8%) (Fig.4.3).

4.5 XPS STUDIES

XPS spectra of the brush plated CdS films grown at different temperatures were measured to analyze the chemical composition of the films. Fig.4.4 shows the binding energies of the Cd(3d_{5/2} and 3d_{3/2}) and S(3d_{5/2} and 3d_{3/2}) levels of the CdS films annealed at 550°C. There is no preferential removal of Cd on annealing, but a small amount of S is lost by evaporation. This is also evidenced from the EDAX results. The peak energy levels associated with the Cd (3d_{5/2} and 3d_{3/2}) appeared at 405 and 412.5 eV respectively. These values are in close agreement with the literature values. The binding energies of S (3d_{5/2} and 3d_{3/2}) levels are observed at 161.0 eV and 168.0 eV respectively. The sulphur binding energies are found to shift to lower energy values after annealing due to a small loss of S by evaporation.
There is no evidence of shifting of the energy levels to higher binding energies corresponding to the oxidation of sulphur or cadmium after annealing.

4.6 OPTICAL STUDIES

Optical absorption measurements were made on the CdS films deposited on conducting glass substrates. Substrate absorption, if any was corrected by placing an uncoated conducting glass substrate in the reference beam. Fig.4.5 shows the $(\alpha h \nu)^2$ vs $h \nu$ plot of the CdS films annealed at 550°C.

Fig.4.3 – EDAX spectrum of CdS films heated at 550 °C
Fig. 4.4 – XPS spectrum of Cd and S for films heated at 550°C
The energy gap obtained from the wavelength at which onset of maximum absorption is obtained corresponds to 2.39 eV. This value is similar to the values obtained on single crystal and thin film CdS [3].
4.7 RESISTIVITY, HALL MOBILITY AND CARRIER CONCENTRATION

4.7.1 MEASUREMENTS

Hall measurements were made on the films adopting the following procedure [56]. In this method, the CdS layer is mechanically transferred from the Indium doped tin oxide conducting substrate onto a non-conductive epoxy resin without the formation of cracks [57, 58]. The electrical properties of the CdS layers were examined at room temperature by resistivity and Hall measurements using Van der Pauw method. The resistivity (\(\rho\)) of the CdS films was calculated using equation 2.5. The influence of annealing temperature on the resistivity of the films is depicted in Fig.4.6 for the resistivities measured at room temperature. The magnitude of the resistivity varies from 0.1 to 20 ohm-cm as the annealing temperature is increased. Fig.4.7 shows the variation of Hall mobility (\(\mu_H\)) of all the films with annealing temperature. The Hall mobility was determined by using the equation 2.7. It was observed that the mobility decreases initially and then attains a constant value as the annealing temperature increases. Fig.4.8 shows the variation of carrier density N, (calculated using equation 2.8) with the annealing temperature. It is evident from the figure that the carrier density decreases from 3.13 x 10^{18} to 2.7 x 10^{17} cm^{-3}. The result that the resistivity increases with increase of annealing temperature may be due to the change in film stoichiometry (excess cadmium or sulphur vacancies, which are electron donor sites that provide the additional carriers and decrease the resistivity). In addition, CdS dissociates during annealing by evaporation modifying the ratio of Cd/S. Further, during annealing oxygen fills the S vacancies in CdS and as these donor sites are eliminated, the free carrier concentration is reduced. Invariably, the absorbed oxygen offsets the decrease in resistivity due to the excess carriers provided by the excess cadmium obtained on heat treatment resulting in a net increase of resistivity.
Fig.4.6 – Variation of resistivity of CdS films with post annealing temperature
Fig. 4.7 – Variation of mobility of CdS films with post annealing temperature
Fig.4.8 – Variation of Carrier density of CdS films with post annealing temperature

The grain boundaries between the crystallites dominate the electrical properties of the polycrystalline thin film semiconductors [59]. Traps at the grain boundaries are responsible for the potential barrier that limits carrier mobility.

4.8 PHOTOCONDUCTIVITY STUDIES

For photoconductivity studies, the CdS films deposited at 80°C and post heat treated at different temperatures were transferred to a non conductive epoxy as described above. Indium Ohmic contacts were provided at the two edges of the film surface and the films were illuminated with 100 W tungsten halogen lamp. Fig.4.9 shows the variation of photosensitivity (PS) with intensity of illumination for the cells prepared by using the powder synthesized in the laboratory. The PS was calculated using the equation. 2.13.
It was observed from the figure, as the intensity of illumination increases, the corresponding photosensitivity also increases. Of all the annealing temperatures, the cells prepared with films annealed at 550°C exhibited maximum photosensitivity. The dependence of PS on light intensity

![Graph showing photosensitivity vs. intensity for different annealing temperatures.](image)

**Fig.4.9 - Dependence of Photosensitivity on illumination intensity for undoped CdS films heated at different temperatures (a) 450°C (b) 475°C (c) 500°C (d) 525°C (e) 550°C**

at room temperature can be described in terms of the oxygen absorption effects at high annealing temperatures. The thermal release of oxygen from the surface is the possible mechanism, which is always dominant for cells annealed in Argon and hence both the dark and photoconductivity are increased. The argon used in the present studies was 99% pure and it
contained a small percentage of oxygen. The increase in photosensitivity may be due to the creation of opposite type of charge carriers in N-type CdS, as oxygen acts here as an acceptor impurity. Similar behaviour has also been observed in CdS photocells. It was reported that CdS films annealed at lower temperatures contained larger electron concentrations because of a slight excess of Cd, and the carrier concentration did not change appreciably on illumination to exhibit maximum photosensitivity, hence further studies were made only on the films annealed at 550 °C.

4.8.1 Effect of doping

Fig. 4.10 represents the plots of illumination intensity versus photosensitivity for all the cells prepared with films doped with 0.001, 0.003, 0.005, 0.007, 0.009 and 0.011 M of copper. Similar to the undoped cells, the photosensitivity increases as the intensity of illumination increases. The magnitude of photosensitivity is increased by two orders when compared to undoped cells. Also, it is observed from the figure, as the copper concentration increases for a particular intensity of illumination and for a particular annealing temperature, the corresponding photosensitivity increases and it reaches a maximum when the copper concentration is 0.005 M and then decreases. Hence, further studies were made only on the films with this doping concentration. The incorporation of copper impurity in the CdS films decreased the dark conductivity. Due to the dual nature of copper impurity, the holes and electrons may recombine with majority carriers in the dark and minority carriers under illumination, thereby increasing the photosensitivity of the cell. In fact studies of copper diffusion in CdS [60] have shown that copper can act both as an acceptor and as a donor depending on whether it occupies substitution or interstitial sites in the lattice. The acceptor dominant behaviour of copper arises when the number of copper ions on cadmium substitutional sites is larger than the number of atoms in the interstitial
positions. It is clear from the results observed here that in the II-VI semiconducting compounds, copper is associated with photoconductivity sensitizing centers.

Fig.4.10 - Plots of illumination intensity versus photosensitivity for all the cells prepared with CdS films deposited at 80°C and post heated at 550°C doped with (a) 0.001 M (b) 0.003 M (c) 0.005 M (d) 0.007 M (e) 0.009 M (f) 0.011 M of copper.

Copper centers are situated at 0.6eV above the valence band as reported by Tyurn et al [61]. The maximum photosensitivity is observed for the doping concentration of 0.005 M. AAS analysis of the Cu concentration corresponding to this doping revealed the presence of 405 ppm of copper. This particular concentration corresponds to a donor to acceptor ratio around unity. For other concentrations of copper doping this ratio deviates from unity and hence the photosensitivity decreases. The acceptor dominant behaviour of
copper arises when the number of copper ions on Cd substitutional sites is larger than the number of atoms in the interstitial positions. Thus to fix the acceptor and donor concentrations as required above, the total donor concentration must be determined and distinction between electrically active impurities and crystal defects as a function of processing variables must be made.

### 4.8.2 Effect of Ageing

Fig. 4.11 exhibits the variation of photosensitivity of both undoped and doped cells with time. The unencapsulated cells when kept upto 220 days indicated a constant value of photosensitivity for both undoped and doped cells. After keeping the cells for 250 days, the value of photosensitivity decreased. This behaviour may be due to the effect of atmospheric oxygen introducing acceptor levels in CdS, since the cells are not encapsulated. For the doped cells, both copper and oxygen introduce acceptor levels in CdS, which in turn decreases the photosensitivity after keeping the cells for 220 days. The encapsulated cells did not show any degradation even after 1000 days.

### 4.8.3 Spectral distribution of photoconductivity

The spectral distribution of photoconductivity of the cells doped with different concentrations of copper (0.001, 0.003, 0.005, and 0.007 M) is shown in Fig. 4.12. It is evident from all the figures, that, for all the four concentrations of copper doping, the normalized photocurrent of the cell increases as the wavelength of the incident light increases and the photocurrent reaches a maximum for \( \lambda = 0.6 \, \mu m \). Above this particular wavelength, the photocurrent starts to decrease and reaches a minimum at
0.9 μm. From the figures it is also evident that the impurity excitation dominates.

Fig. 4.11 - Variation of Photosensitivity of CdS films with time
(a) Undoped (b) copper doped (0.005 M)
the spectrum. Generally pure CdS has a peak photoresponse at $\lambda = 0.52$ $\mu$m. This response is essentially caused by intrinsic excitation. Lattice defects which may be present in the crystal introduce levels in the forbidden gap, which requires less energy than excitation across the band gap. Consequently in crystals with such defects, the peak response shifts to longer wavelengths. Such longer wavelength (in this case 0.6 $\mu$m) response might also be attributed to the presence of incorporated impurities like chloride or copper or the combined effects of copper and chloride centers [62]. The presence of adsorbed oxygen on the annealed CdS films also contributes to the high peak value. The long wavelength tail of the response for the doped cells may be due to the excitation of electrons directly from the sensitizing centers (copper levels) [63].
The sharp decrease in the photocurrent at shorter wavelengths may be partly associated with the corresponding decrease in the lamp response, but this would not have been sufficient, on its own, to account for the observed behaviour. However, this could result from the interaction of the class-II (i.e., the Cu level) center located in the upper half of the band gap with a class-I center located near the middle of the band gap \((\sigma_p/\sigma_n - 1)\). When scanning from the long to short wavelengths, an initial increase in the photocurrent due to the promotion of electrons from the class-II center to the conduction band has been observed. At this stage, the class-I center would be saturated with electrons and therefore would not participate in any recombination process. However, when the energy of illumination exceeds the energy difference between the class-II center and the valence band, holes will be released to the valence band from the class-II center. These will be captured by the class-I center, effectively switching on a fast recombination route. This reduces the lifetime of electrons in the conduction band and hence the photoconductivity gain.

4.8.4 A.C. Photoconductivity Measurements

A.C. photoconductivity measurements were made using a chopper of frequency 90 Hz for the films deposited at different temperatures and for the films doped with different concentrations of copper.

The A.C. photosensitivity of the films were calculated using the relation,

\[
\%S = \frac{E - \Delta V}{V_1(E - V_2)} \times 100
\]
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 when the cell is in dark and $V_2$ is the load voltage on illumination.

$$V_2 = (V_1 + \Delta V), \Delta V$$ is the signal voltage [64].

The sensitivity results are indicated in Table 4.2. It is observed from the table that for the films heat-treated at 525°C, the AC photosensitivity is maximum. The variation of sensitivity was studied using different bias voltages ranging from 30 – 150 V, maximum photosensitivity was obtained for a bias voltage of 150 V with an illumination intensity of 5000 lux.
Table 4.2
AC photosensitivity Measurements of undoped films
Applied bias: 150 V  Intensity: 5000 lx

<table>
<thead>
<tr>
<th>Sl.No.</th>
<th>Heat treatment Temp (°C)</th>
<th>S = (ΔRc/Rc) x 100%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>450</td>
<td>14.61</td>
</tr>
<tr>
<td>2.</td>
<td>475</td>
<td>18.31</td>
</tr>
<tr>
<td>3.</td>
<td>500</td>
<td>24.08</td>
</tr>
<tr>
<td>4.</td>
<td>525</td>
<td>31.74</td>
</tr>
<tr>
<td>5.</td>
<td>550</td>
<td>38.75</td>
</tr>
</tbody>
</table>

Table 4.3
Effect of copper doping on AC photosensitivity
Applied Bias: 150 V  Intensity: 5000 lux

<table>
<thead>
<tr>
<th>Sl.No.</th>
<th>Doping concentration (ppm)</th>
<th>S = (ΔRc/Rc) x 100%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>100</td>
<td>42.52</td>
</tr>
<tr>
<td>2.</td>
<td>200</td>
<td>58.32</td>
</tr>
<tr>
<td>3.</td>
<td>300</td>
<td>64.15</td>
</tr>
<tr>
<td>4.</td>
<td>400</td>
<td>79.32</td>
</tr>
<tr>
<td>5.</td>
<td>500</td>
<td>75.25</td>
</tr>
</tbody>
</table>

In the case of copper doped samples, the value of the AC photosensitivity was observed to be higher than the undoped samples. The AC photosensitivity (Table 4.3) is found to increase up to 400 ppm of copper doping beyond which it starts to decrease due to the possible formation of small amounts of Copper.
4.9 ATOMIC FORCE MICROSCOPY

Fig. 4.13 shows the Atomic Force Micrograph of the CdS films deposited at a deposition temperature of 80°C and post heat treated at different temperatures in argon atmosphere. The grain size and surface roughness are observed to increase with post heat treatment temperature. The grain size is found to increase from 60 nm to 130 nm with increase of post heat treatment temperature. The surface roughness increases from 4.5 nm to 9.0 nm. This is understandable, since higher temperatures improves the crystallinity and causes the small grains to coalesce into bigger grains, hence an increase in surface roughness.

4.10 PHOTO ELECTROCHEMICAL MEASUREMENTS

Photo electrochemical (PEC) cells were prepared using the films deposited on titanium substrates heat treated at different temperatures. The films were lacquered with polystyrene in order to prevent the metal substrate portions from being exposed to the redox electrolyte. These films were used as the working electrode. The electrolyte was 1 M polysulphide. This electrolyte was chosen, as it is well known that CdS electrode has reasonable stability and yield respectable outputs in 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 intensity of illumination was varied changing the distance between the source and the cell. The power output characteristics of the cells were measured by connecting the resistance box and an ammeter in series and the voltage output was measured across the load resistance. The photocurrent, dark current and output voltage were measured with a HIL digital multimeter.
Fig. 4.13 – Atomic force micrographs of CdS films deposited at 80°C and post heat treated at different temperatures (a) 475°C (b) 525°C (c) 550°C
The CdS photoelectrodes were dipped in the electrolyte and allowed to attain equilibrium under dark conditions for about 10 minutes. 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 under illumination and the dark current, and voltage under illumination and dark voltage respectively.

The power output characteristics of the PEC cells made using the photoelectrodes heat treated at different temperatures is shown in Fig.4.14. From the figure, it is observed that the PEC output parameters, viz., open circuit voltage and short circuit current were found to increase for the electrodes heat treated up to a temperature of 500°C. Photoelectrodes heat treated at temperatures greater than this value exhibited lower open circuit voltage and short circuit current due to the reduction in thickness of the films as well as the slight change in stoichiometry. Hence, further studies were made only on the films heat treated at 500°C. The power output characteristics of the electrodes heat treated at 500°C were studied at different intensities of illumination in the range 20-100 mWcm\(^{-2}\). It was observed that both \(V_{oc}\) and \(J_{sc}\) increased with increase of intensity (Fig.4.15). \(V_{oc}\) increased from 0.36 V to 0.50 V as the intensity increased from 20 – 100 mWcm\(^{-2}\). Beyond 80 mWcm\(^{-2}\) illumination, \(V_{oc}\) was found to saturate as is commonly observed in the case of photovoltaic cells and PEC cells. \(J_{sc}\) is found to increase with intensity of illumination. It is observed that the \(J_{sc}\) increases from 3.6 mAcm\(^{-2}\) to 5.2 mAcm\(^{-2}\) as the intensity increased from 20 – 100 mWcm\(^{-2}\). A plot of ln\(J_{sc}\) vs \(V_{oc}\) (Fig.4.16) yielded a straight line and the reverse saturation current density \(J_0\) was 1.5 x 10\(^{-7}\) Acm\(^{-2}\). The ideality factor (n) was calculated from the slope of the straight line and it was found to be 2.65.
The effect of photoetching on the PEC performance was studied by shorting the photoelectrode and the graphite counter electrode under an illumination of 100 mWcm\(^{-2}\) in 1:100 HCl for different durations in the range 0 – 100 s. Both photocurrent and photovoltage are found to increase up to 80 s photoetch, beyond which they begin to decrease (Fig.4.17). Photoetching leads to selective attack of surface states not accessible to chemical etchants. It is observed that during photoetching, the open circuit voltage and short circuit current increase from 0.475 V to 0.60 V and from 4.2 mAcm\(^{-2}\) to 7.4 mAcm\(^{-2}\) respectively for an intensity of 80 mWcm\(^{-2}\). The decrease in the voltage and current beyond 80s photoetching can be attributed to separation of grain boundaries due to prolonged photoetching [65]. The power output characteristics (Fig.4.18) after 80s photoetching indicates a \(V_{oc}\) of 0.60V, \(J_{sc}\) of 7.50 mAcm\(^{-2}\), \(ff\) of 0.53 and \(\eta\) f 3.0% for 80 mWcm\(^{-2}\) illumination. The photovoltaic parameters of the electrodes with and without photoetching are shown in Table.4.4. The efficiency of the photoelectrodes is higher than the earlier reports [66 - 68].

Mott-Schottky plots (1/C\(^2\) vs V) were studied using 1 M Na\(_2\)SO\(_4\) as the blocking electrolyte and an EG & G PARC impedance analyzer model 6310. The CdS films heat treated at different temperatures were used as working electrode, graphite was used as counter electrode and SCE was used as the reference electrode. The frequency was fixed at 1 KHz and the bias voltage was varied in the range –0.8 to +0.4V vs SCE, the value of C was estimated from the imaginary part of the impedance using the equation,

\[
C = \frac{1}{2\pi fZ}
\]
Fig.4.14 – Power Output Characteristics of CdS electrodes annealed in argon atmosphere at different temperatures (a) 450°C (b) 475°C (c) 550°C (d) 500°C
Fig. 4.15 – Variation of open circuit voltage and short circuit current with intensity for the CdS electrodes annealed in argon at 500°C.
Fig. 4.16 - Plot of $\ln J_{sc}$ vs $V_{oc}$ of CdS electrodes annealed in argon atmosphere at 500 °C
Fig. 4.17 - Effect of Photoetching on $V_{oc}$ and $J_{sc}$ of CdS electrodes annealed in argon atmosphere at 500 °C
Fig. 4.18 - Power Output Characteristics of CdS electrodes annealed in argon atmosphere at 500°C after photoetching for 80s and illuminated at 80 mWcm⁻².

Fig. 4.19 exhibits the Mott-Schottky plots for the films heat treated at 550°C. The nature of the plot indicates n-type behaviour. Extrapolation of the plot to the voltage axis yields a Vfb of −1.10 V (SCE). The value of carrier density from the slope of the plot yields a value around 2.0 x 10¹⁷ cm⁻³. This value agrees well with the carrier density obtained from Hall measurements.
Spectral response measurements were carried out on the photoelectrodes by using photophysics monochromator and a 250W Tungsten halogen lamp, 1 M polysulphide as electrolyte, graphite as counter electrode and the photoelectrode as the working electrode. The wavelength was varied in the range 400 – 900 nm and the photocurrent was noted at each wavelength. Plot of $J_{\text{ph}}$ vs $\lambda$ for the CdS electrode heat treated at 500°C is shown in Fig.4.20. The value of $J_{\text{phmax}}$ occurs at 525 nm corresponding to the band gap of 2.38 eV. This value matches well with the band gap value of 2.39 eV estimated from optical absorption measurements.

Table 4.4

Photovoltaic parameters of CdS photoelectrodes

(Intensity–80 mWcm$^{-2}$)

<table>
<thead>
<tr>
<th>Temperature of Heat treatment</th>
<th>$V_{\text{oc}}$ (V)</th>
<th>$J_{\text{sc}}$ (mAcm$^{-2}$)</th>
<th>ff</th>
<th>$\eta$ (%)</th>
<th>$R_s$(Ω)</th>
<th>$R_{sh}$(kΩ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>450</td>
<td>0.300</td>
<td>2.6</td>
<td>0.56</td>
<td>0.66</td>
<td>20.0</td>
<td>2.0</td>
</tr>
<tr>
<td>475</td>
<td>0.375</td>
<td>3.2</td>
<td>0.58</td>
<td>0.93</td>
<td>18.0</td>
<td>3.6</td>
</tr>
<tr>
<td>500</td>
<td>0.480</td>
<td>4.3</td>
<td>0.56</td>
<td>1.43</td>
<td>10.0</td>
<td>5.0</td>
</tr>
<tr>
<td>525</td>
<td>0.450</td>
<td>3.9</td>
<td>0.60</td>
<td>1.20</td>
<td>15.0</td>
<td>2.8</td>
</tr>
<tr>
<td>550</td>
<td>0.425</td>
<td>3.6</td>
<td>0.57</td>
<td>0.93</td>
<td>18.0</td>
<td>3.6</td>
</tr>
<tr>
<td>500 (After photoetch)</td>
<td>0.600</td>
<td>7.5</td>
<td>0.53</td>
<td>3.00</td>
<td>13.0</td>
<td>2.0</td>
</tr>
</tbody>
</table>
Fig. 4.19 – Mott-Schottky plots for the films heat treated at 550 °C
4.11 LASER RAMAN STUDIES

The room temperature Raman spectra of the CdS films deposited at different deposition temperatures are shown in Fig.4.21. The Raman spectra of the CdS films exhibit a well-resolved line at approximately 300 cm\(^{-1}\), corresponding to the first order scattering of the longitudinal optical (LO) phonon mode. CdS can take both hexagonal wurtzite and cubic zinc blende structures, and it was reported that for both the structures, the zone-center longitudinal-optical A\(_1\)(LO) phonon frequency is about 305 cm\(^{-1}\)\[69,70\]. The FWHMs of the 1 LO peak are 27.8, 23.7, and 20.6 cm\(^{-1}\), for the films deposited at 30°C, 50°C and 80°C respectively. These values are much larger than that (6.5 cm\(^{-1}\)) for melt grown single-crystal CdS. Usually, very large width indicates poor crystallinity (lack of long-range order) in the films, but
the well-defined peak indicates the crystalline nature of the films. Hence, the large FWHM in the present case can be attributed to a polycrystalline effect in the films [71]. The broad second-order scattering of LO phonons is also visible at approximately 600 cm\(^{-1}\), regardless of deposition temperature. The main characteristic of the Raman spectra of our films is the broadening of the LO peak in the samples deposited at lower deposition temperatures. The peak position did not change much with change in deposition temperature and remained almost constant.

Fig.4.21 – Laser Raman Spectra of CdS films deposited at different deposition temperatures (a) 30°C (b) 50°C (c) 80°C
4.12 PHOTOLUMINESCENCE STUDIES

Fig. 4.22 shows the room temperature PL spectra for films deposited at different deposition temperatures. In our study, room temperature PL was detected for all the CdS samples deposited by the brush plating technique. All the samples showed two bands in the PL spectra, one localized at 2.30 eV and the other at 1.80 eV. The band in the 1.60–1.85 eV range is associated to sulfur vacancies (VS), whereas the peak around 2.3 eV is usually related to interstitial sulfur (IS) [72,73].

Fig.4.22 – Room temperature Photoluminescence spectra of CdS films deposited at different deposition temperatures (a)30°C (b) 40°C (c) 50°C (d) 60°C (e) 70°C (f) 80°C.