Chapter – IV

Results on CdSe films

Introduction:

In recent years, there has been considerable interest in II-VI semiconductors particularly CdSe for various optoelectronic applications like blue light emitting diodes, laser diodes, catalysis, solar cells and biological labeling. Cadmium selenide is of interest because its band gap can be tuned across the visible region by varying the size of the material. Several thin film techniques have been used for the deposition of CdSe thin films. In this work, CdSe films have been deposited by the pulse plating technique. In this chapter, characteristics of the pulse plated CdSe films are presented and discussed.

Preparation of Thin films:

CdSe films of area 2.5 cm² were deposited on titanium, tin oxide and stainless steel substrates at different duty cycles in the range 6.25 – 50 %, the substrates were first cleaned prior to deposition with dilute hydrochloric acid. All the etched electrodes were thoroughly washed in triple distilled water and finally degreased with acetone or trichloroethylene. AR grade cadmium sulphate and selenium di oxide were the precursors for the deposition bath, pH was adjusted to a value of 2 by the addition of dil.H₂SO₄. The pulse voltage/current, concentration and pH were optimized using the earlier report[83]. Under optimized condition, a concentration of 0.5 M CdSO₄, 0.1 M SeO₂ were taken. The deposition was carried out for a duration of one hour, at - 870mV(SCE) [84,85] at room temperature. The thickness of the films was estimated to be
1.6µm for as deposited films by gravimetric method. The films were heat treated in argon at different temperatures in the range of 450 - 550ºC for a duration of 5 min. The thickness of the films after heat treatment was around 1.5 µm. Reproducibility of the deposition process was checked by depositing about six sets of samples under each condition. The variation in results obtained with the different sets were within 2%.

**X-Ray Diffraction studies:**

Structural analysis was made on the CdSe films deposited at different duty cycles (both as deposited and post-heat treated). All the surfaces of the films were smooth and adhered firmly to the substrate. X-ray diffraction studies were made by using CuKα radiation(λ = 1.541 Å) and JEOL 8030 model x-ray diffractometer. By using the same x-ray diffraction pattern, the full widths at half maximum(FWHM) for all the films were obtained. Phase identification was made and the crystallite size of the films was determined from Scherrer’s equation[41].

X-ray diffractograms of the films deposited at different duty cycles are shown in Fig.4.1a – 4.1e. The XRD patterns indicate the polycrystalline nature of the films. In all the figures, the prominent peaks corresponding to (111), (220) and (311) reflections of CdSe were observed at 2Θ of 25.2º, 42.0º and 49.6º respectively. Two peaks corresponding to Ti(2Θ of 53.2º and 70.5º) and one peak corresponding to Cd were also observed. The as deposited films exhibit cubic structure with preferential orientation in the (111) direction. As the duty cycle decreases, the intensity of the peaks decrease, the width of the (111) peak is observed to increase with decrease of duty cycle for an increase of OFF time.
Fig. 4.1 – X-ray diffraction pattern of pulse plated CdSe films at different duty cycles (a) 100% (b) 50% (c) 33% (d) 15% (e) 10% (f) 6%
from 1s to 15s. As the OFF time increases, the number of peaks are observed to decrease gradually and for OFF times greater than 15s only peaks corresponding to Cd were observed along with the Ti peaks (Fig.4.2). Hence films were prepared with OFF times \( \leq 15 \)s. The thickness of the films are also found to decrease with increase of OFF time, this is understandable, since the number of pulses decrease for the same total deposition duration, viz., one hour.

In order to change the phase from cubic to hexagonal (which is the desired phase for optoelectronic devices), the films were post heat treated in air at different temperatures in the range of 450 - 550\(^\circ\)C\[86]\ for 10 min. As the temperature of heat treatment increased from 450\(^\circ\)C peaks corresponding to hexagonal CdSe are found to appear (Fig.4.3 and Fig.4.4). At a heat treatment temperature of 550\(^\circ\)C only single phase hexagonal CdSe reflection corresponding to (100), (002), (101), (102), (110), (103), (112), (203), (105) and (300) at 2\(\Theta\) of 23.9, 25.4, 27.0, 35.2, 42.0, 45.8, 49.4, 63.7, 70.8 and 76.3\(^\circ\) were observed along with four titanium peaks.

**Optical Absorption Studies:**

Optical Absorption studies were made on the films deposited at different duty cycles and heat treated at 550\(^\circ\)C in argon containing single phase hexagonal CdSe) using the films deposited on tin oxide substrates. Substrate absorption, if any was corrected by placing an identical uncoated tin oxide substrate in the reference beam.

The absorption co-efficient(\(\alpha\)) at various wavelengths has been calculated using the equation\[87\]
Fig. 4.2 – X-ray diffraction pattern of pulse plated CdSe films deposited at a duty cycle of 3.33%
Fig. 4.3 - X-ray diffraction pattern of pulse plated CdSe films at different duty cycles and annealed at 525°C (a) 50% (b) 33% (c) 15% (d) 10% (e) 6%
Fig. 4.4 - X-ray diffraction pattern of pulse plated CdSe films at different duty cycles and annealed at 550°C (a) 50% (b) 33% (c) 15% (d) 10% (e) 6%
\[ \alpha = 2.303A/t \] ........................................... (1)

Where \( A \) is the absorbance value at a particular wavelength and \( t \) is the thickness of the film. The band gap of the films were determined by plotting a graph between \((\alpha h\nu)^2\) vs \( h\nu \). Extrapolation of the linear region to the \( hv \) axis gives the band gap of the material. Fig.4.5 indicates a direct band gap of 1.70 eV for the films heat treated at 550ºC irrespective of duty cycle. An absorption coefficient of \( 10^4 \) cm\(^{-1} \) was obtained [88].

**Hot Probe Measurements:**

The experimental set up used to find out the type of semiconductor (n or p type) is shown in Fig.3.7. The CdSe film deposited on titanium substrate was placed over an aluminum plate and an aluminum probe connected the base metal through a multimeter. The probe was heated with a 25W soldering iron, and while the probe was hot, it was momentarily contacted with the film. The multimeter shows a deflection and depending on the direction of deflection, the type of semiconductor was identified. In this case, the films were found to exhibit p-type behaviour.

**Atomic Force Microscopy:**

Fig.4.6 shows the Atomic force micrograph of the CdSe films deposited at different duty cycles and post heat treated at 550ºC With decrease of the duty cycle, the average grain size decreased from 82.6 nm to 58.3 nm and 41.7 nm, and the grain became more homogeneous. Meanwhile, the surface of the films became smoother. The root-mean-square roughness decreased from 27.31 nm to 18.57 nm and 5.04 nm with decrease of duty cycle.
Fig. 4.5 - \((\alpha h \nu)^2\) vs \(h \nu\) plot of CdSe films heat treated at 550°C
EDAX measurements

EDAX measurements were made on the samples annealed at different temperature. The chemical composition for the films annealed at 475°C is Cd(48.1%) and Se(51.9%). For the films annealed at 525°C the composition was Cd(49.3%) and Se(50.7%)(Fig.4.7).

XPS studies:

The XPS spectra of the CdSe films annealed at different temperatures are shown in Fig.4.8a and Fig.4.8b for the binding energies of the Cd(3d_{5/2} and 3d_{3/2}) and Se(3d_{5/2} and 3d_{3/2}) level. After annealing the area under the selenium binding energy curves decrease indicating a small amount of loss of selenium upon evaporation from the sample due to heat treatment. As shown in the fig.4.8a, the peak energy levels associated with Cd(3d_{5/2} and 3d_{3/2}) appeared at 405 and 411.7 eV respectively, which are in good agreement with the literature[89]. These findings are characteristic of the Cd in CdSe and are in good agreement with the literature [89,90]. Fig.4.8b shows the binding energies of the Se(3d_{5/2} and 3d_{3/2}) levels at 53.9 and 59.2 eV respectively. The selenium binding energies shift to lower energies after annealing due to loss of selenium by evaporation. There is no evidence of shifting of the energy levels to higher binding energies corresponding to SeO$_2$ formation[91]. Atomic concentration measurements made on the heat treated samples yielded an apparent Cd/Se ratio of 1.62, this calculation is based on the consideration of area sensitivity factors for Cd and Se respectively and agrees well with the composition estimated from EDAX measurements.
Fig. 4.6 – AFM micrographs of CdSe films deposited at different duty cycles after post heating at 550°C (a) 50% (b) 25% (c) 6%
Fig. 4.7 - EDAX spectrum of CdSe films deposited at 10% duty cycle and post heated at 525 °C
Fig. 4.8 – XPS binding energies of Cd,Se of CdSe films deposited at a duty cycle of 10% (A) as deposited (B) post heated at 525 °C
Photoelectrochemical Measurements

Photoelectrochemical (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 stop off 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 CdSe electrode has reasonable stability and yield respectable outputs ion polysulphide. The light source used for illumination was an ORIEL 250W 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 mW cm$^{-2}$. 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, the voltage output was measured across the load resistance. The photocurrent as well as dark current were measured with a HIL digital multimeter. The output voltage was measured by a HIL digital multimeter.

The CdSe photoelectrodes were dipped in the electrolyte and allowed to attain equilibrium under dark conditions for about 10 min. The dark current and voltage values were noted. The cells were then illuminated by the light source and the current and voltage were measured for each setting of the resistance box. The photocurrent and photovoltage were calculated as the difference
between the current and voltage under illumination and the dark current and voltage respectively.

The power output characteristics of the PEC cells made using the photoelectrodes deposited at different duty cycles and post heat treated at 550ºC is shown in Fig.4.9a -4.9e. As the duty cycle decreases, both $V_{oc}$ and $J_{sc}$ are found to increase. The variation of photocurrent and photovoltage were studied at different intensities, both photocurrent and photovoltage are found to increase with intensity (Fig.4.10). It is observed that $V_{oc}$ increased from 274 mV to 383 mV and $J_{sc}$ increased from 1.81 mA cm$^{-2}$ to 5.12 mA cm$^{-2}$ as the duty cycle varied from 50% - 6.25%. The value of output parameters are high for the electrodes deposited at 10% duty cycle may be due to optimum number of photoactive centres. Fig.4.11 indicates the plot of ln$J_{sc}$ vs $V_{oc}$ for the CdSe photoelectrodes. The plot yields a straight line. Experimentally obtained PEC parameters such as $R_s$, $R_{sh}$, $\eta$, $ff$ and ideality factor of CdSe photoelectrodes are given in Table.4.1.

Photoetching was done by shorting the photoelectrodes and the graphite counter electrode under an illumination of 100 mW cm$^{-2}$ in 1 : 100 HCl for different durations in the range 0 – 40s. Both photocurrent and photovoltage are found to increase up to 30s photoetch, beyond which they begin to decrease. This is illustrated in Fig.4.12. The decrease of the photocurrent and photovoltage is attributable to separation of grain boundaries due to prolonged photoetching[92]. The power output characteristics of Fig.4.13 for 30s photoetching indicates an increase in the $V_{oc}$, $J_{sc}$, $ff$ and $\eta$ values, the photovoltaic parameters of the photoetched electrodes are given in Table.4.2.
Fig. 4.9 - Load characteristics of the CdSe films deposited at different duty cycles after post heat treatment at 550°C (a) 50% (b) 33% (c) 15% (d) 10% (f) 6%
Fig. 4.10 - Variation of $V_{oc}$ and $J_{sc}$ with intensity for the CdSe films deposited at different duty cycles after post heat treatment at 550°C (a) 50% (b) 33% (c) 15% (d) 10% (e) 6%
Fig.4.11 – Plot of $\ln J_{sc}$ vs $V_{oc}$ for the CdSe photoelectrodes deposited at different duty cycles after post heat treatment at 550°C (a) 50% (b) 33% (c) 15% (d) 10% (e) 6%
Fig. 4.12 – (a) Photoetching time vs $V_{oc}$ (b) Photoetching time vs $J_{sc}$
Fig. 4.13 – Load characteristics of CdSe films deposited at different duty cycles after post heat treatment at 550°C and after photoetching for 30s (a) 50% (b) 33% (c) 15% (d) 10% (e) 6%
Table 4.1 – PEC characteristics of pulse plated CdSe films heat treated at 550ºC

<table>
<thead>
<tr>
<th>Duty Cycle (%)</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>ff (%)</th>
<th>$\eta$ (%)</th>
<th>$R_s$ (Ω)</th>
<th>$R_{sh}$ (kΩ)</th>
<th>n</th>
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<tr>
<td>50.00</td>
<td>295</td>
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<td>0.32</td>
<td>0.29</td>
<td>180</td>
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<tr>
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<td>165</td>
<td>0.99</td>
<td>1.76</td>
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<td>325</td>
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<td>0.33</td>
<td>0.46</td>
<td>115</td>
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<td>1.65</td>
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<tr>
<td>9.99</td>
<td>350</td>
<td>4.57</td>
<td>0.33</td>
<td>0.75</td>
<td>51</td>
<td>1.08</td>
<td>1.42</td>
</tr>
<tr>
<td>6.25</td>
<td>380</td>
<td>4.06</td>
<td>0.33</td>
<td>0.72</td>
<td>140</td>
<td>1.07</td>
<td>1.48</td>
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Table 4.2 – PEC Characteristics of photoetched pulse plated CdSe films
heat treated at 550°C

<table>
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<tr>
<th>Duty Cycle (%)</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>ff</th>
<th>$\eta$ (%)</th>
<th>$R_s$ (Ω)</th>
<th>$R_{sh}$ (kΩ)</th>
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<td>0.42</td>
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<td>1.85</td>
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<td>1.63</td>
<td>1.49</td>
</tr>
<tr>
<td>9.99</td>
<td>377</td>
<td>13.56</td>
<td>0.44</td>
<td>3.20</td>
<td>42</td>
<td>1.96</td>
<td>1.31</td>
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<tr>
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<td>11.04</td>
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<td>2.15</td>
<td>61</td>
<td>1.90</td>
<td>1.31</td>
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Effect of Pulse Reversal

CdSe films were deposited by inverting the pulse voltage / pulse current from cathodic to anodic during a small fraction of the total period (pulse reversal). The main purpose of pulse reversal is to preferentially remove species from areas that tend to overplate during the cathodic part of the duty cycle [82]. Changes in deposit structure, mainly grain size can be achieved, because of forced nucleation at each new cathodic pulse, it is clear that adsorption, desorption as well as recrystallization takes place. The main purpose of carrying out pulse reversal is to obtain better film thickness [81] with good adherence, which in turn will yield higher grain size due to better nucleation sites and hence high conversion efficiencies in PEC cells fabricated using these electrodes.

The films deposited with different pulse reversal times in the range 30 – 90 ms indicate hexagonal phase in their x-ray diffraction patterns (Fig.4. 14). After heat treatment. The intensity of the peak having (100) reflection is found to increase with increase of pulse reversal time.

The surface morphology of the films deposited at 10% duty cycle and with pulse reversal (Fig.4.15) indicates that the average grain size increases from 220 nm to 325 nm with increasing pulse reversal timings, the initial increase in grain size decreases as the pulse reversal time further increases 200 nm. The root-mean square (rms) roughness of these films shows the similar behavior to the size of grain as the substrate temperature changes. The rms roughness of these films was found to increase from 12.80 nm to 16.47 nm with increasing pulse reversal timings then decreases as with further increase of pulse reversal timings.
Fig. 4.14 – X-ray diffraction pattern of CdSe films deposited at a duty cycle of 10% after post heat treatment at 550°C with different pulse reversal times (a) 0 ms (b) 30 ms (c) 60 ms (d) 90 ms.
Fig. 4.15 – AFM micrographs of CdSe films deposited at 10% duty and with different pulse reversal timings (a) 30 ms (b) 60 ms (c) 90 ms
(11.96 nm). The increase in rms roughness with the increase of pulse reversal timings is attributed to the larger grain size. Due to the increase in grain size, the density of grain boundary is smaller than the films grown at other pulse reversal timings.

The power output characteristics of the PEC cells made using the pulse plated films with and without pulse reversal is shown in Fig. 4.16. Both $V_{oc}$ and $J_{sc}$ are found to increase up to 60 ms pulse reversal, beyond which they are found to decrease due to thickness of the film. Fig. 4.17 shows the power output characteristics of the electrodes prepared with and without pulse reversal after photetching. The PEC parameters are indicated in Table 4.3. The $J_{sc}$ is found to increase from 13.56 mA cm$^{-2}$ for the films deposited without pulse reversal to 22.35 mA cm$^{-2}$ for the films deposited with pulse reversal of 60 ms. It appears that the improved characteristics are due to the improved crystallinity and grain size as evident from the x-ray diffraction data.

**Capacitance Voltage Measurements:**

Mott-Schottky plots ($1/C^2$ vs V) were studied using 1M Na$_2$SO$_4$ as the blocking electrolyte and an EG&G PARC electrochemical analyzer model 6310 for the electrodes prepared with and without pulse reversal. The CdSe films were used as working electrode, graphite was used as counter electrode and Saturated Calomel Electrode (SCE) was used as 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
Fig. 4.16 - Load characteristics of CdSe films deposited at a duty cycle of 10% after post heat treatment at 550°C with different pulse reversal times (a) 0 ms (b) 30 ms (c) 60 ms (d) 90 ms.
Fig. 4.17 - Load characteristics of CdSe films deposited at a duty cycle of 10% after post heat treatment at 550°C with different pulse reversal times after photoetching for 30s (a) 0 ms (b) 30 ms (c) 60 ms (d) 90 ms.
Table 4.3 – PEC parameters for the pulse plated electrodes with pulse reversal with and without photoetching

<table>
<thead>
<tr>
<th>Duty Cycle</th>
<th>$V_{oc}$</th>
<th>$J_{Sc}$</th>
<th>ff</th>
<th>$\eta$</th>
<th>$R_s$</th>
<th>$R_{sh}$</th>
<th>n</th>
</tr>
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<tbody>
<tr>
<td>(%)</td>
<td>(mV)</td>
<td>(mA cm$^{-2}$)</td>
<td>(%)</td>
<td>(Ω)</td>
<td>(kΩ)</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>1 : 10</td>
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<td>0.88</td>
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<td>0.74</td>
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<tr>
<td><strong>After Photoetching</strong></td>
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<td>2.08</td>
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<td>1 : 10 : 90</td>
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<td>1.71</td>
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<td>1.18</td>
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impedance using the relation, \( C = 1/(2\pi fZ) \). Fig. 4.18 and Fig. 4.19 indicate the Mott-Schottky plots for the films without and with pulse reversal. The nature of the plots indicate the p-type behaviour[93]. The plots are linear, extrapolation of the straight lines to the voltage axis indicates a flat band potential of 1.2V(SCE) [93,94]. The value of acceptor density(\( N_A \)) estimated from the slope of the plots are around \( 7.045 \times 10^{16} \) and \( 4.974 \times 10^{16} \) cm\(^{-3} \) for the electrodes prepared without and with pulse reversal.

**Spectral response measurements**

Spectral response measurements were made on the photoelectrodes prepared with and without pulse reversal using a photophysics monochromator and a 250W tungsten halogen lamp, 1M polysulphide as electrolyte, graphite as counter electrode and the photoelectrode as the working electrode. The wavelength was varied in the range 550 - 850nm and the photocurrent was noted at each wavelength. These photocurrent values were used for calculation of the quantum efficiency(\( \Phi \)) using the well known relation[88],

\[
\Phi = \frac{1240J_{sc}}{\lambda P_{in}} \tag{2}
\]

Where \( J_{sc} \) is the photocurrent, \( \lambda \) is the wavelength of illumination, \( P_{in} \) is the power of light incident on the photoelectrode. Plot of \( \Phi \) vs \( \lambda \) are shown in Fig. 4.20. The plots indicate maximum at 720 nm corresponding to the band gap of the material, this matches well with the band gap obtained from optical absorption measurements. While a quantum efficiency of 0.55 was obtained for the films deposited without pulse reversal, the value was 0.80 for the electrodes prepared with pulse reversal.
Fig.4.18 - Mott Schottky plots of CdSe films deposited at different duty cycles after post heat treatment at 550°C (a) 6% (b) 10% (c) 15% (d) 33% (e) 50%.
Fig. 4.19 – Mott Shottky plot of CdSe films deposited at a duty cycle of 10% after post heat treatment at 550°C with a pulse reversal time of 60 ms.
Fig.4.20 - Plot of $\Phi$ vs $\lambda$ of CdSe films deposited at a duty cycle of 10% after post heat treatment at 550°C (a) without pulse reversal (b) with 60 ms pulse reversal.
I – V characteristics

The conduction mechanism in semiconductors can be understood by analyzing the current voltage characteristics. 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. I – V characteristics of the films deposited at different duty cycles is shown in Fig.4.21. The voltage was applied using a DC power supply APLAB. The applied voltage varied in the range 0 – 2.5V. The voltage could not be increased beyond 2.5V, since the films got punctured at higher voltages. All the samples indicated linear behaviour.

As in the case of CdS, electronic conduction mechanism in CdSe is associated with lattice vacancies(V_{Se}) which are known to behave both as shallow donor centers and deep electron traps[89].

Selenium vacancies are generated as a result of partial electrode evaporation during annealing. The higher the annealing temperature, the greater the V_{Se} and N_A, and so the thinner W. At higher temperatures (T > 550ºC), though there can be an increase in N_A but L_n is observed to decrease, since increasing concentration of V_{Se} results in V_{Se} behaving as recombination centers[96].

For an efficient control of V_{Se} and N_A, the annealing treatment has to be performed in an inert atmosphere( Eg., He) containing a few ppm of oxygen in order to facilitate oxygen chemisorption.
Fig. 4.21 - I – V characteristics of CdSe films deposited at different duty cycles and post heated at 525°C (a) 6% (b) 10% (c) 15% (d) 33% (e) 50%
Laser Raman Spectra:

Laser Raman spectra were recorded on the films deposited at different duty cycles (Fig. 4.22). In all cases a single peak corresponding to the LO phonon of CdSe at 204 cm\(^{-1}\) is observed, the peak is broad for the films deposited at lower duty cycles. At higher duty cycles, the peak is very sharp indicating the improvement in crystallinity. The peak is shifted to a lower frequency compared with the bulk value of 210 cm\(^{-1}\) [97].
Fig. 4.22 – Raman spectra of CdSe films plated at different duty cycles (a) 6% (b) 10% (c) 15% (d) 33% (e) 50%