CHAPTER 3

STUDIES ON COPPER INDIUM SELENIDE FILMS

3.1 INTRODUCTION

In recent years, copper indium diselenide (CIS) with I–III–VI$_2$ ternary chalcopyrite structure has excited extensive interest for its desirable physical properties such as a direct band gap at \( \sim 1 \text{eV} \) and thus a high absorption coefficient of \( >10^5 \text{ cm}^{-1} \) at photon energies above the band gap, which make it ideal for fabrication of high efficiency polycrystalline thin film based photovoltaic devices (Luque & Hegedus 2006). There are multiple techniques currently available for the preparation of CIS thin films, i.e. co-evaporation (McCandless & Birkmore 1988), sputtering (Vassilev et al 2003), spray pyrolysis (Abernathy et al 1984), molecular beam epitaxy, etc. Among these, electrodeposition is considered to be a promising approach from the viewpoint of non-vacuum large area thin film production. Up to now, laboratory cell efficiency of more than 11% CIS devices have already been developed using electrodeposited films (Pathak et al 2009). Earlier two or three potential pulse electrodeposition method has been successfully employed for the deposition of CIS films. In the present investigation, we report the structural parameters, surface morphology, XPS, transmittance, refractive index, band gap energy, and transport parameters of the pulse plated CIS films deposited at different duty cycles for the first time.
3.2 DEPOSITION OF CuInSe$_2$ THIN FILMS

CIS thin films were deposited on indium tin oxide coated glass substrates (5 ohm/ sq) at different duty cycles in the range of 6 – 50 %. Deposition current density was kept constant at 5 mA cm$^{-2}$ in the present work. The total deposition time was maintained at 60 min. The precursors used were AR grade of 0.3 M of each CuCl$_2$ and InCl$_3$, along with 0.2 M of SeO$_2$ as shown in Figure 3.1. The thickness of the films was estimated by mitutoyo surface profilometer varied in the range of 800 to 1200 nm with increase of duty cycle.

The films were characterized by Xpert panalytical X-ray diffraction unit with Cu$_{k\alpha}$ radiation. Optical measurements were recorded using an Hitachi U3400 UV-VIS-IR spectrophotometer. The composition of the films was estimated by using EDAX attachment to JOEL SEM. The surface morphology of the films was studied by molecular imaging atomic force microscope. The electrical resistivity of the films was measured by Hall Van der Pauw method. Photo electrochemical cell studies were made on the films with 1M polysulphide (1M S, 1M Na$_2$S and 1M NaOH) as the redox electrolyte. A 250 W tungsten halogen lamp was used as the light source and graphite was used as counter electrode.
3.3 STRUCTURAL PROPERTIES

3.3.1 Structural Analysis of Thin Films (XRD)

The typical XRD patterns of CIS films deposited at different duty cycles exhibit the chalcopyrite structure which is easily identified JCPDS card no. 00-040-1487. The films deposited at duty cycles less than 15% show a poor crystallinity with weak and broadened diffraction peaks as shown in Figure 3.2. As the duty cycle increased beyond 15%, the diffraction peaks become sharp and the peak intensity was also greatly enhanced. Three well-defined characteristic peaks at 26.6°, 44.1° and 52.4° correspond to the diffraction of the (112), (204) and (312) planes, respectively were observed for lower duty cycles. For duty cycles greater than 15%, two additional peaks corresponding to (400) and (316) were observed. The crystallite size was determined from Scherrer’s equation

\[
\text{Crystallite size} = \frac{0.9 \lambda}{\beta \cos \theta}
\]  

(3.1)
where $\lambda$ is the wavelength of CuK$_\alpha$ x-rays (1.541Å), $\beta$ is the full width at half maximum and $\theta$ is the Bragg angle. The crystallite size was found to vary in the range from 10 to 40 nm with an increase of duty cycle.

The dislocation density $\delta$, defined as the length of dislocation lines per unit volume of the crystal has been evaluated using the formula (Mustafa et al 2007),

$$\delta = \frac{1}{D^2}$$

(3.2)

The microstructural parameters are presented in Table 3.1. It was observed that the dislocation density decreases with increase in grain size. The particle size and strain of CuInSe$_2$ films were obtained from the full-width at half-maximum of the diffraction peaks. The full-width at half-maximum ($\beta$) can be expressed as a linear combination of the contributions from the particle size(D) and strain ($\varepsilon$) through the relation (Santhosh Kumar & Pradeep 2004),

$$\frac{\beta \cos \theta}{\lambda} = \frac{1}{D} + \frac{\varepsilon \sin \theta}{\lambda}$$

(3.3)

The plot of $\beta \cos \theta/\lambda$ vs $\sin \theta/\lambda$ allows us to determine both strain and particles size from slope and intercept of the graph. The estimated values of films deposited at different duty cycles are listed in Table 3.1. The deviation in the lattice parameter values from the bulk value observed in the present case clearly suggested that the grains in the films are under stress. Such a behavior can be attributed to the change of nature, deposition conditions and the concentration of the native imperfections developed in thin films. It led to either elongation or compression of the lattices and the structural parameters. The density of the film was therefore found to change considerably in accordance with the variations of lattice constant values (Groenik & Janse 1978). The stress developed at higher duty cycles is likely
to be due to the formation of native defects developed from the lattice misfit or dislocations. The defects have a probability to migrate parallel to the substrate surface with the surface mobility greatly influenced by the duty cycle, so that the films can have a tendency to expand and develop an internal tensile stress. This type of change in internal stress is always predominant by the observed recrystallization process in polycrystalline films. The stress relaxation is mainly considered as due to dislocation glides formed in the films. The decrease of internal stress may be attributed to a decrease in dislocation density. The reduction in the strain and dislocation density with increase in duty cycle may be due to the reduction in concentration of lattice imperfections due to the improved crystallinity at higher duty cycles.

Figure 3.2  X-ray diffraction pattern of CuInSe₂ films deposited at different duty cycles (a)15 %  (b) 33 % (c) 50 %
Table 3.1  Structural parameters of CuInSe$_2$ films deposited at different duty cycles

<table>
<thead>
<tr>
<th>Duty cycle</th>
<th>Lattice parameters (Å)</th>
<th>Internal strain</th>
<th>Grain size (nm)</th>
<th>Dislocation density ($10^{16}$linesm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(a)</td>
<td>(c)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>5.785</td>
<td>11.58</td>
<td>0.22</td>
<td>10</td>
</tr>
<tr>
<td>9</td>
<td>5.786</td>
<td>11.59</td>
<td>0.15</td>
<td>17</td>
</tr>
<tr>
<td>15</td>
<td>5.787</td>
<td>11.60</td>
<td>0.12</td>
<td>26</td>
</tr>
<tr>
<td>33</td>
<td>5.787</td>
<td>11.60</td>
<td>0.05</td>
<td>34</td>
</tr>
<tr>
<td>50</td>
<td>5.788</td>
<td>11.61</td>
<td>0.01</td>
<td>40</td>
</tr>
</tbody>
</table>

3.3.2  Analysis of Thin Film Composition

The composition of the films was estimated by recording the EDAX spectrum deposited at different duty cycles (Table 3.2). Figure 3.3 shows the EDS spectrum of CuInSe$_2$ films deposited at 50 % duty cycle. It was observed that films deposited at lower duty cycles are copper rich. For the films deposited at 6 %, 9 % and 15 % duty cycle, the Cu/In ratio was found to be 1.07, 1.04 and 1.01 respectively. As the duty cycle increased, the films became stoichiometric. For the films deposited at 33 % duty cycle, Cu/In ratio was found to be 1.001. At 50 % duty cycle, the Cu/In ratio was found to be less than unity, 0.99. It was observed that at higher duty cycles, more flux of indium ions are available for deposition compared to the flux of indium ions at lower duty cycles, which results in higher concentration of Indium thus decreasing the Cu/In ratio. Based on the defect chemistry model of ternary compounds (Groenik & Janse 1978), the compositional deviation of the CuInSe$_2$ can be expressed by non-stoichiometry parameter ($\Delta y = [2\text{Se}/(\text{Cu} + 3\text{In})] - 1$). The parameter $\Delta y$ is related to the electronic defects. For $\Delta y > 0$, the film has p-type conductivity and it has n-type conductivity for $\Delta y < 0$. In this study it was observed that the value of $\Delta y$ is greater than zero and the films exhibit p-type conductivity.
Figure 3.3  EDAX spectrum of CIS films deposited at 50 % duty cycle

Table 3.2  Composition of CuInSe₂ films deposited at different duty cycles

<table>
<thead>
<tr>
<th>Duty cycle (%)</th>
<th>Cu (at.% )</th>
<th>In (at.% )</th>
<th>Se (at.% )</th>
<th>Cu/In</th>
<th>Δy</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>25.56</td>
<td>23.85</td>
<td>50.59</td>
<td>1.07</td>
<td>1.04</td>
</tr>
<tr>
<td>9</td>
<td>25.08</td>
<td>24.18</td>
<td>50.74</td>
<td>1.04</td>
<td>1.04</td>
</tr>
<tr>
<td>15</td>
<td>24.87</td>
<td>24.56</td>
<td>50.57</td>
<td>1.01</td>
<td>1.03</td>
</tr>
<tr>
<td>33</td>
<td>24.74</td>
<td>24.71</td>
<td>50.55</td>
<td>1.001</td>
<td>1.02</td>
</tr>
<tr>
<td>50</td>
<td>24.62</td>
<td>24.91</td>
<td>50.47</td>
<td>0.99</td>
<td>1.02</td>
</tr>
</tbody>
</table>

3.3.3 Surface Analysis of Thin Films (AFM)

The surface morphology of the films (Fig.3.4) studied in an area of 3 μm x 3 μm indicated that the grain size increases from 15 nm to 40 nm as the duty cycle increases from 6 to 50 %. The surface roughness was also increased from 1.5 nm to 3.2 nm with an increase in duty cycle. The surface roughness increases due to the increase in grain size.
3.3.4 Binding Energy XPS

XPS analysis was performed to identify the chemical binding states of the constituents of the CIS films deposited at 50 % duty cycle. Fig.3.5a represents the Cu 2p core level spectrum. The observed peak located at 931.6 eV coincides with the binding energy for Cu 2p$_{3/2}$ electrons emitted from CIS compound (Wagner et al 1978) and the peak at 951 eV corresponds to the binding energy for Cu 2p$_{1/2}$ electrons emitted from Cu element. Fig. 3.5b shows the In 3d core level spectrum. The observed binding energy peaks located at 441.2 eV and 448.3 eV are attributed to the electronic states of In 3d$_{5/2}$ and In 3d$_{3/2}$. As shown in Figure. 3.5c, there are two peaks for the Se 3d core level spectrum. The peak at 53.6 eV corresponds to the electronic state of Se 3d$_{5/2}$ from the CIS compound (Briggs & Seah 1993).

Figure 3.4 Atomic force micrographs of CuInSe$_2$ films deposited at different duty cycles (a) 6 % (b) 15 % (c) 50 % (Z – I div – 40 nm).
Figure 3.5 XPS spectra of CIS films deposited at 50 % duty cycle
3.4 OPTICAL PROPERTIES

3.4.1 Transmission Spectrum - Refractive Index

Figure 3.6 shows the transmission spectra of the CuInSe₂ films deposited at 50% duty cycle. The spectrum exhibits interference fringes and the value of the refractive index was estimated by the envelope method (Joo & Kim 1999).

\[
n = [N + (N^2 - n_s^2)]^2
\]

(3.4)

Where

\[
N = (n_s^2 + 1)/2 + 2 \frac{n_s}{T_{\text{max}} - T_{\text{min}}}/\frac{T_{\text{max}}}{T_{\text{min}}}
\]

(3.5)

where \(n_s\) is the refractive index of the substrate, \(T_{\text{max}}\) and \(T_{\text{min}}\) are the maximum and minimum transmittances at the same wavelength in the fitted envelope curve drawn on transmittance spectrum. The refractive index calculated from the above equations was found to be 2.60. The refractive index decreases with increases in wavelength (Figure 3.7).

3.4.2 Absorption and Band Gap

The absorption co-efficient (\(\alpha\)) was calculated using the relation,

\[
\alpha = \frac{1}{d} \ln \left\{ \frac{(n-1)(n-n_s)}{(n+1)(n-n_s)} \right\} \left[ \frac{(T_{\text{max}}/T_{\text{min}})^2 + 1}{(T_{\text{max}}/T_{\text{min}})^2 - 1} \right]
\]

(3.6)

where ‘\(d\)’ is the thickness of the film and the other parameters have the usual meaning as given in Equation (3.5). The band gap of the films increased from 1.05 eV to 1.17 eV as the duty cycle decreased (Figure 3.8). The increase in band gap at lower duty cycles is due to small crystallites. The values of the band gap agree very well with the earlier report (Huang et al 2004).
Figure 3.6  Transmission spectra of CIS films deposited at different duty cycles (a) 9 % (b) 15 % (c) 33 % (d) 50 %

Figure 3.7  Variation of refractive index with wavelength for CIS films deposited at different duty cycles (a) 9 % (b) 15 % (c) 33 % (d) 50 %
3.5 ELECTRICAL PROPERTIES

3.5.1 Electrical Measurements

The room temperature transport parameters were measured by Hall Van der Pauw technique using gold ohmic contact. The influence of duty cycle on the resistivity of the films is shown in Table 3.3. The films exhibited p-type conductivity. The EDAX results supported the p-type conductivity, since, the non-stoichiometry parameter is greater than zero. The magnitude of the resistivity increased from 1.5 ohm.cm to 12.4 ohm.cm as the duty cycle was increased. The obtained resistivity values are lower than the earlier report (Luo et al 2008). The variation in resistivity with duty cycle can be explained in terms of the Cu/In ratio obtained from EDAX measurements. At low duty cycles, a high Cu/In ratio was observed. At higher duty cycles, Cu/In ratio is unity, hence as the concentration of copper decreases, the resistivity increases. The variation of room temperature mobility and carrier density with duty cycle is shown in Table 3.3. The increase of resistivity at 50% duty cycle can
also be explained in terms of the decrease in carrier density with increase in duty cycle. The increase of resistivity with decrease in Cu/In ratio has been observed in earlier report (Luo et al 2008). The values of mobility increase and carrier density decrease with increase in duty cycle.

Table 3.3 Transport parameters of CuInSe₂ films deposited at different duty cycles

<table>
<thead>
<tr>
<th>Duty cycles (%)</th>
<th>Resistivity (ohm cm)</th>
<th>Mobility (cm²V⁻¹s⁻¹)</th>
<th>Carrier density (cm⁻³ x 10¹⁷)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>1.5</td>
<td>20</td>
<td>2.08</td>
</tr>
<tr>
<td>9</td>
<td>2.8</td>
<td>23.8</td>
<td>0.90</td>
</tr>
<tr>
<td>15</td>
<td>4.7</td>
<td>27.1</td>
<td>0.49</td>
</tr>
<tr>
<td>33</td>
<td>8.6</td>
<td>30.2</td>
<td>0.24</td>
</tr>
<tr>
<td>50</td>
<td>12.4</td>
<td>34.1</td>
<td>0.14</td>
</tr>
</tbody>
</table>

3.5.2 Current-Voltage Characteristics

Various crystalline imperfections in the film, such as vacancies, dislocations and grain boundaries act as trapping or recombination centers of the carriers and play an important role in photoconduction. These traps act as localized positive potential centers for electrons and negative potential centers for holes. Therefore, some localized discrete energy levels were formed in the band gap, in the vicinity of the conduction and valence bands respectively. Fig.3.9 shows the variation of photocurrent with light intensity of CuInSe₂ films deposited at different duty cycles. The photocurrent was found to increase with an increase of duty cycle due to increase in film thickness and light intensity. As the thickness of the film increases, the crystalline nature increases (Table 3.1) and this helps in the improvement of photocurrent. The increase in photocurrent is attributed to an increase in the majority carrier concentration and an increase in impurity centers acting as traps for minority carriers. The variation of photocurrent with applied voltage in CuInSe₂ films is shown in Figure 3.10.
the figure, it was observed that the photocurrent increases with an increase in voltage.

Photocurrent spectra of CuInSe$_2$ films deposited at different duty cycles are shown in Figure 3.11. The photocurrent spectra show a peak near the absorption edge and the same was observed by Rose (1955). The band gap of CuInSe$_2$ films determined from the spectral response is in the range 1.05 eV – 1.17 eV with decrease of duty cycle. This is in good agreement with the band gap values obtained from optical absorption measurements. The low photocurrent in the short wavelength range may be due to the high absorption coefficient and only surface region where defect states with shorter life times, has been excited. In the high wavelength region, the radiation is partially absorbed giving rise to less photocurrent than the peak value. The spectra extending up to 1300 nm are attributed to direct excitation of the carriers from the defect levels as reported by several workers for CuInSe$_2$ films (Pal et al 1994, Fischer et al 2001).

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

$$\text{Photosensitivity} = \frac{\Delta \sigma}{\sigma} = \frac{I_L - I_d}{I_d}$$

where $I_L$ and $I_d$ represent the currents under illumination and in the dark respectively. It seems that some transitions create additional free carriers effectively and it increases the free life time in order to increase the photosensitivity of the material. Figure 3.12 shows a plot of photosensitivity versus light intensity of CuInSe$_2$ thin films. Thinner films exhibited moderate photosensitivity, whereas thicker films were found to exhibit higher photosensitivity. Crystallographical imperfections acting as trapping centers will enhance the photosensitivity, whereas the recombination centers decrease the photosensitivity.
Figure 3.9  Photocurrent – Intensity characteristics of CuInSe$_2$ films deposited at different duty cycles (a) 6 % (b) 9 % (c) 15 % (d) 33 % (e) 50 %

Figure 3.10  Photocurrent – voltage characteristics of CuInSe$_2$ films deposited at different duty cycles (a) 6 % (b) 9 % (c) 15 % (d) 33 % (e) 50 %
Figure 3.11  Photocurrent spectra of CuInSe$_2$ films deposited at different duty cycles (a) 6 % (b) 15 % (c) 33 % (d) 50 %

Figure 3.12  Photosensitivity vs intensity of CuInSe$_2$ films deposited at different duty cycles (a) 6 % (b) 9 % (c) 15 % (d) 33 % (e) 50 %
3.6 PHOTOELECTROCHEMICAL CELLS

Photoelectrochemical (PEC) cells were prepared using the films deposited on titanium substrates and they were 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. Photoelectrochemical cell studies were made using 1.0 M Na$_2$S, 1.0 M NaOH and 1.0 M S, as the redox electrolyte. Graphite was used as the counter electrode Fig 3.13. The light source used for illumination was 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 by 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.

The CuInSe$_2$ photoelectrode was dipped in the electrolyte and allowed to attain equilibrium under dark condition for about 10 minutes. The dark current and voltage values were noted. The cell was 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.
3.6.1 Photo Electrochemical Measurements

The PEC cells using these films exhibited low photocurrent and photovoltage. The intensity of the light falling on the films deposited at different duty cycles was kept constant at 60 mW cm\(^{-2}\). Figure 3.14 shows the load characteristics of CIS deposited films, prepared at different duty cycles. Films deposited at 50% duty cycle exhibited maximum photo-output. In order to increase the photo-output, the films deposited at 50% duty cycle were post heated in argon atmosphere at different temperatures in the range 450 - 550°C for 15 min. The load characteristics of the post heat treated films are shown in Figure 3.15. From the figure, it was observed that the PEC output parameters, viz., open circuit voltage and short circuit current were found to increase for the electrodes which was heat treated up to a temperature of 525°C. Photoelectrodes heat treated at temperatures greater than this value exhibit 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. The photovoltaic parameters are shown in Table 3.4. For a film deposited at 50% duty cycle, an open circuit voltage of 0.54 V and a short circuit current density of 12.0 mA cm\(^{-2}\) at 60 mW cm\(^{-2}\) illumination. The photo output is higher than earlier report (Lincot et al 1990).

It was observed that both \(V_{oc}\) and \(J_{sc}\) increased with increase in intensity. Beyond 80 mW cm\(^{-2}\) illumination, \(V_{oc}\) was found to be saturated as commonly observed in the case of photovoltaic cells and PEC cells. \(J_{sc}\) was found to linearly increase with intensity of illumination. A plot of \(\ln J_{sc} vs V_{oc}\) (Figure 3.16) yielded a straight line. Extrapolation of the line to the y-axis yielded the value \(J_0\) as 5.1 \times 10^{-7} A cm\(^{-2}\) and the ideality factor (n) was calculated from the slope of the straight line as 1.85.

Photoetching was done by shorting the photoelectrodes and the graphite counter electrode under an illumination of 100 mW cm\(^{-2}\) in 1 : 100 HNO\(_3\) for different durations in the range 0 – 100s. Both photocurrent and photovoltage were found to increase up to 80s photoetch, beyond which they begin to decrease. This is illustrated in Figure 3.17 for the CIS photoelectrode deposited at 50% duty cycle. The decrease of the photocurrent and photovoltage after 80s photoetch is attributable to separation of grain boundaries due to prolonged photoetching (Mangalhara et al 1988).

The power output characteristics (Figure 3.18) after 80s photoetching indicated the data: \(V_{oc} = 0.625V, J_{sc} = 16.0\ mA\ cm^{-2}, ff = 0.71\) and \(\eta = 11.83\ \%\), for 60 mW cm\(^{-2}\) illumination. The photovoltaic parameters of the electrodes with and without photoetching are shown in Table 3.4. The films deposited at lower duty cycles exhibited very poor photo-output after post annealing in Argon atmosphere. Films deposited at lower duty cycles exhibited low output.
Mott-Schottky plot ($1/C^2$ vs V) was studied by using 1 M Na$_2$SO$_4$ as the blocking electrolyte and EG&G PARC impedance analyzer model 6310. The CuInSe$_2$ films deposited at 50 % duty cycle and post heat treated at 500˚C, were used as working electrode and graphite was used as counter electrode. SCE was used as the reference electrode. The frequency was fixed at 1 kHz and the bias voltage was varied from –0.2 to +0.8V vs SCE. The value of C was estimated from the imaginary part of the impedance using the equation,

$$C = 1/2\pi f \varepsilon$$

The Mott-Schottky plots for the films deposited at different duty cycles are shown in Figure 3.19. The nature of the plot indicates the p-type behaviour. Extrapolation of the plot to the voltage axis yielded a Vfb of 0.70V (SCE). The value of carrier density from the slope of the plot yielded the value around $2.0 \times 10^{17}$cm$^{-3}$. This value agrees well with the carrier density obtained from the Hall measurement.

Spectral response measurements were carried out on the photoelectrodes by using Photophysics monochromator with 250 W tungsten halogen lamp source. 1M polysulphide as the electrolyte, graphite as counter electrode and the photoelectrodes as working electrodes were used in this experiment. 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 (Segui 1991),

$$\phi = \frac{1240 \cdot J_{sc}}{\lambda \cdot P_{in}}$$
where $J_{sc}$ is the photocurrent, $\lambda$ is the wavelength of illumination, $P_{in}$ is the power of the light incident on the photoelectrodes. The plot drawn between $J_{ph}$ and $\lambda$ for the CuInSe$_2$ electrodes heat treated at 525°C is shown in Figure 3.20. The value of $(J_{ph})_{max}$ occurs at a wavelength value corresponding to the band gap 1.05 eV. This value is nearly equal to the band gap obtained from optical measurements.

Figure 3.14  Load characteristics of CIS films deposited at different duty cycles (a) 9 % (b) 15 % (c) 25 % (d) 33 % (e) 50 %
Figure 3.15 Load characteristics of CIS films deposited at 50% duty cycle and post heat treated at different temperatures (a) 450°C (b) 475°C (c) 500°C (d) 525°C (e) 550°C
Figure 3.16  Variation of $\ln J_{SC}$ vs $V_{OC}$ for the CIS films deposited at 50 % duty cycle and post heat treatment at 525°C
Figure 3.17 Effect of photoetching of CIS films deposited at 50 % duty cycle and post heat treatment at 525°C
Figure 3.18 Load characteristics of CIS photoelectrodes deposited at 50% duty cycle and post heat treatment at 525°C after photoetching for 80s

\[ J \text{ (mA cm}^{-2}\text{)} \] vs. \[ V \text{ (mV)} \]
Table 3.4   Photovoltaic parameters of CIS photoelectrodes at different post heat treatment temperatures

<table>
<thead>
<tr>
<th>Heat Treatment Temp (°C)</th>
<th>V&lt;sub&gt;OC&lt;/sub&gt; (V)</th>
<th>J&lt;sub&gt;SC&lt;/sub&gt; (mA cm&lt;sup&gt;-2&lt;/sup&gt;)</th>
<th>FF</th>
<th>η(%)</th>
<th>R&lt;sub&gt;s&lt;/sub&gt; (Ohms)</th>
<th>R&lt;sub&gt;sh&lt;/sub&gt; (K ohms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>450</td>
<td>0.40</td>
<td>6.50</td>
<td>0.48</td>
<td>2.08</td>
<td>38</td>
<td>2.00</td>
</tr>
<tr>
<td>475</td>
<td>0.43</td>
<td>7.50</td>
<td>0.50</td>
<td>2.70</td>
<td>35</td>
<td>2.10</td>
</tr>
<tr>
<td>500</td>
<td>0.47</td>
<td>9.00</td>
<td>0.52</td>
<td>3.67</td>
<td>28</td>
<td>2.20</td>
</tr>
<tr>
<td>525</td>
<td>0.54</td>
<td>12.0</td>
<td>0.56</td>
<td>5.95</td>
<td>20</td>
<td>2.50</td>
</tr>
<tr>
<td>550</td>
<td>0.50</td>
<td>10.8</td>
<td>0.55</td>
<td>4.95</td>
<td>26</td>
<td>2.30</td>
</tr>
<tr>
<td>525 (After Photoetch)</td>
<td>0.625</td>
<td>16.0</td>
<td>0.71</td>
<td>11.83</td>
<td>10</td>
<td>2.80</td>
</tr>
</tbody>
</table>

Figure 3.19 Mott schottky plots of CIS films deposited at different duty cycles (a) 15 % (b) 33 % (c) 50 %
3.7 PHOTOLUMINESCENCE STUDIES

Room temperature photoluminescence was studied using Hitachi fluorescence spectrophotometer with 240 nm excitation line. Figure 3.21 shows the PL response of CuInSe$_2$ film deposited at 50% duty cycle. The Cu/In atomic ratio of this sample was 0.95. The photoluminescence from this sample was dominated by the presence of a single peak at approximately 0.94 eV. This observation is agreed with other studies indicating that the optical properties of slightly In-rich CuInSe$_2$ which are dominated by the presence of a donor–acceptor pair transition at about 0.95 eV. This emission process is generally described to the radiative transition between an electron and a hole bound to a selenium vacancy ($V_{Se}$) and a copper vacancy ($V_{Cu}$).
3.8 LASER RAMAN SPECTRA

Figure 3.22 shows the comparison of Raman spectra of CIS films deposited at different duty cycles. The main peak was observed around 175 cm\(^{-1}\) and could be identified as the A1 vibrational mode from I–III–VI\(_2\) chalcopyrite compounds (Tanino & Maeda 1992). The slight peak shift is likely due to the extended defects such as dislocation, twins or grain boundaries at the nanocrystals because even point defects can result in changes in the Raman peak. It was further observed that the intensity of the major peak at 173 Cm\(^{-1}\) increases with the increase of duty cycle. A broad and weak A1 peak was observed for the films deposited at 15 % duty cycle. In addition, two peaks centered at 210 and 228 cm\(^{-1}\) were also observed in the Raman Spectra for the films deposited at higher duty cycles. These two peaks are in agreement with the predicted modes in CIS thin film (Rincon & Ramirez 1992).

![Room temperature PL spectrum of CIS films deposited at 50 % duty cycle](image)
Figure 3.22  Room temperature Raman spectra of CIS films deposited at different duty cycles (a) 15 % (b) 33 % (c) 50 %