CHAPTER 4

PREPARATION, STRUCTURAL, OPTICAL, MORPHOLOGY, BINDING ENERGY, TRANSPORT PARAMETERS AND PHOTOELECTRO CHEMICAL STUDIES OF CuInS₂ THIN FILMS

4.1 INTRODUCTION

Among ternary semiconductor compounds belonging to the I–III–VI₂ series, CuInX₂ (X=Se, Te, S) are promising materials for photovoltaic applications because of the suitability of their electrical and optical properties (Shay et al 1975). CuInS₂ is a promising material to be used as absorber layer in photovoltaic devices because of its direct gap of about 1.55eV and its high absorption coefficient value (10⁵cm⁻¹) (Emst et al 2003). Various techniques have been used for the deposition of CuInS₂ films, such as molecular beam epitaxy (Gossla et al 1995), sulfurization of metallic precursor (Calderon et al 2010), reactive sputtering (Seeger et al 2009), electrodeposition (Lee et al 2012), chemical method (Zheng et al 2012), spray pyrolysis (Suhail 2012), etc. Among them, electrodeposition presents several advantages because of its simplicity, low cost and low energy requirements and further it is ideally suited for large scale production. In this work, the galvanostatic pulse electrodeposition technique has been employed for the deposition of CuInS₂ films. In an earlier article, CuInS₂ films were deposited by potentiostatic pulse electrodeposition technique (Murali et al 2011).
The developments of new materials to be used in organic optoelectronic devices such as polymeric solar cells have become dramatically attractive because they represent a green and renewable energy alternative to fossil energy and nuclear power. In particular, the so called bulk heterojunction (BHJ) concept (Yu et al 1995) has been established thin films of organic solar devices utilizing electron donating conjugated polymers blended with electron accepting species, such as fullerenes (Thompson et al 2008) dicyano based polymers (Kietzke et al 2007, Uhrich et al 2007) or n-type nanoparticles (Moet et al 2007). These hybrid polymer inorganic solar cells utilize the high electron mobility of the inorganic phase to overcome charge transport limitations associated with organic materials.

Taking all of these results into account, the development of new copolymers based on carbazoles should therefore lead to interesting features for photovoltaic applications. A class of polymer that have to date received little attention as p-type materials for use in solar cells is polycarbazoles. Cabazole is a well known electron donating unit, and thus polys(2, 7 – carbazole) are attractive candidates as p-type materials for solar cells (Lecerf et al 2009). In this chapter discuss with various parameters of preparation technique, X-ray diffraction analysis, optical transmission spectral analysis (UV-VIS-NIR spectrum), atomic force microscopy, X-ray photoelectron spectroscopy, Mott-Schottky studies, spectral response studies, photoluminescence studies, Laser Raman spectrum analysis, transport parameters and photovoltaic parameters of CuInS₂ thin films.

4.2 PREPARATION OF CuInS₂ THIN FILMS

The CuInS₂ thin films were deposited on conducting glass substrates at different duty cycles in the range of 6% to 50% and at a current density of 1.0mA cm⁻². The precursors were solutions of 0.1M CuCl₂, 0.1M InCl₃ and
0.2M of sodium thiosulphate. The pH was maintained at 1.5 by HCl. The deposition time was fixed as 60 minutes in all the cases.

4.3 CHARACTERIZATION STUDIES OF CuInS$_2$ THIN FILMS

4.3.1 Structural Analysis of CuInS$_2$ Thin Films

4.3.1.1 X-ray diffraction studies of CuInS$_2$ thin films

Figure 4.1 shows that the XRD patterns of CuInS$_2$ films deposited at different duty cycles. The films are polycrystalline with peaks corresponding to the chalcopyrite phase of CuInS$_2$ JCPDS with number 27-0159. Peaks corresponding to CuS were not present. XRD peaks of the chalcopyrite phase, namely, (112), (204) and (312). The height of the peak increased with increase of duty cycle and decreased the width of the peaks. The grain size (D) of the films has been calculated using Scherrer's formula (Patterson 1939).

$$D = \frac{0.94\lambda}{\beta \cos\theta}$$  \hspace{1cm} (4.1)

Where $\lambda$ is the wavelength of X-ray used, $\beta$ is the full width at half maximum (FWHM) and $\theta$ is the Bragg angle. The full width at half maximum values were 0.0018 radian, 0.0027 radian, 0.0033 radian, 0.0053 radian and 0.0099 radian for the films deposited at 50%, 33%, 15%, 9% and 6% duty cycles respectively.
4.3.1.2 Microstructural parameters of CuInS₂ thin films

The grain size increased from 15nm to 80nm with 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 (Williamson et al 1956)

\[
\delta = \frac{1}{D^2}
\]  

(4.2)

The microstructural parameters are presented in Table 4.1 from the table it is observed that the dislocation density decreases with increase of grain size. Information on the particle size and strain for the CuInS₂ films was 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 (Williamson 1953).
\[
\frac{\beta \cos \theta}{\lambda} = \frac{1}{D} + \frac{\varepsilon \sin \theta}{\lambda}
\]  \hspace{1cm} (4.3)

The plot of $\beta \cos \theta / \lambda$ versus $\sin \theta / \lambda$ allows us to determine strain from the slope of the graph. The estimated values for films deposited at different duty cycles are listed in Table 4.1. The deviation of the lattice parameter values from the bulk value observed in the present case clearly suggests 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. This results in either elongation or compression of the lattice and the structural parameters. The density of the film is therefore found to be change considerably in accordance with the variations observed with the lattice constant values (El Sherrif et al 1996).

The stress developed at lower 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 will 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 of duty cycle may be due to the reduction in concentration of lattice imperfections due to the improved crystallinity at higher duty cycles.
**Table 4.1** Microstructural parameters of CuInS$_2$ films deposited at different duty cycles

<table>
<thead>
<tr>
<th>Duty cycle (%)</th>
<th>Thickness (nm)</th>
<th>Lattice parameters (Å)</th>
<th>β (nm)</th>
<th>D (nm)</th>
<th>ε ($\times 10^{-4}$)</th>
<th>δ ($\times 10^{14}$cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>500</td>
<td>5.54 11.03 0.570</td>
<td>15</td>
<td>3.84</td>
<td>44.40</td>
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</tr>
<tr>
<td>9</td>
<td>580</td>
<td>5.55 11.04 0.305</td>
<td>28</td>
<td>3.45</td>
<td>12.30</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>730</td>
<td>5.56 11.05 0.190</td>
<td>45</td>
<td>2.99</td>
<td>4.93</td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>810</td>
<td>5.56 11.05 0.124</td>
<td>69</td>
<td>2.71</td>
<td>2.10</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>900</td>
<td>5.58 11.04 0.110</td>
<td>80</td>
<td>1.08</td>
<td>1.56</td>
<td></td>
</tr>
</tbody>
</table>

### 4.3.1.3 Thickness measurement of CuInS$_2$ thin films

Thickness of the films was measured by a Mitutoyo surface profilometer and it was observed to be in the range of 500nm to 900 nm with an increase of duty cycle from 6% to 50%.

### 4.3.2 Optical Properties of CuInS$_2$ Thin Films

#### 4.3.2.1 Transmission spectra of CuInS$_2$ thin films

Transmission spectra of the films deposited at different duty cycles were recorded at room temperature in the wavelength range of 300nm to 2500nm. Figure 4.2 shows the transmission spectra of the CuInS$_2$ films deposited at different duty cycles. The cut off of the transmission spectra towards short wavelengths indicates the onset of the intrinsic interband absorption in the CuInS$_2$ films. The intrinsic absorption is corroborated by the sharpness of the absorption edge which increases with duty cycle.
Figure 4.2  Transmission spectra of CuInS$_2$ films deposited at different duty cycles (---) 6% (-■-) 15% (-□-) 33% (-●-) 50%

4.3.2.2  Band gap studies of CuInS$_2$ thin films

Tauc’s plots of CuInS$_2$ thin films deposited at different duty cycles are displayed in Figure 4.3. Bandgap values of 1.39eV, 1.4eV and 1.5eV were obtained. The band gap of the CuInS$_2$ films corresponding to the theoretical value 1.53eV. These changes are directly related to the phase composition of the CuInS$_2$ films. When Cu/In molar ratio increases, the Cu$_{In}$ and V$_{In}$ defect densities may increase, which make the materials p-type degenerate, but when the materials become indium rich, the most probable defects are V$_S$, In$_{Cu}$, which can introduce two donor levels and also the defect V$_{Cu}$ is responsible for producing an acceptor level. Thus the indium-rich materials become n-type degenerate. Obviously, these defects play very important role in the variation of the optical band gap of CuInS$_2$ with Cu/In molar ratio (Ueng et al 1989). The similar behavior of CuInS$_2$ films reported by Gossala et al. (Gossala et al 2000).
Figure 4.3  $(ahv)^2$ versus photon energy of CuInS$_2$ films deposited at different duty cycles (a) 50\% (b) 15\% (c) 6\%

4.3.3 Photoluminescence Studies of CuInS$_2$ Thin Films

The photoluminescence studies was using Hitachi fluorescence spectrophotometer with 240nm excitation line. Figure 4.4 shows the PL Spectrum response of CuInS$_2$ 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 0.94eV. This observation is in good agreement with other studies indicating that the optical properties of slightly In-rich CuInS$_2$ are dominated by the presence of a donor acceptor pair transition at about 0.95eV (Schon et al 1997). This emission process is generally ascribed to the radiative transition between an electron and a hole bound to a selenium vacancy ($V_{Se}$) and a copper vacancy ($V_{Cu}$).
Figure 4.4 Room temperature PL spectrum of CuInS$_2$ films deposited at 50% duty cycle

4.3.4 Raman Scattering of CuInS$_2$ Thin Films

The Raman spectra of CuInS$_2$ thin films deposited at different duty cycle as shown in Figure 4.5. As previously mentioned, A1 modes for chalcopyrite ordering are reported to be observed as the biggest peaks, which appear at 295cm$^{-1}$ (Rudigier et al 2004). The other peaks at 240cm$^{-1}$ ($E_{TO}^3$, $B_{2TO}$) and 340cm$^{-1}$ ($E_{LO}^1$) represent Raman modes for Chalcopyrite ordering (Rudigier et al 2004). The peaks increase in intensity with duty cycle.

The chalcopyrite structure was confirmed by Raman spectra. This Figure 4.5 shows only one peak 295cm$^{-1}$ corresponding to the A1 mode, which is considered to be the dominant vibrational mode of chalcopyrite phase (Bacewicz et al 1994, Sproul et al 2005) and no other peaks are present. The obtained target is dense and not friable. The target morphology was characterized by AFM shows smooth surface without macro defects or cracks. Chemical analysis by energy dispersive X-ray spectroscopy confirmed chalcopyrite composition of the CuInS$_2$ thin film.
4.3.5 Spectral Response of CuInS$_2$ Thin Films

Spectral response measurements were carried out on the photoelectrodes by using a photophysics monochromator and a 250W tungsten halogen lamp, 1M polysulphide was used as the electrolyte, graphite as counter electrode and the photoelectrodes as working electrodes. The wavelength was varied in the range 400nm to 900nm and the photocurrent were noted at all the wavelength.

The photocurrent values were used for the calculation of the quantum efficiency ($\phi$) using the well known relation (Segui et al 1991),

$$\phi = \frac{1240J_{sc}}{\lambda P_{in}}$$

(4.4)

where $J_{sc}$ is the photocurrent, $\lambda$ is the wavelength of illumination, $P_{in}$ is the power of the light incident on the photoelectrodes. Plot of $J_{ph}$ versus $\lambda$ for
the CuInS₂ electrodes heat treated at 525°C is shown in Figure 4.6. The value of $(J_{ph})_{max}$ occurs at a wavelength value corresponding to the band gap value is 1.52eV. This band gap value is nearly equal to the band gap obtained from optical measurements.

![Figure 4.6 Photocurrent density versus wavelength plot of CuInS₂ films deposited at 50% duty cycle and post heat treated at 525°C](image)

**Figure 4.6 Photocurrent density versus wavelength plot of CuInS₂ films deposited at 50% duty cycle and post heat treated at 525°C**

### 4.3.6 EDS Spectrum of CuInS₂ Thin Films

Composition of the films were estimated by recording of the EDS spectrum of the films deposited at different duty cycles. Figure 4.7 shows the EDS spectrum of CuInS₂ films deposited at 50% duty cycle. It is observed from Table 4.2, that the CuInS₂ thin films deposited at lower duty cycles were copper rich. For the films deposited at 6%, 9%, 15% and 33% duty cycle, the Cu/In ratio were 1.09, 1.07, 1.05 and 1.03 respectively. As the duty cycle increased, the films became stochiometric. For the films deposited at 50% duty cycle, Cu/In ratio was ~1.0. This is due to the fact that at higher duty cycles, more flux of Indium ions is available for deposition compared to the flux of ions at lower duty cycles, which results in higher concentrations of
Indium thus decreasing the Cu/In ratio. At lower duty cycles, more copper is deposited relative to Indium, since copper is more noble compared to indium, hence the Cu/In ratio is greater than one. Compositional deviations of the CuInS$_2$ can be expressed by non stoichiometry parameter ($\Delta y = [2S/(Cu + 3In)] - 1$). The parameter $\Delta y$ is related to the electronic defects. For $\Delta y > 0$, the film has a p-type conductivity and it has a n-type conductivity for $\Delta y < 0$. In this study the value of $\Delta y$ is greater than zero for all the films deposited at different duty cycles as presented in Table 4.2. Hence the p-type conductivity exhibited by the films can be explained in terms of $\Delta y$ for the films deposited at different duty cycles.

![Figure 4.7 EDS spectrum of CuInS$_2$ films deposited at 50% duty cycle](image)

**Table 4.2 Composition of CuInS$_2$ films deposited at different duty cycles**

<table>
<thead>
<tr>
<th>Duty cycle (%)</th>
<th>Cu (at %)</th>
<th>In (at %)</th>
<th>S (at %)</th>
<th>Cu/In</th>
<th>$\Delta y$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>25.52</td>
<td>23.28</td>
<td>51.20</td>
<td>1.09</td>
<td>0.07</td>
</tr>
<tr>
<td>9</td>
<td>25.14</td>
<td>23.49</td>
<td>51.37</td>
<td>1.07</td>
<td>0.07</td>
</tr>
<tr>
<td>15</td>
<td>24.95</td>
<td>23.81</td>
<td>51.24</td>
<td>1.05</td>
<td>0.06</td>
</tr>
<tr>
<td>33</td>
<td>24.67</td>
<td>24.05</td>
<td>51.28</td>
<td>1.03</td>
<td>0.06</td>
</tr>
<tr>
<td>50</td>
<td>24.28</td>
<td>24.18</td>
<td>51.54</td>
<td>1.004</td>
<td>0.06</td>
</tr>
</tbody>
</table>
4.3.7 XPS Studies of CuInS$_2$ Thin Films

The binding energy values of Cu-2p$_{3/2}$, In-3d$_{5/2}$ and 3d$_{3/2}$, S-2p peaks in the XPS spectra of the film deposited at 50% duty cycle are given in Figure 4.8. The binding energy of Cu-2p$_{3/2}$, In-3d$_{5/2}$ and S-2p$_{1/2}$ peaks are about 932.4eV, 444.7eV and 162.5eV respectively, which good agreement with that reported by other workers for sprayed pyrolysis method in CuInS$_2$ thin films (Zouaghi et al 2001).

The background signals were subtracted using the Shirley method. Cu-2P$_{3/2}$ and In-3d$_{5/2}$ signals were detected even from the lower peeled surface and which conflicts with a previous study in which no Cu or In signals were detectable (Scheer et al 1995). In addition, weak Mo signals were detected from the upper peeled surface. XPS peaks associated with S-2p$_{3/2}$ and S-p$_{1/2}$ photo electrons from MoS$_2$ have reported at 162.1eV and 163.28eV, respectively (Baker et al 1999 ), which is consistent with the S-2p spectrum from the lower peeled surface is consistent with the SK-edge XANES results. However, a MoS$_2$ layer was not detectable from the GIXRD pattern, which suggests that the layer is very thin. We therefore conclude that a thin MoS$_2$ layer was formed during CuInS$_2$ deposition and that the CuInS$_2$ thin film peeled smoothly at the CuInS$_2$/MoS$_2$ interface during the lift off process. However some Cu and In remained on the lower peeled surface and some Mo remained on the upper surface. The preferential peeling at the CuInS$_2$/MoS$_2$ interface suggests that the interfacial MoS$_2$ acts as a sacrificial layer, similar to the situation reported for an interfacial MoSe$_2$ layer in the case of a Cu(In,Ga)Se$_2$ film (Marron et al 2005).

We now consider the origin of the Cu and In detected on the lower peeled surface. Since we did not perform any intentional sulfurization of the Mo surface, We think that the interfacial MoS$_2$ layer mainly formed during the very early stages of CuInS$_2$ coevaporation. Since we could not confirm
that the MoS₂ layer was continuous across the entire interface, it is possible
that in some spots there was direct contact between the CuInS₂ and Mo. The
presence of Cu and In on the lower peeled surface following the lift off
process might then be due to such spots of direct contact, where peeling
occurred slightly within the CuInS₂ layer rather than at the CuInS₂/MoS₂
interface.

![XPS spectra of Cu, S and In for the CuInS₂ films deposited at 50% duty cycle](image)

Figure 4.8  XPS spectra of Cu, S and In for the CuInS₂ films deposited at 50% duty cycle
4.3.8 Atomic Force Microscopy of CuInS$_2$ Thin Films

The surface morphology of the films deposited at different duty cycles was studied by Atomic force microscopy. Figure 4.9 shows the atomic force three dimensional images of the films. It is observed that the surface roughness and grain size increases with difference duty cycles. The surface roughness increases from 0.85nm to 2.50nm as the duty cycle increases from 6% to 50 %. Fine grains are observed in the films deposited at 6% duty cycle. The grain size of the films deposited at 6%, 9%, 15%, 33% and 50% duty cycle was 15nm to 80nm. The higher surface roughness at higher duty cycle and higher grain size presented in the CuInS$_2$ thin films. The lower surface roughness at lower duty cycle and lower grain size in CuInS$_2$ thin films.

![Atomic force images of CuInS$_2$ films deposited at different duty cycles (a) 6% (b) 15% (c) 50%](image)
4.3.9 Electrical Properties of CuInS$_2$ Thin Films

4.3.9.1 Hall Van der Pauw technique of CuInS$_2$ thin films

The transport parameters were measured by Hall Van der Pauw technique by providing gold ohmic contact. The influence of duty cycle on the resistivity of the CuInS$_2$ films is shown in Table 4.3. The CuInS$_2$ films exhibit p-type conductivity. The EDAX results support the p-type conductivity, since, the non-stoichiometry parameter is greater than zero. The magnitude of the resistivity increased from 0.10ohm cm to 3.67ohm cm as the duty cycle is increased. The resistivity values of this work are lower than the earlier report of 80.5ohm cm for the films with Cu/In ratio of unity (Shi et al 2006). 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 is observed. At higher duty cycle, Cu/In ratio is unity, hence as the concentration of copper decreases, the resistivity increases. The concentration of copper is inversely proportional to the resistivity of the CuInS$_2$ films is observed from values. The variation of mobility and carrier density with duty cycle is also shown in Table 4.3. The increase of resistivity at 50% duty cycle can also be explained in terms of the decrease of carrier density with increase of duty cycle. The increase of resistivity from $3.4 \times 10^{-3}$ohm cm to 80.5ohm cm with the decrease of Cu/In ratio from 2.0 to 1.0. The similar report is very good agreement with SILAR method of CuInS$_2$ films (Shi et al 2006). The values of mobility and carrier density decrease with increase of duty cycle. Mobility is $2.43\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ for Cu/In ratio of unity is lower than $4.92\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ and carrier density value of $3.998 \times 10^{18}\text{cm}^{-3}$ for Cu/In ratio of unity in this study is higher than $1.2 \times 10^{16}\text{cm}^{-3}$ for Cu/In ratio The similar behavior of CuInS$_2$ films reported by Y. Shi et al (Shi et al 2006).
### Table 4.3 Transport parameter values of CuInS$_2$ films deposited at different duty cycles

<table>
<thead>
<tr>
<th>Duty cycles (%)</th>
<th>Resistivity (ohm cm)</th>
<th>Mobility (cm$^2$V$^{-1}$s$^{-1}$)</th>
<th>Carrier density ($\text{cm}^{-3} \times 10^{17}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0.10</td>
<td>15.54</td>
<td>39.98</td>
</tr>
<tr>
<td>9</td>
<td>0.18</td>
<td>12.57</td>
<td>34.60</td>
</tr>
<tr>
<td>15</td>
<td>0.36</td>
<td>7.86</td>
<td>21.90</td>
</tr>
<tr>
<td>33</td>
<td>1.39</td>
<td>3.54</td>
<td>12.70</td>
</tr>
<tr>
<td>50</td>
<td>3.67</td>
<td>2.45</td>
<td>6.95</td>
</tr>
</tbody>
</table>

### 4.3.9.2 Photocurrent measurements of CuInS$_2$ thin films

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 of holes. Therefore, some localized discrete energy levels are formed in, the band gap, in the vicinity of the conduction and valence bands respectively. Figure 4.10 shows the variation of photocurrent with a light intensity of CuInS$_2$ films deposited at different duty cycles. The photocurrent is 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 and this helps in the improvement of photocurrent. Microstructural parameters of CuInS$_2$ films deposited at different duty cycles are reported in the Table 4.1. 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 CuInS$_2$ films is shown in Figure 4.11. The photocurrent increases with an increase in voltage. The similar behaviour of CuInS$_2$ films of the photocurrent has been reported by Shahidi et al (Shahidi et al 1985), wherein, the
photoconductivity increased from 0μV to 20μV as the applied voltage increased from 0V to 0.3V. In this work, the photocurrent increased from 0A to 10x10^{-5}A as the applied voltage increased from 0V to 25V. The samples prepared in this work, can be operated at higher voltages compared to the earlier report (Shahidi et al 1985).

![Graph](image)

**Figure 4.10** Photocurrent versus intensity characteristics of CuInS_2 films deposited at different duty cycles (a) 6% (b) 9% (c) 15% (d) 33% (e) 50%  

![Graph](image)

**Figure 4.11** Photocurrent versus voltage characteristics of CuInS_2 films deposited at different duty cycles (a) 6% (b) 9% (c) 15% (d) 33% (e) 50%
4.3.9.3 Photosensitivity measurements of CuInS$_2$ thin films

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

\[
\text{Photosensitivity} \quad \frac{\Delta \sigma}{\sigma} = \frac{I_L - I_D}{I_D} \tag{4.5}
\]

where $I_L$ and $I_D$ represent the current under illumination and in the dark respectively. It seems that some transitions that create additional free carriers effectively increase the free lifetime, increasing the photosensitivity of the material. Figure 4.12 shows a plot of photosensitivity versus light intensity of CuInS$_2$ thin films. Thinner films exhibit moderate photosensitivity, whereas thicker films are found to exhibit higher photosensitivity. Crystallographic imperfections acting as trapping centers will enhance the photosensitivity, whereas the recombination centers decrease the photosensitivity.

![Graph showing photosensitivity versus intensity of CuInS$_2$ films deposited at different duty cycles](image)

Figure 4.12 Photosensitivity versus intensity of CuInS$_2$ films deposited at different duty cycles (a) 6% (b) 9% (c) 15% (d) 33% (e) 50%
4.3.10 Mott-Schottky Studies of CuInS$_2$ Thin Films

Mott-Schottky plots (1/C$^2$ versus Voltage) were studied using 1 M Na$_2$SO$_4$ as the blocking electrolyte and an EG & G PARC impedance analyzer model 6310. The CuInS$_2$ films deposited at 50% duty cycle and post heat treated at 500°C, were used as working electrode, graphite was used as counter electrode and SCE was used as the reference electrode. The frequency was fixed at 1kHz and the bias voltage was varied in the range of −0.2V to 0.8V versus SCE, the value of C was estimated from the imaginary part of the impedance using the equation,

\[
C = \frac{1}{2\pi fZ}
\]  

(4.6)

Figure 4.13 exhibits the Mott-Schottky plots of the films deposited at different duty cycles. The nature of the plot indicates p-type behaviour. Extrapolation of the plot to the voltage axis yields a $V_{fb}$ of 0.70V (SCE). The value of carrier density from the slope of the plot yields a value around $2.0 \times 10^{17}$ cm$^{-3}$. This value agrees well with the carrier density obtained from Hall measurements.

![Mott Schottky plots](image)

**Figure 4.13** Mott schottky plots of CuInS$_2$ films deposited at different duty cycles (a) 15% (b) 33% (c) 50%
4.3.11 Photo Electrochemical Studies of CuInS\textsubscript{2} Thin Films

Photoelectrochemical (PEC) cells were prepared using the films deposited on titanium substrate 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 1M 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 mWcm\textsuperscript{-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 was measured with a HIL digital multimeter.

The CuInS\textsubscript{2} 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 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 60mWcm\textsuperscript{-2}. Figure 4.14 shows the current density versus voltage of the as deposited films, deposited 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 of 450°C to 550°C for 15 min.

Figure 4.14  Current density versus voltage of CuInS₂ films deposited at different duty cycles (a) 9% (b) 15% (c) 25% (d) 33% (e) 50%

Figure 4.15 shows the current density versus voltage of the post heat treated films. From the Figure 4.15, 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 525°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. The photovoltaic parameters are shown in Table 4.4. For a film deposited at 50% duty cycle, an open circuit voltage of 0.55V and a short circuit current density of 12.0mAcm⁻² at 60mWcm⁻² illumination. The photo output is higher than the earlier report (Long et al 2010).
Figure 4.15  Current density versus voltage of CuInS$_2$ 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

Table 4.4  Photovoltaic parameters of CuInS$_2$ photoelectrodes post heat treated at different temperatures

<table>
<thead>
<tr>
<th>Heat treatment Temp(°C)</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mAcm$^{-2}$)</th>
<th>ff</th>
<th>$\eta$ (%)</th>
<th>$R_s$(ohms)</th>
<th>$R_{sh}$(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</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>
<tr>
<td>(After Photoetch)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
It was observed that both $V_{oc}$ and $J_{sc}$ increased with an increase in intensity. Beyond 80mWcm$^{-2}$ 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 linearly increase with intensity of illumination. The Figure 4.16 is shows the ln$J_{sc}$ versus $V_{oc}$ yielded a straight line. Extrapolation of the line to the y-axis yields a $J_0$ value of $5.1 \times 10^{-7}$Acm$^{-2}$, the ideality factor (n) was calculated from the slope of the straight line and it was found to be 1.85.

![Figure 4.16](image)

**Figure 4.16** ln $J_{sc}$ versus $V_{oc}$ for the CuInS$_2$ films deposited at 50% duty cycle and post heat treated at 525°C

Photoetching was done by shorting the photoelectrodes and the graphite counter electrode under an illumination of 100mWcm$^{-2}$ in 1 : 100 HNO$_3$ for different durations in the range 0 seconds to 100 seconds. Both photocurrent and photovoltage are found to increase up to 80 seconds photoetch, beyond which they begin to decrease. This is illustrated in Figure 4.17 for the CuInS$_2$ films deposited at 50% duty cycle. The decrease of the photocurrent and photovoltage after 80 seconds photoetch is attributable to separation of grain boundaries due to prolonged photoetching (Mangalhara et al 1988).
Figure 4.17 Effect of photoetching of CuInS₂ films deposited at 50% duty cycle and post heat treated at 525°C

From the Figure 4.18 power output characteristics after 80 seconds photoetching indicates a $V_{oc}$ of 0.625V, $J_{sc}$ of 16.0mAcm⁻², $ff$ of 0.71 and $\eta$ of 11.83%, for 60mWcm⁻² illumination. The photovoltaic parameters of the electrodes with and without photoetching are shown in Table 4.4. 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.
4.4 CONCLUSION

The pulse plating technique has been employed for the first time to deposit copper indium sulphide thin films. X-ray diffractograms of the films are of single phase with chalcopyrite structure. Microstructural parameters are evaluated it conforms the grain size increased from 15nm to 80nm to increase of duty cycles. At lower duty cycle the internal stress is maximum due to that native defects developed from the lattice misfits or dislocations. Increase of duty cycle the strain and dislocation was reduced and the improved crystalline is obtained. Thickness of the films was observed in the range of 500nm to 900nm with increase of duty cycle. A transmission spectrum towards short wavelengths indicates the onset of the intrinsic inter band absorption is obtained. Optical absorption measurements indicate energy band gap values lies between 1.39eV to 1.53eV. A Photoluminescence measurement indicates a single peak at 0.94eV. Raman spectra authenticate the chalcopyrite structure. Spectral response measurements indicate the value of photocurrent
density (maximum) occurs at a wavelength value corresponding to the band gap 1.52eV. EDS measurements indicates the Cu/In ratio decreased from 1.09 to 1.00 as the duty cycle increased from 6% to 50%. The films exhibit p-type conductivity from Δy parameter. XPS spectrum exhibit the binding energy of Cu-2p_{3/2}, In-3d_{5/2} and S-2p_{1/2} peaks are about 932.4eV, 444.7eV and 162.5eV. AFM studies results the surface roughness increases from 0.85nm to 2.50nm as the duty cycle increases from 6% to 50%. Transport parameters of CuInS_{2} thin films exhibit the resistivity value is 0.10ohmcm to 3.67ohmcm, the mobility value is 15.54cm^{2}V^{-1}s^{-1} to 2.45cm^{2}V^{-1}s^{-1}, the carrier density 39.98x10^{17}cm^{-3} to 6.95x10^{17}cm^{-3} as the duty cycle increased. Photocurrent increased from 0A to 10x10^{-5}A as the applied voltage increased from 0V to 25V. Thinner films exhibit moderate photosensitivity, whereas thicker films are found to exhibit higher photosensitivity. Crystallographic imperfections acting as trapping centers will enhance the photosensitivity, whereas the recombination centers decrease the photosensitivity. The nature of the Mott-Schottky plot indicates p-type behaviour. Photoelectrochemical cell studies have indicated higher output. The photovoltaic parameters of power output characteristics after 80 seconds photoetching indicates a V_{oc} of 0.625V, J_{sc} of 16.0mAcm^{-2}, ff of 0.71 and η of 11.83%, for 60mWcm^{-2} illumination. The ideality factor of 1.85 and the reverse saturation current density, Jo was 5.1x10^{-7}Acm^{-2}. 