CHAPTER 6

PREPARATION, STRUCTURAL, OPTICAL, MORPHOLOGY, BINDING ENERGY, TRANSPORT PARAMETERS AND PHOTOELECTRO CHEMICAL STUDIES OF CuIn$_{1-x}$Ga$_x$S$_2$ THIN FILMS

6.1 INTRODUCTION

CuIn$_{1-x}$Ga$_x$S$_2$ ($0<x<1$), which belongs to the family of I–III–VI$_2$ semiconducting materials, has potential applications for optoelectronics devices and light emitting diodes (LEDs) (Kato et al 2005, Coe et al 2002). The energy gap ($E_g$) of CuIn$_{1-x}$Ga$_x$S$_2$ can be adjusted from 1.5eV (CuInS$_2$) to 2.49eV (CuGaS$_2$) by the adding of Ga (Courtel et al 2010, Prabukanthan et al 2007, Das et al 2008). In recent years, there is a growing interest to explore low cost routes for the production of solar cell materials. Solvent based routes leading to stable CuIn$_{1-x}$Ga$_x$S$_2$ nanocrystals dispersions are very attractive as they can avoid energy intensive vacuum techniques for the production of the active material (Pein et al 2011). Different synthetic methods have been investigated for the preparation of CuGa$_{1-x}$In$_x$S$_2$ nanocrystals, besides solution growth method (Kato et al 2005) and single source precursor method (Sun et al 2010). In this chapter discuss with preparation, various parameters of 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 pulse electrodeposition technique, a low cost and economical method for growing thin films, was employed for the first time in this investigation to deposit $\text{CuIn}_{1-x}\text{Ga}_x\text{S}_2$ films ($0<x<1$).

### 6.2 PREPARATION OF $\text{CuIn}_{1-x}\text{Ga}_x\text{S}_2$ THIN FILMS

$\text{CuIn}_x\text{Ga}_{1-x}\text{S}_2$ films of different composition were pulse electrodeposited on tin oxide coated glass substrates (1.0ohm/sq) at different duty cycles in the range of 6% to 50%. The deposition current density was 1.0mAcm$^{-2}$. The pH was maintained at 1.5 by HCl. The total deposition time was 60 sec. The precursors used were Analar grade 0.20 M$\text{CuCl}_2$, 0.1M $\text{InCl}_3$, 0.25M $\text{GaCl}_3$ and 0.20M sodium thiosulphate. The concentration of the Indium chloride and gallium chloride precursors were varied as shown in Table 6.1, to obtain films of different composition. A microprocessor controlled pulse plating unit was used. The films were characterized by Xpert panalytical X-ray diffraction unit with Cukα radiation. Optical measurements were recorded using a Hitachi UV-vis-IR spectrophotometer. Composition of the films was estimated by EDAX attachment.

X-ray photoelectron spectroscopic (XPS) studies were made using VG MK II system with Mg kα radiation. The surface morphology of the films was studied by molecular imaging atomic force microscope. Electrical measurements were made by Hall Van der Pauw method. The dark and photo conductivity measurements were carried out at room temperature. The measuring system consists of a regulated dc power supply (Aplab) in series with the sample and a Keithley electrometer (model 610 C). A tungsten lamp of 200W was used for illumination. The intensity of the light source was measured with the help of a power meter. The spectral distribution of photocurrent was measured with the help of Photophysics monochromator. Photoelectrochemical cell measurements were made with 250W tungsten halogen lamp, load resistance box, Digital multimeters for measuring current
and voltage output. Capacitance voltage measurements were made using Electrochemical workstation. Microstructural parameters were estimated by studying the X-ray diffractograms of CuIn$_{1-x}$Ga$_x$S$_2$ films of different composition.

<table>
<thead>
<tr>
<th>Table 6.1</th>
<th>Concentration of InCl$_3$ and GaCl$<em>3$ precursors for deposition of CuIn$</em>{1-x}$Ga$_x$S$_2$ films at different composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition (x)</td>
<td>Conc of InCl$_3$ (mM)</td>
</tr>
<tr>
<td>0.1</td>
<td>90</td>
</tr>
<tr>
<td>0.2</td>
<td>80</td>
</tr>
<tr>
<td>0.3</td>
<td>70</td>
</tr>
<tr>
<td>0.4</td>
<td>60</td>
</tr>
<tr>
<td>0.5</td>
<td>50</td>
</tr>
<tr>
<td>0.6</td>
<td>40</td>
</tr>
<tr>
<td>0.7</td>
<td>30</td>
</tr>
<tr>
<td>0.8</td>
<td>20</td>
</tr>
<tr>
<td>0.9</td>
<td>10</td>
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6.3 CHARACTERIZATION OF CuIn$_{1-x}$Ga$_x$S$_2$ THIN FILMS

6.3.1 Structural Analysis of CuIn$_{1-x}$Ga$_x$S$_2$ Thin Films

6.3.1.1 X-ray diffraction studies of CuIn$_{1-x}$Ga$_x$S$_2$ thin films

Figure 6.1 to Figure 6.9 show the X-ray diffraction patterns of CuIn$_{1-x}$Ga$_x$S$_2$ films of different composition. All the figures indicate the prominent peaks corresponding to (112), (220)/(204), (312)/(116). These are characteristic of the chalcopyrite phase. No other phases were observed in the X-ray diffractograms indicating the formation of single phase material. The
peaks shifted from CuInS$_2$ side to CuGaS$_2$ side as the concentration of Ga increased in the films.

Figure 6.1 X-ray diffraction pattern of CuIn$_{0.5}$Ga$_{0.1}$S$_2$ films deposited at different duty cycles of 50\% (Top), 15\% (Middle), 6\% (Bottom)

Figure 6.2 X-ray diffraction pattern of CuIn$_{0.6}$Ga$_{0.2}$S$_2$ films deposited at different duty cycles of 50\% (Top), 15\% (Middle), 6\% (Bottom)
Figure 6.3  X-ray diffraction pattern of CuIn$_{0.7}$Ga$_{0.3}$S$_2$ films deposited at different duty cycles of 50% (Top), 15% (Middle), 6% (Bottom)

Figure 6.4  X-ray diffraction pattern of CuIn$_{0.6}$Ga$_{0.4}$S$_2$ films deposited at different duty cycles of 50% (Top), 15% (Middle), 6% (Bottom)
Figure 6.5 X-ray diffraction pattern of CuIn$_{0.5}$Ga$_{0.5}$S$_2$ films deposited at different duty cycles of 50% (Top), 15% (Middle), 6% (Bottom)

Figure 6.6 X-ray diffraction pattern of CuIn$_{0.4}$Ga$_{0.6}$S$_2$ films deposited at different duty cycles of 50% (Top), 15% (Middle), 6% (Bottom)
Figure 6.7  X-ray diffraction pattern of CuIn$_{0.3}$Ga$_{0.7}$S$_2$ films deposited at different duty cycles of 50% (Top), 15% (Middle), 6% (Bottom)

Figure 6.8  X-ray diffraction pattern of CuIn$_{0.2}$Ga$_{0.8}$S$_2$ films deposited at different duty cycles of 50% (Top), 15% (Middle), 6% (Bottom)
Figure 6.9 X-ray diffraction pattern of CuIn_{0.1}Ga_{0.9}S_{2} films deposited at different duty cycles of 50% (Top), 15% (Middle), 6% (Bottom)

6.3.1.2 Lattice parameters of CuIn_{1-x}Ga_{x}S_{2} thin films

The lattice parameters were calculated using the following relation (Lee et al. 2011)

\[
\frac{1}{d^2} = \frac{(h^2+k^2)}{a^2} + \frac{l^2}{c^2}
\]  

(6.1)

Where, ‘a’ and ‘c’ is the lattice parameters, “d” is the lattice spacing. Table 6.2 shows the variation of ‘a’ and ‘c’ with an increase of indium concentration. This behaviour is similar to an earlier report on CuInGaSe_{2} films (Rincon et al. 2001)
Table 6.2  Lattice parameter values of CuIn$_{1-x}$Ga$_x$S$_2$ films of different composition deposited at 50% duty cycle

<table>
<thead>
<tr>
<th>Concentration of Ga (x)</th>
<th>a (Å)</th>
<th>c (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>5.56</td>
<td>11.53</td>
</tr>
<tr>
<td>0.2</td>
<td>5.54</td>
<td>10.94</td>
</tr>
<tr>
<td>0.3</td>
<td>5.52</td>
<td>10.89</td>
</tr>
<tr>
<td>0.4</td>
<td>5.50</td>
<td>10.84</td>
</tr>
<tr>
<td>0.5</td>
<td>5.48</td>
<td>10.79</td>
</tr>
<tr>
<td>0.6</td>
<td>5.45</td>
<td>10.74</td>
</tr>
<tr>
<td>0.7</td>
<td>5.43</td>
<td>10.69</td>
</tr>
<tr>
<td>0.8</td>
<td>5.41</td>
<td>10.64</td>
</tr>
<tr>
<td>0.9</td>
<td>5.39</td>
<td>10.59</td>
</tr>
</tbody>
</table>

6.3.1.3  Microstructural parameters of CuIn$_{1-x}$Ga$_x$S$_2$ thin films

The grain size of the films has been calculated using Scherrer’s formula (Mustafa et al 2007),

$$D = \frac{0.94\lambda}{\beta \cos \theta} \tag{6.2}$$

Where $\lambda$ is the wavelength of X-ray used, $\beta$ is the full width at half maximum (FWHM) and $\theta$ the Bragg angle. The grain size varied from 30nm to 70nm as the Gallium concentration increased. The dislocation density $\delta$, defined as the length of dislocation lines per unit volume of the crystal has been evaluated using the formula (Huang et al 2004)

$$\delta = \frac{1}{D^2} \tag{6.3}$$
The microstructural parameters are presented in Table 6.3. 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 CuIn$_{1-x}$Ga$_x$S$_2$ 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 (Santhosh kumar et al 2004)

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

(6.4)

The plot of $\beta \cos \theta/\lambda$ versus $\sin \theta/\lambda$ allows us to determine both strain and particle size from the slope and intercept of the graph. The estimated values for films deposited at different duty cycles are listed in Table 6.3. 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.

**Table 6.3 Microstructural parameters of CuIn$_{1-x}$Ga$_x$S$_2$ films at different composition**

<table>
<thead>
<tr>
<th>Composition (x)</th>
<th>Thickness (nm)</th>
<th>Grain size (nm)</th>
<th>Strain ($x 10^{-4}$)</th>
<th>Dislocation density ($x 10^{12} cm^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9</td>
<td>600</td>
<td>30</td>
<td>2.51</td>
<td>2.77</td>
</tr>
<tr>
<td>0.8</td>
<td>680</td>
<td>39</td>
<td>2.45</td>
<td>2.16</td>
</tr>
<tr>
<td>0.7</td>
<td>750</td>
<td>45</td>
<td>2.24</td>
<td>1.77</td>
</tr>
<tr>
<td>0.6</td>
<td>850</td>
<td>49</td>
<td>2.12</td>
<td>1.38</td>
</tr>
<tr>
<td>0.5</td>
<td>950</td>
<td>52</td>
<td>1.87</td>
<td>1.11</td>
</tr>
<tr>
<td>0.4</td>
<td>1035</td>
<td>57</td>
<td>1.48</td>
<td>0.94</td>
</tr>
<tr>
<td>0.3</td>
<td>1190</td>
<td>62</td>
<td>1.12</td>
<td>0.71</td>
</tr>
<tr>
<td>0.2</td>
<td>1358</td>
<td>66</td>
<td>1.02</td>
<td>0.54</td>
</tr>
<tr>
<td>0.1</td>
<td>1600</td>
<td>70</td>
<td>0.91</td>
<td>0.39</td>
</tr>
</tbody>
</table>
Such a behaviour 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 change considerably in accordance with the variations observed with the lattice constant values. The stress developed at higher Ga concentrations 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 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 decrease of Ga concentration may be due to the reduction in concentration of lattice imperfections at lower Ga concentrations. The similar behavior of CuInGaS$_2$ films was reported by Das et al (Das et al 2008).

6.3.1.4 Thickness measurement of CuIn$_{1-x}$Ga$_x$S$_2$ thin films

Thickness of the films estimated by a Mitutoyo surface profilometer varied in the range of 350nm to 800nm with increase of duty cycle. Thickness of the films was in the range of 0.5 micrometer to 1.4 micrometer with an increase of Indium concentration.

6.3.2 Optical Properties of CuIn$_{1-x}$Ga$_x$S$_2$ Thin Films

6.3.2.1 Transmission spectra of CuIn$_{1-x}$Ga$_x$S$_2$ thin films

Figure 6.10 shows the transmission spectra of the CuIn$_{1-x}$Ga$_x$S$_2$ films of different composition deposited at 50% duty cycle. The spectra exhibits
interference fringes and the value of the refractive index was estimated by the envelope method (Joo et al 1999) as follows:

\[ n = [N + (N^2 - n_s^2)]^2 \quad (6.5) \]

\[ N = (n_s^2 + 1)/2 + 2 n_s (T_{\text{max}} - T_{\text{min}})/T_{\text{max}} T_{\text{min}} \quad (6.6) \]

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 on a transmittance spectrum. The value of the refractive index calculated from the above equations was in the range of 2.695 to 2.55 with a decrease of gallium concentration. The refractive index decreases with wavelength (Figure 6.11). The value of the absorption coefficient \( (\alpha) \) was calculated using the relation

\[ \alpha = 1/d \ln (n-1)/(n-n_s) [(T_{\text{max}}/T_{\text{min}})^2 + 1]/[(T_{\text{max}}/T_{\text{min}})^2 - 1] \quad (6.7) \]

Where ‘d’ is the thickness of the film and the other parameters have the usual meaning as is given in equation (6.6).

Figure 6.10 Transmission spectra of CuIn\(_{1-x}\)Ga\(_x\)S\(_2\) films of different composition deposited at 50 % duty cycle (a) \( x = 0.1 \) (b) \( x = 0.2 \) (c) \( x = 0.3 \) (d) \( x = 0.4 \) (e) \( x = 0.5 \) (f) \( x = 0.6 \) (g) \( x = 0.7 \) (h) \( x = 0.8 \) (i) \( x = 0.9 \)
Figure 6.11 Variation of refractive index with wavelength for the CuIn$_{1-x}$Ga$_x$S$_2$ of different composition deposited at 50% duty cycle (a) x = 0.2 (b) x = 0.4 (c) x = 0.7 (d) x = 0.9

6.3.2.2 Band gap studies of CuIn$_{1-x}$Ga$_x$S$_2$ thin films

The band gap of the films increased from 1.60eV to 2.275eV as the gallium concentration increased (from Figure 6.12 $(\alpha h \nu)^2$ versus photon energy).

Figure 6.12 $(\alpha h \nu)^2$ versus photon energy (eV) of CuIn$_{1-x}$Ga$_x$S$_2$ films of different composition deposited at 50% duty cycle (a) x = 0.1 (b) x = 0.2 (c) x = 0.3 (d) x = 0.4 (e) x = 0.5 (f) x = 0.6 (g) x = 0.7 (h) x = 0.8 (i) x = 0.9
The increase in the band gap at lower duty cycles is due to the small crystallites. The values of the band gap are in the range reported earlier (Courtel et al 2010, Prabukanthan et al 2007 and Das et al 2008)

6.3.3 Photoluminescence Studies of CuIn$_{1-x}$Ga$_x$S$_2$ Thin Films

The photoluminescence spectra were recorded on the films of different composition deposited at 50% duty cycle. PL spectra were obtained using the 457.9nm line of an Ar$^+$-ion laser as an excitation source. After passing through a laser line notch filter, the beam was focused and directed onto the sample. Figure 6.13 shows the PL spectra of the films. From the Figure 6.13, it can be seen that the samples exhibit emission peaks at 540 nm and a broad emission peak at around 820nm. The peak at 540nm exhibits a 40nm red shift relative to bulk CuGaS$_2$, whose strong emission band peaks at $\sim$ 500nm (Metzner et al 2004). The peak reduces in intensity with the decrease of gallium concentration. The broad peak around 820nm corresponds to the excitonic emission from CuInS$_2$. The height of this peak increases with the decrease of gallium concentration.

![Photoluminescence spectrum of CuIn$_{1-x}$Ga$_x$S$_2$ films of different composition deposited at 50% duty cycle](image)

**Figure 6.13** Photoluminescence spectrum of CuIn$_{1-x}$Ga$_x$S$_2$ films of different composition deposited at 50% duty cycle (a) $x = 0.9$ (b) $x = 0.7$ (c) $x = 0.5$ (d) $x = 0.3$ (e) $x = 0.1$
6.3.4 Raman Studies of CuIn$_{1-x}$Ga$_x$S$_2$ Thin Films

The Raman spectra (Figure 6.14) were recorded on the CuIn$_{1-x}$Ga$_x$S$_2$ films of different composition deposited at 50% duty cycle using Renshaw Invia Raman spectrometer fitted with 633nm Helium Neon laser. CuInS$_2$ is known to be grown with two different structures, chalcopyrite (CH) and CuAu (CA) orderings. An A1 mode of CH ordering is reported to appear at ~ 295 cm$^{-1}$ (Rudigier et al 2004). In the present study, a peak corresponding to A1 mode of CH ordering of CuInS$_2$ is observed at 293 cm$^{-1}$. Another peak centered at 303 cm$^{-1}$ is also observed, which corresponds to A1 mode for CuIn$_{1-x}$Ga$_x$S$_2$ (Zhong et al 2012). As the concentration of Ga increases in the films, the peak at 303 cm$^{-1}$ increases in intensity and the peak at 293 cm$^{-1}$ decrease correspondingly.

![Raman spectra of CuIn$_{1-x}$Ga$_x$S$_2$ films](image)

**Figure 6.14** Raman spectra of CuIn$_{1-x}$Ga$_x$S$_2$ films of different composition deposited at 50% duty cycle (a) x = 0.1 (b) x = 0.3 (c) x = 0.5 (d) x = 0.7 (e) x = 0.8 (f) x = 0.9
6.3.5 Spectral Response of CuIn$_{1-x}$Ga$_x$S$_2$ 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 was noted at each wavelength.

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

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

(6.8)

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 $J_{ph}$ vs $\lambda$ for the CuIn$_{1-x}$Ga$_x$S$_2$ electrodes of different composition heat treated at 525°C is shown in Figure 6.15 to Figure 6.23. The value of ($J_{ph}$)$_{max}$ occurs at a wavelength value corresponding to the band gap corresponding to the band gap obtained from optical measurements for that composition.

![Photocurrent spectra of CuIn$_{0.1}$Ga$_{0.9}$S$_2$ films deposited at 50% duty cycle and post heat treated at 500°C](image)
Figure 6.16  Photocurrent spectra of CuIn$_{0.2}$Ga$_{0.8}$S$_2$ films deposited at 50% duty cycle and post heat treated at 500°C

Figure 6.17  Photocurrent spectra of CuIn$_{0.3}$Ga$_{0.7}$S$_2$ films deposited at 50% duty cycle and post heat treated at 500°C

Figure 6.18  Photocurrent spectra of CuIn$_{0.4}$Ga$_{0.6}$S$_2$ films deposited at 50% duty cycle and post heat treated at 500°C
Figure 6.19  Photocurrent spectra of CuIn$_{0.5}$Ga$_{0.5}$S$_2$ films deposited at 50% duty cycle and post heat treated at 500°C

Figure 6.20  Photocurrent spectra of CuIn$_{0.6}$Ga$_{0.4}$S$_2$ films deposited at 50% duty cycle and post heat treated at 500°C

Figure 6.21  Photocurrent spectra of CuIn$_{0.7}$Ga$_{0.3}$S$_2$ films deposited at 50% duty cycle and post heat treated at 500°C
Figure 6.22  Photocurrent spectra of CuIn\textsubscript{0.8}Ga\textsubscript{0.2}S\textsubscript{2} films deposited at 50\% duty cycle and post heat treated at 500°C

Figure 6.23  Photocurrent spectra of CuIn\textsubscript{0.9}Ga\textsubscript{0.1}S\textsubscript{2} films deposited at 50\% duty cycle and post heat treated at 500°C

6.3.6   EDS Spectrum of CuIn\textsubscript{1-x}Ga\textsubscript{x}S\textsubscript{2} Thin Films

Composition of the films was estimated by recording the EDS spectrum of the CuIn\textsubscript{1-x}Ga\textsubscript{x}S\textsubscript{2} thin films deposited of different composition is shown in the Table 6.4. Figure 6.24 to Figure 6.28 show the EDS spectrum of CuIn\textsubscript{1-x}Ga\textsubscript{x}S\textsubscript{2} films deposited at 50\% duty cycle. It is observed that films with lower concentrations of Gallium were copper rich. As the gallium
concentration increased, the films became nearly stochiometric. This is due to
the fact that at as the concentration of gallium chloride increases in the bath,
more flux of gallium ions are available for deposition compared to the flux of
indium ions, which results in higher concentrations of gallium thus decreasing
the Cu/(Ga+In) ratio. Based on the defect chemistry model of ternary
compounds (Groenik et al 1978), compositional deviations of the
CuIn_{1-x}Ga_xS_2 films can be expressed by non stoichiometry parameter
(Δy = [2S/Cu + 3(Ga + In)] - 1). The parameter Δy is related to the
electronic defects. For Δy > 0, the film has a p-type conductivity and it has a
n-type conductivity for Δy < 0. In this study the value of Δy is greater than
zero and the films exhibit p-type conductivity.

![Figure 6.24](image)

**Figure 6.24** EDS spectrum of CuIn_{0.9}Ga_{0.1}S_2 films deposited at 50% duty cycle

![Figure 6.25](image)

**Figure 6.25** EDS spectrum of CuIn_{0.7}Ga_{0.3}S_2 films deposited at 50% duty cycle
Figure 6.26  EDS spectrum of CuIn$_{0.5}$Ga$_{0.5}$S$_2$ films deposited at 50 % duty cycle

Figure 6.27  EDS spectrum of CuIn$_{0.3}$Ga$_{0.7}$S$_2$ films deposited at 50 % duty cycle

Figure 6.28  EDS spectrum of CuIn$_{0.1}$Ga$_{0.9}$S$_2$ films deposited at 50 % duty cycle
Table 6.4 Composition of CuIn$_{1-x}$Ga$_x$S$_2$ films of deposited at 50% duty cycle

<table>
<thead>
<tr>
<th>Comp(x)</th>
<th>Cu (at.%)</th>
<th>In (at.%)</th>
<th>Ga (at.%)</th>
<th>S (at.%)</th>
<th>Cu/(Ga+In)</th>
<th>Ga/(Ga+In)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>26.00</td>
<td>22.50</td>
<td>2.50</td>
<td>49.00</td>
<td>1.04</td>
<td>0.10</td>
</tr>
<tr>
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<td>5.00</td>
<td>49.70</td>
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</tr>
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</tr>
<tr>
<td>0.5</td>
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<td>12.00</td>
<td>51.80</td>
<td>1.01</td>
<td>0.50</td>
</tr>
<tr>
<td>0.6</td>
<td>23.20</td>
<td>9.00</td>
<td>14.00</td>
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<td>1.01</td>
<td>0.61</td>
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<tr>
<td>0.7</td>
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<td>16.00</td>
<td>53.80</td>
<td>1.01</td>
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<tr>
<td>0.9</td>
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<td>19.10</td>
<td>57.60</td>
<td>1.01</td>
<td>0.90</td>
</tr>
</tbody>
</table>

6.3.7 XPS Studies of CuIn$_{1-x}$Ga$_x$S$_2$ Thin Films

XPS studies were made on the CuIn$_{1-x}$Ga$_x$S$_2$ films using MK II VG systems XPS system. From the Cu2p core level spectral region. Figure 6.29 to Figure 6.37 show the XPS spectra of CuIn$_{1-x}$Ga$_x$S$_2$ films of different composition. The observed binding energy values for Cu2p$_{3/2}$ varied from 932.38eV to 932.18eV and Cu2p$_{1/2}$ varied from 952.38eV to 952.18eV as the gallium concentration increased, these values are close to the reported values for Cu$^+$(Cao et al 2011). Besides, the Cu2p$_{3/2}$ satellite peaks characterizing Cu$^{2+}$, which are usually centered at about 942eV, are absent in the Figure. The In 3d$_{5/2}$ varied in the range of 445.53eV to 446.56eV, In 3d$_{3/2}$ varied from 452.53eV to 453.56eV as the gallium concentration increases. The Ga2p core level spectral region indicates that the binding energies for Ga2p$_{3/2}$, which varied from 1118.00eV to 1117.00eV and Ga2p$_{1/2}$ varied from 1143.63eV to 1144.98eV as the gallium concentration increased, these are in good agreement with the respective values for Ga$^{3+}$. The S2p core level spectrum
shows a peak, which varies from 162.48eV to 162.20eV as the gallium concentration increased. This value is typical of metal sulphides (Zhu et al 2011).

Figure 6.29 XPS spectra of Ga, In, Cu and S of CuIn$_{0.9}$Ga$_{0.1}$S$_2$ films
Figure 6.30  XPS spectra of Ga, In, Cu and S of CuIn$_{0.8}$Ga$_{0.2}$S$_2$ films
Figure 6.31 XPS spectra of Ga, In, Cu and S of CuIn$_{0.7}$Ga$_{0.3}$S$_2$ films
Figure 6.32 XPS spectra of Ga, In, Cu and S of CuIn$_{0.6}$Ga$_{0.4}$S$_2$ films
Figure 6.33 XPS spectra of Ga, In, Cu and S of CuIn$_{0.5}$Ga$_{0.5}$S$_2$ films
Figure 6.34  XPS spectra of Ga, In, Cu and S of CuIn\textsubscript{0.4}Ga\textsubscript{0.6}S\textsubscript{2} films
Figure 6.35  XPS spectra of Ga, In, Cu and S of CuIn_{0.3}Ga_{0.7}S_{2} films
Figure 6.36  XPS spectra of Ga, In, Cu and S of CuIn_{0.2}Ga_{0.8}S_{2} films
Figure 6.37 XPS spectra of Ga, In, Cu and S of CuIn\textsubscript{0.9}Ga\textsubscript{0.1}S\textsubscript{2} films

6.3.8 Atomic Force Microscopy of CuIn\textsubscript{1-x}Ga\textsubscript{x}S\textsubscript{2} Thin Films

The surface morphology of the films (Figure 6.38) studied in an area of 13m x 13m indicated that the grain size increased from 30nm to 70nm as the indium concentration increased. The surface roughness also increased
from 0.25 nm to 2.2 nm with an increase of indium concentration. The surface roughness increases due to the increase of grain size.

Figure 6.38 Atomic force micrographs of CuIn$_{1-x}$Ga$_x$S$_2$ films of different composition deposited at 50% duty cycle (A) x=0.9 (B) x=0.7 (C) x=0.5 (D) x=0.3 (E) x=0.1
6.3.9 Electrical Properties of CuIn_{1-x}Ga_xS_2 Thin Films

6.3.9.1 Hall van der pauw technique of CuIn_{1-x}Ga_xS_2 thin films

The electrical resistivity of the CuIn_{1-x}Ga_xS_2 films of different composition was studied by providing gold ohmic contacts (0.1 cm^2) on top of the film surface and the resistance was measured between the top gold contact and the bottom tin oxide coated substrate. Resistivity was calculated from the resistance values and it was observed that the resistivity decreased from 14.74ohmcm to 4.52ohmcm with the decrease of gallium content (Table 6.5). The low resistivity values are due to decrease of resistivity with increasing Cu/In ratio. This is due to an increase in carrier concentration with increasing with Cu/In ratio. In our study the Cu/In ratio increased from 0.98 to 1.15 as the gallium content decreased.

The variation of mobility (μ) of CuIn_{1-x}Ga_xS_2 films of different composition with the decrease of gallium content is indicated in Table 6.5.

<table>
<thead>
<tr>
<th>Conc.of Ga (x)</th>
<th>Resistivity (ohm cm)</th>
<th>Mobility (cm^2V^{-1}s^{-1})</th>
<th>Carrier density (cm^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9</td>
<td>14.74</td>
<td>3.1</td>
<td>1.36 x 10^{17}</td>
</tr>
<tr>
<td>0.8</td>
<td>12.86</td>
<td>2.9</td>
<td>1.67 x 10^{17}</td>
</tr>
<tr>
<td>0.7</td>
<td>11.10</td>
<td>2.8</td>
<td>2.01 x 10^{17}</td>
</tr>
<tr>
<td>0.6</td>
<td>10.55</td>
<td>2.7</td>
<td>2.19 x 10^{17}</td>
</tr>
<tr>
<td>0.5</td>
<td>9.85</td>
<td>2.62</td>
<td>2.42 x 10^{17}</td>
</tr>
<tr>
<td>0.4</td>
<td>8.98</td>
<td>2.58</td>
<td>2.69 x 10^{17}</td>
</tr>
<tr>
<td>0.3</td>
<td>7.09</td>
<td>2.54</td>
<td>3.47 x 10^{17}</td>
</tr>
<tr>
<td>0.2</td>
<td>6.29</td>
<td>2.51</td>
<td>3.95 x 10^{17}</td>
</tr>
<tr>
<td>0.1</td>
<td>4.52</td>
<td>2.49</td>
<td>5.54 x 10^{17}</td>
</tr>
</tbody>
</table>
It is observed from the figure that the mobility decreases from 3.1cm²V⁻¹s⁻¹ to 2.49cm²V⁻¹s⁻¹ as the gallium content decreases. The variation of carrier concentration (n) with in a decrease of gallium content is also indicated in the table. The carrier concentration varies from $1.36 \times 10^{17}$ cm⁻³ to $5.54 \times 10^{17}$ cm⁻³ as the gallium content decreased.

6.3.9.2 Photocurrent measurements of CuIn₁₋ₓGaₓS₂ 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 6.39 shows the variation of photocurrent with a light intensity of CuIn₁₋ₓGaₓS₂ films of different composition. The photocurrent is found to increase with an increase of indium concentration due to increase in film thickness.

![Graph showing photocurrent versus intensity for CuIn₁₋ₓGaₓS₂ films](image)

Figure 6.39 Photocurrent versus intensity for CuIn₁₋ₓGaₓS₂ films of different composition (a) x = 0.1 (b) x = 0.2 (c) x = 0 (d) x = 0.4 (e) x = 0.5 (f) x = 0.6 (g) x = 0.7 (h) x = 0.8 (i) x = 0.9
As the thickness of the film increases the crystalline nature increases (Table 6.2) 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 CuIn$_{1-x}$Ga$_x$S$_2$ films of different composition is shown in Figure 6.40. The photocurrent increases with an increase in voltage.

![Photocurrent versus voltage](image)

**Figure 6.40** Photocurrent versus voltage of CuIn$_{1-x}$Ga$_x$S$_2$ films of different composition (a) $x = 0.1$ (b) $x = 0.2$ (c) $x = 0.3$ (d) $x = 0.4$ (e) $x = 0.5$ (f) $x = 0.6$ (g) $x = 0.7$ (h) $x = 0.8$ (i) $x = 0.9$

Photocurrent spectra of CuIn$_{1-x}$Ga$_x$S$_2$ films of different composition are shown in Figure 6.41. The photocurrent spectra show a peak near the absorption edge which was also observed (Rose 1955). The band gap of the films determined from the spectral response coincided with the band gap determined from optical absorption measurements for that composition. The low photocurrent in the short wavelength range may be due to the high absorption coefficient and only surface region where defect states give a shorter lifetime, is excited. In the high wavelength region the radiation is only
partially absorbed giving rise to less photocurrent than the peak value. Tails of the spectra extending to long wavelength are attributed to direct excitation of the carriers from the defect levels. Similar results have been reported by several researchers for CuInSe$_2$ films (Pal et al 1994, Fischer et al 2001).

![Figure 6.41 Photocurrent versus wavelength of CuIn$_{1-x}$Ga$_x$S$_2$ films deposited at 50% duty cycle (a) x=0.9 (b) x=0.6 (c) x=0.3 (d) x=0.1](image)

6.3.9.3 Photosensitivity measurements of CuIn$_{1-x}$Ga$_x$S$_2$ 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:

\[
\text{Photosensitivity} \quad \frac{\Delta \sigma}{\sigma} = \frac{I_L - I_D}{I_D} \quad (6.9)
\]
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 life time increasing the photosensitivity of the material. Figure 6.42 shows a plot of photosensitivity versus light intensity of thin films of different compositions. Thinner films exhibit moderate photosensitivity, whereas thicker films are found to exhibit higher photosensitivity. Crystallographical imperfections acting as trapping centers will enhance the photosensitivity, whereas the recombination centers decrease the photosensitivity.

![Photoconductivity vs. Intensity](image)

**Figure 6.42 Photosensitivity versus intensity of illumination of CuIn$_{1-x}$Ga$_x$S$_2$ films of different composition (a) x = 0.1 (b) x = 0.3 (c) x = 0.5 (d) x = 0.7 (e) x = 0.8 (f) x = 0.9**

### 6.3.10 Mott Schottky Plots of CuIn$_{1-x}$Ga$_x$S$_2$ Thin Films

Mott-Schottky plot of the CIGS films of different composition with 1M Na$_2$(SO$_4$)$_2$ blocking electrolyte was studied, the AC frequency was 10 kHz linear plots were obtained. The nature of the plot with positive slope indicates p-type behavior. $V_m$ in the range of 0.76V (SCE) to 0.94V (SCE) (Figure 6.43). The value of carrier density from the slope of the plot yields values in the range of $1.2 \times 10^{17}$cm$^{-3}$ to $6.5 \times 10^{16}$ with increase of gallium.
concentration. Figure 6.43 also shows the Mott-Schottky plot of CuIn\textsubscript{0.1}Ga\textsubscript{0.9}S\textsubscript{2} films after photoetching. It exhibits a $V_{fb}$ of 1.00V (SCE).

![Mott-Schottky plot](image)

**Figure 6.43** Mott-Schottky plot of CuIn\textsubscript{1-x}Ga\textsubscript{x}S\textsubscript{2} films of different composition post heat treated at 500°C (a) x = 0.1 (b) x = 0.3 (c) x = 0.5 (d) x = 0.7 (e) x = 0.9

### 6.3.11 Photoelectrochemical Studies of CuIn\textsubscript{1-x}Ga\textsubscript{x}S\textsubscript{2} Thin Films

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 6.44 shows the Photocurrent density versus Photovoltage of the as deposited films of different composition. Films of composition CuIn\textsubscript{0.9}Ga\textsubscript{0.1}S\textsubscript{2} exhibited maximum photo output. The photo output was low, hence, in order to increase the photo output, the films of different composition were post heated in argon atmosphere at different temperatures in the range of 450°C to 525°C for 15min. Figure 6.45 shows the Photocurrent density versus Photovoltage of the post heat treated films of composition CuIn\textsubscript{0.9}Ga\textsubscript{0.1}S\textsubscript{2} 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 a slight change in stoichiometry. The photovoltaic parameters are shown in Table 6.6. Photocurrent density versus Photovoltage of the films of other composition, post heat treated at different temperatures are shown in Figure 6.46 to Figure 6.53. Films of composition CuIn$_{0.7}$Ga$_{0.3}$S$_2$ exhibit maximum V$_{oc}$, since these films indicate maximum V$_{fb}$ (flat band potential) (Mott-Schottky plot) (Figure 6.41).

![Figure 6.44](image1)

**Figure 6.44** Photocurrent density versus photovoltage of CuIn$_{1-x}$Ga$_x$S$_2$ films of different composition deposited at 50 % duty cycles
(a) x = 0.1 (b) x = 0.3 (c) x = 0.6 (d) x = 0.9

![Figure 6.45](image2)

**Figure 6.45** Photocurrent density versus photovoltage of CuIn$_{0.5}$Ga$_{0.1}$S$_2$ films post heat treated at different temperatures (a) 450°C (b) 475°C (c) 500°C (d) 525°C
Table 6.6  Photovoltaic parameters of CuIn$_{1-x}$Ga$_x$S$_2$ films of different composition deposited at 50% duty cycle after post heat treatment at 500°C

<table>
<thead>
<tr>
<th>Conc of Ga (x)</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>ff</th>
<th>η (%)</th>
<th>$R_s$ (Ω)</th>
<th>$R_{sh}$ (kΩ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9</td>
<td>0.385</td>
<td>7.32</td>
<td>0.70</td>
<td>3.29</td>
<td>30</td>
<td>1.90</td>
</tr>
<tr>
<td>0.8</td>
<td>0.380</td>
<td>7.50</td>
<td>0.68</td>
<td>3.25</td>
<td>28</td>
<td>1.90</td>
</tr>
<tr>
<td>0.7</td>
<td>0.400</td>
<td>8.50</td>
<td>0.65</td>
<td>3.68</td>
<td>25</td>
<td>1.95</td>
</tr>
<tr>
<td>0.6</td>
<td>0.420</td>
<td>9.50</td>
<td>0.65</td>
<td>4.32</td>
<td>22</td>
<td>1.95</td>
</tr>
<tr>
<td>0.5</td>
<td>0.470</td>
<td>10.00</td>
<td>0.62</td>
<td>4.86</td>
<td>21</td>
<td>2.00</td>
</tr>
<tr>
<td>0.4</td>
<td>0.575</td>
<td>10.00</td>
<td>0.62</td>
<td>5.94</td>
<td>21</td>
<td>2.10</td>
</tr>
<tr>
<td>0.3</td>
<td>0.595</td>
<td>11.00</td>
<td>0.65</td>
<td>7.09</td>
<td>18</td>
<td>2.20</td>
</tr>
<tr>
<td>0.2</td>
<td>0.385</td>
<td>12.00</td>
<td>0.65</td>
<td>5.01</td>
<td>15</td>
<td>1.90</td>
</tr>
<tr>
<td>0.1</td>
<td>0.330</td>
<td>13.50</td>
<td>0.65</td>
<td>4.83</td>
<td>12</td>
<td>1.80</td>
</tr>
<tr>
<td>0.3</td>
<td>0.710</td>
<td>12.00</td>
<td>0.75</td>
<td>6.39</td>
<td>15</td>
<td>2.30</td>
</tr>
</tbody>
</table>

Figure 6.46  Photocurrent density versus photovoltage of CuIn$_{0.8}$Ga$_{0.2}$S$_2$ films post heat treated at different temperatures (a) 450°C (b) 475°C (c) 500°C (d) 525°C
Figure 6.47 Photocurrent density versus photovoltage of CuIn$_{0.7}$Ga$_{0.3}$S$_2$ films post heat treated at different temperatures (a) 450°C (b) 475°C (c) 500°C (d) 525°C

Figure 6.48 Photocurrent density versus photovoltage of CuIn$_{0.6}$Ga$_{0.4}$S$_2$ films post heat treated at different temperatures (a) 450°C (b) 475°C (c) 500°C (d) 525°C

Figure 6.49 Photocurrent density versus photovoltage of CuIn$_{0.5}$Ga$_{0.5}$S$_2$ films post heat treated at different temperatures (a) 450°C (b) 475°C (c) 500°C (d) 525°C
Figure 6.50 Photocurrent density versus photovoltage of CuIn$_{0.4}$Ga$_{0.6}$S$_2$ films post heat treated at different temperatures (a) 450°C (b) 475°C (c) 500°C (d) 525°C

Figure 6.51 Photocurrent density versus photovoltage of CuIn$_{0.3}$Ga$_{0.7}$S$_2$ films post heat treated at different temperatures (a) 450°C (b) 475°C (c) 500°C (d) 525°C

Figure 6.52 Photocurrent density versus photovoltage of CuIn$_{0.2}$Ga$_{0.8}$S$_2$ films post heat treated at different temperatures (a) 450°C (b) 475°C (c) 500°C (d) 525°C
It was observed that both $V_{oc}$ and $J_{sc}$ increased with an increase of 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. A plot of $\ln J_{sc}$ versus $V_{oc}$ (Figure 6.54) yielded a straight line. Extrapolation of the line to the y-axis yields a $J_0$ value of 1.15 x 10$^{-7}$Acm$^{-2}$, the ideality factor (n) was calculated from the slope of the straight line and it was found to be 2.05
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 0sec to 100sec. Both photocurrent and photovoltage are found to increase up to 80sec photoetch, beyond which they begin to decrease. This is illustrated in Figure 6.55 for the CuIn$_{0.7}$Ga$_{0.3}$S$_2$ photoelectrode after post heat treatment. The decrease of the photocurrent and photovoltage after 80sec photoetch is attributable to separation of grain boundaries due to prolonged photoetching (Mangalhara et al 1988). The power output characteristics (Figure 6.56) after 80sec photoetching indicates a $V_{oc}$ of 0.70V, $J_{sc}$ of 20.0 mAcm$^{-2}$, ff of 0.71 and $\eta$ of 14.33%, for 60mWcm$^{-2}$ illumination. The photovoltaic parameters of the electrodes with and without photoetching are shown in Table 6.6.

![Figure 6.55 Effect of photoetching time on $V_{oc}$ and $J_{sc}$ of CuIn$_{0.7}$Ga$_{0.3}$S$_2$ films post heat treated at 500°C](image)

The charge distribution at the semiconductor and electrolyte interface is often determined by measuring the capacitance of the space charge layer $C_{sc}$ as a function of the electrode potential $V$. The Mott-Schottky
relationship expresses the potential dependence of $C_{sc}$ of a semiconductor electrode under depletion conditions

$$\frac{1}{C_{sc}^2} = \left[\frac{2}{eN_A \varepsilon \varepsilon_0}\right] \left[(V - V_{fb}) - kT/e\right]$$

(6.10)

where, $C_{sc}$ is the space charge capacitance; $V$ represents the applied potential; $V_{fb}$ is the flat band voltage, $N_A$ is the concentration of acceptors, $N_A$ can be determined from the slope of the experimental $1/C_{sc}^2$ versus $V$ plots, while $V_{fb}$ comes from the extrapolation for $1/C_{sc}^2 = 0$. The validity of the Mott–Schottky analysis is based on the assumption that the capacitance of the space charge layer is much less than that of the Helmholtz layer. When the measured frequency is high enough ($> 1 \text{ kHz}$), the contribution of Helmholtz capacitance to the measured electrode capacitance is negligible. Thus the capacitance of the semiconductor electrolyte interface mainly expresses the capacitance of the space charge layer of the semiconductor.

![Figure 6.56](image.jpg) **Figure 6.56** Photocurrent density versus photovoltage of CuIn$_{0.7}$Ga$_{0.3}$S$_2$ films post heat treated at 500°C after photoetching for 80 sec
6.4 CONCLUSION

The CuIn$_{1-x}$Ga$_x$S$_2$ thin films of different composition were pulse electrodeposited on ITO substrates at different duty cycles. X-ray diffractograms indicating the formation of single phase chalcopyrite structure. Lattice parameters decrease with increase of gallium concentration. Microstructural parameters observed that the dislocation density decreases with increase of grain size from the role of gallium concentration. The grain size varied from 30nm to 70nm as the gallium concentration increased. Transmission spectra exhibits interference fringes and the refractive index value was in the range of 2.695 to 2.55 with decrease of gallium concentration. The band gap value of the films increased form 1.60eV to 2.275eV as the gallium concentration increased. Photoluminescence exhibit emission peaks at 540nm and broad emission peak at around 820nm. Laser Raman studies observed a peak corresponding to A1 mode of CH ordering is reported to appear at 293cm$^{-1}$ and 303cm$^{-1}$. The value of ($I_{ph}$)$_{max}$ occurs at a wavelength value corresponding to the band gap value of that composition. EDS spectrum results the gallium concentration increased the film became nearly stiochiometric. Peaks corresponding to Cu, Ga, In and S is obtained. The observed binding energy of Cu2p$_{3/2}$, Cu2p$_{1/2}$, In3d$_{5/2}$, In3d$_{3/2}$ Ga2p$_{3/2}$, Ga2p$_{1/2}$, S2p these are in good agreement with the respective values. The surface roughness increased from 0.25nm to 2.2nm with increase of indium concentration. Transport parameters of CuIn$_{1-x}$Ga$_x$S$_2$ thin films of different composition deposited at 50% duty cycle shows the resistivity and mobility decreases as the gallium content decreases and the carrier density varies from 1.36x10$^{17}$ to 5.54x10$^{17}$ as the gallium content decreases. Photocurrent spectra show a peak near the absorption edge. Thinner films exhibit moderate photosensitivity, whereas thicker films are found to be exhibit higher photosensitivity. The nature of the Mott-Schottky plot with positive slope indicates p-type behavior. $V_{fb}$ in the range of 0.76V (SCE) to 0.94V (SCE).
The value of carrier density from the slope of the plot yields values in the range of $1.2 \times 10^{17}$ cm$^{-3}$ to $6.5 \times 10^{16}$ cm$^{-3}$ with increase of gallium concentration. Photoelectrochemical studies show the film composition of CuIn$_{0.9}$Ga$_{0.1}$S$_2$ exhibited maximum output. Ideality factor calculated from the slope of the straight line was 2.05. The reverse saturation current density, $J_o$ was $1.15 \times 10^{-7}$ A cm$^{-2}$. The power output characteristics after 80sec photoetching indicates a $V_{oc}$ of 0.70V, $J_{sc}$ of 20.0 mA cm$^{-2}$, ff of 0.71 and $\eta$ of 14.33%, for 60mWcm$^{-2}$ illumination.