CHAPTER VIII
CuInSe\textsubscript{2}/CdS SOLAR CELLS

8.1 Introduction

Photovoltaic effect has been discovered nearly a century and half ago\[1\]. However the photovoltaic research has been dominated by solid state technology for large scale energy applications. The energy contained in sunlight is distributed over a wide range of wavelengths and efficient conversion requires a wide spectral response. Wider band gap materials absorb smallest spectral range of the terrestrial solar insolation producing smaller currents than smaller band gap materials which absorb more producing larger short circuit current.

CuInSe\textsubscript{2}, due to its smaller and direct band gap (1.04 eV) is considered to be a promising material for solar cell application. In the present study, CuInSe\textsubscript{2} films deposited by close-spaced vapour transport is used as a p-type absorber layer in the fabrication of solar cells (Quartz/Mo/p-CuInSe\textsubscript{2}/n-CdS). Some of the important heterojunction solar cells are n-Si/p-CdTe, n-Si/p-GaAs, n-GaAs/p-InP, n-ZnSe/p-InP, n-ITO/p-InP,
n-CdTe/p-Cu₂Se, n-GaP/p-InP, p-CdTe/n-CuInSe₂, n-CdS/p-CuInSe₂, n-ZnO/p-CuInSe₂.

Particularly, I-III-VI₂ ternary semiconductors have been receiving attention primarily due to their photovoltaic device potential [2-6]. Among these chalcopyrite type material, CuInSe₂ possesses some exceptional characteristics for heterojunction application with CdS viz.,

a) CuInSe₂ is a direct band gap semiconductor which minimizes the minority carrier diffusion length

b) the lattice match between CuInSe₂ and CdS is exceptionally good (lattice mismatch is only about 1.2 %) thereby introduces only a small amount of interfacial defects and

c) electron affinities of CuInSe₂ and CdS are close enough to minimize any potential barrier to the photo-induced carriers. No interfacial spikes are formed in the conduction band as electron affinities of the two materials are very close.

Kushiya et al [7] have reported an efficiency of 10.3 % for CuInSe₂ based solar cell with the structure ZnO/CdS/ CuInSe₂/Mo/glass. Zweigart
et al[8] have deposited the CuInSe$_2$ absorber layer by sequential deposition process. The CdS buffer layer was deposited by chemical bath deposition technique and a window layer consisting of high and low resistivity ZnO layers were deposited by sputtering. They have reported a cell efficiency of 13.9%.

Fitzgerald and Potrous[9] have fabricated p-CuInSe$_2$/n-CdS and p-CuInSe$_2$/n-Si heterojunctions by spray pyrolysis technique. Arya et al[10] have studied the photovoltaic properties of CuInSe$_2$/CdS solar cell in which CuInSe$_2$ was a large grained polycrystal and a low resistivity CdS was evaporated over it. The device efficiency has been reported as 5.8%. It has been reported that the observed large leakage current and low values of open circuit voltage are due to exposure of CuInSe$_2$ to atmosphere before CdS deposition.

Stolt et al[11] have obtained an active area efficiency of 14.8% for a n-ZnO/n-CdS/p-CuInSe$_2$ solar cell structure deposited on soda lime glass substrate. The obtained low short circuit current has been attributed to the CdS cut off which is at 2.4 eV compared to ZnO which is about 3.2 eV. They have also reported that large grain size with strong (112) orientation
and low porosity resulted in reduced recombination rates, higher open circuit voltage and fill factor.

Schock [12] has reported that highest efficiency is obtained for CuInSe$_2$ thin films whose band gap lies in the range 1 to 1.2eV. Schmidt et al [13] have studied Mo/ CuInSe$_2$/CdS/ZnO solar cells and chemical reactions with reference to the interfaces and band alignment.

ZnO/CuInSe$_2$ heterojunction solar cells have been fabricated by several workers[14-16]. Tomar and Garcia[14] have demonstrated the feasibility of preparing thin film ZnO/p-CuInSe$_2$ solar cells using spray pyrolysis technique. Nishitani et al[15] have fabricated CuInSe$_2$ solar cells using CdS as well as ZnO as window layers. It has been reported that CdS window layer films had a higher efficiency (10.5%) compared to ZnO window layer films.

Kazmerski et al[16] have observed that the electron affinities of CuInSe$_2$ and CdS are close enough to minimize any potential barriers to the photo-induced carriers and have obtained the cell efficiency as 5.7%. Gillespie et al[17] at NREL have measured efficiencies of 7% on flexible
non-sodium containing substrate and 10% on soda-lime silica glass substrate. Homojunction solar cells of area (2 x 2 mm²) using p-CuInSe₂ and n-CuInSe₂ have been fabricated by Nishitani et al[18] and the cell efficiency has been reported as 0.35%.

Yousfi et al[19] have employed atomic layer epitaxy to form CuInSe₂ junction using zincoxysulfide, aluminium oxide and indium sulfide as the options for buffer layers. They have obtained promising results with indium sulfide buffers with an efficiency of 13.5%. The effect of interface defect states on the efficiency of CdS/CuInSe₂ cells have been studied by Ram Janam et al[20]. It has been reported that CdS/CuInSe₂ junctions with the ordered phase exhibited higher photovoltaic efficiencies than the disordered ones. Qiu et al[21] have fabricated CuInSe₂ solar cells by electrodeposition and have achieved an efficiency of 8%. It has been suggested that electrodeposited CuInSe₂ films treated in argon yielded the best results. Kazmerski et al[22] have carried out Auger studies on CuInSe₂/CdS thin film cells and studied the diffusion of cadmium into CuInSe₂ film.

Vidyadharan Pillai and Vijayakumar[23] have explained the characteristics of CuInSe₂/CdS solar cells prepared by chemical bath
deposition technique. The increase in current density with film thickness was ascribed to the increase in grain size with film thickness accompanying reduction of grain boundary scattering. The cell exhibited 3.1 % efficiency. The low value of efficiency has been attributed to the high series resistance arising due to high sheet resistance of CdS layer and high carrier concentration in the absorber layer. Close-spaced vapour transport technique (CSVT) has been used to grow low cost thin films having large area and good crystallinity by Masse and Djessas[24,25]. They have fabricated CuInSe$_2$/SnO$_2$ thin film structures by CSVT technique and have reported an open circuit voltage of the order of 350 mV and short circuit current densities of the order of 30 mA/cm$^2$.

Sities[26] has studied the individual loss mechanisms in polycrystalline thin film solar cells based on CdTe, CuInSe$_2$ and related alloys. It has been reported that the CdS/ CuInSe$_2$ solar cell has a low shunt resistance and the forward current is limited due to a contact barrier.

In the present study an attempt has been made to fabricate n-CdS/ p-CuInSe$_2$ solar cells.
8.2 Theory

Photovoltaic effect can be defined as the generation of potential when radiation ionizes the region in or near the built-in potential barrier of a semiconductor. A potential barrier can be formed in a semiconductor by several means. The two techniques of most interest in photovoltaic cells are:

(i) metal-semiconductor barrier and

(ii) p-n junction.

The schematic diagram of a typical solar cell is shown in figure 8.1 and the equivalent circuit of a solar cell is shown in figure 8.2. Light impinging on a semiconductor gets absorbed and creates electron-hole pairs. If these pairs are brought into an electric field region they are separated and a current is set up. Under short circuit condition this photogenerated current is collected at the terminals. Under open circuit conditions the device structure would have to bias itself to a voltage called open circuit voltage. This voltage is needed to develop a backing current just able to counter the photogenerated current. The typical I-V characteristics of a solar cell in shown figure 8.3.
Fig. 8.1 Schematic diagram of a typical solar cell
Fig. 8.2 Equivalent circuit of a solar cell
Fig. 8.3 I-V characteristics of a solar cell

\[ P_{\text{max}} = I_{\text{max}} \times V_{\text{max}} \]
8.2.1 Photovoltaic parameters

a) Short circuit current (Isc):

The short circuit current is the current that flows through the junction under illumination at zero applied bias and in the ideal case (when series and shunt resistance effects are not present) it is equal to the light generated current and proportional to the incident number of photons i.e., the illumination intensity. Short circuit current increases with minority carrier life time and diffusion length.

b) Open circuit voltage (Voc):

Open circuit voltage is the voltage at zero current through the device, i.e., it is the voltage developed in the cell under illumination when no current flows through the cell. The open circuit voltage of a cell increases with

(i) decrease in temperature of the junction
(ii) increase in band gap of the material
(iii) decrease in resistivity and increase in the minority carrier life time and therefore the diffusion lengths.

c) Power maximum (Pmax):

Power maximum is determined by calculating the product of I and V over the entire range of current voltage output curve. A maximum value
is observed at one particular point on the I-V curve which corresponds to maximum power output. At this point, the current and voltage are designated as $I_{\text{max}}$ and $V_{\text{max}}$ and is given by

$$P_{\text{max}} = V_{\text{max}} I_{\text{max}}.$$  \hspace{1cm} (8.1)

d) Fill factor (FF):

The fill factor measures the squareness of the I-V curve. It is the ratio of the maximum power output of the cell to the product of open circuit voltage ($V_{\text{oc}}$) and short circuit current ($I_{\text{sc}}$). Fill factor indicates the extent of deviation from the ideal output and is given by

$$F.F = \frac{(V_{\text{max}} I_{\text{max}})}{(V_{\text{oc}} I_{\text{sc}})}$$ \hspace{1cm} (8.2)

e) Series resistance ($R_s$):

It is composed of electrical resistance due to metal and semiconductor and due to connecting leads. The series resistance should be very low for a good solar cell. Series resistance can be determined from the inverse of the slope of the I-V curve at $I$ equal to zero.

f) Shunt resistance ($R_{\text{sh}}$):

If the semiconductor layer is defective with pin holes, cracks and impurities it will provide a shunting path for the photogenerated current. For a good solar cell the shunt resistance should be high ($>1000 \ \Omega$). Shunt
resistance is determined from the inverse of the slope of the I-V curve at $V$ equal to zero.

g) Efficiency ($\eta$):

Efficiency is given by the ratio of the electrical energy output to the light energy input, i.e.,

$$\text{Efficiency} (\eta) = \frac{(V_m I_m)}{(P_{in} A)} \quad (8.3)$$

where $P_{in}$ denotes the optical power incident and $A$, the illuminated area of the cell.

### 8.2.2 p-n Heterojunction

A generalised photovoltaic device is composed of three functional elements namely an absorber, a junction region or converter and a collector. There are three basic types of junctions: (i) a p/n homojunction, (ii) a p/n heterojunction and (iii) a metal/semiconductor or conductor/insulator/semiconductor junction.

A p-n homojunction is essentially a single semiconductor with two regions of different conductivity type, n and p-type. The junction is formed at the region where the conductivity changes from one type to another. A
junction formed between two semiconductors having different energy band gap values is termed as heterojunction. If the conductivity type is the same in the two semiconductors then the heterojunction is called an isotype. If the conductivity is different in the two semiconductors it is called as an anisotype heterojunction. Some of the requirements to form a good quality heterojunction are:

(i) lattice constant of the two materials should be nearly equal
(ii) electron affinities should be compatible and
(iii) thermal expansion coefficients should be close.

The energy band diagram of a heterojunction is shown in figure 8.4. The various transport mechanisms that are operative at the interface of a heterojunction solar cell are: (i) the ideal diffusion or emission current for electrons, (ii) recombination – generation currents, (iii) recombination through interface states at the junction, (iv) tunnelling from band states to localized defect states in the gap across the interface and (v) band-band tunnelling.

8.3 Preparation and characterization of CdS films

CdS has been selected to be a heterojunction partner to the p-type CuInSe₂ films in the present study as the lattice match between CdS and CuInSe₂ is exceptionally good and the electron affinities of CdS and
Ohmic contact

$E_{g1}$

$E_{g2}$

$V_{bi1}$

$V_{bi2}$

$E_{g1}, E_{g2}$ - Semiconductor bandgap

$V_{bi}$ - Built-in potential

Fig. 8.4 Energy band diagram of a heterojunction
CuInSe$_2$ are close enough to minimize any potential barriers to the
photoinduced carriers.

CdS thin films can be prepared by different methods such as
thermal evaporation[27,28], MOCVD[29], CSVT[30], chemical bath
deposition[31], flowed liquid film method[32] and by hot wall depositions
 technique[33,34]. Haque et al[35] have reported that CdS films deposited
by hot wall deposition technique can be a promising n-type substrate to
grow epitaxial p-CuInSe$_2$.

One of the techniques that have contributed significantly to the
preparation of epitaxial films of congruently evaporating compound
semiconductors with bulk like properties is the hot wall epitaxy
technique[36]. Hot wall epitaxy is one of the three temperature approaches
to grow quality epitaxial films with controlled stoichiometric deviation[37].
Hot wall deposition technique is a low cost, convenient and scalable
technique which permits film deposition very close to thermodynamical
equilibrium with minimum loss of material. Muthukumarasamy et al[38]
have deposited polycrystalline CdS thin films by hot wall deposition
technique and has also fabricated CdS/ CdSe_{x}Te_{1-x} solar cell by hotwall deposition technique and have reported an efficiency of 3%.

The schematic diagram of the hot wall set up is shown in figure 8.5 and the experimental arrangement is shown in figure 8.6. It consists of a quartz tube of length 7.5 cm and diameter 1 cm with one end open and the other end closed. Kanthal wire closely wound along the length of the quartz tube heats the wall of the quartz tube. Two independent heater coils are used to heat the source and the wall of the tube. The quartz tube is charged with CdS (99.999% purity, Sigma Aldrich, USA) material. The main feature of the hot wall system is the heated-linear quartz tube which serves to enclose and direct the vapour from source to substrate. The substrate is held at a distance of less than 1 mm exactly at the open end of the quartz tube acting almost as a lid closing the tube with the help of a substrate holder. The whole arrangement is placed inside the vacuum chamber in which a pressure of about 10^{-5} Torr is maintained. CdS films have been deposited onto well cleaned and polished quartz substrates at wall temperature \( \approx 750 \text{ K} \). Due to radiation from the hot wall of the quartz tube the substrate temperature automatically rises to 350 K under normal coating conditions.
Fig. 8.5 Schematic diagram of hot wall deposition technique
Fig. 8.6 Experimental arrangement of hot wall deposition technique
Fig. 8.8 SEM micrograph of CdS thin film of thickness 240 nm
Fig. 8.9 Transmittance spectra of CdS film of thickness 240 nm
Fig. 8.10 Plot of $(\alpha h v)^2$ versus $h v$ of CdS film of thickness 240 nm
estimated to be 2.38 eV and is in good agreement with the reported values of 2.4 eV[29-31,40]. Hall measurements were made on CdS films to find the nature of conductivity. Hall measurement results indicated that the hot wall deposited CdS films are n-type in nature.

8.3 Fabrication of Quartz/Mo/p-CuInSe2/n-CdS solar cell

Solar cells of Quartz/Mo/CuInSe2/CdS structure have been fabricated. The fabrication involves:

(i) deposition of molybdenum onto well cleaned polished quartz substrates by electron beam evaporation

(ii) p-CuInSe2 layer has been deposited on the molybdenum layer by CSVT technique at source temperature \(T_s=843\ K\) and

(iii) n-CdS has been deposited on the p-CuInSe2 layer by hot-wall deposition technique.

In the present study molybdenum coated quartz substrates have been used for the fabrication of solar cells. Menna et al[41] have reported that molybdenum/glass substrates are suitable for stabilizing CuInSe2 chalcopyrite phase in a wide Cu/In ratio range. It has been reported that CuInSe2 single phase on molybdenum-coated glass substrates can tolerate
Cu/In ratio variations of 0.8 to 1.8 interval which includes the interval suitable for high efficiency devices. Rockett et al[42] have reported that molybdenum is the unique choice for the back contact in CuInSe$_2$ device fabrication as molybdenum forms ohmic rather than rectifying contact to CuInSe$_2$ and offers a high resistance to selenium corrosion. So molybdenum is used as a back contact for solar cells.

Electron beam evaporation technique is one of the important method for the deposition of metals, alloys and even refractory metals. In this technique an electron beam accelerated with a voltage of 2-10 KV is focussed on the surface of a charge that is normally kept inside a graphite crucible placed on a water-cooled copper block. The high energy electron coming from the cathode impinges on the charge and produces intense heat energy that melts the charge. The electrons lose their kinetic energy mostly as heat and the temperature at the focussed spot can become as high as 3000° C. At such a high temperature most of the refractory metals and compounds get evaporated. Since the temperature is high only at the focussed spot the rest of the material remains cool. The result is lesser interaction between the material and the support and thereby reduces contamination. Since the input power can be very high(several KW)
extremely high rates of evaporation can be achieved even for high melting point materials using this technique. In the present investigation molybdenum (powder 99.99%, Sigma Aldrich, USA) has been deposited onto well cleaned and polished quartz substrates by electron beam evaporation (figure 8.11). These molybdenum coated quartz substrates are used for solar cell fabrication.

P-type CuInSe$_2$ thin films have been prepared by CSVT technique at source temperature 843 K. CdS films of n-type nature have been deposited onto the p-CuInSe$_2$ films by hot wall deposition technique at wall temperature 750 K to form a p-n junction. The structure of the fabricated quartz/Mo/p-CuInSe$_2$/n-CdS solar cell is shown in figure 8.12. The necessary electrical contacts to the fabricated p-CuInSe$_2$/n-CdS solar cell have been made using silver.

### 8.4 Solar cell characterization

The performance of the fabricated quartz/Mo/p-CuInSe$_2$/n-CdS solar cells have been studied by illuminating the solar cells using a tungsten lamp [230 V, 150 W, Philips]. Light intensity has been measured using suryamapi (CEL, India). The current and the voltage have been measured
Fig. 8.11 Preparation of molybdenum base layer by electron beam evaporation technique
Fig. 8.12 Schematic diagram of Quartz/Mo/CuInSe₂/CdS thin film solar cell
The energy dispersive x-ray analysis has been carried out to determine the composition of the hot wall deposited CdS films. The figure 8.7 shows the results of this analysis. The results indicate that hot wall deposited CdS film has a near stoichiometric composition of Cd: 52.25 atomic% and S: 47.75 atomic%. The surface morphology of the deposited CdS film has been analysed using a scanning electron microscope and is shown in figure 8.8. The micrograph reveals that the deposited CdS film is polycrystalline in nature with smooth surface morphology.

The transmittance characteristics of the hot wall deposited CdS films have been studied in the wavelength range 190 to 2500 nm. The transmittance spectra of CdS film is shown in figure 8.9. The film shows good transparency exhibiting interference pattern in the wavelength region 600 to 2500 nm. In the region of the spectrum where the thin film is transparent the transmission spectrum exhibits oscillatory behaviour due to interference between the wavefronts reflected from the two surfaces of the thin film[39]. In order to identify the nature of transition in the hot wall deposited CdS films the various powers of $\alpha h\nu$ has been plotted against $h\nu$ and it has been identified that the transition is direct and allowed (figure 8.10) and is in agreement with the earlier reports. The band gap has been
Fig. 8.7 EDAX result of CdS film of thickness 240 nm

Cd = 52.25 atomic %
S = 47.75 atomic %
using optical power meter [Oriel 70310] and Keithley-2001 electrometer respectively.

8.5 Results and discussion

The I-V characteristic curves for some of the fabricated p-CuInSe$_2$/n-CdS solar cells are shown in figure 8.13. The cell parameters have been calculated and are given in Table 8.1. The conversion efficiencies of the fabricated solar cells are found to be in the range 2.8 - 3.5%. The major limiting factor of the device may be the high series resistance obtained (49 - 275 Ω) as suggested by Basol et al.[43]. The low shunt resistance $R_{sh}$ (620 - 1090 Ω) obtained may be due to leakage across the semiconductor surface because of the presence of grain boundaries in polycrystalline films. Ideally the shunt resistance should be infinite so that there is no leakage. That is observed when the photocurrent – photovoltage plot is perfectly rectangular as in the ideal case. The fill factor is weak probably due to low shunt resistance. The low value of short circuit current may be due to lower CdS cut off at 2.38 eV as mentioned by Stolt[44]. The curvature observed near $V_{oc}$ is due to non-ohmic contact[45].
Fig. 8.13 Current–voltage characteristics of CdS/CuInSe$_2$ solar cells
Table 8.1

Solar cell parameters

<table>
<thead>
<tr>
<th>Cell No.</th>
<th>Cell Area (cm²)</th>
<th>V_{oc} (mV)</th>
<th>I_{sc} (mA)</th>
<th>R_{sh} (Ω)</th>
<th>R_{s} (Ω)</th>
<th>Fill Factor</th>
<th>η %</th>
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<td>5.45</td>
<td>965</td>
<td>160</td>
<td>0.381</td>
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<td>2</td>
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<td>275</td>
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<td>0.226</td>
<td>221</td>
<td>5.92</td>
<td>777</td>
<td>104</td>
<td>0.457</td>
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</tr>
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<td>4</td>
<td>0.173</td>
<td>205</td>
<td>5.25</td>
<td>620</td>
<td>49</td>
<td>0.517</td>
<td>2.8</td>
</tr>
</tbody>
</table>
Only Masse and Djessas[25] have fabricated CuInSe$_2$ solar cell using the simple and low cost close-spaced vapour transport technique. They have illuminated the cell through the SnO$_2$ layer and have obtained open circuit voltage of the order of 350 mV and short circuit current density of the order of 30 mA/cm$^2$. They have attributed the low fill factor to the shunt resistance.

The efficiency achieved for the different CuInSe$_2$/CdS solar cells fabricated in the present study using the simple close-spaced vapour transport technique is in the range 2.8 – 3.5%[46] and the cell parameters are given in detail in Table 8.1.
References


