Chapter 4

Modified Technique for Deposition of CuInSe₂ Thin Films Using Sequential Elemental Evaporation and Characterization

4.1 Introduction

In the last chapter, an economical and eco-friendly method was demonstrated for the deposition of CuInSe₂ (CIS) thin films in which chemically deposited Selenium was used. Optimization of these CuInSe₂ films was carried out and with this optimized sample, an attempt to device fabrication was also made. Here CdS was the buffer layer. But photovoltaic effect could not be observed with this CuInSe₂/CdS junction. One of the possible reasons for this could have been the reduced thickness of the absorber layer, which was < 0.5μm. For the fabrication of solar cells, thickness of the absorber layer should be greater than 0.5 μm in order to have efficient absorption of the solar radiation, even though theoretical calculation predicts efficiency above 17% for an optimized cell with a thickness of 0.3μm.¹ The main drawback of the above mentioned deposition technique was that the thickness of the Se layer could not be increased above a certain limit. As the thickness goes beyond this limit, the films started to peel off. Hence the overall thickness of the CuInSe₂ films, prepared using Se layer deposited using CBD technique, was limited to less than 0.5μm.

With the aim of fabricating a solar cell with better efficiency, a modified technique was developed using vacuum evaporation, whereby the film thickness could be increased. In literature, there are many reports on deposition of CuInSe₂ thin films using vacuum evaporation.²⁻⁶ Interestingly, the record-breaking 19.9% efficient cell was also fabricated using co-evaporation technique.⁷ In all the reported techniques, Cu, In and Se were
Modified technique for deposition of CuInSe₂ thin films using...

deposited either in elemental or in compound form, at very high substrate temperatures starting from 350°C. Moreover, these processes are complex and controlling the deposition parameters is also difficult. In the present work, CuInSe₂ thin films were deposited through sequential evaporation of Se, In and Cu, at moderately low substrate temperature. This method of sequential evaporation is simpler than co-evaporation technique and control of stoichiometry could be easily achieved. We could deposit highly stoichiometric samples through this method. Here we made an attempt to deposit sub-micrometre thick absorber layers and fabricate solar cells using these.

The key issues in the field of CuInSe₂ based solar cells are, reducing the thickness of CIS and the replacement of CdS with non-toxic and low absorbing materials. Typical absorber layer thickness of today’s solar cell ranges between 2 to 3μm. Reducing the thickness of the absorber layer is one of the challenges to minimize the processing time and material usage, particularly of Indium. Work is going on to replace Indium partially by Ga, Al etc. The main reasons to find an alternative buffer layer are the following:

(a) The expected environmental risks arising from implementation of a CBD CdS process in a CIGS module production line could be avoided.

(b) The expected technological problems caused by a non-vacuum CBD process in a vacuum line could be separated.

(c) The potential of increasing current generation in the spectral region of 350–550 nm, and thereby increasing the cell efficiency is another possibility.

(d) As the presence of Cadmium in electrical or electronic equipment has already been prohibited through legal regulations in different countries, there is a marketing problem for the Cd-containing CIGS-based thin-film modules today.

In₂S₃, ZnS, ZnO, ZnSe, In₂Se₃, InZnSeₓ, SnS₂, SnO₂ are reported to be the possible alternative buffer layers for CIS solar cells. In the present work, we chose In₂S₃ prepared through chemical spray pyrolysis as the buffer layer. This was a novel approach as CuInSe₂/ In₂S₃ junctions. This is rather rare as most of the reports are on the devices prepared using vacuum evaporation technique for the entire cell.
4.2 Experimental details

Soda lime glass was used as the substrate in this work. Samples were prepared using thermal evaporation of Cu, In and Se at a pressure of $10^{-5}$ mbar. Quantity of Cu, In and Se to be evaporated was selected such that the film stoichiometry was $1:1:2$. Rates of evaporation were 0.5 nm/sec, 0.3 nm/sec and 0.2 nm/sec for Se, In and Cu respectively. After deposition, the samples were annealed at 400°C for one hour at a pressure of $10^{-5}$ mbar resulting in the formation of CuInSe$_2$.

4.3 Optimization of deposition process

Molybdenum (Mo) coated glass (thickness of Mo ~ 80 Å) was used as the substrate in the optimization work. The Mo substrate was highly resistive so that it did not affect the conductivity measurements of the CIS sample. The deposition process was optimized by varying parameters like, substrate temperature, annealing rate and the sequence in which the three layers were deposited. As a primary step, deposition was carried out by sequential evaporation of Se, In and Cu to get the structure of glass/Mo/Se/In/Cu, keeping the substrate at room temperature. This sample was named as CIS1. After deposition, the sample was annealed at 400°C [heating rate -2.5°C/min] for one hour at a pressure of $10^{-5}$ mbar resulting in the formation of CuInSe$_2$.

A point to be noticed in this course is that an intermediate annealing at 150°C (near the melting point of In) was carried out for these samples, before increasing the temperature to 400°C. This process helped to form Cu-In alloy and subsequent selenization of this alloy lead to formation of CuInSe$_2$.

From the X-ray diffractogram of CIS1 (Fig 4.1), single phase CuInSe$_2$ with chalcopyrite structure was identified. Peaks were at angles $2\theta$=17.1°, 26.6°, 35.45°, 44.02°, 52.32°, 64.32° and 70.8° respectively. On comparing the observed d-spacing with powder diffraction standards (JCPDS card 23-209), planes were identified as (103) at $2\theta$=17.1°, (112) at 26.6°, (211) at 35.45°, (220)/(204) at 44.02°, (116)/(312) at 52.3°, (400) at 65.02° and (316) at 71.51°. The sample showed strong preferential orientation along (112) plane. The characteristic chalcopyrite peaks were obtained at (103), (211) and (400) planes.
Grain size was calculated using Debye-Scherrer’s formula, and was found to be of the order of 45 nm. However the samples were found to be highly porous in nature to the naked eye. Five samples of dimension 3.5x1 cm² were prepared at a time. Among these, at least four were showing similar XRD pattern in spite of being porous in appearance. This proved that the structural properties were repeatable in this type of preparation.

In order to reduce the porosity, the deposition process was repeated by reducing the annealing temperature to 300°C (sample CIS2) keeping all the other deposition parameters identical to that used for sample CIS1. XRD pattern of sample annealed at 300°C is given in fig 4.2. It showed that reduction in annealing temperature lead to the formation of InSe phase together with CuInSe₂ phase.

The peak at 23.3° was corresponding to InSe phase (JCPDS card27-0244). Moreover, on reducing the annealing temperature to 300°C, porous nature of the film did not change and resulted in the decrease of crystallinity compared to the samples annealed at 400°C. The temperature of 400°C has been reported to be the optimum temperature for the deposition of CIS by many authors.
In the next trial, Se was deposited at a substrate temperature of 50°C, while In and Cu layers were deposited at room temperature, followed by annealing of the entire structure at 400°C at a pressure of 2x10^{-5} mbar and this set of samples was named as CIS3. Visual examination revealed reduction in the porosity of the film. With the increase in substrate temperature, the surface mobility of the adsorbed species increased because of which they interacted among themselves, resulting in continuous films with well-defined grains of large size.

As the next step, samples were prepared by keeping the deposition parameters identical to that of CIS3, but changing the heating rate while annealing at 400°C. The heating rate was reduced to 1.2°C /minute from 2.5°C /minute. These samples were named as CIS4. Crystallinity of the sample also improved slightly. But these were still showing porous nature. Fig 4.3 reveals the XRD pattern of samples CIS3 and CIS4 which clearly showed that CIS3 was a better polycrystalline sample compared to CIS4.

**Fig.4.2:** X-ray diffraactogram of CIS2
The deposition process was further modified by depositing ‘In’ first at a substrate temperature of 100°C, followed by Se at 50°C and Cu at room temperature. Such samples [named as CIS5] exhibited better crystallinity without the porous nature. This might be due to the enhanced surface mobility of the adsorbed In atoms which filled the voids. Grain size increased to 60 nm even though this value was less compared to that already reported. Only three prominent peaks were observed corresponding to planes (112) at 2θ = 26.6°, (220)/(204) at 44.1° and (116)/(312) at 52.3° respectively (fig 4.4). The characteristic chalcopyrite peaks were absent in these samples.
Following the same deposition process as that of sample CIS5, deposition was repeated without keeping the samples at 150°C for one hour during the annealing process. These were named as CIS6. Fig 4.5 shows the XRD spectra of these. The sample showed the same polycrystalline quality as that of CIS5, with grain size of 57 nm. This is almost equal to that of CIS5. Hence it was concluded that, when 'In' was evaporated at a substrate temperature of 100°C, intermediate annealing at 150°C was not required. This could save time during deposition, making this method easier. Hence this method was followed for further fabrication process. This process was repeated to check consistency in the results and the properties of the repeated sample showed negligible variations.

![X-ray diffractogram of CIS6](image)

**Fig.4.5:** X-ray diffractogram of CIS6

To evaluate the degree of crystallinity of these samples, Preferred Orientation Quality (POQ\( _{hk\ell} \)) in the (h\(k\ell\)) direction was calculated using the formula\(^{11}\):

\[
POQ_{hk\ell} = \frac{I_{hk\ell}}{\sum I_{hk\ell} (FWHM_{hk\ell} Ri_{hk\ell})}
\]

(4.1)

where \(I_{hk\ell}\) is the actual intensity of the diffracting line \(hk\ell\), FWHM\( _{hk\ell}\) is their full width at half maximum and \(Ri_{hk\ell}\) is the relative intensity of that particular line, in a powder sample. POQ was calculated for all samples and the values are given in table 4.1.
From the table, it could be seen that POQ was maximum for CIS3 which showed that it was more crystalline. But the sample was visibly porous. For CIS1 and CIS2, POQ was below 2 and for samples CIS4 and CIS5, the POQ value is more or less the same. Considering the visual appearance, XRD peaks as well as the POQ value, CIS6 could be taken as the best sample in this group. Compositional, optical, electrical and morphological analyses of this sample were carried out.

4.4 Characterization of Optimized sample

4.4.1 EDAX analysis

Atomic concentration of the constituent elements of CIS6 was determined using EDAX by applying an acceleration voltage of 20kV. The EDAX spectrum is shown in fig.4.6. EDAX spot analysis across the entire sample revealed high degree of compositional uniformity with typical values around 29.01 at%, 17.95 at% and 53.54 at% for Cu, In and Se respectively. This very well indicated that sample was homogeneous. Even though the masses evaporated were for stoichiometric with a ratio 1:1:2, the sample was Cu-rich. As the melting point of In is only 150°C, there is a high probability for Indium getting lost
during the annealing process at 400°C. This could be the reason as to why the films were Cu-rich.

![Graph with peaks labeled Cu, In, and Se]

**Fig. 4.6:** A typical EDAX spectrum of CuInSe$_2$

### 4.4.2 XPS analysis

Fig. 4.7 shows the result of the ‘XPS depth profile’ analysis of CIS6. The results reveal that Cu and Se diffused into the ‘In’ layer due to annealing and this resulted in the formation of CuInSe$_2$.

![Graph with multiple peaks labeled Cu, In, and Se over cycles and binding energy]

**Fig. 4.7:** XPS depth profile of CuInSe$_2$
The binding energy values of Cu, In and Se were in agreement with the standard values reported earlier\(^1\) and these are given in the table 4.2. A slight shift in BE of Cu, In and Se near the interface of film and the substrate was observed which could be due to the presence of oxygen in the substrate.

**Table 4.2: Binding energies for the different elements in CIS**

<table>
<thead>
<tr>
<th>Element</th>
<th>Binding Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu2p(_{3/2})</td>
<td>952.4</td>
</tr>
<tr>
<td>Cu2p(_{1/2})</td>
<td>932.8</td>
</tr>
<tr>
<td>In3d(_{5/2})</td>
<td>452.8</td>
</tr>
<tr>
<td>In3d(_{3/2})</td>
<td>445.2</td>
</tr>
<tr>
<td>Se3d</td>
<td>54.8</td>
</tr>
<tr>
<td>Mo</td>
<td>231.3</td>
</tr>
<tr>
<td>Mo</td>
<td>229</td>
</tr>
<tr>
<td>O</td>
<td>531.1</td>
</tr>
<tr>
<td>O</td>
<td>530.4</td>
</tr>
</tbody>
</table>

From XPS analysis, we could conclude that, even with the Cu-rich composition, film existed in single phase, which is an indication of its large structural tolerance to off-stoichiometry. However, Mo diffused from the substrate up to the surface of the film. Two different binding energies were obtained for Mo, [231.3 and 229 meV]. These values were corresponding to two different phases of Molybdenum oxide namely, MoO\(_2\) and MoO\(_3\). Binding energies of oxygen also supported this assignment. Binding energy of Oxygen was 531.1 eV in MoO\(_2\) and 530.4 eV in MoO\(_3\).
4.4.3 Thickness measurement

Film thickness and sample surface roughness were determined from the one dimensional scan carried out by means of Dektak32 stylus profilometer. Thickness of the sample was found to be 0.79 μm while the average roughness was 93.6 nm. Thickness can be increased by multilayer deposition, if required.

4.4.4 Optical absorption

Absorption spectrum was recorded in the wavelength range 500 nm to 1500 nm for all the samples. Fig 4.8 shows the plot of $(\alpha \nu)^2$ versus $\nu$ for sample CIS6.

![Absorption spectra of CuInSe$_2$](image)

**Fig.4.8: Absorption spectra of CuInSe$_2$**

Band gap obtained, by extrapolating the linear portion of the $(\alpha \nu)^2$ versus $\nu$ graph to $\nu$ axis [0.97 eV], was close to the reported value for Cu-rich films. In all the films, there existed a second absorption edge at energy ~1.1eV. This absorption is attributed to the ‘valence band splitting’, a phenomenon commonly occurring in I-III-VI$_2$ semiconductors.

The valence band of CIS consists of three sub-bands. At the top, there is a broad band built up from Se-4p and Cu-3d states. Next is a narrower band formed from In-5s and Se-
4p bonding states. Finally, well-separated from the first two bands, there exists the Se-4s band. The uppermost valance band is lifted due to simultaneous influence of spin-orbit and crystal field interactions (tetragonal distortion). This splitting is owing to the following reasons.

(1) Ordering of the metal cations relative to one another such that the unit cell is doubled along the optic axis

(2) In the chalcopyrite structure, each cation (Cu and In) has four anions (Se) as nearest neighbours. The anion usually adopts an equilibrium position closer to one pair of cations than to the other. That means, the anions are not located at positions like (½, ½, ½); instead these are placed at (1/4, 1/4, 1/8) which make the In-Se and Cu-Se bond lengths unequal and

(3) The chalcopyrite lattice is slightly compressed along the z-axis.¹⁴⁻¹⁷

Fig 4.9: Splitting of the uppermost valance band in CuInSe₂

Fig 4.9 shows the valence-band splitting due to crystal field and spin-orbit interactions. The 3d or 4d electrons of the noble metal (Cu) hybridize with the p-like valence band due to proximity of their levels. This hybridization p-d resonance cause anion p-state and Cu-d band splitting. Transition can take place between conduction band and split valance bands which create additional absorption edge, as observed in the present case.
4.4.5 Electrical characterization

Hot probe measurement confirmed the samples to be p-type. Generally p-type samples are Cu-rich\textsuperscript{18} and this was consistent with EDAX measurement. Resistivity of the sample was found to be 3 \( \Omega \text{cm} \), from the dark I-V characteristics. For fabrication of solar cells, resistivity of the order of 10 \( \Omega \text{cm} \) is usually preferred. The resistivity could be varied by varying the composition in the film.

4.4.6 Temperature dependant conductivity measurements

Defect levels were identified using temperature dependant conductivity measurements. Measurement was performed in the temperature range 100\textdegree K- 400\textdegree K under ‘dark condition’. The Arrhenius plot of conductivity (fig.4.10) indicated two distinct slopes of activation energies 30 meV and 130 meV. These values agreed with the activation energies of Cu\textsubscript{n}\textsuperscript{-} and V\textsubscript{ln}\textsuperscript{-} respectively.\textsuperscript{20,21} Since the film was Cu-rich, the probability of formation of these defects was high. These are the acceptor levels contributing to p-type conductivity.

![Temperature dependant conductivity of CuInSe\textsubscript{2}](image)

Fig 4.10: Temperature dependant conductivity of CuInSe\textsubscript{2}
4.4.7 Morphological analysis

Morphological analysis of CIS6 was carried out using Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). The image of the sample obtained from SEM analysis is given in fig.4.11 which shows that the film surface was smooth and uniform. It could also be seen that the sample was free of pinholes and micro-cracks.

![Image of CuInSe₂](image)

Fig 4.11: Scanning electron microscopic image of CuInSe₂

Fig 4.12 shows three dimensional AFM image of CIS6. From AFM, pyramidal structure of the grains could be seen, which is a characteristic of Cu-rich CuInSe₂ thin films. This kind of surface structure can be used to increase light trapping. Sample roughness was calculated from an area of 1μm x 1μm. The RMS roughness was found to be 26 nm which was comparable to that obtained from the stylus profilometer (93.6 nm).

The two dimensional AFM image (fig.4.13) showed that the grain size varied in a wide range, from 75 nm to 200 nm and was different from the grain size obtained using Debye-Scherrer formula. From XRD analysis, the average grain size was calculated as 57 nm. Müller et al assigned the value calculated from this formula as “domain size” and one grain contains several domains. From AFM study, we could get grain size of the order of 200 nm and also sub-particles of size ~ 75 nm which can be called as domain.
Fig. 4.12: 3D AFM image in 1 x 1 μm area

Fig. 4.13: 2D AFM image in 0.5 x 0.5 μm area

4.4.8 Inference

Stacked elemental layers of Cu, In and Se were deposited at moderately low substrate temperature. The deposition process was optimized as follows:

(1) Structure of the film: Glass/In/Se/Cu
(2) Indium evaporation at 100°C
(3) Selenium evaporation at 50°C
(4) Copper evaporation at room temperature
(5) Annealing this layer at 400°C
All these processes were carried out at a pressure of $2 \times 10^{-5}$ mbar. On analyzing the characteristics of the sample, we could infer that this procedure can be followed for further deposition. The samples were again deposited at the same condition to ensure repeatability and the film characteristics showed nearly the same values.
Films were characterized by varying the concentration of Cu, In and Se, one at a time.

4.5 Effect of variation of Cu

CuInSe$_2$ thin films were prepared by varying the concentration of Cu keeping In and Se concentrations constant at 110 and 170mg respectively. Concentration of Cu was varied from 40mg to 80mg. These samples were named as CIS7, CIS8, CIS9 and CIS10 depending up on concentration of Cu.

4.5.1 Structural characterization

![X-ray diffractograms of samples CIS7 to CIS10](image)

**Fig.4.14:** X-ray diffractograms of samples CIS7 to CIS10
Fig. 4.14 shows the X-ray diffraction pattern of the samples CIS7, CIS8, CIS9 and CIS10. All the films were preferentially oriented along the (112) plane. Peaks were corresponding to planes (220)/(204) and (312)/(116). In addition, CIS4 showed a peak at 13.14°. The calculated d value of this peak was 6.73 Å, corresponding to (030) plane of Cu₂Se. Formation of this binary phase could be due to the higher Cu concentration.

The POQ<sub>hkl</sub> factor and the grain size were calculated for all samples and the values are given in Table 4.3.

**Table 4.3: Grain size and POQ values of Cu varied samples**

<table>
<thead>
<tr>
<th>Sample name</th>
<th>POQ</th>
<th>Grain size nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIS7</td>
<td>2.2</td>
<td>58</td>
</tr>
<tr>
<td>CIS8</td>
<td>2.6</td>
<td>58</td>
</tr>
<tr>
<td>CIS9</td>
<td>2.4</td>
<td>33</td>
</tr>
<tr>
<td>CIS10</td>
<td>2.3</td>
<td>57</td>
</tr>
</tbody>
</table>

From the table 4.3, it could be seen that, POQ increased to 2.6 for CIS8 and then decreased with further increase in Cu. Grain sizes of the samples were comparable except CIS9 for which it decreased drastically to 33nm. But on considering POQ values, this sample can be considered to be more crystalline than CIS7 and CIS10. However, the grain size obtained through this deposition technique was smaller compared to other reported results obtained using evaporation techniques. Smaller grain size lead to an increase in grain boundaries which cause grain boundary scattering. This degrades conductivity of the samples. Also grain boundaries create potentials which are known to hamper the device performance. Controversial arguments exist about the role of the 'grain boundary potential'. According to some reports, grain boundary potential has beneficial effects in CuInSe₂ solar cell. Even though conclusive evidence in this direction is still missing. 23-25
The calculated values of lattice constants a, b and c are given in the table 4.4 and these values were comparable with the reported ones. Among these, 'a' was high for CIS9, which had the lowest grain size. In the CIS lattice, tetragonal distortion occurs due to the excess and deficiency of bond charge in the In-Se and Cu-Se bonds respectively. This results in shortening of the In-Se bond, compared to the Cu-Se bond with a corresponding shift in the anion (sub-lattice displacement). The In-Se tetrahedron is consequently more rigid and shows little distortion, while Cu-Se tetrahedron is considerably distorted. The bond charge distribution also results in the tetragonal compression because the Cu-Se-In bond-bending force constant is not equal to the average of the corresponding Cu-Se-Cu and In-Se-In force constants and bond-bending energy is lowered by compression. The values of tetragonal distortion, \( \frac{2a}{c} - 1 \) is also shown in table 4.4. With decrease in ‘a’, tetragonal distortion becomes negative.

**Table 4.4: Lattice constants and tetragonal distortion of the CuInSe\(_2\) lattice**

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Lattice parameters in Å</th>
<th>Tetragonal distortion: ( \frac{2a}{c} - 1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIS7</td>
<td>5.84 11.52</td>
<td>0.014</td>
</tr>
<tr>
<td>CIS8</td>
<td>5.76 11.61</td>
<td>-0.007</td>
</tr>
<tr>
<td>CIS9</td>
<td>5.94 11.48</td>
<td>0.035</td>
</tr>
<tr>
<td>CIS10</td>
<td>5.74 11.63</td>
<td>-0.012</td>
</tr>
</tbody>
</table>

**4.5.2 Thickness measurements**

Thickness measurement using stylus profilometer revealed that single layer CuInSe\(_2\) was \( \sim 0.55 \) μm thick. Fig. 4.15 shows the stylus graph depicting a thickness of 0.55 μm for the single layer CIS. There was no variation in thickness with composition in the present samples and all the samples were nearly 0.55μm thick.
Fig. 4.15: Stylus graph showing single layer thickness of 0.55μm

Thickness could be increased to 0.85 μm by depositing a second layer of CuInSe₂, following same steps as for the first layer; this can be further increased by giving a third layer, if necessary. Since CIS possesses a very strong absorption coefficient (~10⁵ cm⁻¹), thickness of about 1μm is sufficient for absorption of the full intensity of sunlight falling on the specimen as these direct band gap semiconductors operate through field assisted carrier collection (carrier ‘drift’) rather depending on diffusion, as in high purity single-crystal region. It is better to have bi-layer structure for the absorber in photovoltaic devices, as back contact recombination can be reduced by making the bottom layer highly conductive. In the present study, this requirement can be achieved by making the back layer slightly Cu-rich. Increase in Cu concentration enhances the conductivity by forming a p' layer. This p' bottom layer can create “Back Surface Field (BSF)” which assists in hole collection and serves as an electron reflector thus reducing the recombination.

4.5.3 EDAX measurements

Deviation in the actual composition from the ideal formula can be described by two parameters, viz., deviation from molecularity (Δm) and the deviation from stoichiometry (Δs). These parameters are defined as.¹⁵⁻¹⁶
\[ \Delta m = \frac{Cu}{In} - 1 \]

and

\[ \Delta s = \frac{2[Se]}{[Cu]+3[In]} - 1 \]

If \( \Delta m > 0 \) and \( \Delta s > 0 \) the sample will be p-type and if \( \Delta m < 0 \) and \( \Delta s < 0 \), the sample will be n-type.

Atomic concentration of the constituent elements was determined using EDAX, at different points along the entire length of the sample. Samples CIS10 was spatially non-uniform in composition. In CIS10, Cu was found to be agglomerated and hence the composition was different at different points. Average composition is given in table 4.5. Also formation of \( Cu_2Se \) phase was identified from the XRD studies, probably due to the increased concentration of Cu. Mass of Cu evaporated was greater for CIS10 than CIS9. But due to the spatial non-uniformity in CIS10, EDAX analysis showed nearly the same composition for both the samples. Typical values are given in table 4.5. With increase in Cu concentration in the solution, the atomic concentration of Cu in the sample (as per the EDAX results) was also increasing.

Cu-rich films should be dominated by antisite \( (Cu_{In}) \) acceptor defects, yielding strongly p-type layers. However, in all cases, auto-compensation may be expected at high intrinsic defect levels in order to maintain overall valence neutrality. \( Cu_{In} \) antisite defects move a \( Cu^{+1} \) atom onto a nominally \( In^{+3} \) site, resulting in a net charge of -2. This can be compensated for by the creation of a Se vacancy (net change in charge of +2) with a resulting decrease in Se concentration as the Cu concentration increases as observed.
Table 4.5: Atomic percentage and deviation from stoichiometry and molecularity of the samples with different Cu concentrations.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Atomic concentration in percentage</th>
<th>( \Delta m )</th>
<th>( \Delta s )</th>
<th>Cu/In ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>In</td>
<td>Se</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CIS7</td>
<td>20.67</td>
<td>23.38</td>
<td>56.05</td>
<td>-0.12</td>
</tr>
<tr>
<td>CIS8</td>
<td>23.89</td>
<td>21.44</td>
<td>54.67</td>
<td>0.11</td>
</tr>
<tr>
<td>CIS9</td>
<td>27.25</td>
<td>19.28</td>
<td>53.47</td>
<td>0.41</td>
</tr>
<tr>
<td>CIS10</td>
<td>27.15</td>
<td>21.71</td>
<td>51.14</td>
<td>0.25</td>
</tr>
</tbody>
</table>

4.5.4 Optical absorption

Fig 4.16 shows absorption spectra of samples CIS7 to CIS10, recorded in the wavelength range 500 nm to 1500 nm at room temperature. The band gap increased from 0.95 eV to 0.99 eV with increase in Cu concentration even though the variation was not regular. CIS8 had lowest \( E_g \) of 0.95 eV and CIS10 had the highest band gap of 0.99 eV in this set of samples. The crystallinity and grain size were high for CIS8, which caused the band gap to decrease. This increase in band gap for CIS10 can be attributed to the presence of \( \text{Cu}_2\text{Se} \) phase in CIS10. The absorbance was found to be larger for CIS8. Table 4.6 gives the band gap variation in the samples.

Table 4.6: Band gap variation

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Band gap eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIS7</td>
<td>0.97</td>
</tr>
<tr>
<td>CIS8</td>
<td>0.95</td>
</tr>
<tr>
<td>CIS9</td>
<td>0.97</td>
</tr>
<tr>
<td>CIS10</td>
<td>0.99</td>
</tr>
</tbody>
</table>

Fig.4.16 Absorption spectra of samples
In all the films, there existed a second absorption edge at energies near 1.1 eV as obtained in the earlier case which could be attributed to the valence band splitting.

4.5.5 Electrical characterization

Table 4.7 gives the type of conductivity, photosensitivity and resistivity of the samples. Type of conductivity was determined to be p-type using hot probe method for all the samples, except CIS7. Interestingly, CIS7 was the only In-rich sample in this series. Excess ‘In’ might have created donor levels like In$_{In}$, In$_{Cu}$, In$_{Se}$ etc in CuInSe$_2$ which converted the conductivity type to n. For CIS7, the deviation from molecularity was <1 and hence the stoichiometry supported the n-type behaviour. For all other samples, deviation from molecularity and stoichiometry was >1, and hence were showing p-type conductivity.

Table 4.7: Type of conductivity and resistivity for the Cu varied samples

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Type of carrier</th>
<th>Photosensitivity</th>
<th>Resistivity Ωcm</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIS7</td>
<td>n</td>
<td>-0.78</td>
<td>10.37</td>
</tr>
<tr>
<td>CIS8</td>
<td>p</td>
<td>0.17</td>
<td>76</td>
</tr>
<tr>
<td>CIS9</td>
<td>p</td>
<td>0.1</td>
<td>3</td>
</tr>
<tr>
<td>CIS10</td>
<td>p</td>
<td>-0.045</td>
<td>1.8×10^{-3}</td>
</tr>
</tbody>
</table>

For the n-type sample, the resistivity was 10.37 Ωcm while resistivity of p-type samples decreased with increase in Cu. Thus highly conductive (ρ~10^{-3} Ωcm) as well as resistive samples (ρ~76 Ωcm) could be prepared using this method.

For device fabrication, usually slightly resistive samples (resistivity of the order of 10^1 Ωcm) are preferred, whereas the highly conductive films are used as the bottom layer of the absorber near the electrode. This low resistivity CIS layer incorporated on the contact-side lowers the series resistance $R_s$ of the device. Photosensitivity of the n-type sample was negative and for the remaining samples its value was fractional. For the
highly conductive sample, CIS10, the photosensitivity again showed negative value. The negative photosensitivity may be due to recombination of light generated minority carriers with holes (electrons) at the top of the valence band (bottom of the conduction band).

4.5.6 Morphological analysis

Morphological analysis carried out using AFM is shown in (Fig.4.17 (a)-(d)). The 3 dimensional AFM image showed that in CIS7 (i.e. the n-type sample), the grains were agglomerated. These agglomerations might be due to the unreacted binary phases which were not revealed in XRD analysis. These grains were separated indicating the reason for low conductivity of this sample. There was a distribution of grain size in the films. Grain size varied over a wide range, (from 61 nm to 202 nm).

Fig. 4.17 Three dimensional AFM images of samples
(a) CIS7 (b) CIS8 (c) CIS9 (d) CIS10
With the increase in Cu concentration, the geometry of the grain changed from spherical to pyramidal. Pyramidal shape could be clearly seen in the case of CIS10. Here the grains were densely packed and hence this could lead to increase in conductivity as observed in the films. The rms value of surface roughness also increased with increase in Cu concentration and this was calculated from AFM for a sample area of 250nm x 250nm. The roughness values are given in Table 4.8.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Roughness in nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIS7</td>
<td>7.64</td>
</tr>
<tr>
<td>CIS8</td>
<td>11.75</td>
</tr>
<tr>
<td>CIS9</td>
<td>16.87</td>
</tr>
<tr>
<td>CIS10</td>
<td>14.32</td>
</tr>
</tbody>
</table>

Roughness increased as we go from In-rich to Cu-rich samples even though variation was negligible. Generally it was observed that Cu-rich films have roughness greater than In-rich films.

4.5.7 PL measurement

PL measurements were taken for the n-type sample CIS7 and the p-type sample CIS10. Fig 4.18 shows the temperature dependence of PL in CIS7. The signal was very noisy as seen in the figure. The highest PL emission in CIS7 was centered at 0.991 eV at 12 K. This emission shifted to lower energy side, as temperature was raised, and this emission was not detected above 50K. This shift indicated that this transition was a ‘donor – acceptor pair’ (DAP) recombination. The activation energy of the shallow center among the DAP was calculated by fitting the plot of log (PL intensity) vs 1000/T as shown in Fig. 4.19 using the equation (3.6).
The activation energy was obtained to be 13 meV which agreed with the activation energy of the $In^{+}_{Cu}$ donor level. Neglecting the Coulomb term and using $E_D = 13$ meV and $E_g = 1.042$ eV in equation (3.5) $E_A$ was obtained as 38 meV which agreed with the activation energy of the $V_{Cu}$ acceptor level. Hence this emission could be assigned to the $In^{+}_{Cu} - V_{Cu}$ DAP recombination.

**Fig. 4.18:** Temperature dependence of PL spectra of sample CIS7 ($Cu/In=0.88$)

**Fig. 4.19:** Plot of $1000/T$ vs log (integrated PL intensity) of CIS7 fitted using equation (4.2)
Fig. 4.18 shows a shoulder on the lower energy side centered at 0.983 eV whose position did not change with increase in temperature. But this was quenched, at a much faster rate, compared to the peak due to the DAP transition. Hence this emission could be assigned to the $(D^0,h)$ transition. From our previous work, it was well established that the 0.983 eV line is representing $Cu_i$-VB transition. For verification, we used equation

$$E_{PL} = E_g - E_D$$

(4.2)

(where $E_{PL}$ is the emission energy, $E_g$ the band gap and $E_D$ the donor activation energy) and obtained $E_D = 59$ meV, which is comparable to the activation energy of ionized $Cu_i$ donor level $^{30,31}$ Figure 4.20(a) reveals the PL spectra of sample CIS10 ($Cu/In=1.25$), which was Cu-excess in composition. The film stoichiometry indicated that this film was highly Cu-rich. In CIS10, the highest PL peak position was at 1.032 eV and was very weak compared to the other emissions in the sample. Also it was not observed above 12 K. Thus this emission could be assigned to the free exciton (FE) line in this sample.

![Fig. 4.20](image)

**Fig. 4.20:** (a) PL emission from sample CIS10($Cu/In=1.25$) at 12 K and (b) Temperature dependence of PL emission in the sample.
Figure 4.21: Multiple curve fitting of the PL spectra obtained from sample CIS10 at (a) 20 K and (b) 80 K.

Figure 4.21(a) and (b) depict the temperature dependent PL of this sample. As the temperature increased, the PL spectra broadened, with the peak position shifting to 0.979 eV. Multiple fitting of the spectra at higher temperatures showed that the broad spectra contained emissions at 0.983 eV and 0.972 eV (Fig. 4.21 a & b). Thus it could be concluded that the two emissions merged, resulting in spectral broadening and shift in peak position. In the de-convoluted spectrum, since there was no change in peak position of the emission at 0.983 eV, it was assumed that this was the Cu$_i$ - VB free-to-bound ($D^0,h$) transition was observed in Cu-rich samples.

Figure 4.22 represents the plot of ratio of the intensities (Cu$_i$ - VB ($D^0,h$) to 0.972 eV transitions) versus 1000/T fitted using the equation

\[
\frac{I_{Dh}}{I} = \exp \left( \frac{-\Delta E}{kT} \right)
\]

where $I_{Dh}$ is the intensity of the ($D^0,h$) emission while $I$ is the intensity of the 0.972 eV emission. It could be realized that the intensity of the emission at 0.983 eV increased
relative to the emission at 0.972 eV. The activation energy, $\Delta E$, was obtained to be $\sim 5$ meV, which agreed with the exciton binding energy in CuInSe$_2$.\textsuperscript{32-34} Hence it was concluded that the emission at 0.972 eV was the 'bound exciton emission' in this sample. Rincon et al had observed emission at 0.973 eV and had assigned it to the transition of exciton bound to the acceptor $Cu_{in}$ (BX2: $Cu_{in}$).\textsuperscript{35} Presently it can only be speculated that this may be the same BX2 transition as the film stoichiometry supported the assignment. The absence of this emission line in In-rich samples once again, supports the assignment.

Fig. 4.22: Ratio of the intensities of the emission ($I_{Dh}(0.983 \text{ eV}) : I(0.972 \text{ eV})$) as a function of temperature fitted using equation (4.3)

4.6 Effect of variation of In-concentration

From the above series of samples, CIS7 to CIS10, we could not obtain a sample having reasonable photosensitivity. CIS8 (Cu-50, In-110 and Se-175mg) and CIS9 (Cu-60, In-110 and Se-175mg) were of comparable photosensitivity [0.17 and 0.1 respectively]. CIS9 had low resistivity and hence the Cu concentration was fixed at 60-mg and Se at 170mg; In concentration was varied from 110mg to 130 and 150mg and the samples are named as CIS11, CIS12 and CIS13 respectively.
4.6.1 Structural Characterization

Fig 4.23 shows the X-ray diffraction pattern of the samples in which concentration of In was varied from 110 to 150mg.

Samples CIS11 and CIS12 showed single phase CuInSe₂, while CIS13 showed In₂Se₃ phase in addition to the CIS phase. All the samples were preferentially oriented along (112) plane. The peak intensity increased drastically for CIS12 in which case, all the three peaks were clearly visible. With further increase in 'In' concentration, secondary phases like In₂Se₃ appeared and the CIS peak intensity decreased with the onset of In₂Se₃ phase. The grain size of these samples, calculated using Debye-Scherrer formula, and the POQ values are given in table 4.9. Even though the sample CIS13 possessed secondary phases, grain size and POQ value were very high for this sample. The peak intensity was greater for CIS12. But the full width at half maximum (FWHM) was lowest for CIS13 and hence the highest grain size.
**Table 4.9** Variation in grain size and POQ values

<table>
<thead>
<tr>
<th>Sample name</th>
<th>POQ</th>
<th>Grain Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIS11</td>
<td>3</td>
<td>35</td>
</tr>
<tr>
<td>CIS12</td>
<td>4</td>
<td>42</td>
</tr>
<tr>
<td>CIS13</td>
<td>5</td>
<td>65</td>
</tr>
</tbody>
</table>

4.6.2 **EDAX measurements**

**Table 4.10**: Atomic concentration and deviation in molecularity and stoichiometry

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Atomic concentration in percentage</th>
<th>Δm</th>
<th>Δs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu</td>
<td>In</td>
<td>Se</td>
</tr>
<tr>
<td>CIS 11</td>
<td>27.25</td>
<td>19.28</td>
<td>53.47</td>
</tr>
<tr>
<td>CIS 12</td>
<td>17.12</td>
<td>31.48</td>
<td>51.39</td>
</tr>
</tbody>
</table>

Table 4.10 clearly indicates that, CIS11 was Cu-rich and CIS12 was highly In-rich. The table also gives the deviation from molecularity and stoichiometry. For the Cu-rich sample, both these values are positive and for the In-rich sample the values are negative.

4.6.3 **Optical Absorption**

Absorption spectra were recorded in the range 1500 to 500nm. Fig 4.24 shows the absorption spectrum of the In-varied samples. From the table 4.11, it was found that band gap varied slightly.
4.6.4 Electrical Characterization

Hot probe analysis proved p-type nature of sample CIS11. This sample was found to be Cu-rich from the EDAX analysis; more over, deviation from molecularity and stoichiometry was >0 in this case. But samples CIS12 and CIS13 were n-type, since In-concentration was high in these samples. CIS12 showed negative values for $\Delta m$ and $\Delta s$. Table 4.12 shows the electrical parameters of samples CIS11-CIS13.

**Table 4.12: Type of conductivity and variation in resistivity and photosensitivity of samples**

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Type of conductivity</th>
<th>Resistivity, $\rho$ ((\Omega)cm)</th>
<th>Photosensitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIS11</td>
<td>p</td>
<td>3</td>
<td>0.09</td>
</tr>
<tr>
<td>CIS12</td>
<td>n</td>
<td>0.005</td>
<td>-0.60</td>
</tr>
<tr>
<td>CIS13</td>
<td>n</td>
<td>1.03K</td>
<td>-0.01</td>
</tr>
</tbody>
</table>

Resistivity was 3\(\Omega\)cm for CIS11 and photosensitivity was 0.09. In the case of CIS12, the resistivity decreased and the photosensitivity became negative. In the normal case, there should be an increase in resistivity with increase in ‘In’ concentration. But in the present case, there occurred a type conversion and the increased ‘In’ concentration in this sample...
gave way to decreased resistivity. With further increase in ‘In’ concentration, [i.e. for CIS13], the resistivity again increased. This increase can be attributed to the presence of binary phase in this sample.

4.6.5 Discussion

‘In’ concentration was varied in the samples. The samples CIS12 and CIS13 were n-type while CIS11 was p-type. Also, on increasing mass of ‘In’ evaporated to 150 mg, there occurred In$_2$Se$_3$ phase in addition to the CIS phase. Hence it was concluded that ‘In’ concentration of 110 or below should be used in the present work. However, this n-type layer can be made use of for the fabrication of homojunction solar cells.

4.7 Minute variations of Cu and In concentrations

From the characterizations carried out above, only CIS8 (Se-170, In-110 and Cu-50) exhibited reasonable photosensitivity. Minute variations in Cu and In concentrations were made to achieve better photosensitivity in the samples. However concentration of Se was fixed in all the cases. Samples were prepared with masses In-112mg and Cu-51mg(CIS14), In-110mg and Cu-46mg(CIS15), In-112 and Cu-50(CIS16), In-114 and Cu50mg(CIS17), In-118 and Cu-50mg(CIS18). Table 4.13 shows the photosensitivity and resistivity of these samples.

**Table 4.13 Electrical parameters of the samples CIS14 to CIS18**

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Resistivity $\Omega$cm</th>
<th>Photosensitivity</th>
<th>Type of Conductivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIS14</td>
<td>0.019</td>
<td>0.02</td>
<td>p</td>
</tr>
<tr>
<td>CIS15</td>
<td>0.114</td>
<td>0.02</td>
<td>p</td>
</tr>
<tr>
<td>CIS16</td>
<td>0.011</td>
<td>-0.02</td>
<td>p</td>
</tr>
<tr>
<td>CIS17</td>
<td>2.6</td>
<td>-0.07</td>
<td>p</td>
</tr>
<tr>
<td>CIS18</td>
<td>9.3</td>
<td>0.1</td>
<td>n</td>
</tr>
</tbody>
</table>
From the table, it is clear that the photosensitivity of the p-type samples was very low and conductivity changed to n type, when In-concentration was increased to 118mg.

4.8 Optimization for solar cell fabrication

In order to get ideal samples for device fabrication, further variation in stoichiometry was carried out. Concentration of Se was fixed at 175 mg and that of Indium at 100 mg and mass of Cu was varied from 20 to 50 mg in steps of 10 mg so that Cu/In ratio was 2.37, 1.48, 1.13, and 0.98 respectively, as obtained from EDAX. The samples were named as CIS0.2, CIS0.3, CIS0.4 and CIS0.5. These samples were fully characterized to find the suitability for device fabrication.

4.8.1 Structural Characterization

Structural characterization was performed using X-ray diffraction and Raman analysis.

(i) XRD: Fig 4.25 shows the XRD pattern of the samples. Peaks were observed in the (112), (220)/(204) and (116)/(312) planes with preferential orientation along (112) direction as observed earlier. As Cu concentration increased, the crystallinity also increased. Cu-rich films are generally more crystalline than In-rich films. In the case of Cu rich films, there occurs a liquid phase of Cu₄Se which enhances the grain growth. Crystallinity was better for CIS0.4 and decreased with further increase in Cu-concentration. In the case of CIS0.5, for which Cu concentration was the maximum, secondary phase of Cu₃Se₂ was observed. However grain size and POQ value were high for CIS0.4 and the values are listed in the table 4.14

The XRD profile contained only the common peaks corresponding to sphalerite and chalcopyrite structures as obtained earlier. To confirm the structure of the CuInSe₂ films, Raman analysis was carried out on these samples.
Table 4.14: Grain size and POQ values

<table>
<thead>
<tr>
<th>Sample name</th>
<th>POQ</th>
<th>Grain size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIS 0.5</td>
<td>3</td>
<td>51</td>
</tr>
<tr>
<td>CIS 0.4</td>
<td>4</td>
<td>63</td>
</tr>
<tr>
<td>CIS 0.3</td>
<td>4</td>
<td>60</td>
</tr>
<tr>
<td>CIS 0.2</td>
<td>3</td>
<td>49</td>
</tr>
</tbody>
</table>

Fig. 4.25: X-ray diffractogram of the samples

(ii) Raman analysis: Raman analysis was performed in the 'back scattering mode' at room temperature using micro Raman system [Jobin Yvon Horibra LABRAM-HR] in visible region (400 -1100 nm) with a spectral resolution of 1cm\(^{-1}\). Argon ion laser of wavelength 488nm was used as excitation source. The chalcopyrite structure is a tetragonal body centered lattice and belongs to the space group \(\text{I}4\overline{2}d\), i.e. to the point group \(D_{2d}\). On the basis of the character table of the group \(D_{2d}\), the general vibrations for the primitive cell, involving optic and acoustic modes are distributed as,

\[
\Gamma = A_1 + 2A_2 + 3B_1 + 4B_2 + 7E
\]

If we take into account that the symmetry of the acoustic modes is \(B_2 + E\), then for the optic modes in the crystal,

\[
\Gamma_{\text{vib}} = A_1 + 2A_2 + 3B_1 + 3B_2 + 6E
\]

Therefore there are 19 Raman active vibrations (\(A_1 + 3B_1 + 3B_2 + 6E\)), nine infra red active (3B_2 + 6E), and two silent modes (2A_2). The observed modes in CuInSe_2 are listed below in Table 4.15.
Table 4.15: The different vibrational modes observed in CuInSe$_2$

<table>
<thead>
<tr>
<th>Frequency(cm$^{-1}$)</th>
<th>Approximate relative strength (%)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>259</td>
<td>15</td>
<td>E</td>
</tr>
<tr>
<td>231</td>
<td>8</td>
<td>B$_2$,E</td>
</tr>
<tr>
<td>215</td>
<td>22</td>
<td>B$_2$,E</td>
</tr>
<tr>
<td>206</td>
<td>10</td>
<td>E</td>
</tr>
<tr>
<td>174</td>
<td>100</td>
<td>A$_1$</td>
</tr>
<tr>
<td>124</td>
<td>20</td>
<td>B$_1$</td>
</tr>
<tr>
<td>76</td>
<td>35</td>
<td>B$_1$</td>
</tr>
<tr>
<td>61</td>
<td>30</td>
<td>B$_2$</td>
</tr>
</tbody>
</table>

Figure 4.26 shows the Raman spectra of the samples. All the samples showed a prominent peak at 174 cm$^{-1}$, which is the characteristic peak of chalcopyrite structure. This peak corresponds to A$_1$ mode in which Se atoms vibrate in the x-y plane with Cu and In atoms at rest. Hence frequency of this mode is associated with Se mass and the cations-Se bond stretching forces, describing the interaction between nearest neighbors. The frequency of the A$_1$ mode is given by

$$\nu = \left( \frac{k}{M_{\text{Se}}} \right)^{1/2}$$

where $k$ is the force constant and $M_{\text{Se}}$, mass of Se atom.$^{36}$ Dependence of $\nu$ on these force constants can be expressed as

$$\nu^2(A_1) = \frac{2(\alpha_{\text{Cu-Se}} + \alpha_{\text{In-Se}})}{M_{\text{Se}}}$$
where $\alpha_{\text{Cu-Se}}$ and $\alpha_{\text{In-Se}}$ are the bond-stretching constants between the corresponding atoms. Because of the dependence on force constants, position of this mode directly depends on the atoms surrounding Se.

$A_1$ mode appears even for non-stoichiometric composition, if the chalcopyrite structure is not distorted. Intensity of Raman peak is directly proportional to crystallinity of the sample which can be verified using X-ray Diffractogram. XRD proved that crystallinity was better for CIS0.4 and Raman peak also showed maximum intensity for this sample.

CIS0.2 showed additional modes at 212 cm$^{-1}$ and 231 cm$^{-1}$ which were due to the transverse optical (TO) and longitudinal optical (LO) phonon mode with $B_2$ or $E$ symmetry respectively. $B_2$ type are excited for light polarized parallel to the optic axis and $E$ type are excited only for light polarized perpendicular to the optic axis. These modes reflect the vibration of In-Se atoms in antiphase. Remaining samples showed weak peaks for these modes, as In and Se concentrations were low compared with CIS0.2.

![Raman spectra of the samples CIS0.2 to CIS0.5](image)

**Fig. 4.26:** Raman spectra of the samples CIS0.2 to CIS0.5
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With the increase in Cu concentration (CIS0.4), B₂ mode showed a slight shift to 226 cm⁻¹ and this may be due to vacancy of Indium or stress in the sample. For CIS0.3 and CIS0.4, an additional mode at 260 cm⁻¹ could be seen. This peak is assumed to be the highest frequency mode in CuInSe₂. This mode is reported to be due to CuₙSe binary phase by many authors.³⁸,³⁹ In the present case, this peak disappeared for the Cu-rich sample CIS0.5 which contained Cu₃Se₂ phase. Hence it was concluded that this peak was not due to any CuₓSe phase and could be attributed to B₂+E mode. Intensity of the A₁ mode was better for CIS0.4 which also shows that it is the most ordered structure.

Raman spectra of CIS0.4 showed a shoulder at 150 cm⁻¹, which corresponds to the highest frequency B₁ mode. This peak showed a slight decrease from the original value of 160 cm⁻¹. This may be due to stress in the sample. The B₁ mode corresponds to the frequency of vibration of Cu and In atoms in antiphase. In this case, the polarizability changes during the vibration due to the stretching of the Cu-In bond are partially compensated by the compression of the In-Se bond and hence this mode is very weak. Frequency of this mode is given by³⁶

\[
v = \frac{k(M_{Cu} + M_{In})^{1/2}}{(M_{Cu}M_{In})^{1/2}}
\]

Mode at 150 cm⁻¹ is also reported to be due to In-Se compounds. As the composition was Cu-rich, in the present case, this possibility could be avoided.

From the Raman analysis of the samples, we could confirm that the structure was chalcopyrite which was the most favorable structure for solar cell fabrication. The compositional variation was reflected in the Raman spectrum also. Intensity of the A₁ mode was directly linked with the crystallinity. Hence from the FWHM of the Raman peak, one could have an idea about the crystallinity of the films.
4.8.2 Compositional analysis

(i) EDAX measurements: Elemental concentrations were determined using EDAX and depth-wise analysis of the sample was carried out using XPS measurements. The atomic concentrations in percentage are given in the table 4.16. CISO.5 has Cu concentration of 32.79% for which Cu$_3$Se$_2$ phase was observed. From the table, it is clear that on decreasing Cu concentration, In and Se concentrations increase correspondingly. On reaching CISO.3, the concentration of In remained almost steady and hence for CISO.2, Se concentration increase sharply to 60.04%.

Table 4.16 Atomic concentration and deviation from stoichiometry and molecularity

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Atomic concentration in percentage</th>
<th>Δm</th>
<th>Δs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu</td>
<td>In</td>
<td>Se</td>
</tr>
<tr>
<td>CISO.5</td>
<td>32.79</td>
<td>13.82</td>
<td>53.39</td>
</tr>
<tr>
<td>CISO.4</td>
<td>27.04</td>
<td>18.29</td>
<td>54.67</td>
</tr>
<tr>
<td>CISO.3</td>
<td>22.84</td>
<td>20.19</td>
<td>56.97</td>
</tr>
<tr>
<td>CISO.2</td>
<td>19.75</td>
<td>20.21</td>
<td>60.04</td>
</tr>
</tbody>
</table>

The deviation from molecularity (Δm) and stoichiometry (Δs) of the samples were also listed in the table. CISO.2 showed a slight negative value for Δm.

(ii) XPS analysis: XPS analyses were performed for the samples CISO.2 and CISO.4. Depth-wise XPS analysis was done, employing argon ion sputtering. Figures 4.27-4.28 show the XPS profile of CISO.2. The shift in the binding energy (BE) of In and Se at the surface layers could clearly be seen. On comparing the binding energies it was observed that In$_2$Se$_3$ was formed at the surface. After two layers, the formation of CuInSe$_2$ was evident from the binding energy shift. In the case of CuInSe$_2$, binding energies of Cu, In and Se are Se-54.6 eV and In-444.7 eV respectively. From EDAX, the sample was identified as highly Se-rich. This may be the reason for the formation of In$_2$Se$_3$. However, from the XRD analysis, we could get only the CuInSe$_2$ phase.
Figure 4.27(a) shows the depth-wise analysis of Cu concentration. It can be seen that, Cu was absent in the surface layers of the sample. The peak intensity was high after two cycles of etching. Binding energies of 932 and 952.2 eV were corresponding to Cu2p\textsubscript{3/2} and Cu2p\textsubscript{1/2} states in CuInSe\textsubscript{2} respectively.

The depth-wise analysis of In (Fig. 4.27(b)) shows a shift in binding energy for the two layers at the surface. The binding energies of 445.5 and 453.5 eV were corresponding to that of In in In\textsubscript{2}Se\textsubscript{3} phase. The shift in the first two layers was also observed in the Se depth analysis (Fig 4.28(a)). The binding energy of these layers was 55.5 eV, which was nearly equal to the BE of Se in In\textsubscript{2}Se\textsubscript{3}. Hence it was concluded that In\textsubscript{2}Se\textsubscript{3} was formed at the surface layers of the sample. Since sample stoichiometry contains 60.04% of Se, the formation of In\textsubscript{2}Se\textsubscript{3} is possible.

The inner layers in the ‘In’ depth profile [with binding energies of 444.7 and 452.1 eV] were corresponding to In3d\textsubscript{3/2} and In3d\textsubscript{5/2} respectively which was the BE of In in CIS. The selenium present in the inner layers was having BE of 54.6 eV, which was corresponding to the BE of Se in CIS.\textsuperscript{40} Hence it could be concluded that CIS was formed in the interior of the sample. At the surface layers, formation of In\textsubscript{2}Se\textsubscript{3} was prominent. Fig 4.28(b) shows the depth-wise analysis of oxygen in the sample. It could be seen that oxygen was
absent in the bulk of the sample. Oxygen occurred as a surface contamination at the top layer of the sample.

Fig. 4.28: XPS depth profile of (a) Se in CIS0.2 (b) of O in CIS0.2

Figs 4.29-4.30 show the XPS depth profile of the sample CIS0.4. The binding energies of Cu, In and Se were corresponding to the BE of these elements in CIS. Hence it may be concluded that single phase CuInSe_2 was formed. No shift in the peak was observed throughout the depth of the sample.

Fig. 4.29: XPS depth profile of (a) Cu and (b) In
The BE of 933eV corresponds to Cu2p1/2 state and 952.6eV corresponds to Cu2p3/2. BEs 445.5 and 452.5eV correspond to In3d3/2 and In3d5/2 respectively. The BE of Se was found to be 54.5eV. All these values correspond to the standard values of these elements in CIS. Fig 4.30(b) shows the depth profile of oxygen. Oxygen was present only at the surface of the sample as the surface contamination.

![Graph](image)

**Fig. 4.30:** XPS depth profile of (a) Se and (b) O

### 4.8.3 Optical characterization

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIS0.5</td>
<td>0.94</td>
</tr>
<tr>
<td>CIS0.4</td>
<td>0.94</td>
</tr>
<tr>
<td>CIS 0.3</td>
<td>0.92</td>
</tr>
<tr>
<td>CIS 0.2</td>
<td>0.93</td>
</tr>
</tbody>
</table>

**Table 4.17:** Band gap

![Graph](image)

**Fig. 4.31:** Absorption spectra of the sample
Optical absorption of the sample CIS0.2-CIS 0.5 was measured in the range from 500 nm to 1500 nm. [Fig 4.31]. There was no significant variation in the band gap of the samples. However, there was a visible change in the value of the absorbance of these samples. CIS0.3 showed higher absorbance and CIS0.2, the least. The $E_g$ values are listed in table 4.17.

4.8.4 Electrical characterization

All the samples showed p-type conductivity. Even though there was deviation from molecularity [$\Delta m<0$] for CIS0.2, the sample showed p-type conductivity. This may be due to the increased Se concentration. Resistivity and photosensitivity were high for CIS0.2. The photosensitivity of the sample gradually changed from positive to negative on increasing the Cu concentration. The high resistivity for CIS0.2 may be due to the presence of $\text{In}_2\text{Se}_3$ phase as observed in XPS analysis.

Table 4.18: Resistivity and photosensitivity variation in the samples

<table>
<thead>
<tr>
<th>Sample name</th>
<th>$\rho$ ($\Omega\text{cm}$)</th>
<th>Photosensitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIS 0.5</td>
<td>$3.2 \times 10^{-2}$</td>
<td>Negative</td>
</tr>
<tr>
<td>CIS 0.4</td>
<td>$5 \times 10^{-2}$</td>
<td>Negative</td>
</tr>
<tr>
<td>CIS 0.3</td>
<td>$8 \times 10^{-2}$</td>
<td>0.001</td>
</tr>
<tr>
<td>CIS 0.2</td>
<td>$8 \times 10^{2}$</td>
<td>4</td>
</tr>
</tbody>
</table>

For device fabrication, both high and low resistivity CIS are needed as Copper cones will be formed at the junction, when low resistivity CIS is used throughout. This will provide shunting paths, destroying junction properties.
4.8.5 Discussion

Highly resistive and highly conductive CuInSe$_2$ samples could be prepared using the technique developed in the present work. CIS0.2 was the most photosensitive sample. However, this sample contained secondary phase of In$_2$Se$_3$ which made it unsuitable for solar cell fabrication. CIS0.3 can be used as the conductive bottom layer of the solar cell because of its low resistivity. For device fabrication, a slightly resistive layer should be used at the junction. To find this Se concentration was varied slightly.

4.9 Variation of Se concentration

Concentration of Se was varied slightly, keeping the concentrations of Cu and In fixed at 20 and 100 mg respectively. 165 and 185 mg of Se were evaporated for further optimization. These samples were named as CIS165, CIS175 and CIS185 with masses of Se as 165, 175 and 185 mg respectively.

4.9.1 Structural Characterization

XRD analysis of CIS165, CIS175 and CIS185 proved the existence of single phase CIS preferentially oriented along (112) plane [Fig.4.32]. (220)/(204) and (312)/(116) planes were also identified from XRD, as in the earlier case.

Fig. 4.32: X-ray diffractogram of the Se varied samples
Among these, crystallinity was high for Se concentration of 165mg and it decreased sharply for CIS 185. The grain sizes together with the quality factors are given in the Table 4.19. Maximum grain size and POQ were obtained for Se concentration of 165mg and it decreases with increase in Se concentration.

Table 4.19 Grain size and POQ variation

<table>
<thead>
<tr>
<th>Sample name</th>
<th>POQ</th>
<th>Grain size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIS165</td>
<td>4.6</td>
<td>54</td>
</tr>
<tr>
<td>CIS175</td>
<td>4.5</td>
<td>51</td>
</tr>
<tr>
<td>CIS185</td>
<td>3.8</td>
<td>45</td>
</tr>
</tbody>
</table>

4.9.2 EDAX measurements

Atomic concentration was determined using EDAX analysis. Table 4.20 gives the atomic concentration and deviation from molecularity and stoichiometry. CIS165 was In-rich, which had a suitable value for device fabrication. In CuInSe2 based solar cells, the layer used near the junction has In concentration ~26%. Hence the layer of CIS165 can be used in solar cells. With the increase in mass of Se, the atomic percentage was also found to increase. For CIS175, the Se concentration reached 60.04%.

Table 4.20 Atomic concentration and deviation from molecularity and stoichiometry

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Atomic concentration in percentage</th>
<th>( \Delta m )</th>
<th>( \Delta s )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu</td>
<td>In</td>
<td>Se</td>
</tr>
<tr>
<td>CIS165</td>
<td>21.55</td>
<td>26.21</td>
<td>52.24</td>
</tr>
<tr>
<td>CIS175</td>
<td>19.75</td>
<td>20.21</td>
<td>60.04</td>
</tr>
<tr>
<td>CIS185</td>
<td>18.62</td>
<td>27.13</td>
<td>54.25</td>
</tr>
</tbody>
</table>

On increasing Se concentration to 185mg, the EDAX results did not show the same trend. A reduction in Se concentration was observed in this case. Re-evaporation of Se may be
the reason for this reduced Se concentration. In all the cases, deviation from molecularity showed a negative value, since Cu concentration was less than the In concentration in these samples. Still, Δs was greater than zero for all the samples.

4.9.3 Optical characterization

The band gap of the film showed a slight variation with change in Se concentration. The band gap was found to be least for the Se-rich sample (0.93eV). [Table 4.21]

Table 4.21: Band gap variation with Se concentration

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Band gap eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIS165</td>
<td>0.95</td>
</tr>
<tr>
<td>CIS175</td>
<td>0.93</td>
</tr>
<tr>
<td>CIS185</td>
<td>0.95</td>
</tr>
</tbody>
</table>

The rest of the two samples showed same band gap of ~ 0.95 eV. In CIS165 and CIS185, In concentration was also high, which leads to the increase in band gap of the films. Figure 4.33 and Fig. 4.34 shows the absorption spectra of the Se varied samples. The absorbance was high for CIS185.

Fig. 4.33 Absorption spectra of CIS175 and CIS185
4.9.4 Electrical characterization

Hot probe measurement proved that all the samples were p-type. Electrical resistivity and photosensitivity are depicted in Table 4.22. With increase in Se concentration, the resistivity shows a decrease. Increase in Se will increase acceptor concentration making the conductivity also high. The photosensitivity increased to 7.7, on decreasing the Se concentration.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Resistivity $\rho$ ((\Omega\text{cm}))</th>
<th>Photosensitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIS165</td>
<td>7916</td>
<td>7.7</td>
</tr>
<tr>
<td>CIS175</td>
<td>800</td>
<td>3.7</td>
</tr>
<tr>
<td>CIS185</td>
<td>720</td>
<td>2.8</td>
</tr>
</tbody>
</table>

From the above analysis, it could be concluded that CIS165 possessed suitable resistivity and photosensitivity for device fabrication and hence this layer could be used near the junction. The sample CIS165 was prepared repeatedly to ensure consistency in the properties.
4.10 Stoichiometric CuInSe₂ films

One of the advantages of this deposition technique was that highly stoichiometric films could be prepared without using ultra high vacuum. We could obtain typical concentrations as Cu: 24.92%, In: 24.98% and Se 50.10%. For this, the quantity of elements taken was Cu-25mg, In-105mg and Se-175mg respectively. XRD pattern (Fig. 4.35) shows the highly crystalline nature of this sample with grain size of 44 nm and POQ of 2.6.

![X-ray diffraction pattern of stoichiometric sample](image1)

**Fig. 4.35:** X-ray diffraction pattern of stoichiometric sample

![Absorption spectra of stoichiometric sample](image2)

**Fig. 4.36:** Absorption spectra of stoichiometric sample
Band gap (Fig 4.36) of this ideal sample was 0.98 eV and thickness was 0.58 μm. The sample was p-type in nature and had a resistivity of 2 Ωcm. The sample exhibited very poor photosensitivity of 0.024, probably due to low resistivity of the sample.

PL spectra of this sample (Fig. 4.37(a)) showed very sharp emission, centered at 0.97 eV at very low temperature (~12K). The intensity decreased with the increase in temperature and completely quenched above 90 K. This emission had a high energy shoulder at 0.976 eV. The FWHM of the emission at 0.971 eV (~2 meV) was the smallest among the samples studied in this work. The emission at 0.971 eV shifted to higher energy, as the temperature was increased, at the rate of $1.1 \times 10^{-5} \text{eV/K}$ which was much smaller than the shift of $4 \times 10^{-5} \text{eV/K}$ expected for $a(e, A^0)$ free-to-bound transition. Hence this was classified as a ‘bound exciton emission’.

![Graphs showing PL intensity and 1000/T vs log(Integrated PL intensity)](image)

**Fig. 4.37:** (a) Variation of PL intensity with temperature and (b) Plot of $1000/T$ vs log (Integrated PL intensity) fitted using equation (4.2)

When excitons are near the defects, the defects can either increase or decrease the binding energy of the exciton. When the defects reduce the total system energy of the exciton, excitons will be trapped in the defects, which lead to the formation of ‘bound
excitons'. This gives rise to PL emission at lower energy than that of free excitons. This could be the reason to the absence of FE line was not observed in this sample. Bound exciton emission lines exhibit narrower line-widths than free exciton emissions due to increased localization. This supported our observation as to why the emission at 0.971 eV exhibited very low FWHM. Since most semiconducting materials contain significant amount of impurities and/or defects which can trap excitons, the identification of the bound exciton states provides an important characterization of impurities, which control the electro-optic properties of semiconductors. Neutral and ionized donors and acceptors can trap excitons and form bound excitons.

The bound exciton emission from the sample was quenched above 80 K. In order to calculate the PL quenching energy, a plot between logarithmic value of integrated PL intensity versus 1000/T was fitted (Fig. 4.37(b)) using the equation (4.2). The activation energy (ΔE) of the impurity was obtained to be 20 meV. This was in good agreement with the reported activation energy of the doubly ionized In$^{+2+}_Cu$ donor level.$^{42, 43}$ As temperature was raised, the localization decreased due to the thermal ionization of the defect center. This caused the bound exciton to become free, resulting in increase of FWHM and PL peak energy. Thus it could be concluded that this was the In$^{+2+}_Cu$ donor bound exciton (BX:D2 ($In_{Cu}$)) emission in this sample.

### 4.11 Double layer CuInSe$_2$

As the thickness of single layer was nearly 0.55 μm, a double layer CIS was prepared for cell fabrication. For this, a highly conductive bottom layer and highly resistive top layer were selected. From the above optimizations, CIS 0.3 with a resistivity of 0.08Ωcm was ideal for the bottom layer and CIS165 with a resistivity of 7916 Ωcm was ideal as the top layer. The thickness of this double layer was 0.9 μm. X-ray diffractogram (Fig. 4.38) proved the existence of single phase CuInSe$_2$. Grain size was calculated to be 52 nm.
Modified technique for deposition of CuInSe\textsubscript{2} thin films using...  

Fig. 4.38: X-ray diffractogram of double layer

Fig. 4.39: Absorption spectra of CIS double layer

Fig 4.39 shows the absorption spectrum of the sample recorded in the wavelength range 500-1500nm. Band gap of this double layer was 0.93eV. The absorbance of this sample was greater as the thickness was also greater.

Figure 4.40 shows the cross-sectional image of double layer CuInSe\textsubscript{2}. The two layers were clearly distinguishable from the SEM image.
The double layer thickness was also verified using the SEM image and was in agreement to that obtained using stylus measurements.

4.12 Conclusions

CuInSe$_2$ thin films were prepared using sequential elemental evaporation at moderately low substrate temperature. Indium, Selenium and Copper were evaporated at a substrate temperature of 100°C, 50°C and room temperature respectively. Annealing this stacked layer at 400 °C resulted in the formation of CuInSe$_2$. Single layer thickness was 0.55 μm which could be increased up to 0.9 μm through double layer deposition, adopting similar steps. This technique was selected for further deposition.

The composition was widely varied to find the suitability in device fabrication. For this Cu and Se were varied, one at a time, keeping the others constant. Both p- and n-type films could be prepared using this technique. From the structural characterizations using XRD and Raman scattering, the structure of CuInSe$_2$ prepared using the present method, was identified as chalcopyrite which was the most suitable and favorable structure for solar cells. The grain size varied from 35 nm to 63 nm in these samples. However this grain size was still lower than the reported values, obtained through other techniques of CuInSe$_2$ fabrication. This lead to increase in the number of grain boundaries which, in
some cases, has beneficial effects on CuInSe₂ devices. Interestingly, the grain size of the
samples prepared using this technique was three times larger than that prepared using
CBD Se (as described in chapter 4).

The band gap varied from 0.93 to 0.99 eV in the samples with variation in elemental
concentrations. The AFM analysis of the sample showed that the geometry of the sample
changed from spherical to triangular on going from In-rich to Cu-rich. The resistivity
varied in the range of 0.002 Ωcm to 7916 Ωcm, from which highly conductive and highly
resistive samples could be selected for the device fabrication. The sample with resistivity
of 0.08 Ωcm can be used as the conductive bottom layer and sample with a resistivity of
7916 Ωcm can be used as the resistive top layer for device fabrication. The
photosensitivity of the highly resistive sample was 7.7. Highly stoichiometric film could
be prepared without using ultra high vacuum which is still a major challenge for many
researchers working in ternary chalcopyrites. Typical concentration of the stoichiometric
sample is Cu: 24.92%, In: 24.98% and Se 50.10%. Hence this technique was proved to be
useful for the fabrication of solar cells.
References