CHAPTER III

STRUCTURAL PROPERTIES

3.1 Introduction

The knowledge of the structure of thin films is essential to understand its nature and for interpreting different physical properties that can be used for device applications. The structural characteristics sensitively influence the optical and electronic properties of thin films. Similarly the electronic behaviour of the photovoltaic junction is also strongly affected by the structural features of the interface at the junction. Therefore study of structural properties of thin films is of great importance in the design of high efficiency solar cells.

Structural properties of thin films can be studied precisely using sophisticated techniques such as x-ray diffraction, electron diffraction, field ion microscopy, electron microscopy, ultraviolet photoelectron spectroscopy etc. Of the various methods x-ray diffraction technique has been used for structural analysis due to its advantages such as the relative ease and convenience, large diffraction angles making accurate measurement of spot patterns possible, the diffraction patterns representing the average crystalline
lattice throughout the film due to increased penetration and simultaneous display of diffraction patterns from the film. Some selected methods for understanding the topography of the films are scanning electron microscopy, scanning tunneling microscopy, atomic force microscopy, interferometry, x-ray topography etc. In the present investigation scanning electron microscope has been used for morphological studies. Elemental identification and composition can be studied by energy dispersive x-ray analysis, wavelength dispersive x-ray analysis, auger electron microscope, x-ray photoelectron spectroscopy, secondary ion mass spectrometry, electron probe microanalysis etc. In the present study energy dispersive x-ray analysis has been employed to know the chemical constituents and their composition in the films.

CuInSe$_2$ is a I-III-VI$_2$ semiconductor with properties making it suitable for applications in solar cells, optical detectors and light emitting diodes[1]. The structural properties of CuInSe$_2$ thin films prepared by different techniques have been reported by many workers[2-44]. X-ray diffraction studies carried out by Sahu et al[2] on electrodeposited CuInSe$_2$ thin films have indicated the presence of chalcopyrite phase for both annealed and indium diffused films. However they have also identified the
presence of sphalerite phase. Kim and Im[3] have reported that the sputter deposition of Cu and In metals with the range of sputtered molecularity, M = 0.28 ~ 0.31 is about the optimum condition for fabricating single chalcopyrite phase CuInSe₂ films. Nishitani et al[4] have prepared CuInSe₂ films by molecular beam deposition method and they have reported that in copper rich films (In/Cu < 1) only the (112) diffraction line appeared to be strong, whereas indium rich films (In/Cu > 1) consisted of randomly oriented polycrystals. The copper rich films have been found to have larger grains when compared to indium rich films.

Senthil et al[5] have observed the intensity of peaks in the x-ray diffractogram of CuInSe₂ films deposited by thermal evaporation technique to increase with increase in film thickness. They have estimated the crystallite size as 170 and 213 Å for films of thickness 175 and 230 nm respectively. X-ray diffraction studies carried out by Szot and Haneman[6] on CuInSe₂ films grown by simultaneous vacuum evaporation show that films grown at substrate temperature greater than 420° C are polycrystalline single phase chalcopyrite. The SEM micrographs indicated the presence of surface hillocks in the region of 0.1 to 0.5 μm in size. Schumann et al[7] have studied the structural properties of CuInSe₂ films grown by flash
evaporation technique on GaAs substrates by reflection high energy electron diffraction technique. They have reported that films grown at substrate temperature less than 570 K are polycrystalline. Above this temperature a gradual transition from polycrystalline to single crystalline state was observed.

Kohiki et al[8] have observed that the composition of CuInSe$_2$ films can be varied precisely by changing both the source and substrate temperatures. They have obtained larger grain size for copper rich films (1-2 µm) than for the indium rich films (less than 0.7 µm) and the grain size of the near stoichiometric film was intermediate (0.5-1 µm). The intensity of the preferred (112) orientation was found to increase with the increase in Cu : In ratio and the copper rich films exhibited only the (112) orientation. The lattice parameters have been reported as $a = 5.78 \text{ Å}$ and $c = 11.62 \text{ Å}$.

Aren et al[9] have reported that CuInSe$_2$ films deposited by two source vacuum evaporation of CuInSe$_2$ and Se powders at a substrate temperature 200° C exhibited three peaks corresponding to (112), (220,204) and (424) orientations, (112) peak was observed to be very intense. Kindyak et al[10] have grown CuInSe$_2$ films by laser evaporation method
and have observed that the films deposited at a substrate temperature 375° C to be highly oriented, single phase with only (112) orientation. Yamaguchi et al[11] have reported the presence of (112), (204) and (220), (116) and (312) planes corresponding to chalcopyrite phase in CuInSe₂ films deposited by r.f. sputtering. The full width half maximum of the (112) peak was found to decrease with increase in Cu/In ratio confirming improvement in crystallinity with increase in copper.

Kavcar et al[12] have reported that columnar growth with (112) preferred orientation is desirable in thin CuInSe₂ films for use in solar cells since there is least crystallographic mismatch with thin film CdS grown on top. They have obtained c/a ratio as 2.009. X-ray diffraction studies on CuInSe₂ films prepared by selenizing co-sputtered Cu-In films have been carried out by Schmidt et al[13]. They have observed the films to be polycrystalline with tetragonal chalcopyrite structure and the XRD studies of the (204) and (220) reflections showed a well-split peak shape due to tetragonal distortion representing a high crystallite quality. Ramjanam and Srivastava[14] have reported chalcopyrite type tetragonal phase with a = 5.78 Å and c = 11.62 Å for both bulk and CuInSe₂ films prepared by thermal evaporation technique.
Pern et al[15] have studied the effect of annealing on structural properties of electrodeposited CuInSe₂ films. As the annealing temperature was increased the films exhibited a relatively preferred orientation along the (112) plane. The grain size obtained was 1.96 µm for copper rich films annealed at 400° C for about one hour. Varela et al[16] have reported a columnar structure with a grain size in the range 0.1-0.3 µm for CuInSe₂ films deposited by co-evaporation of Cu, In and Se. The XRD spectra exhibited peaks corresponding to chalcopyrite or sphalerite phases depending on growth parameters. Hachiuma et al[17] have deposited CuInSe₂ thin films by evaporation of mixed powder of Cu₂Se and In₂Se₄ and by stack of Cu-Se and In-Se. The optimum annealing temperature was found to be 400° C for the formation of nearly single-phase chalcopyrite CuInSe₂ films.

Masse and Djessas[18] have reported the growth of CuInSe₂ films by close-spaced vapour transport technique. They have obtained CuInSe₂ films with composition very close to the stoichiometric composition for source temperatures above 550° C. Hama et al[19] have studied the structural properties of CuInSe₂ films deposited by three-source co-evaporation and also by selenization of Cu/In/Se stacked layers. Films prepared by
co-evaporation were found to exhibit a stronger (112) orientation and the peak position was observed to have composition dependence. The lattice spacing ($d_{112}$) was found to decrease as Cu/In ratio decreased. From the surface morphological studies they have observed the good adhesion of CuInSe$_2$ film to molybdenum layer for films deposited on Mo coated substrates. For films formed by selenization the dependence of (112) plane spacing on Cu/In ratio was not so large.

Varela et al[1] have analyzed the dependence of grain size on deposition rate and substrate temperature. The influence of film thickness on grain size was found to be very weak when compared to that of substrate temperature or deposition rate. The broadening observed in the diffraction peaks were attributed to the non-uniformity in the interplanar spacing because of stress in crystallites. The lattice constant ‘a’ of the film was found to vary with the ratio of copper to indium and had a maximum value of 5.82 Å near the stoichiometric composition. Isomura et al[20] have deposited CuInSe$_2$ films by vacuum evaporation of each element. They have studied the influence of indium content on the film properties. CuInSe$_2$ films deposited for an indium source temperature of 900, 940 and 980° C showed a strong line of (112) diffraction corresponding to
chalcopyrite phase. The best single phase was obtained for 940° C. At 900 and 980° C the secondary phases of Cu₂Se and InSe were present.

Masse and Djessas[21] have grown CuInSe₂ films by vertical closed tube systems. They have identified that 450° C is the low limit temperature for which the films are nearly stoichiometric with no CuI phase for iodine saturated vapour pressure of the order 2 x 10⁻³ atmospheres. They have identified the upper limit for film growth as 600° C above which In₂Se₃ and InSe phases were detected. Ramjanam and Srivastava[22] have reported chalcopyrite type tetragonal phase with \( a = 0.5789 \pm 0.0005 \) nm and \( c = 1.160 \pm 0.0005 \) nm for as-sintered annealed and unannealed CuInSe₂ pellets. But when annealed at 1050 K in vacuum of \( \approx 10^{-7} \) Torr they observed the chalcopyrite phase transforming into sphalerite type cubic structure.

The microstructure of CuInSe₂ layers formed by selenization of the precursor layer has been analyzed by Norsworthy et al[23]. They have noticed the crust of the film to be well fused and dense. No clear grain structure was observed for film with Cu/In ratio of 0.88. For films with Cu/In ratio of 0.98 they have observed visible network of consolidated
regions where as filamentary grains of less than 1 \( \mu \text{m} \) was observed around the voids in copper rich films. Castaneda and Rueda[24] have deposited CuInSe\(_2\) films by electron beam evaporation and by flash evaporation. The grain size of films deposited by flash evaporation was found to lie in the range \( 47-190 \) nm. They have observed round prisms of size about \( 600 \) nm. Isomura et al[25] have reported that CuInSe\(_2\) grown on SnO\(_2\) substrate had fine grain size and the (112) peak intensity is more when compared to films grown on glass substrates. They have observed the presence of smooth surface for both but columnar structure has been observed only in films grown on SnO\(_2\).

Zegadi et al[26] have deposited CuInSe\(_2\) films by three source co-evaporation technique. They have observed for the as-grown films low intensity diffraction peaks and have been attributed to chalcopyrite or sphalerite phase. The appearance of (101) and (211) peaks after annealing confirmed the chalcopyrite structure. Subbaramaiah and Sundararaja[27] have analyzed spray deposited CuInSe\(_2\) films by electron probe microanalysis. The analysis revealed that the films are chalcopyrite in structure with a strong (112) reflection. The lattice parameters were found to be \( a = 5.647 \) Å and \( c = 11.245 \) Å respectively. Grain sizes of the order
of 200 – 800 nm for copper rich and 10 – 100 nm for near stoichiometric and indium rich composition have been reported by Tseng et al[28].

CuInSe₂ films have been deposited using vacuum evaporation by Fray and Lloyd[29]. They have observed a sharp and intense line in the x-ray diffractogram corresponding to (112) orientation. Kumar et al[30] have reported that flash annealing of the Cu-In/Se layer at 400° C, yielded CuInSe₂ films with chalcopyrite structure. Adurodija et al[31] have carried out detailed studies on CuInSe₂ films obtained by close-spaced selenization. They have reported that highly indium rich films yielded ordered defect chalcopyrite compound with small crystallite sizes while slightly indium rich or copper rich alloys yielded single phase CuInSe₂ films with dense crystals and sizes of about 5 μm.

Single-phase CuInSe₂ films have been obtained by selenizing the near stoichiometric Cu-In-O film prepared using r.f. magnetron sputtering by Terauchi et al[32]. Pal et al[33] have deposited CuInSe₂ films on glass substrates by three-source evaporation technique. They have reported a very rough surface texture. The crystallites became more spherical with
increasing Cu/In where as with increasing indium content it showed plate like features. The grain size was found to lie in the range 0.1 to 0.4 μm. Intense peak corresponding to (112) orientation and small peaks corresponding to (220) and (204) planes were observed in the diffraction pattern. The (112) peak indicating chalcopyrite structure has been observed to increase considerably with increase in Cu/In ratio near stoichiometry.

Garcia et al[34] have prepared CuInSe$_2$ thin films by co-evaporation. The grain size was found to be in the 100 nm range. Menna et al[35] have reported that CuInSe$_2$ single phase on Mo-coated glass can tolerate Cu/In ratio variations in the 0.8 – 1.1 interval and be as single phase. For Cu/In ratio less than 0.8, a secondary ordered vacancy phase was found to be formed. Durny et al[36] have reported the formation of amorphous CuInSe$_2$ films with no preferred crystallite orientation by flash evaporation technique. Adurodija et al[37] have studied about the formation of CuInSe$_2$ by annealing Cu-In-Se stacked elemental layers. They have reported that at temperatures above 400° C Cu$_2$Se and β-In$_2$Se$_3$ phases react to form CuInSe$_2$. An annealing time of 60 seconds was found to be sufficient for the formation of single-phase chalcopyrite CuInSe$_2$. 

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X-ray diffraction studies of CuInSe₂ films produced in Ar/O₂ atmospheres as a function of (O₂/Ar) + O₂ have been carried out by Yamaguchi[38]. The x-ray diffractogram exhibited peaks at 20 = 26.7°, 44.4° and 52.5° corresponding to (112), (204) and (220), (116) and (312) planes of the chalcopyrite phases of CuInSe₂. The (112) diffraction line was found to be very strong.

Dhanam et al[39] have deposited CuInSe₂ films by chemical bath deposition technique. The peaks (105), (213), (103), (101), (211) and (301) present in the x-ray diffractogram confirmed the chalcopyrite structure of the films. The tetragonal distortion was found to be in the range -0.097 to + 0.014. Uniform and smooth morphology containing the accumulation of small grains has been observed from the SEM micrographs. The sizes of the grain aggregation of CuInSe₂ films have been reported to lie in the range 0.55 to 0.15 μm. Tanaka et al[40] have grown CuInSe₂ films on GaAs substrates by r.f.diode sputtering. The films were found to have chalcopyrite structure with the c-axis of the CuInSe₂ perpendicular to the surface of (001) GaAs substrate.
Malar et al[41] have prepared CuInSe$_2$ films by flash evaporation method. They have studied the electron beam induced recrystallization in copper indium films and have reported that the grain size of as-deposited film is 390 Å and it changed to 1540 Å on irradiation by electron beam. CuInSe$_2$ films with compositional ratios Cu/In = 0.9 and Se/(Cu+In) have been grown by r.f.diode sputtering by Tanaka et al[42] and the films were found to exhibit chalcopyrite structure. Bindu et al[43] have prepared CuInSe$_2$ films by an eco-friendly selenisation technique and have reported that the films are polycrystalline with chalcopyrite structure.

Masse et al[44] have deposited nearly stoichiometric CuInSe$_2$ films by close-spaced vapor transport technique for source temperatures in the range of 400 – 580° C. They have observed only one phase with (112), (204, 220) and (312,116) orientations and the grain size obtained from SEM micrographs show an increase with the source and substrate temperatures up to 10 μm and even more for thick layers. Experimental details and results of structural characterization, composition analysis and surface analysis of CuInSe$_2$ films deposited by CSVT technique are projected in this chapter.
3.2 Experimental techniques

Several analytical techniques are available for the analysis of the structure, few of them being x-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM), scanning tunneling electron microscope (STEM) etc. Among these, x-ray diffraction is a very simple and non-destructive technique requiring only very small area of the sample. X-ray diffraction is a well-established technique for determining crystalline order in three-dimensional solids [45, 46]. With the advancement in technology and computer control over the high power x-ray sources, diffractometers and counters this method of analysis has become very popular and is widely used. Hence in the present study the structural characterization has been carried out using x-ray diffraction method and various microstructural parameters have been estimated.

Determination of chemical composition is one of the most important study in thin film characterization because compound materials dissociate during evaporation due to their different melting points and vapour pressures. The major microchemical analysis that is adapted to chemically characterize a thin film is energy dispersive analysis of x-rays (EDAX) [47]. In the present work energy dispersive analysis of x-rays has been used to
determine the composition. Surface analysis of the films has been carried out using scanning electron microscope.

3.2.1 X-ray diffractometer

The x-ray diffractometer consists of three parts namely, a basic diffraction unit, a counter goniometer and an electronic circuit panel with an automatic recorder. The collimated x-ray beam produced at a rating of 40 KV – 20 mA is allowed to be incident on the sample and the diffracted rays are received by a proportional (or scintillation) counter through a crystal monochromator or a Ni-filter for CuKα radiation(λ=1.5418 Å). The perfect alignment of the goniometer with respect to x-ray beam and the monochromator assembly with reference to the diffracted beam from the surface ensures minimum error in the measurement of diffraction angle (2θ) and intensity (I) values. The proportional counter receives the diffracted intensity and the diffraction response is converted to electrical pulses and preamplified. The preamplified signal is then fed to the electronic system control for further amplification and process. The single channel analyzer displays the analog output according to the present conditions.
The basis of x-ray diffraction is the Bragg’s law, which describes the conditions for constructive interference of x-rays scattered from atomic planes of a crystal. The condition for constructive interference is

\[ 2d \sin \theta = n\lambda \]  

(3.1)

where \( \lambda \) is the wavelength of x-rays, \( d \) is the lattice spacing, \( n \) is the order of diffraction and \( \theta \) is the glancing angle of x-rays. The factor \( d \) is related to the (hkl) indices of the planes and the dimension of the unit cell. It is therefore seen that the diffraction direction is solely determined by the structure and size of the unit cell.

The crystallite sizes are calculated using the Scherrer’s formula [48-50]

\[ D = \frac{0.94 \lambda}{\beta \cos \theta} \]  

(3.2)

The strain (\( \varepsilon \)) is calculated using the relation

\[ \beta = \frac{\lambda}{D \cos \theta} - \varepsilon \tan \theta \]  

(3.3)
The dislocation density (\(\delta\)) defined as the length of dislocation lines per unit volume of the crystal can be evaluated from the formula [51]

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

(3.4)

The intensities of the diffracted beams depend on the possible diffraction directions and the lattice parameters such as ‘a’ and ‘c’ in the case of tetragonal symmetry which can be expressed by the relation [52]

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

(3.5)

The lattice parameters ‘a’ and ‘c’ are calculated from the above equation (3.5). In the present investigation the structure of the films have been analyzed using a x-ray diffractometer (model – JOEL 8030) with a nickel filtered CuK\(\alpha\) radiation (\(\lambda = 0.15418\) nm) at 40 KV and 20 mA in the 2\(\theta\) range.
3.2.2 Energy dispersive analysis of x-rays

Energy dispersive x-ray spectrometer helps to determine the elemental contents in the specimen very accurately. In this technique an energetic beam of electrons is allowed to be incident on the thin film. These incident electrons interact inelastically with both the inner shell electrons and outer shell electrons of the atoms of the film material, generating x-rays. The outer shell electrons generate soft x-rays due to this interaction where as the inner most shells generate characteristic x-rays, which are characteristic of the energies of these shells and hence are characteristic of the atoms radiating these x-rays. Hence by analyzing the energy of these characteristic x-rays, typical of which are $K_a$, $K_β$, $L_a$, $L_β$ and etc., information about the types of atoms present in the film and their concentration can be determined. In the present study Leica S – 440i EDAX spectrometer has been used to determine the elemental contents in the deposited CuInSe$_2$ thin films.

3.2.3 Scanning electron microscope

The scanning electron microscope is the most widely used instrument for obtaining topographical features of a film. In this the areas to be examined or the microvolumes to be analyzed are irradiated with a fine electron beam produced by the electron gun and focused by electron lenses.
The scanning coils deflect this beam and sweep it over the film surface. A cathode ray tube is scanned synchronously with the electron beam. The brightness of the display tube is modulated by the signal that arises from the interactions of the beam with the film surface element under study. The strength of this signal is thus translated into image contrast. The types of signals produced when the electron beam impinges on the specimen surface include secondary electrons, Auger electrons, characteristic x-rays and photons of various energies. The emanating secondary electrons are used for the z-modulation in a corresponding raster on a television or oscilloscope screen. For topographical feature determination the secondary electron mode is generally preferred since these electrons emanate only from about 10 Å or less from the film surface and hence the picture obtained is a faithful reproduction of the surface features.

In the present investigation the surface of the CuInSe₂ films of different thicknesses lying in the range 400 to 6000 nm deposited on polished quartz substrates at three different source temperatures 713, 758 and 843 K have been examined using JSM 35CF JOEL model scanning electron microscope.
3.3 Results and discussion

The x-ray diffractogram of the CuInSe$_2$ films of thickness 410 nm, 412 nm and 1234 nm deposited at source temperature 713 K is shown in figure 3.1. X-ray diffractogram of the film with thickness 410 nm shows diffraction peaks with orientation along (101), (112), (103) and (105) planes corresponding to the CuInSe$_2$ phase. The presence of these peaks indicates that the CuInSe$_2$ film exhibits chalcopyrite structure. The scanning electron micrograph of CuInSe$_2$ films deposited at source temperature 713 K on to quartz substrates are shown in figures 3.2(a) and 3.2(b). The micrograph revealed that the deposited films are polycrystalline in nature. The results of the energy dispersive x-ray analysis of the film with thickness 410 nm is shown in figure 3.3. The composition of the film determined from the energy dispersive x-ray analysis pattern gives a composition of Cu = 17.02 atomic %, In = 24.53 atomic % and Se = 58.44 atomic %. The compositional analysis indicates that the film is copper deficient and indium rich with Cu/In ratio equal to 0.69. Similar results have been reported by Hama et al[19] for CuInSe$_2$ films deposited by three-source co-evaporation at a substrate temperature of 420° C. They have obtained a Cu/In ratio equal to 0.58 for which they have observed InSe peak. In the present study on the CSVT deposited CuInSe$_2$ films InSe peak has not been observed.
Fig. 3.1 X-ray diffractogram of CuInSe$_2$ films deposited at source temperature 713 K
Fig. 3.2 (a) SEM micrograph of CuInSe$_2$ film of thickness 410 nm ($T_s = 713$ K)

Fig. 3.2 (b) SEM micrograph of CuInSe$_2$ film of thickness 1234 nm ($T_s = 713$ K)
Source Temperature = 713K
Cu = 17.02 atomic %
In = 24.53 atomic %
Se = 58.44 atomic %

Fig. 3.3 Composition study of CuInSe$_2$ film of thickness 410 nm


CuInSe$_2$ films with thickness 412 nm exhibited diffraction peaks (101), (103), (211), (105) and (213) which are characteristic of the chalcopyrite structure. Film with thickness 1234 nm shows diffraction peaks corresponding to (112), (204), (220), (301), (116) and (312) orientations. Masse et al[44] have reported the presence of similar peaks for CuInSe$_2$ films deposited by CSVT technique. The EDAX pattern of CuInSe$_2$ film with thickness 1234 nm is shown in figure 3.4. Energy dispersive x-ray analysis results shows that the deposited film with thickness 1234 nm has a composition of Cu = 10.62 atomic%, In = 18.76 atomic% and Se = 70.62 atomic %. This copper deficient and selenium rich film has a Cu/In ratio = 0.57. Films with excess selenium correspond to ordered phases as disorder gets created through the occurrence of planar faults which inturn is produced by the nucleation of selenium vacancies.

CuInSe$_2$ films deposited at source temperature 713 K are found to be selenium rich and copper deficient with non-stoichiometric composition. The structural parameters of the films deposited at source temperature 713 K are shown in Table 3.1.
Fig. 3.4 EDAX result of CuInSe$_2$ film of thickness 1234 nm

Source Temperature = 713 K
Cu = 10.62 atomic %
In = 18.76 atomic %
Se = 70.62 atomic %
Table 3.1

Structural parameters of CuInSe$_2$ films prepared by close-spaced vapour transport technique

<table>
<thead>
<tr>
<th>Source Temperature (K)</th>
<th>Sample thickness (nm)</th>
<th>Observed (hkl) planes</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>c/a ratio</th>
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<td>713</td>
<td>410</td>
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<td>(103)(105,213)</td>
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<tr>
<td>713</td>
<td>412</td>
<td>(101)(103)</td>
<td>6.22</td>
<td>11.36</td>
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<tr>
<td>1234</td>
<td>412</td>
<td>(112)(220,204)</td>
<td>5.70</td>
<td>11.61</td>
<td>2.03</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>(301)(116)</td>
<td></td>
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<td></td>
<td></td>
<td>(312)</td>
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<tr>
<td>838</td>
<td>412</td>
<td>(112) (103)</td>
<td>5.70</td>
<td>11.60</td>
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<td>758</td>
<td>838</td>
<td>(112) (211)</td>
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<td>11.60</td>
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<td>(217) (411)</td>
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<td>758</td>
<td>1690</td>
<td>(112) (211)</td>
<td>5.77</td>
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<td>2304</td>
<td>1690</td>
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X-ray diffractogram of CuInSe$_2$ films with thickness 838 nm, 1690 nm and 2304 nm deposited at a source temperature 758 K is shown in figure 3.5. Film with thickness 838 nm show the characteristic peaks (112), (103), (204) and (220) corresponding to chalcopyrite structure. CuInSe$_2$ films with thickness 1690 nm exhibited only two peaks corresponding to (112) and (211) orientations. Film with thickness 2304 nm exhibits characteristic peaks (211), (204), (220), (301), (305), (323), (217) and (411) corresponding to chalcopyrite structure. Figure 3.6 depicts the SEM micrograph of CuInSe$_2$ film of thickness 838 nm deposited at source temperature 758 K. The micrograph shows the formation of fine-grained polycrystals with less porous and uniform deposit distribution. The results of the composition study on the CuInSe$_2$ film with of thickness 838 nm is shown in figure 3.7. The film is found to exhibit a composition of Cu = 6.2 atomic %, In = 34.3 atomic% and Se = 59.50 atomic%. The result shows that it is an indium rich film exhibiting chalcopyrite structure. Qiu and Shih[53] have reported chalcopyrite structure for both copper rich and indium rich films. The chemical composition details of energy dispersive analysis spectrum of CuInSe$_2$ film of thickness 2304 nm is shown in figure 3.8. The plot exhibits a composition of Cu = 21.26 atomic%, In = 22.27 atomic% and Se = 56.48 atomic%. The structural parameters of the films deposited at
Fig. 3.5 X-ray diffractogram of CuInSe$_2$ films deposited at source temperature 758 K
Fig. 3.6 SEM micrograph of CuInSe$_2$ film of thickness 838 nm ($T_s = 758$K)
Fig. 3.7 The result of composition studies of CuInSe$_2$ film of thickness 838 nm

Source Temperature = 758K
Cu = 6.20 atomic %
In = 34.30 atomic %
Se = 59.50 atomic %
Fig. 3.8 The result of composition studies of CuInSe$_2$ film of thickness 2304 nm

Source Temperature = 758K
Cu = 21.26 atomic %
In = 22.27 atomic %
Se = 56.48 atomic %
source temperature 758 K are shown in Table 3.1. The lattice parameter values ‘a’ and ‘c’ of the CuInSe₂ films of various thicknesses are in good agreement with JCPDS values (23-209).

The x-ray diffractogram of CuInSe₂ films with thickness 399 nm, 1640 nm, 2553 nm and 5796 nm deposited at source temperature 843 K is shown in figure 3.9. All those films deposited at source temperature 843 K exhibit sharp peaks which confirm the polycrystalline nature of the films. The presence of (112), (103), (204) and (220) diffraction peaks confirm the chalcopyrite structure[54]. The presence of an intense peak (112) corresponding to chalcopyrite structure have been reported by Pal et al[33]. The lattice parameter values of the CuInSe₂ films deposited at source temperature 843 K are in good agreement with JCPDS values. Varela et al[1] have reported the lattice parameter value a = 5.82 Å for near stoichiometric composition. The c/a ratio is found to lie around 2.0. Sharma and Garg[55] have reported that CuInSe₂ films with chalcopyrite structure and having a lattice constant ratio c/a = 2.0 as the most suitable ones for the fabrication of CdS/CuInSe₂ heterojunction solar cells. Figures 3.10 and 3.11 show the results of the composition studies on CuInSe₂ films of thicknesses 5796 nm and 1640 nm respectively. The composition of the
Fig. 3.9 X-ray diffractogram of CuInSe$_2$ films deposited at source temperature 843 K
Fig. 3.10 EDAX result of CuInSe$_2$ film of thickness 5796 nm

Source Temperature = 43K
Cu = 24.51 atomic %
In = 23.34 atomic %
Se = 52.16 atomic %
Fig. 3.11 EDAX result of CuInSe₂ film of thickness 1640 nm

Source Temperature = 843K
Cu = 22.34 atomic %
In = 20.21 atomic %
Se = 57.45 atomic %
chemical constituents in the CuInSe$_2$ films of thickness 5796 nm are 
Cu = 24.51 atomic%, In = 23.34 atomic% and Se = 52.16 atomic%; and the 
results for the film of thickness 1640 nm are Cu = 22.34 atomic%, 
In = 20.21 atomic% and Se = 57.45 atomic% respectively. The films 
deposited at source temperature 843 K are Cu rich and as Cu/In ratio is 
greater than one the (112) diffraction lines are found to be sharp. Several 
workers[4,8-10,15,20,27,33,38] have reported a similar observation for 
copper rich films. This observed value of Cu/In greater than one have been 
reported by Menna et al[35] as suitable for high efficiency devices. Figures 
3.12(a) and 3.12(b) show the micrograph of CuInSe$_2$ films deposited at 
source temperature 843 K. It is seen that the films are smooth and uniform 
having a large grain size. The micrograph also reveals the agglomeration of 
particles in a uniform dense layer on the substrate as the thickness increases.

The absence of elemental copper even in copper rich films could be 
due to its high reactive state which is thought to be favoured by broad 
atomic distribution of copper and indium within the entire mass of the alloy 
materials which means the condition of deposition is good[31]. For all the 
films deposited at source temperature 843 K it is found that (112) orientation 
is the preferred orientation. The structural parameters of the films deposited
Fig. 3.12(a) SEM micrograph of CuInSe$_2$ film of thickness 399 nm ($T_S = 843$K)

Fig. 3.12(b) SEM micrograph of CuInSe$_2$ film of thickness 1640 nm ($T_S = 843$K)
at 843 K are shown in Table 3.2. The grain size is found to increase with film thickness. A large grain size of 703 Å has been observed for a film of thickness 5796 nm. The large grain size may also be due to the excess copper which promotes grain growth. The crystallinity of grains in copper rich films is much better than in indium rich films and this has also been observed by several other workers[4,8,11,33]. The presence of sharp and intense (112) peak suggests that polycrystalline films of CuInSe$_2$ exhibit columnar growth with a preferred (112) orientation. This orientation is desirable in thin films of CuInSe$_2$ for use in solar cells since there is a least crystallographic mismatch with thin film CdS grown on top[12].
Table 3.2

Structural parameters of CuInSe$_2$ films prepared by close-spaced vapour transport technique

<table>
<thead>
<tr>
<th>Source Temperature (K)</th>
<th>Sample thickness (nm)</th>
<th>Observed (hkl) planes</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>c/a ratio</th>
<th>Tetragonal distortion 2- c/a</th>
<th>Grain size (Å)</th>
<th>Dislocation density lines/m$^2$</th>
<th>Strain</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>observed ASTM</td>
<td>observed ASTM</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>843</td>
<td>399</td>
<td>(112)(204,220) (116)(312)</td>
<td>5.829</td>
<td>11.9</td>
<td>2.04</td>
<td>-0.04</td>
<td>298</td>
<td>8.36x10$^{-4}$</td>
<td>8.98x10$^{-4}$</td>
</tr>
<tr>
<td></td>
<td>1640</td>
<td>(112)(103) (105,213) (204,220)(116) (312)(316)(332)</td>
<td>5.828</td>
<td>11.91</td>
<td>2.043</td>
<td>-0.043</td>
<td>366</td>
<td>7.05x10$^{-4}$</td>
<td>8.495x10$^{-4}$</td>
</tr>
<tr>
<td></td>
<td>2553</td>
<td>(112)</td>
<td>5.789</td>
<td>11.62</td>
<td></td>
<td></td>
<td>390</td>
<td>6.54x10$^{-4}$</td>
<td>8.2x10$^{-4}$</td>
</tr>
<tr>
<td></td>
<td>5796</td>
<td>(112) (103) (220,204)</td>
<td>5.835</td>
<td>11.83</td>
<td>2.027</td>
<td>-0.027</td>
<td>703</td>
<td>2.1x10$^{-4}$</td>
<td>4.782x10$^{-4}$</td>
</tr>
</tbody>
</table>
References


