CHAPTER 4

STRUCTURAL PROPERTIES

4.1 INTRODUCTION

The microstructure of the film is found to have profound influence on the optical, electrical, structural and mechanical properties of the film. The physical properties of thin films are known to differ widely from those of bulk materials. This is evidently connected with the small size of the crystallites and in particular, with the large faults, grain boundaries, etc. The method of film deposition, the electrical and thermal conditions of the substrate also influences the structure of the deposited film. Mechanical, chemical or electrical property of the material depends strongly on its internal structure. An understanding of the structure of the materials has become essential in the world of novel materials. Today a wide range of experimental methods are available for the evaluation of structure of materials with high accuracy and precision. This chapter begins with theory of structural parameters, followed by introduction about the different analytical techniques that are used to study the structural properties of the film. The techniques discussed are X-ray diffraction measurements and Raman spectroscopy. Finally, discussions about compositional variations in as-prepared samples and thermally treated samples are obtained from the results.

X-Ray Diffraction (XRD) technique has played a vital role in coordination chemistry and determination of bond lengths, band angle, residual stress, preferential orientation, grain size and temperature factor etc.,
X-ray studies gives information about the size of the individual micro-
crystallites capable of diffracting the X-ray coherently. The techniques based 
on X-ray probe have dominated the field mainly because of their simplicity, 
more reliability, quantitative and non-destructive nature. Tarey et al. (1987) 
explained that of all these techniques, X-ray diffraction plays a leading role, 
as fundamental for material characterization. Raman spectroscopy is a 
powerful tool for elucidating detailed structural and compositional 
information about the structure of the materials.

4.2 THEORY

4.2.1 Bragg's Law

Diffraction occurs only when Bragg’s law is satisfied, which 
describes the condition of constructive interference for X-ray scattering from 
atomic planes of crystal.

When monochromatic X-rays impinge upon the atoms in a crystal 
lattice, each atom acts as a series of parallel reflecting planes. The intensity of 
the reflected beam will be maximum at certain angles when the path 
difference between the two reflected waves from the two different planes is 
integral multiple of \( \lambda \). The condition for constructive interference is

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

(4.1)

where ‘d’ is the distance between the atomic planes parallel to the axis of the 
incident beam, ‘\( \theta \)’ is the angle of incidence relative to the planes, ‘\( n \)’ is the 
order of reflection, and ‘\( \lambda \)’ is the wavelength of the X-rays.

Bragg’s law requires that \( \theta \) and \( \lambda \) should be matched for diffraction. 
The condition may be satisfied by \( \lambda \), or by varying the orientation of the 
single crystal. In thin films, the distribution of crystallite orientations is nearly
continuous and diffraction occurs from crystallites that happen to be oriented at the angle to satisfy the Bragg’s law condition. From the XRD profiles the interplanar spacing \( d_{hkl} \) has been calculated using the Bragg’s relation (4.1)

\[
d_{hkl} = \frac{n\lambda}{2\sin \theta}
\]  

(4.2)

where \( h,k,l \) are miller indices.

### 4.2.2 Grain Size

The size of the grains in a polycrystalline material has pronounced effects on many of its properties, namely increase in strength and hardness, accompanied by a decrease in grain size. The most accurate method of determining grain size is by microscopic examination; and the usual procedure is to determine the average number of grains per unit area of the surface and is represented in terms of ‘index number’. Although X-ray diffraction is inferior to microscopic examination in the accurate measurement of grain size, one diffraction pattern can yield semi-quantitative information about the grain size, together with information about the preferential orientation.

Analysis of diffraction pattern and comparison with the standard ASTM data can reveal the existence of different crystallographic phases in the film, the relative abundance, lattice parameters and any preferred orientation. The average grain size \( D \) of the film from the Full Width at Half Maximum (FWHM) can be calculated using Scherer’s formula (Cullity 1967)

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

(4.3)
where the constant ‘K’ is the shape factor = 0.94, ‘λ’ is the wavelength of X-rays (1.5406 for CuKα), ‘θ’ is the Bragg’s angle and ‘β’ is the FWHM.

### 4.2.3 Crystal Orientation

Each grain in a polycrystalline aggregate has a crystallographic orientation different from that of its neighbor i.e., the orientations of all grains are randomly distributed in relation to some selected frame of reference. Preferred orientation is a very common condition and any aggregate characterized by the particular orientation is said to have a preferred orientation.

### 4.2.4 Internal Stress

When a polycrystalline piece of metal is deformed elastically in such a manner that strain is uniform over a relatively large distance, the lattice plane spacing in the constituent grains change from their stress free value to some new value corresponding to the magnitude of the applied stress. This new space is essentially constant from one grain to another for any particular set of planes similarly oriented with respect to the stress. Due to this strain causes a shift in the diffraction of lines to 2 new positions. This non-uniform micro strain causes a broadening of the corresponding diffraction line. From the XRD shift, strain may be calculated and then the presence of stress can be determined. The origin of the micro strain is related to the lattice misfit, which in-turn depends upon the deposition conditions. The micro strain (ε) can be calculated from the relation

\[ \varepsilon = \frac{\beta \cos \theta}{4} \]  

(4.4)

where ‘β’ is the angular line width, at half maximum intensity in radians; ‘θ’ is the Bragg’s angle.
4.2.5 Dislocation Density ($\delta$)

Dislocation density ($\delta$) can be evaluated from crystallite size (D) given by Nelson and Riely (1945)

$$\delta = \frac{1}{D^2} \quad (4.5)$$

4.2.6 Lattice Parameter (a)

The lattice parameter (a) can be evaluated from the relation

$$a = \sqrt{h^2 + k^2 + l^2} \quad (4.6)$$

where h; k; l are Miller indices.

4.3 X-RAY DIFFRACTION (XRD)

The X-ray diffractometer is used as a powerful tool in diffraction analysis. This instrument is known as diffractometer when it is used with X-rays of known wavelength to determine the unknown spacing of crystal planes. X-ray Diffraction is decidedly inferior to microscopic examination in the accurate measurement of grain size. The advantage is that dynamic measurements can be made with the diffractometer. XRD is a versatile, non-destructive analytical technique for identification and quantitative determination of the various crystalline compounds known as ‘phases’ present in the polycrystalline films. X-ray techniques based on monochromatic radiation are generally important because it enables to determine ‘d’ spacing from observed diffraction angles. An important feature of X-ray diffraction is their ability to focus into a sharp diffraction line, which is Bragg-reflected from a sharp extended area and considerably improves the signal to noise
ratio. One of the main applications of XRD techniques in thin films is in fact to make use of their good resolution of ‘d’ spacing to investigate strains in the film. X-ray diffraction has many field applications not only in the structural analysis of crystalline and amorphous materials, but also in various metallurgical fields. X-ray diffraction methods have advantages of relative ease and convenience, large diffraction angles making accurate measurement of spot pattern possible and simultaneous display of diffraction pattern from film and the substrate.

4.4 RAMAN SPECTROSCOPY

Raman spectroscopy is a technique used to study vibrational, rotational, and other low-frequency modes in a system. It relies on inelastic scattering, or Raman scattering, of monochromatic light, usually from a laser in the visible, near infrared, or near ultraviolet range. The laser light interacts with molecular vibrations, phonons or other excitations in the system, resulting in the energy of the laser photons being shifted up or down. The shift in energy gives information about the vibrational modes in the system. In solid-state physics, spontaneous Raman spectroscopy is used to characterize materials and to find the crystallographic orientation of a sample. Raman spectroscopy is a viable method for thin film and monolayer characterization. It is primarily used to investigate the structure of both amorphous and crystalline solids.

4.5 EXPERIMENTAL PROCEDURE

4.5.1 X-Ray Diffraction

Samples were analyzed by a Shimadzu XRD-6000 X-ray diffractometer. Samples mounted on the specimen holder using silica gel were scanned at a rate of 0.5°/min with CuKα radiation. The radiation was filtered
using a 1° divergence slit, a 1° slatter slit and a 0.15 mm receiving slit. Structural identification of Cu₂S films were carried out from the analysis of the X-ray diffractogram taken in the range of 2θ between 20 and 80°. The generated raw data files were then computer processed to smooth data prints, to remove the amorphous background scatter, and to remove the Kα2 analytical spectrum component. Integrated intensities were calculated using a profile fitting software package that performs mathematical modeling of the diffractogram pattern.

4.5.2 Raman Spectroscopy

Raman spectra of the films were recorded by using a Horiba’s Lab Ram High Resolution spectrometer equipped with a multichannel detection system in the backscattering configuration. The incident laser light (λ=532 nm) could be focused on the sample within a spot of 1μ m in diameter.

4.6 RESULTS ANS DISCUSSION

4.6.1 Structural Study

It is well known that various Cu-S phases, namely chalcocite, djurleite, digenite and covellite have different crystallographic structures and hence show different X-ray diffraction patterns. X-ray diffraction can thus be used to identify the Cu-S phases present in vacuum evaporated Cu₂S film. Figure 4.1 to 4.4 shows the X-ray diffraction patterns of as-deposited Cu₂S films of various thicknesses (namely 1000Å, 3000Å, 5000Å and 7000 Å) prepared on glass substrates at room temperature. The crystallite of as-deposited films were thought to be amorphous but the presence of humps in Figures 4.1 to 4.3 reveals that the prepared film exhibit mixed state of amorphous and polycrystalline nature of Cu₂S films. However a strong peak
observed in Figure 4.4 clearly leads us to understand that the film coated at higher thickness bears polycrystalline nature. This improvement in the crystallite of the deposited films has been previously reported by Grozdanov and Najdoski (1995), Xu and Ding (2008) using different methods.

The peak observed near $2\theta = 22.9^0$ in Figure 4.1 is a good diagnostic line for chalcocite Cu$_2$S phase and are in agreement with the JCPDS value (ISCD 200986). The peaks obtained in XRD spectrum are compared with standard JCPDS values and are reported in Table 4.1 along with various planes of Cu$_2$S film. It is thus observed from XRD pattern that the formed film is a mixture of either or both phases of chalcosite (Cu$_2$S) and covellite (CuS) as reported by Jiban Podder et al (2005). Moreover (110) plane arrives at $2\theta$ equal to 46.78$^0$, 47.9$^0$, 45.91$^0$ and 47.4$^0$ for films of thickness 1000Å, 3000Å, 5000Å and 7000 Å thickness respectively as obtained earlier by He et al (2001), Kazinets et al(1977).

![X-ray diffraction spectra of Cu$_2$S films of 1000Å thickness](image)

**Figure 4.1** X-ray diffraction spectra of Cu$_2$S films of 1000Å thickness
Figure 4.2 X-ray diffraction spectra of Cu$_2$S films of 3000Å thickness

Figure 4.3 X-ray diffraction spectra of Cu$_2$S films of 5000Å thickness
In Figure 4.4 one small diffraction peak at $2\theta = 27.76^0$ from (101) plane and one strong prominent diffraction peak at $2\theta = 46.26^0$ from (110) plane are observed for Cu$_2$S film of 7000Å thickness. These peaks near $27.76^0$ and $46.26^0$ are closely associated with covellite phase and no other characteristic phase corresponding to intermediate Cu$_x$S structure was observed. Hence it is noted that, after 5000 Å film thickness the XRD patterns of Cu$_2$S distinguishes itself from the hexagonal Cu$_2$S to CuS phases depending on film thickness. Because of sulphur enrichment with minor rearrangements of copper atoms, the Cu$_2$S changes its crystal structure from Cu$_2$S to CuS ie, phase transformation exists in the film prepared at higher thickness. Calculated ‘d’ spacing values are compared with standard JCPDS (78-0878) values for various thicknesses of Cu$_2$S film and are given in Table 4.1. The calculated values are in good agreement with the standard values.

![X-ray diffraction spectra of Cu$_2$S films of 7000Å thickness](image)

**Figure 4.4** X-ray diffraction spectra of Cu$_2$S films of 7000Å thickness
The interplanar distance has been calculated for 1000 Å and 7000 Å film thickness and is given in Table 4.2. It is found to be $a = 5.94$ Å, $c = 9.64$ Å for 1000 Å thickness which shows a slight contradiction with the values ($a = 3.95$ Å, $c = 6.78$ Å) reported for Cu$_2$S films. The interplanar distance calculated for 7000 Å film thickness is found to be $a = 2.99$ Å, $c = 13.36$ Å which agrees with the values of CuS Films ($a = 3.79$ Å, $c = 16.34$ Å) reported by Grozdanov and Najdoski (1995).

<table>
<thead>
<tr>
<th>Thickness (Å)</th>
<th>2θ values (°)</th>
<th>d – spacing values (Å)</th>
<th>hkl planes</th>
<th>Phase</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Standard</td>
<td>Observed</td>
<td>Standard</td>
<td>Observed</td>
</tr>
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<td></td>
<td>54.3</td>
<td>53.3</td>
<td>1.69</td>
<td>1.61</td>
</tr>
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<td>55.3</td>
<td>58.06</td>
<td>1.66</td>
<td>1.58</td>
</tr>
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<td>24.1</td>
<td>3.72</td>
<td>3.68</td>
</tr>
<tr>
<td></td>
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<td></td>
<td>54.3</td>
<td>54.1</td>
<td>1.63</td>
<td>1.62</td>
</tr>
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<td>23.5</td>
<td>24</td>
<td>3.72</td>
<td>3.67</td>
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<td>48.7</td>
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<td>1.63</td>
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</tr>
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<td>25.9</td>
<td>24.1</td>
<td>3.37</td>
<td>3.68</td>
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<td></td>
<td>47.4</td>
<td>46.3</td>
<td>1.90</td>
<td>1.89</td>
</tr>
</tbody>
</table>

Table 4.1 Comparison of observed XRD data of Cu$_2$S films with the JCPDS values
Deviation in the lattice parameters of this film is connected with lattice mismatch between the atoms in the plane of Cu$_2$S and the generation of strains within the film as reported by Dheepa et al (2004).

**Table 4.2 Cell parameters value for Cu$_2$S films of different thicknesses**

<table>
<thead>
<tr>
<th>Thickness (Å)</th>
<th>Cell parameter (Å)</th>
<th>Crystal System</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Standard</td>
<td>Observed</td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>3.95</td>
<td>5.94</td>
<td>Hexagonal</td>
</tr>
<tr>
<td></td>
<td>6.78</td>
<td>9.64</td>
<td></td>
</tr>
<tr>
<td>7000</td>
<td>3.79</td>
<td>2.99</td>
<td>Hexagonal</td>
</tr>
<tr>
<td></td>
<td>16.34</td>
<td>13.36</td>
<td></td>
</tr>
</tbody>
</table>

Grain size (D) of Cu$_2$S films are calculated using Equation (4.3) and the values are reported in Table 4.3. The calculated value shows that the grain size of lower thickness film is 207 nm, which is due to the growth of grains at the initial stage of film. But as thickness increases, the grain size of Cu$_2$S film decreases from 207 nm to 19.77nm, suggesting the formation of new grains over older ones as explained by Loptez Otero (1977) and Lalitha et al (2004). Moreover, sudden increase in the grain size from 19.77nm to 103.79 nm is observed, and it may be because these grains continued to grow into bigger islands that increase the grain size of the film.
Strain of Cu$_2$S films are calculated using Equation (4.4) and the values are given in Table 4.3. An important issue observed in the film is the increasing tensile strain that is accumulated during the deposition process with an increasing layer of film thickness. Moreover the strain of Cu$_2$S film decreases at higher thickness (Figure 4.6) which indicates that the deposited higher thickness film exhibits transition from tensile strain (5000 Å) to compressive strain (7000 Å).

**Figure 4.5 Variation of grain size with Cu$_2$S film thickness**

**Figure 4.6 Variation of strain with Cu$_2$S film thickness**
Since the crystallite of the as-deposited films were amorphous, they are not suitable for exact phase identification of the films. Therefore Raman spectroscopy was used to confirm the composition of the film. Figure 4.7 shows the Raman spectra of two different thicknesses of Cu$_2$S films. Raman studies of Cu$_2$S film indicates that peaks of 1000 Å and 7000 Å thickness are located at 472 cm$^{-1}$ and 474 cm$^{-1}$ respectively. It can be seen that the peak of 7000 Å thickness shifted to higher frequency from 472 to 474 cm$^{-1}$ probably indicative of being a non-stoichiometric sulphur rich phase (Shen-Yue Wang et al 2003, Bollero et al 2009). Hence it is inferred that lower thickness film was Cu$_2$S and transferred to CuS at higher thickness.

### Table 4.3 Structural parameters of Cu$_2$S film of different thicknesses

<table>
<thead>
<tr>
<th>Thickness (Å)</th>
<th>Grain size(D) (nm)</th>
<th>Strain (ε) $10^{-4}$ lines m$^{-2}$</th>
<th>Dislocation density (δ) $10^{14}$ lines/m$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>207.59</td>
<td>1.7439</td>
<td>23.2</td>
</tr>
<tr>
<td>3000</td>
<td>138.40</td>
<td>2.615</td>
<td>52.2</td>
</tr>
<tr>
<td>5000</td>
<td>19.773</td>
<td>18.309</td>
<td>0.255</td>
</tr>
<tr>
<td>7000</td>
<td>103.79</td>
<td>3.4879</td>
<td>92.8</td>
</tr>
</tbody>
</table>
From the analysis it is inferred that for the film deposited at lower thickness, the films presented mixed phases of Cu$_2$S and CuS, and for the higher thickness the main crystalline phase was just CuS. Moreover, the results indicate that the appropriate increase of thickness will enhance the crystalline growth of single CuS phase. Thus it is concluded that glass substrate must be maintained at subsequently higher temperature in order to obtain copper-rich phase and in contradiction if the substrate has a lower temperature during condensation, the phases obtained for the higher thickness, would be excess of sulphur (copper-poor phase) than that of copper as reported by Luminita Isac et al (2007).

### 4.6.3 Effects of Annealing

Annealing effects of Cu$_2$S thin films are performed in the presence of air for 1 hr at 100$^0$C and 200$^0$C. X-ray diffraction pattern of Cu$_2$S film of 1000 Å thickness annealed at 200$^0$C is shown in Figure 4.8. The close observations between as-deposited and annealed films show that the peaks of
the annealed films are improved with increasing annealing temperature. It is also observed that annealing the film at 200°C becomes polycrystalline in nature. The peaks obtained in XRD spectrum are compared with standard JCPDS values and are reported in Table 4.4 along with various planes of Cu$_2$S thin film. The planes (102), (108) and (100) indicate covellite (CuS) phase with hexagonal structure. Moreover (110) plane arrives at 2θ equal to 47.4°. The lattice constants obtained from the data are $a=3.05\,\text{Å}$, $c=14.41\,\text{Å}$ that agree well with CuS phase. It is relevant that as-deposited lower thickness Cu$_2$S film was high chalcocite (Cu$_2$S) phase however after annealing, the phase obtained were comparatively of high content of sulphur ie, covellite (CuS). Therefore it is supposed that lower thickness Cu$_2$S film annealed at 200°C, started to transform from Cu$_2$S to CuS phase (Nien and Chen 2009).

![X-ray diffraction pattern](image)

**Figure 4.8** X-ray diffraction spectra of Cu$_2$S film of 1000 Å thickness annealed at 200°C

Figure 4.9 shows the X-ray diffraction pattern of Cu$_2$S film of 7000 Å thickness annealed at 200°C. Analysis of the sample annealed at 200°C revealed that the diffraction angles are at 27.7°, 33.5°, 48.2° and 52.4°. The (hkl) planes responsible for the diffraction patterns are (002), (044), (103)
and (112). The peaks obtained in the XRD spectrum are compared with standard values and are reported in Table 4.4. It is thus observed that the planes obtained correspond to Cu$_2$S phase. From the results it is inferred that for the film deposited at higher thickness, the initially formed phase was CuS and after annealing the sample at 200$^\circ$C results in Cu$_2$S phase. When the samples are heat treated in air at 200$^\circ$C, they appear to lose sulphur and the stoichiometry becomes Cu$_x$S with $x$ increasing with annealing temperature. As $x$ increases the atomic percent of sulphur decreases, new phases are formed corresponding to changes in the solid state that lead to the most stable phase for each composition (Nair et al 1998). Therefore it is inferred that higher thickness Cu$_2$S film annealed at 200$^\circ$C, exhibit phase transformation from CuS to Cu$_2$S. The grain size calculated using Equation (4.4) for 7000 Å thickness annealed at 200$^\circ$C is found to be 180 nm which showed that there is an average increase in the grain size of the film when compared to as-deposited film.

Figure 4.9  X-ray diffraction pattern of Cu$_2$S film of 7000 Å thickness annealed at 200$^\circ$C
The structural studies revealed the change in the stoichiometric composition of copper sulfide compounds from chalcocite (Cu$_2$S) to covellite (CuS) for the sample deposited at higher thickness. From the result it can be concluded that lower thickness Cu$_2$S film annealed at higher temperature have strong intensity than at lower temperature and significant change in the crystalline phase was observed from Cu$_2$S to CuS. Further, higher thickness Cu$_2$S film annealed at higher temperature results in the formation of Cu$_2$S phase while the initially formed phase was CuS.