Structural and optical properties of CuS thin films deposited by Thermal co-evaporation

A K Sahoo, P Mohanta and A S Bhattacharyya

1Department of Metallurgical Engineering and Materials Science, Indian Institute of Technology Bombay, Mumbai - 400076, India
2Center for Research in Nano-Technology and Science, Indian Institute of Technology Bombay, Mumbai - 400076, India
3School for Engineering and Technologies, Central University of Jharkhand, Ranchi, 835205, India

E-mail: ashishkumarsahoo443@gmail.com

Abstract. Copper sulfide (CuS) thin films with thickness 100, 150 and 200 nm have been deposited on glass substrates by thermal co-evaporation of Copper and Sulphur. The effect of CuS film thickness on the structural and optical properties have investigated and discussed. Structural and optical investigations of the films were carried out by X-ray diffraction, atomic force microscopy, high-resolution transmission electron microscopy and UV spectroscopy. XRD and selected area electron diffraction conforms that polycrystalline in nature with hexagonal crystal structure. AFM studies revealed a smooth surface morphology with root mean-square roughness values increases from 24 nm to 42 nm as the film thickness increase from 100 nm to 200 nm. AFM image showed that grain size increases with thickness of film increases and good agreement with the calculated from full width half maximum of the X-ray diffraction peak using Scherrer’s formula and Williamson-Hall plot. The absorbance of the thin films were absorbed decreases with wavelength through UV-visible regions but showed a increasing in the near-infrared regions. The reflectance spectra also showed lower reflectance peak (25% to 32%) in visible region and high reflectance peak (49 % to 54 %) in near-infrared region. These high absorbance films made them for photo-thermal conversion of solar energy.

1. Introduction
The last few decades transition metal chalcogenides have been widely studied due to their excellent physical and chemical properties. Among them, copper sulfide is an important p-type semiconductor material which has great interest due to their importance in basic scientific research and potential applications for solid state solar cells, electro conductive coatings, lithium ion batteries, electrodes. The high absorbance of the films also used for photo-thermal conversion of solar energy. Generally copper sulfide can easily form a series of nonstoichiometric compounds, depends on the exact composition Cu$_x$S$_y$ (x = 1 - 2) with a crystal structure varying from orthogonal to hexagonal. Copper sulfide thin films have been synthesized by several growth methods such as thermal evaporation [2], sputtering, spray pyrolysis [1], chemical bath deposition [3,5-7,9], electro deposition [8], atomic layer deposition and electrochemical methods. In most of the reports, CuS films were deposited by chemical roots techniques using harmful chemical and long deposition time for film
preparation, these are main disadvantage of this technique. There are also few reports for the growth of CuS thin films by thermal co-evaporation of elemental constituents.

Here we report, the synthesis and characterization of CuS thin film have been deposited on glass substrates by thermal co-evaporation of copper and sulphur. The effect of CuS film thickness on the structural, morphological and optical properties have been investigated and discussed. The structural, morphological and optical properties of these samples were studied by using X-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM), atomic force microscopy (AFM) and UV–visible spectrophotometer.

2. Experimental
Copper sulfide based thin films were deposited on glass substrate by thermal co-evaporation of Cu and S with 99.999 % purity. A home-made thermal evaporation system was used for this purpose. The base vacuum was of ~5 x 10^-6 mbar. The distance between the source and substrate was of about 20 cm. Keeping all other parameter constant changing the evaporation time, different thicknesses of films such as 100, 150 and 200 nm were deposited on glass substrate at the substrate temperature of 250 °C. Quartz crystal thickness monitor was mounted close to the substrate, to estimate the thickness and deposition rate. All these films thickness were also measured by surface profile meter (model Ambios XP-2). The effect of CuS film thicknesses on the structural, morphology and optical properties were investigated. Structural and composition analysis of these films were performed using a X’Pert PRO PANalytical X-ray powder diffractometer with CuKα radiation (λ = 1.54056 Å). The surface morphology of the grown films were studied by using AFM carried out in a contact mode with silicon nitride probes using Digital Instruments Nanoscope IV multimode SPM. Absorption and reflectance were carried out on Perkin-Elmer Lambda-950 UV – visible spectrophotometer. A JEOL model JEM-2100F HRTEM operated at 200 kV was used to record the bright field images and selected area electron diffraction pattern (SAED). For the TEM analysis, the CuS film was scratched by using sharp bleat and put into the beaker containing de-ionized water. The CuS film was found completely floating on the surface of de-ionized water. Then this film was transferred to carbon coated copper grid.

3. Results and Discussion
X-ray diffraction pattern have been carried out (see figure 1) for deposited films with different thickness of 100, 150 and 200 nm. It shows that a broad humps at 22.5° which corresponding to glass

![Figure 1](image-url)

**Figure 1.** (a) X-ray diffraction patterns for CuS thin films of different thickness, (b) Bright field TEM image of 200 nm film and corresponding SAED pattern.
substrate. The intensities of (101), (102), (006), (105) and (110) XRD peaks are comparable with JCPDS (780876) (figure 1). We are not getting higher intensity peaks of CuS covellite phase in case of lower thickness films and additionally minor presence of CuS phase. Thus, XRD result conform that deposited CuS films are polycrystalline and hexagonal. On the other hand, the crystalline size was also calculated from the full width half maximum (FWHM) of all these peaks using the Debye–Scherrer formula (1).

\[ t = \frac{0.9 \lambda}{\beta \cos \theta} \]  

(1)

where, \( \lambda \) is the X-ray wave length and \( \theta \) is the diffraction Bragg angle. The calculated crystallite size ranged from about 28, 32 and 54 nm with increase the film thickness from 100 to 200 nm. We also used another procedure based on the Williamson–Hall equation to calculate strain and crystallite size of all deposited films. The Williamson–Hall equation (2) is

\[ \beta \cos \theta = k \lambda (t)^{-1} + 2 \varepsilon \sin \theta \]  

(2)

where, \( \beta \) is the FWHM of the XRD all peaks, \( K \) is Scherrer constant, \( t \) is the crystalline size, \( \lambda \) is the wave length of the X-ray, \( \varepsilon \) is the lattice strain, and \( \theta \) is the Bragg angle. In this method, \( \beta \cos \theta \) is plotted against \( 2 \sin \theta \). Using a linear extrapolation to this plot, the intercept gives the crystallite size and slope gives the strain. These crystallite values are comparable with the crystalline size which is calculated in Debye–Scherrer (see table 1). In order to study the crystal structure, transmission electron microscopy analysis was carried out on the 100 nm thick film. The electron diffraction pattern represent that the film is polycrystalline and the diffraction rings indexed as (101), (006), (105), (110), (202) (In figure 1(b)), which are properly match with the hexagonal covellite CuS film. This is in good agreement with the XRD result. Thus, TEM and XRD result conform that deposited films are hexagonal covellite CuS film.

![AFM images of CuS films of different thickness](image)

**Figure 2.** AFM images of CuS films of different thickness (a) 100 nm and (b) 200 nm.

AFM image have been carried out for the deposited CuS films of different thickness from 100 to 200 nm (Figure 2). It is clearly seen that grain size increases, values ranged from 32 nm to 61 nm for film with thickness increase from 100 nm to 200 nm, respectively. AFM image showed that grain size increases with thickness of film increases and good agreement with the calculated crystallite size from full width half maximum of the the XRD peak using Scherrer’s formula and Williamson-Hall plot (see table 1). Also we observed that the grain size values obtained from AFM images were slightly larger than those calculated from the XRD measurement. AFM studies also reveal a smooth surface morphology with root mean-square roughness values increases from 24 nm to 42 nm as the film thickness increase from 100 nm to 200 nm (see table 1).
Table 1. Comparison between crystalline size calculated from XRD using Debye–Scherrer formula, Williamson–Hall plot and AFM image for different thickness.

| Film thickness (nm) | Debye–Scherrer crystalline size (nm) | Williamson–Hall crystalline size (nm) | Particle size from AFM (nm) |
|---------------------|--------------------------------------|---------------------------------------|-----------------------------|
| 100                 | 28                                   | 24                                    | 31                          |
| 150                 | 32                                   | 29                                    | 37                          |
| 200                 | 54                                   | 56                                    | 58                          |

Figure 3. Optical (a) absorption (b) reflectance for deposited CuS thin films.

The optical absorption and reflectance measurement were carried out for all the deposited films (see figure 3). The absorbance of the thin films were absorbed decreases with wavelength through UV-visible regions but showed a increasing in the near-infrared regions, clearly absolved in case of 200 nm thick CuS film. The reflectance spectra also showed two prominent peak in all these deposited films, lower reflectance peak (~ 25 % to 32 %) in visible region and high reflectance peak (~ 49 % to 54 %) in near-infrared region.

4. Conclusions
CuS thin films with hexagonal have been successfully deposited on glass substrate by thermal co-evaporation of copper and sulphur. XRD and TEM results confirm that deposited films are hexagonal covellite CuS films. The increased in crystallite size are absorbed as film thickness increases from 100 nm to 200 nm and conformed from XRD and AFM studies. The deposited films also exhibit good optical properties, which make it for application in photo-thermal conversion of solar energy.

References
[1] Majhi S K, Mukherjee N, Dutta A K, Srivastava D N, Paul P, Karmakar B, Mondal A and Adhikary B 2011 Mater. Chem. Phys. 130 392
[2] Bollero A, Grossberg M, Asenjo B and Gutelerrez M T 2009 Surf. Coat. Technol. 204 593
[3] Hu H and Nair P K 1996 Surf. Coat. Technol. 81 183
[4] Yuan K D, Wu J J, Liu M L, Zhang L L and Xu F F 2008 Appl. Phys. Lett. 93 132106
[5] Güneri E, Kariper A 2012 J. Alloys Compd. 516 20
[6] Castillo S J, Apolinar-Iribe A, León D A and Ruvalcaba-Cornejo C 2011 J. Optoelectron. Adv. Mater. 13 1258
[7] Rodríguez-Lacanzo Y., Martínez H, Calixto-Rodríguez M and Rodríguez A N 2009 Thin Solid Films 517 5951
[8] Chen Y, Davoise C, Tarascon J M and Guery C 2012 J. Mater. Chem. 22 5295
[9] Xin M, Li K and Wang H 2009 Appl. Surf. Sci. 256 1436