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# Structural, compositional, and optical properties of electrochemically deposited $Cu_2S$ thin films

**B. Bharathi[1], S.Thanikaikarasan[1]* and K.Ramesh[1]**

**[1]Centre for Scientific and Applied Research, School of Basic Engineering and Sciences, PSN College of Engineering and Technology, Tirunelveli – 627 152, Tamil Nadu, India.**

***Corres. author: s_thanikai@rediffmail.com**

**Abstract:** Thin films of copper sulphide have been deposited on indium doped tin oxide coated glass substrates. X-ray diffraction analysis revealed that the deposited films possess polycrystalline in nature. Optical absorption analysis showed that the deposited films possess band gap value around 2.35 eV.
**Keywords:** Metal Chalcogenides, $Cu_2S$; Thin Films, Electrodeposition, X-ray diffraction.

## 1. Introduction

Copper Sulfide ($Cu_2S$) is a p-type semiconductor with a band gap value in the range between 1.2 and 1.8 eV which make them interesting for solar energy conversion [1]. Copper Sulfide is found to exist in five stable phases at room temperature such as CuS in ''S-rich region'' and $Cu_{1.75}S$, $Cu_{1.8}S$, $Cu_{1.95}S$ and $Cu_2S$ in the ''Cu-rich region'' [2]. $Cu_2S$ thin films are usually crystallized in cubic structure (JCPDS ICDD 2003, File No: 65-2980) with lattice constants (a = b = c = 5.600 Å).Numerous techniques have been used to obtain $Cu_2S$ thin films: hydrothermal synthesis [3], atomic layer deposition [4], spray pyrolysis [5], chemical bath deposition [6]. Electrodeposition technique provides many advantages over vacuum and other processes, such as low temperature growth, control of film thickness and morphology, potentially low capital cost, etc., [7]. In this paper, thin films of $Cu_2S$ have been prepared on indium doped tin oxide (ITO) coated glass substrates using electrodeposition technique. Deposited films are subjected to X-ray diffraction, Scanning electron microscopy, Energy dispersive analysis by X-rays and Optical absorption techniques, respectively. The experimental observations are discussed in detail.

### 1.1. Experimental Details

$Cu_2S$ thin films were deposited on ITO substrate (sheet resistance 20Ω/ sq) from an aqueous electrolytic bath containing 0.05M $CuSO_4$ and 0.05M $Na_2S_2O_3$. The electrochemical experiments were carried out using a Potentiostat/Galvanostat (BioLogic-SP50, France) employing three electrode configuration with ITO substrate as working electrode, graphite plate as counter electrode and saturated calomel electrode (SCE) as reference electrode, respectively. The bath temperature and solution pH were maintained at 70°C and 2.0 ± 0.5, respectively. Deposition potential was fixed as -1000 mV Vs SCE using cyclic voltammetry. Thickness of the deposited films was estimated using weight difference method. X-ray diffraction data of the deposited films was

recorded using an X-ray diffractometer (X'PERT PRO PANalytical X-ray diffractometer, Netherland). Surface morphology and film composition were analyzed using scanning electron microscope and Energy dispersive analysis by X-rays (Philips, Model XL 30). Optical absorption analysis of the deposited films was recorded using an UV-Vis-NIR spectrophotometer (Shimadzu Model 2600, Singapore).

## 2. Results and Discussion

### 2.1. Film Thickness

Thickness of the deposited films is measured using weight difference method. Thickness value of films obtained at bath temperature 75°C under various deposition time is given in Table 1. It is observed from table that value of film thickness increases with deposition time and reaches its maximum value at a deposition time of 30 minutes. Further increasing deposition time thickness value decreases which is not given in table. Hence, films with maximum thickness value are obtained at bath temperature around 75°C at a deposition time of 30 minutes.

### 2.2. Structural Properties

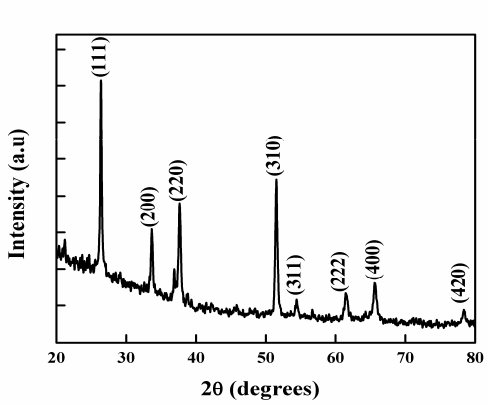


**Figure 1.** XRD pattern of $Cu_2S$ thin films obtained at bath temperature around 70°C

X-ray diffraction pattern of $Cu_2S$ thin films deposited at bath temperature 70 ºC is shown in Fig.1. XRD patterns revealed that the deposited films possess polycrystalline nature with cubic structure with lattice constants (a = b = c = 5.600 Å). The different peaks in the diffractogram are indexed and the corresponding values of interplanar spacing ''d'' is calculated and compared with standard JCPDS ICDD file for cubic $Cu_2S$ [8]. The height of (111) peak is found to be higher than all other peaks in the XRD pattern indicated that the crystallites are preferentially oriented along (111) plane. The value of crystallite size is determined using Debye Scherrer formula which is given in Eq.(1) [7]

$$D = \frac{0.9\lambda}{\beta \cos\theta} \qquad (1)$$

where $\lambda$ is the wavelength of $CuK_\alpha$ target used ($\lambda$=1.5406 Å), $\beta$ is full width at half maximum of the peak position in radian, $\theta$ is Bragg's diffraction angle at peak position in degree. The structural parameters such as crystallite size, strain and dislocation density are calculated for $Cu_2S$ films and given in Table1. It is observed from Table 1, we have concluded that the value of crystallite size is found to increase, whereas the value of strain and dislocation density are found to decrease while increasing the deposition time from 10 to 30 minutes, thereafter both them changes vice versa.

**Table 1.** Variation of structural parameters **with deposition time for $Cu_2S$ thin films**

| Sl.No | Deposition Time (minutes) | Film Thickness (nm) | Crystallite Size, D (nm) | Strain, ε ($lines^{-2}/m^4$) x$10^{-3}$ | Dislocation Density, δ ($lines/m^2$)x$10^{14}$ |
|---|---|---|---|---|---|
| 1. | 10 | 450 | 35.56 | 38.52 | 79.08 |
| 2. | 20 | 580 | 41.13 | 45.13 | 59.11 |
| 3. | 30 | 730 | 52.39 | 51.96 | 36.43 |

### 2.3. Morphological, Compositional, Optical Properties

SEM image of $Cu_2S$ thin films prepared at 70 ºC bath temperature is shown in Fig.2**.** It is observed from Figure number of crystallites are joined together to form grain as shown in Fig.2. The non-uniform and undefined grain boundaries with different sizes are observed. The atomic percentage (Cu:S) of $Cu_2S$ thin films obtained at optimized condition is found to be (71.21 : 28.79) indicating approximate stoichiometry ratio (2.473:1) of the deposited films.

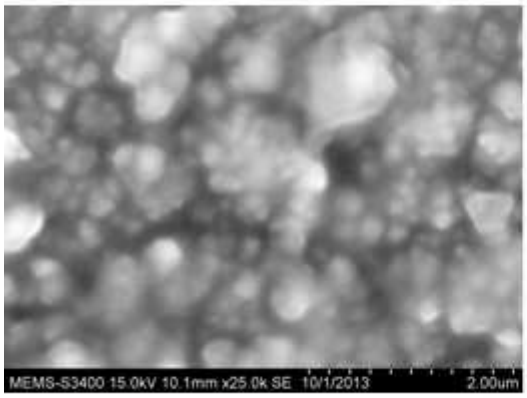


**Figure 2.** SEM image of $Cu_2S$ thin films obtained at bath temperature around 70°C

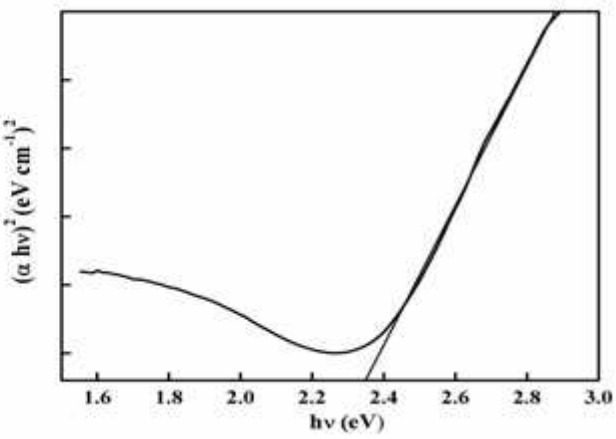


**Figure 3.** Tauc's plot of $Cu_2S$ thin films prepared bath temperature around 70°C

The plot of $(h\upsilon)$ versus $(\alpha h\upsilon)^2$ for $Cu_2S$ thin films obtained at optimized condition is shown in Fig.3. Extrapolation of linear portion of the graph to the energy $(h\upsilon)$ axis gives band gap energy of the material. The band gap value of the deposited film is found to be 2.35 eV.

## 3. Conclusions

Electrodeposition of $Cu_2S$ thin films have been carried out on ITO coated substrates. XRD patterns revealed that the deposited films were found to exhibit cubic structure with preferential orientation along (002) plane. Structural parameters were found to exhibit monotonic variation with deposition time and film thickness. Optical absorption analysis showed that the band gap value of the deposited film was found to be 2.35 eV.

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