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EFFECT OF DEPOSITION PERIOD AND BATH TEMPERATURE ON THE PROPERTIES OF ELECTRODEPOSITED Cu_4SnS_4 FILMS

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ABSTRACT

Cu_4SnS_4 thin films were prepared by electrodeposition method in aqueous solutions. The effect of various bath temperatures (25, 35, 45 °C) and deposition periods (15, 30, 45 min) on growth of these films was reported. The structure and morphology characteristics of thin films of Cu_4SnS_4 grown on indium tin oxide glass substrates were investigated by X-ray diffraction and atomic force microscopy techniques. The optical properties were measured to determine the transition type and band gap value. The thin films produced were found to be polycrystalline with orthorhombic structure. The X-ray diffraction data showed that the most prominent peak at $2\theta = 30.2°$ which belongs to (221) plane of Cu_4SnS_4. The atomic force microscopy image indicated that the films deposited at 25 °C for 45 min exhibited smaller crystal size with uniformly distributed on indium tin oxide substrates. Photoelectrochemical test shows a p-type conduction mechanism. The bandgap was found to be 1.68 eV with direct transition.

INTRODUCTION

Recently, ternary compounds have received much attention in the field of solar cells owing to their interesting properties of band gap and lattice constant modulation by composition. There are many techniques for preparing thin films such as chemical bath deposition [1], vacuum evaporation [2], electrodeposition [3], molecular beam epitaxy [4], close spaced sublimation [5], thermal evaporation [6], spray pyrolysis [7], sputter deposition [8], metal organic chemical vapor deposition [9] and plasma-enhanced chemical vapor deposition [10]. The preparation of thin films by the electrodeposition is currently attracting a great deal of attention, as the method is simple, inexpensive, no requirement of sophisticated instruments and possibility for large-scale production. At present, electrodeposition has been proved as a suitable method of preparing binary compounds like CdS [11], ZnS [12], CdSe [13], PbS [14], SnS [15], SnSe [16], Cu_2S [17] and ternary semiconductors such as $CdIn_2S_4$ [18], $SnS_{0.5}Se_{0.5}$ [19], $CuInS_2$ [20], $CuInSe_2$ [21], ZnCuTe [22].

In this work, we investigated the influence of the various bath temperatures (25, 35 and 45 °C) and deposition periods (15, 30 and 45 min) on structural, morphological and

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optical properties of electrodeposited Cu_4SnS_4 films. The structure of the film was studied by XRD. The morphology and optical absorption properties were determined by using atomic force microscope and UV-Visible Spectrophotometer, respectively.

METHODOLOGY

All the chemicals used for the deposition were analytical grade. It includes copper sulfate ($CuSO_4$), tin chloride ($SnCl_2$), sodium thiosulfate ($Na_2S_2O_3$) and hydrochloric acid (HCl). All the solutions were prepared in deionised water (Alpha-Q Millipore). The deposition bath contained 0.01 M of $CuSO_4$, $SnCl_2$ and $Na_2S_2O_3$.The pH of the bath was adjusted to 1.5 by using HCl. The electrodeposition was carried out in a conventional three-electrode cell. The indium-doped tin oxide (ITO) was used as the working electrode. The ITO was cleaned ultrasonically in ethanol and distilled water before use. The counter electrode and reference electrode was made from platinum wire and Ag/AgCl, respectively. The EG&G Princeton Applied Research potentiostat driven by a software model 270 Electrochemical Analysis System was used to control electrodeposition process and to monitor current and voltage profiles. In order to determine the optimum condition for the deposition process, the films were deposited at –600 mV versus Ag/AgCl under different bath temperatures (25, 35 and 45 °C) and deposition periods (15, 30 and 45 min). After deposition, the deposited films were tested for adhesion by subjecting it to a steady stream of distilled water. The deposited films were kept for further analysis.

X-ray diffraction analysis was carried out, using a Philips PM 11730 diffractometer for the 2θ ranging from 25° to 60° with CuK_α (λ=0.15418 nm) radiation. Topography was measured by using an atomic force microscopy (Quesant Instrument Corporation, Q-Scope 250) operating in contact mode, with a commercial Si_3N_4 cantilever. Photoelectrochemical (PEC) experiments were performed using a $[Fe(CN)_6]^{3-}$ /$[Fe(CN)_6]^{4-}$ redox system, by performing linear sweep voltammetry between -500 to -1000 mV. The sequence of constant illumination, chopped illumination and dark period were performed on the PEC cell to study the effect on photoactivity behavior. A halogen lamp (300 W, 120 V) was used for illuminating the electrode. Optical absorption study was carried out using the Perkin Elmer UV/Vis Lambda 20 Spectrophotometer. The film-coated indium doped tin oxide glass was placed across the sample radiation pathway while the uncoated ITO glass was put across the reference path. From the analyses of absorption spectra, the band gap energy was determined.

RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction patterns of films deposited at –600 mV versus Ag/AgCl under room temperature for various deposition periods. There are two peaks, observed at the diffraction angles of 27.6°and 38.8° for the films deposited for 15 min of deposition period. These two peaks were assigned to (002) and (222) plane, respectively. Meanwhile, the films prepared at 30 min showed five peaks at 2θ = 30.3°, 35.1°, 38.7°, 45.3° and 50.5° corresponding to interplanar distances of 2.96, 2.54, 2.33,

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2.00 and 1.80 Å respectively. However, the films prepared at longer deposition period (45 min) showed only four peaks at 2θ = 30.3°, 35.1°, 43.3° and 50.4° corresponding to interplanar distances of 2.96, 2.54, 2.07 and 1.80 Å, respectively. All these peaks are related to the compound of Cu_4SnS_4 (Reference code: 010710129) of orthorhombic structure. (a =13.5580 Å, b = 7.6810 Å, c =6.4120Å, α = β = γ =90°). The strongest peak occurred at 2θ =30.1° with d=2.96 Å. It indicates that the preferred orientation lie along the (221) plane for electrodeposited Cu_4SnS_4 thin films. The appearance of copper sulfide (Reference code: 000653556) was detected at 2θ = 31.5° for the films deposited at 30 min, probably due to the Cu_4SnS_4 formation reaction is not complete during electrodepositon process.

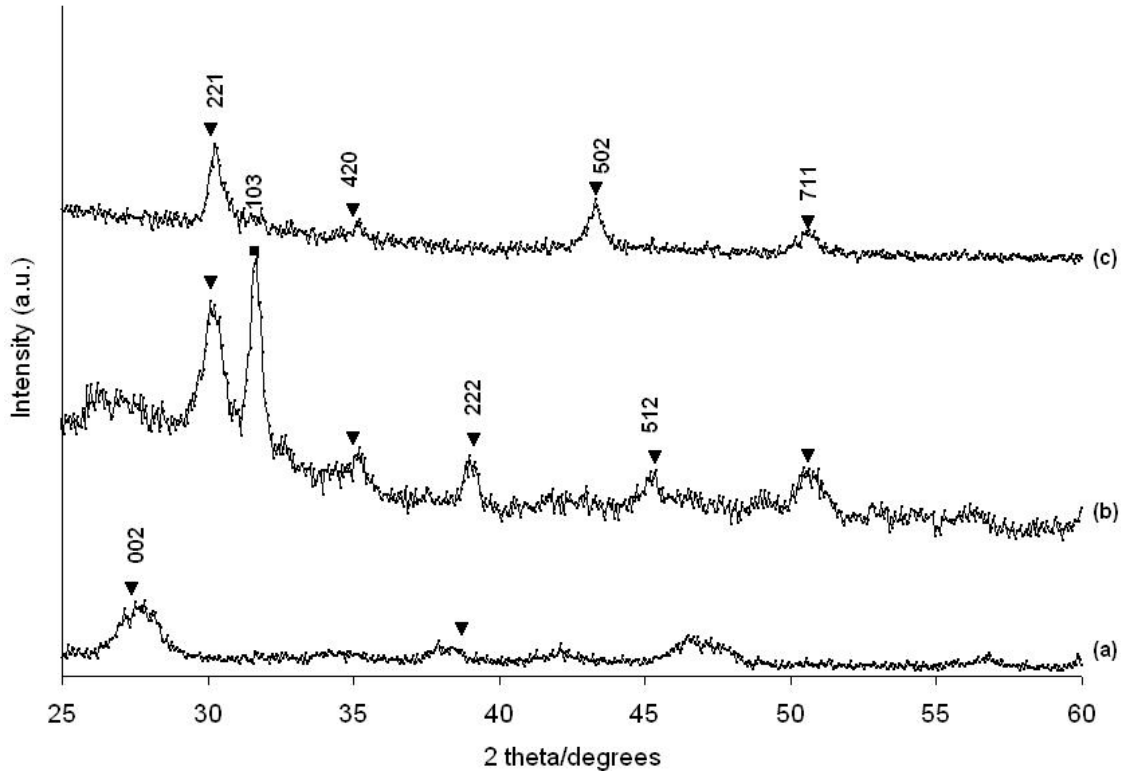

Figure 1: X-ray diffraction patterns of Cu_4SnS_4 thin films deposited at various deposition periods (a) 15 min (b) 30 min (c) 45 min [Cu_4SnS_4 (▼), CuS (■)]

The Cu_4SnS_4 thin film was morphologically characterized by using atomic force microscopy. Figure 2 shows the three-dimensional representation of a 20 μm X 20 μm area of the Cu_4SnS_4 thin film deposited at various deposition periods. It is indicated that the deposited thin films are crystalline and their grain size varies with the different deposition periods. The grain size decreases as the deposition period was increased from 15 min to 45 min. The average grain size of around 2.5 μm and 1 μm were observed on the film prepared at 15 min (Figure 2a) and 45 min (Figure 2c) , respectively.

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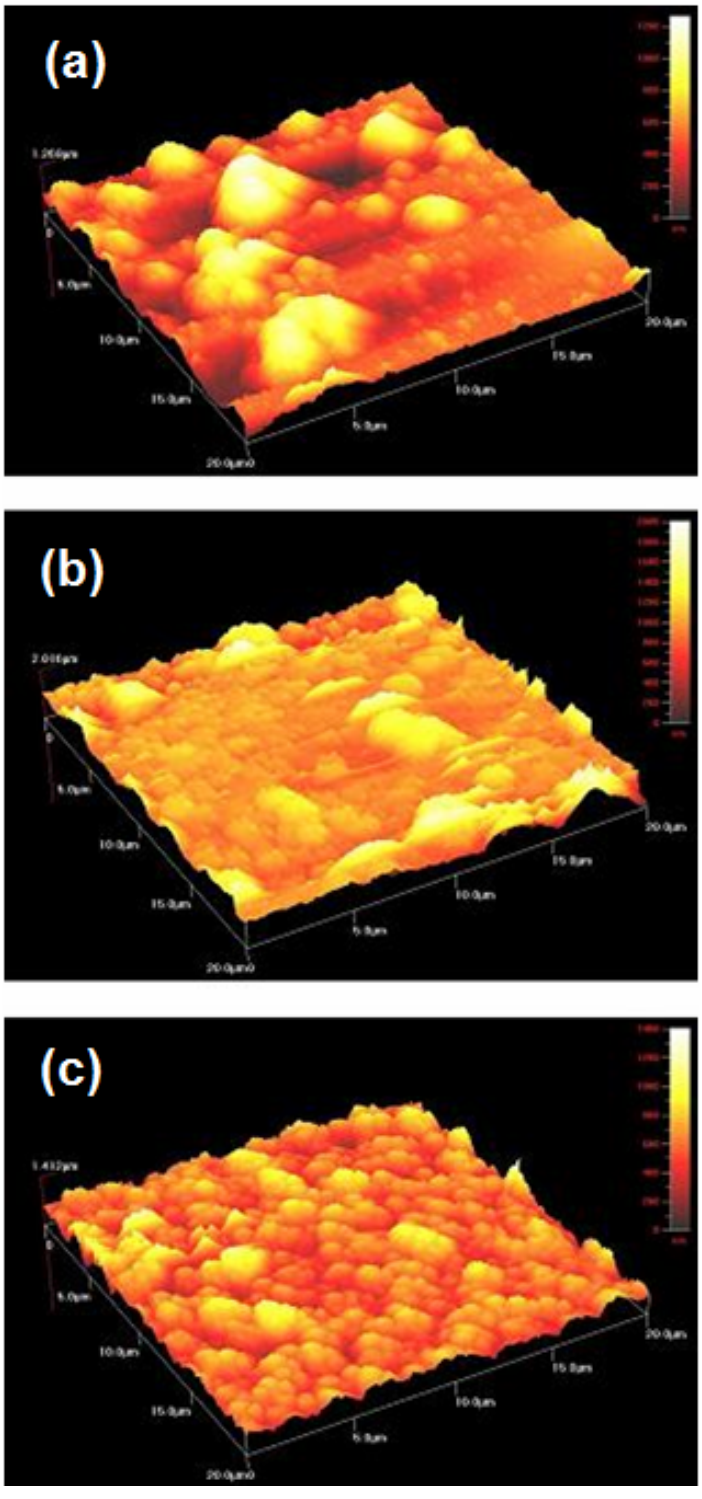

Figure 2: Atomic force microscopy images of Cu_4SnS_4 thin films deposited at various deposition periods (a) 15 min (b) 30 min (c) 45 min

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The film thickness and root mean square roughness (RMS) are observed by using atomic force microscopy. The results indicated an increase in the film thickness as the deposition time was increased from 15 min (1269 nm) to 30 min (2016 nm). The increase in deposition time allows more material to be deposited onto the substrate and thicker films to be formed. However, the film thickness decreased to 1412 nm when the deposition time was extended to 45 min. The RMS roughness values of the surfaces were found to increase from 149 nm to 244 nm as the deposition time was increased from 15 to 30 min. However, when the deposition period was increased to 45 min, the decrease in RMS values was obtained. It could be noted that the surface roughness decreases with decreasing films thickness.

Figure 3 shows the difference between the photocurrent (I_p) and darkcurrent (I_d) versus potential for the deposited films in contact with Fe^{2+}/Fe^{3+} solution. The current change with illumination confirms that the films possess semiconducting properties. The films prepared at 45 min showed the highest photoresponse activity as compared with other deposition periods. This could be due to sufficient material deposited onto surface of substrate. The photocurrent occurs on the negative potential indicates that the films prepared are of p-type semiconductor.

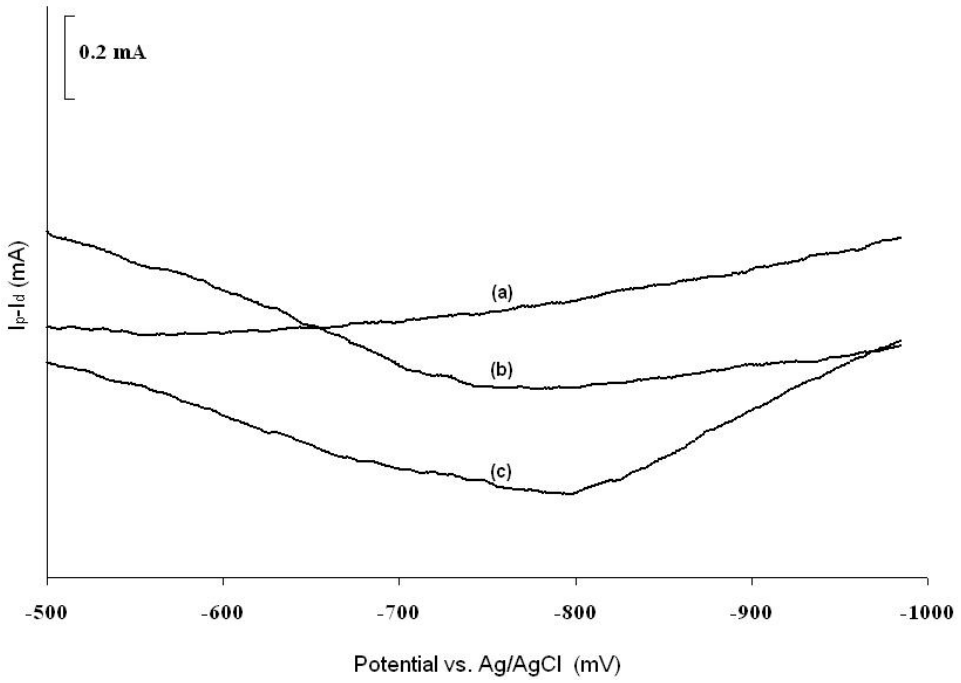

Figure 3: Difference between photocurrent and darkcurrent (I_p-I_d) of Cu_4SnS_4 thin film deposited at 25 °C under various deposition periods. (a) 45 min (b) 30 min (c) 15 min

Figure 4 shows the X-ray diffraction patterns for the films deposited for 45 min under various bath temperatures. There are four peaks at 2θ =30.2°, 35.4.°, 43.5° and 50.7°

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were detected for films deposited at 25°C. The corresponding interplanar distances are well in agreement with JCPDS data (Reference code: 010710129) of 0.296, 0.255, 0.207 and 0.180 nm which attributed to the (221), (420), (502) and (711) planes, respectively. All these peaks are related to the compound of Cu_4SnS_4 of orthorhombic structure. On the other hand, raising the bath temperature further to 35 °C and 45 °C, resulted in the appearance of (222) plane could be observed in XRD patterns. The most prominent peak obtained at 2θ =30.2° corresponding to interplanar distance of 0.296 nm. The presence of copper sulfide (Reference code: 000653556) was detected at 2θ =31.4° for the film deposited at higher bath temperature (35 °C and 45 °C). This is probably due to the fact that these temperatures are unfavorable to produce Cu_4SnS_4 thin films.

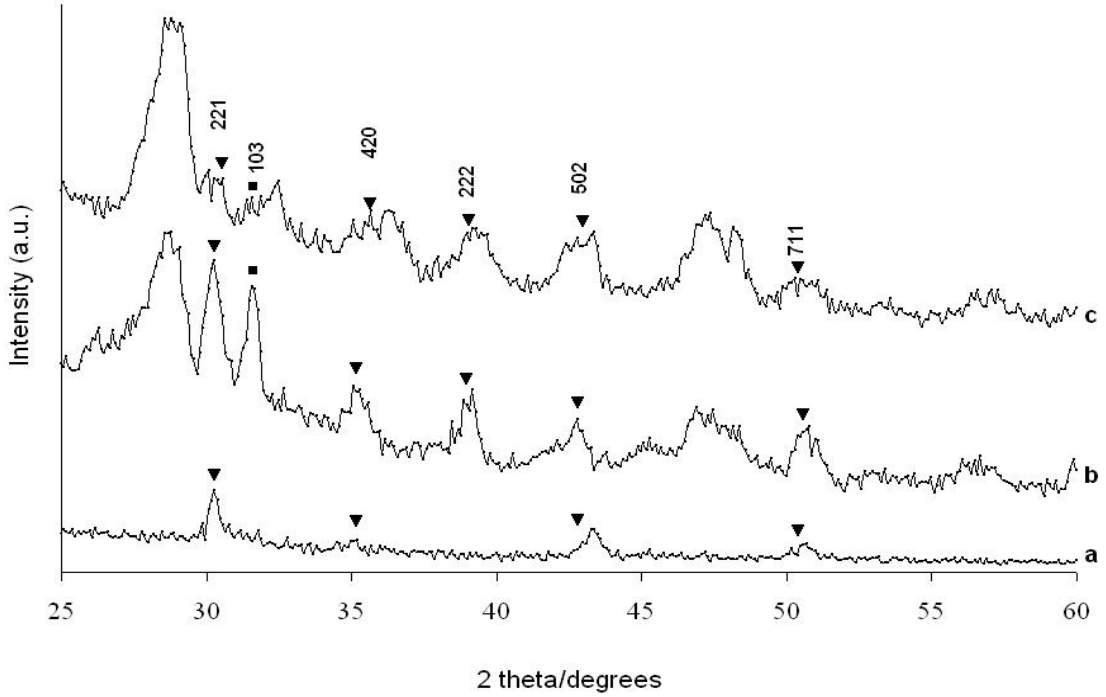

Figure 4: X-ray diffraction patterns of Cu_4SnS_4 thin films deposited at various bath temperatures (a) 25 °C (b) 35 °C (c) 45 °C [Cu_4SnS_4 (▼), CuS (■)]

Figure 5 shows the three-dimensional representation of a 20 μm X 20 μm area of the Cu_4SnS_4 thin films deposited at different bath temperatures. The AFM images reveal that these films have a granular morphology. The films deposited at 25 °C showed a smooth, uniform surface and well cover the glass substrate (Figure 5a). The average sizes of smaller grains are found to be in the range between 1 um. With the increase of the bath temperature, the grain size of the thin films becomes larger. Several small grains are found to agglomerate and form a few larger grains. The average grain sizes are around 2 um as can be seen from the Figure 5 b, c. The bath temperature plays an important role in the electrodeposition and properties of thin films. The film deposited

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at 25 °C, yielding thinner (0.8 um) deposits on indium tin oxide glass substrates. However, at higher temperature (35 and 45 °C), the thicker films (2 um) may have resulted because the deposition rate usually increases with deposition temperature.

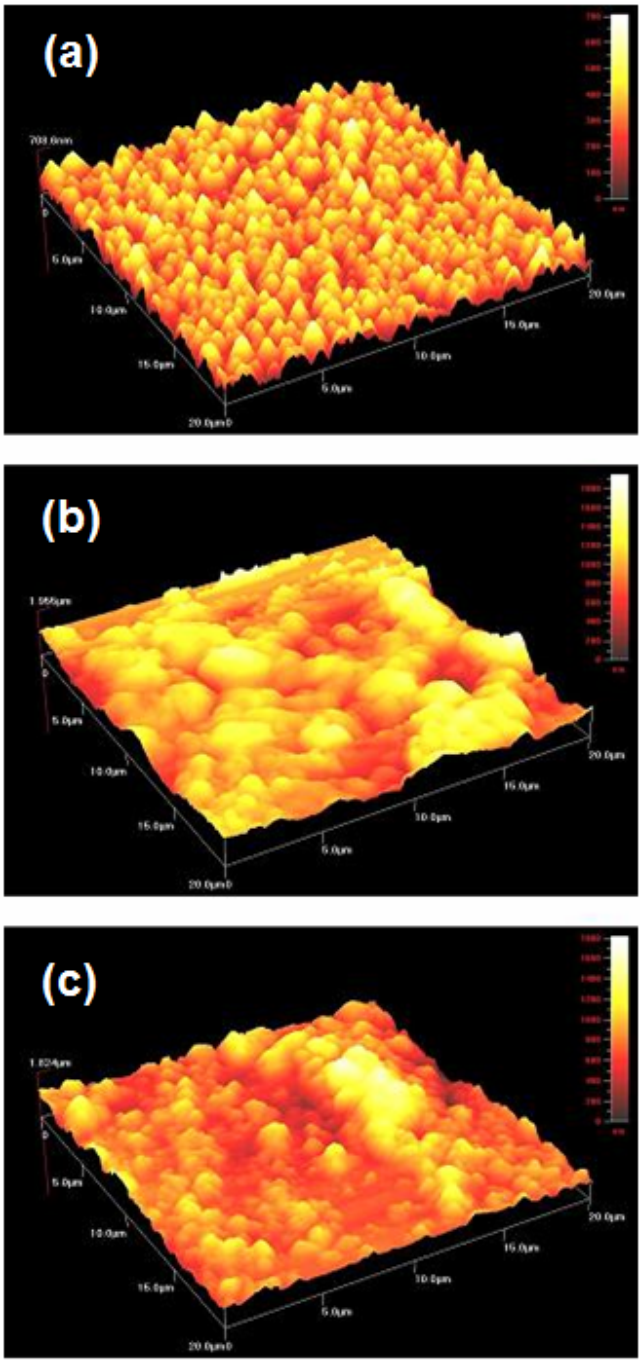

Figure 5: Atomic force microscopy images of Cu_4SnS_4 thin films deposited for 45 min at various bath temperatures (a) 25 °C (b) 35 °C (c) 45 °C

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Figure 6 shows the difference between the photocurrent (I_p) and darkcurrent (I_d) versus potential for the films prepared at 45 min under different bath temperatures in contact with Fe^{2+}/Fe^{3+} solution. The current change with illumination confirms that the films possess semiconducting properties. The films prepared at 25 °C showed the highest photoresponse activity as compared with other bath temperature. This could be due to sufficient material deposited onto surface of substrate. The photocurrent occurs on the negative potential indicates that the films prepared are of p-type semiconductor. This indicates that the majority carriers generated are holes.

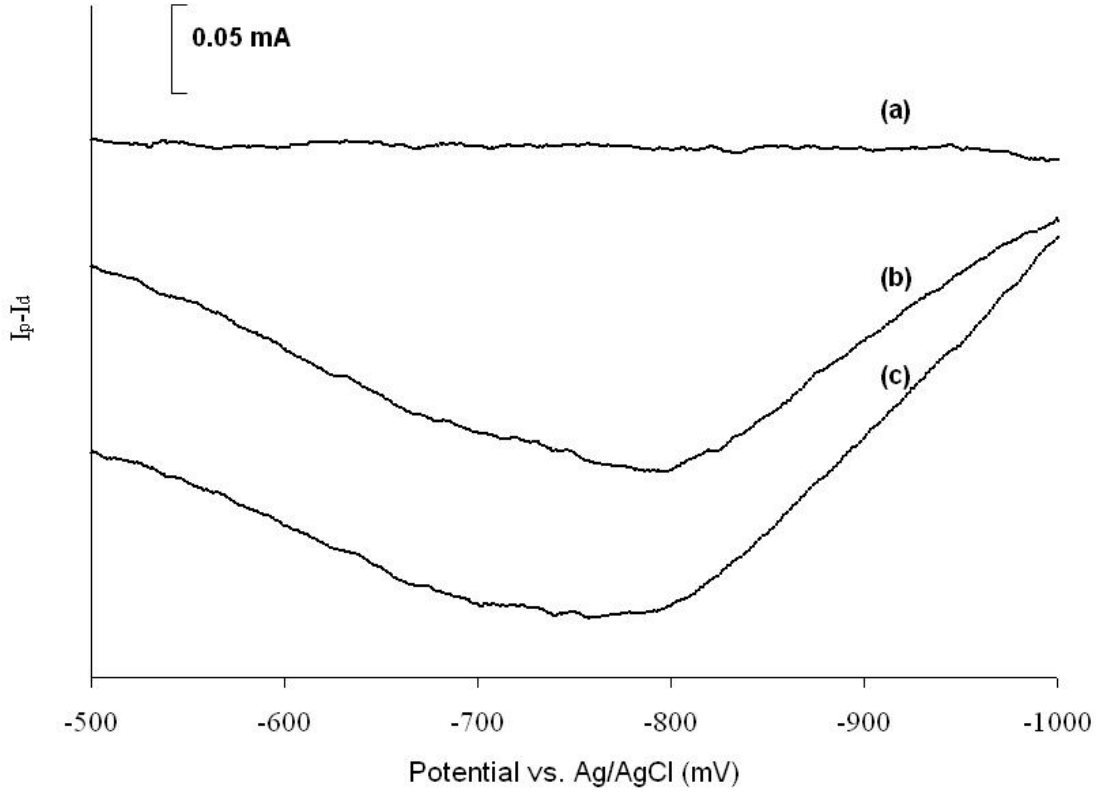

Figure 6: Difference between photocurrent and darkcurrent (I_p-I_d) of Cu_4SnS_4 thin film deposited for 45 min at various bath temperatures (a) 25 °C (b) 35 °C (c) 45 °C

The optical absorption spectra of Cu_4SnS_4 thin films deposited onto indium tin oxide glass substrate were studied at 25 °C for 45 min in the range of wavelengths 300 –800 nm. The plot of optical absorption versus wavelength is as shown in Figure 7. The films show a gradually increasing absorbance throughout the visible region, which make it possible for this material to be used in a photoelectrochemical cell.

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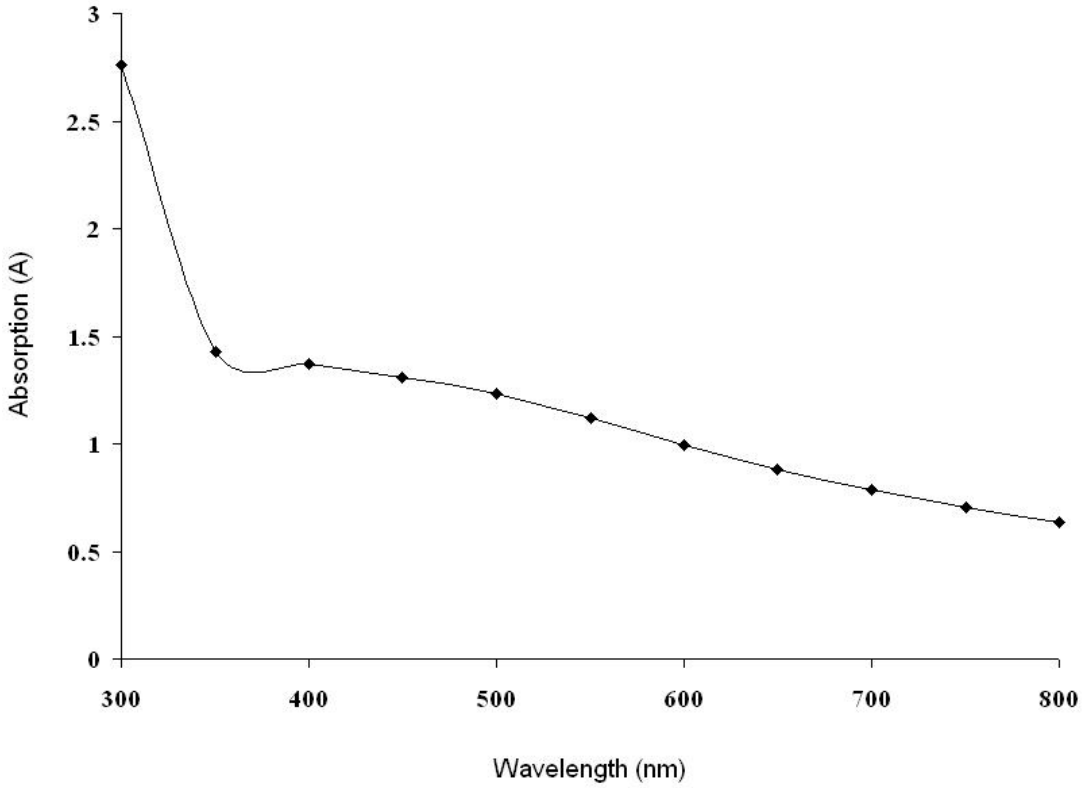

Figure 7: The typical optical absorbance versus wavelength of Cu_4SnS_4 thin films deposited at 25 °C for 45 min

Band gap energy and transition type can be derived from mathematical treatment of data obtained from optical absorbance versus wavelength with Stern relationship of near-edge absorption:

$$A = \frac{[k(h\nu - E_g)^{n/2}}{h\nu} \quad (1)$$

where v is the frequency, h is the Planck's constant, k equals a constant while n carries the value of either 1 or 4. The value of n is 1 and 4 for the direct transition and indirect transition, respectively. The band gap (E_g) could be obtained from a straight line plot of $(Ahv)^{2/n}$ as a function of hv. Extrapolation of the line to the base line, where the value of $(Ahv)^{2/n}$ is zero, will give E_g. The $(Ahv)^{1/2}$ versus hv plot is a straight line (Figure 8) indicating that the energy band gap of Cu_4SnS_4 is direct and intercept on the hv axis yield a band gap of 1.68 eV for the film deposited at 25 °C for 45 min.

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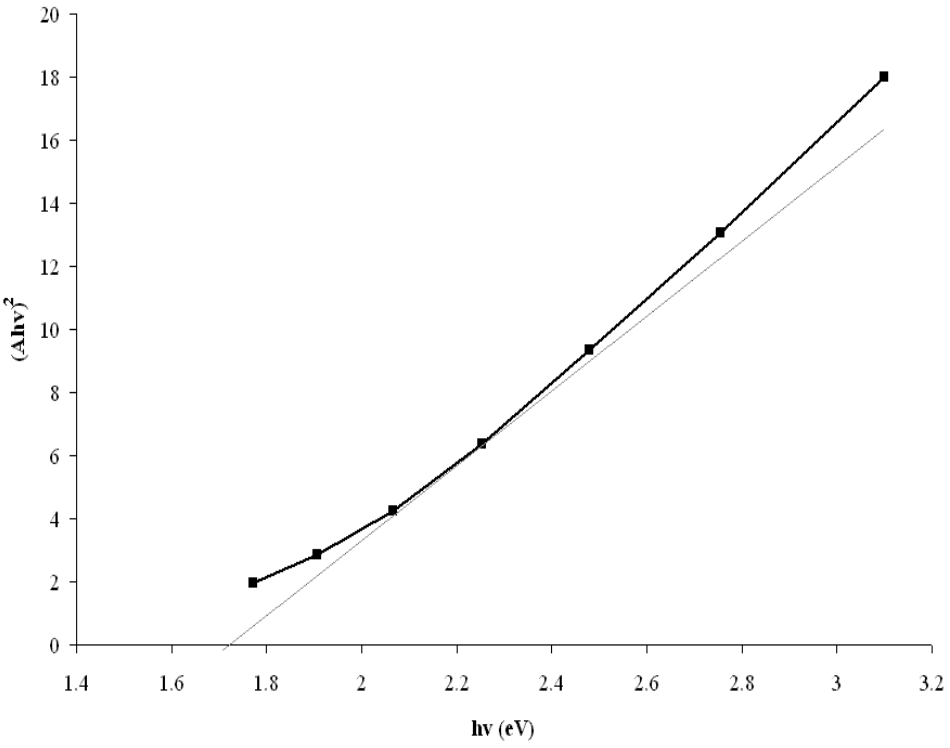

Figure 8: Plot of $(Ahv)^{2/n}$ versus hv when n=4 for Cu_4SnS_4 thin films deposited at 25 °C for 45 min

CONCLUSION

The polycrystalline Cu_4SnS_4 thin films can be deposited on indium tin oxide glass substrates by the electrodeposition technique. The Cu_4SnS_4 thin films have orthorhombic structure and preferred orientation in the (221) plane. The AFM images indicated that higher bath temperature leads to larger crystal size. The films deposited at 25 °C have a homogeneous, uniform surface and well cover the substrate. Deposition at 45 min is sufficient to produce films with the highest photoresponse activity and better surface coverage. The films deposited at 25 °C for 45 min are considered as the optimum bath temperature to produce good quality thin films. The band gap energy was found to be 1.68 eV with direct transition. The photoresponse in the cathodic region indicated the p-type semiconductor.

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