EFFECTS OF pH VALUE ON THE ELECTRODEPOSITION OF Cu_4SnS_4 THIN FILMS

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abstract: Copper tin sulfide thin films were electrodeposited on the indium tin oxide substrates in a bath containing $CuSO_4$, $SnCl_2$ and $Na_2S_2O_3$ solutions. Various pH values ranging from 1.1 to 1.5 were attempted in order to determine the optimum condition for electrodeposition process. The structure and morphology of the films were studied by using X-ray diffraction and atomic force microscopy, respectively. The band gap energy and absorption properties were determined using UV-VIS spectrophotometer. The thin films produced were polycrystalline in nature. The XRD patterns showed that the most intense peak at $2\theta = 30.2°$ which belongs to (221) plane of Cu_4SnS_4. As the pH was increased, the grain size of this film was much smaller and has complete coverage over the substrate surface. The film showed good uniformity and produced higher absorbance value at pH 1.5. The band gap energy of this film was found to be 1.5 eV.

key words: bandgap energy; electrodeposition method; X-ray diffraction; thin films

Introduction

The research for thin film materials for solar energy conversion and other related applications has been recently initiated. It is not surprising that a lot of effort has been geared towards metal chalcogenides as this class of materials had shown somewhat superior performance when compared to others. There are many techniques for preparing thin films such as chemical bath deposition, flash evaporation, electrodeposition, vacuum evaporation, close spaced sublimation, thermal evaporation, spray pyrolysis, sputter deposition, metal organic chemical vapor deposition and plasma-enhanced chemical vapor deposition. Amongst these deposition methods, electrodeposition is more attractive, since it has the advantages of being a simple, low temperature and inexpensive large-area deposition technique. To this date, many thin films deposited by electrodeposition technique have been reported including ZnSe [1], CdSe [2], ZnTe [3], $FeSe_2$ [4], PbSe [5], CdS [6], Cu_2S [7],

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SnSe [8], CuInSe$_2$ [9], Cd$_{1-x}$Fe$_x$S [10], Zn$_{1-x}$Hg$_x$Se [11], Cd$_{0.7}$Zn$_{0.3}$Se [12], SnS$_{0.5}$Se$_{0.5}$ [13] and CdIn$_2$S$_4$ [14].

In the present work, thin Cu$_4$SnS$_4$ films were prepared by electrodeposition technique, and the effects of pH on the properties of these materials have been studied. These thin films have been characterized by using X-ray diffraction, atomic force microscope and UV-Visible Spectrophotometer for structural, surface morphological and optical absorption properties studies.

Experimental

The chemicals were of analytical grade and used as obtained without further purification. All the solutions were prepared using deionized water. The deposition bath contains 0.01 M copper sulfate (CuSO$_4$), tin chloride (SnCl$_2$) and sodium thiosulfate (Na$_2$S$_2$O$_3$) solutions [15]. Films were deposited using a three-electrode cell. 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. The electrodes were: an indium-doped tin oxide (ITO) glass substrate as the working electrode, a platinum wire as the counter electrode and a silver-silver chloride (Ag/AgCl) as the reference electrode. The substrates were cleaned ultrasonically in water and ethanol before use. The deposition process was carried out at room temperature [16] at –0.6 V versus Ag/AgCl for 45 min by varying the pH values (pH 1.1, 1.3, 1.5). Hydrochloric acid was added into bath to adjust the pH at the desired value. During deposition process, the bath was kept undisturbed. The deposited films were tested for adhesion by subjecting it to a steady stream of distilled water.

X-ray diffraction (XRD) analysis was carried out, using a Philips PM 11730 diffractometer for the 2θ ranging from 25° to 60° with CuK$_\alpha$ (λ=1.5418 Å) radiation. Surface morphology was measured by using an atomic force microscope (Quesant Instrument Corporation, Q-Scope 250) operating in contact mode, with a commercial Si$_3$N$_4$ cantilever. 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 in the sample radiation pathway while the uncoated ITO glass was put across the reference path. The data obtained from the film was used to determine the band gap energy and transition type of the semiconductor film.

Results and discussion

Fig. 1 shows the XRD patterns of Cu$_4$SnS$_4$ thin films deposited under different pH values ranging from 1.1 to 1.5. The XRD patterns were found to be polycrystalline with orthorhombic structure. For the films prepared at pH 1.1, six peaks at 2θ = 28.7°, 30.2°, 35.1°, 39.0°, 47.3° and 50.6° corresponding to interplanar distances of 3.11, 2.96, 2.56, 2.32, 1.93 and 1.81 Å, respectively were observed. These interplanar distances are in good agreement with JCPDS data (Reference code: 010710129). The lattice parameter values for the dominant orthorhombic structure are: a = 13.558 Å, b = 7.681 Å, c = 6.412 Å [17]. As

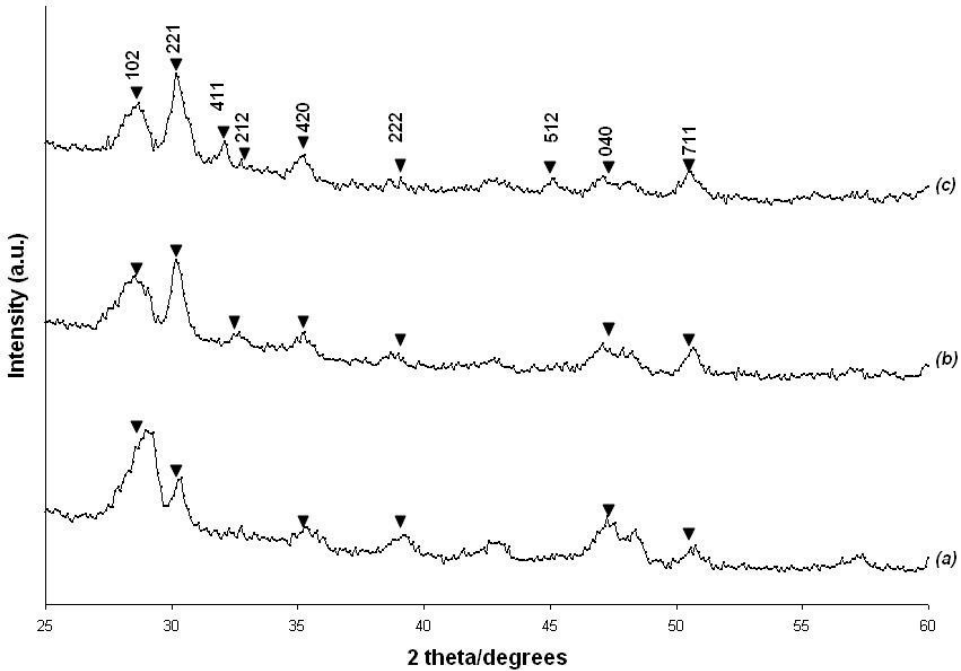the *p*H was increased to 1.3 and 1.5, the Cu_4SnS_4 peak increased to seven and finally nine, respectively.

Fig. 1 *X-ray diffraction patterns of films prepared at different pH values*
(a) *p*H 1.1 (b) *p*H 1.3 (c) *p*H 1.5 [Cu_4SnS_4 (▲)]

Fig. 2 shows the three-dimensional representation of a 20 μm × 20 μm area of the Cu_4SnS_4 thin films deposited at different *p*H values varied from 1.1 to 1.5. Larger grain sizes were observed on the surface of Cu_4SnS_4 films deposited at *p*H 1.1 (Fig. 2a) and 1.3 (Fig. 2b). These films also revealed an incomplete coverage of the substrate surface and grains are not distributed uniformly over the substrate (Fig. 2a, 2b). As the *p*H was increased to 1.5, the grain size of this film was much smaller and has complete coverage over the substrate surface (Fig. 2c).

The Table 1 shows the film thickness and root mean square (RMS) roughness observed by atomic force microscopy. The results indicated an increased in the film thickness from 1170 nm to 1930 nm as the *p*H was increased from 1.1 to 1.3. However, the film thickness decreased to 708 nm when the pH was further extended to 1.5. On the other hand, the RMS roughness values of the surfaces were found increased from 144 nm to 166 nm as the *p*H was increased from 1.1 to 1.3. However, the RMS value was reduced to 100 nm at higher *p*H value.

Fig. 3 shows the absorbance spectra of Cu_4SnS_4 films at different *p*H values. The film deposited at *p*H 1.5 produced the largest absorption value (Fig. 3c) as compared with other *p*H values. This response associated with the formation of smaller grain sizes which normally related higher surface area as shown in Fig. 2c. This result was consistent with the

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observation from X-ray diffraction pattern and atomic force microscopy images. Thus, deposition at pH 1.5 produced better quality of Cu_4SnS_4 films on ITO glass substrate.
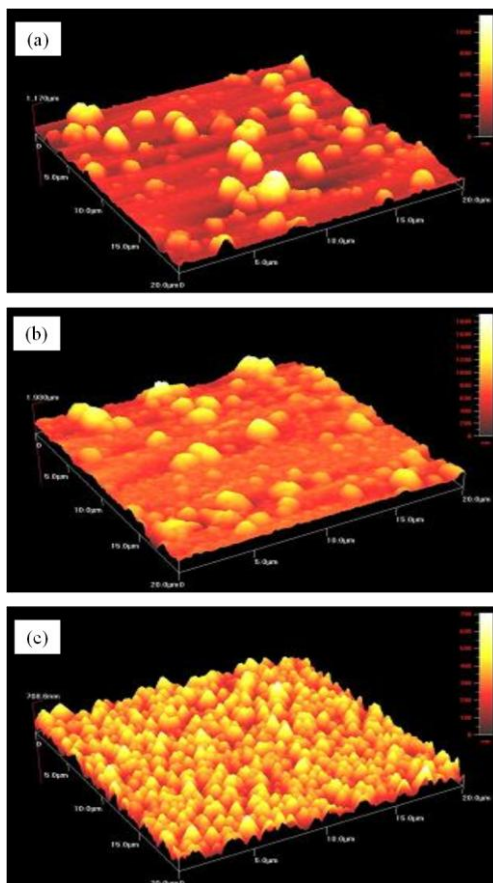

Fig. 2 *Atomic force microscopy images of Cu_4SnS_4 thin films prepared at different pH values:*
(a) pH 1.1 (b) pH 1.3 (c) pH 1.5

Table 1 Thickness and root mean square (roughness) determined from atomic force microscopy
for films prepared at different pH values

pH value	Thickness (nm)	RMS (nm)
1.1	1170	144
1.3	1930	166
1.5	708	100

The band gap energy and transition type was derived from mathematical treatment of data obtained from optical absorbance versus wavelength with the following relationship for near-edge absorption:

$$A = \frac{\left[k\ hv - E_g{}^{n/2}\right]}{hv} \quad (1)$$

where v is the frequency, h is the Planck's constant, k equals to 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. The line to determine the band gap was plotted by using Microsoft Excel software (least square method). The R^2 value obtained from the graph shown is 0.9922 which is almost equal to the value of 1. This value shows that all the data is fitted well by using this least square method technique. Extrapolation of the line to the base line, where the value of $(Ahv)^{2/n}$ is zero, will give E_g. The Fig. 4 showed the band gap energy of Cu_4SnS_4 film prepared at *p*H 1.5, which has 1.5 eV for the direct transition.
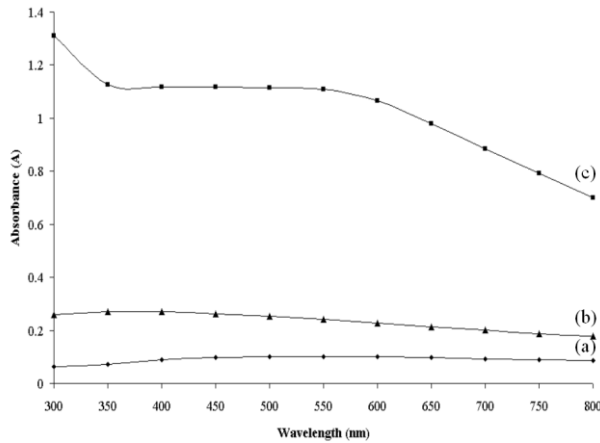
Fig. 3 *Optical absorbance versus wavelength of Cu_4SnS_4 films deposited at different pH values:*
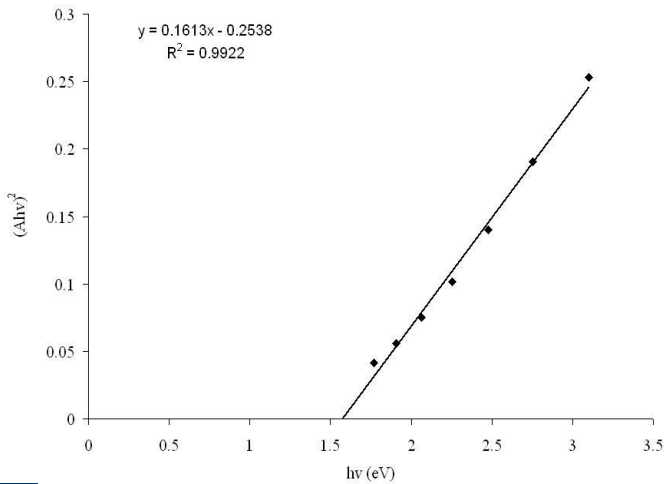*(a) pH 1.5 (b) pH 1.3 (c) pH 1.1*

Fig. 4 *Plot of* $(Ahv)^{2/n}$ *versus hv when n=1 for Cu_4SnS_4 films deposited at pH 1.5.*

Conclusions

The Cu_4SnS_4 thin films can be electrodeposited using $CuSO_4$, $SnCl_2$ and $Na_2S_2O_3$ solutions. X-ray diffraction patterns showed that the intensity of major peak at 2.96 Å which belongs to (221) plane of Cu_4SnS_4 change with *p*H. As the *p*H was increased, the grain size of this film was much smaller and has complete coverage over the substrate surface. The film showed good uniformity and exhibited higher absorbance value at *p*H 1.5. The band gap energy of this film was found to be 1.5 eV. Therefore, the *p*H values do effect the formation of thin film and *p*H 1.5 was the best condition observed.

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