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INFLUENCE OF COMPLEXING AGENT (Na_2EDTA) ON CHEMICAL BATH DEPOSITED Cu_4SnS_4 THIN FILMS

Anuar Kassim[1*], Saravanan Nagalingam[2], Zulkefly Kuang[1], Atan Sharif[1], Tan Wee Tee[1] and Ho Soon Min[1]

[1]Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia
[2]Department of Bioscience and Chemistry, Faculty of Engineering and Science, Universiti Tunku Abdul Rahman, 53300 Kuala Lumpur, Malaysia

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ABSTRACT. The quality of thin film is influenced by the presence of complexing agents such as Na_2EDTA. The Cu_4SnS_4 thin films were deposited onto indium tin oxide glass substrate by chemical bath deposition method. The structural, morphological and optical properties of the deposited films have been studied using X-ray diffraction, atomic force microscopy and UV-Vis spectrophotometer, respectively. The XRD data showed that the films have a polycrystalline and orthorhombic structure. It also indicated that the most intense peak at $2\theta = 30.2°$ which belongs to (221) plane of Cu_4SnS_4. The film deposited with 0.05 M Na_2EDTA showed good uniformity, good surface coverage with bigger grains and produced higher absorbance value. The band gap energy varies with the variation of Na_2EDTA concentration which ranging from 1.56-1.60 eV. Deposition at concentration of 0.05 M Na_2EDTA proved to offer a reasonably good Cu_4SnS_4 thin film.

KEY WORDS: Chemical bath deposition, Complexing agents, Thin films, X-ray diffraction

INTRODUCTION

The synthesis and characterization of metal chalcogenides thin film of different groups have attracted attention due to their applications such as in solar cells, sensor and laser materials. A variety of techniques have been used to prepare thin films including chemical bath deposition [1-9], vacuum evaporation [10], electrodeposition [11], successive ionic layer adsorption reaction [12], electron beam evaporation [13], atomic layer deposition [14], spray pyrolysis [15], flash evaporation [16] and plasma-enhanced chemical vapor deposition [17]. Among these techniques, the chemical bath deposition technique is most commonly used because it is a time saving, simple, cost effective and economically reproducible technique that can be applied in large area deposition at low temperature. The use of complexing agent is very common in the preparation of thin films through chemical bath deposition. Researchers use various complexing agents such as thiourea [18], ammonia [19-20], triethanolamine [21-22], disodium ethylene diamine tetra-acetate [23], nitrilotriacetic acid [24], ammonium hydroxide [25], hydrazine [26], sodium citrate [27] and tartaric acid [28-29] during deposition of thin films. Ternary copper tin chalcogenides form a large family of compounds such as Cu_2SnS_3, $Cu_2Sn_3S_7$, Cu_4SnS_6 and Cu_4SnS_4. All these compounds are represented by the general formula I-IV-VI and they are suitable candidates for photovoltaic cell materials and small band gap semiconductors.

In this paper, we prepare Cu_4SnS_4 thin films by chemical bath deposition technique using Na_2EDTA as a complexing agent. There is no report on deposition of Cu_4SnS_4 thin films from aqueous solution in the presence of Na_2EDTA. The influence of Na_2EDTA on the properties of thin films was studied. X-ray diffraction was used to study the structural properties of films. Meanwhile, the morphological and optical properties of Cu_4SnS_4 thin films were investigated by using atomic force microscope and UV-Visible spectrophotometer, respectively.

*Corresponding author. E-mail: anuar@science.upm.edu.my

EXPERIMENTAL

All the chemicals used for the deposition were analytical grade and all the solutions were prepared in deionised water (Alpha-Q Millipore, USA). The Cu_4SnS_4 thin films were prepared from an acidic bath using copper sulfate ($CuSO_4$), tin chloride ($SnCl_2$) and sodium thiosulfate ($Na_2S_2O_3$) acted as a source of copper, tin and sulfide ion, respectively. The disodium ethylenediaminetetraacetic acid (Na_2EDTA) was used as a complexing agent during deposition process. In order to investigate the influence of the complexing agent on the chemical bath deposited films, the deposition was carried out under different concentrations of Na_2EDTA ranging from 0.01 M to 0.10 M. 10 mL of Na_2EDTA solution was added into 10 mL of 0.05 M $SnCl_2$ and 0.05 M $CuSO_4$ in 100 mL beaker, respectively. Then solution was stirred. 10 mL of 0.05 M $Na_2S_2O_3$ solution was then added into a beaker slowly. The resultant solution was stirred for few minutes. The pH of the chemical bath was maintained at 1.5 by using hydrochloric acid. The indium doped tin oxide (ITO) glass was used as the substrate. The ultrasonically cleaned glass substrates were immersed vertically into acidic bath. The deposition process was carried out for 2 h at 50 °C. After deposition, the glass substrates coated with sample were washed by distilled water to remove the contamination in the surface.

The crystal structure of the film was monitored by X-ray diffraction (XRD) with a Philips PM 11730 diffractometer (Netherlands) equipped with a CuK_α (λ = 1.5418 Å) radiation source. Data were collected by step scanning from 20° to 60° (2θ) with a step size of 0.05° (2θ) and 1s counting time per step. Surface morphologies of the films were observed by using a Q-Scope 250 (Quesant Instrument Corporation, USA) atomic force microscope in a contact mode. The optical properties of the film were measured with a Perkin Elmer UV/Vis Lambda 20 Spectrophotometer (USA) in the wavelength range of 300 to 800 nm. The film-coated indium tin oxide glass was placed across the sample radiation pathway while the uncoated indium tin oxide glass was put across the reference path. From the analyses of absorption spectra, the band gap energy (E_g) was determined.

RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of the films deposited at different concentrations of Na_2EDTA. All the samples showed a polycrystalline in nature. There are nine peaks occurred at 2θ = 22.3°, 28.4°, 30.2°, 35.1°, 39.1°, 42.8°, 47.0°, 50.6° and 56.6° were detected for the films deposited with 0.05 M Na_2EDTA (Figure 1b). The XRD data obtained match the standard JCPDS [30] data (Reference code: 010710129) for orthorhombic phase of Cu_4SnS_4 (a = 13.5580 Å, b = 7.6810 Å, c = 6.4120Å, α = β = γ = 90°). However, the number of Cu_4SnS_4 peaks decreased to three (Figure 1a) and five (Figure 1c) for the films deposited with 0.01 M and 0.10 M Na_2EDTA, respectively. From the XRD patterns, it is observed that the intensities of the Cu_4SnS_4 peaks are decreased as the concentration of Na_2EDTA exceeds 0.05 M. This phenomenon was also observed by Whang *et al.* [31] in the electrodeposition of $CuInSe_2$. On the other hand, the strongest peak for all samples occurred at 2θ = 30.2° with *d*-spacing value of 2.96 Å. This indicates that the preferred orientation lies along (221) direction for the chemical bath deposited Cu_4SnS_4 thin film. However, the (221) plane showed the highest intensity peak for the film deposited using 0.05 M Na_2EDTA indicating more favorable condition for the formation of thin film.

The atomic force microscopy (AFM) measurements were performed to study the differences in the surface morphology for the samples deposited under different concentrations of Na_2EDTA. Figure 2 shows the AFM images of thin film deposited with 0.01 M, 0.05 M and 0.10 M Na_2EDTA on a scale of 20 μm x 20 μm. Comparing the three AFM images, it is clearly seen that the surface of the film deposited with 0.05 M Na_2EDTA is very smooth. The material was found to cover the surface of the substrate completely (Figure 2b). The sizes of each grain differ from others, varying from 0.9 to 1.2 μm. There are several big grains in the thin film, which due to the agglomeration of the smaller crystallites. However, the images show the film is more uniform and compacter than that prepared in other concentrations of Na_2EDTA. The AFM images show that the thin films obtained with 0.01 M and 0.10 M Na_2EDTA are very thin, not compact and incomplete coverage over the substrate surface (Figure 2a, c).

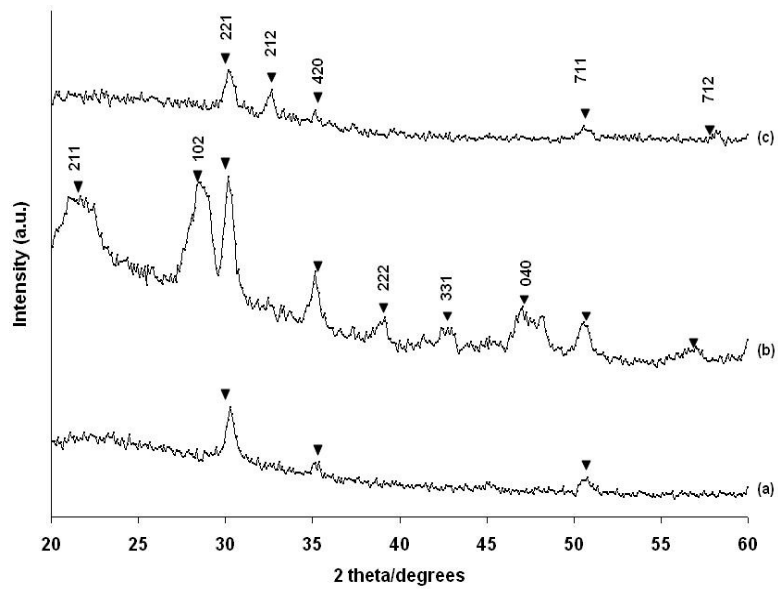

Figure 1. X-ray diffraction patterns of the Cu_4SnS_4 thin films deposited at different concentrations of Na_2EDTA. (a) 0.01 M, (b) 0.05 M, and (c) 0.10 M.

The thickness of the films was studied using AFM images. At the right side of the images, an intensity strip is shown, which indicates the depth and height along the *z*-axis. The thickness of thin film was increased from 640 nm to 981 nm as the concentration of Na_2EDTA was increased from 0.01 M to 0.05 M. However, the thickness of the thin films was reduced (125 nm) as the concentration of Na_2EDTA was further increased to 0.10 M. It is probably due to the complexing reaction was complete with high concentration (0.05 M) of complexing agent. Therefore, hinders the deposition of thin films [31]. The AFM results are consistent with the results obtained from XRD patterns.

The optical properties of thin films were measured in the range of 300-800 nm by using UV-Vis spectrophotometer. Figure 3 shows the absorption spectra of the samples deposited with different concentrations of Na_2EDTA, ranging from 0.01 M to 0.10 M. With increasing concentration of Na_2EDTA from 0.01 M (Figure 3c) to 0.05 M (Figure 3a), the absorption value of the films increases and then decreases at higher Na_2EDTA concentration (Figure 3b). This could be due to more Cu_4SnS_4 thin films (thicker film) deposited onto the surface of substrate using 0.05 M of Na_2EDTA providing better absorption properties.

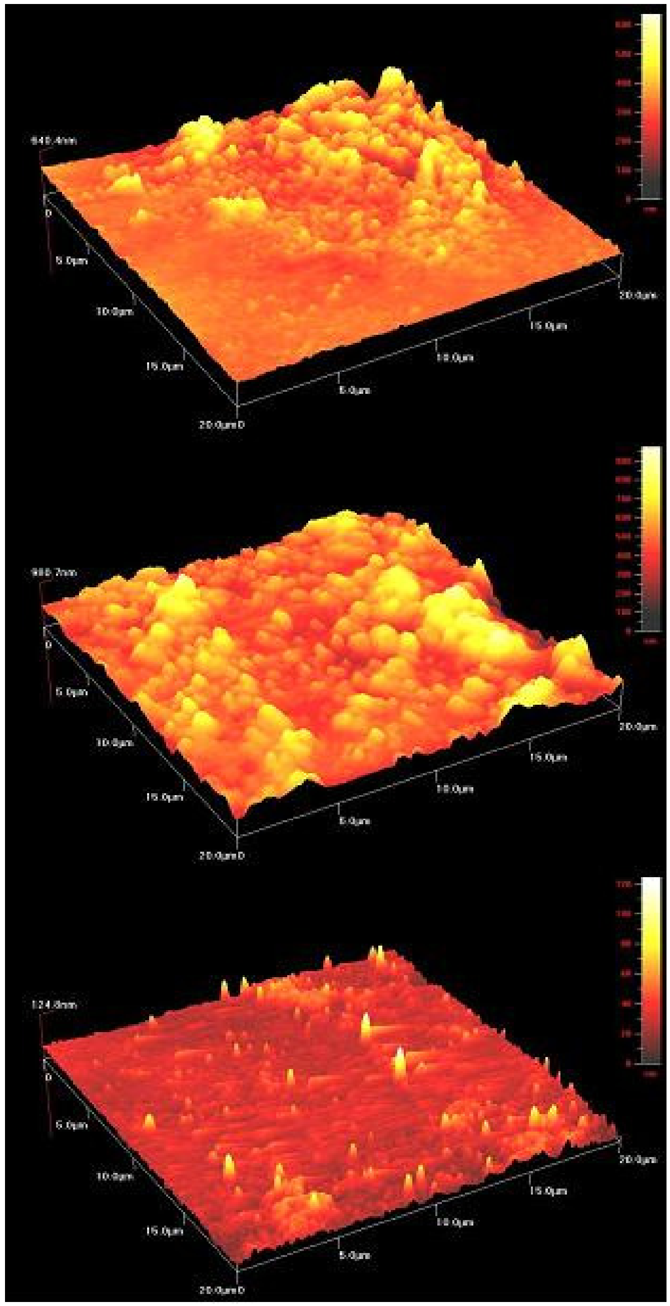

Figure 2. The atomic force microscopy images of the Cu_4SnS_4 thin films deposited at different concentrations of Na_2EDTA. (a) 0.01 M, (b) 0.05 M, and (c) 0.10 M.

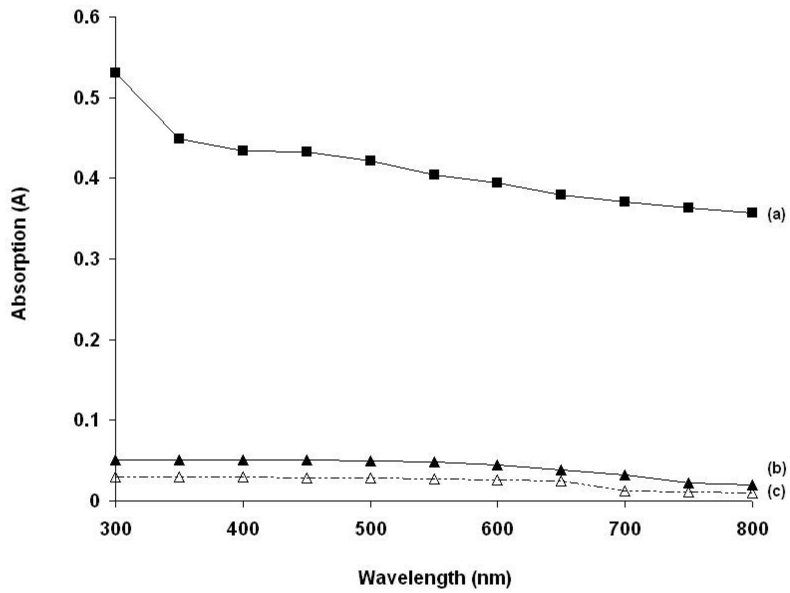

Figure 3. The optical absorption versus wavelength of the Cu_4SnS_4 thin films deposited at different concentrations of Na_2EDTA. (a) 0.05 M, (b) 0.10 M, and (c) 0.01 M.

Band gap energy and transition type can be derived from mathematical treatment of data obtained from optical absorbance versus wavelength with Stern [32] relationship of near-edge absorption (Equation 1):

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

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 [33]. Figure 4 shows the plot of $(Ahv)^2$ versus hv for Cu_4SnS_4 thin films deposited with different concentrations of Na_2EDTA. The band gap values were determined from the intercept of the straight-line portion of the $(Ahv)^2$ against the hv graph on the hv-axis using computer fitting program. The linear part shows that the mode of transition in these films is of direct nature. The band gaps deduced for all thin films in this manner increased from 1.56 eV (Figure 4a) to 1.60 eV (Figure 4b) as concentration of Na_2EDTA was increased from 0.01 M to 0.05 M. However, the band gap was found decreased to 1.59 eV (Figure 4c) as the concentration of Na_2EDTA was further increased to 0.10 M.

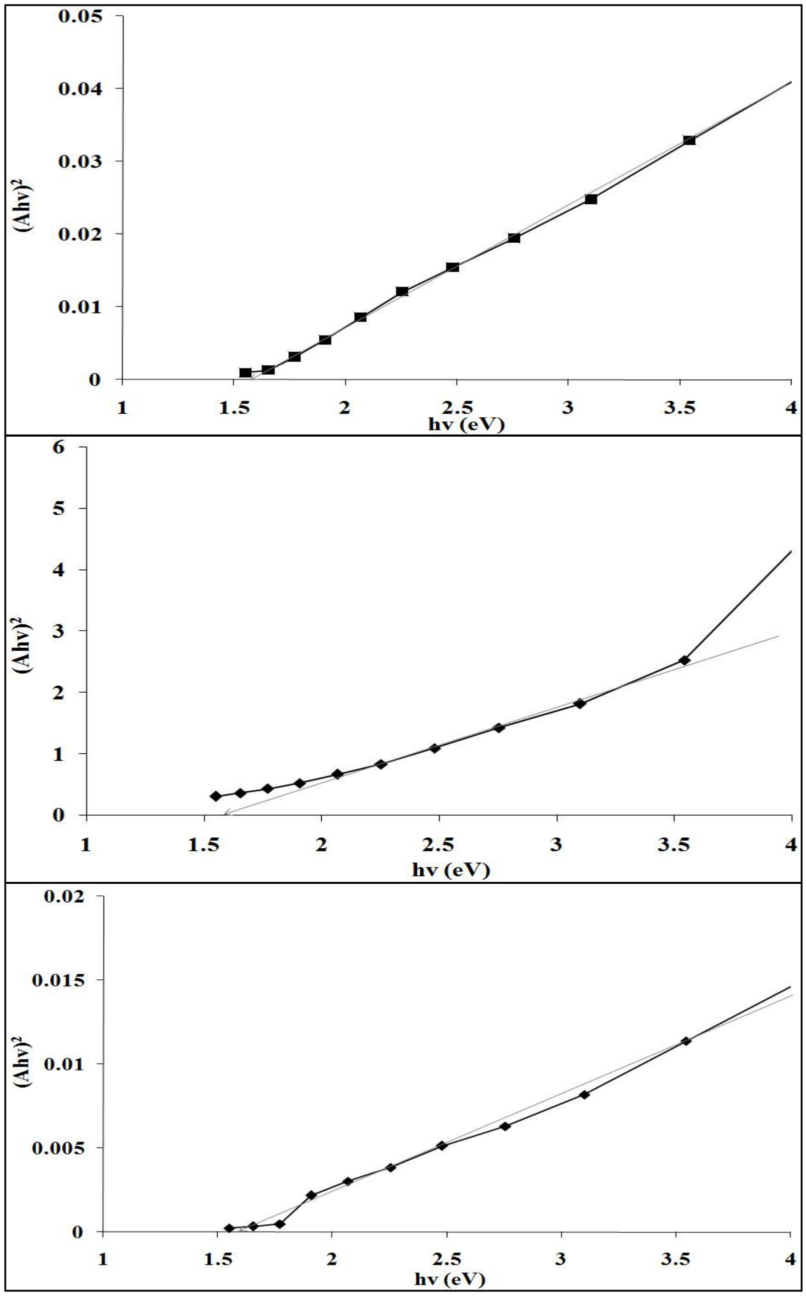

Figure 4. Plot of $(Ahv)^{2/n}$ versus hv when n = 1 of the Cu_4SnS_4 thin films deposited at different concentrations of Na_2EDTA. (a) 0.01 M, (b) 0.05 M, and (c) 0.10 M.

CONCLUSIONS

The Cu_4SnS_4 thin films were prepared by the chemical bath deposition method onto indium tin oxide glass substrates using aqueous solution of copper sulfate, tin chloride, sodium thiosulfate and Na_2EDTA. The Na_2EDTA acted as complexing agent has some influences on the structure, morphology and optical properties of Cu_4SnS_4 thin films. The XRD data showed that the films have a polycrystalline, orthorhombic structure with preferential orientation along (221) plane. According XRD patterns, there are less Cu_4SnS_4 peaks could be observed for the films deposited using 0.01 M and 0.10 M of Na_2EDTA. Also, the AFM images show that these films are very thin, not compact and incomplete coverage over the substrate surface. However, the films deposited with 0.05 M Na_2EDTA showed good uniformity, good surface coverage with bigger grains and produced higher absorbance value. Meanwhile, the band gap energy varies with the variation of Na_2EDTA concentration which ranging from 1.56-1.60 eV. Deposition at concentration of 0.05 M Na_2EDTA proved to offer a reasonably good Cu_4SnS_4 thin film.

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