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Composition, structure and photoelectrochemical characterization of electrodeposited Cu_4SnS_4 thin films

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ABSTRACT

Cu_4SnS_4 thin films were deposited on indium tin oxide glass substrate using the electrodeposition method. The thin films were obtained in a reaction bath at pH values of 1.1, 1.3, 1.5, 1.7 and 2.0. The structure and chemical composition of the thin films were studied by X-ray diffraction and energy dispersive analysis of X-ray, respectively. The photoresponse of the deposited films and their conduction types were evaluated using the photoelectrochemical technique. The X-ray diffraction data indicated that the number of peaks increased as the pH was increased up to 1.5. However, the total Cu_4SnS_4 peaks reduced to three peaks as the pH was further increased to 2. Based on the energy dispersive analysis of X-ray analysis, the composition ratio Cu:Sn:S of the films was varied with pH. When the pH was lower or higher than pH 1.5, the content of Cu and Sn is slightly greater than that of elemental S. Therefore, the pH had significant influence on the composition of the deposited films.

Key words: Electrodeposition method, X-ray diffraction, photocurrent, thin films.

INTRODUCTION

The binary and ternary compound semiconductor thin films are promising materials for a variety of optical device applications such as solar cells, UV light emitting diode, photocatalysis, phosphors in flat panel displays, electroluminescent and photoconductor devices. Several techniques have been applied to obtain thin films such as pulsed laser deposition[1], electrochemical atomic layer epitaxy[2], successive ionic layer adsorption reaction[3], metal organic chemical vapor deposition[4], thermal evaporation[5], sputtering[6], electrodeposition[7] and chemical bath deposition[8]. Among these deposition methods, electrodeposition method is more attractive. This method is simple, low cost and can operate at low processing temperature to produce large deposition area. The preparations of various ternary compounds using electrodeposition technique such as HgCdTe[9], $CuInS_2$[10], $SnS_{0.5}Se_{0.5}$[11], $CdIn_2S_4$[12] and $CuInSe_2$[13] have been reported by several researchers.

Previously, Anuar *et al*.[14] reported the influence of pH (pH 1.1, 1.3 and 1.5) on the properties of Cu_4SnS_4 thin films using electrodeposition method. 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. In this work, for the first time, the chemical composition of the thin films deposited at various pH values (1.1-2.0) was studied by energy dispersive analysis of X-ray. The photoresponse of the deposited films and their conduction types were evaluated using the photoelectrochemical technique.

MATERIAL AND METHODS

All the chemicals used for the deposition were analytical grade reagents and all the solutions were prepared in deionised water (Alpha-Q Millipore). The Cu_4SnS_4 thin films were prepared

from an acidic bath using aqueous solutions[15] of 0.01 M copper sulfate ($CuSO_4$), tin chloride ($SnCl_2$) and sodium thiosulfate ($Na_2S_2O_3$) acted as a source of Cu^{2+}, Sn^{2+} and S^{2-} ions, respectively. The EG&G Princeton Applied Research potentiostat driven by a software model 270 Electrochemical Analysis System was used for the Cu_4SnS_4 thin films electrodeposition in a three-electrode cell. The cell consisted of indium doped tin oxide (ITO) glass substrate as working electrode, platinum wire as counter electrode and silver-silver chloride (Ag/AgCl) as reference electrode, separately. Before deposition, the glass substrate was degreased with ethanol for 10 min. Then, ultrasonically cleaned with distilled water for another 10 min and dried in desiccator. Purified nitrogen was flowed into the deposition bath for few minutes to create oxygen free environment. The deposition process was carried out at room temperature[16] at –0.6 V versus Ag/AgCl[17] for 45 min by varying the pH values (pH 1.1, 1.3, 1.5, 1.7 and 2.0). The pH was adjusted by using hydrochloric acid under the control of a pH meter. After the deposition, the thin films were washed with distilled water and kept for analysis.

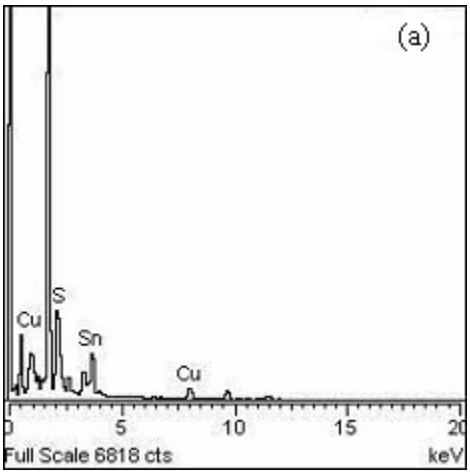
The structure of the thin films was monitored by X-ray diffraction (XRD) with a Philips PM 11730 diffractometer equipped with a CuK_α (λ=0.15418 nm) radiation source. Data were collected by step scanning from 25° to 60° with a step size of 0.05° (2è). The elemental composition of the films was studied by scanning electron microscope (JEOL JSM 6400) attached with energy dispersive analysis of X-ray (EDAX) analyzer. The photoelectrochemical experiment was performed in $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ redox system by running linear sweep voltammetry (LSV) between -200 to –1000 mV versus Ag/AgCl. A halogen lamp (300 W, 120 V) was served as the light source. The voltage scan speed was 10 mV/s and light was manually chopped.

RESULTS AND DISCUSSION

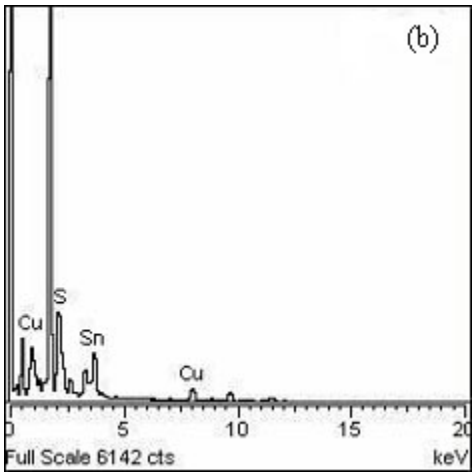
Table 1 shows the XRD data of the Cu_4SnS_4 thin films prepared at different pH values ranging from 1.1 to 2.0. At pH 1.1, only six peaks attributable to orthorhombic phase of Cu_4SnS_4 are observed. The number of peaks increased to seven and nine, as the pH is increased to 1.3 and 1.5, respectively. The XRD results confirm that the thin films deposited at pH above 1.5, proved less favourable as the number of peaks assigned to Cu_4SnS_4 reduced. As the pH is further increased to 1.7 and 2, only four and three peaks of Cu_4SnS_4 are obtained from the XRD analysis. From the XRD results, we can conclude that the films are polycrystalline and the best pH for the formation of Cu_4SnS_4 thin films is pH 1.5. At pH 1.5, the peaks obtained indicate that an orthorhombic Cu_4SnS_4 structure with (102), (221), (411), (212), (420), (222), (512), (040) and (711) planes have been deposited. The *d*-spacing values obtained for Cu_4SnS_4 thin films

Table 1: Comparison between *d*-spacing values of Cu_4SnS_4 thin films and JCPDS data

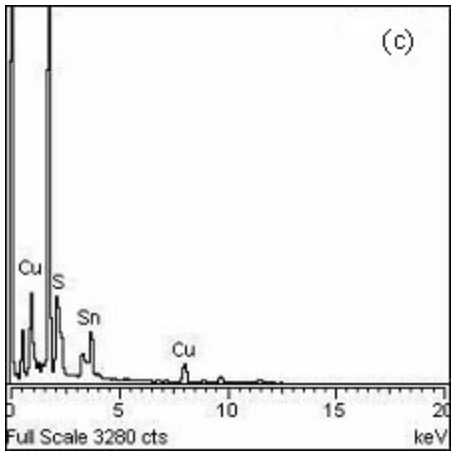
pH	2*ô* (°)	hkl	*d*-spacing (Å)	
			Obtained values	JCPDS values
1.1	28.7	102	3.11	3.12
	30.2	221	2.96	2.96
	35.2	420	2.56	2.54
	39.0	222	2.32	2.31
	47.3	040	1.93	1.92
	50.6	711	1.81	1.80
1.3	28.7	102	3.11	3.12
	30.2	221	2.96	2.96
	33.1	212	2.73	2.71
	35.2	420	2.56	2.54
	39.0	222	2.32	2.31
	47.3	040	1.93	1.92
	50.6	711	1.81	1.80
1.5	28.7	102	3.11	3.12
	30.2	221	2.96	2.96
	32.3	411	2.77	2.79
	33.1	212	2.73	2.71
	35.2	420	2.56	2.54
	39.0	222	2.32	2.31
	45.0	512	2.03	2.00
	47.3	040	1.93	1.92
	50.6	711	1.81	1.80
1.7	28.7	102	3.11	3.12
	30.2	221	2.96	2.96
	47.3	040	1.93	1.92
	50.6	711	1.81	1.80
2.0	28.7	102	3.11	3.12
	30.2	221	2.96	2.96
	47.3	040	1.93	1.92



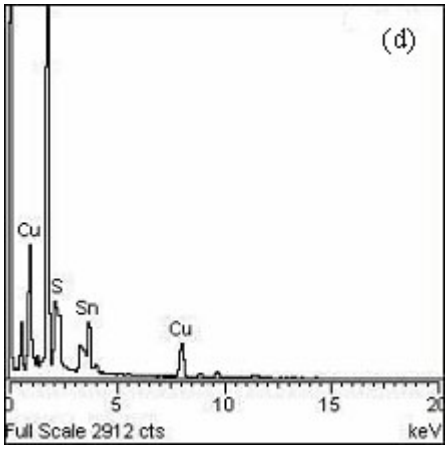
(a) pH 1.1



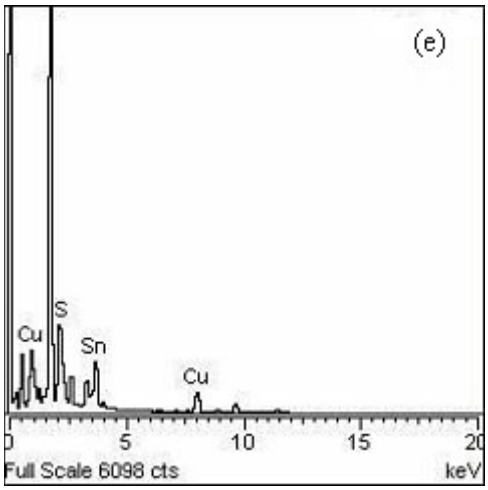
(b) pH 1.3



(a) pH 1.5



(b) pH 1.7



(b) pH 2.0

Fig. 1: The EDAX spectra of the Cu_4SnS_4 thin films prepared under various pH values

prepared at this pH value are found to match the standard JCPDS[18] data (JCPDS Reference code: 01-071-0129). The lattice parameter values are a=1.3558 nm, b = 0.7681 nm, c = 0.6412 nm.

The compositional analysis of the thin films is investigated by energy dispersive analysis of X-ray (EDAX) technique. The EDAX spectra of the Cu_4SnS_4 thin films prepared under various pH values are shown in Fig. 1 (1a-1e). The quantitative elemental analysis is carried out only for Cu, Sn and S. The Table 2 shows the ratio of Cu, Sn to S obtained from the EDAX analysis. For the thin films prepared at pH 1.5, the atomic percentage (%) for these elements is 49.13, 12.59 and 38.28 %, respectively. The ratio of 4:1:3 of copper (Cu), tin (Sn) and sulphur (S) has been confirmed by EDAX analysis. It is observed that the atomic percentage of the thin films is altered as the thin films are prepared at other pH values. When the pH is lower or higher than pH 1.5, the content of Cu and Sn is slightly greater than that of elemental S. Therefore, the pH has significant influence on the composition of the deposited films.

In the growth of the Cu_4SnS_4 thin films from a reaction bath, the copper sulfate, tin chloride and sodium thiosulfate acted as a source of Cu^{2+}, Sn^{2+} and S^{2-} ions, respectively. In aqueous bath, sodium thiosulfate dissociates[19] as

$$Na_2S_2O_3 \rightarrow 2Na^+ + S_2O_3^{2-} \quad ...(1)$$

By virtue of half-cell reaction[20],

$$2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^- \quad ...(2)$$

The pH value of the reaction mixture is controlled by the addition of hydrochloric acid. The addition of HCl increases the presence of hydrogen ions (H^+) in the solution. In an acidic medium, the dissociation of sodium thiosulfate takes place[21]

$$S_2O_3^{2-} + H^+ \rightarrow HSO_3^- + S \quad ...(3)$$

The electrons released in reaction [2] react with sulphur released in reaction [3] to produce sulphide ions (S^{2-}).

$$S + 2e^- \rightarrow S^{2-} \quad ...(4)$$

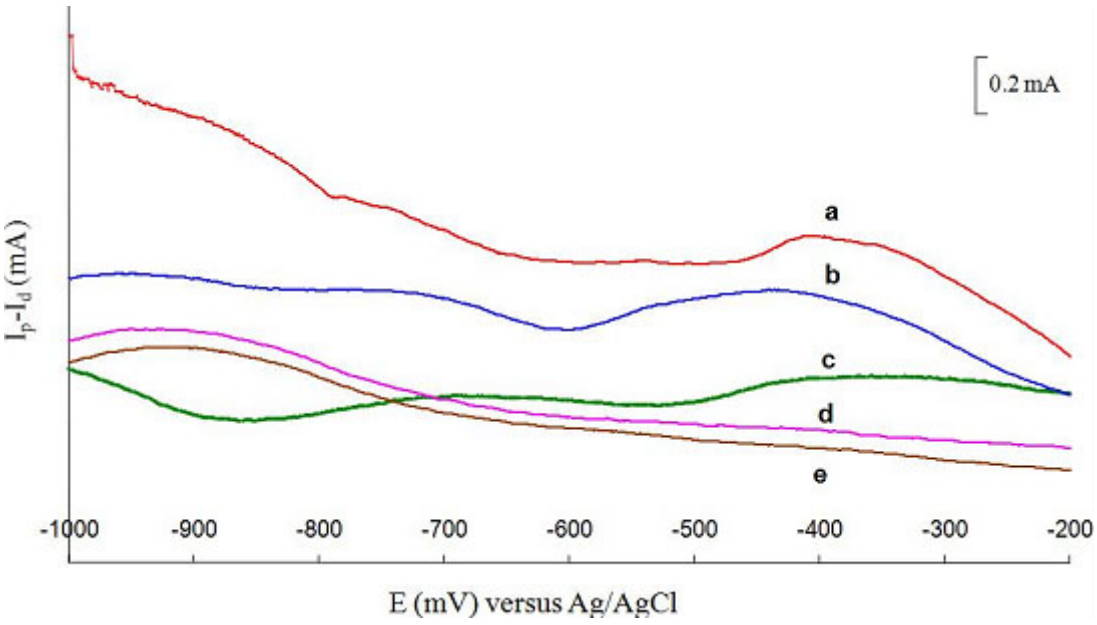


Fig. 2: Comparison of the difference between the photocurrent and darkcurrent (I_p-I_d) of Cu_4SnS_4 thin films deposited at different pH values

When a photoelectrode is immersed in an electrolyte, an electrode-electrolyte interface is formed, which is called photoelectrochemical (PEC) cell. Fig. 2 shows difference between the photocurrent and dark current when the samples are illuminated under halogen lamp. The films deposited at pH 1.5 produced the highest photoresponse compared to the films prepared at other pH values. This is due to more polycrystalline Cu_4SnS_4 thin films are formed at this pH value, which is also supported by the number of Cu_4SnS_4 peaks in the XRD data. The films deposited at other pH values did not display good photoresponse due to unfavourable amount of deposits. This leads to minimal interaction of semiconductor-electrolyte phase, which produces low photocurrent upon illumination. On the other hand, a steady increase in the current could be observed for all the samples as the potential is swept to more negative region. This indicates that the films prepared are of *p*-type semiconductor.

Table 2: The atomic percentage of Cu, Sn and S for the films deposited at different pH values

pH	Atomic percentage (%)			Ratio of
	Cu	Sn	S	Cu:Sn:S
1.1	53.81	13.96	32.23	3.85 : 1: 2.31
1.3	51.43	13.78	34.79	3.73 : 1: 2.52
1.5	49.13	12.59	38.28	4 : 1: 3.04
1.7	53.34	12.64	34.02	4.22 : 1: 2.69
2.0	60.74	12.69	26.57	4.79 : 1: 2.09

CONCLUSIONS

Cu_4SnS_4 thin films were deposited on indium tin oxide glass substrate using the electrodeposition method. The X-ray diffraction data indicated that the number of peaks increased as the pH was increased up to 1.5. However, the total Cu_4SnS_4 peaks reduced to three peaks as the pH was further increased to 2. Based on the energy dispersive analysis of X-ray analysis, the composition ratio Cu:Sn:S of the films was varied with pH. When the pH was lower or higher than pH 1.5, the content of Cu and Sn is slightly greater than that of elemental S. Therefore, the pH had significant influence on the composition of the deposited films. According to photoelectrochemical analysis, all the films exhibited *p*-type semiconductor behavior and the highest photoresponse was obtained for the films deposited at pH 1.5. Based on the above results, deposition at pH 1.5 could produce good Cu_4SnS_4 thin films.

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