

DEPOSITION AND CHARACTERIZATION OF Cu_4SnS_4 THIN FILMS BY CHEMICAL BATH DEPOSITION METHOD

Anuar Kassim¹, Tan WeeTee¹, Abdul Halim Abdullah¹, Saravanan Nagalingam², Ho Soon Min¹

¹Department of Chemistry, Faculty of Science, Universiti Putra Malaysia,
43400 Serdang, Selangor, Malaysia

²Department of Bioscience and Chemistry, Faculty of Engineering and Science,
University Tunku Abdul Rahman, 53300 Kuala Lumpur, Malaysia
anuar@science.upm.edu.my

A low cost chemical bath deposition method has been used for the preparation of Cu_4SnS_4 thin films onto indium tin oxide glass substrate. The deposition parameters such as bath temperature (50 °C), deposition time (120 min), electrolyte concentration (0.05 M) and bath pH (1.5) were optimized to obtain good quality thin films. The structural, surface morphological and optical properties of thin films were studied by X-ray diffraction, an atomic force microscopy and an UV-Vis Spectrophotometer, respectively. The X-ray diffraction study revealed that the Cu_4SnS_4 films were polycrystalline in nature with the preferential orientation along the (221) plane. The atomic force microscopy results indicated that the films were smooth, uniform and the substrate surface was covered completely at these experimental conditions. These films exhibited *p*-type semiconductor behavior with the band gap energy about 1.57 eV.

Key words: thin film; chemical bath deposition; X-ray diffraction

ДЕПОЗИЦИЈА И КАРАКТЕРИЗАЦИЈА НА ТЕНКИ ФИЛМОВИ ОД Cu_4SnS_4 СО МЕТОД НА ХЕМИСКА ДЕПОЗИЦИЈА

Употребен е евтин метод на хемиска депозиција за добивање тенки филмови од Cu_4SnS_4 врз стаклен супстрат покриен со оксид на индиум и калај. За да се добие добар квалитет на тенките филмови, направена е оптимизација на параметрите на депозиција: температура на бањата (50 °C), време на депозиција (120 min), концентрација на електролитот (0,05 M) и pH на бањата (1,5). Структурните, површинско-морфолошките и оптичките својства на тенките филмови се проучени со рендгенска дифракција, со микроскопија заснована на (меѓу)атомски сили и со УВ-видлива спектрометрија. Истражувањето со рендгенската дифракција покажа дека филмовите од Cu_4SnS_4 се поликристални со преферирана ориентација наддолж (221) рамнината. Резултатите од микроскопијата заснована на (меѓу)атомски сили покажуваат постоење на рамни (мазни) и униформни филмови, како и целосно прекриена површина на супстратот при споменатите експериментални услови. Добиените филмови покажуваат *p*-тип на полупроводничко однесување со енергетска ширина на забранетата зона од околу 1,57 eV.

Клучни зборови: тенки филмови; хемиска депозиција; рендгенска дифракција

1. INTRODUCTION

The investigation of thin films has received a great deal of attention during the last few years due to their important semiconducting properties. Thin films can be used as optoelectronic devices, photovoltaic cells, solar selective coatings and la-

ser materials. Photovoltaic cells at present furnish the most important long duration power supply for satellite, space vehicle and terrestrial applications. The solar energy is considered a major candidate for obtaining energy from the sun, since it can convert sunlight directly into electricity. In recent years, considerable efforts have been made

to find out low cost materials such as metal chalcogenide materials [1–3] for solar energy conversion application. There are several methods that can be used to prepare thin films such as chemical bath deposition [4], electrodeposition [5], molecular beam epitaxy [6], close spaced sublimation [7], sputter deposition [8], metal organic chemical vapor deposition [9] and plasma-enhanced chemical vapor deposition [10]. The properties of thin films depend on the deposition process and deposition parameters. Each deposition method has its own advantages and disadvantages. The chemical bath deposition method is preferred for its simplicity, inexpensive and capability to achieve large area coatings. Over the past several years, many researchers have prepared thin films such as ZnS [11], PbS [12], SnS [13], CdS [14], FeS₂ [15], CuBiS₂ [16], PbSnS₃ [17], Cd_{1-x}Zn_xS [18] and Cd_{0.5}Zn_{0.5}Se [19] by the chemical bath deposition method. Nair *et al.* [20] have reported the results on the formation of Cu₄SnS₄ thin films when a chemically deposited SnS-CuS layer is heated at 400 °C under a 300 mTorr pressure of nitrogen.

In the present study, we describe the deposition of Cu₄SnS₄ thin films onto indium tin oxide glass substrate using the chemical bath deposition technique. We report for the first time chemical bath deposition of Cu₄SnS₄ thin films in the presence of Na₂EDTA at 50 °C in a strong acidic medium (pH = 1.5). The deposition parameters were optimized to obtain good quality thin films. The structural and morphological properties of thin films were investigated by the X-ray diffraction and the atomic force microscopy, respectively. Meanwhile, the optical properties of thin films were studied by the UV-Visible Spectrophotometer.

2. EXPERIMENTAL

Preparation of samples

All the chemicals used for the deposition were analytical grade reagents and all the solutions were prepared using deionised water (Alpha-Q Millipore). The chemicals used were copper sulfate (CuSO₄), tin chloride (SnCl₂), sodium thiosulfate (Na₂S₂O₃), disodium ethylenediaminetetraacetic (Na₂EDTA) and hydrochloric acid (HCl). The copper sulfate, tin chloride and sodium thiosulfate were acted as a source of copper, tin and sulfide ion, respectively. The Na₂EDTA was used as a complexing agent to chelate with Cu²⁺ and Sn²⁺ to

obtain Cu-EDTA and Sn-EDTA complex solutions. The presence of Na₂EDTA was found to improve the lifetime of the deposition bath as well as the adhesion of deposited films on the indium tin oxide glass substrate. Before deposition, the indium tin oxide (ITO) glass substrate was degreased with ethanol for 10 min, followed by ultrasonically cleaned with distilled water for another 15 min. Depositions of Cu₄SnS₄ thin films were carried out by using the following procedure: Firstly, 10 ml of CuSO₄ (0.05 M) and 10 ml of SnCl₂ (0.05 M) solutions were complexed with 10 ml of Na₂EDTA (0.1 M), respectively and stirred for several minutes to get clear and homogeneous solutions. Thereafter, 10 ml of Na₂S₂O₃ (0.05 M) was added under stirring conditions. Finally, hydrochloric acid was added to make the solution acidic and the pH was maintained at 1.5. The clean ITO glass substrate was then placed vertically inside the beaker without disturbing it. This beaker was then kept in constant temperature water bath. The beaker was allowed to stand for 120 min at 50 °C constant temperature. After completion of film deposition, the ITO glass substrate was removed from the beaker and cleaned with distilled water. Then the deposited films were dried in the desiccator and subjected to further analyses.

Characterization method

The structural characterization of the films was carried out using a Philips PM 11730 X-ray diffractometer with CuK_α radiation ($\lambda = 1.5418 \text{ \AA}$) in scanning the angle (2θ) from 20 ° to 60 °. The surface morphology of the films was investigated by atomic force microscopy (Quesant Instrument Corporation, Q-Scope 250). It was operated in a contact mode with the Si₃N₄ cantilever. The value of root mean square (RMS) roughness was calculated from the height values in the atomic force microscopy (AFM) image using the commercial software. The elemental composition of the films was studied by scanning the electron microscope (JEOL JSM 6400) attached with energy dispersive analysis of the 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 -400 to -1000 mV versus Ag/AgCl (silver-silver chloride electrode). A halogen lamp (300 W, 120 V) was served as the light source. The voltage scan speed was 10 mV/s and the light was manually chopped. The absorption was recorded in the range of 350–

800 nm using the Perkin-Elmer Lambda 20 UV-Vis 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. Thus, the absorbance measurement included only the contribution from Cu_4SnS_4 thin films. From the analyses of absorption spectrum, the band gap energy (E_g) was determined.

3. RESULTS AND DISCUSSION

The X-ray diffraction (XRD) pattern of thin films deposited onto the indium tin oxide glass

substrate at optimized deposition parameters is shown in Fig. 1. This pattern contains eight diffraction peaks indicating that these films are polycrystalline in nature. The XRD peaks are at $2\theta = 22.3^\circ, 28.9^\circ, 30.2^\circ, 35.2^\circ, 39.1^\circ, 47.0^\circ, 50.6^\circ$ and 57.0° . Fig. 1 shows that the films exhibit a high intensity peak at $2\theta = 30.2^\circ$. All other peaks and their relative planes are listed in Table 1. The comparisons of observed d -spacing values with standard d -spacing values (JCPDS Reference code: 010710129) [21] clearly indicate the formation of orthorhombic phase of Cu_4SnS_4 . The lattice parameter values are $a = 1.3558$ nm, $b = 0.7681$ nm, $c = 0.6412$ nm.

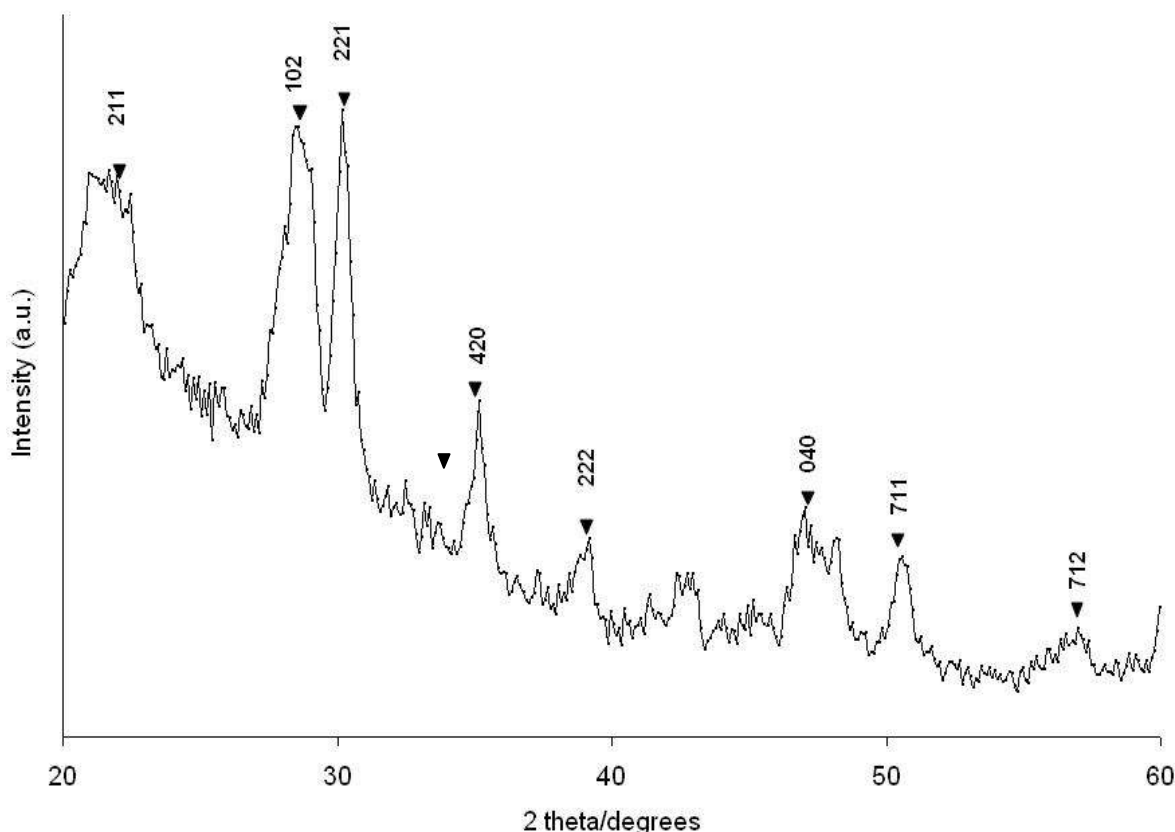


Fig. 1. X-ray diffraction pattern of Cu_4SnS_4 thin films deposited at optimized deposition parameters. (Cu_4SnS_4)

The compositional analysis of the films is investigated by the energy dispersive analysis of the X-ray (EDAX) technique. The EDAX spectrum of the Cu_4SnS_4 thin films deposited under optimized deposition conditions is shown in Fig. 2. The quantitative elemental analysis is carried out only for Cu, Sn and S. The atomic percentage (%) for

these elements is 49.1, 12.6 and 38.3 %, respectively. The ratio of 4:1:3 of copper (Cu), tin (Sn) and sulphur (S) has been confirmed by EDAX analysis. We can conclude that the sulphur concentration is slightly less as compared to stoichiometric of Cu_4SnS_4 .

Table 1

Comparison of the JCPDS *d*-spacing data for Cu_4SnS_4 thin films to experimentally observed values for the sample deposited at optimized deposition parameters

2θ ($^\circ$)	<i>hkl</i>	<i>d</i> -spacing	
		Observed	JCPDS value
22.3	211	3.99	3.98
28.9	102	3.08	3.12
30.2	221	2.96	2.96
35.2	420	2.55	2.54
39.1	222	2.30	2.31
47.0	040	1.93	1.92
50.6	711	1.80	1.80
57.0	712	1.61	1.62

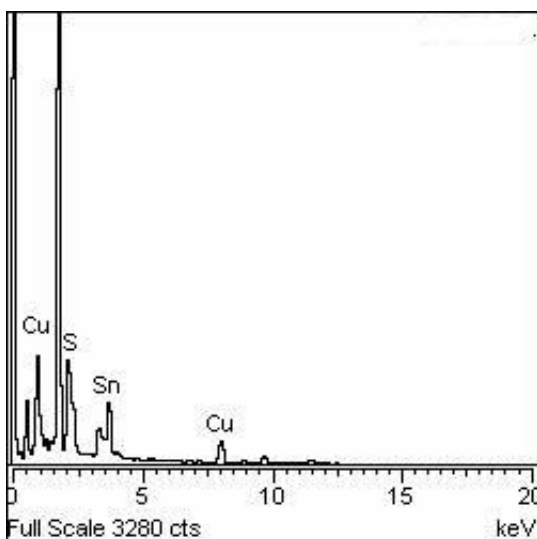
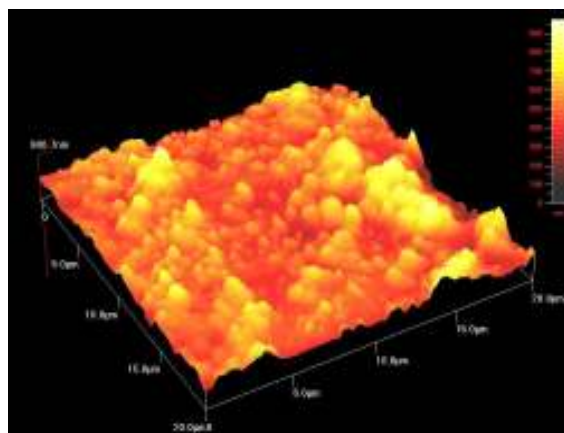


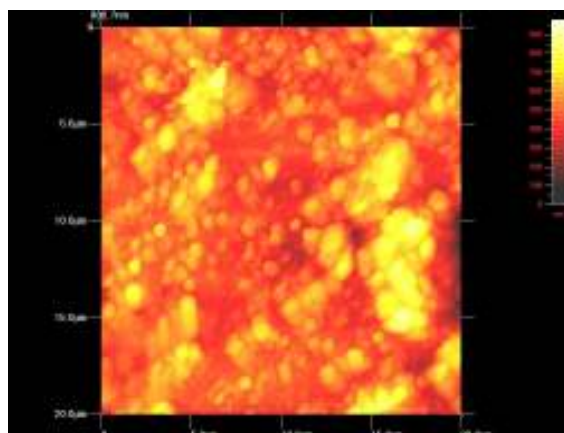
Fig. 2. EDAX spectrum of Cu_4SnS_4 thin films deposited at optimized deposition parameters

Surface morphology is observed with the atomic force microscopy (AFM) technique. Figs. 3a and 3b show two-dimensional and three-dimensional images of films deposited onto the indium tin oxide glass substrate at optimized deposition parameters, measured over an area of $20\ \mu\text{m} \times 20\ \mu\text{m}$. Fig. 3a shows that the small spherical grains of approximately $0.8\text{--}1\ \mu\text{m}$ size are uniformly distributed over the surface of substrate. Fig. 3b indicates the formation of hill-like structure which shows the growth of thin films during the deposition process. The AFM images show that the

grains are distributed to cover the surface of the substrate completely.



a)



b)

Fig. 3. Two-dimensional (a) and three-dimensional (b) AFM images of Cu_4SnS_4 thin films deposited at optimized deposition parameters

The root mean square (RMS) roughness which is defined as the standard deviation of the surface height profile from the average height, is the most commonly reported measurement of surface roughness [22]. The surface roughness is small (67 nm) and is unavoidable due to the three-dimensional growth of films. The thickness of the films is also 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 is measured from the AFM images and is found to be 980 nm.

Figure 4 shows the optical absorption spectrum of Cu_4SnS_4 thin films in the wavelength region from 350 to 800 nm. As seen in the Figure 4, the spectrum of thin films shows high absorption

(at wavelengths less than 750 nm) throughout the visible region indicating that these materials can

be used for photoelectrochemical cells

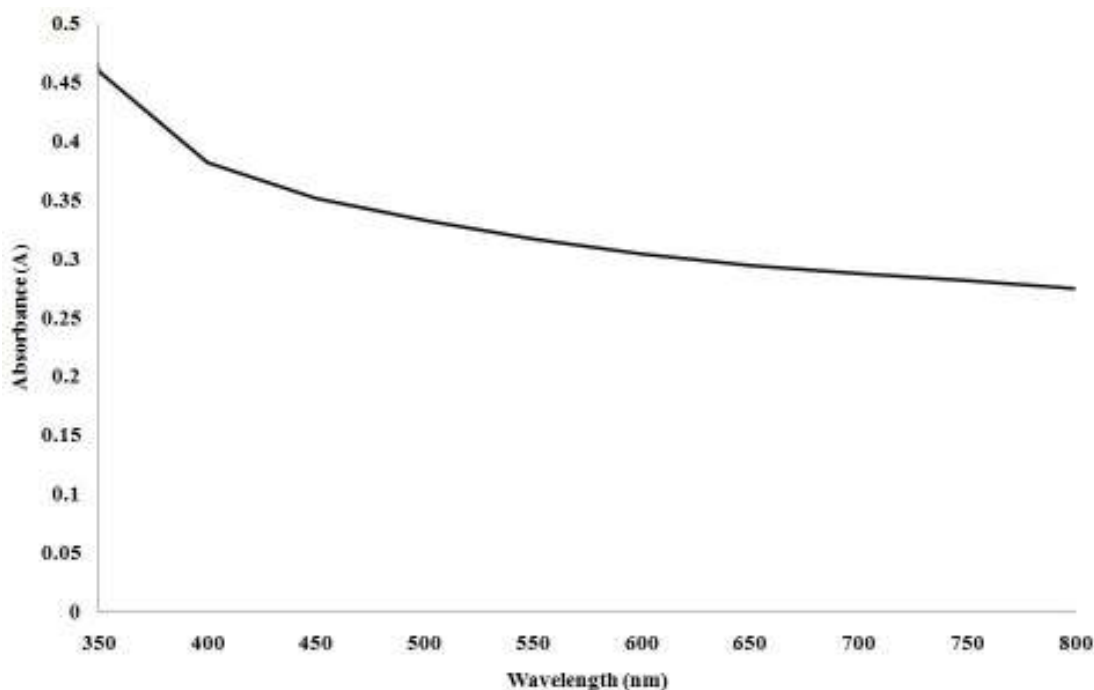


Fig. 4. Optical absorbance versus wavelength of Cu_4SnS_4 thin films deposited at optimized deposition parameters

The band gap energy and transition type can be derived from mathematical treatment of data obtained from optical absorbance versus wavelength with the Stern [23] relationship of near-edge absorption (Equation 1):

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

where ν is the frequency, h is the Planck's constant, k equals a constant while n carries value which is either 1 or 4. The plot of $(Ah\nu)^2$ versus $h\nu$ for the films deposited at optimized deposition conditions is shown in Fig. 5. The band gap energy is obtained by extrapolating the linear portion of $(Ah\nu)^{2/n}$ versus $h\nu$ to the energy axis at $(Ah\nu)^{2/n} = 0$. The line to determine the band gap is plotted using Microsoft Excel software (least square method). The R^2 value obtained from the graph shown is 0.962 which is almost to the value of 1. This value shows that all the data is fitted well by using this

least square method. The linear nature of the plot indicates the existence of direct transition [24]. The band gap value is found to be 1.57 eV.

Figure 6 shows the photoresponse of Cu_4SnS_4 thin films in contact with the $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ redox system. The current-potential response when lights are shone and chopped at an almost constant frequency is overlaid on the results of this test carried out in dark condition for a better delineation of photocurrent and darkcurrent. The photocurrent can be explained by the fact that once transition of electrons occurs, holes are left in the valence band with a lifetime adequate for them to participate in electrochemical reaction at the electrode/electrolyte interface [25]. The current changes with the illumination indicating the films possess semiconductor behavior. The fact that photocurrent occurs on negative potential indicates that the films prepared are of p -type and they can be deployed as photocathode in the photoelectrochemical cell.

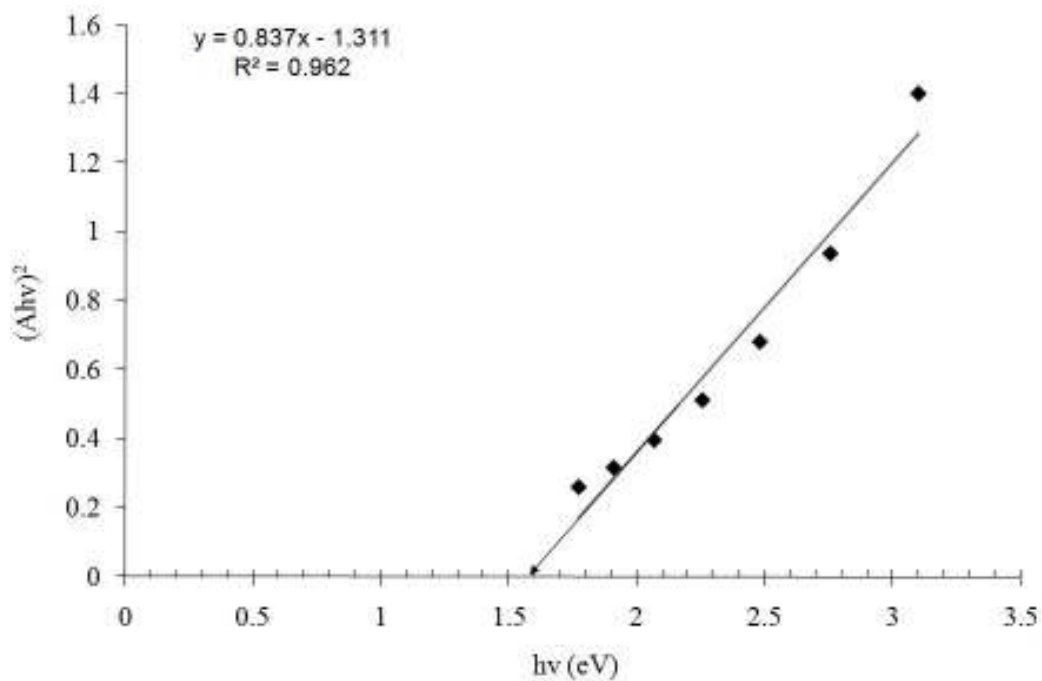


Fig. 5: Plot of $(Ah\nu)^2$ versus $h\nu$ of Cu_4SnS_4 thin films deposited at optimized deposition parameters

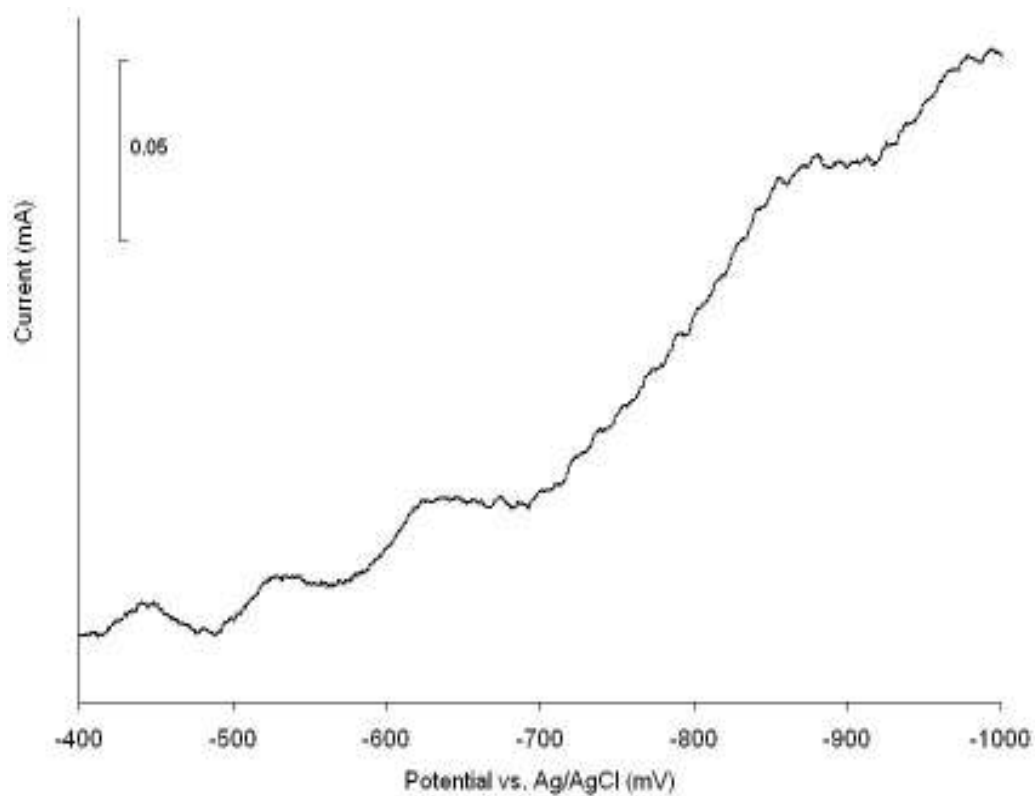


Fig. 6. The photosensitivity of Cu_4SnS_4 thin films deposited at optimized deposition parameters

4. CONCLUSION

Cu_4SnS_4 thin films were successfully deposited onto the indium tin oxide glass substrate using the chemical bath deposition method. The chemical bath consisted of CuSO_4 , SnCl_2 and $\text{Na}_2\text{S}_2\text{O}_3$ as the starting materials while Na_2EDTA was used as the complexing agent. The X-ray diffraction study revealed that Cu_4SnS_4 films were polycrystalline in nature with the preferential orientation along (221) plane. The atomic force microscopy results indicated that the films were smooth, uniform and the substrate surface was covered completely at this experimental condition. These films exhibited *p*-type semiconductor behavior with the band gap energy which was about 1.57 eV.

Acknowledgement: The authors would like to thank the Department of Chemistry, University Putra Malaysia for the provision of laboratory facilities and MOSTI for the National Science Fellowship.

REFERENCES

- [1] S. Messina, M.T.S. Nair, P. K. Nair, Antimony sulfide thin films in chemically deposited thin film photovoltaic cells, *Thin Solid Films*, **515**, 5777–5782 (2007).
- [2] M. Ristov, G. Sinadinovski, M. Mitreski, M. Ristova, Photovoltaic cells based on chemically deposited *p*-type SnS, *Sol. Energy Mater. Sol. Cells*, **69**, 17–24 (2001).
- [3] A. M. Fernandez, M. G. Merino, Preparation and characterization of Sb_2Se_3 thin films prepared by electrodeposition for photovoltaic applications, *Thin Solid Films*, **366**, 202–206 (2000).
- [4] Z. Zainal, N. Saravanan, K. Anuar, M. Z. Hussein, W. M. M. Yunus, Chemical bath deposition of tin selenide thin films, *Mater. Sci. Eng., B*, **107**, 181–185 (2004).
- [5] W. L. Li, X. T. Meng, X. Liang, H. Wang, H. Yan, Electrodeposition and characterization of PbSe films on indium tin oxide glass substrates, *J. Solid State Electrochem.*, **10**, 48–53 (2006).
- [6] C. Gautier, G. Breton, M. Nouaoura, M. Cambon, S. Charar, M. Averous, Sulfide films on PbSe thin layer grown by MBE, *Thin Solid Films*, **315**, 118–122 (1998).
- [7] S. Armstrong, P. K. Datta, R. W. Miles, Properties of zinc sulfur selenide deposited using a close-spaced sublimation method, *Thin Solid Films*, **403–404**, 126–129 (2002).
- [8] Y. B. He, A. Polity, H. R. Alves, I. Osterreicher, W. Kriegseis, D. Pfisterer, B. K. Meyer, M. Hardt, Structural and optical characterization of RF reactively sputtered CuInS_2 thin films, *Thin Solid Films*, **403–404**, 62–65 (2002).
- [9] R. A. Berrigan, N. Maung, S. J. C. Irvine, D. J. C. Hamilton, D. Ellis D, Thin films of CdTe/CdS grown by MOCVD for photovoltaics, *J. Cryst. Growth*, **195**, 718–724 (1998).
- [10] M. A. Atif, I. Takao I., H. Seiichi, Structural and photoluminescence properties of nanocrystalline silicon films deposited at low temperature by plasma-enhanced chemical vapor deposition, *Appl. Surf. Sci.*, **253**, 1198–1204 (2006).
- [11] A. Antony, K. V. Murali, R. Manoj, M. K. Jayaraj, The effect of the pH value on the growth and properties of chemical-bath-deposited ZnS thin films, *Mater. Chem. Phys.*, **90**, 106–110 (2005).
- [12] S. Seghaier, N. Kamoun, R. Brini, A. B. Amara, Structural and optical properties of PbS thin films deposited by chemical bath deposition, *Mater. Chem. Phys.*, **97**, 71–80 (2006).
- [13] A. David, D. Guadalupe, M. T. S. Nair, P. K. Nair, Structural and chemical transformations in SnS thin films used in chemically deposited photovoltaic cells, *Thin Solid Films*, **515**, 5771–5776 (2007).
- [14] A. Cortes, H. Gomez, R. E. Marotti, G. Riveros, E. A. Dalchiale, Grain size dependence of the bandgap in chemical bath deposited CdS thin films, *Sol. Energy Mater. Sol. Cells*, **82**, 21–34 (2004).
- [15] K. Anuar, W. T. Tan, N. Saravanan, S. M. Ho, S. Y. Gwee, Influence of pH values on chemical bath deposited FeS_2 thin films, *Pacific J. Sci. Technol.*, **10**, 801–805 (2009).
- [16] P. S. Sonawane, P. A. Wani, L. A. Patil, T. Seth, Growth of CuBiS_2 thin films by chemical bath deposition technique from an acidic bath, *Mater. Chem. Phys.*, **84**, 221–227 (2004).
- [17] A. M. Salem, M. O. Abou-Helal, Preparation and characterization of chemically deposited PbSnS_3 thin films, *Mater. Chem. Phys.*, **80**, 740–745 (2003).
- [18] Z. Khfacha, Z. Benzarti, M. Mnari, M. Dachraoui, Electrical and optical properties of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ ($0 \leq x \leq 0.18$) grown by chemical bath deposition, *J. Cryst. Growth*, **260**, 400–409 (2004).
- [19] R. B. Kale, C. D. Lokhande, R. S. Mane, S. H. Han, $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{Se}$ wide range composite thin films for solar cell buffer layer application, *Appl. Surf. Sci.*, **253**, 3109–3112 (2007).
- [20] M. T. S. Nair, C. Lopez-Mata, O. GomezDaza, P. K. Nair, Copper tin sulfide semiconductor thin films produced by heating SnS-CuS layers deposited from chemical bath, *Semicond. Sci. Technol.*, **18**, 755–759 (2003).
- [21] S. Jaulmes, J. Rivet, P. Laruelle, Cuivre-etain-soufre Cu_4SnS_4 , *Acta Crystallogr. B*, **33**, 540–542 (1977).
- [22] T. Jiang, N. Hall, A. Ho., S. Morin, Quantitative analysis of electrodeposited tin film morphologies by atomic force microscopy, *Thin Solid Films*, **417**, 76–85 (2005).
- [23] F. Stern, Elementary theory of the optical properties of solids, *Solid State Phys.*, **15**, 299–408 (1963).
- [24] C. D. Lokhande, A. U. Ubale, P. S. Patil, Thickness dependent properties of chemically deposited Bi_2S_3 thin films, *Thin Solid Films*, **302**, 1–4 (1997).
- [25] S. J. Fonash, in: *Solar Cell Device Physics*, Academic Press, Sydney, 1981.