Photoactivity of Cu_2S Thin Films Prepared through Electrodeposition

Anuar Kassim, Ph.D.*, Zulkarnain Zainal, Ph.D., R. Vikneshwari,

and N. Saravanan

Department of Chemistry, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia.

*Author for Correspondence.

ABSTRACT

Cathodic electrodeposition in the presence of sodium dodecylsulphate in aqueous solution was used to prepare copper sulphide thin films deposited on titanium substrates. The effect of the deposition potential, concentration, and deposition time was studied to determine the optimum conditions for electrodeposition process. Cyclic voltammetry was performed to elucidate the electrodic processes that occur while potentials for electrodeposition were applied to determine the optimum potential for electrodeposition. The films were characterized by X-ray diffraction and photo-electrochemical technique.

(Key words: electrodeposition, metal chalcogenides, thin film electrochemistry)

INTRODUCTION

There has been an increasing interest during the past few decades in semiconducting chalcogenide thin films, because of their wide applications in various fields of science and technology. This has resulted in a drastic cut in the cost of production of semiconductor devices. Metal chalcogenide films have been extensively studied because of their promise in electronic, optical, and superconductor devices as well as solar energy conversion studies by photovoltaic (PV) means (Rai, 1993, Singh, 1989, Mishra et al, 1989, Sharon et al, 1987, Engelken et al 1986). Binary semiconductors are considered important technological materials because of their potential applications in optoelectronic devices, solar cells, IR detectors and lasers (Hodes, 1995, Pandey et al, 1996, Makhnii et al).

Semiconductor materials for terrestrial solar cells must meet the following two requirements: (1) the material should have appropriate electrical and optical properties for solar cells and (2) its constituent elements should be abundant, cheap and non-toxic. Due to these factors, electrodeposition is probably the cheapest method to deposit large area thin films, and has been widely used for metal plating (Fernandez, A.M et al, 2000).

Thin film semiconducting materials are now widely used and researchers are working on various methods to prepare good quality films. In this paper we report on the preparation and photoactivity of copper sulphide thin films that could be used as a semiconducting device in a photo-electrochemical cell.

MATERIALS AND METHODS

The deposition for this research was carried out potentiostatically using an EG&G Priceton Applied Research potentiostat, driven by a software model 270 Electrochemical Analysis System. A conventional three-electrode cell is employed, where the reference electrode is a Ag/AgCl and Pt is the counter electrode. Titanium (99.99%) was used as the working electrode. Sodium dodecylsulphate (SDS) was used as a complexing agent to chelate with Cu^{2+} to obtain Cu-SDS solution. The presence of a complexing agent in aqueous solution was found to improve the lifetime of the deposition bath as well as the adhesion of the deposited film on the Ti substrate (Ghazali et al, 1988).

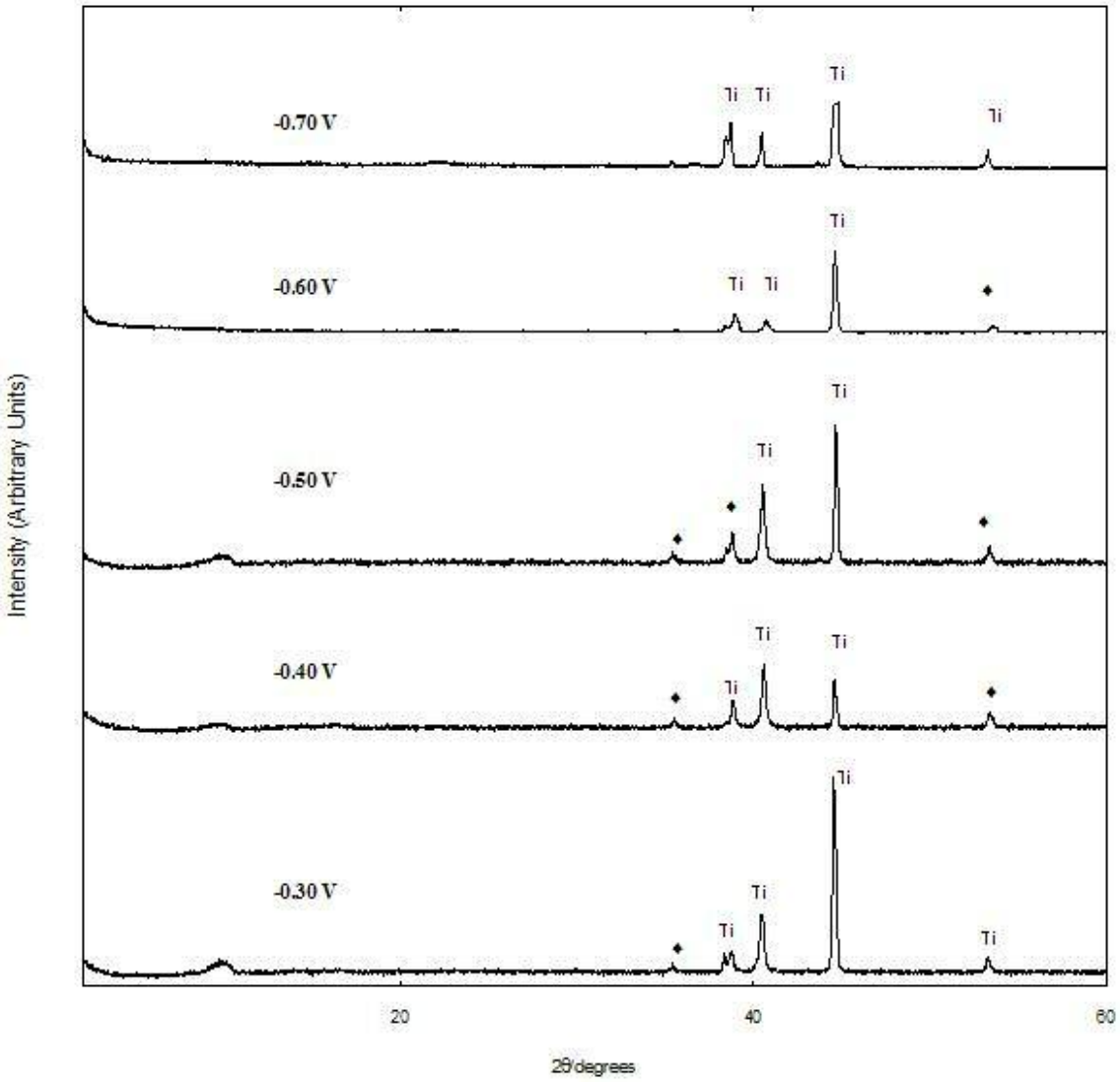
An electrodeposition test was carried out on the cell containing the two solutions, Cu-SDS and $Na_2S_2O_3$. The deposition bath consisted of 0.01 M Cu-SDS (45 ml) and 0.01 M $Na_2S_2O_3$ (45 ml) solution. The experiment was performed at room temperature (27 ° C) under N_2 blanket without stirring. The pH was maintained at 2.5 using HCl. HCl was added to prevent the formation of hydroxyl species and insoluble compounds. The substrate and the counter electrode were polished prior to the insertion into the electrolyte cell. The surface of the working electrode that is not contact with the electrolyte was sealed using PTFE tape.

The films were prepared at various deposition potentials, solution concentrations, and deposition times. The deposited films were rinsed with distilled water and kept for further comparison and analysis. The films were characterized by X-ray diffraction (XRD) and photo-electrochemical technique (PEC). XRD analysis was performed using a Philips PM 1730 diffractometer for the 2θ (range = 2° - 60°) with CuKα radiation. Photo-electrochemical experiments were performed by running linear sweep voltammetry (LSV) between two potential limits (-0.30 to -1.00 V). An electrolytic bath was used containing 80 ml 0.010 M $Na_2S_2O_3$ as prepared using deionized water. The sequence of constant chopped illumination was performed on the PEC cell to study the effect on photoactivity behavior. A halogen tungsten lamp (300 W, 120 V) was used for illumination of the electrode.

RESULTS AND DISCUSSION

Varying deposition potential: The deposition potential was carried out at different potentials: -0.30V -0.40, -0.50, -0.60 and -0.70V. The XRD pattern (Figure 1) indicates that the peaks belonging to the polycrystalline Cu_2S material are detected for films prepared at potentials less than -0.60V. For the films prepared at -0.30V, there is only one peak at 2θ = 34.6º corresponding to interplanar distance of 2.58 Å, which is in good agreement with the JCPDS value (File No: 12-0227) (Table 1). The film deposited at potential -0.40V showed two peaks at 2θ = 36.6° and 54.9° corresponding to interplanar distances of 2.58 Å and 1.66 Å, respectively, which matches the correlating theoretical values of 2.59 Å and 1.67 A. Three peaks were detected for the film prepared at -0.50V at 2θ = 34.6° , 38.1° and 52.4° corresponding to interplanar distances of 2.58 Å, 2.37 Å and 1.74 Å. Only one peak was detected at 2θ = 52.4° corresponding to interplanar distance of 1.74 Å for the film prepared at -0.60V. No peaks were observed for potential at -0.70V.

Figure 1. XRD Patterns of Cu_2S Samples Prepared at Different Deposition Potentials.



Cu_2S (♦)

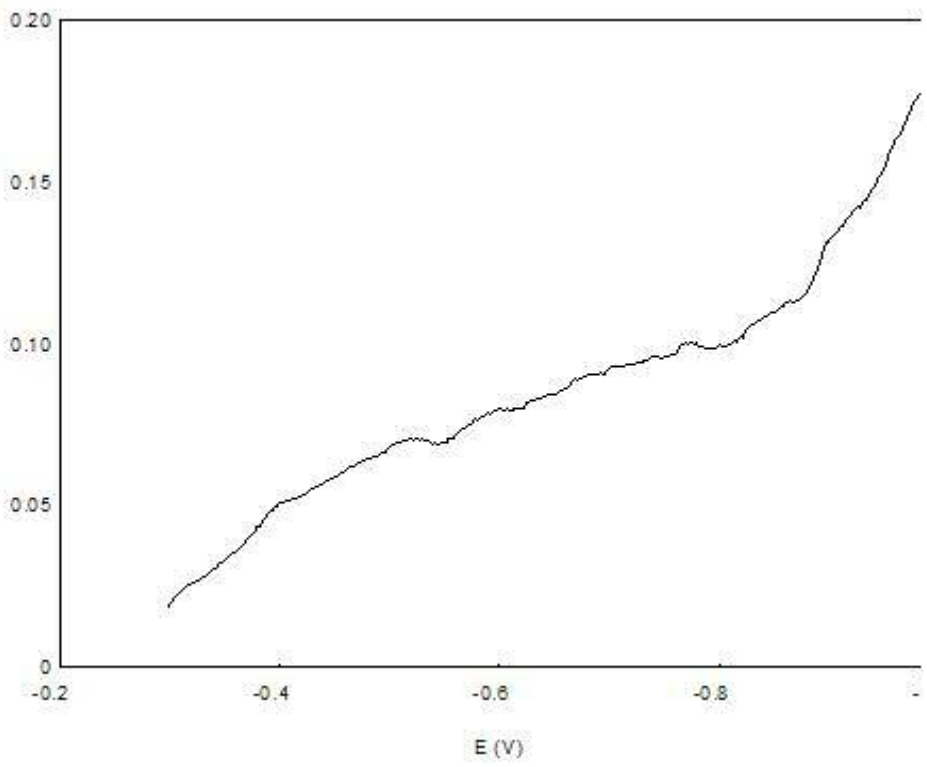
Table 1. X-ray Diffraction Data of Samples Prepared at Various Potentials.

Potential (V)	2θ	d-value (Å)	JCPDS value (Å)
-0.30	34.6°	2.58	2.59
-0.40	36.6° , 54.9°	2.58, 1.65	2.59,1.67
-0.50	34.6° , 38.1° , 52.4°	2.58, 2.37, 1.74	2.59, 2.36, 1.75

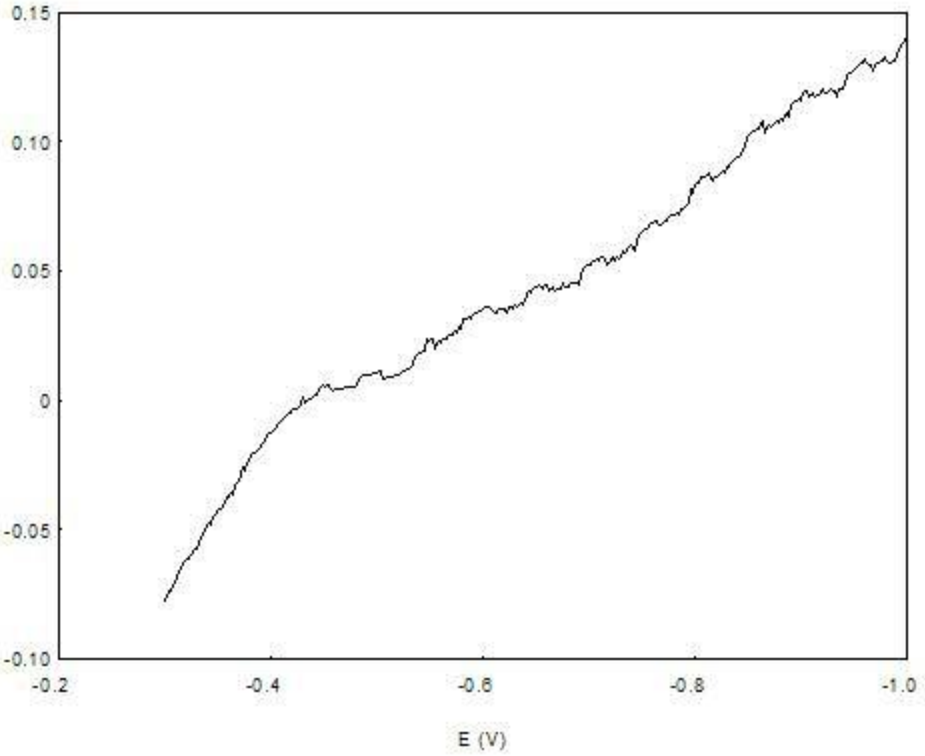
-0.60	52.4°	1.74	1.75

Figure 2 shows the light photoresponse of the film deposited at different potentials with 0.010 M $Na_2S_2O_3$ solution. The graph shows the resulting changes in the current when the sample employed as a cathode in the electrochemical cell, has been illuminated intermittently. This current change with the illumination, confirms that the films possess semiconducting behavior. The upper value corresponds to the current when the samples were illuminated, while the lower value corresponds to the darkcurrent, due to the chopping of the light. The photocurrent output in mA, can be regarded as relatively high values.

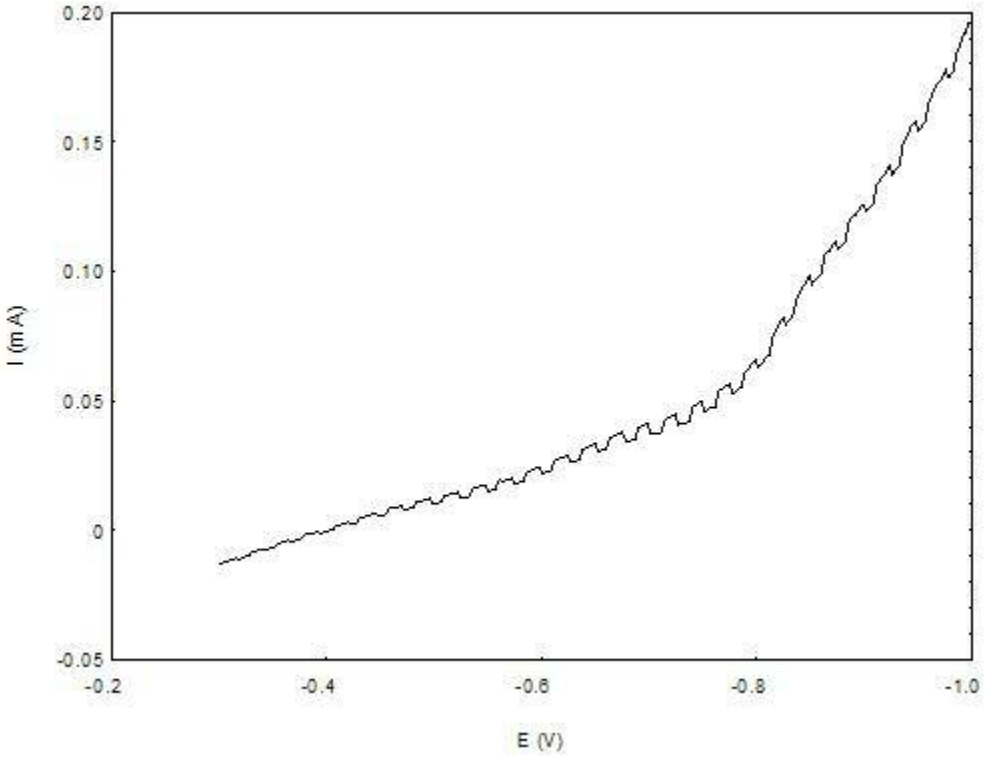
Figure 2. Comparison of Photosensitivity of Cu_2S Thin Films Deposited at Different Potentials



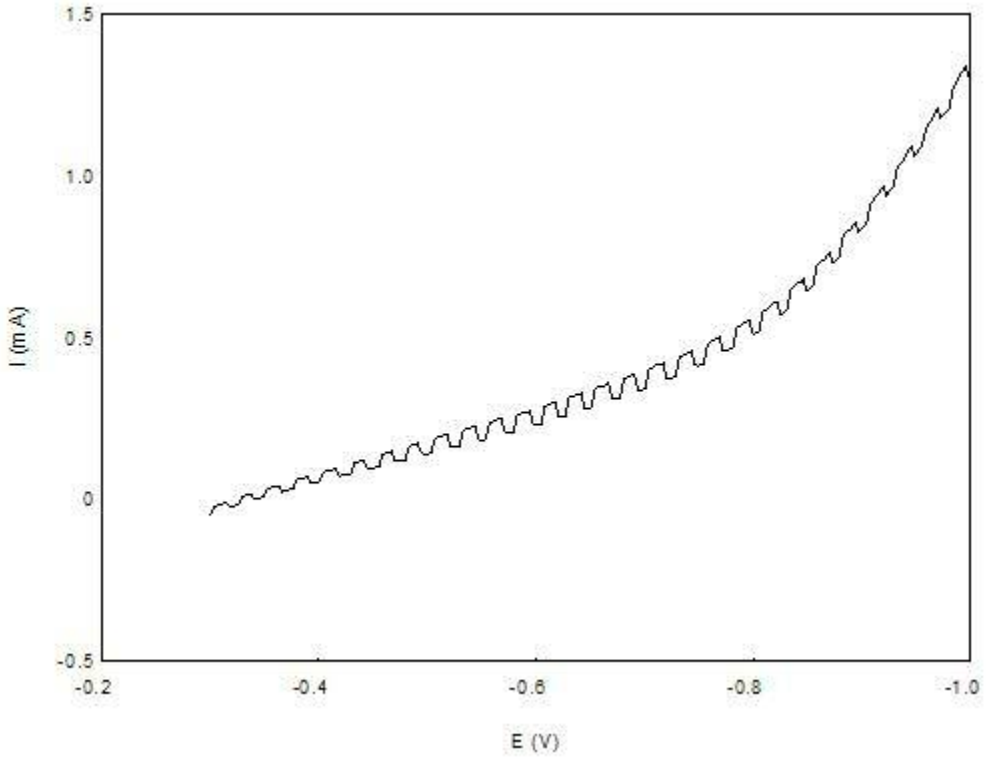
a) -0.30V


0.15
0.10
0.05
0
-0.05
-0.10
-0.2
-0.4
-0.6
-0.8
-1.0
E (V)

b) -0.40V


0.20
0.15
0.10
0.05
0
-0.05
I (mA)
-0.2
-0.4
-0.6
-0.8
-1.0
E (V)

c) -0.50V



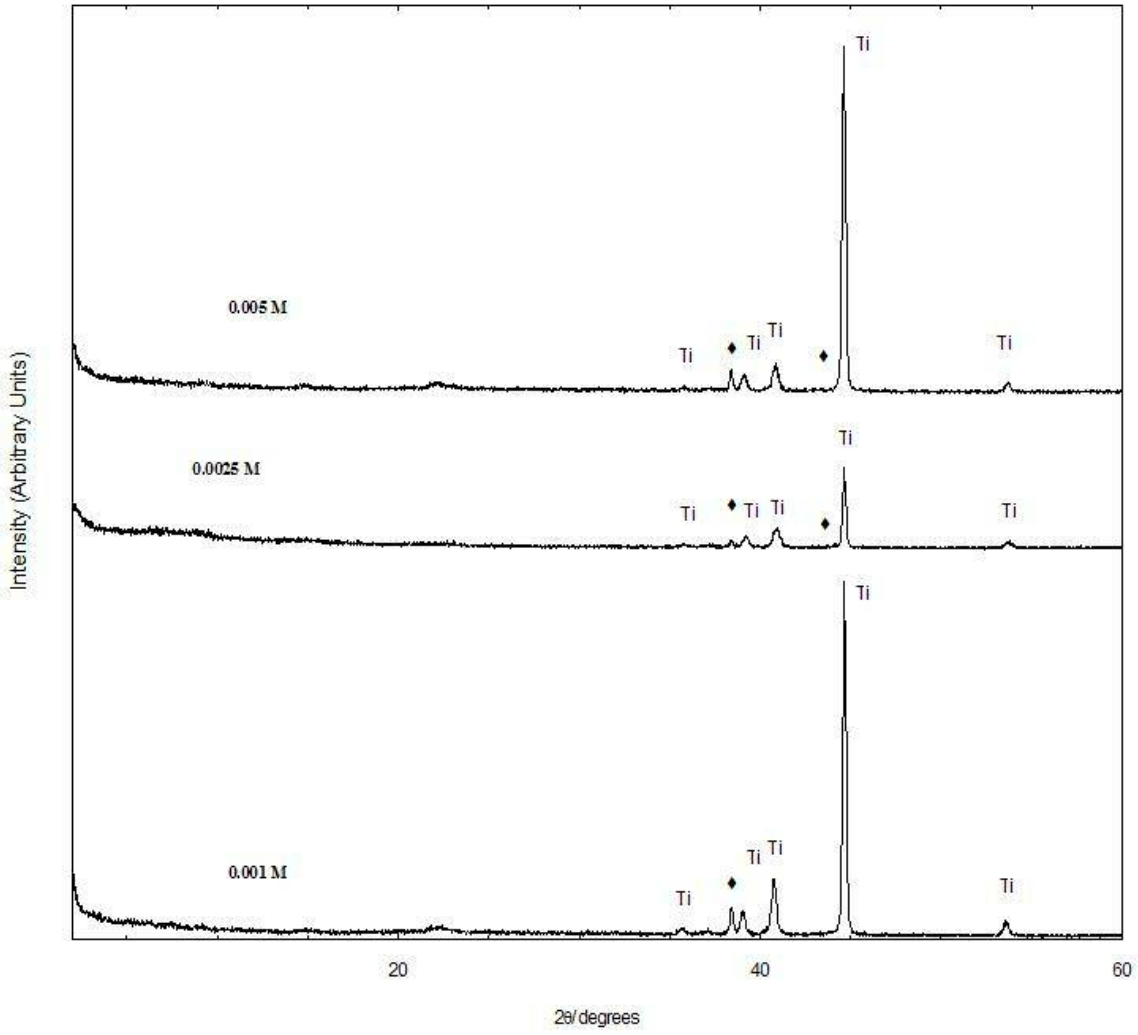
d) -0.60V

The fact that the photocurrent occurs on the negative (cathodic) potential indicates that the films prepared are of p-type (positive). The samples prepared at -0.50 V and -0.60 V have better photosensitivity.

Varying concentration of $Na_2S_2O_3$: Various concentration of $Na_2S_2O_3$

(0.001 M, 0.0025 M, and 0.005 M) with a fixed concentration of 0.010 M of $CuSO_4$, were used to prepare Cu_2S thin films. The deposition was carried out for 45 minutes at the deposition potential of -0.50 V (vs. Ag/AgCl). XRD patterns of the deposited samples (Figure 3) indicate a peak at $2\theta = 38.1°$ corresponding to interplanar distance of 2.37 Å, which is in good agreement with the JCPDS value of 2.36 Å. Two peaks corresponding to interplanar distances of 2.37 Å and 2.04 Å were observed for the film prepared from 0.0025 M $Na_2S_2O_3$. There were also two peaks obtained at $2\theta = 38.1°$ and 44.3° for 0.005 M $Na_2S_2O_3$ preparation, with corresponding interplanar distances of 2.37 Å and 2.04 Å (Table 2).

Figure 3. XRD Patterns of the Samples Prepared at Different $Na_2S_2O_3$ Concentrations



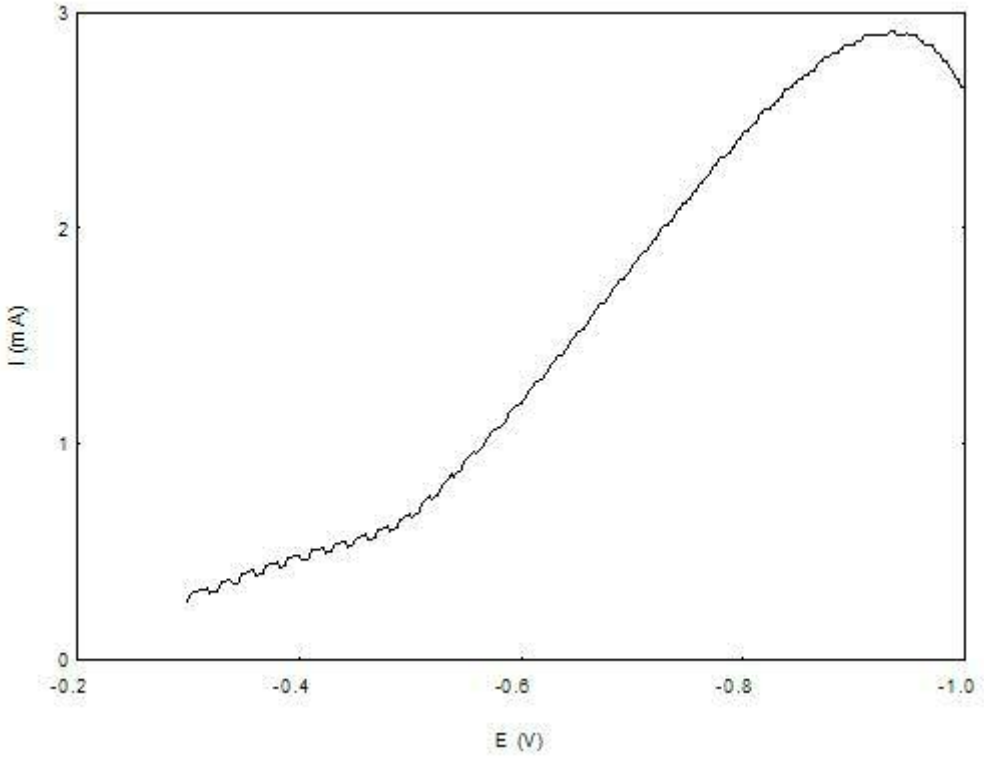
The CU-SDS concentration was fixed at 0.010M. Cu_2S (♦).

Table 2. X-ray Diffraction Data of Samples Prepared at Various Concentrations of $Na_2S_2O_3$ (concentration of Cu-SDS was fixed at 0.010 M).

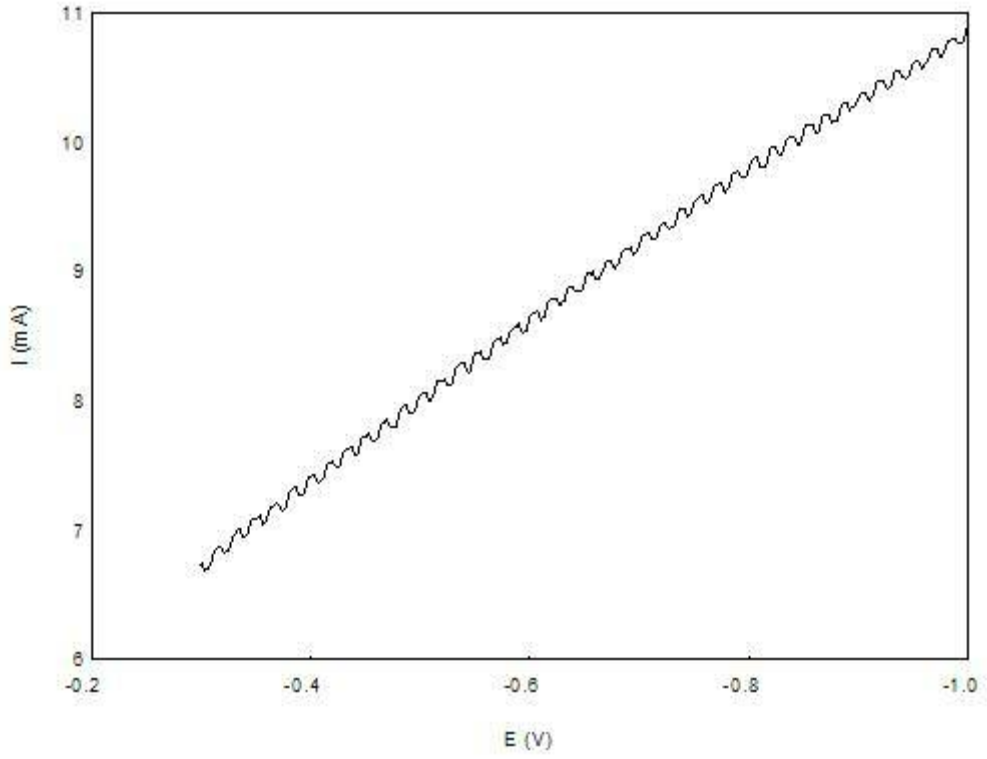
Concentration of $CuSO_4$ (M)	2θ	d-value (Å)	JCPDS value (Å)
0.001	38.1°	2.37	2.36
0.0025	38.1° , 44.3°	2.37, 2.04	2.36, 2.05
0.005	38.1° , 44.3°	2.37, 2.04	2.36, 2.05

Figure 4 shows the photoactivity of the samples prepared in various $Na_2S_2O_3$ concentrations at constant concentration of $CuSO_4$ (0.010 M). The photocurrent is obviously in the cathodic direction; thus cathodic polarization minority carriers, which are indicative of p-type semiconductor films, were deposited. Different samples show different photosensitivities. The best PEC was obtained from the samples deposited with 0.0025 M of $Na_2S_2O_3$ as the chopping signals are very clear.

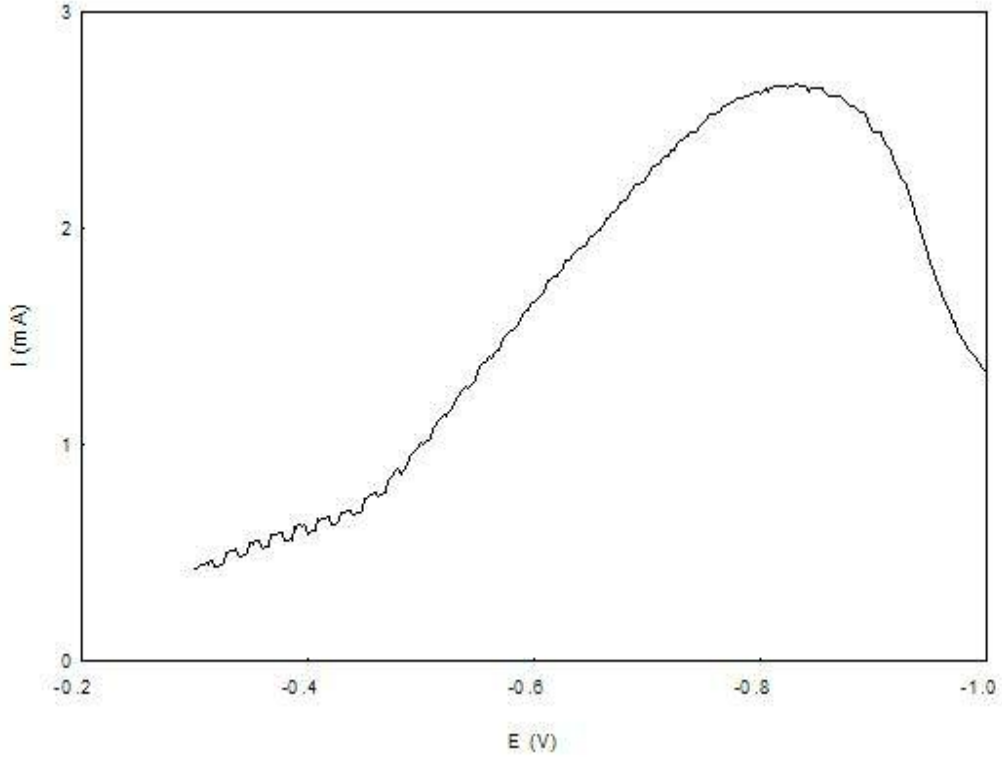
Figure 4. The Photosensitivity of Samples Prepared at Different $Na_2S_2O_3$ Concentrations ($CuSO_4$ fixed at 0.010M).



a) 0.001M



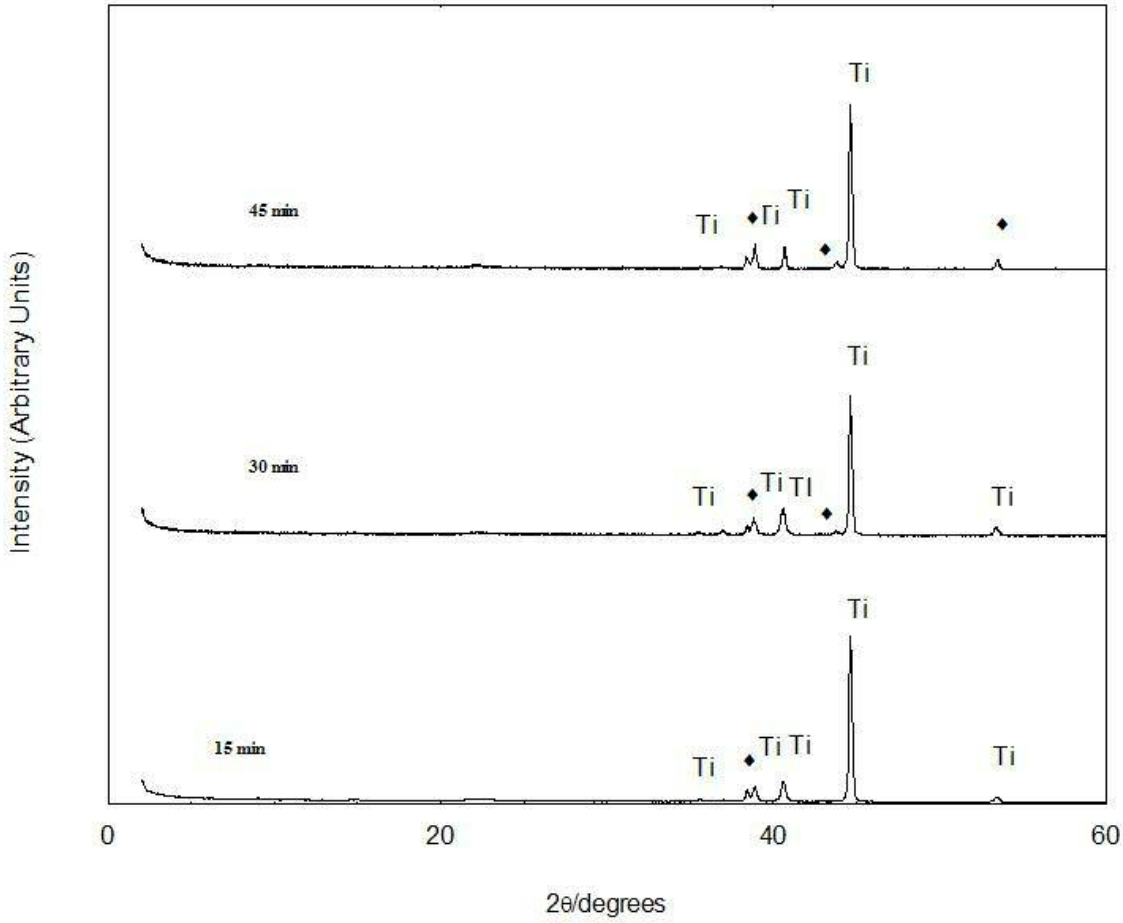
b) 0.0025M



c) 0.005M

Varying deposition periods: Deposition was performed at varying times ranging from 15 to 45 minutes using concentrations of 0.010 M of $CuSO_4$ and 0.010 M $Na_2S_2O_3$. The pH of the deposition bath was maintained in the range 2.50-2.60. The XRD pattern (Figure 5) for samples deposited for 15 minutes shows a peak belonging to Cu_2S at $2\theta = 38.1°$ corresponding to the interplanar distance of 2.37 Å. Two peaks at $2\theta = 38.1°$ and 44.3° were detected for samples prepared at 30 minutes, corresponding to interplanar distances of 2.37 Å and 2.04 Å, respectively, which are in good agreement with the JCPDS values of 2.36 Å and 2.05 Å (Table 3). Three peaks were observed at $2\theta = 38.1°$, 44.3° and 52.4° corresponding to the interplanar distances of 2.37 Á, 2.04 Å and 1.74 Á when the deposition time was extended to 45 minutes.

Figure 5. XRD Patterns of Cu_2S Samples Prepared at Different Deposition Periods: 15, 30 and 45 Minutes.



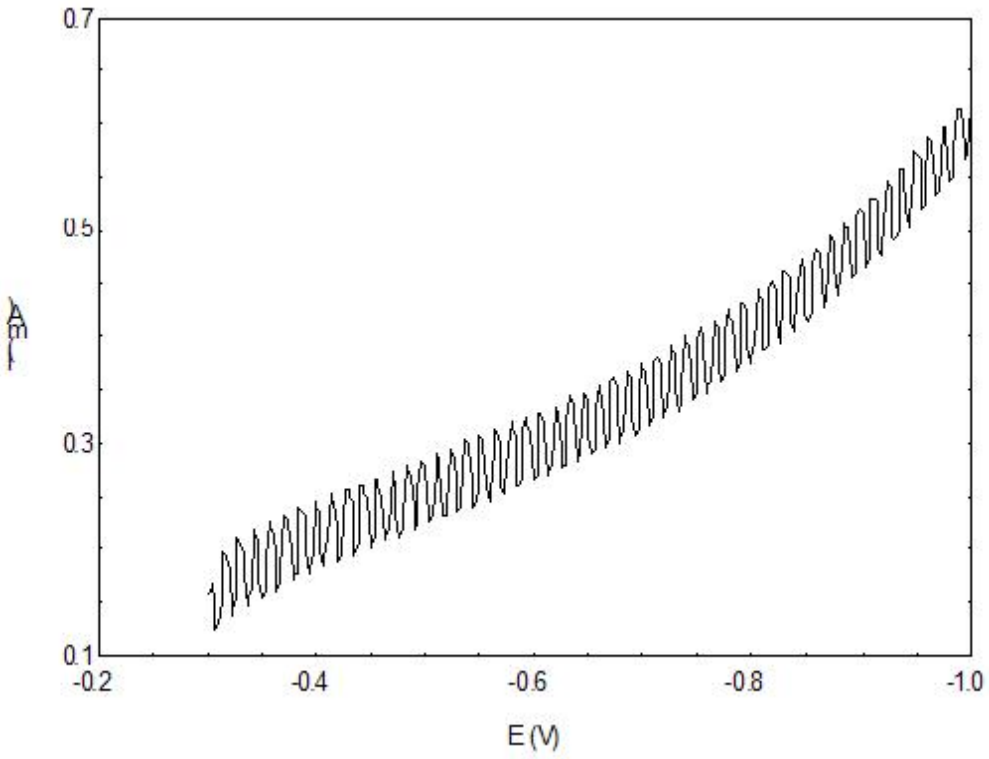
Cu_2S (♦).

Table 3. X-ray Diffraction Data of Samples Prepared at Various Deposition Times.

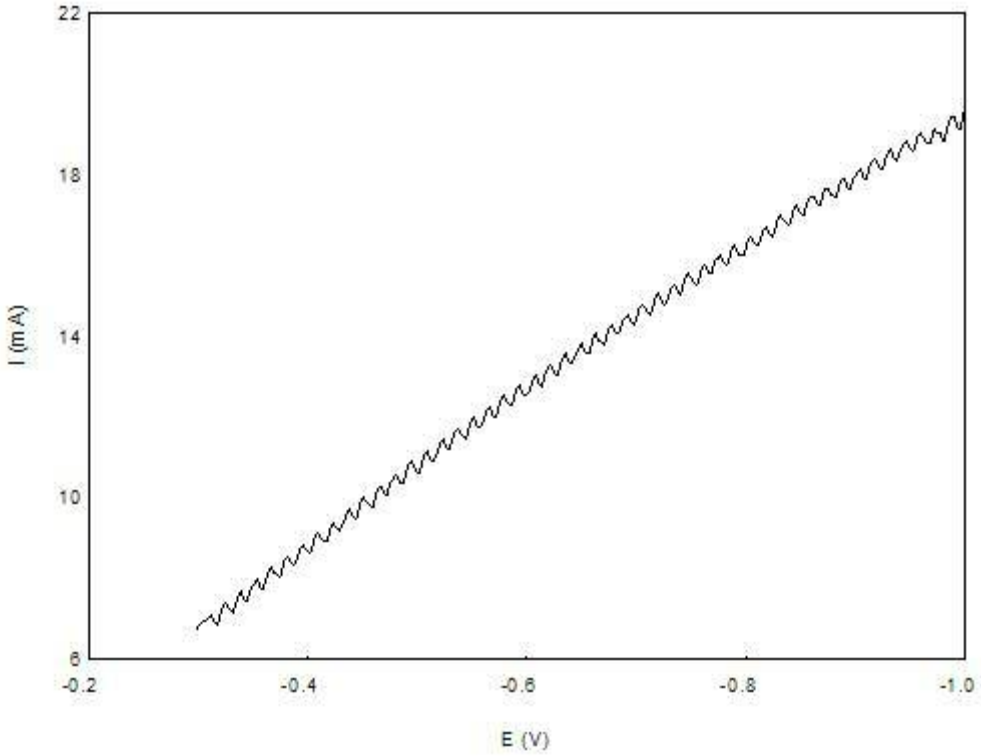
Deposition time (min)	2θ	d-value (Å)	JCPDS value (Å)
15	38.1°	2.37	2.36
30	38.1° , 44.3°	2.37, 2.04	2.36, 2.05
45	38.1° , 44.3° , 52.4°	1.74, 2.37, 2.04	1.75, 2.36, 2.05

The results obtained from the PEC experiments carried out at different deposition periods are shown in Figure 6. The sample prepared for 30 minutes indicates the best photoactivity and shows the highest photocurrent.

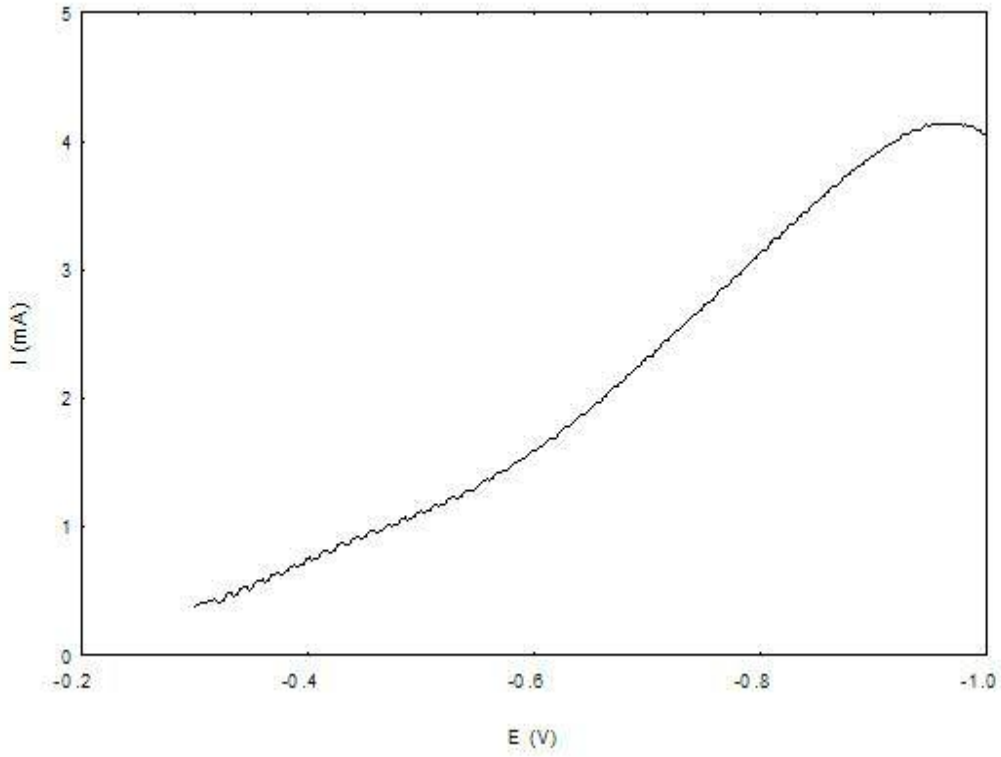
Figure 6. The Photosensitivity of the Samples Prepared at Different Deposition Periods: (a) 15, (b) 30 and (c) 45 minutes.



a) 15 minutes



b) 30 minutes



c) 45 minutes

CONCLUSIONS

The optimum potential to prepare the Cu_2S films was found to be -0.50 V. Films prepared at lower concentration of $Na_2S_2O_3$ (0.0025 M) shows better photoactivity. The optimum deposition time was found to be at 30 min.

ACKNOWLEDGMENTS

The authors are very grateful for the grant given by the Malaysian Government under IRPA-7 Grant No: 09-02-04-0101.

REFERENCES

Engelken, R. D., Berry, A. K., Van Doren, T. P., Boone, J. L., and Shahnazary, A. 1986. Electrodeposition and Analysis of Tin Selenide Films. *J. Electrochem. Soc.* 133:581-585.

Ghazali, A., Zainal, Z., Hussein, M.Z., and Kassim, A. 1988. Cathodic Electrodeposition of SnS Thin Films Using EDTA as Chelating Agent. *Sol. Energy Mater*. Sol. Cells 55:237-243.

Hodes, G. 1995. Physical electrochemistry. I. Rubinstein (Ed.), Principles, Methods and Applications, Marcel Dekker Inc., New York, pp. 515-554.

Fernandez, A.M., and Merino, M.G. 2000. Preparation and Characterization of Sb_2Se_3 Thin Films Prepared by Electrodeposition for Photovoltaic Applications. Thin Solid Films. 366: 202-206.

Rajeshwar, K. 1992. Electrosynthesized Thin Films of Group II-Iv Compound Semiconductors, Alloys and Superstructures. 4:23-29.

Mishra, K. K., and Rajeshwar, K. 1989. A Re-examination of the Mechanism of Electrodeposition CdX and ZnX (X = Se, Te) Semiconductors by the Cyclic Photovoltammetric Technique. J. Electroanal. Chem. 273:169.

Pandey, R.K., Sahu, S.N., Chandra, S. 1996. Handbook of Semiconductor Electrodeposition (Ed.), Marcel Dekker Inc., New York, pp. 27-60, 82-85, 205-238.

Rai, J.P. 1993. Electrosynthesis of Zinc Selenide and Thallium Containing Zinc Selenide Thin Films and Their Characterization. *Solar Energy Mater.* 30:119.

Sharon, M. and Basavaswaran, K. 1987. Photoelectrochemical Studies on p-SnSe Electrodes. *Solar Cells* 20:323.

Singh, K., and Rai, J.P., 1989. Electrosynthesis and Photoelectrochemical Characterization of Zinc Selenide Doped With Thallium. Ind. J. Chem. 28A 557.

About the Authors:

Dr. Anuar Kassim is an Associate Professor in the Department of Chemistry, Universiti Putra Malaysia. Dr. Kassim's research interests relate to thin films, conducting polymers, surfactants, and activated carbon.

Dr. Zulkarnain Zainal is an Associate Professor in the Department of Chemistry, Universiti Putra Malaysia. Dr. Zainal's research interests focus on semiconductor electrodeposition, photo-catalysis, and activated carbon and nanocomposite applications.

R. Vikneshwari is a post-graduate student in the Department of Chemistry, Universiti Putra Malaysia.

N. Saravanan is a post-graduate student in the Department of Chemistry, Universiti Putra Malaysia.

Cite As: Kassim, A. Z. Zainal, R. Vikneshwari, and N. Saravanan. 2003. Photoactivity of CU_2S Thin Films Prepared Through Electrodeposition. *Greenwich Journal of Science and Technology*. 3(2):76-89.

Return to GJST Home Page