Solid State Science and Technology, Vol. 17, No 2 (2010) 74-83
ISSN 0128-7389

PULSE ELECTRODEPOSITION AND SOLID PHASE VOLTAMMETRY OF COPPER INDIUM DISULFIDE SEMICONDUCTOR THIN FILMS

S. L. Teo, Z. Zainal, W. T. Tan and M. Z. Hussein

Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor Darul Ehsan, Malaysia.

ABSTRACT

$CuInS_2$ thin films were deposited onto fluorine doped tin oxide coated glass (FTO) using pulse electrodeposition from aqueous solutions comprising Cu-EDTA, $In_2(SO_4)_3$ and $Na_2S_2O_3$. Deposited films were polycrystalline with tetragonal structure and behavior as a p-type semiconductor. A smooth and adherent film was obtained at pulse height of -1.00 V and the band gap energy was found to be 1.40 eV with indirect transition. The Cu:In:S compositions of the films was 1.1:1.0:1.8. From morphological studies, the particles had worm like structure which interconnected with each other. Solid phase voltammetry resulted in redox couple of Cu^{2+}/Cu^{+} and Cu^{+}/Cu^{0}.

INTRODUCTION

Recently, $CuInS_2$ has attracted much interest as absorber layer in photovoltaic cell applications because of its direct band gap energy of ~1.5 eV, high conversion efficiency and high absorption coefficient. Many deposition techniques have been studied for the preparation of $CuInS_2$ thin films, such as sulfurization of eletrodeposited Cu-In precursor, spray pyrolysis, co-evaporation, etc [1]. Electrodeposition was found suitable for the commercial and large scale application because of its simplicity and low cost. Pulse electrodeposition refers to deposition when the potential is alternated rapidly between two different values [2]. Variables like pulse magnitude, pulse time and duty cycle are varied to control macroscopic properties of the films such as morphology, porosity and adhesion [3].

EXPERIMENTAL DETAILS

Preparation of films

In this work, cyclic voltammetry, pulse electrodeposition and solid phase voltammetry were carried out using a μ-type III AUTOLAB potentiostat driven by General Purpose Electrochemical System software. A three electrode-cell was used, where Ag/AgCl as the reference electrode, FTO as the working electrode and platinum wire as the counter electrode. The deposition bath comprised of Cu-EDTA, $In_2(SO_4)_3$ and $Na_2S_2O_3$. The solution pH was adjusted using sulphuric acid. The probable potential range for deposition was predetermined by running cyclic voltammetry. Pulse height of -0.90 V, -0.95 V and -1.00 V were applied.

Corresponding Author: zulkar@science.upm.edu.my

Solid State Science and Technology, Vol. 17, No 2 (2010) 74-83
ISSN 0128-7389

Characterizations of films

X-ray Diffraction (XRD) analysis (Philips PM 1730) was used to determine the phase composition, crystal structure and crystallite size of the deposited samples. The photoelectrochemical (PEC) behavior of the films were evaluated using linear sweep photovoltammetry by intermittently illuminating the samples with halogen lamp (120 V 300 W) in 0.01 M $Na_2S_2O_3$ electrolyte. Atomic force microscopy (AFM) was performed using contact mode of AFM Quesant Q Scope 250 to analyze the roughness means square (RMS) of the film. Field emission scanning electron microscopy (FESEM) was performed using SUPRA™ 40VP Versatile High Performance VP SEM with superb resolution and image quality at low operating voltages to analyze the surface morphology. Transmission electron microscopy (TEM) was performed using TEM Hitachi H-1700. Energy dispersive analysis of X-rays (EDAX) was performed using JSM 6400 JEOL Scanning Microscope attached with Oxford INCA Energy 200 EDX to determine the elemental composition in the sample. The transition type and band gap energy were determined using Perkin-Elmer Lambda 20 UV-visible spectrophotometer. Solid phase voltammetry was run to investigate the electrochemical properties of the film.

RESULTS AND DISCUSSION

Pulse current profile

The pulse current profile of the first 6 s deposition at pulse height of -1.00 V is shown in Figure 1. During ON time, high current is observed due to nucleation and growth because more evenly distributed ions are available for deposition. During the OFF time, the elemental copper and indium which are bounded to sulfur will redissolves into the bulk solution [4] and allows the region of the solution near the film surface to be replenished with Cu^{2+}, In^{3+} and S colloids through diffusion. The concentration of these metal ions will reach the equilibrium concentration of the bulk electrolyte if enough time is allowed. Thus, the nucleation rate can be kept high throughout the deposition process. As shown in Figure 1, deposition at -1.00 V was able to generate high current of 12 mA. Some inverse (anodic) current was observed in the OFF time and will approach null in the adequate OFF time, which means that the initial solute concentration will recover within that time [5].

Corresponding Author: zulkar@science.upm.edu.my

Solid State Science and Technology, Vol. 17, No 2 (2010) 74-83
ISSN 0128-7389

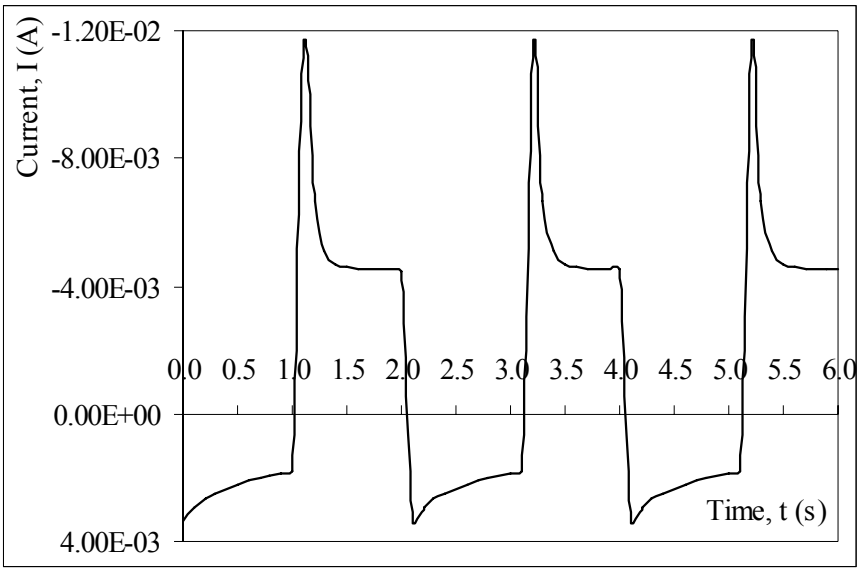


Figure 1: Pulse current profile.

XRD analysis

XRD patterns are shown in Figure 2. $CuInS_2$ films were polycrystalline with tetragonal structure. Peaks belonging to $CuInS_2$ were present at $2\theta = 29.3^o$, 43.2^o, 47.5^o, 48.6^o and 54.7^o for all applied potentials. Peak intensity at $2\theta = 29.3^o$ increased as the potential increased from -0.90 V to -1.00 V. In this potential range, films thickness is depends on applied potential, higher potential will contribute to thicker film. The darker film color was observed by naked eye which represents the thicker film. With appropriate thickness obtained at -1.00 V, the observed peak intensity was the highest among them.

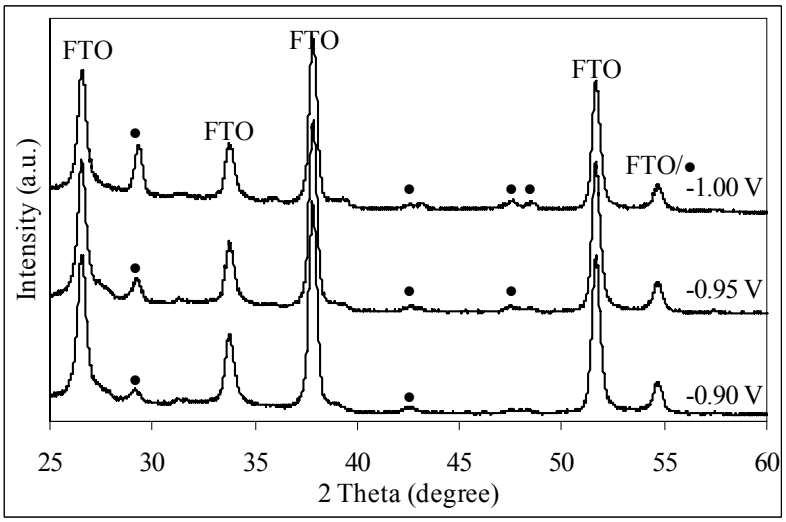


Figure 2: XRD patterns for films deposited at different pulse potentials.

Corresponding Author: zulkar@science.upm.edu.my

Solid State Science and Technology, Vol. 17, No 2 (2010) 74-83
ISSN 0128-7389

Photoelectrochemical experiments

PEC experiments were performed to evaluate the photoresponse of $CuInS_2$ thin films. To be expected as semiconductor, a material should be sensitive to light, with energy higher than its band gap by showing a photocurrent in the region corresponding to their majority carriers current flow.

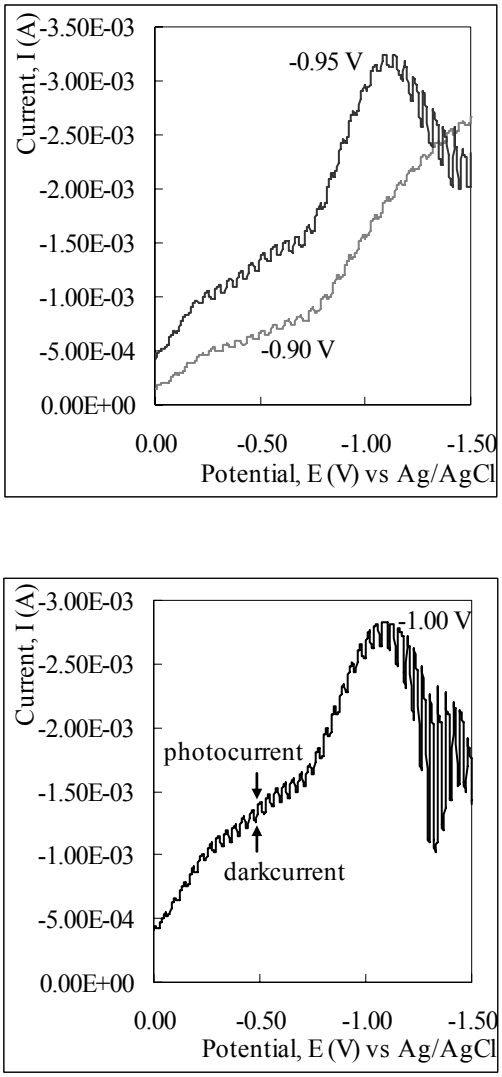


Figure 3: Photoresponse of films deposited at different pulse potentials.

The reactions at semiconductor/electrolyte interface occur as the electrons flow through the junction and reduced some species in the electrolyte. The holes left in $CuInS_2$ are collected at the back contact (FTO) to produce a cathodic photocurrent. This observation suggests that the electrons are preferentially scavenged by the electrolyte while holes diffuse to the back contact where they are withdrawn as a photocurrent [6]. Formation of spikes at cathodic region is due to the generation of photocurrent when the sample was intermittently illuminated. Thus, $CuInS_2$ is a p-type semiconductor with

Corresponding Author: zulkar@science.upm.edu.my

holes as majority carriers.

As pulse potential increase from -0.90 V to -1.00 V, the formation of spikes became more significant (Figure 3). The spike height represents the different between photocurrent and dark current. From XRD and PEC results, pulse potential at -1.00 V was selected as the optimum potential.

Morphological studies

AFM images in Figure 4 showed the film had smooth surface with uniformly distributed fine structure. The surface roughness was 74.73 nm.

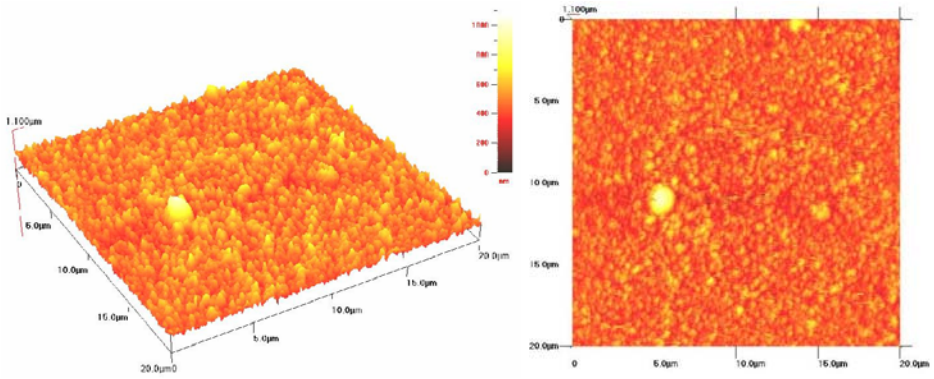
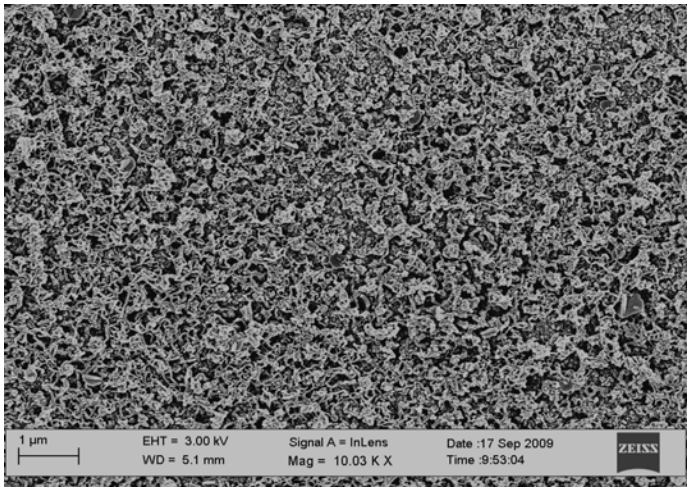


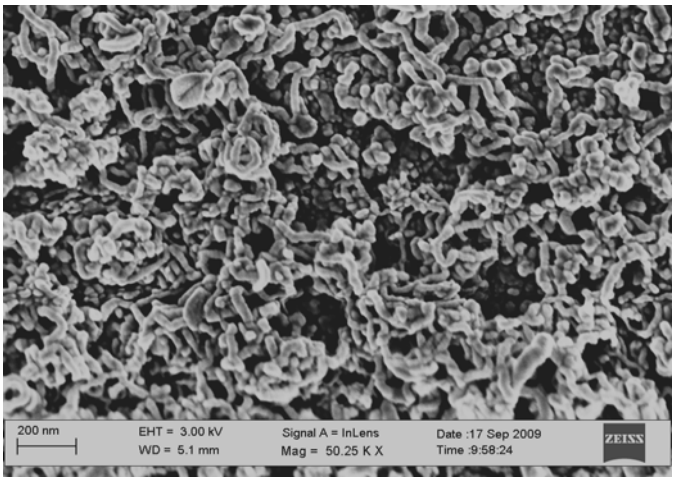
Figure 4: AFM images of film deposited at potential of -1.00 V.

From FESEM micrographs (Figure 5), the film was compact, dense and has a very fine structure without crack or pinhole. The particles have worm like structure which are interconnected with each other can be observed at higher magnification.



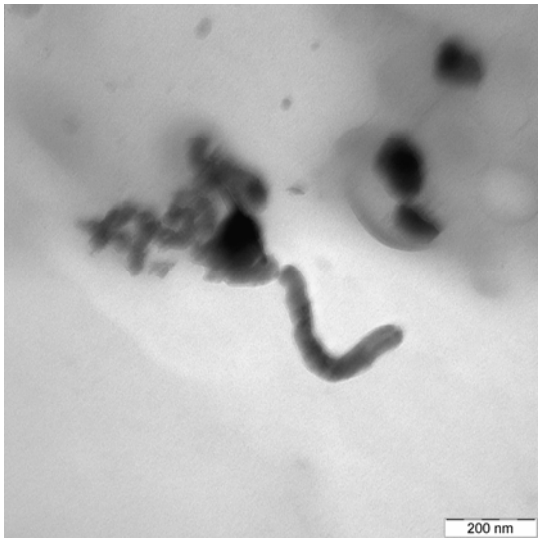
(a)

Corresponding Author: zulkar@science.upm.edu.my



(b)

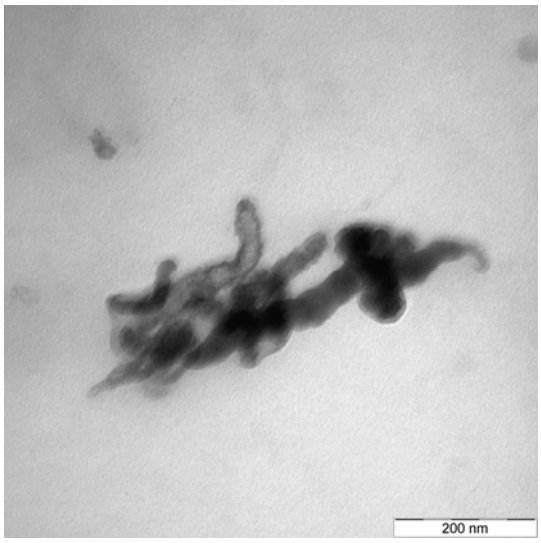
TEM provides unique capabilities to reveal the small particles (nano) structure feature and interaction at high magnification. If samples are too thick, they absorb too much electron beam and cause dark images. Worm like particles were observed in the TEM micrographs (Figure 6) and correlated with FESEM result. The particles width was estimated in the range of 36.63-59.06 nm with different length.



(a)

Corresponding Author: zulkar@science.upm.edu.my

Solid State Science and Technology, Vol. 17, No 2 (2010) 74-83
ISSN 0128-7389



(b)

Figure 6: TEM micrographs of film deposited at potential of -1.00 V at magnifications of (a) 100, 000 X and (b) 150, 000 X.

Elemental composition and estimated crystallite sizes
The ratio of Cu:In:S was determined using EDAX resulted in 1.1:1.0:1.8. Table 1 shows the comparison of estimated crystallite size values determined from XRD (using Scherrer's formula at $2\theta = 29.3^{o}$), FESEM and TEM. The obtained values using different instrumentations resulted approximately in agreement values.

Table 1: Comparison of estimated crystallite size obtained from XRD, FESEM and TEM.

Crystallite size (nm)		
XRD	FESEM	TEM
40.45	42.79	47.08

Optical absorption study
Pronounced absorption spectrum was observed between 320 and 800 nm (Figure 7a). Thus, the films are active in the visible portion of the spectrum, so they have potential to be applied as visible light energy conversion material.

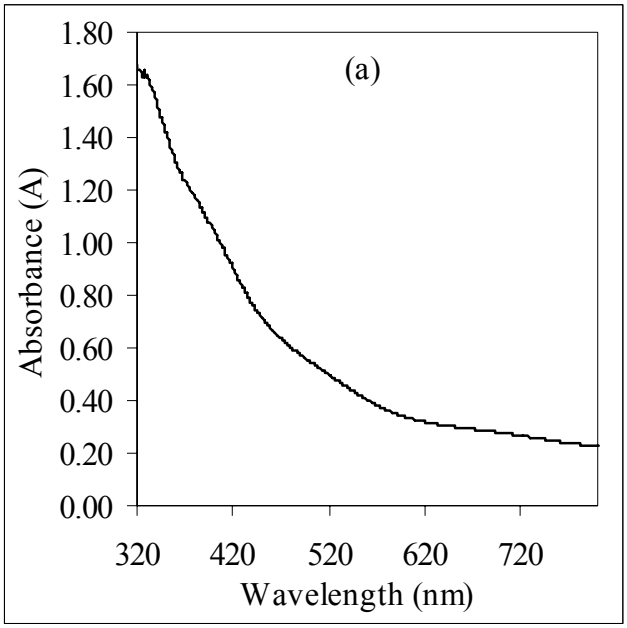
The band gap energy was calculated using following equation:

$$(Ahv)^{\frac{2}{n}} = k'(hv - E_g) \quad (1)$$

Corresponding Author: zulkar@science.upm.edu.my

Solid State Science and Technology, Vol. 17, No 2 (2010) 74-83
ISSN 0128-7389

where A is absorbance, ν is frequency, h is Planck's constant, E_g band gap energy and k', k, n= constant. The plot of $(Ahv)^{2/n}$ as the function of hν with n=1 indicated direct transition (Figure 7b). The obtained band gap was 1.40 eV with indirect transition.



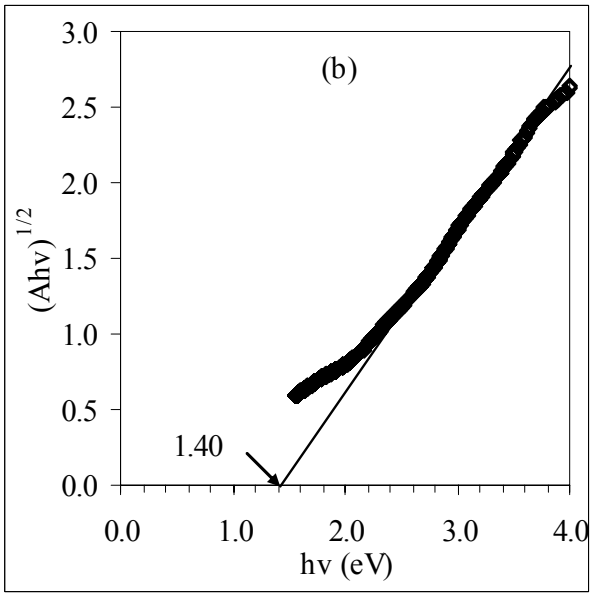


Figure 7: Optical study.

(a) absorbance versus wavelength and (b) plot of $(Ahv)^{1/2}$ versus hν

Corresponding Author: zulkar@science.upm.edu.my

Solid State Science and Technology, Vol. 17, No 2 (2010) 74-83
ISSN 0128-7389

Solid phase voltammetry

Study of solid phase voltammetry involves electrochemical characteristics and stability of redox active film immersed in supporting electrolyte. Cyclic voltammogram of $CuInS_2$ immersed in 0.10 M NH_4Cl is shown in Figure 8.

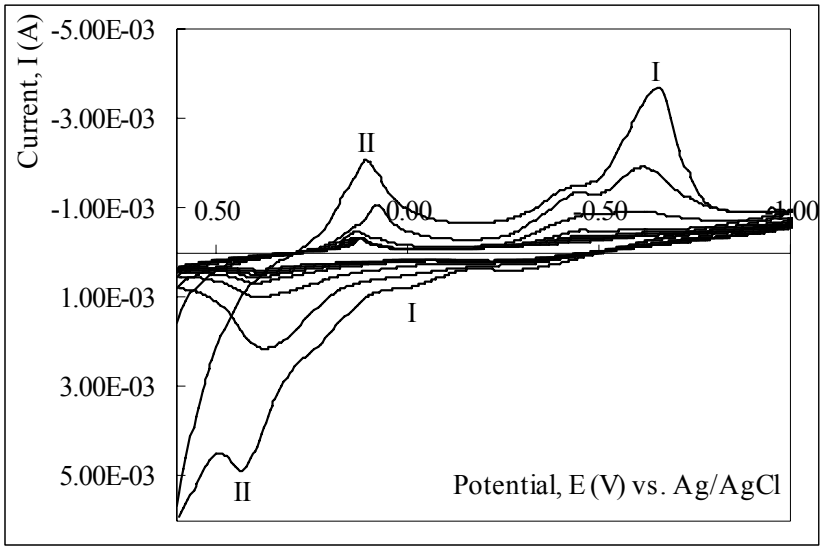


Figure 8: Solid phase voltammogram of $CuInS_2$ film immersed in 0.10 M NH_4Cl using scan rate of 20 mV/s.

At first cycle, the curve was deviated from second cycle because the redox reaction was not completed yet and the curve became more stable after second cycle. Consequently, data of the third cycle were used for the investigation. The redox reaction was identified as process (I) and (II). Voltammetric data of anodic potential (E_{pa}), anodic current (I_{pa}), cathodic potential (E_{pc}) and cathodic current (I_{pc}) are simplified in Table 2.

The presence of NH_4^+ ions in the electrolyte can act as complexing agent toward copper ion. The mechanism of redox peaks of Cu^{2+}/Cu^+ and Cu^+/Cu^0 detected is shown as following:

$$Cu + NH_4Cl \longrightarrow Cu(NH_3)_4^{2+} + Cl^- \quad (2)$$

$$Cu(NH_3)_4^{2+} + e \leftrightarrow Cu(NH_3)^+ + 2NH_3 \quad (3)$$

Process (I): $CuL^{2+} + e \rightarrow CuL^+$ L = NH_3 or related ligand (4)

Process (II): $CuL^+ + e \rightarrow Cu$ (5)

Corresponding Author: zulkar@science.upm.edu.my

Table 2: Voltammetric data of $CuInS_2$ films immersed in 0.10 M NH_4Cl using scan rate of 20 mV/s.

Potential (V)				Current (mA)			
I		II		I		II	
E_{pa}	E_{pc}	E_{pa}	E_{pc}	I_{pa}	I_{pc}	I_{pa}	I_{pc}
0.05	-0.67	0.46	0.09	0.80	3.53	4.67	1.93

CONCLUSION

The optimum pulse potential for deposition of $CuInS_2$ film was at -1.00 V. $CuInS_2$ films were polycrystalline with tetragonal structure. $CuInS_2$ was p-type semiconductor with indirect band gap energy of 1.40 eV. Morphological studies showed the film surface roughness was 74.73 nm, compact and dense with worm like particles. The estimated crystallite sizes were in the range 40.45-47.08 nm. Solid phase voltammetry represented the redox couples of Cu^{2+}/Cu^{+} and Cu^{+}/Cu^{0}.

ACKNOWLEDGEMENTS

We thank the Malaysian Government for financial support, Universiti Putra Malaysia for providing research facilities and Ministry of Science, Technology and Innovation for the National Science Fellowship.

REFERENCES

[1] Wijesundera, R. P. and Siripala, W. (2004). Preparation of $CuInS_2$ thin films by electrodeposition and sulphurisation for applications in solar cells. *Solar Energy Materials & Solar Cells* **81** 147-154.

[2] Ghaemi, M. and Binder, L. (2002). Effects of direct and pulse current on electrodeposition of manganese dioxide. *Journal of Power Sources* **111** 248-254.

[3] Sharma, R. K., Singh G. and Rastologi, A. C. (2004). Pulsed electrodeposition of CdTe thin films: effect of pulse parameters over structure, stoichiometry and optical absorption. *Solar Energy Materials & Solar Cells* **82** 201-215.

[4] Fathy, N., Kobayashi, R. and Ichimura, M. (2004). Preparation of ZnS thin films by the pulsed electrochemical deposition. *Materials Science and Engineering B***107**(3) 271-276.

[5] Takeuchi, K., Ichimura, M., Arai, E. and Yamazaki, Y. (2003). SnS thin films fabricated by pulsed and normal electrochemical deposition. *Solar Energy Materials and Solar Cells* **75** (3-4) 427-432.

[6] Nasr, T. B., Kamoun, N. and Guasch, C. (2006). Structure, surface composition, and electronic properties of zinc sulphide thin films. *Materials Chemistry and Physics* **96** (1) 84-89.

Corresponding Author: zulkar@science.upm.edu.my