

ELECTROPHORETIC DEPOSITION AND CHARACTERIZATION OF CuSe THIN FILMS

Zulkarnain Zainal and Mohd Fairul Sharin Abdul Razak

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

ABSTRACT

Various methods have been developed for the preparation of copper selenide thin films. One of the promising method is by electrophoretic deposition (EPD) using copper selenide powder synthesized by chemical precipitation technique. The powder and deposited thin films at various deposition voltages were analysed using X-ray diffractometry (XRD) and scanning electron microscopy (SEM). XRD data of the thin film indicate the formation of polycrystalline materials. The SEM micrographs showed more compact and smaller granular shape for the film deposited at 300V compared to CuSe powder. The films produced were found to display p-type semiconducting behavior.

INTRODUCTION

Semiconducting metal chalcogenide are important materials for applications in various photoelectric and other devices. In recent years, there has been considerable interest in the study of copper selenide due to their composition's complexity [1] and wide application as solar cell materials and superionic conductors [2-5]. Copper selenide usually exists as copper (I) selenide (Cu_2Se or Cu_{2-x}Se) or copper (II) selenide (CuSe or Cu_3Se_2). Cu_3Se_2 is often reported as an impurity phase along with CuSe phase [6-7]. A number of method have been reported for the deposition of copper selenide thin films of different crystalline modification and varying stoichiometries including various preparation techniques such as flash evaporation [8-9], selenisation [10], vacuum evaporation [11] and chemical bath deposition [12]. In this paper, we report a relatively new electrophoretic deposition method to produce copper selenide thin films.

Electrophoretic deposition (EPD) is essentially a two-step process. In the first step, the particles suspended in a liquid are forced to move toward an electrode by applying an electric field (electrophoresis). In the second step, the particles collected at one of the electrode form a coherent deposit. This technique has attracted attention due to several advantages such as shorter deposition time, simple experiment set up, applicability for depositing layer on the substrate of complicated shape, and easy control of layer thickness. This paper deals with preparation, characterization and the photoelectrochemical properties of the copper selenide thin films prepared by this method.

EXPERIMENTAL

The chemicals were of Analar grade and used as obtained without further purification. All solutions were prepared using deionised water. CuSe powder was synthesized by chemical precipitation technique. The desired amount of elemental selenium was dissolved in NaOH (12 M) solution and rapidly stirred for 20 min. Upon complete dissolution of elemental selenium, Cu^{2+} solution was added and the rapid stirring process was maintained for almost 15 minutes. Black precipitate obtained was centrifuged and washed with deionised water and dried in an oven overnight. The dried paste precipitate was ground to a fine powder then a required amount of the synthesized powder was added in the organic solvent. Organic solvent was used as a medium for suspension due to their high density, good chemical stability and low conductivity. Ageing and prolong ultrasonication which was carried out in order to disperse the material and produce conducive conditions for deposition of smooth films.

A simple apparatus was set up to carry out the electrophoretic deposition. It comprises of an electrophoretic bath that can accommodate two electrodes, the working and counter electrodes which were made from titanium (Ti, 99.99%) and platinum, respectively. The Ti substrate and Pt electrode was polished and rinse with deionised water before the deposition process. The electrophoretic deposition experiment were performed in a 100 ml beaker containing 80 ml of suspension. Two electrodes were kept parallel in the suspension and a DC power supply was used to apply an electric field. The potential difference was varied from 50 to 300V for 1 minute deposition time. The films deposited were dried in an oven at 100°C for 30 minutes.

X-ray diffraction (XRD) analysis was carried out on the sample using a Philips PM 1730 Diffractometer for the 2θ ranging from 20° to 60° with $\text{CuK}\alpha$ line ($\lambda = 1.5418\text{\AA}$) was used as an incident beam. Scanning electron microscopy (SEM) was performed on a JEOL JSM 6400 Scanning microscope. Photoelectrochemical (PEC) test were run in $\text{Na}_2\text{S}_2\text{O}_3$ (0.02M) solution by running linear sweep voltammetry (LSV) between - 0.30 V and - 0.07 V. An EG&G Princeton Applied Research potentiostat driven by a software model 270 Electrochemical Analysis System was used to control the LSV process and to monitor the current and voltage profile in a conventional three-electrode cell.

RESULTS AND DISCUSSION

Figure 1. Shows the XRD plot of the copper selenide powder obtained through the chemical precipitation method. All peaks obtained are well matched with the JCPDS data (File No. 0604027)

The observed data obtained indicate hexagonal phase of CuSe was formed by this method. No selenium peaks or phase impurity are observed indicating that high purity CuSe powder was obtained. Fig. 2 shows the XRD patterns of the films prepared at different deposition voltages. The peaks corresponding to the formation of CuSe phase for all films and more intense peaks were observed at higher deposition voltages.

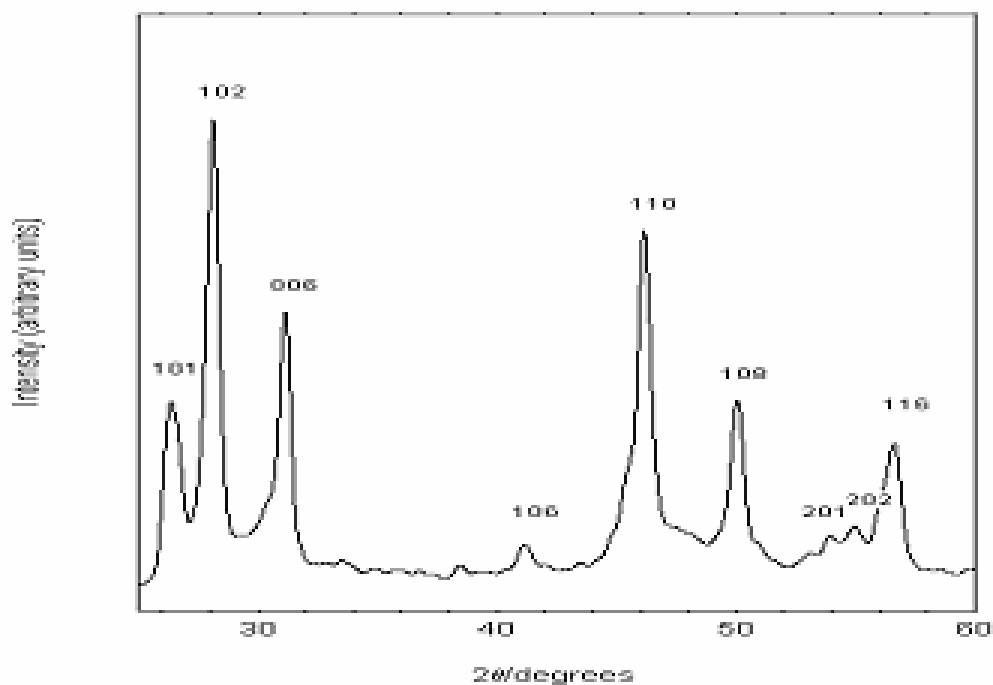


Figure 1 : XRD pattern of CuSe powder prepared by precipitation technique

Table 1 : XRD data of CuSe powder

2θ (°)	d-spacing (Å)		hkl	Compound
	experimental values	JCPDS values		
26.6	3.36	3.35	101	CuSe
28.2	3.18	3.18	102	CuSe
31.1	2.88	2.88	006	CuSe
41.1	2.19	2.19	106	CuSe
46.1	1.96	1.97	110	CuSe
50.1	1.82	1.82	108	CuSe
53.9	1.69	1.70	201	CuSe
54.9	1.66	1.62	202	CuSe
56.6	1.62	1.62	116	CuSe

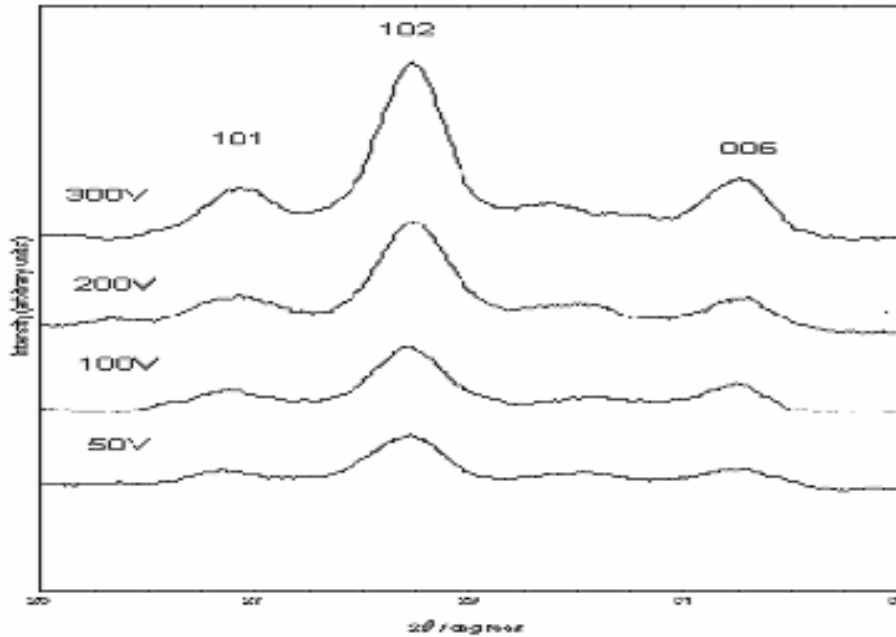


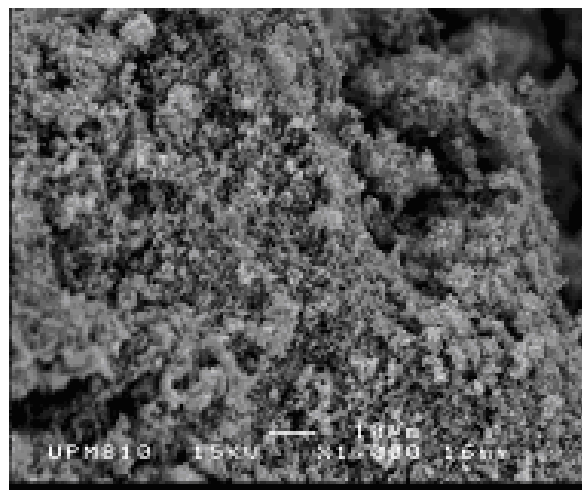
Figure 2: XRD patterns of the CuSe films prepared at different deposition voltages

Table 2: XRD data of CuSe films at different deposition voltages.

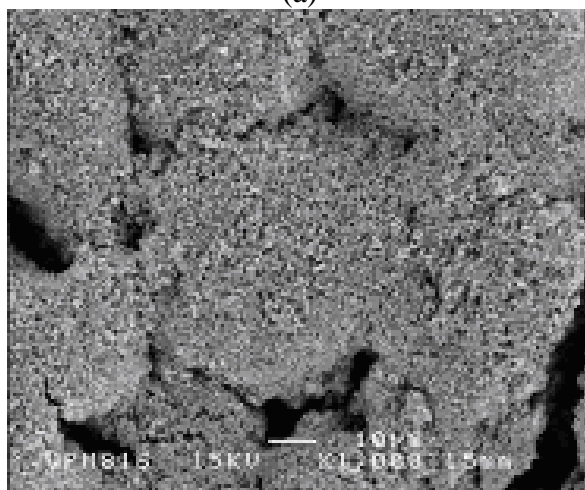
Voltage(V)	2θ (°)	d-spacing (Å)		hkl
		experimental values	JCPDS data	
50V	26.6	3.34	3.35	101
	28.2	3.14	3.18	102
	31.1	2.84	2.88	006
100V	26.6	3.34	3.35	101
	28.2	3.15	3.18	102
	31.1	2.84	2.88	006
200V	26.6	3.33	3.35	101
	28.2	3.15	3.18	102
	31.1	2.88	2.88	006
300V	26.6	3.33	3.35	101
	28.2	3.15	3.18	102
	31.1	2.88	2.88	006

Figure 3(a) and figure 3(b) show SEM micrographs of CuSe powder and thin film prepared at 300 V. It can be seen that the film contains densely packed CuSe particles.

These particles were much finer than the powders. This indicates that organic suspension was effective in breaking up the agglomerates present in the powder to produce a colloidal stable suspension.



(a)



(b)

Figure 3: (a) SEM micrograph of CuSe powder, (b) SEM Micrograph of CuSe film deposited at 300V

Figure 4 shows the photoresponse of the copper selenide films at different voltages in the presence of $\text{Na}_2\text{S}_2\text{O}_3$ upon illumination with a halogen lamp (100W). CuSe film deposited at 300V produced the highest photosensitivity. This probably due to more material deposited high voltages and larger crystallite size based on the XRD result. The fact that the photocurrent occur on the negative (cathodic) potential indicate that the film prepared are of p-type (positive).

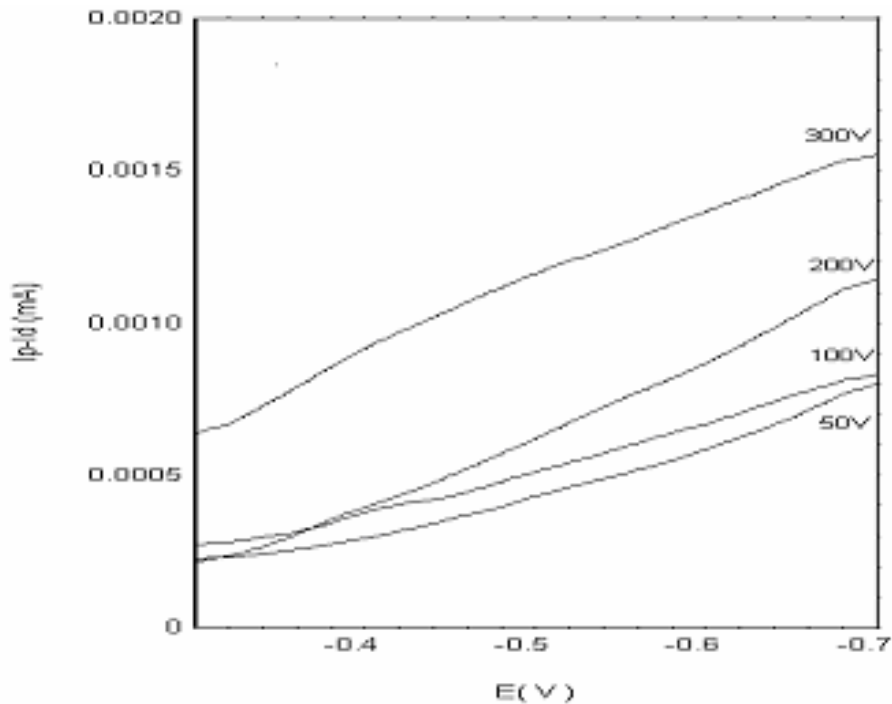


Figure 4: Comparison of the photocurrent to darkcurrent (I_p-I_d) of CuSe film at different voltages.

CONCLUSION

Polycrystalline copper selenide thin film could be prepared by electrophoretic deposition method. The method employed is a simple and less time-consuming compared to other conventional method. The XRD data confirmed the formation of polycrystalline materials. This study showed that by increasing the deposition voltages, the deposited amount of CuSe is also increased. The SEM micrographs show more compact and smaller granular morphology after electrophoretic process. CuSe thin films prepared are of p-type behaviour and the deposit photosensitivity increasing with applied voltage.

REFERENCES

- [1]. A. L. N.Stevens, F. Jellinek, *Recueil*, (1971), pg 273.
- [2]. H. Okimura, T. Matsumae, R. Makabe, *Thin Solid Films* (1980) 71, pg 53.
- [3]. W. S. Chen, J. M. Stewart, R. A. Mickelsen *Appl.Phys. Lett.* (1988) 46, pg 1095 .
- [4]. R. C Kainthla, D. K. Pandya, K.L. Chopra, *J. Electrochem. Soc.* (1982) **15**, pg 101.
- [5]. A. A. Korzhuev, *Fiz. Khim. Obrab. Mater.* (1981) **3**, pg 131
- [6]. R. B. Shafizade, I.V.Ivanova, M. M. Kazinets, *Thin Solid Films* (1978) **55**, pg 211.

- [7]. C. A. Estrada, P. K. Nair, M. T. S. Nair, R. A. Zingaro, E. A. Meyers, J. Electrochem. Soc. (1994) **141**, pg 802.
- [8]. S. G. Ellis, J. Appl. Phys. (1967) **38**, pg 2906.
- [9]. B. Tell, J. J. Weigang, J. Appl. Phys. (1977) **48**, pg 5321.
- [10]. T. L. Chu, S. S. Chu, S. C. Lin, J. Yu, J. Electrochem. Soc. (1984) **131**, pg 31
- [11]. W. S. Chen, J. M. Stewart, R. A. Mickelson, Appl. Phys. Letter.(1985) **46**. pg 1.
- [12]. J. G. Garg, R. P. Sharma, K. C. Sharma, Thin Solid Films (1988) **164**, pg 269.