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ELECTROPHORETIC DEPOSITION AND CHARACTERIZATION OF COPPER SELENIDE THIN FILMS

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Abstract

Copper selenide thin films were prepared by electrophoretic deposition (EPD) using copper selenide powder synthesized by precipitation method. EPD is a combination of two processes which is electrophoresis and deposition. EPD was found suitable in a mixture of methanol and toluene which allows the particles to be well suspended and migrated to the electrode surface. X-ray diffraction (XRD) results on the powder showed the formation CuSe as a major phase with few $CuSe_2$ peaks. The scanning electron microscopy (SEM) micrograph of the powder showed irregular surface structures due to polycrystalline form. Thermal gravimetric curve showed that copper selenide powder was preferable heated below 350 °C for heat treatment analysis. The deposition of CuSe films was able to be carried out in a short period of time due to high deposition rate with appropriate amount deposited on the substrate. The photoresponse did not show any significant dependent to the bath temperature. The sample showed indirect transition with band gap energy of 1.51 eV.

Abstrak

Lapisan nipis kuprum selenida dihasilkan menggunakan teknik pengenapan elektrophoretik daripada serbuk kuprum selenida yang disediakan melalui keadah pemendakan. Pengenapan elektrophoretik adalah kombinasi dua proses iaitu elektroporesis dan pngenapan. Di dapati pengenapan elektophoretik ini sesuai dilakukan dalam pelarut campuran metanol dan toluena kerana ia membenarkan butiran terampai dengan baik seterusnya membantu dalam penghijrahan butiran ke permukaan elektrod. Keputusan pembelauan sinar (XRD) ke atas serbuk kuprum selenida menunjukkan sebahagian besar adalah fasa CuSe dengan sedikit fasa $CuSe_2$.

Manakala keputusan mikroskop pengimbasan elektron (SEM) terhadap serbuk mempamerkan struktur permukaan yang tidak seragam disebabkan pembentukan kristal yang bersifat polihablur kristal. Penentuan suhu pemanasan ke atas serbuk di dapati fasa CuSe berada dalam keadaan stabil pada suhu di bawah 350 °C. Pembentukan lapisan CuSe dapat disediakan pada tempoh yang singkat disebabkan kadar pengenapan kadar yang tinggi dengan jumlah pemendakan yang berpatutan. Di dapati tiada peningkatan fotosensitiviti pada sampel apabila suhu pengenapan dinaikkan. Sampel yang terhasil menunjukkan keadaan peralihan tidak langsung dengan nilai luang tenaga lapisan kurum selenida 1.51 eV.

Introduction

Intensive research has been performed in the past to study the fabrication and characterization of copper selenide in the form of thin films because of its potential application in solar cell technology. Copper selenide is a semiconductor with a wide range of stoichiometric compositions and also with various crystallographic forms. Recently, the techniques of thin film growth of this compound has become of interest in fabricating low cost photocells. Thin films of copper selenide can be obtained by variety of techniques like vacuum evaporation, melting of Cu and Se, electrodeposition and chemical bath deposition [1-2]. Electrophoretic deposition (EPD) also seems to be a simple and inexpensive method for fabricating semiconductor films. EPD is essentially a two-step process which is 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 deposit on the electrode surface forming coherent deposit via particle coagulation. The phenomenon of electrophoresis has been known since the beginning of the 19th century and it has found applications during the past 40 years mainly in traditional ceramic technology. [3-6]. This technique has attracted attention due to several advantages such as short deposition time, simple experimental set up, applicability for depositing layer on the substrate of complicated shape, and easy control of layer thickness. In any application of electrophoresis the composition of the suspension is of great importance. Most of the work on EPD has been done in non-aqueous medium [3,5,8-13] The use of aqueous suspension causes a number of problems in electrophoretic forming such as electrolysis of water occurs at low voltages (~5 V) and producing gas evolution on cathode which affect the formation and the quality of deposit. [4]

Experimental

Copper selenide synthesized powder (0.5g) prepared by precipitation method was added in 80 ml organic solvent mixture of methanol and toluene to form copper selenide EPD suspension. Various volumetric ratios of methanol and toluene of organic solvent were tested when preparing an EPD suspension. For achieving a uniform coating, the acquirement of relative stable suspension seems to be essential. For this reason, mixture of methanol and toluene was preferable due to high chemical stability and lower conductivity compared to water. However, there is still some difficulty to get real stable suspension due to an easy sedimentation of copper selenide powder. Therefore, the suspension was ultrasonically agitated about 15 minutes before performing EPD process. The EPD process was carried out in room temperature by applying a high voltage (300V) between a platinum counter electrode (anode) and a titanium plate (cathode). The electrodes were set parallel to each other with separation distance of 1 cm and immersed into the suspension. Besides the constituents of EPD suspensions, the effects of EPD process parameters such as deposition time (15 -120 s) and different bath temperature (28 - 65 ºC) also have been investigated.

Characterization of copper selenide powder and CuSe films

Copper selenide powder was characterized by thermogravimetric analysis (TGA, PERKIN-ELMER) to determine solid phase content in the powder. The phase composition and structure of the powder and copper selenide films were determined by X-ray diffraction (XRD, Philips PM 1730). The microstructure and elemental composition of the materials were examined by scanning electron microscopy and energy dispersive analysis of X-ray (SEM and EDAX, JSM 6400 JEOL). The photosensitivity of the films were determined by photoelectrochemical (PEC) test in $Na_2S_2O_3$ (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

Characterization of copper selenide powder

Figure 1 shows the XRD pattern of copper selenide powder obtained through the chemical precipitation method. The presence of sharp structural peaks in XRD traces confirmed the polycrystalline nature of the sample. The peaks in the pattern indicate the formation of heterogeneous phase of CuSe and $CuSe_2$. The results are well matched with the standard JCPDS values (File No. 06-0427) for CuSe and (File No. 019-0400) for $CuSe_2$ (Table 1). From the XRD results, we can see that CuSe phase are dominant in the powder. Six main peaks belong to CuSe were detected at 2θ = 26.6°, 28.2°, 31.1°, 46.1°. 50.1° and 56.6° corresponding to interplanar distances of 3.36 , 3.18 , 2.88, 1.96, 1.82 and 1.62 Å respectively. However, only two peaks belong to $CuSe_2$ were observed at 2? = 38.4 ° and 41.1° corresponding to d-spacing values of 2.34 and 2.19 Å.

Figure 2(a-b) showed the granules display sharp edges of particles due to the crystalline form which evidence by intense CuSe peaks in XRD analysis. The particles were formed in various crystal shaped with different sizes. This indicates that the powder produced was not uniform using precipitation technique. TGA curve of the copper selenide powder are shown in Figure 3 in the temperature range between 30 and 1000 °C. The thermal stability of the powder depends o the stability of CuSe phase. The TGA curve of copper selenide powder exhibited three characteristic weight loss stages. The first stage was observed from 30 to 160 °C as been shown in Figure 3.3 with a sharp peak at 160 °C in the DTG curve due to desorption of water molecules adsorbed on the crystallites surface. The calculated weight loss is about 4.16 %. The major weight loss of 10.94 % occurs around 160 -389 °C.

The high amount of weight loss in this stage probably due to the release of elemental Se due to the occurrence of phase changes of this temperature range. The third stage of negligible weight loss at temperature above 400 °C due further release of Se which cause subsequent phase transformation

Characterization of CuSe films using EPD technique

Electrophoretic deposition (EPD) was carried out at high voltage (300V) due to better distribution of copper selenide deposited on the substrate. As being shown in Fig. 4, the samples were deposited at different period of time. The film deposited for 15 second shows low intense peaks at 2? = 26.4, 28.2, 31.4 and 46.4 with interplanar distances of 3.37, 3.16, 2.84 and 1.96 Å. As the deposition time increased from 30 to 120 second, the intensity of the CuSe peaks increased and reducing the titanium signal due to more particles were deposited to build thicker layer. This indicates that EPD process provided a very quick deposition process with appropriately mass deposited on the substrate.

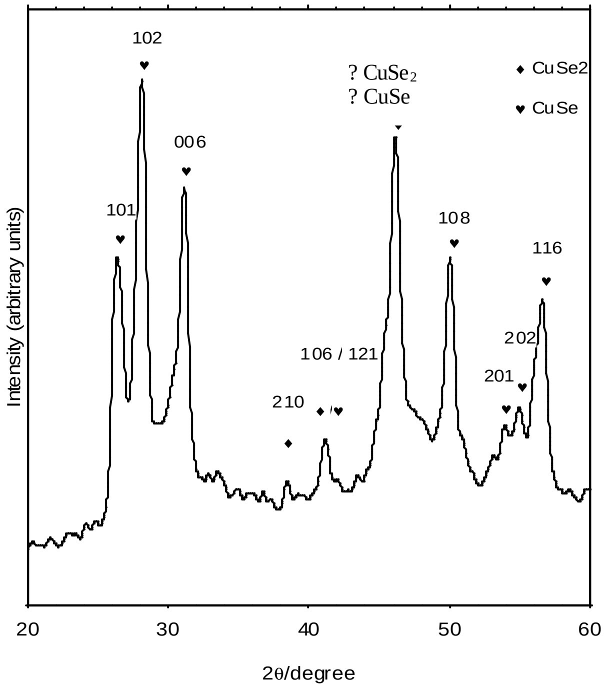
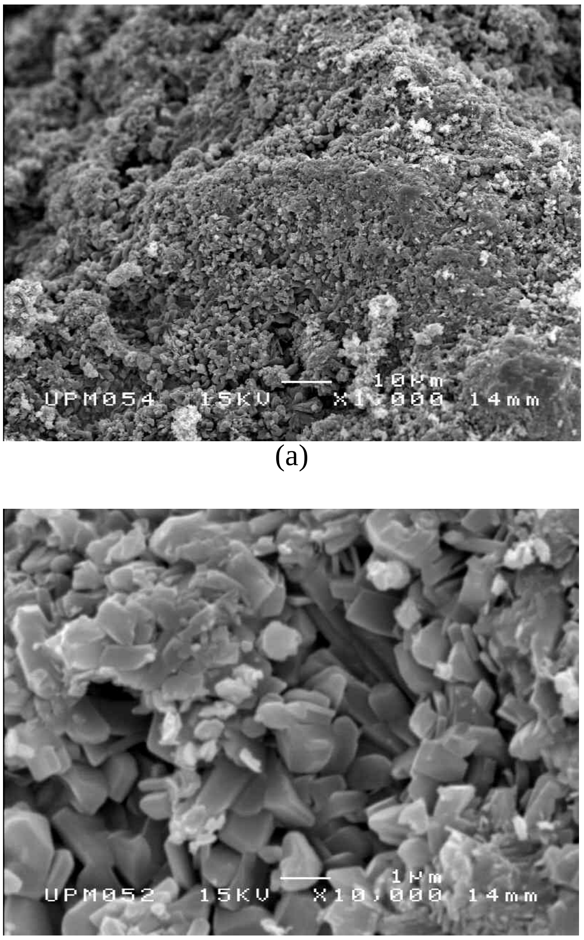


Figure 1: XRD pattern for copper selenide powder.

Table 1: The comparison between the JCPDS d-spacing for CuSe and $CuSe_2$ to experimentally observed values for copper selenide powder.

2? (°)	d-spacing (Å)		hkl	Compound
	experimental values	experimental 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
38.4	2.34	2.33	210	$CuSe_2$
41.1	2.19	2.16	106/121	CuSe, $CuSe_2$
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



(a)

(b)

Figure 2: SEM micrograph of copper selenide powder at magnifications (a) 1000 X and (b) 10,000 X

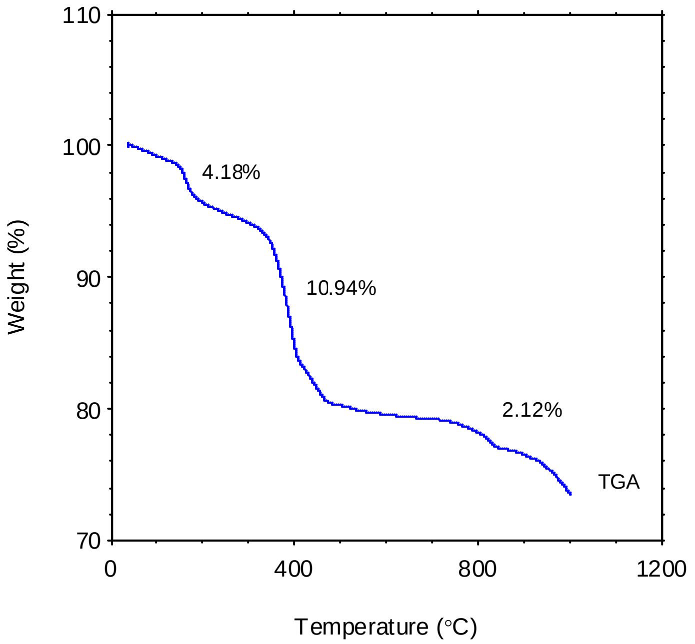


Figure 3: TG curve of copper selenide powder from 30 to 1000 °C

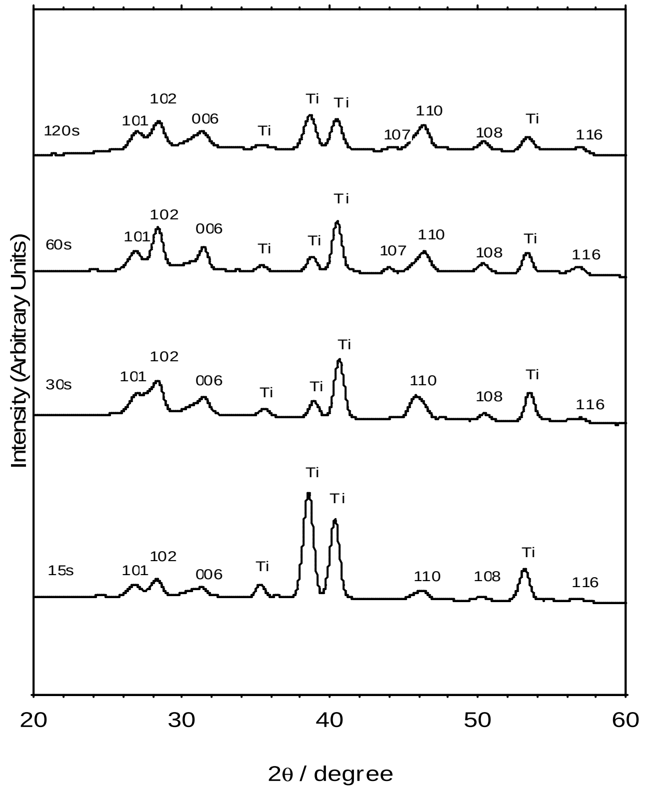


Figure 4: XRD pattern of CuSe deposited for different deposition time.

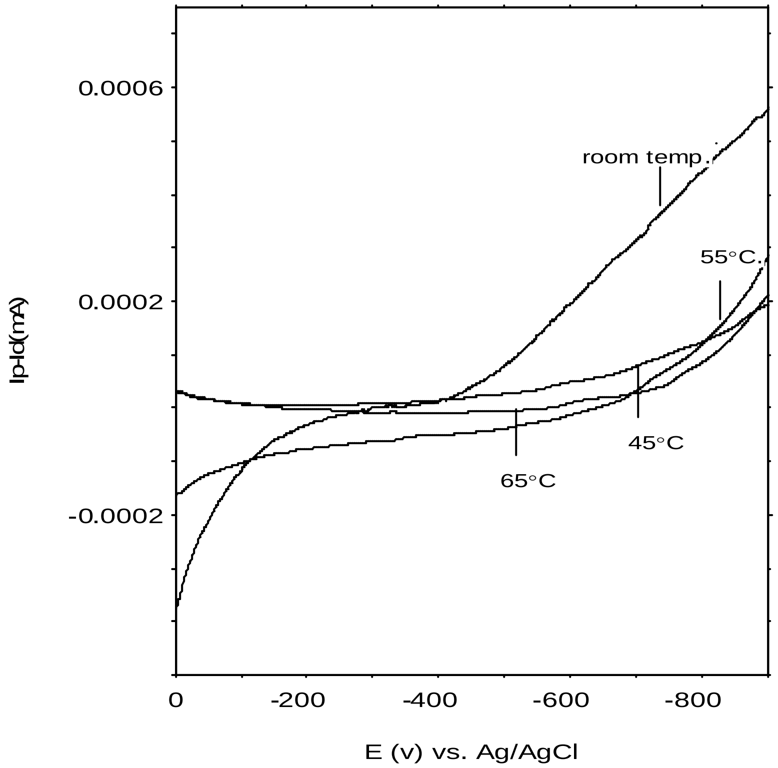


Figure 5: Comparison of the difference between photocurrent and darkcurrent (Ip-Id) of copper selenide samples deposited at room temperature, 45, 55, 65 °C

As shown in Figure 5, the increasing temperature in deposition process does not improve the photoactivity of the deposit. Therefore, film deposited at room temperatures can be considered as the best temperature for electrophoretic process due to better photosensitivity compared to other. The copper selenide thin films were deposited on ITO coated glass substrate instead of titanium in order to study the optical behavior of the film. Figure 6a shows the optical absorbance of the film versus wavelength graphs obtained from UV-visible spectrophotometer. The optical absorbance spectra of the films were recorded in the wavelength range from 400 to 800 nm. Extrapolation of this curve to zero absorption coefficients as shown in Figure 6b gives the optical energy gap of the semiconductor, which is about 1.51 eV.

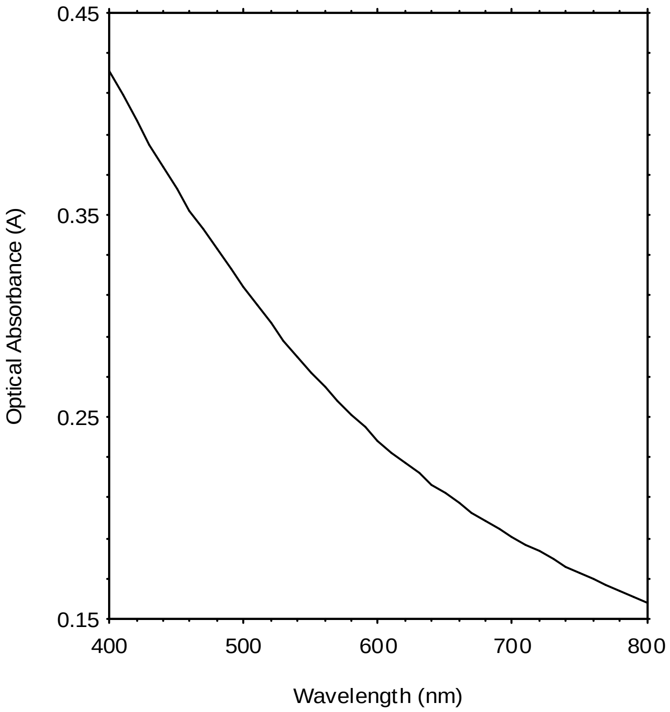


Figure 6a: The optical absorbance of the film vs. wavelength copper selenide deposited on ITO glass

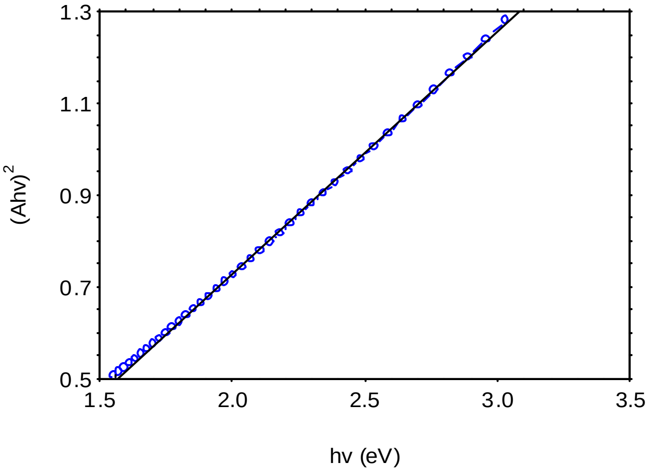


Figure 6b: Plot of $(Ahv)^{2/n}$ vs. hv for film deposited on ITO glass.

Conclusion

The study of copper selenide powder synthesized by precipitation method was carried out for preparation copper selenide thin film using electrophoretic deposition (EPD) technique. Based on the study, it was clearly showed that EPD technique enable less deposition time due to simple process with low cost production of CuSe thin films. High voltage (300 V) was needed to produce CuSe film with better distribution of materials on the substrate. The film deposited at room temperature can be considered as the preferable temperature for electrophoretic process due to better photosensitivity than other temperatures. The result of this experimental study show that EPD, being simple and inexpensive, provides an attractive potential method for producing films for a variety of application in thin film industries.

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