
UNIVERSITI PUTRA MALAYSIA

# ELECTROCHEMICAL DEPOSITION AND CHARACTERIZATION OF COPPER INDIUM DISULFIDE SEMICONDUCTOR THIN FILMS

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**DOCTOR OF PHILOSOPHY**
**UNIVERSITI PUTRA MALAYSIA**

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# ELECTROCHEMICAL DEPOSITION AND CHARACTERIZATION OF COPPER INDIUM DISULFIDE SEMICONDUCTOR THIN FILMS

**By**

**TEO SOOK LIANG**

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirements for the Degree of Doctor of Philosophy**

**April 2011**

*Dedicated to my lovely family and Boon Song for their love, support and encouragement.*

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Doctor of Philosophy

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**April 2011**

**Chairman : Professor Zulkarnain bin Zainal, PhD**

**Faculty : Science**

Copper indium disulfide ($CuInS_2$) 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, high absorption coefficient and free from hazardous chalcogenides, selenium or tellurium. In this work, three electrochemical deposition techniques were used in the preparation of $CuInS_2$ thin films namely potentiostatic deposition, pulse electrodeposition and potentiodynamic deposition.

$CuInS_2$ thin films were deposited onto fluorine doped tin oxide coated glass (FTO) from deposition bath comprised of Cu-EDTA, $In_2(SO_4)_3$ and $Na_2S_2O_3$, and the pH was adjusted to ~2.30 by using sulfuric acid. A three electrode-cell was used, where Ag/AgCl/3M NaCl as the reference electrode, FTO as the working electrode and platinum wire as the counterelectrode. Cyclic voltammetry was used to investigate the probable range of deposition potential and the potential range obtained was at -0.80 V to -1.00 V. Deposition parameters such as potential (-0.85 V to -1.20 V), time (10 min to

50 min), pulse magnitude (-0.85 V to -1.20 V), duty cycle (10% to 90%), scan rate (5 mV/s to 40 mV/s), potential cycling (5 cycles to 50 cycles), concentration of $CuSO_4$ (0.004 M to 0.020 M), concentration of $In_2(SO_4)_3$ (0.004 M to 0.020 M) and annealing temperature (250 $^oC$ to 400 $^oC$ ) were studied.

X-ray diffraction (XRD) patterns showed that the deposited $CuInS_2$ films were polycrystalline with tetragonal structure at hkl planes of (200), (112) and (204). The photoelectrochemical (PEC) properties of the films were evaluated using linear sweep photovoltammetry by intermittently illuminating the samples which was immersed in 0.01 M $Na_2S_2O_3$ electrolyte with a halogen lamp (120 V 300 W). Photocurrent was observed due to cathodic reaction involving generated minority carriers of electrons. Thus, $CuInS_2$ is a p-type semiconductor as deposited in this study. The XRD and PEC results suggested the suitable electrolyte bath composition for $CuInS_2$ deposition was 0.01 M Cu-EDTA, 0.01 M $In_2(SO_4)_3$ and 0.40 M $Na_2S_2O_3$. A smooth adherent film was obtained at potential -1.00 V with deposition time of 30 min in potentiostatic deposition. While for pulse electrodeposition, pulse potential of -1.00 V at 50% duty cycle showed good PEC behaviour. Besides, for potentiodynamic deposition, a significant PEC effect was obtained at potential range of -0.40 V to -1.00 V with scan rate of 25 mV/s for 20 cycles. Annealing improved the film crystallinity, but caused the formation of impurity phases and resulted in poor photoresponse.

The band gap energy of samples prepared by these techniques was found to be within 1.20-1.40 eV with indirect transition. The surface roughness mean squares of 218.60 nm, 74.73 nm and 93.30 nm were respectively obtained for potentiostatic, pulse and

potentiodynamic deposition as examined using atomic force microscopy. The morphology of the films was further studied using scanning electron microscopy (SEM), field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). Based on SEM cross sectional images, the thicknesses of potentiostatic, pulse and potentiodynamic deposited films were estimated to be 5.06 μm, 1.55 μm and 3.32 μm respectively. From FESEM and TEM, the obtained grain shape varied from spherical to worm like for potentiostatic, pulse and potentiodynamic deposition. The crystallite sizes estimated from XRD, FESEM and TEM were 24.27-29.59 nm for potentiostatic technique, 40.45-47.08 nm for pulse electrodeposition and 31.93-36.41 nm for potentiodynamic deposition. The Cu:In:S compositions of the films were evaluated using energy dispersive X-ray analysis which resulted in 1.0:1.1:2.1, 1.1:1.0:1.8 and 1.2:1.0:1.7 respectively for potentiostatic, pulse and potentiodynamic deposition. The reasons for these compositional trends are elaborated in the text.

Cyclic voltammetry was run to investigate the electrochemical properties of the films in various supporting electrolytes ($NH_4Cl$, $(NH_4)_2SO_4$, KCl, $K_2SO_4$), concentration (0.01 M to 2.00 M), pH (1.35 to 10.00) and potential cycling (1 cycle to 10 cycles). $Cu^{2+}/Cu^{+}$ and $Cu^{+}/Cu^{0}$ redox peaks were observed for all films. The film deposited using potentiostatic technique showed a good electrochemical stability compared to other techniques. Chronocoulometry study showed potentiostatic deposited film had a high surface charge of 0.115 Coulomb.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

**PENGENAPAN ELEKTROKIMIA DAN PENCIRIAN FILEM NIPIS SEMIKONDUKTOR KUPRUM INDIUM DISULFIDA**

Oleh

**TEO SOOK LIANG**

**April 2011**

**Pengerusi : Profesor Zulkarnain bin Zainal, PhD**

**Fakulti : Sains**

Kuprum indium disulfida ($CuInS_2$) telah menarik perhatian sebagai lapisan penyerap dalam aplikasi sel solar kerana ia mempunyai luang tenaga terus ~1.5 eV, kecekapan penukaran yang tinggi, pekali penyerapan yang tinggi dan bebas daripada chalcogenides berbahaya seperti selenium atau tellurium. Dalam kajian ini, tiga teknik enapan elektrokimia digunakan untuk menyediakan filem nipis $CuInS_2$, iaitu enapan potentiostatik, pengenapan denyutan dan enapan potentiodinamik.

Filem nipis $CuInS_2$ dienapkan atas kaca bersadur timah oksida terdop fluorin (FTO) daripada larutan yang mengandungi Cu-EDTA, $In_2(SO_4)_3$ dan $Na_2S_2O_3$, pH diubah kepada ~2.30 dengan menggunakan asid sulfurik. Sel tiga elektrod digunakan, Ag/AgCl/3M NaCl sebagai elektrod rujukan, FTO sebagai elektrod kerja dan wayar platinum sebagai elektrod perantaraan. Kitar voltametri dijalankan untuk menentukan julat kemungkinan keupayaan enapan dan julat keupayaan yang diperoleh ialah antara -0.80 V hingga -1.00 V. Parameter-parameter enapan seperti keupayaan (-0.85 V hingga -

1.20 V), masa (10 min hingga 50 min), magnitud denyutan (-0.85 V hingga -1.20 V), kitar kerja (10% hingga 90%), kadar imbasan (5 mV/s hingga 40 mV/s), kitar keupayaan ( 5 hingga 50 kitar), kepekatan $CuSO_4$ (0.004 M hingga 0.020 M), kepekatan $In_2(SO_4)_3$ (0.004 M hingga 0.020 M) dan suhu pemanasan (250 $^oC$ hingga 400 $^oC$) telah dikaji.

Keputusan pembelauan sinar-X (XRD) menunjukkan filem $CuInS_2$ yang terenap bersifat polihablur dengan struktur tetragonal pada satah (200), (112) dan (204). Pencirian fotoelektrokimia (PEC) dinilai menggunakan fotovoltametri pengimbasan linear dengan menerangkan sampel yang direndam dalam elektrolit 0.01 M $Na_2S_2O_3$ secara bersela menggunakan lampu halogen (120 V 300 W). Arus foto diperhatikan di bahagian katodik kerana lubang yang tertinggal di jalur valen telah mengambil bahagian dalam tindak balas elektrokimia. Maka, $CuInS_2$ yang dienapkan dalam kajian ini merupakan semikonduktor jenis p. Berdasarkan keputusan XRD dan PEC, komposisi larutan yang sesuai untuk enapan $CuInS_2$ ialah 0.01 M $CuSO_4$, 0.01 M $In_2(SO_4)_3$ dan 0.40 M $Na_2S_2O_3$. Filem yang rata dan melekat didapati pada keupayaan -1.00 V dengan masa 30 min untuk enapan potentiostatik. Sementara bagi pengenapan denyutan, denyutan keupayaan pada -1.00 V untuk 50% kitar kerja menunjukkan cirian PEC yang bagus. Di samping itu, enapan potentiodinamik memberikan kesan PEC yang jelas pada julat keupayaan -0.40 V to -1.00 V dengan kitar imbasan 25 mV/s untuk 20 kitar. Pemanasan membaiki kristal filem, tetapi turut menyebabkan pembentukkan fasa lain yang mengurangkan cirian PEC filem.

Luang tenaga untuk sampel yang disediakan oleh teknik tersebut didapati berada dalam julat 1.20-1.40 eV dengan peralihan tak langsung. Kekasaran permukaan untuk enapan

potentiostatik, denyutan dan potentiodinamik masing-masing ialah 218.60 nm, 74.73 nm dan 93.30 nm seperti yang diperiksa menggunakan mikroskop daya atom. Morfologi filem dikaji menggunakan mikroskopi pengimbasan elektron (SEM), pancaran mikroskop pengimbasan elektron pemancaran medan (FESEM) dan mikroskopi pemancaran electron (TEM). Berdasarkan imej keratan rentas SEM, ketebalan filem yang dienapkan oleh potentiostatik, denyutan dan potentiodinamik masing-masing dianggarkan ialah 5.06 μm, 1.55 μm dan 3.32 μm. Daripada imej FESEM dan TEM, bentuk zarah untuk potentiostatik, denyutan dan potentiodinamik masing-masing ialah sfera, cacing dan campuran kedua-duanya. Saiz kristal boleh dianggarkan dengan menggunakan XRD, FESEM dan TEM dimana ialah 24.27-29.59 nm untuk teknik potentiostatik, 40.45-47.08 nm untuk enapan denyutan dan 31.93-36.41 nm untuk enapan kitar voltammerik. Nisbah komposisi Cu:In:S dinilai menggunakan analisis penyerakan tenaga sinar-X, keputusan yang didapati ialah 1.0:1.1:2.1, 1.1:1.0:1.8 dan 1.2:1.0:1.7 masing-masing untuk pengenapan potentiostatik, denyutan dan potentiodinamik. Penerangan untuk trend composisi tersebut dijelaskan kandungan teks.

Kitar voltametrik dijalankan untuk menyiasat cirian elektrokimia filem dalam kepelbagaian elektrolit sokongan ($NH_4Cl$, $(NH_4)_2SO_4$, KCl, $K_2SO_4$), kepekatan (0.01 M hingga 2.00 M), pH (1.35 hingga 10.00) dan kitar keupayaan (1 hingga 10 kitar). Pasangan redox $Cu^{2+}/Cu^{+}$ dan $Cu^{+}/Cu^{0}$ didapati dalam semua filem. Filem yang dienapkan secara potentiostatik mempunyai kestabilan elektrokimia yang bagus berbanding teknik lain. Khronokoulometri menunjukkan filem yang dienapkan secara potentiostatic mempunyai cas permukaan yang tinggi iaitu 0.115 Koulomb.

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I certify that a Thesis Examination Committee has met on 19 April 2011 to conduct the final examination of Teo Sook Liang on her thesis entitled "Electrochemical Deposition and Characterization of Copper Indium Disulfide Semiconductor Thin Films" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the degree of Doctor of Philosophy.

Members of the Thesis Examination Committee were as follows:

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Date: 28 October 2011

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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## DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.

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**TEO SOOK LIANG**

Date: 19 April 2011

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