UNIVERSITI PUTRA MALAYSIA

PULSE ELECTROCHEMICAL DEPOSITION AND PHOTOCORROSION OF COPPER INDIUM DISELENIDE THIN FILM

NIMA GHAMARIAN

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By

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Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for Degree of Master of Science

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Dedicated to my family for their love, support and encouragement

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirements for the degree of Master of Science

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Supervisor : Professor Zulkarnain Bin Zainal, PhD

Faculty : Faculty of Science

Copper indium diselenide ($CuInSe_2$) because of its features such as suitable band gap value, positive flat band potential and good chemical stability made it a promising energy conversion material in photo-electrochemical cell. In this work, polycrystalline thin film of $CuInSe_2$ (CIS) was prepared by pulse electrodeposition on clean activated ITO glass substrates from aqueous solution containing $CuSO_4$, $In_2(SO_4)_3$ and SeO_2. During pulse electrodeposition duty cycles of 33- 90% were applied for fifteen minutes (total on time) to produce different surface morphologies. The probable potential for deposition was predetermined from cyclic voltammogram (CV). The deposited film was annealed at 400 ^oC under nitrogen gas flow to provide neutral atmosphere to improve the crystalline structure and remove excess deposited selenium.

The crystalline structure of the thin film was determined from X-ray diffraction which confirmed that the deposited CIS had a tetragonal chalcopyrite structure. The CIS phase is consistent for samples deposited for all duty cycles. The optical property of thin film was determined base on the measurement by using UV-Vis spectrophotometer. The direct band gap of the deposited CIS thin film is around 1.21 eV. Thus, the electrodeposited CIS thin film is a potential candidate to be used in solar cell and energy conversion devices.

Atomic force microscope (AFM) was employed to monitor the effect of duty cycles on the morphology of the thin film. It was revealed that with increasing duty cycle the surface morphology shifted from smooth to dendritic structure. Photo-electrochemical characterization (PEC) was performed under chopped white light in acidic redox medium. The CIS film was found to be a photosensitive material and showed p and n-p type semiconductoring behavior when deposited at different duty cycles.

The effect of varying surface morphology on photocorrosion behavior of CIS was studied in acidic and alkaline electrolytes. Polarization curves were acquired in selected corrosive electrolytes which contained 0.5 M KCl + H_2SO_4 as the acidic media and 0.5 M KCl + NaOH as the alkaline media. The photocorrosion rates were evaluated from the electrochemical polarization data.

The photocorrosion rates for different morphologies were estimated from current density (i_{corr}) extracted from Tafel plots for all pH range. Finally activity and passivity behavior of the thin films were determined by interpreting the values from polarization curve peaks (E_{corr}) and the rate of photocorrosion. The photocorrosion behavior of deposited CIS thin film was found to be affected by the surface morphology, photoactivity and pH of medium. The deposited thin film displayed an outstanding stability with corrosion rate of 0.122 mm per year in alkaline media for sample deposited with duty cycle 90% (the least corroded morphology) and 11.96 mm per year in acidic media for duty cycle 33% (the most corroded morphology).

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Sarjana Sains

PENGELEKTROENAPAN DENYUT DAN FOTOKAKISAN FILEM NIPIS KUPRUM INDIUM DISELENIDA

Oleh

Nima Ghamarian

Disember 2012

Pengerusi : Profesor Zulkarnain Bin Zainal, PhD

Fakulti : Sains

Oleh kerana sifatnya seperti nilai ruang tenaga yang sesuai, keupayaan jalur rata yang positif dan kestabilan kimia yang baik menjadikan kuprum indium diselenide ($CuInSe_2$) sebagai bahan penukaran tenaga yang berpotensi untuk sel foto-elektrokimia. Dalam kajian ini, filem nipis polihablur $CuInSe_2$ telah disediakan daripada larutan akueus yang mengandungi $CuSO_4$, $In_2(SO_4)_3$ dan SeO_2 melalui teknik pengelektroenapan denyut. Semasa pengelektroenapan, kitaran kerja 33-90% telah dikenakan selama 15 minit (jumlah masa) untuk menghasilkan morfologi permukaan yang berbeza. Nilai keupayaan yang mungkin telah ditentukan terlebih dahulu daripada kitar voltametri (CV). Filem

yang dienapkan telah dipanaskan pada suhu 400°C di bawah aliran gas nitrogen untuk menyediakan persekitaran neutral bagi meningkatkan struktur hablur dan menyingkirkan lebihan selenium yang terenap.

Struktur kristal filem nipis telah dikenalpasti daripada pembelauan sinar- X yang mengesahkan bahawa CIS yang telah dienapkan mempunyai struktur kalkopirit tetragon. Fasa CIS adalah konsisten untuk sampel yang telah dienapkan bagi semua kitaran kerja. Sifat optikal bagi filem nipis telah dikenalpasti berdasarkan pengukuran dengan menggunakan spektrofotometer UV-Vis. Luang tenaga terus bagi filem nipis CIS yang telah dienapkan adalah sekitar 1.21 eV. Oleh itu, filem nipis CIS yang dienapkan adalah berpotensi digunakan dalam sel solar dan alatan penukaran tenaga.

Mikroskop daya atom (AFM) telah digunakan untuk memantau kesan kitaran kerja terhadap morfologi filem nipis. Ia telah dibuktikan bahawa dengan peningkatan kitaran kerja, morfologi permukaan telah berubah daripada berstruktur licin kepada dendrit. Pencirian foto-elektrokimia telah dijalankan di dalam media redoks berasid, di bawah cahaya putih yang dicincang. Filem nipis CIS telah didapati fotosensitif dan menunjukkkan ciri semikonduktor p dan n-p apabila dienapkan pada kitaran kerja yang berbeza.

Kesan mempelbagaikan morfologi permukaan terhadap tindak balas fotokakisan CIS telah dikaji di dalam elektrolit asid dan alkali. Lengkungan polarisasi telah diperolehi dalam elektolit mengkakis terpilih yang mengandungi 0.5 M KCl + H_2SO_4 untuk media berasid dan 0.5 M KCl + NaOH untuk media beralkali. Kadar kakisan telah diperincikan daripada data lengkungan polarisasi. Kadar fotokakisan untuk morfologi yang berbeza telah dianggarkan daripada ketumpatan arus (i_{corr}) yang diperolehi dari plot Tafel untuk kesemua julat pH. Aktiviti dan tindak balas pasif filem nipis telah dikenalpasti dengan mentafsirkan nilai dari puncak lengkungan polarisasi (E_{corr}) dan kadar fotokakisan. Tindakbalas fotokakisan filem nipis CIS yang dienapkan telah didapati dipengaruhi oleh morfologi permukaan, fotoaktiviti dan media pH. Filem nipis yang dienapkan menunjukkan kestabilan yang sangat baik dengan kadar kakisan 0.122 mm setahun dalam media beralkali bagi sampel yang dienapkan pada kitaran kerja 90% (morfologi yang paling sedikit kakisan) dan 11.96 mm setahun dalam media berasid pada kitaran kerja 33% (morfologi yang paling banyak kakisan).

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

Zulkarnain Zainal, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Tan Wee Tee, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

BUJANG BIN KIM HAUAT, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

DECLARATION

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

NIMA GHAMARIAN

Date: 14 December 2012

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