



UNIVERSITI PUTRA MALAYSIA

***PULSE ELECTROCHEMICAL DEPOSITION AND PHOTOCORROSION
OF COPPER INDIUM DISELENIDE THIN FILM***

NIMA GHAMARIAN

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**PULSE ELECTROCHEMICAL DEPOSITION AND PHOTOCORROSION OF
COPPER INDIUM DISELENIDE THIN FILM**



By

NIMA GHAMARIAN

**Thesis Submitted to the School of Graduate Studies, Universiti Putra
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Science**

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A large, light gray watermark of the UPM logo is oriented diagonally across the page. The logo features a shield with a red and white stylized 'U' and 'M' shape, a book, and the letters 'UPM' in a red box at the top.

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

**PULSE ELECTROCHEMICAL DEPOSITION AND PHOTOCORROSION OF
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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 , $\text{In}_2(\text{SO}_4)_3$ 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 $400\text{ }^\circ\text{C}$ 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 semiconducting 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 + H₂SO₄ 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 , $\text{In}_2(\text{SO}_4)_3$ 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 diaplikasikan telah dipanaskan pada suhu 400°C di bawah aliran gas nitrogen untuk menyediakan persekitaran neutral bagi meningkatkan struktur hablur dan menyingkirkan lebih selenium yang terapan.

Struktur kristal filem nipis telah dikenalpasti daripada pembelauan sinar- X yang mengesahkan bahawa CIS yang telah diaplikasikan mempunyai struktur kalkopirit tetragon. Fasa CIS adalah konsisten untuk sampel yang telah diaplikasikan 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 diaplikasikan adalah sekitar 1.21 eV . Oleh itu, filem nipis CIS yang diaplikasikan 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 menunjukkan ciri semikonduktor p dan n-p apabila diaplikasikan 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 elektrolit mengkakis terpilih yang mengandungi 0.5 M KCl + H₂SO₄ 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 dikenakan telah didapati dipengaruhi oleh morfologi permukaan, fotoaktiviti dan media pH. Filem nipis yang dikenakan menunjukkan kestabilan yang sangat baik dengan kadar kakisan 0.122 mm setahun dalam media beralkali bagi sampel yang dikenakan 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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I certify that a Thesis Examination Committee has met on 14 December 2012 to conduct the final examination of Nima Ghamarian on his thesis entitled "Pulse Electrochemical Deposition and Photocorrosion of Copper Indium Diselenide Thin Film" in accordance with the Universities and University College 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 Master of Science.

Members of the Thesis Examination Committee were as follows:

Abdul Halim bin Abdullah, PhD

Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Mohd Zobir bin Hussein, PhD

Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Tan Kar Ban, PhD

Senior Lecturer
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Madzlan Aziz, PhD

Associate Professor
Faculty of Science
Universiti Teknologi Malaysia
(External Examiner)



SEOW HENG FONG, PhD
Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 26 February 2013



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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