ELECTROCHEMICAL DEPOSITION AND CHARACTERIZATION OF COPPER INDIUM DISULFIDE SEMICONDUCTOR THIN FILMS

TEO SOOK LIANG

FS 2011 40
ELECTROCHEMICAL DEPOSITION AND CHARACTERIZATION OF COPPER INDIUM DISULFIDE SEMICONDUCTOR THIN FILMS

TEO SOOK LIANG

DOCTOR OF PHILOSOPHY
UNIVERSITI PUTRA MALAYSIA

2011
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.
ELECTROCHEMICAL DEPOSITION AND CHARACTERIZATION OF COPPER INDIUM DISULFIDE SEMICONDUCTOR THIN FILMS

By

TEO SOOK LIANG

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$_2$S$_2$O$_3$, 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 °C to 400 °C ) 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$_2$S$_2$O$_3$ 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$_2$S$_2$O$_3$. 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 (NH₄Cl, (NH₄)₂SO₄, KCl, K₂SO₄), concentration (0.01 M to 2.00 M), pH (1.35 to 10.00) and potential cycling (1 cycle to 10 cycles). Cu²⁺/Cu⁺ and Cu⁺/Cu⁰ 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

PENGGENAPAN 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 (CuInS₂) 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 CuInS₂, iaitu enapan potentiostatik, pengenapan denyutan dan enapan potentiodynamik.

Filem nipis CuInS₂ dienapkan atas kaca bersadur timah oksida terdop fluorin (FTO) daripada larutan yang mengandungi Cu-EDTA, In₂(SO₄)₃ dan Na₂S₂O₃, 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 °C hingga 400 °C) 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$_2$S$_2$O$_3$ 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$_2$S$_2$O$_3$.

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 potentiodynamik 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 membahagi 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 potentiostatik 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 pengimbas 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 potentiostatik masing-masing
dianggarkan ialah 5.06 \( \mu m \), 1.55 \( \mu m \) dan 3.32 \( \mu m \). Daripada imej FESEM dan TEM,
bentuk zarah untuk potentiostatik, denyutan dan potentiostatik 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 didapi 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
potentiostatik. Penerangan untuk trend composisi tersebut dijelaskan kandungan teks.

Kitar voltametrik dijalankan untuk menyiasat cirian elektrokimia filem dalam
kepelbagaian elektrolit sokongan (\( \text{NH}_4 \text{Cl}, (\text{NH}_4)_2\text{SO}_4 \), 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 \( \text{Cu}^{2+}/\text{Cu}^+ \) dan \( \text{Cu}^+/\text{Cu}^0 \) 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.
ACKNOWLEDGEMENTS

I would like to forward my greatest thanks to all who contributed in my research. My sincere appreciation is greatly expressed to my supervisor, Professor Dr. Zulkarnain Zainal for his continuous supervision, constructive comments and support throughout my research. My greatest appreciation is also extended to my co-supervisors, Professor Dr, Mohd. Zobir and Associate Professor Dr. Tan Wee Tee for their guidance, supportive advices and comments.

Thousands of thanks are expressed to all my fellow lab-mates and friends for their assistance and help. Also thanks to the staff in Faculty of Science and Institute of Bioscience for analyzing my samples. National Science Fellowship sponsored by Ministry of Science, Technology and Innovation throughout my study is gratefully acknowledged.

Last but not least, I would like to express my appreciation to my lovely family and Boon Song for their support and encouragement.
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:

**Anuar bin Kassim, PhD**  
Professor  
Faculty of Science  
Universiti Putra Malaysia  
(Chairman)

**Nor Azah binti Yusof, PhD**  
Associate Professor  
Faculty of Science  
Universiti Putra Malaysia  
(Internal Examiner)

**Tan Kar Ban, PhD**  
Senior Lecturer  
Faculty of Science  
Universiti Putra Malaysia  
(Internal Examiner)

**Krishnan Rajeshwar, PhD**  
Professor  
The University of Texas at Arlington  
United State of America  
(External Examiner)

---

**NORITAH OMAR, PhD**  
Associate Professor and Deputy Dean  
School of Graduate Studies  
Universiti Putra Malaysia

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:

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

**Mohd. Zobir bin Hussein, PhD**  
Professor  
Faculty of Science  
Universiti Putra Malaysia  
(Member)

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

---

**HASANAH MOHD GHAZALI, 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 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.

TEO SOOK LIANG

Date: 19 April 2011
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEDICATION</td>
<td>ii</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>iii</td>
</tr>
<tr>
<td>ABSTRAK</td>
<td>vi</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>ix</td>
</tr>
<tr>
<td>APPROVAL</td>
<td>x</td>
</tr>
<tr>
<td>DECLARATION</td>
<td>xii</td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td>xiii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>xvi</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xix</td>
</tr>
<tr>
<td>LIST OF ABBREVIATIONS</td>
<td>xxvi</td>
</tr>
</tbody>
</table>

## CHAPTER

1 INTRODUCTION | 1
1.1 The Challenges | 2
1.2 Copper Indium Disulfide Thin Films | 3
1.3 Electrochemical Deposition Techniques | 5
1.3.1 Potentiostatic Deposition | 5
1.3.2 Pulse Electrodeposition | 6
1.3.3 Potentiodynamic Deposition | 6
1.4 Voltammetry Techniques in Solid Phase Analysis | 7
1.4.1 Solid Phase Voltammetry | 7
1.4.2 Chronocoulometry | 7
1.5 Semiconductor | 8
1.5.1 Intrinsic and Extrinsic Semiconductor | 8
1.5.2 Band Gap Energy | 9
1.6 Thin Film Solar Cells | 10
1.6.1 Solid State Photovoltaic Cells | 11
1.6.2 Photoelectrochemical Cells | 12
1.7 Objectives | 16

2 LITERATURE REVIEW | 17
2.1 Previous Preparation Techniques on CuInS$_2$ | 17
2.1.1 Ion Layer Gas Reaction Method | 17
2.1.2 Spray Pyrolysis | 18
2.1.3 Co-evaporation | 19
2.1.4 Sputtering | 20
2.1.5 Chemical Bath Deposition | 21
2.1.6 Sulfurization of Cu-In Precursors | 21
2.2 Potentiostatic Deposition of Metal Chalcogenide Thin Films | 23
2.3 Pulse Electrodeposition of Metal Chalcogenide | 26
3 MATERIALS AND METHODOLOGY
3.1 List of Materials and Chemicals 29
3.2 Preparation of Solutions 30
3.3 Preparation of Electrodes 30
  3.3.1 Working Electrode 30
  3.3.2 Counter Electrode 30
  3.3.3 Reference Electrode 31
3.4 Cyclic Voltammetry Experiment 31
3.5 Electrochemical Deposition 32
  3.5.1 Potentiostatic Deposition 32
  3.5.2 Pulse Electrodeposition 34
  3.5.3 Potentiodynamic Deposition 35
3.6 Characterizations 36
  3.6.1 X-ray Diffraction 36
  3.6.2 Photoelectrochemical Test 37
  3.6.3 Optical Absorption Study 38
  3.6.4 Atomic Force Microscopy 39
  3.6.5 Scanning Electron Microscopy 39
  3.6.6 Field Emission Scanning Electron Microscopy 39
  3.6.7 Transmission Electron Microscopy 40
  3.6.8 Energy Dispersive Analysis of X-rays 40
3.7 Solid Phase Voltammetry 40
4 RESULTS AND DISCUSSION
4.1 Cyclic Voltammetry 42
4.2 Reaction Mechanism of CuInS$_2$ Formation 47
4.3 Potentiostatic Deposition of CuInS$_2$ Thin Films 48
  4.3.1 Effect of Varying Potential 49
  4.3.2 Effect of Varying Time 55
  4.3.3 Effect of Varying CuSO$_4$ Concentration 57
  4.3.4 Effect of Varying In$_2$(SO$_4$)$_3$ Concentration 62
  4.3.5 Effect of Varying Annealing Temperature 67
4.4 Pulse Electrodeposition of CuInS$_2$ Thin Films 71
  4.4.1 Effect of Varying Pulse Potentials 72
  4.4.2 Effect of Varying Duty Cycle 77
  4.4.3 Effect of Varying CuSO$_4$ Concentration 78
  4.4.4 Effect of Varying In$_2$(SO$_4$)$_3$ Concentration 83
  4.4.5 Effect of Varying Annealing Temperature 87
4.5 Potentiodynamic Deposition of CuInS$_2$ Thin Films 91
  4.5.1 Effect of Varying Potential Ranges 92
  4.5.2 Effect of Varying Scan Rate 97
  4.5.3 Effect of Varying Number of Cycles 99
  4.5.4 Effect of Varying CuSO$_4$ Concentration 102
  4.5.5 Effect of Varying In$_2$(SO$_4$)$_3$ Concentration 106
  4.5.6 Effect of Varying Annealing Temperature 110
4.6 Morphological Studies
  4.6.1 Atomic Force Microscopy 114
  4.6.2 Scanning Electron Microscopy 116
  4.6.3 Field Emission Scanning Electron Microscopy 128
  4.6.4 Transmission Electron Microscopy 135
4.7 Energy Dispersive Analysis of X-rays 138
4.8 Optical Studies 140
4.9 Crystallite Size Analysis 143
4.10 Solid Phase Voltammetry 144
  4.10.1 Effect of Varying Supporting Electrolytes 144
  4.10.2 Effect of Varying Concentration of Electrolytes 149
  4.10.3 Effect of Varying pH 155
  4.10.4 Effect of Varying Potential Cycling 164
  4.10.5 Chronocoulometry 170
5 CONCLUSIONS 175

BIBLIOGRAPHY 179
APPENDICES 189
BIODATA OF STUDENT 207
LIST OF PUBLICATIONS 208