ELECTRODEPOSITION OF COPPER TIN SELENIDE FILMS FROM AQUEOUS SOLUTION

By

CHUAH HANG CHING

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

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DEDICATION

I would like to dedicate my work to both my beloved parents for their full support to carry out my Master Degree Program in Universiti Putra Malaysia

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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Chairman: **Associate Professor Zulkarnain Zainal, Ph.D.**

Faculty: **Science and Environmental Studies**

Thin films of Cu_2SnSe_4 have been electrodeposited potentiostatically from aqueous solution containing $CuCl_2$, $SnCl_4$ and Na_2SeO_3 on titanium substrates at room temperature. The disodium salt of ethylenediaminetetraacetic acid (Na_2-EDTA) was used as a complexant. Cyclic voltammetry was performed at room temperature to elucidate the electrodic processes occurred and to determine the potential range for electrodeposition. The effect of parameters such as deposition potential, electrolyte concentration, deposition time, bath temperature, annealing time and temperature and concentration of complexant on the film properties were studied. The films have been characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDAX), X-ray photoelectron spectroscopy (XPS) and linear sweep photovoltammetry (LSPV) technique. The band gap energy and type of optical transition were determined from optical absorbance data.

XRD studies confirmed the formation of polycrystalline Cu_2SnSe_4 on the titanium substrate and showed a cubic structure with strong (111) orientation. The films prepared in this study showed p-type semiconductor behaviour. SEM micrographs confirmed the polycrystalline nature of the deposit. The photoactivity, composition, grain size and shape of the film were dependent on the electrodeposition condition.

Nearly stiochiometric for Cu_2SnSe_4 film was obtained from 0.02 M Cu-EDTA, 0.02 M Sn-EDTA and 0.02 M Na_2SeO_3 solution at potential -0.60 V vs Ag/AgCl. Further investigation at -0.50 V shows that this potential was not suitable for the deposition of copper tin selenide. Increasing the deposition time allowed more materials to be deposited onto the substrate and thicker films were formed. The electrodeposition of the Cu_2SnSe_4 film was most suitable to be carried out at room temperature. Increasing the bath temperature could not improve the crystallinity of Cu_2SnSe_4 compound, but lead to formation of binary phase, CuSe. Annealing also could not improve the crystallinity of film but other binary phases such as $CuSe_2$ and Cu_2Se appeared. Minimum concentration of EDTA obtained for Cu_2SnSe_4 film. The film thickness was controlled by the time of deposition and changing the concentration of the reaction.

XPS spectrum confirms the presence of Cu, Sn and Se. The optical absorption studies revealed that the transition is direct and band gap energy E_g was 1.2 eV.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

ELEKTROENAPAN LAPISAN NIPIS KUPRUM TIMAH SELENIDE DARIPADA LARUTAN LARUTAN BERAKUEUS

Oleh

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November 2003

Pengerusi: **Profesor Madya Zulkarnain Zainal, Ph.D.**

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Lapisan filem nipis Cu_2SnSe_4 telah dienapkan dari larutan akueous yang mengandungi $CuCl_2$, $SnCl_4$ dan Na_2SeO_3 diatas substrat titanium pada suhu bilik melalui kaedah elektroenapan. Proses elektroenapan in dijalankan dengan menggunakan agen pengkomlpex EDTA. Kesan parameter seperti nisbah keupayaan elektroenapan, kepekatan larutan elektrolit, masa elektroenapan, suhu, pemanasan dan kepekatan komplex EDTA telah dikaji. Voltametri siklik dilakukan untuk mengenal pasti julat keupayaan yang sesuai untuk proses pengenapan. Struktur, morfologi, komposisi dan fotosentiviti sample telah dianalisis dengan menggunakan teknik pembelauan sinar-X (XRD), mikroskopi pengimbasan electron (SEM), analisis penyerakan tenaga sinaran-X (EDAX), spektroskopi fotoelektron sinar-X (XPS) dan voltammetri pengimbasan linear (LSPV). Nilai luang tenaga dan jenis peralihan optik telah ditentukan dari data serapan optik.

Analisis pembelauan sinar-X membuktikan terdapat pembentukan polihablur Cu_2SnSe_4 diatas substrat titanium dan berbentuk kiub. Filem yang disediakan dalam kajian ini menunjukkan sifat semikonduktor jenis-p. Mikroskopi pengimbasan elektron telah membuktikan kewujudan polihablur. Fotosentiviti, komposisi, saiz butiran dan bentuknya adalah bergantung kepada keadaan pengenapan.

Larutan yang mengandungi kepekatan 0.02 M Cu-EDTA, 0.02 M Sn-EDTA dan 0.02 M Na_2SeO_3 pada keupayaan -0.60 V menunjukan nilai yang hampir stiochiometric. Penyelidikan lanjutan pada keupayaan -0.50 V menunjukkan keupayaan ini adalah tidak sesuai untuk pengenapan filem nipis Cu_2SnSe_4. Penambahan masa elektroenapan membenarkan lebih banyak bahan mengenap diatas substrat dan filem yang lebih tebal terbentuk. Suhu bilik adalah suhu yang terbaik untuk pengenapan filem Cu_2SnSe_4. Peningkatan suhu tidak meningkatkan penghabluran Cu_2SnSe_4, tetapi menunjukkan pembentukan CuSe. Pemanasan juga tidak meningkatkan penghabluran, tetapi menunjukkan pembentukkan $CuSe_2$ dan Cu_2Se. Kepekatan EDTA yang minimum adalah cukup untuk membentuk filem Cu_2SnSe_4. Ketebalan filem adalah bergantung kepada masa elektroenapan dan kepekatan larutan elektrolit.

Spektroskopi fotoelektron sinar-X (XPS) membuktikkan kewujudan Cu, Sn dan Se. Serapan optik memberikan nilai luang tenaganya (E_g) 1.2 eV serta dalam keadaan peralihan terus.

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I certify that an Examination Committee met on 21st November, 2003 to conduct the final examination of Chuah Hang Ching on her Master of Science thesis entitled "Electrodeposition of Copper Tin Selenide Films from Aqueous Solution" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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This thesis submitted to the Senate of Universiti Putra Malaysia has been accepted as partial fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee are as follows.

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DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

CHUAH HANG CHING

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