ELECTRODEPOSITION OF NICKEL TIN SELENIDE THIN FILM

By

KARTINI BT ABD RAHIM

Thesis Submitted to School of Graduate Studies

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in Fulfilment of the Requirements for the

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Especially to my supervisor, family and friends. Thanks for all your support and couragement.

Abstract of the 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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July 2003

Chairman : Associate Professor Zulkarnain Zainal, Ph.D.

Faculty : Science and Environmental Studies

Nickel tin selenide thin films have been potentiostatically electrodeposited on titanium substrate from aqueous solution consisting of nickel sulphate ($NiSO_4$), tin chloride ($SnCl_2$) and sodium selenide (Na_2SeO_3). Ethylenediaminetetraacetic acid (EDTA) was used as additive to improve the quality of deposit and longevity of the deposition bath. The electrodeposition potential was selected from the cyclic voltammetry (CV) experiment. The crystalline structure, morphology, composition and photoactivity of the films deposited were characterised by using X-ray diffractometry (XRD), scanning electron microscopy (SEM), energy disperse analysis of X-rays (EDAX) and linear sweep photovoltammetry (LSPV). X-ray photoelectron spectroscopy (XPS) was performed to the selected sample. The band gap energy and type of optical transition were determined from optical absorbance data.

The formation of polycrystalline $NiSnSe_4$ was confirmed by comparing the XRD results to that of a powder which was synthesized by precipitation method. Elemental analysis of

the powder determined from XPS spectrum showed the presence of nickel, tin and selenium as ternary compound. The stoichiometric ratio of 1:1:4 of nickel, tin and selenium has been confirmed by EDAX analysis and this value was used as reference.

The deposition was carried out at varying parameters such as different potentials, bath temperatures, concentrations of electrolytes and complexing agent, and deposition times. The photoactivity, composition, grain size and shape of the films were dependent on the electrodeposition conditions. The electrodeposition of $NiSnSe_4$ film is most suitable to be carried out at -0.5 V vs. Ag/AgCl with 0.02 M $NiSO_4$, $SnCl_2$, Na_2SeO_3 while the concentration of complexing agent, EDTA was 0.02 M. This film was obtained in p-type semiconductor.

Shorter deposition time also effected the composition of the films which resulted in a non-stoichiometric selenium rich deposit. The best time to deposit nickel tin selenide thin film was obtained at 60 minutes. The optimum bath temperature was 45 °C. Higher bath temperature could not improve the crystallinity, but also resulted in the formation of binary compound. The optical absorption studies revealed that the film has direct transition with band gap energy of 1.55 eV.

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

ELEKTROENAPAN LAPISAN NIPIS NIKEL TIN SELENIDA

Oleh

KARTINI BT. ABD. RAHIM

Julai 2003

Pengerusi : Profesor Madya Zulkarnain Zainal, Ph.D.

Fakulti : Sains dan Pengajian Alam Sekitar

Lapisan nipis nikel timah selenida telah dienapkan secara elektro di atas substrat titanium dari larutan akueus nikel sulfat ($NiSO_4$), timah klorida ($SnCl_2$) dan natrium selenida (Na_2SeO_3). Ethylenediaminetetraacetic asid (EDTA) telah digunakan sebagai aditif untuk meningkatkan kualiti enapan dan tempoh hayat larutan enapan. Keupayaan pengenapan telah dipilih berdasarkan ujian kitar voltammetri. Struktur, morfologi, komposisi dan kesan cahaya telah di analisis menggunakan teknik pembelauan sinar-X (XRD), mikroskop pengimbasan elektron (SEM), analisis penyerakan tenaga sinaran-X (EDAX) dan pengimbasan linear fotovoltammetri (LSPV). Di dalam kes tertentu, spektroskopi fotoelektron sinar-X (XPS) juga digunakan. Nilai luang tenaga dan jenis peralihan telah ditentukan daripada data serapan optik.

Pembentukan polihablur $NiSnSe_4$ telah ditentukan dengan membandingkan keputusan XRD yang dijalankan ke atas serbuk yang disediakan dari kaedah pengenapan. Manakala spektrum XPS membuktikan kehadiran nikel, timah dan selenium sebagai sebatian

ternari. Analisis EDAX dijalankan ke atas serbuk juga membuktikan kehadiran nikel, timah dan selenium dengan nisbah stoikiometri 1:1:4 dan nisbah ini digunakan sebagai rujukan.

Pengenapan telah dijalankan ke atas beberapa parameter seperti perbezaan keupayaan, suhu larutan, kepekatan larutan, kepekatan agen pengkompleks dan tempoh pengenapan. Fotoaktiviti, komposisi, saiz dan bentuk butiran adalah bergantung kepada keadaan pengenapan. Lapisan nipis nikel timah selenida sesuai dienapkan pada keupayaan -0.50 V vs. Ag/AgCl dengan kepekatan larutan pada 0.02 M ($NiSO_4$, $SnCl_2$, dan Na_2SeO_3) serta kepekatan agen pengkompleks, EDTA adalah 0.02 M. Filem yang disediakan dari kajian ini menunjukkan sifat semikonduktor jenis-p.

Tempoh pengenapan yang singkat juga mempengaruhi komposisi filem di mana lebih banyak elemen selenium akan ditemui dengan nisbah yang tidak stoikiometri. Masa yang paling sesuai untuk mengenapkan filem ini adalah pada 60 minit. Keadaan suhu larutan yang optimum adalah pada 45°C. Peningkatan suhu yang lebih tinggi tidak dapat meningkatkan penghabluran tetapi juga menyebabkan kehadiran sebatian binari. Sampel menunjukkan keadaan peralihan langsung dengan nilai luang tenaga 1.55 eV.

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I certify that an Examination Committee met on 20 July 2003 to conduct the final examination of Graduate Student on her Degree of Master thesis entitled "Electrodeposition of Nickel Tin Selenide Thin Film" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulation 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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Date: **20 NOVEMBER 2004**

This thesis submitted to the Senate of Universiti Putra Malaysia has been accepted as fulfilment of the requirement for the degree of Master of Science

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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.

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KARTINI BT ABD RAHIM

Date:

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