PREPARATION AND CHARACTERIZATION OF TIN SELENIDE THIN FILMS FOR APPLICATION IN PHOTOELECTROCHEMICAL CELL

By

SARAVANAN NAGALINGAM

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

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PREPARATION AND CHARACTERIZATION OF TIN SELENIDE THIN FILMS FOR APPLICATION IN PHOTOELECTROCHEMICAL CELL

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

Faculty: Science

Tin selenide (SnSe) thin films have been prepared using various methods such as electrodeposition, chemical precipitation, thermal evaporation and chemical bath deposition. The variation in the deposition process produced thin films exhibiting various characteristics. The films have been characterised using x-ray diffractometry (XRD), scanning electron microscopy (SEM), energy dispersive analysis of x-ray (EDX) and x-ray photoelectron spectroscopy (XPS). The photoactivity of the films were evaluated using linear sweep voltammetry (LSV) in the presence of $K_4Fe(CN)_6/K_3Fe(CN)_6$ redox system. The band gap energy and transition type was determined from optical absorbance data obtained using UV-VIS spectrophotometry technique.

The electrodeposition process was carried out by varying deposition potentials, solution temperature, solution concentrations and deposition time.

The films prepared were found to be polycrystalline in nature. XRD studies confirmed the formation of orthorhombic SnSe phase with the preferred orientation along the (111) plane. Annealing at 150 °C in the presence of nitrogen atmosphere was found to improve the crystallinity of the film. This treatment also results in an increase in the photoresponse of the films deposited. The electrodeposited SnSe film shows photoresponse in the cathodic region conforming the p-type nature. It was an indirect transition with a bandgap energy of about 1.08 eV.

The SnSe film was also prepared using the combination of chemical precipitation and brush coating method. The crystalline powder was coated onto indium doped tin oxide glass substrates using polyvinyl alcohol solution as a binder. Tin selenide powder was prepared using chemical precipitation method in alkaline aqueous medium. The XRD data obtained confirmed the SnSe powder to be free of impurities. The coatings were subjected to annealing at various times and temperatures in order to study these effects towards the structure, morphology and composition of the materials. XRD data obtained from the films indicated formation of polycrystalline materials. Annealing at 150 °C for 1 h in nitrogen atmosphere was found to be the optimum conditions to produce films of this nature. The photoresponse behaviour of the film in the cathodic region confirms the p-type conduction. The optical absorbance data exhibited indirect transition with a bandgap energy of about 1.00 eV.

The SnSe powder synthesised was also used as a source material to prepare SnSe thin films using thermal evaporation method. The combination of this experimental procedure has resulted in the reduction of time to develop a particular thin film. The currently employed solid-state method, which needs 2 days to develop metal chalcogenide thin films, could be replaced with this method, which takes not more than 5 hours. The films were found to be smooth and free of pinholes. Clear transparent SnSe films with different thickness could conveniently be prepared by this method. XRD data indicated that the preferred orientation lies along the (111) plane. The films were found to be p-type semiconductors. The thicker SnSe film indicates higher photoactivity. The optical data confirmed the indirect transition with an energy gap of 1.25 eV.

Tin selenide thin films could also be deposited onto indium tin oxide glass slides in alkaline medium. The method is based on simple bath deposition technique that requires fewer chemicals, less monitoring, simple and economical. Uniform and well-adhered films were obtained upon required deposition period. XRD data for the as-deposited film confirms polycrystalline material formation. The preferred orientation lies along the (201) plane. The material covered the surface of the substrate completely. The photoresponse in the cathodic region indicates formation of a p-type semiconductor. The bandgap energy obtained was 1.25 eV corresponding to direct transition. The optical absorption in the visible region makes it possible to be used in a photoelectrochemical cell or as semitransparent layer in high-speed detectors working in visible region.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

PENYEDIAAN DAN PENCIRIAN TERHADAP LAPISAN FILEM NIPIS STANUM SELENIDA UNTUK KEGUNAAN DALAM SEL FOTOELEKTROKIMIA

Oleh

SARAVANAN NAGALINGAM

November 2004

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

Fakulti: Sains

Lapisan filem nipis stanum selenida (SnSe) telah disediakan menggunakan kaedah elektroenapan, pemendakan kimia, sejatan panas dan enapan dalam larutan kimia. Kaedah yang berlainan dalam proses penyediaan telah menghasilkan lapisan filem nipis yang menunjukkan ciri-ciri yang berbeza. Lapisan filem nipis yang telah disediakan dianalisis dengan menggunakan teknik pembelauan sinar-X (XRD), mikroskopi pengimbasan elektron (SEM), analisis penyerakan tenaga sinar-X (EDX) dan spektroskopi fotoelektron sinar-X (XPS). Sifat fotoaktif lapisan filem nipis dianalisis dengan menggunakan kaedah voltammetri pengimbasan linear (LSV) dalam larutan $K_4Fe(CN)_6/K_3Fe(CN)_6$. Nilai jurang tenaga dan jenis peralihan optik telah ditentukan dengan menggunakan kaedah serapan optik.

Proses elektroenapan dijalankan dengan mengubah ciri-ciri seperti keupayaan enapan, suhu larutan, kepekatan larutan dan tempoh enapan.

Lapisan filem yang disediakan dengan kaedah ini wujud dalam bentuk polihablur. Analisis XRD mengesahkan pembentukan fasa ortorombik SnSe dengan penyusunan pada satah (111). Sepuh lindap pada suhu 150 °C dengan kehadiran gas nitrogen didapati meningkatkan kehabluran filem tersebut. Filem SnSe yang telah disediakan menunjukkan kesan fotoaktif pada bahagian katod dan ini mengesahkan pembentukan sifat semikonduktor jenis-p. Teknik serapan optik memberikan nilai jurang tenaga sebanyak 1.08 eV dengan keadaan peralihan tidak langsung.

Lapisan filem SnSe juga dapat disediakan dengan menggunakan teknik pemendakan kimia. Bahan semikonduktor yang termendak ini dapat dijadikan sebagai lapisan filem dengan menggunakan kaedah penyapuan ke atas substrat menggunakan berus halus. Lapisan filem ini dapat melekat dengan sempurna apabila bahan campuran seperti larutan alkohol polivinil digunakan. Keputusan XRD mengesahkan serbuk SnSe adalah tulen dan tidak mengandungi bendasing. Lapisan filem yang disediakan dipanaskan pada suhu dan masa yang berbeza untuk mengkaji kesan terhadap struktur, keadaan permukaan dan komposisi filem tersebut. Keputusan XRD menunjukkan wujud lapisan polihablur SnSe. Pemanasan pada suhu 150 °C selama 1 jam dalam kehadiran gas nitrogen merupakan keadaan paling sesuai untuk menghasilkan lapisan filem menggunakan kaedah ini. Filem SnSe yang disediakan menunjukkan kesan fotoaktif pada bahagian katod sekaligus mengesahkan pembentukan semikonduktor jenis-p. Teknik serapan optik memberikan nilai jurang tenaga sebanyak 1.00 eV dengan keadaan peralihan tidak langsung.

Serbuk SnSe yang dihasilkan itu digunakan sebagai bahan sumber bagi menyediakan lapisan filem nipis SnSe menggunakan kaedah sejatan panas. Dengan penghasilan teknik ini, masa yang diperlukan untuk menyediakan lapisan filem dapat dikurangkan daripada 2 hari kepada tidak lebih 5 jam. Kaedah ini diharapkan dapat mengantikan teknik penyediaan keadaan pepejal yang biasa digunakan sekarang. Keputusan XRD menunjukkan lapisan filem dengan fasa ortorombik SnSe yang mempunyai orientasi keutamaannya pada satah (111). Kaedah ini dapat digunakan untuk menghasilkan lapisan filem yang berlainan ketebalan. Filem SnSe yang tebal menunjukkan kesan fotoaktif yang lebih tinggi pada bahagian katod yang mengesahkan pembentukan sifat semikonduktor jenis-p. Teknik serapan optik memberikan nilai jurang tenaga sebanyak 1.25 eV dengan keadaan peralihan tidak langsung.

Lapisan filem SnSe juga telah disediakan dalam keadaan larutan beralkali. Kaedah ini berasaskan teknik enapan larutan kimia yang ringkas, mudah dan melibatkan kos yang rendah. Lapisan filem yang seragam dan mempunyai kelekatan yang baik pada substrat telah diperolehi dengan menggunakan kaedah ini. Data XRD bagi filem yang terenap mengesahkan ia adalah bahan polihablur. Orientasi keutamaannya terletak pada satah (201). Filem ini menutupi seluruh permukaan substrat. Kesan fotoaktif pada bahagian katod mengesahkan pembentukan sifat semikonduktor jenis-p. Teknik serapan optik memberikan nilai jurang tenaga sebanyak 1.25 eV dengan keadaan peralihan langsung. Keupayaan lapisan filem ini untuk menunjukkan kesan terhadap sinaran nampak membolehkan bahan ini

dijadikan sebagai bahan utama dalam pembuatan sel fotoelektrokimia atau lapisan semilutsinar pada pengesan berkelajuan tinggi yang berfungsi dalam julat spektrum sinaran nampak.

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I certify that an Examination Committee met on 8th November 2004 to conduct the final examination of Saravanan Nagalingam on his Doctor of Philosophy thesis entitled "Preparation and Characterization of Tin Selenide Thin Films for Photoelectrochemical Cell" 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:

Mohd. Zaizi Desa, Ph.D.
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Abdul Halim Abdullah, Ph.D.
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

Tan Wee Tee, Ph.D.
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

Abdul Razak Daud, Ph.D.
Professor
Faculty of Science and Technology
Universiti Kebangsaan Malaysia
(Independent Examiner)

GULAM RUSUL RAHMAT ALI, Ph.D.
Professor/Deputy Dean
School of Graduate Studies,
Universiti Putra Malaysia

Date :

This thesis 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 are as follows:

Zulkarnain bin Zainal, Ph.D.
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Anuar bin Kassim, Ph.D.
Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

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

Wan Mahmood bin Mat Yunus, Ph.D.
Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

AINI IDERIS, Ph.D.
Professor/Dean
School of Graduate Studies
Universiti Putra Malaysia

Date :

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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SARAVANAN NAGALINGAM

Date:

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