UNIVERSITI PUTRA MALAYSIA

ELECTRODEPOSITION AND PROPERTIES OF TIN SELENO SULPHIDE

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FS 2005 2

ELECTRODEPOSITION AND PROPERTIES OF TIN SELENO SULPHIDE

By

LEE TIEN PING

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

December 2005

UPM

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

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By

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December 2005

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Thin film semiconductors such as tin seleno sulphide films are considered important technological materials because of their potential applications in solar cells, infrared detectors and lasers. These thin films can be prepared by electrodeposition because of its simple, low cost and easy to control parameters.

In this research, tin seleno sulphide thin films have been electrodeposited potentiostatically from aqueous solution containing $SnCl_2$, Na_2SeO_3 and $Na_2S_2O_3$ on titanium substrate. Disodium salt of ethylenediaminetetraacetic acid (Na_2-EDTA) was used as a complexant to improve the adhesion of the deposited film on the substrate. Cyclic voltammetry was performed to elucidiate the electrodic processes occurred and determine the potential range for electrodeposition.

The effect of parameters such as bath temperatures, the presence of EDTA, deposition potentials, electrolytes concentrations, deposition times, pH, and annealing temperatures on the film properties were studied. The deposited films

were characterized by powder X-ray diffraction (PXRD), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDAX) and linear sweep photovoltammetry (LSPV). The band gap energy and transition type were determined from optical absorbance data. PXRD results showed the formation of polycrystalline orthorhombic crystal structure of $SnSe_{0.5}S_{0.5}$ with strong (111) being the most intense orientation. SEM micrographs revealed the morphological nature of the deposit which is depended on the deposition condition. EDAX results showed that less sulfur was deposited for the samples. All films prepared in this study showed rectifying behaviour in cathodic polarization regime signifying p-type conduction.

A good quality tin seleno sulphide film was obtained from equal volume mixture of 0.005 M Sn-EDTA, 0.0025 M Na_2SeO_3 and 0.0025 M $Na_2S_2O_3$ solutions at potential -0.70 V in the presence of 0.010 M EDTA. Binary phase of SnS_2 was found present in films deposited at more negative potentials than -0.70 V. The presence of EDTA has improved the quality of the samples.

Increasing the bath temperature improve the crystallinity, morphology and photosensitivity of the films. The electrodeposition is most suitable to be carried out at 60 °C. However, when bath temperature is increased to 70 °C, the grain size and surface coverage of the deposits was reduced, which may due to dissolution of deposit because of high temperature. Increasing the deposition time allowed more material to be deposited onto the substrate and the most suitable deposition time was found to be 60 min. pH 1.0 was found to be the optimum condition to prepare

tin seleno sulphide. The photosensitivity and crystallinity of the films decreased when pH 1.5 and pH 2.0 was used.

Annealing at 400 °C for 20 min could improve the crystallinity of the films. The energy gap is around 1.20 eV with indirect transition type as determined by optical absorption data.

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

ELEKTROENAPAN DAN SIFAT TIMAH SELENIDA SULFIDA

Oleh

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Lapisan filem nipis semikonduktor seperti timah selenida sulfida dianggap sebagai bahan sumber teknologi yang penting disebabkan aplikasi penggunaannya yang berpotensi tinggi dalam bidang sel solar, pengesan inframerah dan laser. Lapisan filem nipis ini boleh disediakan melalui kaedah elektroenapan kerana kaedah ini mudah, berkos rendah dan parameternya senang dikawal.

Dalam kajian ini, lapisan filem nipis timah selenida sulfida dihasilkan dengan enapan larutan akueus yang mengandungi $SnCl_2$, Na_2SeO_3 and $Na_2S_2O_3$ pada substrat titanium. EDTA digunakan sebagai agen pengkompleks dalam proses elektroenapan ini untuk memperbaiki kelekatan filem nipis pada substrat titanium. Kitar voltametri dijalankan untuk menerangkan proses-proses elektrodik yang berlaku dan mengenal pasti julat keupayaan yang sesuai untuk proses pengelektroenapan ini.

Kesan parameter seperti suhu larutan, kehadiran EDTA, keupayaan elektroenapan, kepekatan elektrolit, tempoh elektroenapan, pH and kesan pemanasan telah dikaji.

Lapisan filem nipis yang dihasilkan kemudian dikaji dengan pembelauan sinar-X (PXRD), mikroskop pengimbasan elektron (SEM), analisis penyerakan tenaga sinaran-X (EDAX) dan fotovoltametri pengimbasan linear (LSPV). Nilai luang tenaga dan jenis peralihan optik ditentukan daripada data serapan optik. Keputusan XRD mengesahkan pembentukan polihablur timah selenida sulfida jenis ortorombus dengan penyusunan yang optimum pada satah (111). SEM mempamerkan sifat morfologi filem adalah bergantung kepada keadaan pengenapan. EDAX menyatakan bahawa kandungan sulfur yang telah dienapkan pada lapisan filem nipis adalah rendah. Semua filem yang dienapkan itu menunjukkan sifat semikonduktor jenis p.

Lapisan filem nipis timah selenida sulfida yang berkualiti boleh diperoleh daripada larutan yang mengandungi 5.0×10^{-3} M Sn-EDTA, 2.5×10^{-3} M Na_2SeO_3 dan 2.5×10^{-3} M $Na_2S_2O_3$ dengan isipadu yang sama pada -0.70 V. SnS_2 didapati terbentuk pada filem yang disediakan pada keupayaan yang lebih negative daripada -0.70 V. Kehadiran EDTA telah memperbaiki kualiti filem nipis timah selenida sulfida.

Peningkatan suhu larutan telah memperbaiki kehabluran, morfologi dan fotosensitiviti sampel. Elektroenapan paling sesuai dijalankan pada suhu 60 °C. Walau bagaimanapun, apabila suhu larutan ditingkatkan kepada 70 °C, saiz butiran dan lingkungan permukaan saput nipis telah berkurangan. Peningkatan tempoh enapan menghasilkan lebih banyak bahan enapan pada substrat. Dengan ini, tempoh masa yang paling sesuai untuk menghasilkan lapisan nipis ini adalah sebanyak 60 minit. pH 1.0 didapati merupakan keadaan optimum bagi

ACKNOWLEDGEMENTS

I would like to express my sincere appreciation to all who contributed in my research. My greatest gratitude forwarded to my project supervisor, Professor Dr. Zulkarnain Zainal for his guidance, constructive comments, untiring support, invaluable advices and suggestions to complete my research successfully.

My sincere appreciation is also extended to the committee members, Professor Dr. Mohd. Zobir bin Hussein and Professor Dr. Anuar bin Kassim for their guidance, effort and encouragement throughout this research. Many thanks to the staffs in Institute of Bioscience and all my fellow lab-mates for their assistance and help. Without them, my studies would not have come to fruition.

I would also like to express my heartiest gratitude and appreciation to my family and friends for their support, encouragement and understanding throughout my studies.

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LIST OF ABBREVIATIONS

2θ	Two theta
CV	Cyclic voltammetry
eV	electronvolt
Ec	Energy level of the bottom of the conduction band
EDAX	Energy Dispersive of Analysis of X-Ray
E_g	Energy gap or band gap
Ev	Energy level of the top of the valence band
Id	Darkcurrent
Ip	Photocurrent
JCPDS	Joint Committee on Powder Diffraction Standards
PEC	Photoelectrochemical test
SEM	Scanning Electron microscopy
$SnSe_{0.5}S_{0.5}$	Tin Seleno Sulphide
UV-VIS	Ultravoilet-Visible
XRD	X-ray Diffraction

CHAPTER 1

INTRODUCTION

For centuries, mankind has been facing problems concerning the availability and distribution of energy. Traditional fossil energy resources, coal, oil, and gas, are not only limited, but they also contribute to environmental problems in the near future through the emission of carbon dioxide. From this perspective, the use of sunlight offers a conceivable alternative to the worldwide energy problems.

Solar energy is known for its abundant, inexpensive and decentralized energy source. Solar cells are devices that convert the direct conversion of sunlight into electrical energy. Solar cell technology dated to 1839 when French physicist Antoine-Cesar Becquerel observed that when metal plates immersed in a suitable electrolyte were exposed to sunlight, a small voltage and current were produce. In 1941, the first silicon solar cell was invented and is today the most extensively studied semiconductor. The advantages of silicon are its non-toxicity, material abundance, stability and high efficiency potential. However, the production cost of silicon based photovoltaic cells is too high due to the sophisticated processing steps involved.

Binary and ternary chalcogenides semiconductors are considered important technological materials because of their potential applications in the field of photo-catalysis, solar cells, IR detectors and lasers. Thin films of these compounds are usually prepared by chemical vapor deposition (Fischer *et al.*, 2001), chemical bath deposition (García *et al.*, 1999) and electrodeposition (Sharma *et al.*, 2004).

Electrodeposition could be a cost effective technology for the production of terrestrial photoelectrochemical cell. The main advantage of thin film solar cells is their promise of being low cost, due to the low cost production and the use of the relatively low cost materials.

Previous investigations devoted to the electrochemical synthesis of chalcogenide semiconductors have shown the suitability of the electrodeposition method for the preparation of tin chalcogenides thin films. The optical and structural properties of the tin chalcogenides have a variety of application in the optical and optoelectronic application. Out of all the tin-based chalcogenides, tin sulphide (SnS) and tin selenide (SnSe) have received much attention in this respect. SnS a layered semiconductor compound is a promising candidate in the field of photoelectrochemical solar energy conversion due to its highly stable nature. It is basically the combination of tin, an element from group IV and S the member of group VI. In layered type chalcogenides, within each layer, the atoms are predominantly bound together by covalent forces. The bonds between the layers are extremely week due to Van der Waals forces. It crystallises in orthorhombic structure and has an optical band gap of 1.0 to 1.3 eV.

In 1996, Zainal and his co-workers have electrodeposited SnS on ITO glass and Ti substrate. They found that the films are of p-type semiconductor and exhibited indirect band gap of 0.9 to 1.1 eV. Ichimura and his group in 2000 have characterized the deposited SnS films chemically, structurally and optically. The effect of the deposition parameters on the film properties was studied. In 2001, Subramaniam *et al.* have prepared SnS on tin oxide coated substrate. The

materials properties and the results on the photoelectrochemical cell performance was reported.

SnSe is a narrow band gap binary IV-IV semiconductor displaying a variety of application such as infrared optoelectronic devices and memory switching devices with an orthorhombic crystal structure. It exists as a layered compound and is chemically and electrochemically stable in alkaline or acid condition. The band gap of SnSe is about 1.0 eV.

In this research, tin seleno sulphide semiconductor material was prepared by electrodeposited and this continous series of mixed crystal is formed by the two compound, SnSe and SnS. Electrodeposition is a simple, economical and viable technique which produces films with good quality for device application. The film thickness, morphology and composition can be easily controlled by adjusting the electrical parameters. An elaborate research is carried out on the structural, photoelectrochemical, morphological and optical properties of electrodeposited tin seleno sulphide.

1.1 Semiconductor

Electrically, we can divide all materials into three classification; relating to the ability of a specific material to carry electrical current. Conductors are those materials that contain many free electrons; electrons that are not bound to specific sites within the material and, hence, are free to move, and thereby constitute a current. An insulator, on the other hand, has not mobile electrons and therefore, is unable to sustain an electrical current. Semiconductors are those materials whose ability to carry an electrical current lies between these two extremes.

Solar cells are constructed from materials commonly known as semiconductors. Semiconductor materials for terrestrial solar cells must meet the following two requirements: (1) the material should have appropriate electrical and optical properties for solar cells and (2) its constituent elements should be abundant, cheap, and non-toxic.

Several ternary and quaternary semiconductors are currently investigated for their potential for photovoltaic applications. The study of these materials is important due to the fact that the band gap and lattice parameters can be varied by changing the cation composition. $CuInGaSe_2$ (CIGS) chalcopyrite thin film absorber material is one of the most promising candidates for high efficiency, low cost, solar cells (Jain *et al.*, 2003).

Semiconductors exhibit three forms of crystal arrangement; crystalline, polycrystalline and amorphous form. Many of the properties that we find to be useful in semiconductors and solar cells arise from basic crystal structure of the semiconductor and are dependent on the direction in the crystal toward which the observer is facing.

1.1.1 Electrons and holes

One often encounters a graphical representation of semiconductors known as the energy-band diagram. The upper line in Figure 1.1 is the conduction--band edge, representing the lowest energy that conducton electron may have. The two line are separated by bandgap energy , E_g, the energy difference between the top of the

valence band and the bottom of the conduction band in insulators and semiconductors (Hu and White, 1983).

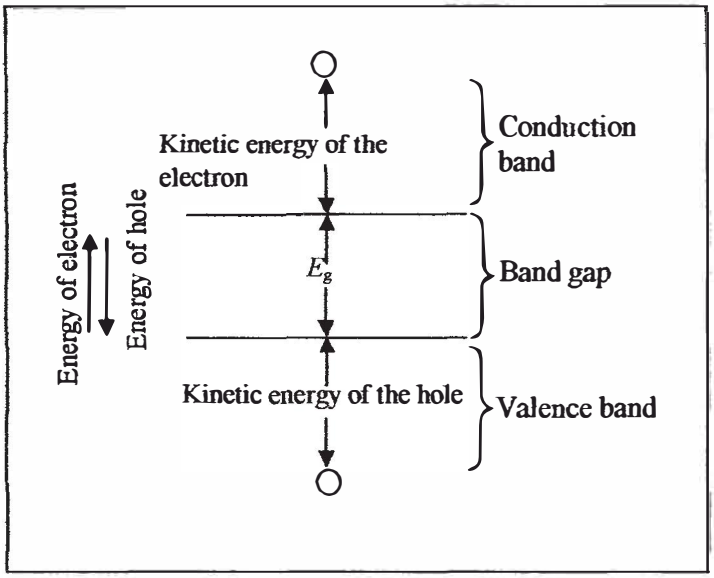

Figure1.1: Energy-band diagram.

1.1.2 Intrinsic and extrinsic semiconductors

An intrinsic semiconductor is one which is pure enough that impurities do not appreciably affect its electrical behavior. In this case, all carriers are created by thermally or optically exciting electrons from the full valence band into the empty conduction band (Figure 1.2). Thus equal numbers of electrons and holes are present in an intrinsic semiconductor.