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ELECTROCHEMICAL SYNTHESIS OF TIN SULPHIDE IN AQUEOUS MEDIA

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Chairman : Associate Professor Zulkarnain Zainal, Ph. D.

Faculty : Science and Environmental Studies

Chalcogenide semiconductor of the type tin sulphide or stannous sulphide (SnS) has been synthesised in aqueous media under the presence and absence of EDTA complexing agent. It was found that electrodeposition performed in the presence of EDTA is more reproducible, better adhered to titanium substrate, more leveled, more crystalline and offers better photoconductivity properties in comparison to electrodeposition carried out without EDTA. These were determined by means of Energy Dispersive Analysis of X-ray (EDAX), Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD), UV-visible Spectroscopy, Linear Scan Photovoltammetry (LSPV) and in special cases, X-ray Photoelectron Spectroscopy (XPS). The main improvement in photoconductivity property which is a basic requirement for any solar energy materials and semiconductor was due

to factors that stem from good adhesion, crystallinity, surface coverage and composition.

Optimisation of the electrodeposition condition was the prerequisite of synthesising an outstanding SnS quality. In the optimisation study, the optimum amount of thiosulphate, EDTA and tin source (stannous ions) has been determined based upon the degree of reproducibility of Sn/S values from analysis of stoichiometry (via EDAX) and degree of reproducibility of deposits quantity (up to XRD detection limit for SnS deduction) at a fixed deposition time. The optimum deposition potential of –0.7V (vs. SCE) was clear cut from microscopic analysis by means of scanning electron micrographs and quantification by way of EDAX. Under the optimum condition, an average Sn/S found from the study was 1.12 ± 0.05, which is within the expected stoichiometry found in literature. The average energy gap estimated on samples prepared on ITO substrate was 1.29 ± 0.29 eV for a direct optical transition and 0.74 ± 0.20 eV for indirect optical transition. In terms of proportion, this correlates with an advanced study on SnS property via valence band spectra by Ettema *et al.* published in Physical Review B, 1992, 46(12): 7363-7386, which reported the optical transitions to be 1.39 eV for direct transition and 0.2-0.4 eV for indirect transition.

Examination of the effect of sodium dodecylsulphate (SDS) on the electrodeposit shows a significant adverse effect on the electrodeposits. SDS was suspected to cause electrode poisoning and had resulted in raise of pH, which was non favourable for cathodic electrodeposition of SnS.

As in the case of tartaric acid, however, the leveling effect expected of it might be insignificant and this could have been the masking effect of EDTA. To ascertain the slight enhancement of crystal growth following addition of tartaric acid into the electrodeposition bath, further investigation may be required.

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

SINTESIS ELEKTROKIMIA TIMAH SULFIDA DI DALAM LARUTAN AKUEUS

Oleh

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Semikonduktor kalkogenida, timah sulfida (SnS), telah disintesis di dalam larutan akueus dengan kehadiran dan tanpa kehadiran agen pengkompleks EDTA. Elektroenapan, yang dilakukan dengan kehadiran EDTA didapati mempunyai kebolehulangan yang lebih baik, di mana enapan dapat melekat pada titanium dengan lebih kuat, lebih rata, mempunyai kehabluran yang lebih baik dan mempamerkan sifat fotokonduksi yang lebih baik. Ini telah diperhatikan daripada analisis penyerakan tenaga sinaran-X (EDAX), mikroskopi elektron imbasan (SEM), pembelauan sinaran-X (XRD), spektroskopi ultra lembayung nampak (UV-visible), imbasan linear fotovoltametri (LSPV), dan di dalam kes-kes tertentu, spektroskopi fotoelektron sinar-X (XPS). Penigkatan dalam fotokonduksi yang merupakan satu sifat asas penting bagi peranti sel suria atau semikonduktor,

telah berjaya dicapai hasil daripada penambahbaikan daya lekatan, kehabluran, pelitupan permukaan dan komposisi.

Pengoptimuman pengelektroenapan adalah perlu bagi mendapatkan SnS yang berkualiti. Amaun optimum bagi tiosulfat, EDTA dan ion timah telah ditentukan berdasarkan pemerhatian kepada darjah keterulangan pada nisbah Sn/S daripada analisis stoikiometri (daripada EDAX), daya lekatan kepada substrat titanium, kehabluran dan sifat fotokonduksi yang baik. Keupayaan pengelektroenapan –0.7 V (terhadap SCE) telah dipilih keupayaan optimum berdasarkan mikroskopi elektron imbasan dan stoikiometri. Enapan yang dihasilkan pada keadaan optima ini menghasilkan nisbah stoikiometri pada nilai 1.12 $\pm$ 0.05 Sn/S, iaitu terlingkung di dalam julat nilai Sn/S yang boleh diterimapakai. Nilai luang tenaga, E_g bagi enapan yang disediakan di atas ITO di bawah keadaan optima ini ialah 1.29 $\pm$ 0.29 eV bagi peralihan terus dan 0.74 $\pm$ 0.20 eV bagi peralihan tidak terus. Ini bersesuaian dengan yang dilaporkan oleh Ettema *et al.* pada tahun 1992 di dalam jurnal Physical Review B, jilid 46, nombor 12, yang menjumpai jurang tenaga bagi peralihan terus 1.39 eV dan bagi peralihan tidak terus 0.2-0.4 eV.

Kehadiran bahan aktif permukaan SDS didapati menunjukkan kesan negatif kepada pengelektroenapan SnS. SDS tidak membantu pengelektroenapan sebaliknya menyebabkan keracunan elektrod. Keracunan ini dijangka berpunca daripada peningkatan pH, yang tidak sesuai untuk pengelektroenapan SnS.

Keupayaan asid tartarik untuk meratakan permukaan tidak dapat dilihat dengan jelas dan ini mungkin disebabkan kesan kehadiran EDTA di dalam larutan pengelektroenapan. Penambahan saiz yang dapat dilihat pada hablur menunjukkan kemungkinan asid tartarik mampu meningkatkan kadar pengelektroenapan. Kajian lanjut diperlukan bagi melihat kesan ini dengan lebih terperinci.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF PLATES

LIST OF ABBREVIATIONS

A	Absorbance
AE	Auxilary electrode
a-Si	Amorphous silicon
CE	Counter electrode
CIS	Copper indium diselenide
CV	Cyclic voltammetry/voltammogram
E	Potential in volts
E_{dep}	Deposition potential
EDAX	Energy dispersive analysis of x-ray
EDTA	Ethyl diamine tetra acetic acid
E_g	Energy gap
eV	Electron volts
FF	Fill factor
I_{dark}	Dark current
I_{max}	Current maximum
I_{photo}	Photocurrent
ITO	Indium doped tin oxide
JCPDS	Joint committee on Powder Diffraction Standard
LCL	Lower control limit
LSV	Linear scan voltammetry/voltammogram

LSPV	Linear scan photovoltammetry
M^{n+}	Metal ion with n charge, where n=1,2,3, etc.
PEC	Photoelectrochemical analysis
PVC	Polyvinyl chloride
Q	Outlier (statistical term)
σ	Standard deviation (statistical term)
SCE	Saturated calomel electrode
SDS	Sodium dodecyl sulfate
SEM	Scanning electron microscopy
μ	Mean (Statistical term)
µpdsm	Micro powder data search match
UCL	Upper control limit
UKM	Universiti Kebangsaan Malaysia
UM	Universiti Malaya
UPM	Universiti Putra Malaysia
USM	Universiti Sains Malaysia
2θ	Two theta
WE	Working electrode
W_p	Watt power
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

CHAPTER I

INTRODUCTION

The era of science and technology will be left for the ionic and protonic technology, by which this work is motivated. Reducing the dimensions of devices is one of the aspects in focus [1]. One of the works prompted by this is the development of thin films from which the idea of electrochemical technique stems for the synthesis of tin sulphide, SnS. This phase of Sn-S compounds reveals the features of an ideal semiconductor with E_g falling in the range of 1-2 eV (Table 1.1), making it suitable for photoelectrochemical, photovoltaic and optoelectronic applications, for instance.

The thin film form of SnS and other more common binary compounds such as CdS, GaAs, ZnS, ZnSe and CdSe, capture a significant interest of scientists in many fields, vis-a-vis Energy, Solar Cell Devices, Silicon and Tin Technology, Materials, Chemistry Electronic Industry and etceteras. In Malaysia, thin film technology is one of the most important technologies in the electronic industry to account for its being world's third largest exporter of semiconductor. With Sn and Si abundance, Malaysia is in even better position for the world market of USD100 billion for thin film [1].