STRUCTURAL CHARACTERIZATION OF TUNGSTEN SULPHOSELENIDES (WSSe) THIN FILMS FOR SEMICONDUCTOR APPLICATION

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DECLARATION

I hereby, declared this report entitled "Structural Characterization of Tungsten Sulphoselenide (WSSe) Thin Films for Semiconductor Application" is the results of my own research except as cited in references.

Signature : ……………………………

Author's Name : TEE KOK CHEN

Date : 8th JUNE 2016

UNIVERSITI TEKNIKAL MALAYSIA MELAKA

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TAJUK: **STRUCTURAL CHARACTERIZATION OF TUNGSTEN SULPHOSELENIDE (WSSe) THIN FILMS FOR SEMICONDUCTOR APPLICATION**

SESI PENGAJIAN: 2015/16 Semester 2

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ABSTRAK

Teknologi filem nipis merupakan salah satu teknologi yang kian memberangsangkan dalam perkembangan sel fotovolta. Peralihan logam dwi-chalkogenida (TMD) merupakan semikonduktor dengan formula MX_2 yang digunakan sebagai bahan fotovolta yang efisien. Kajian ini beramal untuk menghasilkan filem nipis yang kos efisien, mementingan keselamatan dan kemudahan teknik untuk dalam sintesis peralihan logam dwi-chalkogenida. Dalam kumpulan TMD, tungsten sulpho selenide (WSSe) merupakan salah satu bahan yang digunakan dalam pengeluaran filem nipis. Objektif kajian ini adalah untuk mengsintesis WSSe filem nipis dengan teknik pemendapan. Selepas filem nipis telah disintesis, ia akan diteruskan dengan mencirikan struktur melalui penganalisian parameter yang berbeza. Filem nipis Maksudnya, WSSe akan dielektrosintesis pada permukaan Indium Tin Oxida (ITO) dengan salutan subtrat gelas. Analisis struktur dengan menggunakan pembiasan X-ray akan didedahkan pada filem nipis. Informasi penstrukturan boleh didapati dengan menggunkan radiasi CuK α (λ=1.5418 Å) pada sudut 2θ dalam linkungan 10^o-90^o. Imbasan Mikroskop Electron (SEM) akan dikaji pada filem nipis WSSe untuk menentukan penumbuhan granula filem dengan kristal pada permukaannya. Serakan kuasa X-ray (EDS) juga dikaji untuk menntukan komposisi dalam WSSe filem nipis. Potensi pemendapan dijangka akan dijalankan dalam linkugan potensi -2.0V hingga 2.0V. Ketebalan filem juga dijanka dalam linkungan 0.6μm-1.0μm.

ABSTRACT

Thin film technology is one of the most developing technologies nowadays that involve in the development of photovoltaic cell. Transition metal dichalcogenide (TMD) are semiconductors, which are also known as ternary thin film with the formula MX_2 that can be used as an efficient photovoltaic material. This research intent to predict safe, non-toxic, cost- efficient and relatively convenient technique to synthesize the transition metal dichacogenides thin films. Among TMDs, tungsten supho selenide (WSSe) is the one of the promising material that can be used in the thin film technology. The objectives of this paper are to synthesize stoichiometric of ternary tungsten sulpho selenides thin film via electrodeposition method. After the thin film has been prepared, the structural characterization of tungsten sulpho selenide thin film is analyzed by changing its various deposition parameters. WSSe will be electrodeposited on Indium Tin Oxide (ITO) coated glass substrate. Structural analysis via X-ray Diffraction (XRD) will reveal the crystallography nature of the thin film. The structural information can be obtained by using monochromatic CuKα radiation (λ=1.5418 Å) at 2θ angle in the range of 10^o-90^o. Scanning Electron Microscope (SEM) studies will reveal the nature grain growth of the film with crystallite on the surface. Energy Dispersive X-ray Spectroscopy (EDX) analysis was used to confirm the composition of WSSe thin film. The deposition potential is expected to be in the range of -2.0V to 2.0V whereas the thickness of the film is expected to be in the range of 0.6μm-1.0μm.

DEDICATION

To my beloved parents, supervisor, examiners, siblings, lecturer and fellow friends

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It is a genuine pleasure to express my deep sense of thanks and gratitude to my Supervisors, Dr. Zurina Binti Shamsudin and Prof. Madya Dr.T Joseph Sahaya Anand. Their dedication and keen interest above all overwhelming attitude for lending me a hand had been solely and mainly responsible for guiding me in the subject BMFG 4932 successfully. Their timely advice, meticulous scrutiny, scholarly advice and scientific approach have helped me to a very great understanding in my project field.

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LIST OF ABBREVIATIONS

PEC	-	Photoelectrochemical
CVD	-	Chemical Vapour Deposition
PV	-	Photovoltaic
WSSe	-	Tungsten Sulphoselenide
Si	-	Silicon
XRD	-	X-ray Diffraction
SEM	-	Scanning Electron Microscopy
EDS	-	Energy Dispersive X-ray Spectroscopy
CV	-	Cyclic Voltammetry
eV	-	Electron volt
ZnS	-	Zinc Sulfide
Cu2O	-	Copper(II) Oxide
PbS	-	Lead(II) Sulfide
PbSe	-	Lead Selenide
PbTe	-	Lead telluride
$MoSe_2$	-	Molybdenum selenide
CIS	-	Copper Indium Sulfide
CdTe	-	Cadmium telluride
Cl	-	Chloride
WSe_2	-	Tungsten Selenide
WS_2	-	Tungsten Sulfide
PL	-	Photoluminescence

MoS - Molybdenum Sulfide

TMPD - Tetramethyl-p-phenylenediamine

AgCl - Agentum chloride

WE - Working Electrode

CE - Counter Electrode

RE - Reference electrode

SCE - Saturated Calomel Electrode

PTA - Peroxotungstic acid

MoO_2 - Molybdenum dioxide

WO_3 - Tungsten trioxide

PBI_2 - Lead(II) iodide

TCA - Triethanol amine

ITO - Indium Tin Oxide

H_2WO_4 - Tungstic acid

$Na_2S_2O_3 \cdot 5H_2O$ - Sodium thiosulphate pentahydrate

SeO_2 - Selenium dioxide

CdSSe - Cadmium Sulphoselenide

JCPDS - Joint Committee on Powder Diffraction Standards

TEM - Transmission Electron Microscopy

CHAPTER 1

INTRODUCTION

1.1 Research background

Dholakia *et al*. (2003) describe that the semiconducting layered metal dichalcogenides have been classified as new materials that for energy conversion in photochemical (PEC) cells and in solid state (p-n Schotty) solar cells. Through exploratory of nature, transition metal dichalcogenides serve to bring out the potential for photoelectronic devices, in which it has the efficiency to convert sunlight into electricity.

The need to develop the semiconducting layered metal dichalcogenides is to minimize of the production cost and confirm the energy band gap in order to match the solar spectrum as well as due to unique layer lattice structure. The transition metal dichalcogenides are very interesting solids since they display the whole spectrum of electronic properties covering insulators, semiconductors, conductor and superconductor. Transition metal dichalcogenides not only provide the better efficiency but it also minimizes the manufacturing cost.

There are several techniques to produce the thin film such as sputtering, vacuum evaporation, chemical vapour deposition (CVD) and electrodeposition. Rajeshwar (1992) has found electrodeposition is most preferred techniques in the preparation of the film as it is the most economical budget and it is suitable used for substrates of variable size and shape. The analysis of stoichiometry of the transition metal dichalcogenides is found to play an important role by adjusting the parameter such as pH value, deposition time and temperature. Besides, it is also going to study the surface morphology, optical and composition of transition metal dichalcogenides thin film.

1.2 Problem Statement

It is expected that our earth will run out of the oil reserves in future, even though solar energy is free but the application of solar system required large area of surface to capture the sun that will adversely affect the cost and size of solar panel. Besides, most of the other energy technologies, solar energy also limited by cost of conversion and intermittency in time. Furthermore, most of the Photovoltaic (PV) cells, usually required high cost and have low conversion of efficiency. PV cell is quite small, and it required the combination to window-size panels, just can generate the electricity between 60 and 200 W in full sunlight, depending on technology and size. To some extent, solar energy like photovoltaic cells are frequently connected with environmental problems such as toxic substances, but is more or less free from problems that other renewables face. Thin film is one of the renewable energy, which convert the sunlight energy to electrical energy in our daily life. According to Choubey *et al.* (2012), most of the existing material used as the thin film in solar panel such as amorphous silicon, crystalline silicon and polycrystalline silicon has the lower conversion of efficiencies for generating power.

1.3 Objectives

1. To synthesize stoichiometric ternary WSSe thin films by electrochemical route.
2. To analyze the structural characterization of these WSSe thin films for its various deposition parameters.

1.4 Scope

This project will implement the Tungsten Sulphoselenides, WSSe thin film by electrodeposition technique. This experiment will focus on the stoichiometry, optical properties and microstructural characterization of the WSSe thin film. The scale of the thin film ranging from nanometer to micrometer will be carry out by using scanning electron microscopy and X-ray diffractometer. Observation of energy conversion efficiency based on the performance of tungsten film will be implementing.

1.5 Project Outline

This project will divide into five chapters, which include:

1. Introduction
2. Literature review
3. Methodology
4. Result and Discussion
5. Conclusion and Reccomendation

This report will cover on Chapter 1 (Introduction), Chapter 2 (Literature Review), Chapter 3 (Methodology), Chapter 4 (Result and Discussion) and Chapter 5 (Conclusion). In Chapter 1, it will explain about the background of this project, objective of implementation of the project and scope based on project title.

In Chapter 2, the literature review is going to elaborate based on the understanding from the previous research paper such as journals and books. Besides, this chapter will also include the background study for the new research based on previous research.

In Chapter 3, methodology, the experiment will be carrying out to produce the thin film step-by-step. The weight of the aluminium substrates before and after will be recorded in order to calculate the thickness of the thin film. Flow chart of the procedure will implement by the appropriate technique based on the structural characterization of the WSSe thin film.

In Chapter 4, result and discussion will be covered by analyzing the suitable potential from the cyclic voltammogram in order to carry out the electrodeposition process. The crystallographic of the thin film is analyzed by using X-ray Diffractogram (XRD), microstructure analysis is carry out by using Scanning Microscopy (SEM) and the composition analysis is carry out by using Energy Dispersive X-ray Spectroscopy (EDS).

In Chapter 5, the conclusion will be discussed based on the result gained from Chapter 4 and the objective of this project. The recommendation is also discussed for further study in order to enhance the properties of the WSSe thin film.

CHAPTER 2
LITERATURE REVIEW

2.0 Introduction

This chapter focus on semiconductor based thin film preparation and their structural analysis. Structural and morphological studies of the thin film will discuss based on the previous research. Cyclic voltammetry (CV), X-Ray Diffractometry (XRD) Scanning Electron Microscopy (SEM) and Electron Dispersive Spectroscopy (EDS) will be discussed in this chapter. The tungsten sulphoselenides (WSSe) material is chosen as the choice of semiconductor material that will focus in its synthesis and characterization.

2.1 Semiconductor

Semiconductor is defined as a material with resistivity between the ranges of 10^{-2}-10^{9} $\Omega cm.$ It can also defined as a material whose energy gap for electron excitation lies between 1 to 4 electron volts (eV). Semiconductor is material that has intermediate conductivity between a conductor and insulator.

Silicon has become the best-known semiconductor as it purified to very high degree, 99.99999%. The movement of the electrons and the purity of silicon are very closely with the semiconductor behaviour. In contrast, there are also many minerals founded to have semiconductor properties in nature such as zinc-blende (ZnS) cuprite (Cu_2O) and galena (PbS). Owing to the science transformation, semiconductors can be made from vary chemical composition with large variety of crystal structures. Semiconductor growth as three-dimensional bulk crystal or as thin, two-dimensional epitaxial layers on bulk crystals that serve as substrates. (Peter & Manuel, 2010)

2.1.1 Thin Film

Thin film can defined as the layer of the material scale from fraction in nanometer to micrometer. The random nucleation and growth processes can create the thickness of the film by several type of substrate coating such as metallic coating, and dielectric coating depended on a large number of deposition parameters in order to obtain the structural, chemical, metallurgical and physical properties.

There are several thick-film techniques leads into thinning bulk material such as screen-printing, slurry spray, and electrophoresis and plasma gun. Those techniques still left some question to the technologist from the liquid phase technique. The technique involved the impact of the relationship in the final morphology and photovoltaic performance in dealing with the different thin film of the solar cell. (Poortmans & Arkhipov, 2007)

2.1.2 Crystalline based thin film

Heini *et al*. (1998) have used lead chalcogenides (PbS, PbSe, PbTe) in which the materials have narrow band gap of semiconductor grown by various methods such as chemical bath deposition, molecular beam epitaxial, vacuum deposition and electrodeposition. Hence, the electron will excite from valence band to conduction band easily. Thin films were grown at the natural pH of the solution 3.4 and deposited at various potential more than -0.5V. In summary, Heini *et al.* (1998) achieve nearly stoichiometric films with lower lead concentration between potentials of -0.06 and -0.8V, whereas higher lead concentration -0.4 and -0.75V.

Anand *et al.* (2000) described the binary crystalline molybdenum dicalcogenides, $MoSe_2$ thin film have the best solid-state cell and the optical absorption spectra prove the material has an indirect band gap where its photon cannot be emitted because the electron must pass through an intermediate state and transfer momentum to the crystal lattice. The band gap between valence band and conduction band is large. The high optical absorption of $MoSe_2$ located in-group VI in periodic table, which have the ability to absorb visible and near-IR light for photoelectrochemistry solar energy conversion. The study of photoelectrochemical (PEC) with $MoSe_2$ was carried out on single crystal. Molybdenum have an electron configuration $1s^2\ 2s^2p^6\ 3s^2p^6d^{10}\ 4s^2p^6d^5\ 5s^1$. It indicates the molybdenum ion stabilized by its half-filled 4d orbitals as it hybridized with $5s^1$ and $4p^6$ orbitals. It resulted in higher thermal stability as the energy required to break the hybridization is exceed the energy of cathodic discharge of hydrogen. Moreover, Mo atoms have non-bonding d-d orbital atom, which helps to curb the electrolyte corrosion. Besides, the electrodeposition of Mo in the presence of other metal ions is also referred to as induced co-deposition.

Liu *et al.* (2008) have developed the ternary polycrystalline thin film copper indium diselenide ($CuInSe_2$, CIS) by using pulse-plating electrodeposition method. CIS material is a good absorber for thin films cell as it has direct energy band gap in which the momentum of electrons and holes is the same in both the conduction band and the valence band. It permits thin films with the thickness in the range of 1-2 μm and have long-term opto-electronic stability. Besides, CIS material has good homogeneity, high open circuit voltage and low current density. Furthermore, it has the feasibility of the monoclinic integration.

Li *et al.* (2014) described cadmium telluride (CdTe) is one of the most promising thin-film materials which made of many grains of CdTe single crystals. Compared to single crystal, polycrystalline grain boundaries are detrimental. During $CdCl_2$ treatment, Cl takes the place of a large fraction of Te atoms at the grain boundaries and this turns the boundaries into local p-n junctions. CdTe is an excellent material which has the highest theoretical conversion efficiency with the direct band gap 1.5eV and high optical absorption.

2.1.3 Amorphous based thin film

Patil *et al.* (2005) have used molybdenum oxide thin film, which consist of ceramic properties to conduct the structural and optical properties experiment. Mo is an element located at group 6 in periodic tables that the oxygen is categorized as chalcogenides located at group 16 in periodic table. The experiment was done by Auborn and Barberio (1987) who prove that MnO_2 is suitable used as anode for lithium batteries because it has single-phase monoclinic structure. Most of the amorphous thin film required the annealing treatment in order to enhance the surface aesthetic and physical of structural properties.

2.1.4 Research based WSSe thin film material

Dohlakia *et al.* (2003) have studied the crystals grown of tungsten sulphoselenide. Binary WSe_2 and WS_2 have been widely investigated in theirs attractive properties of these materials include the band gap of optical solar energy conversion efficiency, anisotropy in their electric behavior and stability against photoconversion reaction. The conversion energy values up to 17% and 22% for n-WSe_2 photoelectrodes. It found that WSe_2 and WS_2 have a direct energy gap between 1.3-1.5eV. The growth parameters used to synthesize single crystal of WS_xSe_{2-x} is analyzed as shown in the Table 1.1.