



**OPTICAL AND PHOTOELECTROCHEMICAL STUDIES OF
TUNGSTEN DISELENIDE (WSe₂) THIN FILMS FOR
SOLAR PANELS**

This report is submitted in accordance with requirement of the Universiti Teknikal Malaysia
Melaka (UTeM) for the Bachelor Degree of Manufacturing Engineering
(Engineering Materials)(Hons.)

by

IZLIN ANNE KAMELIA BINTI KAMARULBAHRIN

B051310332

941223-10-6510

FACULTY OF MANUFACTURING ENGINEERING

2017

BORANG PENGESAHAN STATUS LAPORAN PROJEK SARJANA MUDA

Tajuk : **OPTICAL AND PHOTOELECTROCHEMICAL PROPERTIES OF TUNGSTEN DISEENIDE (WSe₂) THIN FILMS FOR SOLAR PANELS**

Sesi Pengajian: **2016/2017 Semester 2**

Saya **IZLIN ANNE KAMELIA BINTIKAMARULBAHRIN (941223-10-6510)**

mengaku membenarkan Laporan Projek Sarjana Muda (PSM) ini disimpan di Perpustakaan Universiti Teknikal Malaysia Melaka (UTeM) dengan syarat-syarat kegunaan seperti berikut:

1. Laporan PSM adalah hak milik Universiti Teknikal Malaysia Melaka dan penulis.
2. Perpustakaan Universiti Teknikal Malaysia Melaka dibenarkan membuat salinan untuk tujuan pengajian sahaja dengan izin penulis.
3. Perpustakaan dibenarkan membuat salinan laporan PSM ini sebagai bahan pertukaran antara institusi pengajian tinggi.
4. *Sila tandakan (√)

SULIT (Mengandungi maklumat yang berdarjah keselamatan atau kepentingan Malaysiasebagaimana yang termaktub dalam AKTA RAHSIA RASMI 1972)

TERHAD (Mengandungi maklumat TERHAD yang telah ditentukan oleh organisasi/ badan di mana penyelidikan dijalankan)

TIDAK TERHAD

Disahkan oleh:

Alamat Tetap:
19, Persiaran Wangsa Baiduri 7,
47500 Subang Jaya,
Selangor, Malaysia

Cop Rasmi:

Tarikh: _____

Tarikh: _____



Universiti Teknikal Malaysia Melaka
Hang Tuah Jaya,
76100 Durian Tunggal,
Melaka, Malaysia.

Tel : +606 555 2000
Faks : +606 331 6247
www.utm.edu.my

FAKULTI KEJURUTERAAN PEMBUATAN

Tel : +606 331 6429/6019 | Faks : +606 331 6431/6411

Ruj. Kami (Our Ref.) :
Ruj. Tuan (Your Ref.) :

10 Jun 2017

Ketua Pustakawan
Perpustakaan UTeM Kampus Induk
Univerisiti Teknikal Malaysia Melaka
Hang Tuah Jaya, 76100 Durian Tunggal
Melaka.

Tuan/Puan,

PENKELASAN LAPORAN PSM SEBAGAI TERHAD LAPORAN PROJEK SARJANA MUDA KEJURUTERAAN PEMBUATAN (BAHAN KEJURUTERAAN): IZLIN ANNE KAMELIA BINTI KAMARULBAHRIN

Sukacita dimaklumkan bahawa Laporan PSM yang tersebut di atas berjudul “*Optical and Photoelectrochemical Studies of Tungsten Diselenide (WSe₂) Thin Films for Solar Panels*” mohon dikelaskan sebagai TERHAD untuk LIMA tahun dari tarikh surat ini.

2. Hal ini adalah kerana ia mengandungi hasil data yang diklasifikasikan sebagai sulit. Oleh itu, pengguna yang ingin menggunakan data di dalam laporan ini hendaklah merujuk kembali kepada laporan yang berkaitan.

Sekian dimaklumkan. Terima kasih.

Yang benar,

Prof. Madya Dr T. Joseph Sahaya Anand
Profesor Madya,
Fakulti Kejuruteraan Pembuatan,
Universiti Teknikal Malaysia Melaka.

KOMPETENSI TERAS KEGEMILANGAN



DECLARATION

I declare that this thesis entitled “Optical and Photoelectrochemical Studies of Tungsten Diselenide (WSe₂) Thin Films for Solar Panels” is the result of my own research except as cited in the references.

Signature :

Name : IZLIN ANNE KAMELIA BINTI KAMARULBAHRIN

Date : 6 June 2017

APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of Universiti Teknikal Malaysia Melaka as a partial fulfillment of the requirements for the degree of Bachelor of Manufacturing Engineering (Engineering Materials) (Hons.).

The members of the supervisory committee are as follow:

.....
(PM Dr. T. Joseph Sahaya Anand)

.....
(PM Dr. Zulkifli bin Mohd Rosli)

ABSTRAK

Tungsten Diselenide (WSe_2) adalah salah satu sebatian logam peralihan dichalcogenide (MX_2 , di mana $\text{M} = \text{Mo}, \text{W}, \text{Sn}, \text{Ni}, \text{Cd}, \text{Zn}$ dan $\text{X} = \text{Se}, \text{S}, \text{Te}$) yang mempunyai potensi untuk digunakan bagi tujuan sel solar. Filem nipis telah berkembang dengan elektroenapan dengan parameter yang berbeza semasa pemendapan (10-30 minit dengan selang 5 minit) dan potensi pemendapan (-1.384 V dan -1.372 V) yang telah diambil dari kitaran voltammetri. Ketebalan filem nipis telah dikira dengan kaedah perbezaan berat gravimetrik dimana peningkatan pada masa pemendapan adalah berkadar terus dengan ketebalan filem itu. Kajian struktur telah mendedahkan struktur heksagon ($a = b = 0.3297 \text{ nm}$ dan $c = 1.2982 \text{ nm}$). Kajian permukaan morfologi melalui Mikroskop Imbasan Elektron (SEM) menunjukkan permukaan tidak rata dan berlubang pada filem nipis yang telah dideposit. Filem yang telah disintesis pada 25 minit menunjukkan filem nipis yang paling rata dan seragam di atas substrat kaca. Penyepuhlindapan dilakukan pada 1 jam pada 300°C telah dilakukan pada filem nipis untuk mendedahkan butiran lebih terperinci yang mendedahkan ciri-ciri filem nipis dengan lebih lanjut. Kajian optik telah dijalankan menggunakan UV-Visible Spektrofotometer dan menghasilkan filem nipis yang memberikan nilai jurang paling optimum pada 1.25eV untuk filem nipis yang telah dimasukkan pada tempoh 30 minit. Plot Mott-Schottky mendedahkan semikonduktor jenis p dengan parameter semikonduktor lain.

ABSTRACT

Tungsten Diselenide (WSe_2) is a metal dichalcogenide compound (MX_2 , where $\text{M} = \text{Mo}, \text{W}, \text{Sn}, \text{Ni}, \text{Cd}, \text{Zn}$ and $\text{X} = \text{Se}, \text{S}, \text{Te}$) that has the potential to be used for solar cell purposes. The thin film had been grown via electrodeposition with the varying parameters of deposition time (10, 15, 20, 25, 30 minutes) and deposition potential (-1.384 V and -1.372 V). Thickness of the thin film had been calculated by the Gravimetric Weight Difference Method where an increase in deposition time is directly proportional to the thickness of the the film. The surface morphology studies via Scanning Electron Microscope (SEM) revealed irregular and pinholes on the thin film deposited. The film that had been deposited at 25 minutes show the smoothest and uniform thin film deposited on the glass substrate. Annealing at 1 hour at 300°C had been done to the thin film to reveal more prominent grains which revealed further thin film characteristics. Structural studies have revealed a hexagonal structure ($a = b = 0.3297 \text{ nm}$ and $c = 1.2982 \text{ nm}$). The optical studies had been conducted using a UV-Visible Spectrophotometer and produced a thin film with the lowest bandgap value of 1.25eV for the thin film that had been deposited at 30 minutes. Mott-Schottky plots revealed a p-type semiconductor.

DEDICATION

For those who wish to save Mother Nature to make a better future.

ACKNOWLEDGEMENT

I would like to express my upmost gratitude to Associate Professor Dr. T. Joseph Sahaya Anand for his continuous support, guidance and patience while I conducted my study. I cannot imagine having a better supervisor and mentor for my study. My sincerest thank you to Associate Professor Dr. Zulkifli bin Mohd Rosli, my co-supervisor for my study, for his guidance, advices, and motivation.

I would also like to take this opportunity to thank Shariza Sharir for guiding me. Without her guidance and patience, I would have a much harder time in conducting, and finishing my study. Also not forgetting, En. Bahatiar bin Zaid and En. Azhar Shah for helping me with handling the technical equipments while carrying out my study. To Ling Hung Kit who helped me out while I was stuck in a pinch. Your friendship in the lab will not be forgotten.

Last but not least, I would like to express my gratitude to my family and friends. To my parents, for their continuous support and motivation for me to finish my study, and especially those of the Engineering Materials, Graduating Class of 2017 for their continuous motivation.

TABLE OF CONTENT

| | |
|--|------|
| Abstrak | i |
| Abstract | ii |
| Dedication | iii |
| Acknowledgement | iv |
| Table of Content | v |
| List of Tables | viii |
| List of Figures | ix |
| List of Abbreviations, Symbols and Nomenclatures | xi |

CHAPTER 1: INTRODUCTION

| | | |
|-----|---------------------------|---|
| 1.1 | Background Studies | 1 |
| 1.2 | Problem Statement | 3 |
| 1.3 | Objectives of the Project | 4 |
| 1.4 | Scopes and Limitations | 4 |
| 1.5 | Project Layout | 5 |

CHAPTER 2: LITERATURE REVIEW

| | | |
|-----|---|---|
| 2.1 | Thin Film | 6 |
| 2.2 | Synthesis of Thin Films via Electrodeposition | 7 |

| | | |
|-----|--|----|
| 2.3 | Cyclic Voltammetry | 10 |
| 2.4 | Studies using X-Ray Diffraction (XRD) | 12 |
| 2.5 | Scanning Electron Microscope (SEM) | 15 |
| 2.6 | Optical Characterisation using UV-Visible Spectrophotometer | 18 |
| 2.7 | Photoelectrochemical Cell (PEC) Studies via Mott-Schottky Plot | 22 |
| 2.8 | Summary | 23 |

CHAPTER 3: METHODOLOGY

| | | |
|-----|--|----|
| 3.1 | Introduction | 25 |
| 3.2 | ITO Coated Glass Substrate and Electrolyte Preparation | 28 |
| 3.3 | Cyclic Voltammetry (CV) and Electrodeposition Experiments | 29 |
| 3.4 | Thin Film Thickness Measurement | 29 |
| 3.5 | Structural Studies via X-Ray Diffraction | 30 |
| 3.6 | Surface Morphological Studies via Scanning Electron Microscope (SEM) | 31 |
| 3.7 | Optical Studies via UV-Visible Spectrophotometer | 31 |
| 3.8 | Semiconducting Parameters by Mott-Schottky Plot | 32 |
| 3.9 | Expected Results | 33 |

CHAPTER 4: RESULT AND DISCUSSION

| | | |
|-------|--|----|
| 4.1 | Cyclic Voltammetry and Electrodeposition of WSe ₂ | 34 |
| 4.2 | Characterisation of Thin Films | 35 |
| 4.2.1 | Thin film measurement | 36 |
| 4.2.2 | Structural Studies | 37 |
| 4.2.3 | Surface Morphological Studies via SEM | 40 |
| 4.2.4 | Optical Absorption Studies | 44 |
| 4.2.5 | Semiconducting Parameters by Mott-Schottky Plot | 47 |

CHAPTER 5: CONCLUSION AND RECOMMENDATION

| | | |
|-----|------------------------------------|----|
| 5.1 | Conclusions | 53 |
| 5.2 | Recommendation for Further Studies | 54 |
| 5.3 | Sustainability Elements | 54 |

| | |
|-------------------|----|
| REFERENCES | 56 |
|-------------------|----|

| | |
|-------------------|----|
| APPENDICES | 60 |
|-------------------|----|

LIST OF TABLES

| | | |
|-----|--|----|
| 2.1 | Optical bandgaps for ZnO samples calcined at different temperatures | 20 |
| 3.1 | Measurements needed for preparation of H ₂ WO ₄ + SeO ₂ electrolytic solution | 28 |
| 4.1 | Weight (prior and after deposition) and total area calculated of the WSe ₂ thin film | 36 |
| 4.2 | Thickness of WSe ₂ thin films calculated | 37 |
| 4.3 | Comparison of experimental 'd' values with the JCPDS data for WSe ₂ thin films deposited at different times | 40 |
| 4.4 | Bandgap obtained from the WSe ₂ thin films | 44 |
| 4.5 | Capacitance reading of WSe ₂ thin films using LCR meter | 47 |
| 4.6 | Semiconducting parameters of WSe ₂ thin films with different deposition durations | 52 |

LIST OF FIGURES

| | | |
|------|---|----|
| 2.1 | A schematic diagram of a simple electrolytic cell | 7 |
| 2.2 | Visual of a basic cyclic voltammetry graph | 10 |
| 2.3 | Visual of flux with different scan rates showing CV Characteristics | 11 |
| 2.4 | Cyclic voltammograms in aqueous bath (a) 0rpm (b) 100rpm (c) 200rpm | 12 |
| 2.5 | XRD pattern of WSe ₂ thin films at optimized condition for: (a) as deposited (b) annealed with 300° for 1 hr | 13 |
| 2.6 | XRD diffractogram for MoSe ₂ | 14 |
| 2.7 | Diagram of SEM column and specimen chamber | 16 |
| 2.8 | SEM photograph of MoSe ₂ thin film | 17 |
| 2.9 | Various types of crystallite present on differently aged CdZnO thin films | 18 |
| 2.10 | UV-Vis absorption spectra of ZnO at different temperatures (a) 300°C (b) 500°C (c) 700°C (d) 900°C | 19 |
| 2.11 | Optical bandgap energy of Cu ₂ ZnSnS ₄ films deposited at different pulses | 20 |
| 2.12 | Optical bandgap energy of MoS ₂ , MoSe ₂ and MoTe ₂ thin films | 21 |
| 2.13 | I-V characteristics of tungsten diselenide photoelectrode | 23 |
| 3.1 | Process flow for project | 27 |
| 4.1 | Cyclic Voltammogram of WSe ₂ | 35 |
| 4.2 | XRD Graphs for 15, 20, 25, 30 (-1.384 V) and 30 (-1.372 V) minutes | 38 |

| | | |
|-----|---|----|
| 4.3 | WSe ₂ thin films as observed under Scanning Electron Microscope (SEM) | 41 |
| 4.4 | 30 minute (-1.384 V) films at (a) 1000× (b) 3000× (c) 5000× (d) 5000× magnification | 43 |
| 4.5 | Plots of $(ah\nu)^2$ with respect to photon energy, E_g for WSe ₂ thin films with different deposition times | 45 |
| 4.6 | Bandgaps of WSe ₂ thin films deposited at -1.384V with different deposition times | 46 |
| 4.7 | Mott-Schottky Plots for WSe ₂ thin films with different deposition times | 49 |

LIST OF ABBREVIATION, SYMBOLS AND NOMENCLATURES

| | | |
|------------------------------------|---|---|
| Å | - | Angstrom |
| A | - | Optical absorption, angle between solar ray and vertical line |
| Ag | - | Silver |
| AgCl | - | Silver Chloride |
| a.u. | - | arbitrary unit |
| BCC | - | Body Centered Cubic |
| °C | - | Celcius |
| Cd | - | Cadmium |
| cm | - | Centimeter |
| Cu ₂ S | - | Copper Sleenide |
| CuK α | - | Copper K-alpha |
| Cu _x Se _y | - | Copper Selenide |
| CdZnO | - | Cadmium Zinc Oxide |
| Cu ₂ ZnSnS ₄ | - | Copper Tin Zinc Sulfide |
| CZTS | - | Copper Zinc Tin Sulfide |
| CV | - | Cyclic Voltammetry |

| | | |
|---------------|---|---|
| DC | - | Direct Current |
| D_p | - | Crystallite size |
| g | - | Gram |
| K | - | Kelvin |
| EDS | - | Energy Dispersive Spectroscopy |
| EDX | - | Energy Dispersive X-Ray Spectroscopy |
| E_g | - | Band gap energy |
| E_{pa} | - | Anodic Peak Potential |
| E_{pc} | - | Cathodic Peak Potential |
| eV | - | Electron volt |
| FCC | - | Face Centered Cubic |
| HCP | - | Hexagonal Closed Pack |
| keV | - | Kilo Electron Volt |
| h | - | Planck's constant ($6.62607004 \times 10^{-34} \text{ m}^2 \text{ kg / s}$) |
| HCl | - | Hydrogen Chloride |
| IL | - | Ionic Liquid |
| I_{pa} | - | Anodic Peak Current |
| I_{pc} | - | Cathodic Peak Current |
| ITO | - | Indium Tin Oxide |
| kT/e_0 | - | Temperature dependant correction term |
| MX_2 | - | Metal Dichalcogenide |

| | | |
|------------------|---|------------------------------|
| mA | - | Miliampere |
| μA | - | Microampere |
| Mo | - | Molybdenum |
| MoSe_2 | - | Molybdenum Selenide |
| MoX_2 | - | Molybdenum Chalcogenide |
| mm | - | Milimeter |
| mV | - | Milivolt |
| NaOH | - | Sodium Hydroxide |
| N_D | - | Dopant density |
| Ni | - | Nickel |
| nm | - | Nanometer |
| PEC | - | Photoelectrochemical cell |
| pH | - | Potential of Hydrogen |
| rpm | - | Rotation pre minute |
| S | - | Sulfur |
| Se | - | Selenium |
| Se^{2-} | - | Selenide |
| SeO_2 | - | Selenium Dioxide |
| SEM | - | Scanning Electron Microscope |
| Sn | - | Tin |
| t | - | Film thickness |

| | | |
|--------------|---|---|
| T | - | Transmittance |
| TCO | - | Transparent Conductive Oxide |
| Te | - | Telurium |
| TMC | - | Transition Metal Chalcogenide |
| UV-Vis | - | Ultraviolet Visible |
| ν | - | Frequency of light in hz |
| V | - | Electrical potential |
| V | - | Electrode applied potential |
| V_{FB} | - | Flat band potential |
| W | - | Tungsten |
| W^+ | - | Tungsten ion |
| WO_3 | - | Tungsten Trioxide |
| WSe_2 | - | Tungsten Diselenide |
| XRD | - | X-Ray Diffraction |
| Zn | - | Zinc |
| ZnO | - | Zinc Oxide |
| ZnSe | - | Zinc Selenide |
| α | - | Absorption coefficient in cm^{-1} |
| ϵ | - | Dielectric constant of electrode material |
| ϵ_0 | - | Permittivity of vacuum |
| Θ | - | Angle of diffraction |

- λ - Wavelength
- β - Full width half maximum
- $\beta_{1/2}$ - Broadening diffraction line measured at half of its maximum intensity

CHAPTER 1

INTRODUCTION

This chapter is for the introduction of the final year project that covers the research background as well as the motivation, problem statement of the project. The problem statement has been stated in detail. In this chapter, the project scope is determined and outline has been progressed.

1.1 Background Studies

With the continuous growing population globally, there is always an increase in demand for energy. Although fossil fuels are now used to fulfill 86% of these needs, there is a need to find more alternate resources since non-renewable energy such as using petroleum or natural gases will eventually exhaust (Mediavilla *et. al.*, 2008). A steady growth in energy demand would probably result in a necessity for 55% more energy by 2030 (Mediavilla *et. al.*, 2008).

Semiconductors have been highly considered for its direct light energy to electrical energy conversion, with some studies showing semiconductors with indirect bandgaps

reaching up to 1.42eV (Delphine *et. al.*, 2003). Studies have also been conducted on various metal-oxides as a favourable alternative material to be used in solar energy conversion due to its photoelectrochemical abilities. It is based on the water decomposition reaction by using semiconductor photoelectrodes, with a direct solar energy to chemical with high caloric fuel conversion as a result (Aroutiounian *et. al.*, 2005).

There are two types of films; thick and thin. They both are categorized with their thickness with thin films being defined as an extremely thin layer of substance measuring up from a fraction of a nanometer to a maximum of 1 micron thick (provided it does not have a substrate). Anything thicker than 1 micron is considered a thick film but anything thicker than 5 micron is known as a foil. Thin film characteristics might differ from its bulk characteristics. As an example, in a bulk an iron substance might possess higher strength than that of aluminium in every layer; but in thin films, the aluminium substance would be far stronger due to its crystallographic nature. Nanoparticles are highly dependent on the atomic nature of a material itself. Films require a base material or substrate but foils do not.

High quality thin films can be synthesized using various methods including chemical vapour deposition, pulsed laser, evaporation, molecular beam epitaxy, and sputtering. An alternative method using electrodeposition can also produce similar quality thin films and is the chosen technique to synthesis for this research. Electrodeposition is preferred due to its low cost and simplicity. It can be carried out in ambient atmosphere without requiring a vacuum system (Dharmadasa *et. al.*, 2006).

Electrochemical deposition (electrodeposition) is the process of flowing current from an external source through an electrochemical cell. The experiment usually consists of the working electrode which is used in conjunction with a counter electrode and a reference electrode. All of the electrodes will then be immersed in an electrolyte. A DC power (usually within the milliwatt range of ~2.0V and ~1.0mA) is applied across the anode and cathode at which the cathode will attract the positive ions, discharged and will chemically react to form Tungsten Diselenide (Dharmadasa *et. al.*, 2005).

Cyclic Voltammetry is the method of acquiring the potential range about electrochemical reactions (Andrienko, 2008). It is done by measuring the cycling potential of a

working electrode and its resulting current that develops in the electrochemical cell under conditions at which the voltage is in excess and is predicted by the Nernst equation.

1.2 Problem Statement

Since the need to engineer renewable energy source increases, one must consider the materials used to make the solar panels. The existing solar panels used globally typically use pure silicon for their semiconducting wafers since it is the most available resource as it is made of silicon dioxide more known as sand. Even though it is abundant, the process needed to create the pure wafer silicon form is quite expensive, thus we have come up with another resource to possibly lower the cost for producing the wafers.

Next, silicon as an intrinsic semiconductor is highly dependent on its existing conducting properties to be able to generate electricity; hence we have tried out a possibly more resourceful way to combine transition metal dichalcogenide compounds (MX_2 , where $M = Mo, W, Sn, Ni, Cd, Zn$ and $X = Se, S, Te$) as to not exhaust a single resource too fast. Silicon also has a low conversion efficiency of 12~14% while an ideal efficiency would be around 1~2% which would have an efficiency of a conductive material.

A compound consisting of tungsten and selenium is chosen as the material to be studied for the synthesis of solar cell panels as theoretically, it will be better in comparison to silicon as well as the combination of other transition metals. This is also supported in some of the previous studies which will be stated in the literature review. Further support for the study of Tungsten Diselenide will be explained further in this report.

1.3 Objectives of the Project

The objective for conducting this research study based on WSe₂ thin films is as follows;

- a) To synthesis stoichiometric Tungsten Diselenide (WSe₂) binary thin films by electrochemical route
- b) To analyse the deposition parameters and structural studies of Tungsten Diselenide (WSe₂) by X-Ray Diffraction and Scanning Electron Microscopy
- c) To study the optical and photoelectrochemical properties of binary WSe₂ thin films due to the effect of variable deposition times and deposition potential

1.4 Scopes and Limitations

The WSe₂ thin films will be synthesized using electrochemical deposition method at ambient atmosphere. The electrolyte that will be used for development of the thin films will be composed of Tungsten Trioxide (WSO₃) and Selenium Dioxide (SeO₂) as well as distilled water and Sodium Hydroxide in order to encourage more Se²⁻ development. Thickness of the formed thin films is to be measured using the gravimetric weight difference method at which the thin film samples are broadly cleaned for removal of interfering substance. Morphological and compositional analysis of the WSe₂ will be done via optical microscope, Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray Spectroscopy (EDX). Optical studies of the WSe₂ will be done via UV-Visible Spectrophotometer and semiconducting parameters is investigated using the Mott-Schottky Plot.