OPTICAL AND PHOTOELECTROCHEMICAL STUDIES OF TUNGSTEN DISULFIDE (WS_2) THIN FILMS FOR SOLAR PANEL

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

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DECLARATION

I hereby, declared this report entitled “Optical and Photoelectrochemical studies of Tungsten Disulfide WS_2 Thin Films for Solar Panels” is the result of my own research except as cited in reference.

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APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of Universiti Teknikal Malaysia Melaka as a partial fulfillment of the requirement for the degree of Bachelor of Manufacturing Engineering (Engineering Material) (Hons.). The members of the supervisory committee are as follow:

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ABSTRAK

Polihabluran Tungsten disulfida (WS_2) filem nipis disimpan di atas Indium Tin Oxide (ITO) bersalut substrat kaca telah disediakan dengan kaedah elektroenapan. Masa pemendapan ditetapkan antara 10 hingga 30 minit dengan setiap selang 5 minit. Potensi optimum untuk pemendapan nipis WS_2 ditentukan dengan teknik voltmmetry kitaran dan tebalnya diukur dengan menggunakan kaedah berat badan. Filem nipis WS_2 dengan ketebalan 1.23 mikron berjaya disimpan atas substrat kaca bersalut ITO pada potensi optimum, -0.40V pada 30 minit masa pemendapan. Kemudian, analisis struktur dengan menggunakan X-ray pembelauan (XRD) mendedahkan bahawa polihabluran filem meningkat dengan peningkatan keamatan puncak untuk filem tebal dan analisis permukaan morfologi dengan pengimbas mikroskop elektron (SEM) telah menunjukkan pertumbuhan filem yang seragam dan juga pengabungan yang baik antara WS_2 filem nipis dengan substract kaca bersalut ITO. Walau bagaimanapun, jurang jalur tenaga optik filem nipis WS_2 menunjukkan 1.60 eV pada 10 minit masa pemendapan dan menurun kepada 1.30 eV apabila masa pemendapan meningkat kepada 30 minit. WS_2 filem nipis adalah bahan semikonduktor jenis-p seperti yang ditentukan oleh Mott-Schottky plot berdasarkan semikonduktor analisis parameter. Nilai lebar pengurangan filem nipis WS_2 yang berkurangan menunjukkan perjanjian yang baik dengan nilai jurang jalur tenaga yang diperoleh daripada kajian optik sebagai kenaikan masa pemendapan. Semua nilai parameter semiconducting filem nipis WS_2 menunjukkan persamaaan dengan nilai-nilai parameter bahan semikonduktor TMDS yang lain dan ini membuktikan bahawa filem nipis WS_2 sesuai digunakan sebagai bahan untuk aplikasi sel solar.

ABSTRACT

Polycrystalline Tungsten Disulphide (WS_2) thin films deposited on Indium Tin Oxide (ITO) coated glass substrate were prepared by electrodeposition method. Deposition times were set between 10 to 30 minutes with every 5 minutes interval. Optimum potential for WS_2 thin deposition was determined by cyclic voltmmetry technique and its thickness was measured by using weight gain method. WS_2 thin films were well adherent with the ITO coated glass substrate at optimum potential -0.40V with 1.23 μm at 30 minutes deposition time. Then, structural analysis by using X-ray diffraction (XRD) reveals that the films are polycrystalline with the increasing of peak intensity for thicker films and surface morphology analysis by scanning electron microscope (SEM) which shows uniform growth and well adhere of WS_2 thin films with glass substrate for thicker films. However, the optical energy band gap of the WS_2 thin films was measured as 1.60 eV at 10 deposition time and decreased to 1.30 eV as deposition time increased to 30 minutes. WS_2 thin films was p-type semiconductor material as determined by Mott-Schottky plot based on semiconducting parameter analysis. The values of depletion width of WS_2 thin films that decrease from shows good agreement with the energy band gap values obtained from optical studies as deposition time increases. All the semiconducting parameter values of WS_2 thin films falls in the range as other transition metal dichalcogenides (TMDs) material's semiconducting parameter values and this proved that WS_2 thin films are capable as material for solar cell application.

DEDICATION

To my beloved father, Ling Nai Seng

my appreciated mother, Chieng Liong Kii

my adored sister Ling Hung Zin, Ling Hung Lin and Ling Hung Yee

my little brother Ling Hung Khin

for giving me moral support, money, cooperation, encouragement and understandings

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LIST OF ABBREVIATIONS

Ag	-	Silver
AgCl	-	Silver Chloride
$AgNO_3$	-	Silver Nitrate
a-silicon	-	Amorphous silicon
$CdCl_2$	-	Cadmium Dichloride
CdS	-	Cadmium sulfide
CdSe	-	Cadmium selenide
CdTe	-	Cadmium Telluride
CIGS	-	Copper Indium Gallium Selenides
Cl	-	Chlorine
CV	-	Cyclic voltammetric
CVD	-	Chemical Vapor Deposition
DBTT	-	Ductile to brittle temperature profile
EB-PVD	-	Electron Beam Physical Vapor Depostition
EDS	-	Energy Dispersive Spectroscopy
H_2MnO_4	-	Ammoniacal Molybdenum Sulphide
H_2WO_4	-	Tungstic Acid
HCl	-	Hydrochloric acid
Hg	-	Mercury
ITO	-	Indium Tin Oxide
JCPDS	-	Joint Committee on Powder Diffraction Standards
MBE	-	Molecular Beam Epitaxy
MnO_2	-	Molybdenum dioxide
MoS_2	-	Molybdenum Dilsulfide
$MoSe_2$	-	Molybdenum Diselenides

MoSSe	-	Molybdenum sulfide selenide
$Na_2S_2O_3$	-	Sodium thiosulphate pentahydrate
NbS_2	-	Niobium Disulfide
NiS_2	-	Nickel Disulfide
PbS_2	-	Lead Disulfide
PEC	-	Photoelctrochememical cell
PL	-	Photoluminescence
PV	-	Photovoltaic
PVD	-	Physical Vapor Deposition
QSC	-	Quantum size effect
RF	-	Radio Frequency
S	-	Sulphur
SCE	-	Saturated Calomel electrode
Se	-	Selenide
SEM	-	Scanning Electron Microscope
Te	-	Telluride
TEA	-	Triethylamine
TMDs	-	Transition Metal Dichalcogenides
UV/Vis/NIR	-	Ultraviolet-Visible-Near Infrared
VSe_2	-	Vanadium Diselenides
WS_2	-	Tungsten Disulfide
WSe_2	-	Tungsten Diselenides
WSSe	-	Tungsten sulfide selenide
XRD	-	X-ray diffraction
ZnCdS	-	Zinc Cadmium Sulfide
ZnTe	-	Zinc Telluride

LIST OF SYMBOLS

%	-	Percentage
η_{max}	-	Maximum coefficient
Å	-	Angstrom
A	-	Contact area (2.25 x 10^{-6} m^2)
C	-	Capacitance
c	-	Speed of light 3 x 10^8 m/s
cm	-	Centimeter
cm^2	-	Centimeter square
cm^3	-	Centimeter cube
cos	-	cosine
C_{SC}^2	-	Space charge capacitance
d	-	Thickness of the crystal
D_{XRD}	-	Crystalline size (nm)
e	-	Dielectric constant
E	-	Photon energy
E_c	-	Conduction band edge
E_g	-	Energy gap
e_o	-	Dielectric constant of free space (8.854 x 10^{12} F/m)
eV	-	Electron volt
E_v	-	Valence band edge
g	-	Gram
h	-	Plank constant 6.63 x 10^{-34} J/S
k_B	-	Boltzmann's constant (1.38 x 10^{23} J/K)
keV	-	Kilo electron volt
m	-	Meter

M	-	Molarity
m^2	-	Meter square
ml	-	Milliliter
mm	-	Millimeter
N	-	Charge carrier concentration
n	-	Transition probability, n= 0.5, 1.5, 2 and 3
N_C	-	Conduction band
N_D	-	Doping density
nm	-	Nanometer
^{o}	-	Degree
^oC	-	Degree Celsius
T	-	Temperature
V	-	Volt
V_b	-	Band bending
V_{FB}	-	Flat band potential
W	-	Depletion layer width
β	-	Broadening of diffraction line measured at half of its maximum intensity
θ	-	Angle of diffraction
λ	-	Wavelength
μm	-	Micrometer
α	-	Absorption Coefficient

CHAPTER 1

INTRODUCTION

1.1 Background Study

Nowadays, we greatly depend on natural gas and fossil fuel as our main energy resources for transportation and industrial purpose but these natural resources are non-renewable and will be used up in next tenths year. The significant of growing dependence on fossil fuels has contributed to several environment issues such as green house effect and global warming (Mane *et al.*, 2014). Utilization of renewable solar energy has become major intention as the continuously increasing the fossil fuel consumption (Meng *et al.*, 2016). In recent years, application of thin film solar cell or photoelectrochemical (PEC) cell has become a great intention in solar cell research due to rapid development in term of both efficiency cost deviation and improvement (Hao *et al.*, 2015). Renewable solar energy is the alternative energy that is reproducible, eco-friendly and will not bring any harm to the environment.

There is several research studies have been carrying out to determine thin film material for solar cell application. The best semiconducting materials for direct conversion of light to electrical energy application are the material with a narrow band gap provides the value 1-2 eV in bulk or thin film form. Films come in 2 types which is thick film and thin film in term of different thickness. Thin films are those thin layers of deposited material on the substance with thickness from tenth of nanometer (nm) to 1 micrometer (μm) which differ in bulk characteristic. For example, aluminium thin film in bulk with have 5 times stronger strength than iron substance due to its nature of crystallography which comes from layer by layer. Thick film are normally material for weld base which has thickness of 1-5μm while thickness of foil are more than 5μm and its does not depend on any support such as substrate or base material if compared to thin film. Hence, there are relative growing interest in layered semiconducting materials consisting of group 16 transition metal dichalcogenides MX_2 (M=Mo, W and X= S, Se and Te) (Anand *et al.*, 2013). Transition metal dichalcogenides (TMDs) compounds especially in thin film condition are identified as suggested material in the photovoltaic industry for the development of solar cell panels and photoelectrochemical (PEC) due to its optical and semiconducting material.

There are many techniques for thin films such as Physical Vapor Deposition (PVD) and Chemical Vapor Deposition (CVD). Electrodeposition method is chosen for this research which is one of the CVD methods and it has increasingly applied to thin film synthesis nowadays. Electrodeposition provides simple and large scale deposition, film thickness controlling, arbitrary substrate shapes, composition and band gap width, and relatively low cost technique that provide good quality of the film deposited (Shariza and Anand, 2011). Other method preparations such as sputtering, molecular beam epitaxy (MBE), chemical bath deposition, sulphurization and electrolytic reduction are costly and may cause some special problems for the TMDs preparation.

Cyclic voltammetric (CV) analysis will be done by using electrochemical analyzer to fix the deposition potential. The voltammograms will be collected at different aqueous alkaline solution in various rate of sweep. A conventional three electrode system is then employed (Alghamdi, 2016). Hence, CV analysis was implemented to find the suitable region for potential growth for the electrochemical reaction to growth the thin films as it deposited on the glass substrate.

There are also a lot of techniques that had been developed to analyze the microstructure and properties of material. Ultraviolet-Visible-Near Infrared spectrophotometer (UV/Vis/NIR spectrophotometer) are used to measure optical properties and optical absorption spectra effectiveness of thin films while Mott-Schottky plots are applied to measure the semiconducting parameters such as doping density (N_D), depletion layer width(W), band bending (V_b) and flat band potential (V_{FB}) of thin films. Then, Scanning Electron Microscope (SEM) is carried out to observe the surface morphology properties of thin film whereas Energy Dispersive Spectroscopy (EDS) is used to analyze the composition of thin films. X-ray Diffraction (XRD) is used to reveal the structure properties of thin films.

1.2 Problem Statement

Fossil fuels are the most common world's non-renewable resources for us but consumption of this kind of energy will cause pollution such as green house effect and global warming. These valuable and non-renewable resources of the earth will be used up in next tenths year. Hence, the research of renewable, clean and economical energy source has been carried out to overcome this problem and energy with low price is more preferred. Solar energy is one of the renewable energies that can replace fossil fuels consumption which is safe, reproducible and eco-friendly energy sources. Besides that, thin film solar cells as energy conversion device have become the most interesting field in solar cell research and development recently. Solar cells able absorb light spectrum in the form of photons and convert into electrical energy.

Silicon is the well known material for solar cells due to its good stability, well-balanced set of the electron, physical and chemical propertie (Hao *et al.*, 2015). Although silicon is a common considered material but it still was an expensive material in pure silicon wafer which may involve complicated alignment and design during the manufacturing process. Conversion efficiency of silicon material is poor which only 12-14 percentage while small area (1cm^2) of silicon based thin films for solar panels has conversion efficiency up to 20% in order to compete with other photovoltaic (PV) technology (Isabella *et al*, 2014). However, the research of alternative material with low cost, ease of fabrication, excellent visible light absorption, and good semiconducting parameter is investigated to replace the utilization of silicon material for solar cells.

Recently, transition metal dichalcogenides (TMDS) thin films such Cadmium Selenide (CdSe) and Zinc Telluride (ZnTe) has been identified as material for solar cell and solar panel application. TMDs thin films have good optical and semiconducting properties which can be applied as efficient photovoltaic (PV) material. TMDs thin film can be prepared by low costing and relatively simple electro-deposition technique, ones of the chemical vapor deposition methods (CVD).

In this research, transition metal dichalcogenides (TMDS) material, tungsten disulfide (WS_2) thin film will be prepared by simple and low cost electrodeposition method to replace existed silicon thin film for solar cell application.

1.3 Objective

There are several objectives to be achieved for this project, such as:

1) To synthesis stoichiometric binary Tungsten Disulfide (WS_2) Thin Film by using electrodeposition method
2) To analyze the structural characterization such as crystallography structure of Tungsten Disulfide WS_2 thin film by using X-ray diffraction(XRD) and morphological properties by using scanning electron microscope(SEM)
3) To determine the optical properties of the Tungsten Disulfide WS_2 Thin Film using UV/Vis/NIR spectrophotometer
4) To analyze the semiconductor parameters of Tungsten Disulfide WS_2 thin film using Mott-Schottky plot

1.4 Scope

This project will synthesis Tungsten Disulfide WS_2 thin film by using electrodeposition method and focus the properties studies of WS_2 thin film for the application in photoelectrochemical (PEC) solar cells. This experiment will focus on the stoichiometry, optical and photoelectrochemical study, structural analysis, morphological analysis and composition analysis of Tungsten Disulfide WS_2 thin film

It will start with cyclic voltammetry (CV) to obtain the range of deposition potentials where as the film grow. After that, analyze the optical properties of Tungsten Disulfide WS_2 thin film by using UV/vis/NIR spectrophotometer and semiconductor parameter by using Mott-Schottky plot. Then, the structural properties of the WS_2 thin film will be determined by X-ray Diffraction (XRD) technique while the morphological properties are determined by using Scanning Electron Microscope (SEM) and lastly the composition analysis is carried out by using Energy Dispersive X-ray Spectroscope (EDS).

In conclude, the main intention of this research is to determine the optical and photoelectrochemical studies of Tungsten Disulfide WS_2 thin films for solar panels application.