

FABRICATION OF  $\text{Cu}_2\text{O}$  BASED HOMOSTRUCTURE THIN FILMS USING  
ELECTRODEPOSITION METHOD

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## DEDICATION

*Every challenging work need self-efforts as well as guidance of elders especially those who very close to our hearts. My humble effort I dedicate to my dearest husband, Muhammad Sallehudin Bin Khalid, my beloved mother and father, Rahamah Binti Sumani and Mohamad Arifin Bin Sirat whose affection, love, encouragement and prays of days and nights make me able to complete this project.*

*Alhamdulillah. Thank you.*



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## ABSTRACT

Copper oxide ( $\text{Cu}_2\text{O}$ ) is one of inorganic materials used in photovoltaic (PV) technology. It was reported that  $\text{Cu}_2\text{O}$  that acts as the p-n junction semiconductor material was preferable in extensive studies for solar cell application. However, the heterojunction interface between p-type  $\text{Cu}_2\text{O}$  to other materials has lower conversion efficiency due to lattice mismatch. Thus, a p-n  $\text{Cu}_2\text{O}$  homojunction thin film had been introduced to acquire higher efficiency due to similar interface which can promote less defects between layers. In this experiment, both n and p-type  $\text{Cu}_2\text{O}$  thin film was fabricated by using copper acetate based solution through electrodeposition method. Firstly, the effects of pH value and deposition time were optimized for fabrication of n-type  $\text{Cu}_2\text{O}$  thin film on fluorine doped thin oxide (FTO) glass. The deposition potential optimization was conducted using Cyclic Voltammetry Measurement. Then, the effects of bath temperature and deposition time were optimized for p-type  $\text{Cu}_2\text{O}$  on n-type  $\text{Cu}_2\text{O}$ /FTO substrate to obtain p-type based homostructure. Structural, morphological, topological and optical properties were characterized by using Cyclic Voltammetry, X-ray diffraction (XRD), Field Emission-Scanning Electron Microscope (FE-SEM), Atomic Force Microscopy (AFM) and Ultraviolet-Visible Absorption Spectroscopy (UV-Vis), respectively. The conduction type for n-type and p-type  $\text{Cu}_2\text{O}$  thin film also have been characterized by using Photoelectrochemical Measurement (PEC). The optimum parameters obtained for n-type  $\text{Cu}_2\text{O}$  were pH of 6.3, deposition time of 30 minutes, bath temperature of 60 °C and deposition potential of -0.125V vs Ag/AgCl. Meanwhile, the optimum parameters for fabrication of p-type  $\text{Cu}_2\text{O}$  on n-type  $\text{Cu}_2\text{O}$ /FTO substrate were pH of 12.5, deposition time of 2 hours, bath temperature of 40 °C and potential deposition of -0.4 V vs Ag/AgCl. The p-type  $\text{Cu}_2\text{O}$  based homostructure thin film was successfully fabricated and can be implemented in fabrication of  $\text{Cu}_2\text{O}$  homojunction thin film in photovoltaic for solar cell.



## ABSTRAK

Kuprum Oksida ( $\text{Cu}_2\text{O}$ ) adalah bahan bukan organik yang digunakan dalam teknologi fotovolt.  $\text{Cu}_2\text{O}$  yang bertindak menjadi bahan semikonduktor simpang p-n adalah lebih diutamakan dalam kajian aplikasi sel solar. Walaubagaimanapun, permukaan heterosimpang antara  $\text{Cu}_2\text{O}$  jenis p dengan bahan-bahan lain mempunyai kecekapan perubahan yang rendah berdasarkan tiada kesepadanan kekisi. Oleh itu, filem nipis  $\text{Cu}_2\text{O}$  jenis p-n homosimpang telah diperkenalkan untuk memperoleh kecekapan perubahan lebih tinggi berdasarkan permukaan sama yang mengurangkan kecacatan antara lapisan. Dalam kajian ini, kedua-dua  $\text{Cu}_2\text{O}$  jenis p dan n telah difabrikasi menggunakan campuran berasaskan kuprum asetat melalui teknik pengelektropendapan. Pertamanya, kesan nilai pH dan masa telah dioptimumkan untuk memfabrikasi filem nipis  $\text{Cu}_2\text{O}$  jenis n diatas kaca Fluorin Dop Stanum Oksida (FTO). Optimum potential ini telah dijalankan menggunakan pengukur voltammetri berkitar. Kemudian, kesan suhu dan masa dioptimumkan untuk filem nipis  $\text{Cu}_2\text{O}$  jenis p diatas filem nipis  $\text{Cu}_2\text{O}$ /FTO jenis n untuk membentuk homostruktur jenis p. Sifat struktur, morfologi, topologi dan optik filem nipis tersebut masing-masing telah dikenalpasti dengan menggunakan Belauan Sinar-X, Mikroskop Elektron Pengimbas Pancaran Medan (FE-SEM), Mikroskop Daya Atom (AFM) dan Spektrum Serapan Nampak Ultraviolet (UV-Vis). Jenis konduktor untuk filem nipis  $\text{Cu}_2\text{O}$  jenis n dan p juga telah dikenalpasti dengan menggunakan Pengukur Fotoelektrokimia (PEC). Parameter optimum yang didapati untuk filem nipis  $\text{Cu}_2\text{O}$ /FTO jenis n adalah nilai pH 6.3, masa selama 30 minit, suhu campuran  $60^\circ\text{C}$  dan potential  $-0.125\text{V}$  vs  $\text{Ag}/\text{AgCl}$ . Manakala, kajian juga mendapati parameter yang optimum untuk filem nipis  $\text{Cu}_2\text{O}$  jenis p diatas  $\text{Cu}_2\text{O}$ /FTO jenis n adalah nilai pH 12.5, masa pemendapan selama 2 jam, suhu campuran  $40^\circ\text{C}$  dan potential  $-0.4\text{V}$  vs  $\text{Ag}/\text{AgCl}$ . Homostruktur  $\text{Cu}_2\text{O}$  jenis p telah berjaya difabrikasi dan boleh dilaksanakan dalam homosimpang  $\text{Cu}_2\text{O}$  fotovolt untuk aplikasi sel solar.

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## LISTS OF SYMBOLS AND ABBREVIATIONS

%	- Percentage
°	- Degree
μm	- micrometer
A	- Absorbance
a.u	- Absorbance unit
Ag/AgCl	- Silver/Silver Chloride
Al	- Aluminium
C	- Columb
CE	- Counter electrode
cm	- Centimeter
CO <sub>2</sub>	- Carbon Dioxide
Cu	- Copper
Cu <sub>2</sub> O	- Copper Oxide
CuSO <sub>4</sub>	- Copper Sulphate Pentahydrate
CV	- Cyclic Voltammetry
e	- Electron
ECL	- Electrochemiluminescence
E <sub>g</sub>	- Band gap
Fe <sub>2</sub> O <sub>3</sub>	- Iron Oxide
FE-SEM	- Field Emission-Scanning Electron Microscopy
FF	- Fill factor
FTO	- Fluorine doped tin oxide
h	- Plank's constant
H <sub>2</sub> O	- Water
ITO	- Indium tin oxide
I-V	- Current-voltage

$J_{sc}$	- Short Circuit Current
k	- kilo
KOH	- Potassium Hydroxide
M	- Mol
mA	- miliAmpere
MiNT-SRC	- Microelectronic and Nanotechnology Shamsuddin Research Centre
mV	- milivolt
MW	- Megawatt
NaCl	- Sodium Chloride
NaOH	- Sodium hydroxide
nm	- Nanometer
OCP	- Open circuit potential
°C	- Degree calcius
PEC	- Photoelectrochemical
ppm	- Parts per million
Pt	- Platinum
Pt	- Platinum
PV	- Photovoltaic
RE	- Reference electrode
RF	- Radio frequency
SCE	- Saturated calomel electrode
TCOs	- Transparent Conducting Oxide
TiO <sub>2</sub>	- Titanium Dioxide
UV	- Ultraviolet
UV-Vis	- Ultraviolet-Visible Absorption Spectroscopy
V	- Volt
V/sec	- Volt per second
V <sub>oc</sub>	- Open Circuit Voltage
vs	- Versus
WE	- Working electrode
XRD	- X-Ray Diffraction
ZnO	- Zinc Oxide
$\alpha$	- Alpha

$\theta$  - Theta

$\Omega$  - Ohm



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## CHAPTER 1

### INTRODUCTION

This chapter discussed on the introduction of the project. This section consists of project overview, problem statement, research objectives, scopes and limitations of the project.

#### 1.1 Project overview

Nowadays, the population of the world seem grow rapidly and varies of industries had demand an energy which renewable for consumer. The renewable energy sources are including wind, hydro, solar, geothermal, and some producer of biomass. Based on International Energy Agency (IEA)'s statistic in 2012, the world trusted on renewable sources for around 13.2% of its total main energy supply. At 2013, renewables accounted for 22% of global electricity generation, which is a 5% increase from 2012 [1].

Fossil fuel is the primary renewable source of energy among others. However, it is facing several challenges including high prices and pollution's effect by carbon dioxide emission. Carbon dioxide (CO<sub>2</sub>) is one type of gases which rises global temperature that cause climate change. Based on the increment rate of fossil fuel consumption, the concentration of CO<sub>2</sub> is predicted to reach the dangerous level of 750 ppm in 2050. Since there is no natural decomposition of CO<sub>2</sub> in the atmosphere, the pollution effect will take 500 to 2000 years to reduce [2]. Thus, finding new alternative on renewable energy source has received attention by consumers to

decrease CO<sub>2</sub> emission as alternative energy sources and invention for new technologies.

Solar energy is one of renewable energy through natural processes which use sun as the main source. It is consumable resource which provides more energy in one hour than the entire energy consumed by human in a whole year [2]. Hence, the photovoltaic industry, which is the direct conversion of solar energy to electricity, grew at a rate exceeding 30% per year in the last decade. The efficiency of solar-to-electron conversion is very important in the development of photovoltaic solar cells [4, 5].

Currently, wafer silicon acts as photovoltaic material for most industries. In 2009, solar cells based on large-grain polycrystalline and single-crystal silicon wafers include more than 80% of the photovoltaic market. However, the potential for price reduction is restricted by the bulk silicon wafer's cost. The high cost of these modules are caused by the processing and material cost. As a result, the electrical power production cost by solar energy higher than product by combustion of fossil fuels [4, 6].

Fabrication of thin film solar cell is one of major strategy to overcome the cost of electricity produced by photovoltaic modules. Thin film solar cells are known as the second generation photovoltaic devices which rapidly growing method in the photovoltaic technology. Thin film solar cells based on amorphous, microcrystalline, and polycrystalline silicon compound semiconductors have ascertained their commercial viability. Their market share increased steadily to 15% in 2009. In addition, by increase the efficiency beyond the Shockley–Queisser limit, it can reduce the cost of photovoltaic electricity. A variety of models are proposed along this venue to achieve high efficiency multi-junction solar cell based on III-V binary semiconductor. Initially, they are used in space application but now it is being developed for terrestrial application.

In this development, researchers found that p-n junction semiconductor is essential as a base for solid-state electronic devices including solar cell [6]. This concept was developed since study on movement of charge carriers in photovoltaic process was introduced. It was including both electron and hole formed a junction either in the same material which called homojunction or different materials known as heterojunction [7].

## 1.2 Problem statement

Nowadays, one of invention method for solar cell application is focusing on heterojunction energy conversion efficiency of copper oxide ( $\text{Cu}_2\text{O}$ ) solar cell to improve the efficiency conversion energy. However, there was low efficiency of solar cell based on the interface in heterojunction between p-type  $\text{Cu}_2\text{O}$  when other material create a loss mechanism for photo-carrier separation and collection [8]. In other research, the defects also most probably exist on the silicon interface in heterojunction especially order defect compound layer during deposition. So, it may affect the performance of the solar cells [9]. Therefore, another approach was introduced to improve the efficiency conversion such as p-n homojunction of  $\text{Cu}_2\text{O}$  solar cells. By using electrodeposition method with optimum parameters, it was reported that pH solution is one of the parameter that could control the total of oxygen into the growth of  $\text{Cu}_2\text{O}$  thin film [8]. Thus, the significant approach to increase efficiency in  $\text{Cu}_2\text{O}$  solar cells is to produce a homojunction of  $\text{Cu}_2\text{O}$  by optimizing the parameter such as pH value, deposition time and bath temperature using electrodeposition techniques. Thus, this research was purposed to fabricate n-type and p-type  $\text{Cu}_2\text{O}$  homostructure thin film by obtaining the optimum deposition parameters. The characterizations of  $\text{Cu}_2\text{O}$  homostructure also were carried out to enhance the performance of thin film's properties.

## 1.3 Research objectives

This research will be carried out in order to the following objectives:

1. To fabricate n-type  $\text{Cu}_2\text{O}$  thin film on FTO substrate and p-type  $\text{Cu}_2\text{O}$  on n-type  $\text{Cu}_2\text{O}$ /FTO substrate.
2. To optimize parameters such as pH value, deposition time and bath temperature for fabrication of n-type  $\text{Cu}_2\text{O}$  thin film on FTO substrate and p-type  $\text{Cu}_2\text{O}$  on n-type  $\text{Cu}_2\text{O}$ /FTO substrate.
3. To investigate the structural, morphological, topological and optical properties for both n-type  $\text{Cu}_2\text{O}$  and p-type  $\text{Cu}_2\text{O}$  based homostructure thin film.



#### 1.4 Scope and limitation

The scopes of this project are as follow:

1. Copper (II) acetate monohydrate was used in this experiment as the based solution in electrodeposition method.
2. Deposition process were carried out using three electrodes set up which fluorine doped thin oxide (FTO) glass substrate as a working element, platinum (Pt) as a counter element and silver/silver chloride (Ag/AgCl) as a reference element.
3. The parameters of various pH value from 6.0 to 6.5 and deposition time between 20 and 40 minutes were conducted to optimize the performance of n-type  $\text{Cu}_2\text{O}$  thin film.
4. Cyclic voltammetry measurement of p-type  $\text{Cu}_2\text{O}$  thin film was carried out by using the same setting of three electrode set up as electrodeposition method.
5. Several parameters including bath temperature at 40 and 50 °C and deposition time for 1 hour and 2 hours were used to obtain the optimized p-type  $\text{Cu}_2\text{O}$  based homostructure thin film.
6. The characterization tools used were Field Emission Scanning Electron Microscopy (FE-SEM), X Ray Diffraction (XRD), Surface Profiler, Ultraviolet-Visible Absorption Spectroscopy (UV-Vis) and Atomic Force Microscopy (AFM).

#### 1.5 Thesis layout

This thesis was discussed on fabrication of  $\text{Cu}_2\text{O}$  based homostructure thin films using electrodeposition method. The homostructure was constituted by two deposition layers which n-type and p-type  $\text{Cu}_2\text{O}$  thin films. Based on the objectives and scopes of project, there were five main chapters which explaining whole fabrication process.

In chapter 1, some introduction was briefing about project overview, problem statement, research objectives and scope. Several literature reviews were devoted in related subtopic such as copper oxide fabrication, homostructure, cyclic measurement, photoelectrochemical and photovoltaic concept. In addition, chapter 3

presented fabrication of  $\text{Cu}_2\text{O}$  thin films flowchart which including solution and substrate preparation, electrodeposition process and characterization properties. After that, chapter 4 showed the final results and discussion on structural, morphological, topological and optical properties for performances both n-type  $\text{Cu}_2\text{O}$  and p-type  $\text{Cu}_2\text{O}$  based homostructure thin film. Finally, conclusion was made up and recommendations for future works in this research was provided in chapter 5.



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