PERFORMANCE ANALYSIS OF SOLID-STATE DYE SENSITIZED SOLAR CELLS BY USING SCAPS-1D SIMULATION

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This report is submitted in partial fulfilment of the requirements for the degree of Bachelor of Electronic Engineering with Honours

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DECLARATION

I declare that this report entitled "Performance Analysis of Solid State Dye Sensitized Solar Cells by using SCAPS-1D simulation" is the result of my own work except for quotes as cited in the references.

Signature :

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Date : 24 JUNE 2020

APPROVAL

I hereby declare that I have read this thesis and in my opinion this thesis is sufficient in terms of scope and quality for the award of Bachelor of Electronic Engineering with Honours.

Signature :

Supervisor Name : Dr. Zul Atfyi Fauzan Bin Mohammed Napiah

Date : 01 July 2020

DEDICATION

I'm so grateful to finish this project with a lot of experience gained. Therefore, I want to dedicate my Final Year Bachelor Degree Project to my very supportive parents, Mr. Sha'aban Bin Zakaria and Mrs. Sharipah Binti Mahat. Lastly, without forgetting my supervisor and co-supervisor Dr. Zul Atfyi Fauzan Bin Mohammed Napiah and Dr. Faiz Bin Arith.

ABSTRACT

Energy consumption has become a hot topic in our beloved earth. It has been increasing and demanding. A lot of energy generation has created along the hundred years. Unfortunately, energy consumption has overused instead of the energy generation has decreasing. Therefore, a lot of studies and research about energy harvesting through other approaches. One of them are solid-state dye-sensitized solar cells (SDSC). This device is one of the photovoltaic cells as solar cells with improvement of material consumption, cost reduction and environmental friendly. Also, a lot of test needed to find the best conversion efficiency for SDSC while it is high in cost and time taken to produce a single cell. Due to modern technology, this test can be run by using software, for this project SCAPS-1D software was applied. In SDSC, a lot of researcher has done with variation of material to find the best efficiency. This software can calculate C-V and A-C characteristic. Material tested for this device has compared to select the best material for solar cells. The measured output parameter are open-circuit voltage (Voc), short-circuit current density (Jsc), fill factor (FF) and efficiency (eta%). Hence, to find all of these output parameters, firstly need to insert the input parameter in SCAPS-1D. These parameters are layer thickness, annealing temperature, defect at the interface and doping density. As a result, the main objective of this project has achieved with CuO was the best hole transport material (HTM) layer. The conversion efficiency was 25.33% which higher compared to the other HTM layers.

ABSTRAK

Penggunaan tenaga telah menjadi topik hangat di bumi tercinta kita. Ia semakin meningkat dan permintaan tinggi. Banyak penjanaan tenaga telah dihasilkan sepanjang seratus tahun. Malangnya, penggunaan tenaga telah berlebihan dan bukannya penjanaan tenaga menurun. Oleh itu, banyak kajian dan penyelidikan mengenai pengambilan tenaga melalui pendekatan lain. Salah satunya adalah sel solar dye-sensitized keadaan pepejal (SDSC). Peranti ini adalah salah satu sel fotovoltaik sebagai sel solar dengan peningkatan penggunaan bahan, pengurangan kos dan mesra alam. Banyak ujian yang diperlukan untuk mencari kecekapan penukaran terbaik untuk SDSC sementara kos dan masa yang tinggi diperlukan untuk menghasilkan satu sel. Oleh kerana teknologi moden, ujian ini dapat dijalankan dengan menggunakan perisian, untuk projek ini perisian SCAPS-1D diterapkan. Di SDSC, banyak penyelidik telah melakukan variasi bahan untuk mencari kecekapan terbaik. Perisian ini dapat mengira ciri C-V dan A-C. Bahan yang diuji untuk peranti ini dibandingkan dengan memilih bahan terbaik untuk sel solar. Parameter output yang diukur adalah voltan litar terbuka (Voc), ketumpatan arus litar pintas (Jsc), faktor pengisian (FF) dan kecekapan (eta%). Oleh itu, untuk mencari semua parameter output ini, pertama sekali perlu memasukkan parameter input dalam SCAPS-1D. Parameter ini adalah ketebalan lapisan, suhu penyepuhlindapan, kecacatan pada antara muka dan kepadatan doping. Keputusannya, objektif utama projek ini berjaya dicapai dengan CuO merupakan lapisan HTM terbaik. Perubahan penukaran effisiensi sebanyak 25.33% lebih tinggi berbanding lapisan-lapisan HTM yang lain.

ACKNOWLEDGEMENTS

I would love to give a big thank you to my supervisor Dr. Zul Atfyi Fauzan Bin Mohammed Napiah for giving me the opportunity to run this project under his supervision. He have help me a lot from the beginning of the Bachelor Degree Final Year Project and helping me to plan my project. Besides, I want to thank to my co-supervisor Dr. Faiz Bin Arith as he also helping me a lot about solar cells and giving an overview on how to start this project. Not forgetting my friends who have helping me directly and indirectly. Lastly, a special thanks to my parents who have help me in giving moral support and support me financially. Without them I could not finish my project.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF SYMBOLS AND ABBREVIATIONS

DSSC	:	Dye-Sensitized Solar Cells
SDSC	:	Solid-state Dye-Sensitized Solar Cells
PV	:	Photovoltaic
TiO2	:	Titanium Dioxide
CuO	:	Cupric Oxide
Cu2O	:	Cuprous Oxide
CuI	:	Copper Iodide
HTM	:	Hole Transport Material
ETL	:	Electron Transfer Layer
UV	:	Ultra Violet
η	:	Conversion Efficiency
Pm	:	Maximum Output
Pin	:	Incident Power
Voc	:	Voltage Open Circuit
Jsc	:	Current Density in Short Circuit
FTO	:	Fluorine-doped Tin Oxide
ITO	:	Indium Tin-Oxide

CHAPTER 1

INTRODUCTION

Energy consumption in our world has increasing and demanding. However, the energy generation was not much easy to produce. Since then, there are fossil fuel, steam energy and renewable energy. Particularly, there are some research and progress has made in the development of renewable-energy technologies, such as solar cells, fuel cells, and biofuels. In order to produce the new research and technology required a lot of money to produce them and may harm the environment. Solar cell was one of the best solution for the renewable energy. A solar cell can generate energy at any places without creating any pollution as long as it can receive a few amount of light illumination. Since it can move anywhere, it proves that solar cell was portable and efficient compared to biofuels and fuel cells that produce chemical vapour that creates air pollution. Therefore, dye-sensitized solar cells (DSSC) was one of the photo-voltaic cell technologies developed and it is very favourable as it is valuable in cost of product of photovoltaic electricity generation. There has been a lot of research and studies about the solar generating technology since the last 20 years. During the research, a lot of improvement achieved during the progress of the materials composition of such devices either to enhance device efficiency or to improve stability and process ability and to reduce production costs. Photovoltaic property was related to the incidence of the photons to a conductor/semiconductor and the generation of the electron-hole pairs, creating an electric potential difference across the interface of two different materials.

1.1 Introduction

In the past times, the first person who have discovered this beneficial technology was Gratzel and O'Regan in 1991. They have discovered about the new type of PV cells which this new device use the principal of photosynthesis of plant. The name of the PV cells is Dye-sensitized solar cell (DSSC). Therefore, their achievement during the discovered new PV cells was the efficiency of the DSSC reached to 7.9%. According to Michael Gratzel and Brian O'Regan they have discovered a new type of solar cells called dye-sensitized solar cells (DSSCs), instead this new device has reduced the cost of fabrication by 50% other than conventional semiconductor solar cell, by using solution processes in 1988. Mainly, the working principle of DSSC is a photo induced charge separation at the metal oxide/dye/electrolyte interface. Therefore, energy conversion process has become the primary process in DSSC. Theoritically, the charge separation were largely based upon model system studies such as dye sensitized metal oxide films in the absence of redox electrolyte or solar irradiation. This fabricated design consists of a working electrode with a layer of TiO_2/dye composite particles. The organic dye monolayer in the photo electrochemical or dye-sensitized solar cell replaces light absorbing pigments (chlorophyll). The use of natural dye extracts will provide natural, non toxic and low cost dye sources with high absorbance level of UV. Examples of dye sources are Henna and Raspberries. The prepared samples were characterized by X-ray Diffraction (XRD), Atomic Force Microscopy (AFM) and Ultraviolet-visible spectroscopy (UV-Vis), Field Emission Scanning Electron Microscopy (FESEM) and Raman Spectroscopy.

The parameters that required to measure a solar cell are the output characteristics of the device including short-circuit current (Jsc), open-circuit voltage (Voc), fill factor (FF) and power conversion efficiency (eta%). The maximum output voltage of solar cells resulting in the open circuit voltage. Results appear when the value of the output current is zero. While for the short circuit current, it is when setting a solar cell expose to any source of light while the output is in short circuit state, and the voltage is 0. Current called short-circuit current where it defines as the maximum output current. Conversion efficiency is the value of maximum output power to the open circuit voltage divided by the value of short circuit current. Next, is the fill factor where fill factor is related with maximum output power. A higher fill factor means it has larger output power. Fill factor has a value where it depends on series resistance and voltage. Fill factor can be calculated as

$$\mathrm{FF} = \frac{Pm}{Voc Jsc}$$

Where, Pm is the maximum output power. V_{oc} is the open-circuit voltage. J_{sc} is the short circuit current. Finally, the main parameter to define the device performance is the power conversion efficiency. Power conversion efficiency (PCE) is a significant parameter. Definitely, PCE is the ratio of the maximum output power to the incident light power. The equation for PCE is $\eta = \frac{FF \text{ X } Jsc \text{ X } Voc}{Pin}$. Where FF, I_{SC}, V_{OC}, Pin fill factor, short circuit current, open circuit voltage and incident power respectively ($100mW/cm^2$).

1.1.1 Problem Statement

Based on the research study, most of it has a lot of process to successfully fabricated the DSSC. There are preparation of anode and cathode layer, preparing and synthesis dye and combination of anode and cathode. Therefore, a lot of times and material are used to create a single DSSC. Other than that, DSSC is quite harmful because of the electrolyte. Instead of creating DSSC, a modification has been made to create the DSSC into solid-state dye-sensitized solar cells (SDSC). This new modification has created the device as an environmental friendly device which can preserve our earth. Next, to find the best device efficiency will required a lot experiments by using materials multiple time. Even though the materials were cheap, the time taken to make a DSSC was not short. It required a lot of time to synthesize the TiO^2 and varying the parameters to increase the device efficiency. Therefore, the best way to find the best parameter that will increase the device efficiency was by doing simulation. There are software that calculate and show the result after inserting the parameter of the DSSC.

1.1.2 Objectives

The main objectives for this project are :

a) To simulate the solid-state dye-sensitized solar cells (SDSC) by using SCAPS-1D software.

b) To characterize the selected Hole Transport Material (HTM) structure such as CuO, CuI and Cu2O.

c) To compare the performance of selected HTM layer.

1.1.3 Scope

Depending on the objectives, the scope of this project is to simulate the SDSC on software to compare and analysis the results. The simulation of the SDSC is applying the DSSC structure, which in this project will manipulate the TiO^2 as photoanode. Therefore, the main parameter that need to measure are open-circuit voltage (Voc), short-circuit current density (Jsc), fill factor (FF) and efficiency (eta%). All of this parameter are required to get the comparing and analysis of the DSSC. By the potential functionality of the device (DSSC) parameter setting, SCAPS-1D can insert all of the physical parameter, which is advantageous to study the composite layer formed by the interdiffusion between different layers. Based on the development progress, there are some charactistic required some setting in order to find the best efficiency of the DSSC.

1.1.4 Thesis Outline

The framework of this study is divided into five (5) main chapters, including their sub-chapters. There are Chapter 1 Introduction, Chapter 2 Background Study, Chapter 3 Methodology, Chapter 4 Results and Discussion and Chapter 5 Conclusion and Future Works.

Chapter 1 is the introduction where the significant of this project is stated in the objectives through problem statement. This chapter also determined the scope of work to find where and what are the things to achieve.

Chapter 2 tells everything about the basic of this project which is by examines on the past work or research that had been done in a similar field and the enhancement towards the task.

Chapter 3 will explain the procedures and techniques used in order to complete this project. There are flow chart which need to follow to run this project.

Chapter 4 is where the data is recorded and then the analysis. This chapter is the crucial part where the analysis is important to find the best optimization among the past researchers.

Chapter 5 is the conclusion of the experimental results which has been done due to overall project accomplished from objective. This chapter also contain a recommendation for future work that can be made to this project to make it more reliable.

CHAPTER 2

BACKGROUND STUDY

The point of literature review is to brief about the dye-sensitized solar cell (DSSC) from its working principle into the application in commercialization. Firstly, the vital component of DSSC is about the role of the sensitizer and the parameter that required to monitor in order to increase the performance/efficiency of DSSC [1]. The relationship between the solar cell efficiency and the electron injection efficiency is directly proportional while in the wide bandgap nanostructured semiconductors [2]. Moreover, DSSC is an inexpensive solar cell that can be developed within the massive amount of solar cell that ever been created. Unfortunately, the efficiency cannot compete with the conventional solid state junction in converting the energy.

2.1 Structure of DSSC

DSSC was developed as a sandwich constructed component. At the surface of the glass there is a thick nanoparticle film that works to enhance the light absorption as to increase the efficiency. The sandwich consists of 4 main parts which is a nanostructured wide bandgap semiconducting layer, electrode, dye molecule and electrolyte [2]. Anodes of dye-sensitized solar cells are typically constructed using TiO2 thick film (~10 μm) that was deposited as a paste and sintered to produce electrical continuity. Moreover, the uniqueness of this nanoparticle film is to provide a large internal surface area. It can be defined by characterizing the roughness factor by using microscope. Therefore, it will assist very much on accepting the light going through the substrate along 400 to 800 nm region where it can be found a lot of solar flux incident [3]. Theoritically, based on quantum physics theory, by leaving a hole which leaves a positive charge at the valence band can excite an electron through the conduction band in the nanoparticle semiconductor film.

Indium tin oxide (ITO) is a soda lime glass coated with indium tin oxide layer. It is commonly used as an efficient electrode since it combines good conductivity and transparency in the visible range [4]. In this project, ITO has been applied as a substrate. Dye-sensitized solar cell (DSSC) is a semiconductor photovoltaic device that directly converts solar radiation into electric current. ITO films characteristics are material transmittance of over 80% and sheet resistance 18Ω/cm2, while FTO films has a better transmittance of about 75% in the visible region and sheet resistance of 8.5/cm2 [5]. In order to get the maximum sunlight recflecting through active area of the solar cell, the substrates should be highly transparent with the transparency percentage is more than 80%. Moreover, the substrate should also have higher electrical conductivity to get higher efficiency of charge transfer and to minimize energy loss. Referring to the research studies photoanodes which are applied on FTO and ITO glass substrates were sintered at 450 ◦C for 2h in an oxygen atmosphere. The results shows that the sheet resistance of ITO increased from 18 Ω/cm2 to 52 Ω/cm2 while for FTO it remain constant upon sintering. Therefore, the overall efficiency of a DSSC based on FTO is 9.4%, while for an identical cell based on ITO it is 2.4% [5]. Definitely, unstable compound in ITO substrate occurs at high temperature during experimental comparison in parallel with the sheet resistance to cell efficiency. Even though the result of the experiment shows that FTO can get a better efficiency

Unfortunately, since the synthetic dye was expensive and required a complicated synthesizing method, a group of natural dyes was selected from fruits and leaves where it can save cost, a lot of resources and does not harmful. Dyes contain an significant compound that forms a pigment that is crucial for the measurement of DSSC performance. Pigments from carotenoids, betalains, anthocyanins and chlorophyll are one of the major contributors to a pigment coloring. A research studies using mangosteen pericarp has gain as much as 1.17% and it was the highest DSSC efficiency for nature based dye. The common dye has the ability to absorb all the light from the visible spectrum, meaning that the choice is to combine two separate colors to absorb both the lower and higher wavelength areas.

Characteristics to choose the best dye-sensitizer :

- The sensitizer will be able to detect all incident lights below the near-IR wavelength of roughly 920 nm.
- Must have a carboxylate or phosphonate group fixed on the surface of the semiconductor oxide
- Lowest unoccupied molecular orbital (LUMO) of the sensitizer has to minimize potential energy losses during the electron transfer reaction to match the edge of the oxide conduction band.
- The highest occupied orbital (HOMO) of the sensitizer must be electron donation from an electrolyte or a hole conductive substance must be relatively small to accept electron donation.
- It should be stable enough to endure 10^8 turnovers corresponding to 20 years exposure to sunlight without apparent degradation.

2.2 Working Principle of DSSC

DSSC is a upgrade version of the conventional silicon photovoltaic cells. It is also known as the third generation of the photovoltaic cells. The reasons to get the name of the third generation photovoltaic cells is reasonable where it has low production costs, simple manufacturing process and will function properly under ambient condition with better power conversion efficiency. Despite of the simple manufacturing process, it is full of working principle under this small device. Firstly, the most important of the DSSC is the monolayer of the organic dye that attached to the mesoporous metal oxide semiconductor with wide band gap [7]. The mesoporous oxide layer (typically,TiO2) deposited on the anode to activate electronic conduction. The incident light is the main source which absorbed by the dye. According to the equation $E = h*(c / \lambda)$ (where E stands for the energy of light, h stands for the Planck's constant, c stands for the speed of light and λ stands for the wavelength of light). Anatase TiO2 can absorb ultra-violet light which has wavelength less than 387 nm because it has a band gap of 3.2 ev, but it cannot absorb visible light which is between 400 nm and 700 nm.

Dyes contain an important compound that forms a pigment which are essential in the DSSC efficiency calculation. A monolayer charge transfer dye covalently bonded to the surface of the mesoporous oxide layer to enhance light absorption. The electron of the dye will be excited and injected to the conduction band of TiO2 and flow through the external wire to the load. Ruthenium complex is the most widely used dye, which also has best solar cell efficiency at present assembled with TiO2 electrode and volatile iodide/triodide electrolyte. The electron lost from the dye will be substituted by the electron from the electrolyte through redox reaction of iodide (I-) oxidized into triiodide (I3-) and releasing electron. The new electron collected from the load will flow back to DSSC through the counter electrode (Pd/Au-coated FTO) which act as a catalyst to assist the reduction reaction of the electrolyte triiodide (I3-) into iodide (I-) and re-used in the conversion process of light into electrical energy in DSSC.

The chemical reactions of this DSSC can be given as follows:

(1) Dye is excited by light and the electrons jump to the excited state form the ground state.

$$S + hv = S^* \qquad \text{(eq.1)}$$

S: ground state of dye S^*: excited state of dye S^+: Oxidized state of dye

(2) Electrons inject into the conduction band of semiconductor from the dye excited state.

$$S^* = e^- \text{ (in } TiO_2 \text{ conduction band)} + S^+ \qquad \text{(eq.2)}$$

(3) Electrolyte redox couple reaction is.

$$S^+ + 3I^- = S + I_3^- \qquad \text{(eq.3)}$$

(5) Recombination between electrons in TiO_2 conduction band and oxide dye occurs.

$$S^+ + e^- \text{ (in } TiO_2 \text{ conduction band)} = S \qquad \text{(eq.4)}$$

(6) Electrons in conduction band conduct to outer circuit

$$e^- \text{ (in } TiO_2 \text{ conduction band)} = e^- \text{ (Back contact)} \qquad \text{(eq.5)}$$

(7) Electrons in nano-crystalline semiconductor combine with I3- ions

$$I_3^- + 2e = 3I^- \qquad \text{(eq.6)}$$

(8) I3- ions spread to the counter electrode and electrons lead to the re-generation of I- ions

$$I_3^- + 2e \text{ (in } TiO_2 \text{ conduction band)} = 3\,I^- \qquad \text{(eq.7)}$$

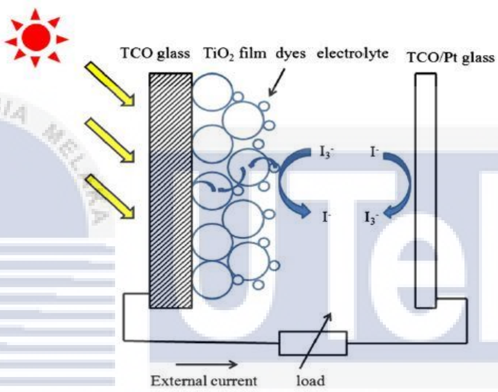

Figure 1 : Device working principle

2.3 Screen printing manufacturing processing

DSSC is competitive because its manufacture process is less expensive, less contamination and most of the materials are plenty comparing to those used in silicon based solar cell. Using thick film printing technique such as screen printing, the DSSC electrode can be massively manufactured and the film thickness is able to be controlled between 10 to 15 microns, a desirable thickness. The objective in this study is to deposit TiO2 and select a screen printing TiO2 paste for DSSC anode material. When manufacturing a DSSC, the anode semiconductor material is usually printed on a conductive glass and then cure at 450^{o}C. Sensitizers, the dyes, are first dispersed in solution such as acetonitrile. Place the cured TiO2 into sensitizer solution overnight for dye adsorption. Finally, electrolyte is injected if using liquid electrolyte and the solar cell is sealed with spacer material. Screen printing technique is often used to print the thick film TiO2, which is ideally about 10 microns, on a conductive glass, such as FTO or ITO. This thick film screen printing technology has been developed for the electronic industries to produce miniature and robust electronics circuits in a cost-effective manner, as this technology is massive and automated. This technology can produce well-defined, highly reproducible structures, and these characteristics are very desirable for manufacturing DSSC.

2.4 TiO2 as photoanode

Advantage of sensitized wide bandgap semiconductors such as TiO2 give a high impact due to high chemical stability of the cell due to their resistance to photo corrosion. It assured that high photovoltaic efficiency cannot be achieved by using a flat layer of semiconductor or wide bandgap semiconductor oxide surface but instead by applying the nanostructured layer of very high roughness factor (surface area). Therefore, Gratzel and his co-workers replaced the huge layer of titanium dioxide (TiO2) with nanoporous TiO2 layer as a photoelectrode. Nanoporusity of the TiO2 paste (or colloidal solution) is achievable by sintering (annealing) of the deposited TiO2 layer at approximately 450 ◦C in a well ventilated zone for about 15 minutes [2]. The nano-crystalline semiconductor anode is not only where the sensitizers adhere, but also where the charge transfer occurs. Consequently, it is acknowledgeable that the quality of the semiconductor electrode directly affects the efficiency of DSSC. Reducing charge recombination is the most direct means to improve DSSC efficiency, and the quality of TiO2 film is one of the most important key parameter. There are four fundamental requirements of the electrode material which are large surface area, roughness and sponge-like nano-crystalline structure and good electronic contact. The anode material structure should allow electrolyte redox couple regenerates the oxide dye and charge should also be able to rapidly inject into the semiconductor. At the meantime, backward charge recombination should be the slowest step. TiO2 is an optimal material with suitable band gap and electronic properties as mentioned. The nano-crystalline semiconductor anode is not only where the sensitizers adhere, but also where the charge transfer occurs. Consequently, it is a fact that the quality of the semiconductor electrode directly affects the efficiency of DSSC. Quality of TiO2 film is the most important part where when reducing charge recombination has the characteristic to improve DSSC efficiency. There are four fundamental requirements of the electrode material: large surface area and roughness, sponge-like nano-crystalline structure with good electronic contact. The anode material structure should allow electrolyte redox couple regenerates the oxide dye and charge should also be able to rapidly inject into the semiconductor. At the meantime, backward charge recombination should be the slowest step. The characteristic to find the conversion efficiency are stated in the formula below.

Conversion efficiency is calculated using equation, η

$$\eta = FF \times I_{SC} \times V_{OC}/Pin$$

Where FF, I_{SC}, V_{OC}, Pin are fill factor, short circuit current, open circuit voltage and incident power, respectively [8].

An efficient photosensitizer has several basic fabrication requirements. Firstly, by strong dye adsorption particles on to the semiconductor surface. Second, by large visible light harvesting capacity while the next requirement is the ability to inject the electron into the conduction band of the semiconductors. Finally, =O or ─H groups capable of anchoring on the TiO2 surface to ensure high rates of electron transfer [9]. Therefore, the high surface area of the nanocrystalline TiO2 film plays a crucial role to increase the performance of the photoelectrochemical cell in energy conversion [10].

2.5 General comparison between semiconductor based solar cells and dye sensitized solar cells

In fact, in semiconductor p-n junction solar cell charge separation is under control by the junction built in electric field, while in dye sensitizes solar cell charge separation is by kinetic competition as in photosynthesis. The organic dye monolayer in the photoelectrochemical or dye sensitized solar cell replaces light absorbing pigments (chlorophylls), the wide bandgap nanostructured semiconductor layer replaces oxidized dihydro-nicotinamideadenine-dinucleotide phosphate (NADPH), and carbon dioxide acts as the electron acceptor. Moreover, the electrolyte replaces the water while oxygen as the electron donor and oxidation product, respectively.

Table 1 : Comparison DSSC with Semiconductor Solar Cells

	Semiconductor solar cells	DSSC
Transparency	Opaque	Transparent
Pro-Environment (Material & Process)	Normal	Great
Power Generation Cost	High	Low
Power Generation Efficiency	High	Normal
Color	Limited	Various

2.6 Solid-state Dye-sensitized Solar Cell (SDSC)

Solid state DSCs (SDSCs) allow a lower driving force for efficient dye regeneration, resulting in greater open circuit voltage compared to liquid DSCs.[11] Various forms of HTMs, including inorganic materials (e.g. CuI, CuSCN)[12][13], low molecular weight organic molecules and organic conductive polymers, have also been tested for use in SDSCs. There were researchers has tested TiO2/CuO and TiO2/Cu2O solar cells as a best devices for photovoltaic applications. Resulting to conversion efficiency of these cells. However, the efficiency still maintaining low. The research studied using the SCAPS-1D program to perform simulations of n-TiO2/p-Cu2Oand n-TiO2/p-CuO thin-film solar cells. Parameters collected were efficiency and short circuit current where 13.7% 22.4%, and 13.3mA cm−2, 28.4mA cm−2 respectively[14].

2.6.1 Advantage of SDSC

Recently, DSSC was a potential devices to replace conventional semiconductor photovoltaic cells. However, DSSC shows several drawbacks such as corrosion, photoreactive, dye desorption, evaporation, and leakage of solvent while using liquid iodide as electrolyte I-/ I3– , thus lead to changing to quasi solid and solid state DSSC[15]. Instead of applying DSSC in application to power generation, the best option in order to get higher efficiency without polluting or harmful was by replacing DSSC into SDSC. Therefore, inorganic hole transport material (HTM) was substituting the harmful liquid electrolyte which was investigated by Tennakone and coworkers with copper iodide (CuI). Indeed, CuI was more promising for HTM compared to CuSCN[15].

2.7 SCAPS-1D Software

Solar Cells Analysis Program (SCAPS) is a one-dimensional solar cell simulation program that has been developed by many researchers at the Department of Electronics and Information Systems (ELIS) of the University of Gent, Belgium. In SCAPS, the features are a lot to explore and parameters taken to find the best efficiency. The features in SCAPS are layers can be constructed up to 7 layers into the device , almost all of the physical parameter from the real device can be insert to simulate in the software. Main function of this software is to calculate the device efficiency, current in short circuit, voltage open circuit and fill factor. Besides, it can calculate C-V and A-C characteristic. If the user wants to calculate a lot of simulation, this software can run in batch which can reduce time to run the simulation done one by one. SCAPS-1D is a numerical simulation where a lot of equation were programmed to calculate the photovoltaic cells device output.

SCAPS performs a complete simultaneous numerical solution of the two continuity equations and Poisson's equation conditional on the boundary conditions appropriate to one and two-dimensional cells[16]. The equations are :

$$\nabla^2 v = -q / \epsilon \ (p - n + N_D - N_A) \qquad \text{(eq.8)}$$

$$\nabla . J_p = -q \ (G - R) \qquad \text{(eq.9)}$$

$$\nabla . J_n = -q \ (R - G) \qquad \text{(eq.10)}$$

General terms of eq (eq.9) and (eq.10) represented as :

$$G(x) = \int_0^\infty \emptyset a e^{-ax} d\lambda \qquad \text{(eq.11)}$$

Hole and electron current densities in eq (eq.9) and (eq.10) are given by:

$$Jp = -q\,\mu_p p \nabla V_p - kT\,\mu_p \nabla p \qquad \text{(eq.12)}$$

$$Jn = -q\,\mu_n n \nabla V_n - kT\,\mu_n \nabla n \qquad \text{(eq.13)}$$

$$V_p = V - (1 - \gamma)\ \Delta G / g \qquad \text{(eq.14)}$$

$$V_n = V + \gamma\ \Delta G / g \qquad \text{(eq.15)}$$

where vp and vn represent the effective potentials expressed in (eq.14) and (eq.15). ΔG and γ account for variations in the band structure, such as the density of band gap and states, and account for Fermi-Dirac statistics. Expression Jn and Jp represent the current density of the electron and holes respectively. Similarly, μn and μp represent the mobility of electron and hole respectively.

CHAPTER 3

METHODOLOGY

In this chapter, the methodology explained upon experiment and process that had been developed for this project. Accordingly, this section is discussing about the strategies and methodologies that have been utilized from the earliest starting point until the end of this project. Each part of the project and the step process discussed in detail.

3.1 Flow chart of the project

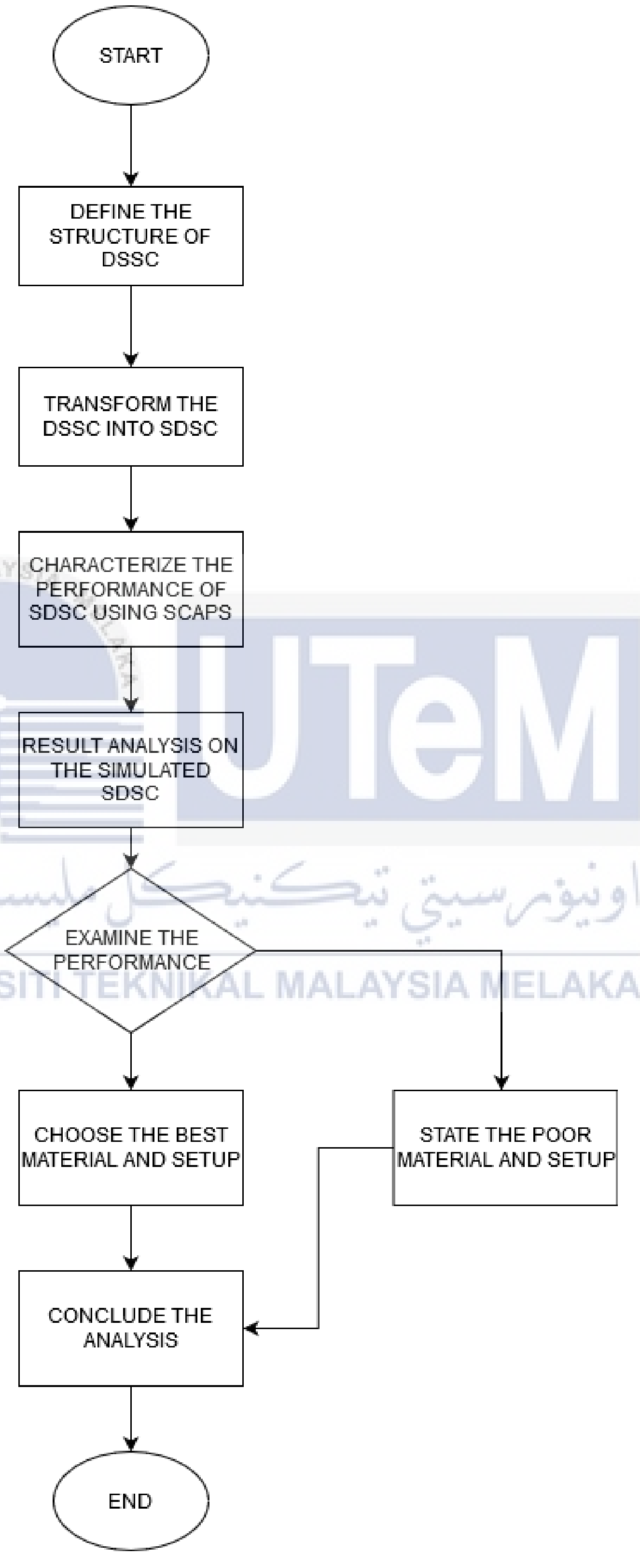

Figure 2 : Flow chart of project

Based on the flow chart, first we need to define the structure of DSSC on SCAPS by referring the journal that has the parameter of the structure. In SCAPS, the structure with most similarity to DSSC is solid state dye-sensitized solar cells (SDSC). Therefore, an SDSC structure build are two types of layer. These layer consists of electron transport layer (ETL) and hole transport material (HTM). Optimization of HTM layer is conducted in this project while it is the main objective to find the best efficiency among the type of HTM layer. By collecting the data on the journal, the structure of SDSC can be developed to run the simulation and to get the measurement. The measurements that need to collect to observe are Voltage open circuit (Voc), Short-circuit current density (Jsc), Fill Factor (FF) and Efficiency (eta%). Then, by varying the thickness of different layer, the performance of the DSSC can be determined. The results are based on each layer with different thickness. After that, the result are going into the analysis to find the best performance of DSSC. Effectiveness of the simulated SDSC depends to various type of parameters. Main focus of this project to observe the best efficiency by varying the layer thickness of both HTM and ETL, the annealing temperature, the electron and hole capture cross-section of defect at the interface, doping density of HTM (N_A) and ETL (N_D)

3.1.1 Define the structure of DSSC

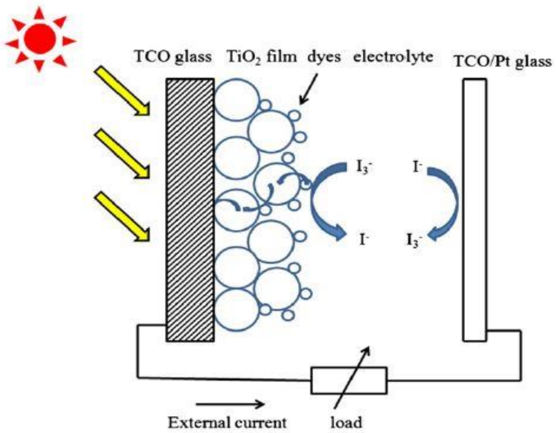

Figure 3 : Structure of DSSC

DSSC was developed as a sandwich constructed component. At the surface of the glass there is a thick nanoparticle film that works to enhance the light absorption as to increase the efficiency. The sandwich consists of 4 main parts which is a nanostructured wide bandgap semiconducting layer, electrode, dye molecule and electrolyte. Anodes of dye-sensitized solar cells are typically constructed using TiO2 thick film (~10 µm) that was deposited as a paste and sintered to produce electrical continuity. Moreover, the uniqueness of this nanoparticle film is to provide a large internal surface area. Internal surface area was the characteristic that will affect the conversion efficiency.

Firstly, the structure for this project was determined by choosing TiO2 as the photoanode while CuI, CuO and Cu2O as counter-electrode. Then, the structure includes electrolyte (I-/ I3–) act as to perform conductivity in the device. Dye was the agent to work as enhancement of electron transfer which acting as photosynthesis process. Finally, by choosing FTO glass to complete the working device structure.

3.1.2 Transforming the DSSC into SDSC

Purposely, in DSSC dye is an important part of the device. However, DSSC is not safe and cannot stand too long in the exposure of sun. Therefore, in this project DSSC will transform into SDSC by capturing almost all the criteria of DSSC. The only difference between DSSC and SDSC are the dye and electrolyte. In this project, the component are used to apply the DSSC are hole transport material (HTM) and electron transfer layer (ETL). Hence, SDSC is created and ready to do the analysis. Since the analysis is about simulating the device, the parameter of the device used for simulation using SCAPS-1D software was done by researcher[14].

3.1.3 SCAPS-1D

Numerical simulation is important and efficient way to explore the physical structure of a solar cell system without really creating a device. It can save both time and money on device development. A lot of simulation software has been built and applied to the study of solar cell systems such as AMPS-1D, PC1D, AFORS-HET and so on. SCAPS-1D is a one-dimensional simulation software developed by the University of Gent, Belgium. It has applied to the study of different types of solar cells.

Difference between SCAPS with other software which are SCAPS has build in operation window and a lot of models for grading, defects and recombination. The main features in SCAPS including materials and defects properties and can insert into 7 layers of material grading, as shown in Figure 4 and Figure 5, where a lot of grading regulation are given for almost all substance and defect parameters. While the defect definition panel function as to set in both bulky material and interface. There are five different types of defect and the distributions available in the software where it has variety of features that has significant value for solar cells, such as energy bands, concentrations, currents, I-V characteristics, C-V, C-f, and QE can be determined by SCAPS. SCAPS-1D can help most of researchers where it has compliant calculation and collectible data record functionality including single shot, batch calculation, curve fitting, data and diagram recording.

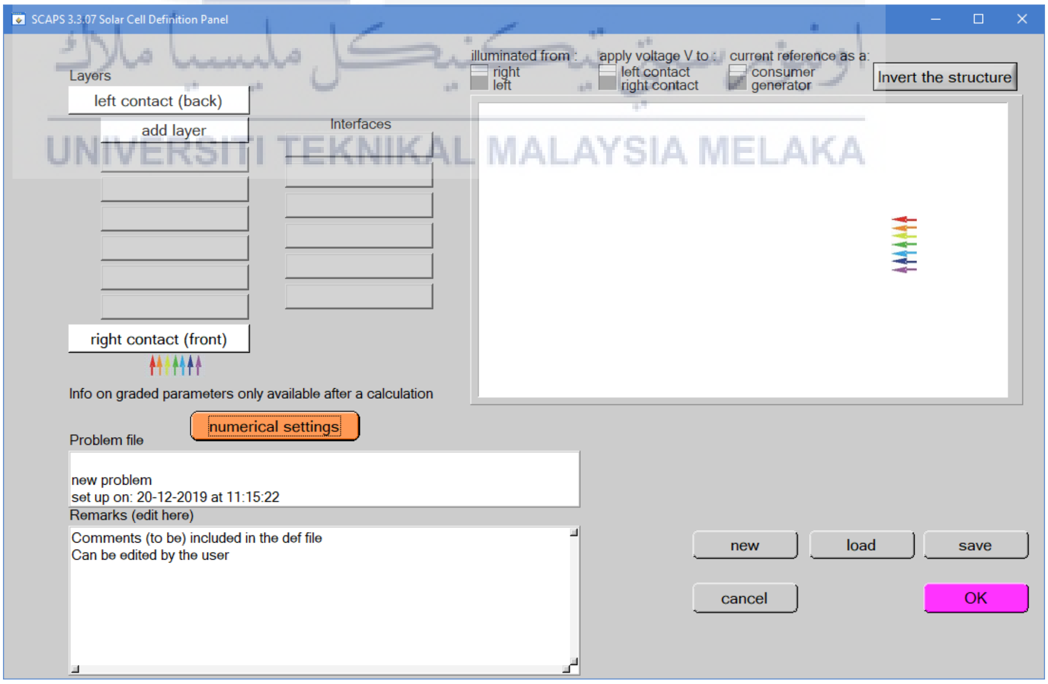

Figure 4 : Set problem panel

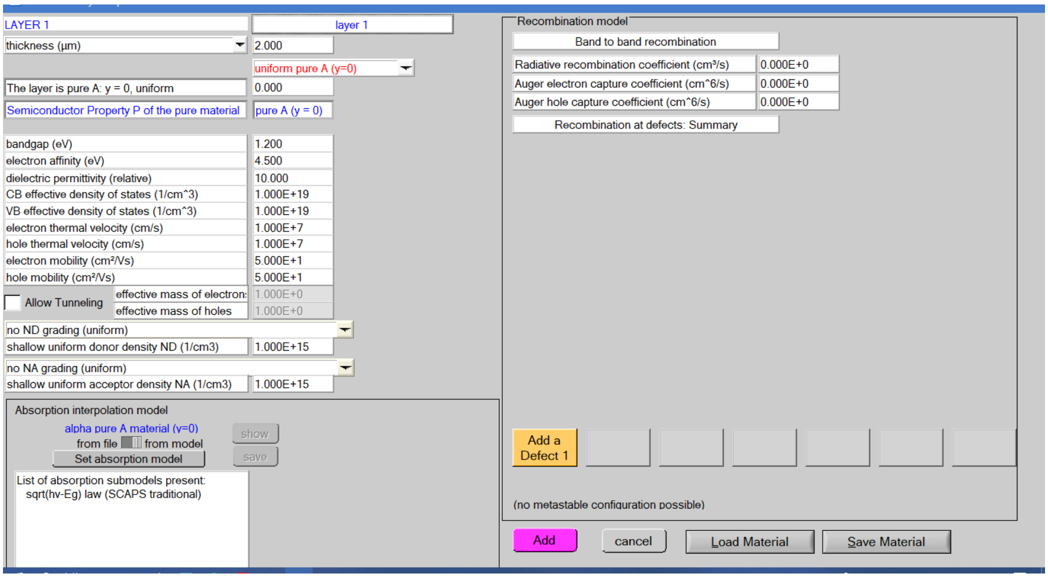

Figure 5 : Material and defect definition panel

There are characteristic that are fixed for the material and the parameter are required to insert into SCAPS software. All the parameter required from the research which are bandgap, electron affinity, dielectric permittivity, covalent bond, valence bond, electron mobility and hole mobility.

Table 2 : Parameter for TiO2/CuO

Layer	TiO2	CuO
Bandgap	3.20	1.51
Electron Affinity	4.20	4.07
Dielectric permittivity	10.00	18.10
CB	2.00E+17	2.20E+19
VB	6.00E+17	5.50E+20
Electron Mobility	1.00E+02	1.00E+02
Hole Mobility	2.50E+02	1.00E-01
Thickness	0.05	2.50

Table 3 : Parameter for TiO2/Cu2O

Layer	TiO2	Cu2O
Bandgap	3.20	2.20
Electron Affinity	4.20	3.20
Dielectric permittivity	10.00	7.11
CB	2.00E+17	2.00E+17
VB	6.00E+17	1.10E+19
Electron Mobility	1.00E+02	2.00E+02
Hole Mobility	2.50E+02	8.00E+01
Thickness	0.50	3.00

Table 4 : Parameter for TiO2/CuI

Layer	TiO2	CuI
Bandgap	3.20	3.10
Electron Affinity	3.90	2.10
Dielectric permittivity	9.00	6.50
CB	1.00E+19	2.50E+19
VB	1.00E+19	2.50E+19
Electron Mobility	2.00E+01	1.00E+02
Hole Mobility	1.00E+01	4.39E+01
Thickness	0.05	3.00

3.1.3.1 SCAPS-1D Panel

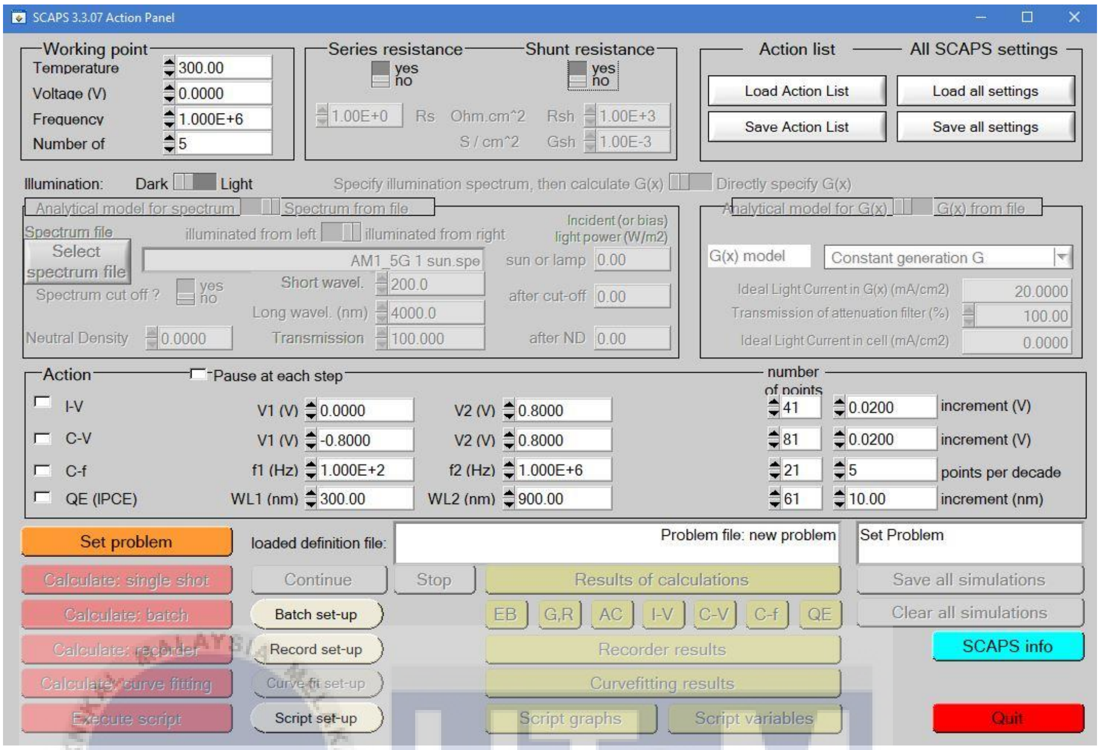

Figure 6 : SCAPS-1D Working Panel

After downloading the software, the working panel of SCAPS-1D shows on the figure 6 above. Inside the panel, there are a lot of parameter that plays a role to get a better conversion efficiency. Along with the research, the parameter that will manipulate the conversion efficiency is the working/annealing temperature. Other than that, the variable parameters that can manipulate the conversion efficieny is by executing the set problem panel as shown in Figure 4.

Then, by clicking the add layer, it will show the parameter for layer characteristic. All of these parameter can be obtain from the research which the parameters are shown as in Figure 5. While the parameter are shown as in

Table 2, 3 and 4. After all the parameter inserted, the illumination in the working panel need to turn on to the light as the conversion efficiency can be calculated as photovoltaic cells works from getting the sunlight under standard illumination (AM1.5G, 100mWcm−2). Therefore, to get the software to calculate the efficiency make sure to click the I-V and C-V in the action around the working panel.

3.1.3.2 Analysis 1 : Layer thickness

First analysis was about varying the layer thickness to find the optimal setup for best efficiency. The properties of layer thickness were choose based from the studies[17]. In this project, the layer thickness was tested in a big range and then the selected layer thickness was selected for TiO_2/CuO. At constant thickness of CuO (2.5µm), the value of layer thickness of TiO_2 (in µm) were 0.5, 1.0, 1.5, 2.0, 2.5, and 3. While at constant value of TiO_2 (0.05µm), the value of layer thickness (in µm) of CuO were 1.5, 2.0, 2.5, 3.0, 3.5, and 4. Table 5 below shows the parameter for layer thickness of TiO_2/CuO.

Table 5 : Thickness Value for TiO_2/CuO

Constant Thickness of CuO	Thickness of TiO_2 (µm)	Constant Thickness of TiO_2	Thickness of CuO
2.5	0.50	0.05	1.50
	1.00		2.00
	1.50		2.50
	2.00		3.00
	2.5		3.50
	3		4.00

Next test for Cu2O as HTM layer, at constant thickness of Cu2O (3µm), the value of layer thickness of TiO2 (in µm) were 0.5, 0.7, 0.9, 1.1, 1.3, and 1.5. While at constant value of TiO2 (0.3µm), the value of layer thickness (in µm) of Cu2O were 1.0, 1.4, 1.8, 2.2, 2.6, and 3. Table 6 below shows the parameter for layer thickness of TiO2/Cu2O.

Table 6 : Thickness Value for TiO2/Cu2O

Constant Thickness of Cu2O	Thickness of TiO2 (µm)	Constant Thickness of TiO2	Thickness of CuO
3	0.50	0.3	3.00
	0.70		2.60
	0.90		2.20
	1.10		1.80
	1.3		1.40
	1.5		1.00

Lastly, test for CuI as HTM layer, at constant thickness of CuI (3µm), the value of layer thickness of TiO2 (in µm) were 0.05, 0.10, 0.15, 0.20, 0.25, and 0.30. While at constant value of TiO2 (0.05µm), the value of layer thickness (in µm) of CuI were 1.0, 2.0, 3.0, 4.0, 5.0, and 6.0. Table 7 below shows the parameter for layer thickness of TiO2/CuI.

Table 7 : Thickness value for TiO2/CuI

Thickness of CuI	Thickness of TiO2 (µm)	Thickness of TiO2	Thickness of CuI
3	0.30	0.05	1.00
	0.25		2.00
	0.20		3.00
	0.15		4.00
	0.10		5.00
	0.05		6.00

3.1.3.3 Analysis 2 : Annealing temperature

Annealing temperature also affect the conversion efficiency, where in the test for TiO2/CuO the value of temperature range from 190K~250K. While for TiO2/Cu2O the value of temperature range from 290K~360K and for TiO2/CuI the value of temperature range from 290K~360K where the value of temperature measured in Kelvin(K).

3.1.3.4 Effect of the defect at the interface

Defect at the interface are working on the electron and hole capture cross-section of the defect. It is define as the probability of trap capturing the free carrier. Electron and hole capture cross-sections of defect at n-TiO2/p-

CuO interface range of 1.00E−17 to 1.00E−19 cm2. In general, it is believed that Coulombic attraction between the trap and the carrier increases capture cross-section, while Coulombic repulsion decreases the capture cross-section, by orders of magnitude. Therefore, this method is used to find the best efficiency.

3.1.3.5 Doping density

In general, higher doping usually contributes to decreased conductivity due to the higher concentration of carriers. Doping density occurred at both HTM and ETL where in HTM it has N_A and ETL it has N_D. The value of N_A and N_D was determined with value range of 1.00E+15~1.00E+17.

3.1.4 Result and analysis

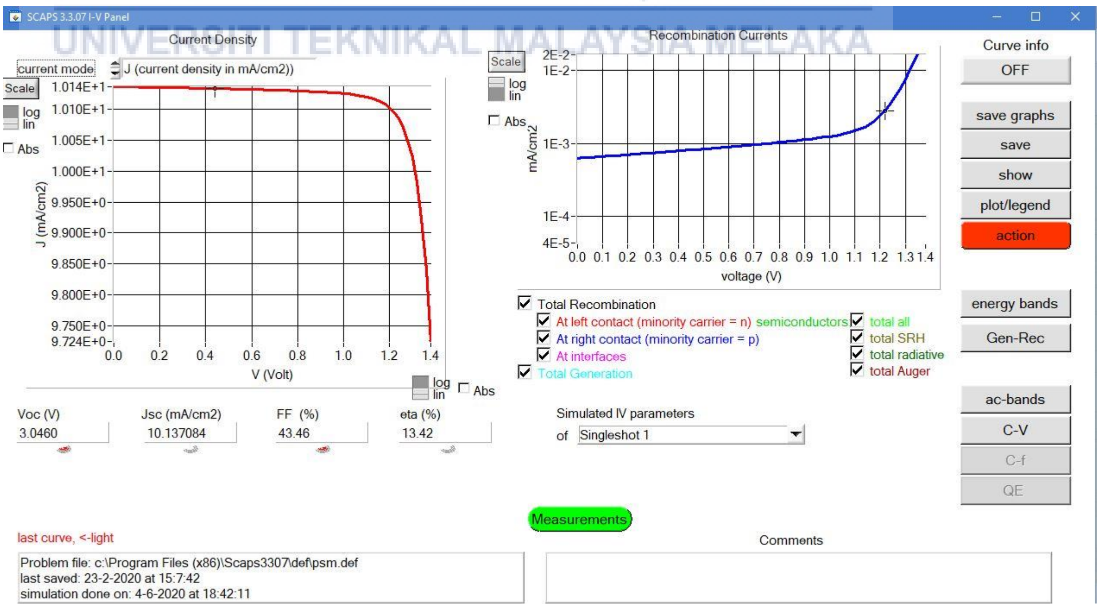

Figure 7 : I-V Characteristic

Parameters were set and the software are ready to run. Run the software by clicking the calculate : single shot and then click the I-V at the working panel for both process. Results will be shown as in Figure 7. All the result for analysis will be recorded from the I-V panel. Voltage open circuit (Voc), Current density in short circuit (Jsc), Fill Factor (FF) and efficiency (eta%) were recorded in Microsoft Excel for futher analysis. These process is applicable to run the test for all HTM (CuO, Cu_2O and CuI). Therefore, throughout all of the analysis, conclusion can be made where which material has the optimum characteristic for the best efficiency

CHAPTER 4

RESULTS AND DISCUSSION

In this chapter, all the data and results collected after every process has already run through. Data are recorded in Microsoft Excel and the graph were made from Microsoft Excel as well for easier analysis. Every data were sort out in table so that it is easier to trace the data if there are any error while doing the analysis. Main objective is to find the best optimization of HTM in SDSC through layer thickness, annealing temperature, effect of the defect at the interface and doping density. HTM that used in this project are CuO, CuI and Cu2O. The data are voltage open circuit (Voc), current density in short circuit (Jsc), fill factor (FF) and conversion efficiency (eta%).

4.1.1.1 Solid-State Dye-Sensitized Solar Cells (TiO2 with CuO)

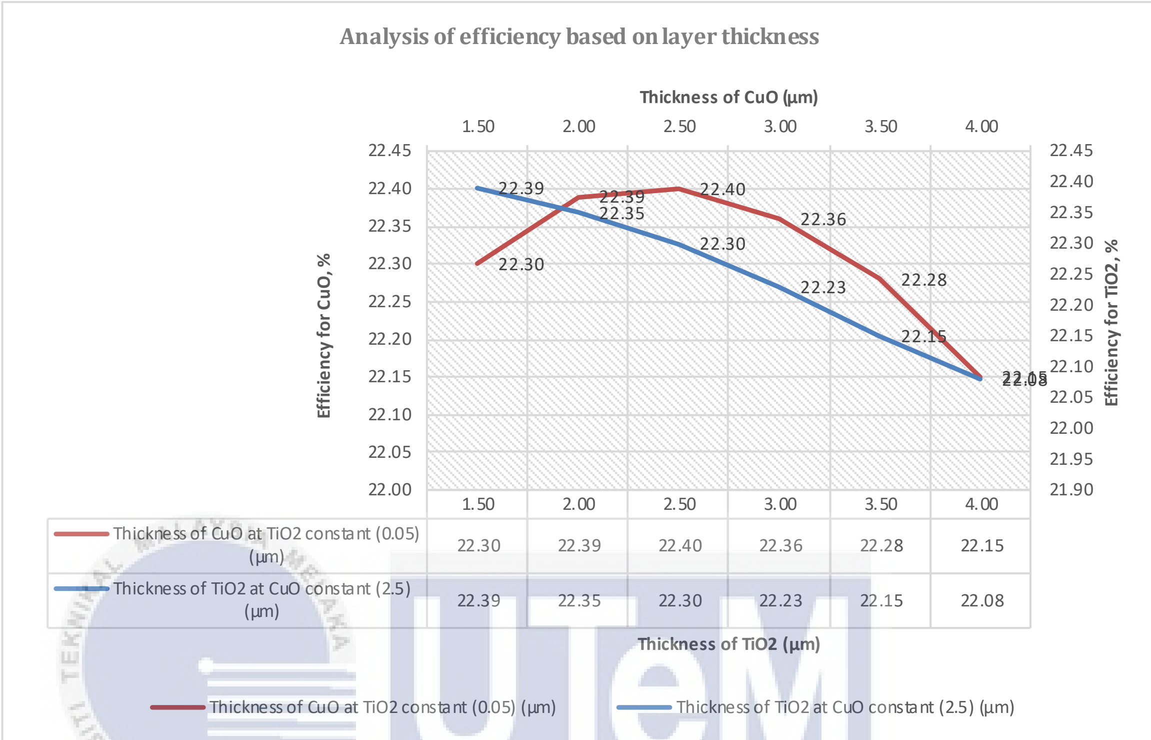

Figure 8 : Effectiveness of the layer thickness of CuO

In this segment, the results are about layer thickness that effect conversion efficiency for CuO as HTM layer. Results show that when the layer thickness increase for both layer, the efficiency also decreasing. 22.4% is the best efficiency recorded for layer thickness of TiO2 (0.05 µm) and CuO (2.5 µm).

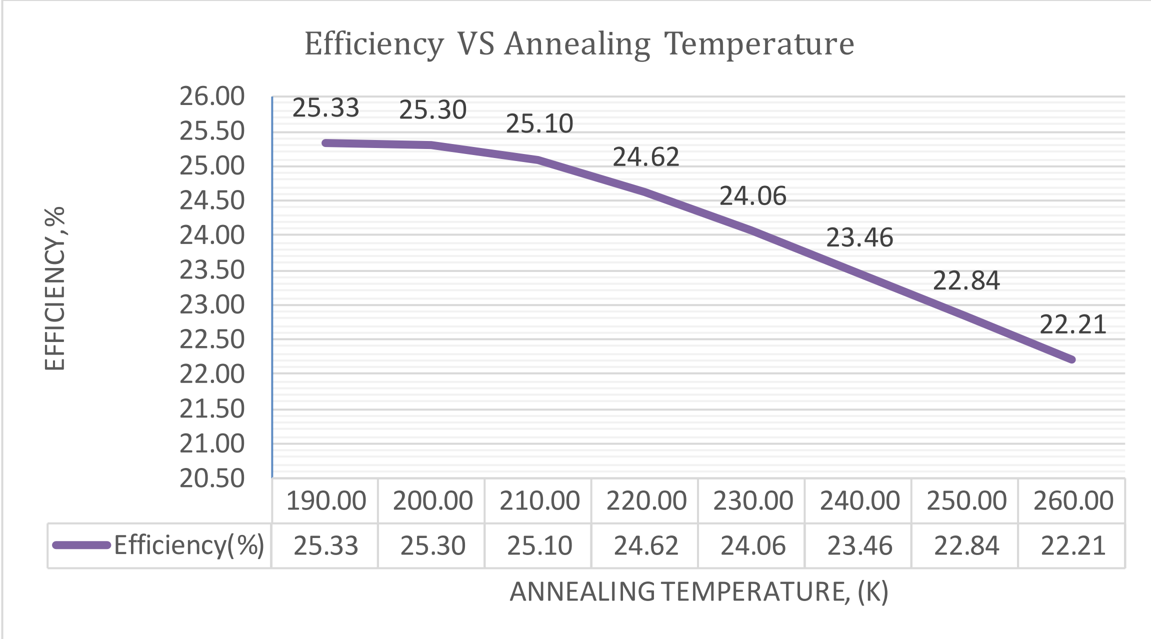

Figure 9 : Effect of annealing temperature for TiO2/CuO

Next analysis for TiO2/CuO is for annealing temperature that effect conversion efficiency. Results show that when the temperature increase, the efficiency is decreasing. 25.33% is the best efficiency recorded for temperature at 190K. Table below shows the parameter required to get this efficiency.

Table 8 : Parameter to get 25.33% at 190K

Layer	TiO2	CuO
Bandgap	3.20	1.51
Electron Affinity	4.20	4.07
Dielectric permittivity	10.00	18.10
CB	2.00E+17	2.20E+19
VB	6.00E+17	5.50E+20
Electron Mobility	1.00E+02	1.00E+02
Hole Mobility	2.50E+02	1.00E-01
Thickness	0.50	3.00

Table 9 : Result for annealing temperature

Operating Temperature (K)	Voc(V)	Jsc(mA/cm2)	FF(%)	Efficiency(%)
190.00	5.04	33.47	15.01	25.33
200.00	3.64	33.52	20.72	25.30
210.00	2.30	33.56	32.45	25.10
220.00	1.45	33.60	50.46	24.62
230.00	1.05	33.63	68.12	24.06
240.00	0.88	33.66	78.79	23.46
250.00	0.82	33.68	82.94	22.84
260.00	0.79	33.71	83.39	22.21

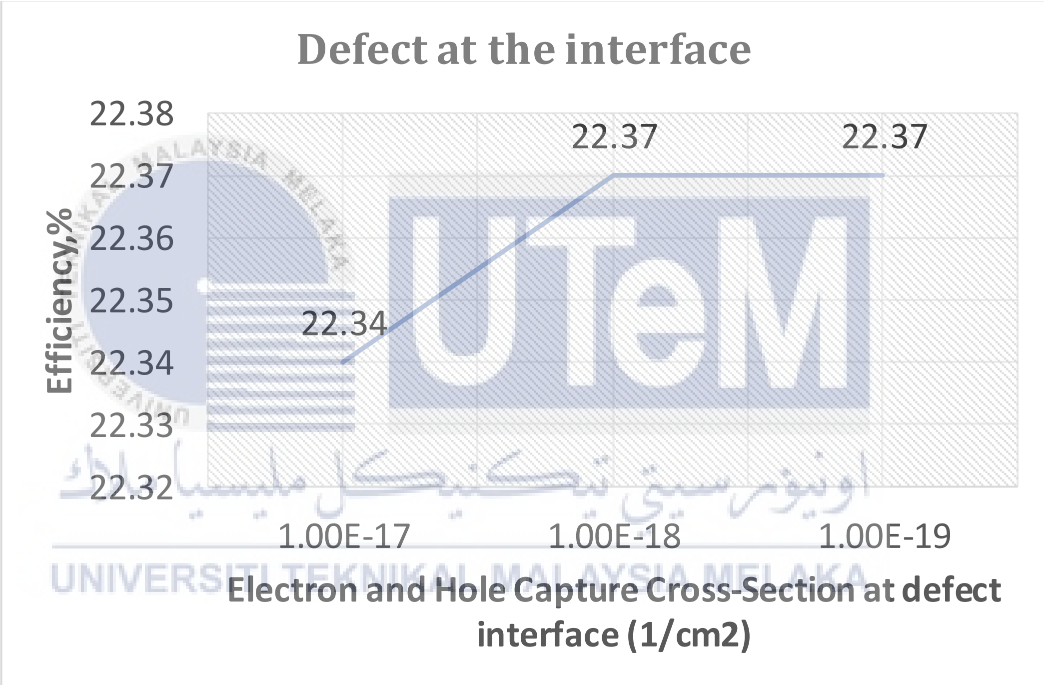

Figure 10 : Efficiency when controlling the defect of interface

This results show that by varying the electron and hole capture cross-section at defect interface from 1.00E-17~1.00E-19, tha conversion efficiency increase. Even though, the results show increasing but it can not achieved the best efficiency at the annealing temperature of 190K with 25.33%.

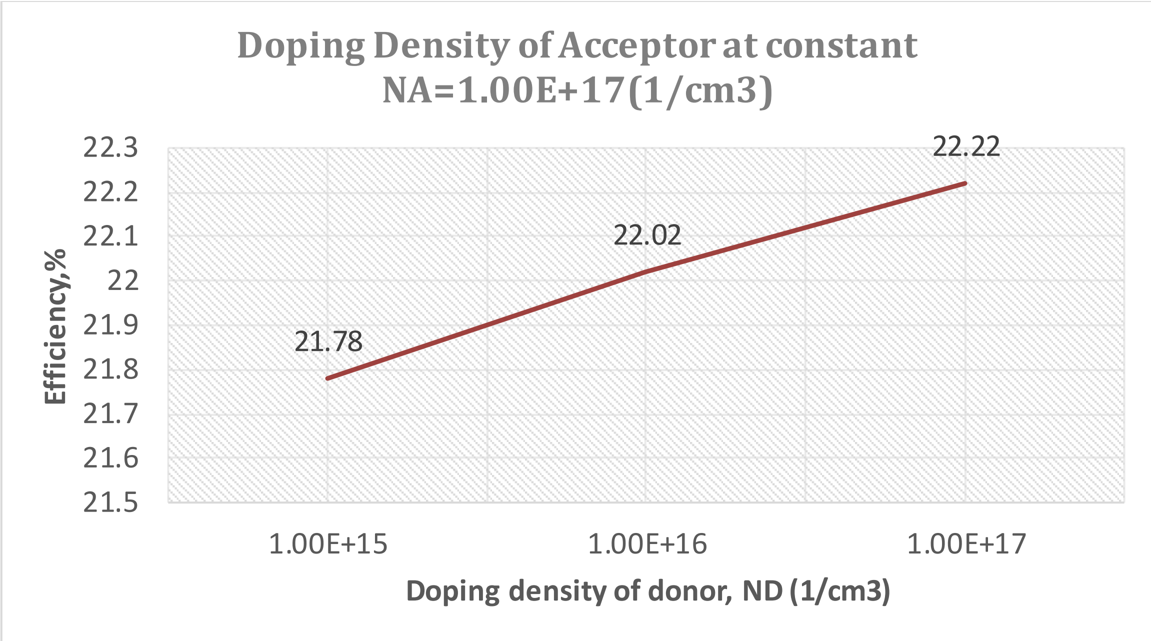

Figure 11 : Effect of controlling the doping donor density

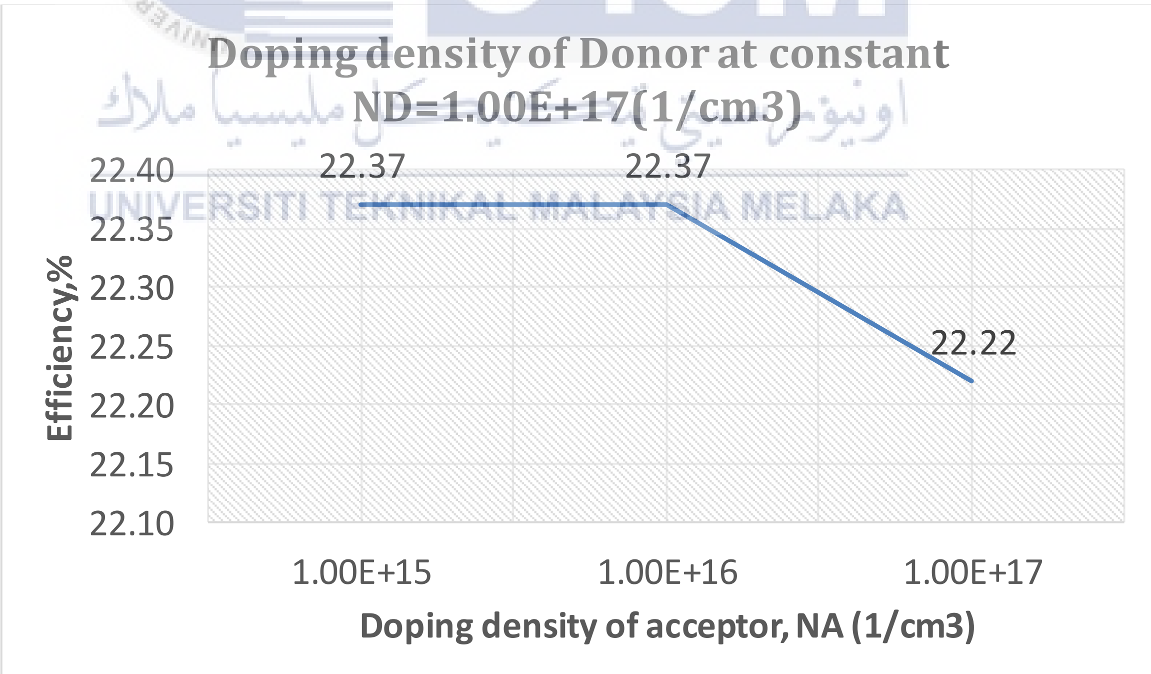

Figure 12 : Effect of controlling the acceptor donor density

Analysis for doping density resulting as shown in Figure 11 & 12. In this analysis, the best efficiency were recorded at doping density of donor N_D at 1.00E+17(1/cm^3) and doping density of acceptor at 1.00E+15(1/cm^3) at 22.37 of efficiency.

4.1.1.2 Solid-State Dye-Sensitized Solar Cells (TiO2 with CuI)

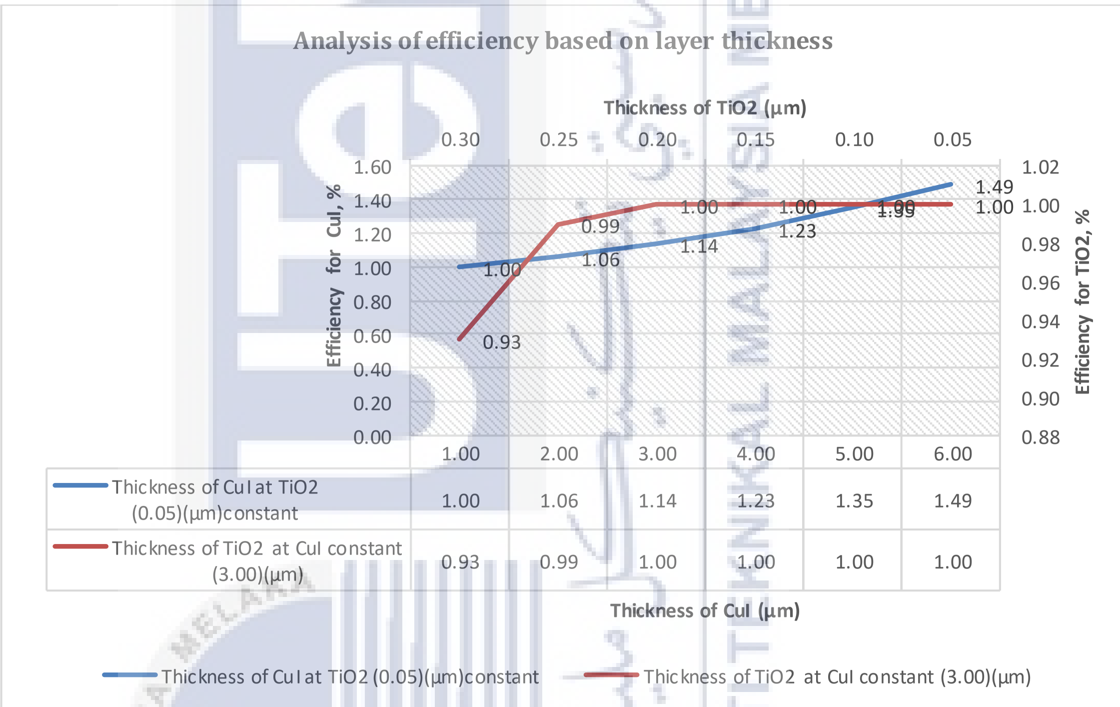

Figure 13 : Effectiveness of the layer thickness of CuI

In this segment, the results are about layer thickness that effect conversion efficiency for CuI as HTM layer. Results show that when the layer thickness increase for both layer, the efficiency also increasing. 1.49% is the best efficiency recorded for layer thickness of TiO2 (0.05µm) and CuI (6.0µm).

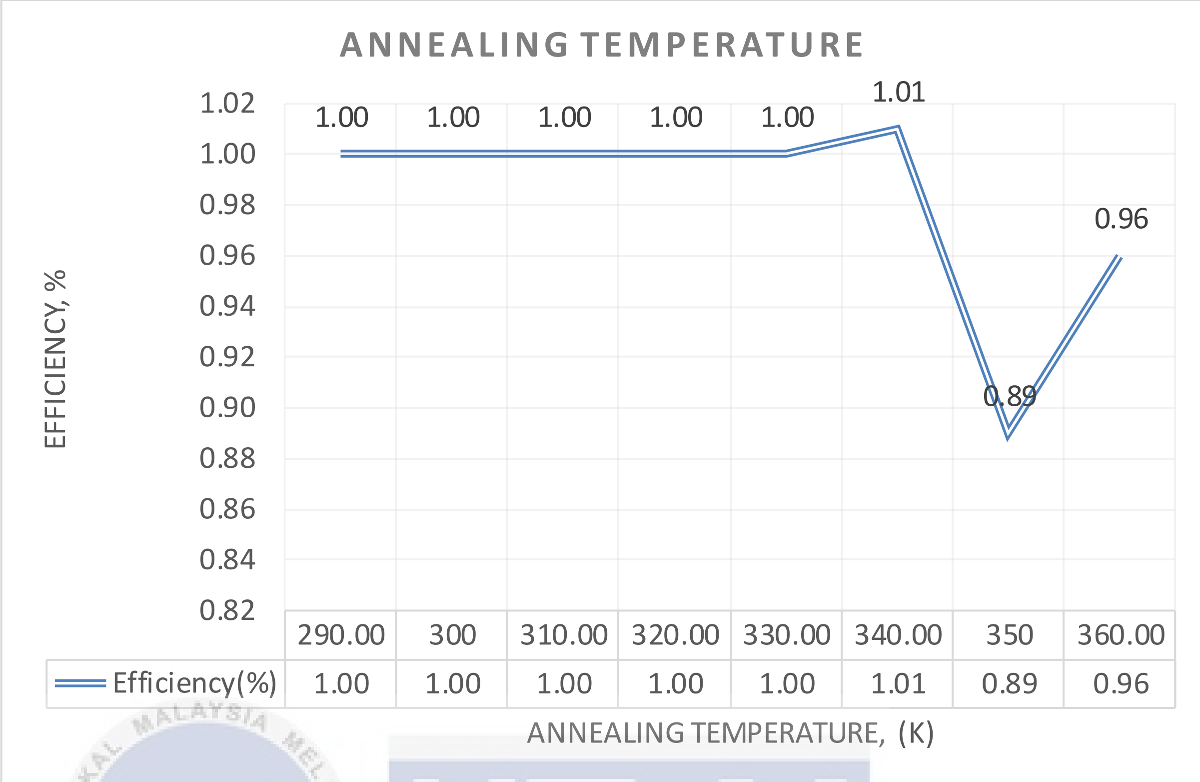

Figure 14 : Effect of annealing temperature for TiO2/CuI

Next analysis for TiO2/CuI is for annealing temperature that effect conversion efficiency. Results show that when the temperature increase, the efficiency will increase and a slight decrease and continue increasing. Every material have its best annealing temperature. If the material have a wide bandgap, therefore it can sustain higher temperature in conducting electricity. 1.01% is the best efficiency recorded for temperature at 350K. Table below shows the parameter required to get this efficiency.

Table 10 : Parameter for annealing temperature of TiO2/CuI

Layer	TiO2	CuI
Bandgap	3.20	3.10
Electron Affinity	3.90	2.10
Dielectric permittivity	9.00	6.50
CB	1.00E+19	2.50E+19
VB	1.00E+19	2.50E+19
Electron Mobility	2.00E+01	1.00E+02
Hole Mobility	1.00E+01	4.39E+01
Thickness	0.05	3.00

Table 11 : Result for annealing temperature of TiO2/CuI

Operating Temperature (K)	Voc(V)	Jsc(mA/cm2)	FF(%)	eta(%)
290.00	2.48	0.92	43.62	1.00
300.00	2.52	0.92	42.85	1.00
310.00	2.56	0.93	42.20	1.00
320.00	2.58	0.93	41.69	1.00
330.00	2.59	0.94	41.35	1.00
340.00	2.57	0.95	41.27	1.01
350.00	2.59	1.16	29.82	0.89
360.00	2.30	1.18	35.45	0.96

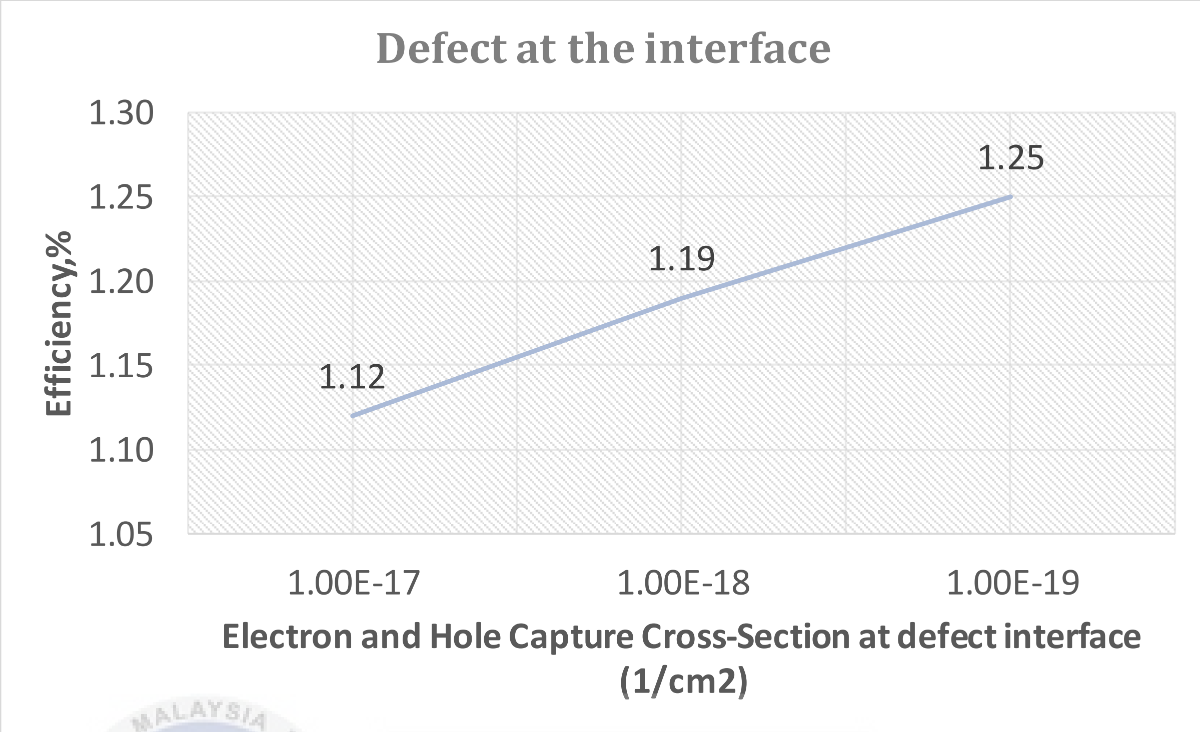

Figure 15 : Efficiency when controlling the defect of interface

This results show that by varying the electron and hole capture cross-section at defect interface from 1.00E-17~1.00E-19, tha conversion efficiency increase. Even though, the results show increasing but it can not achieved the best efficiency at the layer thickness of TiO_2 (0.05µm) and CuI (6.0µm) at 1.49% of efficiency.

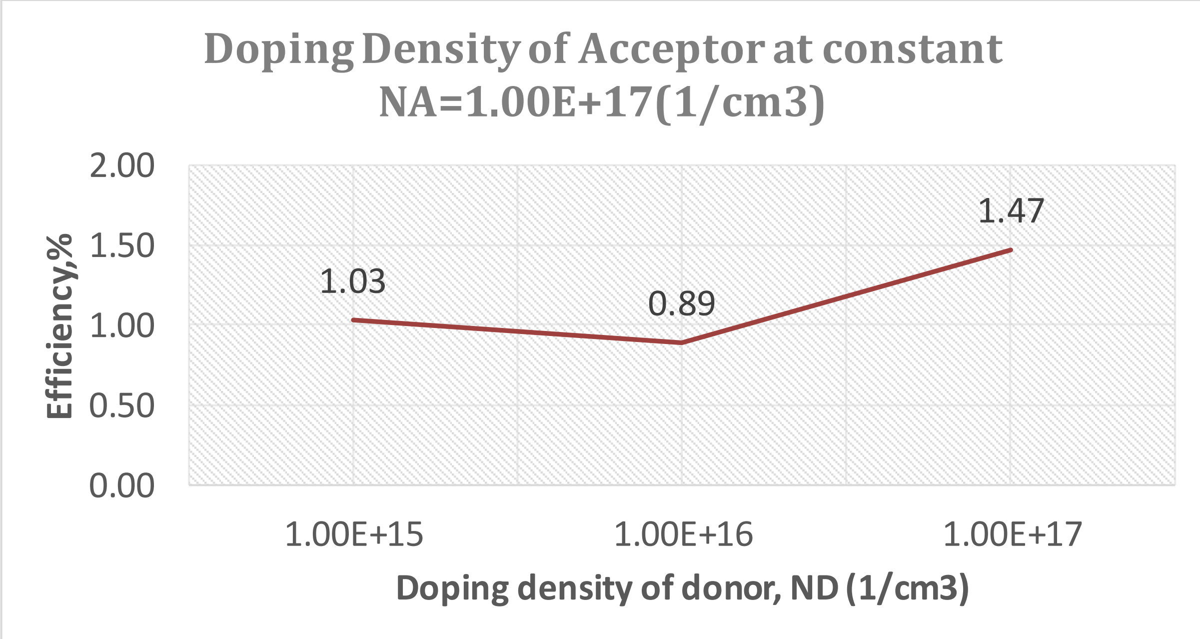

Figure 16 : Effect of controlling the doping donor density

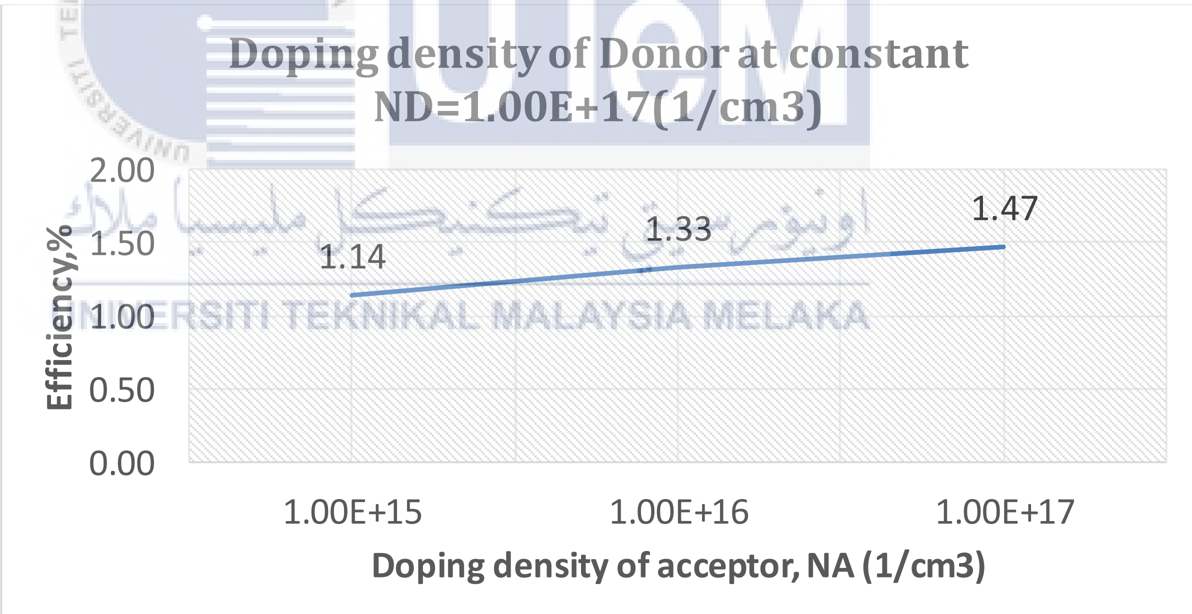

Figure 17 : Effect of controlling the doping acceptor density

Analysis for doping density resulting as shown in figure 16 & 17. In this analysis, the best efficiency were recorded at doping density of donor N_D at 1.00E+17(1/cm^3) and doping density of acceptor at 1.00E+17(1/cm^3) at 1.7% of efficiency

4.1.1.3 Solid-State Dye-Sensitized Solar Cells (TiO2 with Cu2O)

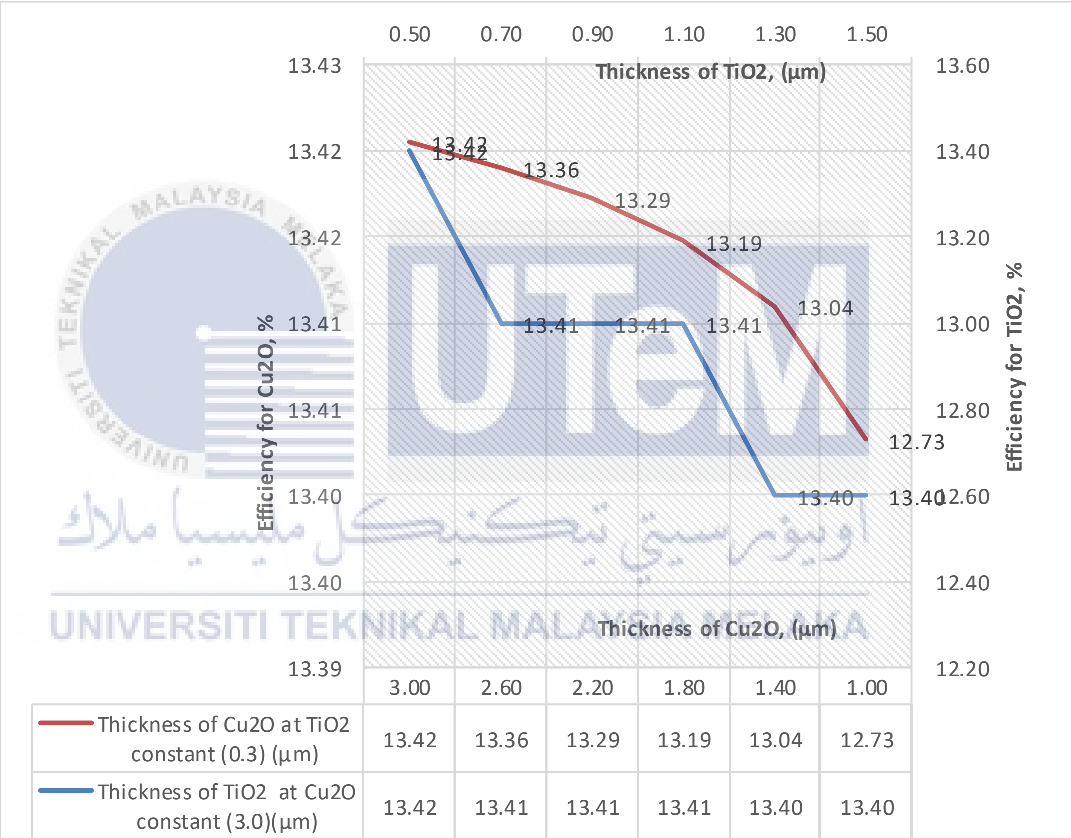

Figure 18 : Effectiveness of the layer thickness of Cu2O

In this segment, the results are about layer thickness that effect conversion efficiency for Cu2O as HTM layer. Results show that when the layer thickness increase for both layer, the efficiency will decreasing. 13.42% is the best efficiency recorded for layer thickness of TiO2 (0.5µm) and CuI (3.0µm).

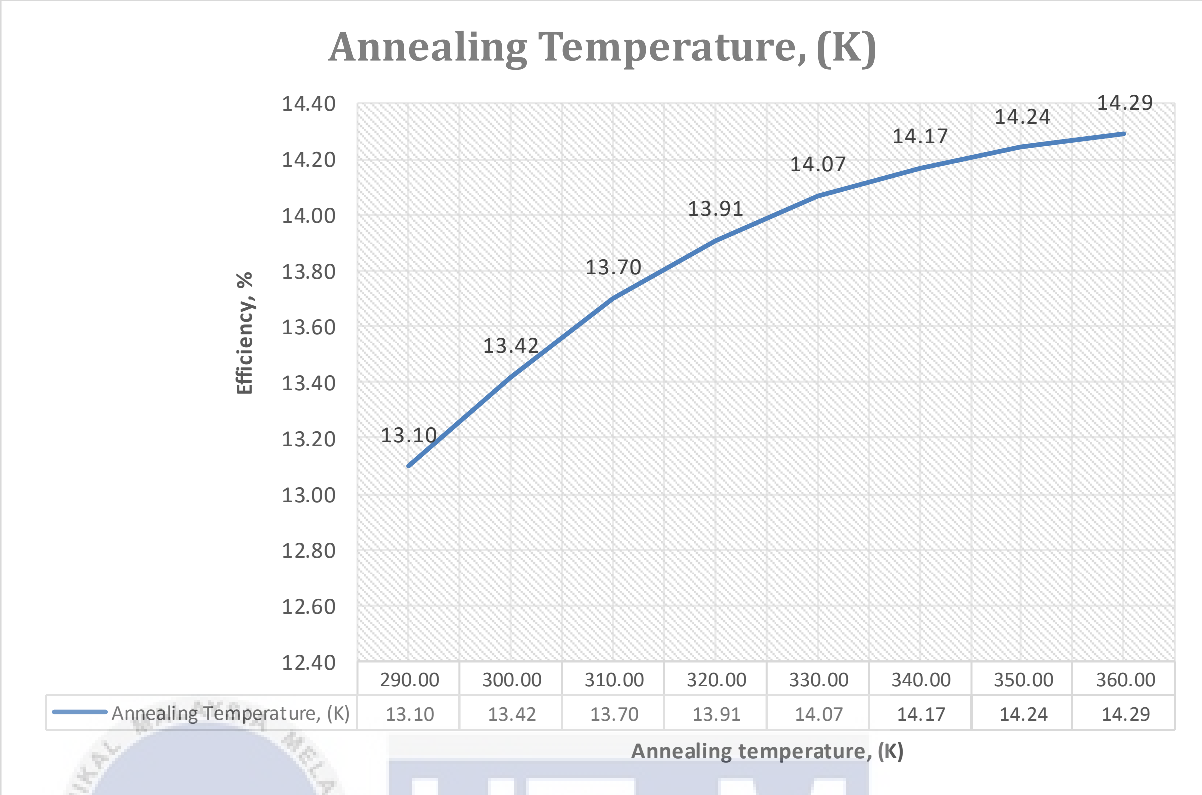

Figure 19 : Effect of annealing temperature for TiO2/Cu2O

Next analysis for TiO2/Cu2O is for annealing temperature that effect conversion efficiency. Results show that when the temperature increase, the efficiency will increase. 14.29% is the best efficiency recorded for temperature at 360K. Table below shows the parameter required to get this efficiency.

Table 12 : Parameter setting for annealing temperature

Layer	TiO2	Cu2O
Bandgap	3.20	2.20
Electron Affinity	4.20	3.20
Dielectric permittivity	10.00	7.11
CB	2.00E+17	2.00E+17
VB	6.00E+17	1.10E+19
Electron Mobility	1.00E+02	2.00E+02
Hole Mobility	2.50E+02	8.00E+01
Thickness	0.30	3.00

Table 13 : Result for annealing temperature of TiO2/Cu2O

Operating Temperature (K)	Voc(V)	Jsc(mA/cm2)	FF(%)	eta(%)
290.00	2.56	10.03	51.05	13.10
300.00	3.05	10.14	43.44	13.42
310.00	3.81	10.22	35.20	13.70
320.00	4.97	10.29	27.21	13.91
330.00	6.71	10.34	20.28	14.07
340.00	9.26	10.37	14.75	14.17
350.00	9.32	10.42	14.45	14.24
360.00	9.46	10.50	13.98	14.29

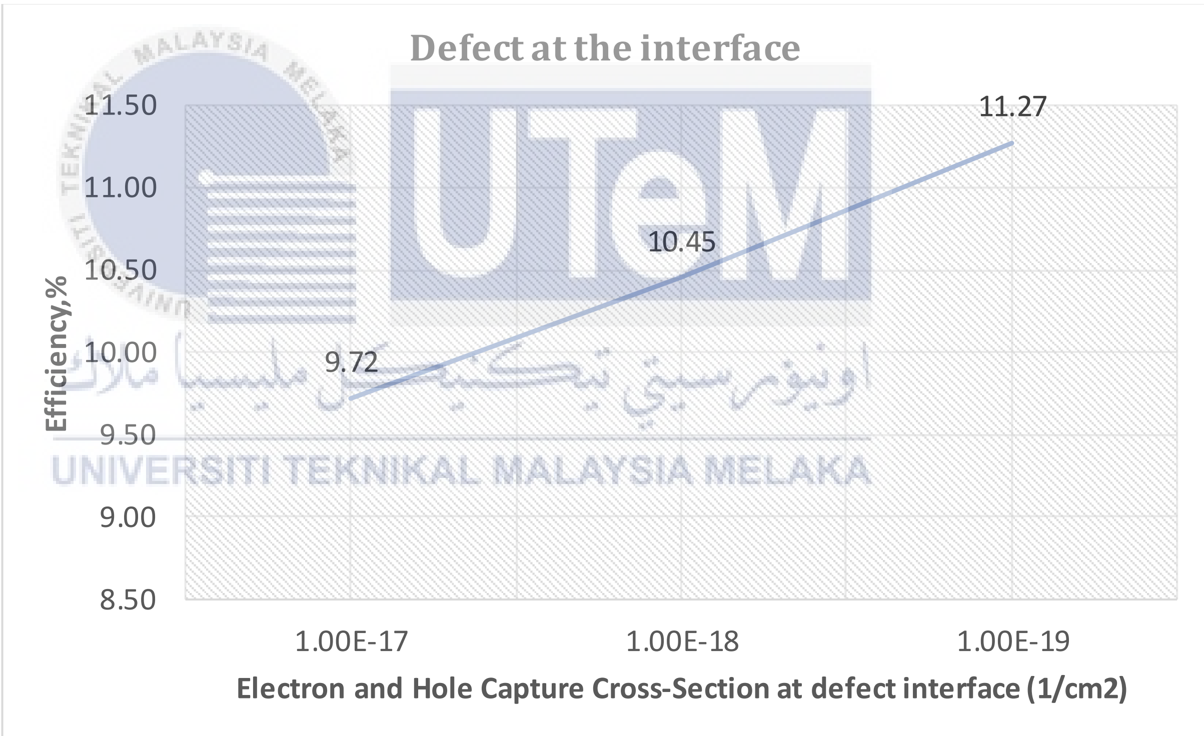

Figure 20 : Efficiency when controlling the defect of interface

This results show that by varying the electron and hole capture cross-section at defect interface from 1.00E-17~1.00E-19, the conversion efficiency increase. Even though, the results show increasing but it can not achieved the best efficiency at the layer thickness of TiO2 (0.5µm) and CuI (3.0µm) with 13.42% of efficiency.

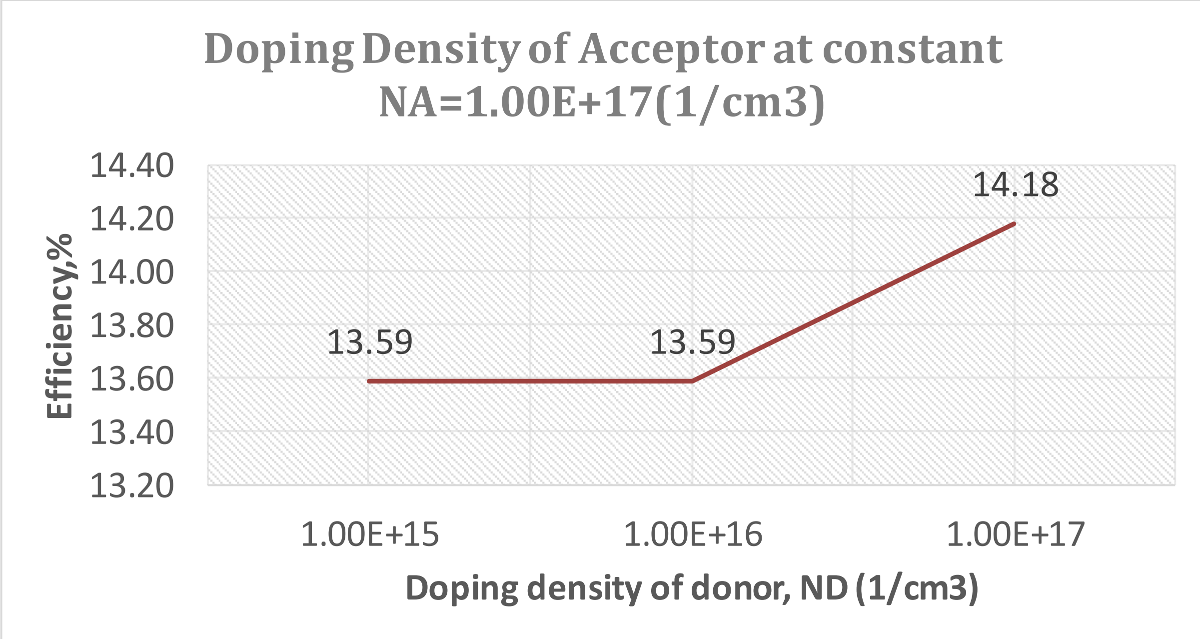

Figure 21 : Effect of controlling the doping donor density

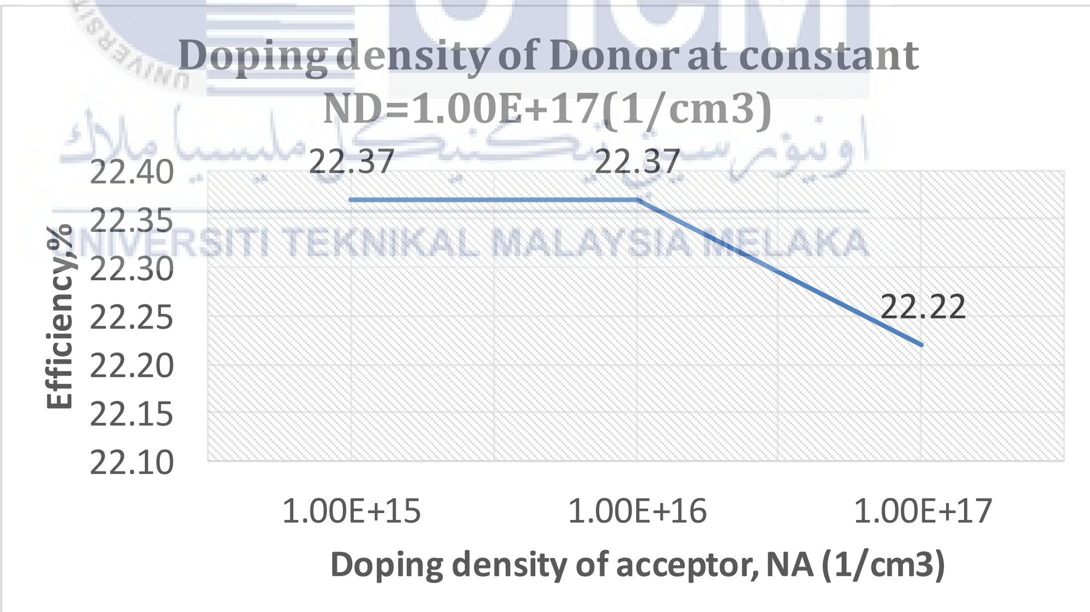

Figure 22 : Effect of controlling the doping acceptor density

Analysis for doping density resulting as shown in Figure 21 & 22. In this analysis, the best efficiency were recorded at doping density of donor N_D at 1.00E+17(1/cm^3) and doping density of acceptor at 1.00E+17(1/cm^3) at 1.7% of efficiency.

CHAPTER 5

CONCLUSION AND FUTURE WORKS

Among all of the HTM, it seems like CuO has the biggest efficiency at 25.33%. It is a successful to simulate in SCAPS-1D and verify HTM layer by varying the thickness value, the annealing temperature, the electron and hole capture at defect interface and by using the doping density can affect the conversion efficiency. SCAPS-1D simulation is successful with applying CuO, Cu2O and CuI as HTM layer in SDSC. Therefore, CuO will be picked as the best HTM layer while CuI was the worst within this project.

Finally, for futher work this project need an improvement in conversion efficiency. Therefore, a lot of studies needed to increase the efficiency. A lot of improvement needed for CuI as in this project it does not reach higher. In addition, more research needed for annealing temperature to find what does affect the efficiency and temperature.

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