Stability and Degradation Factors of Natural Dyes as Photosensitizer in Solar Cell

by

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A thesis submitted in fulfillment of the requirements for the degree of Master of Science in (Microelectronic Engineering)

School of Microelectronic Engineering
UNIVERSITI MALAYSIA PERLIS

2015

ACKNOWLEDGEMENT

I would like to thank Dr. Mukhzeer Mohamad Shahimin for giving me an interesting research topic and for his guidance from the beginning till the end of my research. I would also like to thank the Failure Analysis Laboratory and Tun Abdul Razak Laser Laboratory (TAReL), School of Microelectronic Engineering (SoME), Universiti Malaysia Perlis for providing the facilities in carrying out this work, especially Mr. Bahari and their helping hand in practical problems. A big appreciation also to Mr. Mohd Hishamuddin Che Mat from Institute of Sustainable Agrotechnology, Universiti Malaysia Perlis, for the cooperation to provide the freshest fruits for this research and also for consultation regarding this matter.

I would like to thank my parents, my fiance and all my family for their never ending support during my studies. The dearest and greatest thanks to all final year project's students of Photonic Engineering, School of Microelectronic Engineering under the supervision of Dr. Mukhzeer Mohamad Shahimin, for their invaluable help, and unconditional support during the work.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF SYMBOLS

η	Efficiency
θ	Theta
Ω	Resistance (Ohm)
V_{oc}	Open Circuit Voltage
V_{max}	Maximum Voltage
I_{sc}	Short Circuit Current
J_{sc}	Current Density
P_{in}	Input Power
P_{max}	Maximum Power
FF	Fill Factor
I_3^-	Triiodide
I^-	Iodide
TiO_2	Titanium Dioxide
SiH_4	Silane
Nb_2O_5	Niobium Pentoxide
WO_3	Tungsten Trioxide
Ta_2O_5	Tantalum Pentoxide
W	Power (Watt)
℃	Temperature (Degree Celcius)
E_g	Energy Bandgap
E_g	Fermi Level
E_{FC}	Energy Level Conduction Band
E_{FV}	Energy Level Valence Band
eV	Electron Volt

LIST OF ABBREVIATIONS

DSSCs	Dye-sensitized Solar Cells
PV	Photovoltaic
CIGs	Copper indium Gallium Selenide
CdTe	Cadmium Telluride
CdSe	Cadmium Selenide
CdS	Cadmium Sulfide
Cd	Cadmium
Pb	Plumbum
Se	Selenide
Si	Silicon
a-Si	Amorphous Silicon
PECVD	Plasma Enhanced Deposition
ZnO	Zinc Oxide
AM	Air Mass
TCO	Transparent Conductive Oxide
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Occupied Molecular Orbital
QV	Maximum Potential
CE	Counter Electrode
UV-Vis	Ultra Violet Visible
FTO	Fluorine Tin Oxide
ITO	Indium Tin Oxide
C343	Coumarin 343
COOH	Carboxyl
HTM	Electron Hole Transport Material
Pt	Platinum
MWCNT	Multiwall Carbon Nanotube
CBNT	Carbon Black Nanotube
Ti	Titania

Faktor-faktor Kestabilan dan Degradasi Pewarna Semulajadi Sebagai Foto Pemeka Dalam Sel Suria

ABSTRAK

Sel suria adalah sumber kuasa yang paling berpotensi sebagai sumber yang bersih dan berterusan, dijana daripada radasi suria. Walaubagaimanapun, sel suria berhadapan dengan beberapa isu berkaiatan dengan kestabilan jangka panjang di mana memerlukan perhatian dan diperbetulkan. Projek ini menyiasat prestasi foto pemeka warna sel suria daripada segi kestabilan dan degradasi. Sel difabrikasi menggunakan tujuh jenis pewarna semulajadi yang diekstrak daripada Rosella, Bawang Sabrang, Cherry Barbados, Mulberry, Ardisia, Oxalis Triangularis, dan mangga Harum Manis sebagai foto pemeka. Pewarna tulen diekstrak di dalam air dan etanol dengan nisbah yang sama, digunakan pada filem nipis titanium dioksida. Pewarna diekstrak pada empat suhu berbeza (suhu bilik, 50℃, 75℃ dan 100℃) untuk mendapatkan keadaan paling optimum pada sel. Berdasarkan keputusan, Rosella mencapai kecekapan paling tinggi iaitu 1.05% pada suhu bilik berbanding dilaporkan oleh Wongcharee iaitu 0.37%. Selepas sel disimpan selama 24 jam, Mulberry menghasilkan keputusan yang konsisten dalam pelarut etanol dan air yang menunjukkan kriteria sebagai foto pemeka yang stabil. Mulberry mencapai kecekapan yang tinggi iaitu 0.33% dalam pelarut air pada suhu bilik dan 0.22% pada suhu 50℃ (suhu optimum) dengan penurunan kecekapan kepada 0.21% selepas disimpan selama 24 jam, selari dengan nilai arus voltan yang boleh diterima berbanding pewarna lain. Variasi suhu pewarna yang diekstrak dalam pelarut menunjukkan suhu optimum pewarna pemeka adalah berbeza, yang mana berkait rapat dengan kestabilan dan degradasi pewarna. Walaubagaimanapun ada di anatara pewarna, menghasilkan keputusan yang tidak boleh diaplikasi sebagai sel suria disebabkan oleh nilai isikan faktor yang tinggi selepas keadaan pewarna diubah. Ini mungkin disebabkan oleh ikatan antara molekul pewarna dengan permukaan titanium dioksida dan perubahan pH pewarna. Keseluruhan prestasi penukaran kecekapan yang dicapai oleh pewarna semulajadi; Rosella, Bawang Sabrang, Cherry Barbados, Mulberry, Ardisia, Oxalis Triangularis dan mangga Harum Manis dalam penyelidikan ini mempunyai potensi untuk dibangunkan sebagai foto pemeka sel suria.

Stability and Degradation Factors of Natural Dyes as Photosensitizer in Solar Cell.

ABSTRACT

Solar cell is the most potential power sources as a clean and inexhaustible source that utilize solar radiation. However, the solar cell technology is facing several issues regarding the long term stability which need to be concerned and corrected. The project investigated the performance of photosensitizer dye-sensitized solar cells in terms of stability and degradation of the cell. The cell was fabricated with seven types of natural dye extract which are Rosella, Bawang Sabrang, Cherry Barbados, Mulberry, Ardisia, Oxalis Triangularis and Harum Manis mango as a photosensitizer. The pure dyes are extracted in water and ethanol with the same ratio, and applied to titanium dioxide thin film. The dyes are extracted at four different temperatures (room temperature, 50℃, 75℃ and 100℃) to obtain the best optimum condition for the device. Based from the results, pure Rosella achieved a highest efficiency about 1.05% at room temperature, which is higher compared to the reported by Wongcharee et al., about 0.37%. After the cell have been stored for 24 hours, Mulberry show the most consistent results in both ethanol and water solvent, which indicate a criteria as stable photosensitizer. Mulberry achieved an efficiency up to 0.33% in water solvent at room temperature and 0.22% at temperature 50℃ (optimum temperature) with decreasing efficiency to 0.21% after 24 hours being stored with an acceptable value of current-voltage, compared to other dyes. The variation of dye extracting temperature in different extracting solvent showed different optimum condition of the dye sensitizer which is relatively related to the stability, and degradation of the dye. However, some of the dyes resulted inapplicable results due to the high value of Fill Factor that caused after varied the condition of the dyes. This might be due to the poor bonding between the dye molecule with titanium dioxide surface based from absorption spectrum and the pH changing of dyes. Overall performance of the conversion efficiency achieved by the novel natural dyes; Rosella, Bawang Sabrang, Cherry Barbados, Mulberry, Ardisia, Oxalis Triangularis, and Harum Manis mango in this research have a potential to develop as a photosensitizer in dye-sensitized solar cells.

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Nowadays, the fossil fuel, which is oil, coal and natural gas take place as the important energy sources which contribute to the overall usage of worldwide power consumption about 14 terawatts (TW) and expected to increase twicely within the upcoming 30 years (Grätzel et al., 2009) due to growing of human population and the improvement of living standards. The use of fossil fuels faces the two major problems regarding the limited resources and the environmental impact that have been urging the solutions by developing a clean sustainable energy. A nuclear, hydroelectric, geothermal, wind, biomass and solar (Lewis et al., 2006) is the different alternative power sources that existing today. In the 21st century, a clean and energy sustained will consider as one of the most significant challenges and issues that facing humanity and driving forces of the global economy (Lewis et al., 2006).

Among the different alternative power sources, solar energy shows the most potential energy sources which significantly increases across the world as a clean and inexhaustible. In fact, the sun provides the energy consumption approximately 100000 TW which is almost 10000 times more on earth (Grätzel et al., 2007). The efficient of worldwide solar potential which is about 600 TW (Hagfeldt et al., 2010) promising as abundant energy in the world with the nature's energy flow by utilizing directly from solar radiation to generate the electricity. Solar energy is growing as an energy technology in a variety of applications, ranging from small scale distribute power systems in electronic devices to megawatt scale that used in power plants. Moreover, the massive of theoretical and practical potential of the solar electricity bring about an attractive for large scale utilization. Many types of photovoltaic cells have been developed with different material that produced different conversion efficiency.

Photovoltaic technology has been known since 1839 by Alexandre Edmond Becquerel by discovered of the photovoltaic effect (Becquerel et al., 1839). In 1954, the first practical photovoltaic cell using diffused silicon p-n junction was designed at Bell Laboratories with an efficiency of 6%. Silicon solar cell has reached an electricity conversion efficiency up to 15% to 20% (Grant et al., 2002). Crystalline silicon solar cells dominate the largest market of the solar cell as first reported by Chapin et al. in 1954 (Chapin et al., 1954). However, high fabrication cost and highly purified silicon used toxic chemical in their manufacturing encouraged the searching for environmentally friendly with low cost solar cell. Furthermore, the cost calculations for the thin film photovoltaic technologies more or less are on the same line as standard silicon technology (Halme, 2002). Therefore, prevailing is necessary to produce the low cost and highly efficient solar cells by using new types of materials for photovoltaic operation in order to cut the cost.

Many kinds of solar cell have been explored and developed since 1950s. The trend of nanotechnology that booming in material engineering, recently emerged also in photovoltaic field that potentially lead for low cost solar cell materials and systems in the future. The materials also include the different types of synthetic organic and inorganic nanoparticle basically for organic solar cell. In order to develop new photovoltaic material, the chemistry and physics process are required. In 1991, Grätzel developed an unconventional photovoltaic system which is nanostructured dye sensitized solar cell (DSSC). Dye sensitized solar cell based on titanium dioxide, TiO_2 nanoparticle photoelectrode sensitized by organic dye is a unique photoelectrochemical as promising solar cell that offers alternatively for solar cell based on silicon as well as thin film generation. As compared to conventional solar cell principles, the semiconductor uses a light absorption and charge carrier together in order to operate, while DSSCs separates the two functions. DSSC has an advantage in terms of flexibility, energy payback in a short time and approximately have high a performance for light diffusion (Hagfeldt et al., 2010). The research activity is being advanced by focusing on structural substrates and better material for light harvesting, for example, organic polymers semiconductor, macromolecules, dye sensitizer, pigments or liquid crystalline materials.

To date, most of the work on DSSCs in literature dealt with the research of new materials and new structures in intention to obtain an efficient power conversion, but just a few researchers focused towards the reliability of DSSCs. However, recent findings pointed out the possibility of a severe degradation which directly affects the device performances (Bari et al., 2013). Reliability and stability of the DSSCs are two key issues which are still little explored in literature. From the viewpoint of reliability, DSSC should sustain at least 10^8 redox cycles which corresponds to about 20 years of sunlight exposure (Bari et al., 2011). During the past years of development of this technology, the long term stability nanocrystalline DSSC systems have been a subject of concern (Sommeling et al., 2004). The aim of this research is to study the long term stability and degradation of solar cells sensitized with organic dyes which is available in Malaysia. Investigation of theoretical works combined with the fabrication process studies is established to improve the DSSCs performance. This fundamental research is expected to pave the way for a new generation of DSSCs with long term stability, high reliability, high power conversion efficiency and low manufacturing cost.

1.2 Problem Statement

Solar cells based on dye sensitized nanocrystalline have drawn much attention since 1991. The resultant device was shown to be as the promising new power generating device in the renewable energy market with an acceptable performance. DSSCs must have long term stability and the function must retain after millions of times of turnover for the catalytic cycle which is excitation, charge injection and regeneration (Chiang et al., 2013). The choice of material and structure of each layer is the critical issues as they can have a strong impact on the reliability and the efficiency of the solar cells.

The performance of the cell mainly depends on the dye used as a sensitizer (Grätzel et al., 2003). A DSSC consists of an indium-tin oxide (ITO) layers, dye modified wide band semiconductor electrode, a counter electrode and a redox electrolyte (Figgemeier et al., 2004) (Xue et al., 2012). The dye absorption spectrum and the dye anchorage to the semiconductor oxide are important criteria that determining the performance of the cell. Basically, transition metal coordination compounds (ruthenium polypyridyl complexes) have an excessive charge transfer absorption in the all visible range and the most efficient metal-to-ligand charge transfer (Grätzel et al., 2003) that make the Ru-complex as the most efficient sensitizers.

However, Ru-complexes contain a heavy metal that caused the complexity of synthesization, costly and highly undesirable. The challenge is to produce a long thermal stability and reliability of DSSCs based on organic dye as a sensitizer by evaluating each of the materials involved in DSSCs structure in order to investigate the degradation mechanism of the device. The nanocrystalline DSSCs is probably susceptible to different types of the degradation mechanism (Figure 1.1) : i) the device systems containing an organic liquid have a high risk to leak out of the cell or become evaporate at certain temperature; ii) efficient photocatalyst the titanium dioxide, TiO_2 have potential problem that putting at risk the organic materials (dye sensitizer, electrolyte, solvent) in its direct vicinity under the natural illumination, including the UV light; iii) at high thermal stress, only lower expected mode of degradation occur.

The challenge is to fabricate the device and produce the long stability with high performance, low cost of material and able to have high conversion efficiency by reducing and preventing the device from degradation mechanism. The degradation mechanism factor includes the material and also the condition involved in the fabrication of DSSCs. There are two main approaches to figure out the degradation of the material: (i) by using light absorption spectra measurement and (ii) photoelectrochemical characterization such as open circuit voltage (V_{oc}), short circuit current (I_{sc}), fill factor (FF) and conversion efficiency (η). To date, research into degradation based on the reliability and stability of DSSCs is still in its infancy in developing a high performance of DSSC.

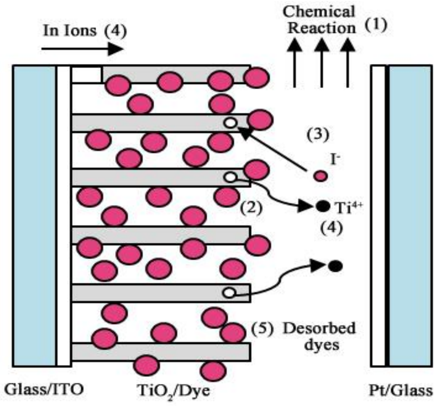

Figure 1.1: Schematic illustration of DSSCs degradation mechanism. (1) Electrolyte react; (2) release ions from TiO_2 nanoparticle and defect vacancies created; (3) penetration (I^-/I_3^-) redox mediator species into the TiO_2 (4) ITO ions diffuse into the TiO_2 nanostructure even electrolyte; (5) dyes desorb from the TiO_2 surface, the redox mediator molecules (I^-/I_3^-) regeneration process will begin (Xue et al., 2012).

1.3 Research Objective

This study embarks on solving the fundamental issues of the reliability and the stability of the dye-sensitized solar cells (DSSCs) based from the degradation mechanism factor. The following objectives describe in details the ultimate aims of the project:

1) To design a solar cell and investigate the various material involved in DSSCs which is the transparent conductive oxide (TCO), semiconductor oxide material, dye sensitizer, counter electrode and the redox electrolyte; including the material that influence the degradation mechanism of DSSCs.
2) To evaluate experimentally the performance of DSSCs based from the photoelectrochemical characterization: efficiency, fill factor, short circuit current and open circuit voltage based on the varied photosensitization compound, extracting temperature and extracting solvent.
3) To assess experimentally the effect of the degradation mechanism to the reliability and stability of the DSSCs performance based on time irradiation by using selected material.

1.4 Hypothesis

There are three hypotheses involved in this research project. First hypothesis are based on the material that are used in the fabrication of the DSSCs. Each of the materials involved owning some specific properties that influence the degradation effect of the device. The second hypothesis are focusing on the performance of DSSCs which most related towards the stability of the device. The efficiency and the stability of the DSSCs can be enhanced by adjusting the extract with the optimum temperature and dye extracting solvent. The last hypotheses are involving the variation of parameters which is temperature and solvent extracted of dyes. By adjusting the temperature and of dye extract solvent to the optimum condition the performance of the DSSCs is expected to improve and indirectly affect the stability of the device for long time operation period.

1.5 Research Scope

The research is focused on the degradation mechanism which has included the term of stability and reliability of DSSCs. In order to discover the stability and reliability of the device, several measurements and characterization which are surface morphology, absorption spectrum and photoelectrochemical characterization was obtained by using UV-Visible Spectroscopy (UV-Vis), X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM), Atomic Force Microscope (AFM) and Semiconductor Parametric Analyzer (SPA). The SEM, XRD and AFM characterized the porous surface and the compound (anatase/rutile) of titanium dioxide (TiO_2). Based from the SPA measurement, the efficiency (η), open circuit voltage (V_{oc}), short circuit current (I_{sc}) and fill factor was determined. Seven natural dyes which are Rosella, Ardisia, Mulberry, Cherry Barbados, Bawang Sabrang, Harum Manis mango and Oxalis

Triangularis are used as a photosensitizer due to availability in tropical areas as in native Malaysia climate. The adjusting temperature (room temperature, 50℃, 75℃ and 100℃), different extracting solvent (water and ethanol) and irradiated time (before and after 24 hours being stored) are used as a parameter to determine the stability of the device. The parameter was controlled by using the same concentration of acidity in titanium dioxide (TiO_2) paste and using the soot as the counter electrode. The device was exposed under the 100 W/cm^2 bulb inside black box. All of the recorded data are necessary to obtain the degradation mechanism occur in the device that influence the stability and reliability of the solar cell.

1.6 Thesis Structure

The thesis is structured with five chapters. The first chapter contain of the thesis introduction by outlining the research background, problem statement and research objective as the purpose of study as well as the outline of the thesis. Chapter 1 briefly described in general the overall content of the research purpose.

Chapter 2 is intended to introduce the photovoltaic generation backgrounds and dye-sensitized solar cells, in order to highlight the primary subjects of this study in the right context for reader understanding. The overview of the generation photovoltaic technology is discussed in details, followed by a description of basic principle and structure of photovoltaic. A DSSC background is briefly described, followed by a short description about the device structure, basic principle and material involved in the second part with some of qualitative discussion together with figure cell operation in order to assist the reader to gain a clear physical picture on how the DSSCs actually works together. This chapter also gives the widely view upon the degradation mechanism in the solar cell and the review of the previous research by using natural dyes as the photosensitizer.

Chapter 3 aimed to describe the method that has been used in this research. The short introduction described the process flow of the fabrication process of DSSCs, followed by the fabrication and the structural study in this research. In the structural study part, the equipment (SPA, UV-Vis, AFM, SEM and XRD) that has been used for measuring the surface morphology of the thin film photoanode and the electrical output is briefly described together with the basic principle and operation.

Chapter 4 presented the results from the experimental method of the work. The first part, presented results from the characterization of nanoparticle and the absorption spectrum of the dye are shortly demonstrated. The figure illustrated the structure of nanoparticle with short descriptive to ensure the readers clear about the characterization part of this work. The second part describes the results of photoelectrochemical parameters that described based on graphical results. The last part shows the results of pH monitoring as verification of overall performance achieved by the DSSCs, followed by the overall conclusion. Mulberry in water extracting at temperature 50℃ was obtained the best performance among all dye sensitizer that has been used.

The conclusion from this work is summarized in Chapter 5. The description area mainly about the overall research view, including the conclusion about an experimental result that correlated with the theoretical. The future direction and several recommendation of this work for further research is shortly described.

CHAPTER 2

DYE-SENSITIZED SOLAR CELLS

2.1 Overview of Photovoltaic Technology

Photovoltaic (PV) is the fastest growing power generation technology sectors and the photovoltaic systems are expected to have over a 30 year (Oliver & Jackson, 2000). The operating lifetime of photovoltaic systems is one of the requirements of sustainability of photovoltaic energy conversion. The solar cell technologies are divided into three generation cells that growing due to different types of materials and properties. In general, 1st generation PV cells, between doped n-type and p-type bulk silicon contain the electric interface resultant the highest conversion efficiency so far, followed by 2nd generation PV cells which made on thin film technology. As a comparison, 2nd generation PV utilizes less material that drop the production cost as return. Basically, both of the early generation of PV cells are made from opaque materials and required a light illuminated from the front face and moving supports to follow the sun's position (Stathatos, 2008). For 3rd generation solar cell, the material is based on nanostructure materials and produce from pure organic or a mixture of organic and inorganic materials, hence allowing widely and inexhaustible choice of materials.

However, the PV technology raises concerns about the disposal method into municipal landfills due to the containing small amounts of different hazardous and regulated materials, such as Cadmium (Cd), Plumbum (Pb) and Selenide (Se) that pave a way for solar cells recycling technology. The progress records of the solar cell