LIMITATION OF LITHIUM FLUORIDE (LiF) PROPERTIES FOR PASSIVATION LAYER IN ORGANIC SOLAR CELLS APPLICATION

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ABSTRACT

Organic solar cell (OSC) is a low cost renewable energy. Instead of semiconductor silicon solar cell; it is a device that converts the energy of light into electrical energy using photovoltaic effect. Nowadays, global warming and emission of greenhouse effect are the sources of the destruction of our mother nature. One of the best organic solar cell is polymer-fullerene cell with poly (3-hexylthiopene) (P3HT) as the donor and the fullerene [6,6] - phenyl-C61 butyric acid methyl ester (PCBM) as the acceptor. The organic solar cell preparation in a lot of research is prepared by the evaporation of organic solar cell layers. This method seems impractical in the large-scale production because the vacuum step requires large power supply. The solar cell preparation using spin coating techniques are the most compatible. As a conclusion, Lithium Fluoride (LiF) prevent metal electrode from diffusing into PEDOT: PSS (poly (3,4-ethylenedioxythiophene) poly(styrenesulfonate)) and ITO (Indium Thin Oxide) because LiF is an interfacial chemistry model for metal cathode that act as a buffer layer and coupling layer to enhance electron injection. Lithium Fluoride can also enhance metal cathode performance, characterize Lithium fluoride (LiF) thickness and test LiF as interlayer between active layer and metal layer by using sol-gel method to improve metal cathode performance if the thickness is less than 10nm.

ABSTRAK

Organik solar sel ialah salah satu sumber tenaga yang boleh diperbaharui selain daripada solar sel yang diperbuat daripada bahan semikonduktor yang berasaskan silikon yang mana menukarkan sumber tenaga solar kepada tenaga elektrik melalui proses fotovolta. Pada masa kini, kesan rumah hijau adalah punca kemusnahan alam semulajadi di dunia kini. Salah satu organik solar sel yang menjadi ujikaji ataupun rujukan ialah polimer fullerene sel dengan menggunakan *poly (3-hexylthiopene) (P3HT)* sebagai penderma dan fullerene *[6,6]- phenyl-C61 butyric acid methyl ester (PCBM)* yang bertindak sebagai penerima. Kebanyakan proses yang digunakan untuk menyediaan solar sel ialah dengan menggunakan proses penyejatan lapisan demi lapisan sel solar tersebut. Kaedah ini tidak sesuai untuk produksi pada skala yang besar kerana salah satu proses ini memerlukan penggunaan vakum yang menggunakan bekalan tenaga yang tinggi. Oleh sebab itu, penyedian solar sel dengan menggunakan proses salutan lebih praktikal. Kesimpulan daripada projek ini, *Lithium Fluoride (LiF)* telah digunakan untuk menghalang metal elektrod daripada menembusi *PEDOT: PSS (poly (3,4-ethylenedioxythiophene) poly(styrenesulfonate))* dan *ITO (Indium Thin Oxide)* kerana keserasian *Lithium Fluoride* bertindak sebagai lapisan penampan dan penganding untuk meningkatkan pengerakan electron. Lapisan *Lithium Fluoride* digunakan untuk meningkatkan prestasi, ciri-ciri *Lithium Fluoride* dengan mengubah ketebalanya yang betindak sebagai pengantara diantara lapisan aktif dan metal elektrod dengan menggunakan teknik sol-gel bagi meningkatkan prestasi metal katod organic solar sel jika ketebalan lapisan *Lithium Fluoride* kurang dari 10nm.

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CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Organic solar cell (OSC) is a low cost renewable energy. Instead of semiconductor silicon solar cell; it is a device that converts the energy of light into electrical energy using photovoltaic effect [1]. Nowadays, global warming and emission of green house effect are the sources of the destruction of our mother nature. To make things worse, energy crisis and economic recession creates an unstable future for oil and gas sectors. Therefore, renewable energy source gained a lot of attention from consumer countries to replace high cost energy sources such as fossil fuel. In the entire renewable energy field, photovoltaic energy is the one secure and promising source that can be considered by the majority of consumers as a clean, sustainable ecosystem and safe energy conversion method to be used in the future.

By referring to the National Renewable Energy Laboratory (NREL) Fig.1.1, the efficiency of organic solar cell is around 10% with respect to silicon based solar cell 44%. To achieve the efficiency of 44%, high investments are needed to support all the facilities and materials. For example, Crystalline silicon photovoltaic are very stable, with estimated operational lifetime in more than 25 years and module power conversion efficiency as high as 20%, but if is discussed about the cost, it is too high and this is seen as the main reason for the scarcity of photovoltaic technologies. So, other alternative is to research on organic solar cell and enhance the material to achieve higher efficiency with respect to green environment constraint nowadays.

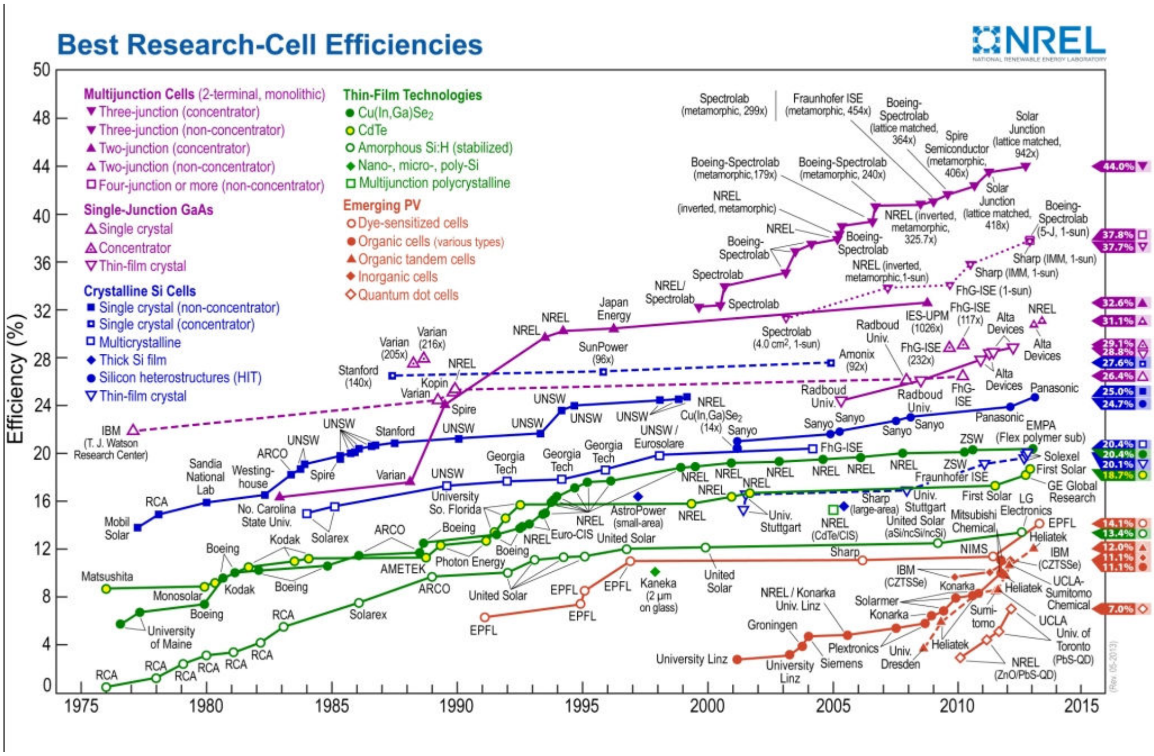

Fig.1.1: Efficiency of various type of Solar Cell Reseach by NREL

Organic photovoltaic uses organic materials such as polymer as an active layer to absorb light and produce free electrons. In addition, polymer can be dissolved in solvents and deposited on substrates using wet-processing techniques such as spin coating. One of the best organic solar cell is polymer-fullerene cell with poly (3-hexylthiopene)(P3HT) as the donor and the fullerene [6,6]- phenyl-C_{61} butyric acid methyl ester (PCBM) as the acceptor [2]. The starting point of organic solar cell base on the bulk heterojunction concept is shown in Fig.1.2. This solar cell, the donor material is combined with an acceptor in an organic solvent and went through spin coating process on a substrate of indium-tin oxide (ITO) on glass as refered to Frederik C. Krebs, Polymer Photovoltaics: A Practical Approach.

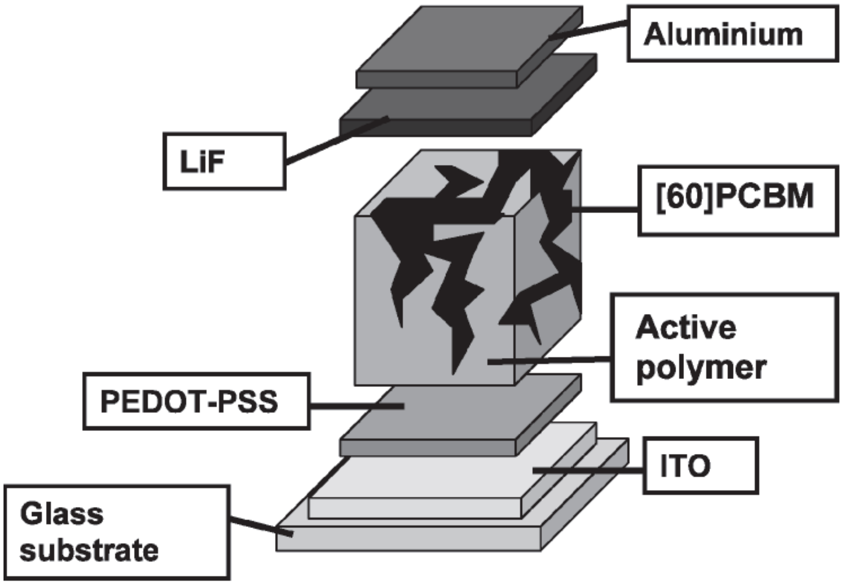

Fig. 1.2: Conventional Layer of Organic Solar Cell from Frederik C. Krebs, Polymer Photovoltaics: The Polymer Solar Cell

1.2 Problem Statement

The organic solar cell preparation in a lot of research is prepared by evaporating the organic solar cell layers. This method seems impractical in large-scale production because the vacuum step requires large amount of energy. Method of deposition Lithium Fluoride is costly and the limitation of Lithium Fluoride is not reported in detail. The solar cell preparation using spin coating techniques are most compatible to suit the low cost organic solar cell fabrication.

The problem to achieve functional solar cell devices depends on the recipe to spin coat solar cell material. By using the recipe of inverted solar cell (Au/PEDOT: PSS/Active layer/ITO) Fig.1.3, it seems that, the metal electrode diffuse through PEDOT: PSS, active layer and short to ITO layer Fig.1.4. This short circuit will damage solar cell's active area and reduce the efficiency of the cell device.

[redacted]

[redacted]

Fig.1.3: Inverted Organic Solar Cell Model Fig.1.4: Metal electrode short to ITO

1.3 Objective of the Project

The aim of this proposal is to enhance metal cathode performance, characterize Lithium fluoride (LiF) thickness and test LiF as interlayer between active layer and metal layer by using sol-gel method to improve metal cathode performance of organic solar cell application.

(i) To examine the effect of different spin coating technique of LiF solution.
(ii) To characterize the properties of Lithium Fluoride (LiF)
(iii) To prove the limitation of LiF for organic solar cell application.

1.4 Scope of the Project

The scope that encompasses the entire project for this master project is stated as below for guideline;

(i) To explore and understand the principle of basic organic solar cell device structure and the function of Lithium Fluoride thru literature review and background study.

(ii) To identify solvent of Lithium Fluoride solution in which the solvent is needed to spin coat with different speed on individual glass.

(iii) To prepare different speed of spin coater recipe using Lithium Fluoride solution to produce uniformity on glass substrate.

(iv) To fabricate and characterize organic solar cell without Lithium Fluoride of individual glass ITO/P3HT: PCBM/PEDOT: PSS/Au structure.

(v) To characterize and enhance organic solar cell device using ITO/P3HT: PCBM/PEDOT: PSS/LiF/Au with different thickness of Lithium Fluoride. The morphology of Lithium Fluoride will be characterized using Atomic Force Microscopy (AFM) and surface profiler.

(vi) To test the organic solar cell device electrical characteristic under AM 1.5 illumination using current voltage (I-V) test system.

1.5 Project Report Outline

This project report consists of 5 main chapters, and is organized as follows:

Chapter 2 provides brief overview of organic solar cell, basic explanation on Lithium Fluoride and basic theory of fabrication and measurement tools of solar cell's project. Chapter 3 describes material and experimental methods involved in this project. Chapter 4 describes the process to achieve Lithium fluoride thickness and solution to be introduced as an interlayer between active layer and metal electrode and the limitation of LiF properties for passivation layer. Chapter 5 provides the conclusion and future work.

CHAPTER 2

LITERATURE REVIEW

2.1 Background History

In 1959, Kallmann and Pope observed a photovoltaic effect in a single crystal of anthracene when sandwiched between two identical electrodes and illuminated from one side (Kallmann et al. 1959). Later, they also observed a photovoltaic effect in a tetracene–water system (Geacintov et al. 1966) [3].

The heterojunction was introduced by Tang in 1986 and it proved to be a great step forward for organic photovoltaics (Tang 1986). Tang described a two-layer device that employed copper phthalocyanine (CuPc) as the donor and a perylene tetracarboxylic derivative (PV) as the acceptor. The device had a power conversion efficiency of about 1%, which was an order of magnitude greater than single-material organic photovoltaics developed at that time [4]. The photovoltaic effect investigated (Hall et al. 1996a) by using thin film of poly(p-phenylenevinylene) (PPV) and poly(2-methoxy,5-(2'-ethylhexyloxy)-1, 4-phenylenevinylene)(MEH-PPV) in a simple single layer, polymer photovoltaic cell, a thin conjugated polymer film sandwiched between electrodes of differing work function. This model estimate an exciton diffusion range of 6nm – 8nm [5]. The estimated exciton diffusion lengths in CuPc [$L_{CuPc} = (68 \pm 20)$ nm and in PPV [$L_{PPV} = (12 \pm 3)$nm reported by Stubinger et al. 2001 [6]. This means that only excitons generated within a short distance of the donor–acceptor interface have the possibility of dissociating into free electrons and holes. Padinger and coworkers (2000) fabricated large area devices on flexible polyester substrates. They made several devices containing either MDMOPPV or P3OT as the electron-donating conjugated polymer. They used unmodified C60 or PCBM (mono-adduct) as the acceptor in the P3OT devices and C60 or one of two different PCBM adducts in the MDMO-PPV devices: a mono-adduct and a bis-adduct, which was a mixture of isomers. The multi-adduct derivative was used to increase the solubility/miscibility of the fullerene. The MDMO-PPV/ PCBM and P3OT/C60 devices exhibited power conversion efficiencies of about 1.5% under monochromatic illumination at 488 nm [7].

Shaheen and coworkers (2001) fabricated devices by spin-coating active layers containing 1:4 mixtures of MDMO-PPV/PCBM. They used either toluene or chlorobenzene as the casting solvent and found that the films cast from chlorobenzene were smoother than those cast from toluene. The combination of increased short-circuit density and fill factor of the chlorobenzene-cast solar cell combined to produce a 2.5% efficient device (under AM1.5) [8]. Martens et al. (2002) studied not only the effect of casting solvent, but also the casting method (drop-cast versus spin-coated) on phase separation in MDMO-PPV/PCBM layers. Based on this and other phase studies, they proposed that the matrices of the films were a 1:1 mixture of polymer and PCBM, while the spherical domains were predominantly PCBM. Furthermore, they observed generally smaller PCBM-rich domains in spin-coated films than in drop-cast films. The reason for smaller domains was related to the faster evaporation rate in spin coating than in drop-casting [9]. Heeger and coworkers (2007) investigated the use and function of PCBM blended into PCPDTBT is the great detail, and reported solar cells with uncertified efficiencies beyond 5% for PCPDTBT/PCBM composites. Konarka has explored the cyclopentadithiophene class in great detail, and, as one of the outcomes, it shows an efficiency certificate for a device submitted to NREL. The solar cell delivers a short-circuit current of ~15mAcm_2 and a Voc of 575mV, which results, together with an FF of 61%, in an efficiency of ~5.2% [3].

The effects of the interface structure between Al cathode and polymer photo-active thin film are investigated regarding the performance of bulk heterojunction polymer solar cells by changing the Al cathode e-beam evaporation rate. The result shows that without much loss of Voc by increasing the evaporation rate, power conversion efficiency enhancement from 1.35% to 3.6% [10]. Influences of metal electrode on the performance of organic photovoltaic device were studied. An appropriate energy level was set between HOMO of donor material and LUMO of acceptor material used to fabricate device and metals with work function above, below and within this appropriate range were selectively chosen to form electron collecting electrode [11]. In order to maximize the performance of organic solar cell, several thickness profile of Lithium Fluoride will be conducted on this report to study the limitation of LiF properties passivation layer between P3HT: PCBM and metal cathode.

2.2 Lithium Fluoride (LiF)

Organic solar cell device has a basic model of anode, active layer and cathode. To improve solar cell efficiency, the Lithium fluoride thin interfacial layer is inserted between active layer (P3HT: PCBM) and cathode electrode (Aluminum or Gold) [12, 13]. Based on the performance improvement of organic light emitting diode research, the interlayer structures of Lithium Fluoride decrease the resistance and lowered the electron injection barrier between Aluminum and active layer in organic light emitting diode [14].

By adding the lithium Fluoride interlayer it will increase device lifetime and prevents the formation of trap state due to oxidation of the metal Aluminum interface. With the buffer layer protection, the metallic surface constructed from gold diffusing into the organic layer can be prevented to some extent [15].

Insertion of thin layer Lithium Fluoride less than 15 Angstroms increases the fill factor of the organic solar cell device. The increased of the fill factor is due to the formation of buffer layer ohmic contact [16-18].

2.3 Sol gel method

The idea behind sol gel synthesis is to dissolve the compound in a liquid in order to bring it back as a solid in a controlled manner. Multi component compounds may be prepared with a controlled stoichiometry by mixing sols of different compounds. This method also enables mixing at an atomic level, results in small particles, which are easily sinterable.

This method was developed in the 1960s mainly due to the need of new synthesis methods in the nuclear industry. A method was needed where dust was reduced (compared to the ceramic method) and which needed a lower sintering temperature. Sol gel synthesis may be used to prepare materials with a variety of shapes, such as porous structure, thin fibers, dense powders and thin films.

A sol is a dispersion of the solid particles (~0.1-1 μm in a liquid where only the Brownian motions suspend the particles. A gel is a state where both liquid and solid are dispersed in each other, which presents a solid network containing liquid components. The sol gel coating process usually consists of 4 steps:

(i) Desired particles once dispersed in a liquid to form a sol.

(ii) Deposition of sol solution produces the coatings on the substrates by spraying, dipping or spinning.

(iii) Particles in sol are polymerized through the removal of the stabilizing components and produce a gel in a state of a continuous network.

(iv) Final heat treatments pyrolyze the remaining organic or inorganic components and form an amorphous or crystalline coating.

2.4 Fabrication tools

Fabrication tools in producing organic solar cell including cleaning, sol-gel method, pre-bake, hard bake and depositing the metal are shown below;

2.4.1 Spin coater machine

Spin coater machine are used to coat a substrate with a uniform thin film materials. The thickness of the materials can be varied by controlling the spin coater machine's speed and time. Material's thickness also may vary depending on materials types itself, solution's concentration, solution's drop quantity or user's spin coating technique (either spin-drop or drop-spin)

Fig.2.1: Spin coater machine to coat LiF layer on glass or active layer substrate

2.4.2 Magnetic stirrer machine

A magnetic stirrer machine below provide stirring and heating features in which stirring speed and heating temperature may be controlled by the user. A solution can be stirred by inserting a magnetic bar into the solution and place onto rotating magnetic at the center of the machine while the heating features can be used for substrate's heating treatment by placing samples onto the surface plate.

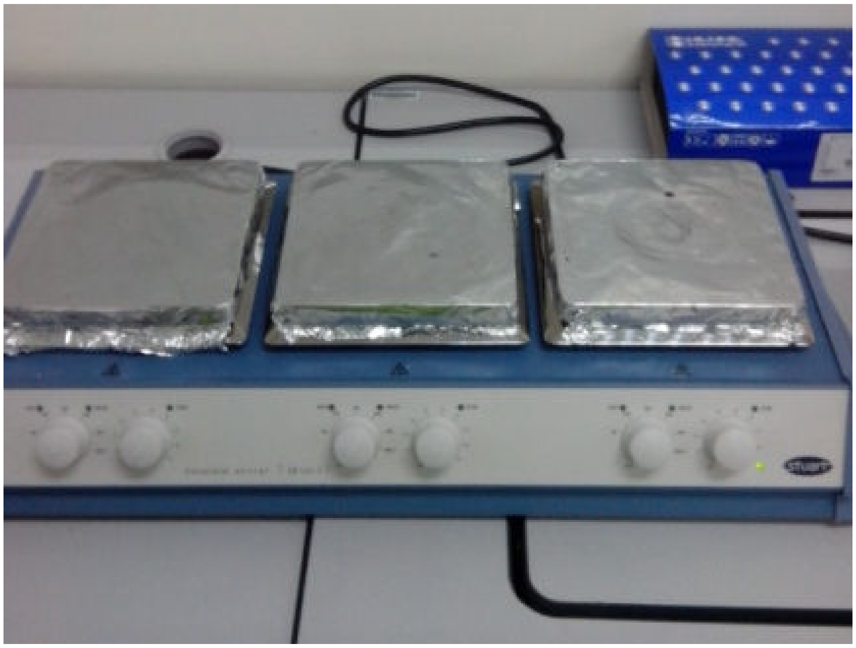

Fig.2.2: Magnetic stirrer machine to dilute LiF and active layer solution

2.4.3 Ultrasonic bath cleaner

Ultrasonic cleaner is a cleaning device that uses ultrasound (usually from 20-400 kHz) and an appropriate cleaning solvent to clean dedicated items. It uses cavitations bubbles induced by high frequency pressure (sound waves) to agitate a liquid. The agitation produce high forces on contaminants adhering to substrates like metals, plastics, glass, rubber and ceramics. Also penetrates blind holes, cracks and recesses to remove all traces of contamination.

Fig.2.3: Ultra sonic bath cleaner taken from MiNT-SRC, UTHM

2.4.4 Annealing chamber

Annealing is a heat treatment, involves heating a material to above its critical temperature, maintain a suitable temperature and then cooling. It can induce ductility, soften material, relieve internal stresses, refine structure by making it homogeneous and improve cold working properties.

Fig.2.4: Annealing chamber of post annealing process organic solar cell procedure

2.4.5 Sputter coater

Sputter coating is a sputter deposition process to cover a substrate with a thin layer of conducting material such as gold (Au). Thickness of the metal can be controlled by varying current and sputtering time. The sputter coating process happens in vacuum.

Fig. 2.5: Sputter coater gold/platinum to coat metal electrode of organic solar cell

2.5 Characterization and measurement tools

2.5.1 FESEM/EDS machine

This is a Field Emission Scanning Electron Microscope (FESEM) equipped with Energy Dispersive Spectroscopy (EDS). FESEM features allows imaging metallic and ceramic based materials that produce image of a sample by scanning it with a focused beam of electrons, containing information about the sample's surface topography and composition. On the other hand, EDS is an analytical technique used for the elemental analysis or chemical characterization of a sample.

Fig.2.6: FESEM/EDS to characterize LiF composite and size

2.5.2 AFM machine

AFM stands for Atomic Force Microscope. AFM provide picture of atoms on or in surfaces. Like Scanning Electron Microscope (SEM), the purpose of AFM is to look at the objects at the atomic level, provides higher resolution, and it does not need to operate in vacuum.

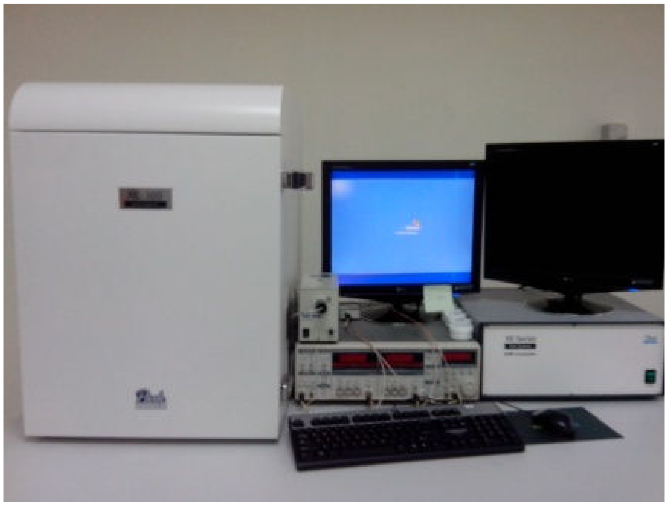

Fig. 2.7: Atomic Force Microscope (AFM) to characterize surface roughness of LiF compare to glass substrate

2.5.3 Surface profiler

Alpha-Step IQ surface profiler is a high measurement precision. It is ideal for semiconductor pilot lines and materials research. This profiler provides 2D surface profiling analysis and determines thin step height, surface micro roughness and overall form error on thin film surface coatings.

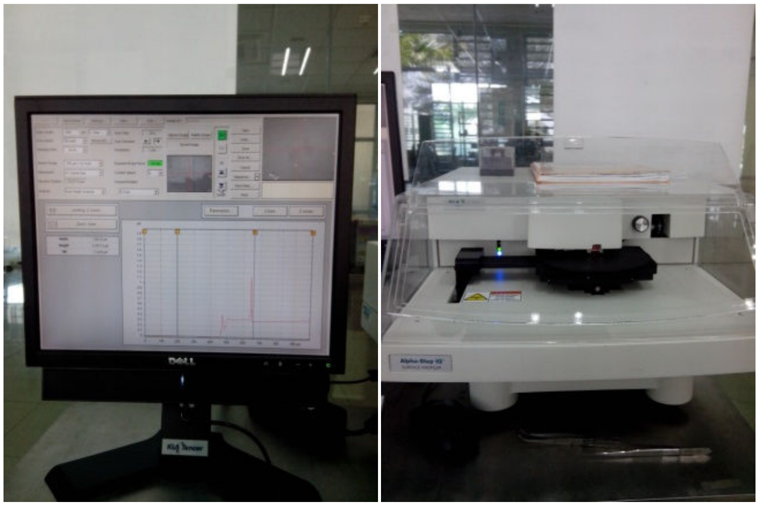

Fig 2.8: Alpha-Step IQ surface profiler to check LiF thickness after spin coater process

2.5.4 I-V characteristic measurement with solar simulator

The illuminated current versus voltage (I-V) characteristics of a photovoltaic device typically measured with respect to standard reference conditions is defined by a spectrum, intensity, temperature and area.

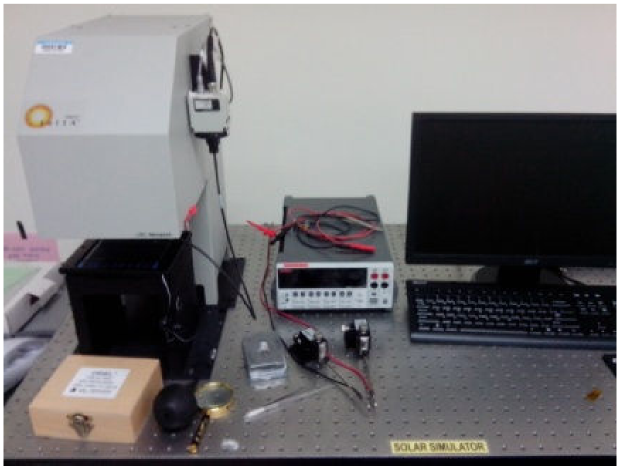

Fig 2.9: I-V characteristic measurement with solar simulator taken from MiNT-SRC, UTHM

CHAPTER 3

METHODOLOGY

This chapter will discuss the process flow of organic solar cell fabrication without lithium Fluoride (LiF) interlayer and with Lithium Fluoride (LiF) layer between metal cathode and active layer P3HT: PCBM as in Appendix A and Appendix B.

3.1 P3HT: PCBM Solvent Preparation

First process is to prepare active layer by 1:1 ratio mixing the 15mg poly (3-hexylthiopene)(P3HT) in Fig.3.1 and 15mg [6,6]- phenyl-C61 butyric acid methyl ester (PCBM) in Fig.3.2, from Sigma Aldrich added with 1ml 1,2 Dichlorobenzene in Fig.3.3 that act as a solvent to produce active layer solution in sol-gel method.

Fig.3.1: 15mg poly (3-hexylthiopene) (P3HT)

Fig.3.2: 15mg [6, 6] - phenyl-C61 butyric acid methyl ester (PCBM)

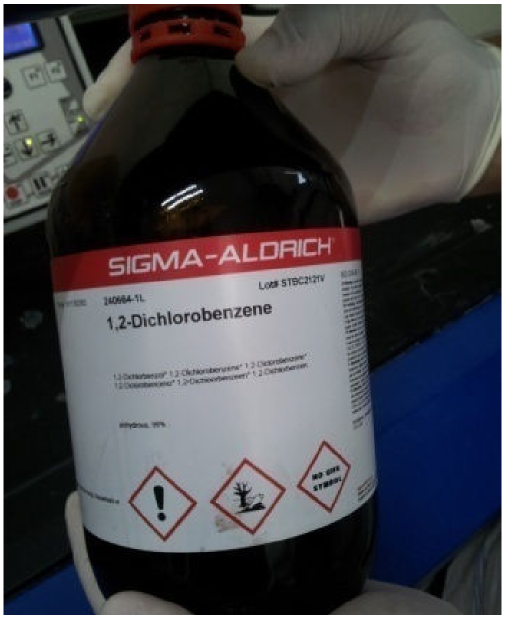

Fig.3.3: 1ml 1, 2 Dichlorobenzene from Sigma-Aldrich as

All three materials are then stirred together by using magnetic stirrer in a room temperature to produce mixture solvent for 24 hours in ageing process as shown in Fig.3.4. The thickness of P3HT: PCBM solvent is about 70nm to 150nm to avoid any exciton recombination in photovoltaic process.

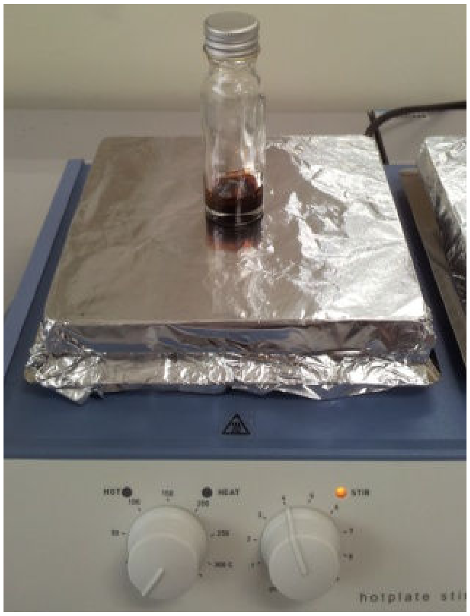

Fig.3.4: Ageing process of P3HT: PCBM

3.2 Organic Solar Cell Fabrication

The basic structure of organic solar cell consists of cathode, active layer and anode to generate the exciton and transfer the electron collected from photovoltaic process. First of all, the active layer P3HT: PCBM will be prepared on a clear glass coated with transparent and colorless Indium Thin Oxide (ITO) with 2.5cm × 2.5cm dimension which act as a conductive transparent metal electrode for inverted solar cell fabrication as shown in Fig.3.5.

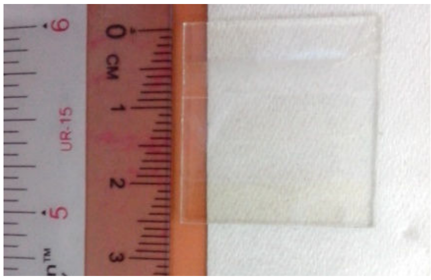

Fig.3.5: ITO etched on glass substrate 2.5cm X 2.5cm dimension

The first process is to remove ITO from glass substrate by attaching Kapton tape around the glass surface to cover the active area and exposed unwanted. The exposed area need to be etched as in Fig3.6. The glass substrate coated with ITO soaked in Hydrochloric Acid mixed with water in about 15 minutes to remove the unwanted or exposed ITO.

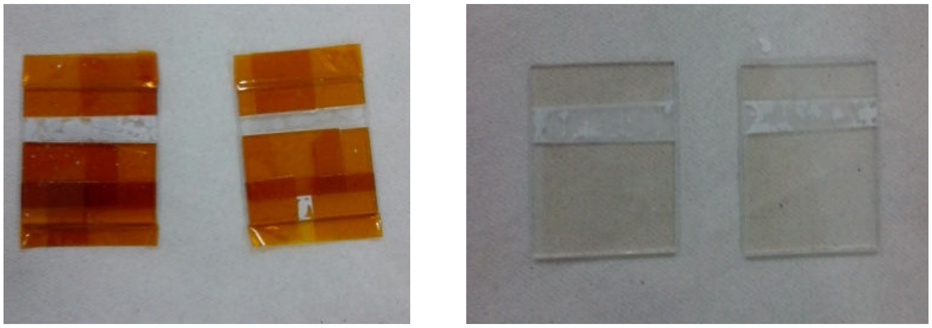

Fig.3.6: Cover glass substrate coated with ITO by using Kapton tape

The next process is to apply the P3HT: PCBM solution to the etched ITO glass substrate by using spin coating machine in Fig.3.7. Dispense 1 drop at different places on the glass substrate with the P3HT: PCBM solution onto the glass surface using plastic pipette. The desired thickness of organic active layer in organic solar cell is between 70nm to 150nm. Two different speeds will be set on spin coater machine, for the first 30s the speed of the coater is 500rpm. The second speed is 1000rpm for 60s to keep the active layer solvent spread through the entire glass surface evenly.

Fig.3.7: Spin-Coater Machine is used to coated active layer and LiF solution on glass substrate

The coated glass substrate with P3HT: PCBM solution sample by using spin coater machine need to go through pre-bake process about 5 minutes with 60 degree temperature using Hotplate Stirrer to remove water particles in organic active layer as shown in figure 3.8.

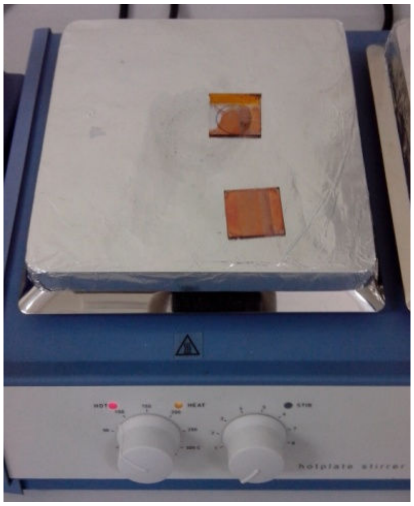

Fig.3.8: Pre-bake sample on Hotplate stirrer

After finishing the pre-bake process for 5 minutes, wipe small area beside the etched of the glass sample to expose ITO by using Iso Propil Alchohol and cotton bud that will act as anode terminal for organic solar cell device. Next step is applying metal cathode by using sputter coater machine to deposit Gold (Au) as a metal cathode to organic solar cell device as shown in Fig.3.9.

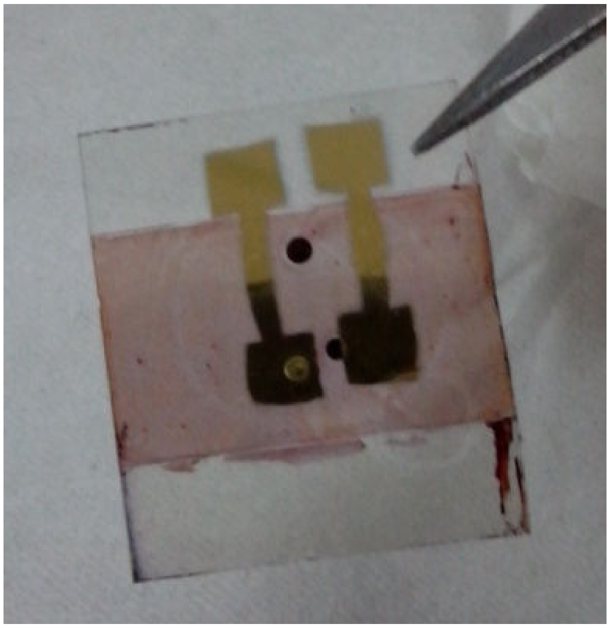

Fig.3.9: Organic Solar cell device

3.3 Lithium Fluoride (LiF) Solvent Preparation

Another layer is attached between active layer and metal cathode to improve the charge injection and to stop diffusion of metal cathode through active layer of the devices in theory. The Lithium Fluoride (LiF) layer coated after P3HT: PCBM process by using sol-gel method that prepared using water mixture and Isopropyl Alcohol mixture.

3.3.1 Lithium Fluoride (LiF) by using distilled water mixture solution

Lithium Fluoride is much less soluble in water and the thickness target is about less than 10nm to deposit between active layer and metal cathode. The first step is to prepare 0.24g Lithium Fluoride (LiF) by using digital weight scale. Mix the Lithium Fluoride (LiF) with 30ml distilled water with 150 degree temperature and 4000rpm magnetic bar stirrer for 24 hours as shown in Fig.3.10.

Fig.3.10: Lithium Fluoride sol-gel preparation

After finishing the stirrer process for 24 hour, the solution is then filtered by using medium fast filter paper to remove large and unwanted or large LiF particles in the solution to achieve the target below than 10nm thickness such as shown in Fig.3.11.

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