Zinc Oxide Nanostructures for Efficient Energy Conversion in Organic Solar Cell

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Abstract: We present a new approach of solution-processed using zinc oxide (ZnO) nanostructures as extraction layer material for organic solar cells. It is low chemical reaction compatibility with all types of organic blends and its good adhesion to both surfaces of ITO/glass substrate and the active layer (blends). Parameters such as the thickness and the morphology of the films were investigated to prove that these factors greatly affect the efficiency of organic solar cells. In this work, ZnO layer with thickness of approximately 53 nm was used as an interlayer to prevent pin-holes between the electrode and the polymer layer. The polymer layer was coated on the ZnO layer with the thickness of about 150 nm. The thick polymer layer will form a non-uniform surface because of the solvent, 1-2dichlorobenzene will etch away some region of the polymer layer and forming pin-holes. ZnO nanostructures layer was used to prevent pin-holes between the polymer layer and electrode. From the surface morphology of ZnO layer, it shows a uniform surface with particle grain size obtained between 50 -100 nm. The presence of the interlayer has a positive effect on the electrical characteristics of the solar cells. It was found that an organic solar cell with thickness less than 150 nm shows the optimum performance with efficiency of 0.0067% and Fill Factor (FF) of about 19.73.

Keywords: Nanostructures, extraction layer, pin-holes, poly (3-hexylthiophene) (P3HT), [6,6]-phenyl C_{61}-butyric acid methyl ester (PCBM).

1. INTRODUCTION

Over the past decades, much effort has been imposed in order to improved energy efficiency, to develop renewable energy and clean fuel sources, and to reduce overall greenhouse gas emission. In particular, the abundance of clean energy from the sun has drawn much attention [1]. Recently, solution-processed organic solar cells have been attracted considerable interests potential next-generation solar cells due to the rapid increased in power conversion efficiency (PCE) towards 10% (the threshold for commercial production) [2]. They can be processed by simple methods which compatible with mass production and cost effective (flexible) photovoltaic devices, with low environmental load, and as lightweight alternatives to currently used silicon solar cells [2]. The combination of poly (3-hexylthiophene) (P3HT) and [6,6]-phenyl C_{61}-butyric acid methyl ester (PCBM) in organic blends exhibits particularly promising photovoltaic performance [3]. It was reported by Gang Li *et al.* on the fabrication of a blend organic solar cells using P3HT and PCBM which produced the significant improvement results from the crystallinity of the blend solution. The best performance from the optimized blend organic solar cells was 4.4% [4].

Basically, the advancements in the field of organic solar cells are strongly driven by development of new materials and device architectures. The electrodes material is one of the important parameter for the organic solar cells operation. Commonly, silver (Ag) or aluminium (Al) and indium tin oxide (ITO) are used as transparent and reflective electrodes. In this work, indium tin oxide (ITO) and gold (Au) was used as transparent and reflective electrodes, respectively.

However, the efficiency of the organic solar cells might suffer of non-optimum interfaces (provides pin-holes) between the active layer and the electrodes with such conductors and decreasing short circuit current density (J_{sc}), open circuit voltage (V_{oc}) and Fill Factor (*FF*) [5].

In order to improve the efficiency, stability and optimum interfaces between the electrodes and the active layers, an inverted structure have been demonstrated. One common approach is to use low work function metals such as Sm, Ca or metal oxide such as zinc oxide (ZnO) as the electron extraction layer [6].

In recent years, the use of ZnO in photovoltaic devices has been expanding. In 2008, a ZnO electron selective layer was prepared by Kyaw *et al.* using a sol-gel process in an inverted organic photovoltaic (OPV) device on a glass substrate to achieve a PCE of 3.09% [7]. Then, Hau *et al.* adopted spin-coated ZnO nanoparticles as the electron selective layer for

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inverted OPV devices fabricated on a glass and plastic substrates, respectively. The maximum PCEs of 3.78% and 3.58% were achieved [6]. In addition, Krebs *et al.* produced solution-processed ZnO which was successfully applied to roll-to-roll processing for inverted PV devices [8]. The ZnO nanorods can improve the electron transport in bulk-heterojunction solar cells and it was reported by Takanezawa *et al.* [9].

The aim of this work is to study the effect of ZnO nanostructures for efficient energy conversion in organic solar cells. The ZnO is use as the acceptor-electrode interface and the energy band will be aligned to have enough lifetime and energy for the carrier transport for the polymer layers. The organic blend of P3HT and PCBM was used as the polymer layer.

2. SUBSTRATE PREPARATION

Indium tin oxide (sheet resistance of 10 Ω/sq) coated on a glass substrate (20 mm × 20 mm) was cleaned in ultra-sonic baths with acetone, ethanol, and rinsed with DI water for 20 min, respectively. Then, the substrate was slowly dried with high purity nitrogen gas. The etching process was applied to etch away the unwanted ITO coated glass region on the substrate. The ITO coated glass was coated with mask to protect the conductive region while the unwanted region was left unprotected. It was dipped into hydrofluoric (HF) acid for 1 minute. Then, the substrate was rinsed-off into de-ionized (DI) water and dried in ambient. After that, the electrical contact between ITO-trench-ITO was measured using multimeter in order to ensure either the etching was completed.

3. EXPERIMENTS

There are two solutions prepared to fabricate the organic solar cell which are (i) ZnO thin film and (ii) organic thin film. Figure **1a-b** shows the substrate containing the ZnO and polymer layer. For solution (i), an aqueous solution containing same molarity of zinc acetate dehydrates $[Zn(O_2CCH_3)_2(H_2O)_2]$ and monoethanolamine $[H_2N\text{-}CH_2CH_2OH]$ was diluted in 30 ml of isopropyl alcohol (IPA). The solution was aged and stirred for 24 hours at room temperature. Then, spin coating technique was used to deposit the ZnO layer and preheated the sample at 280 °C in 3 minutes. After that, annealed the sample at 500 °C for 1 hour and cooled down at room temperature.

For solution (ii), an aqueous solution containing of P3HT:PCBM powder with the same molarity 1:1 was diluted in 1 ml 1-2dichlorobenzene. The solution was stirred and aged for 24 hours at room temperature. After that, the polymer layer was deposited using spin coating technique for 10, 8, 4 and 1 layers. Then, the sample was preheated at 60 °C for 5 minutes and annealed at 500 °C, 3 minutes later for 1 hour.

Finally, the electrode was deposited on the polymer layer using a d.c. sputter coater assisted by mask. The material used is gold (Au). The metal

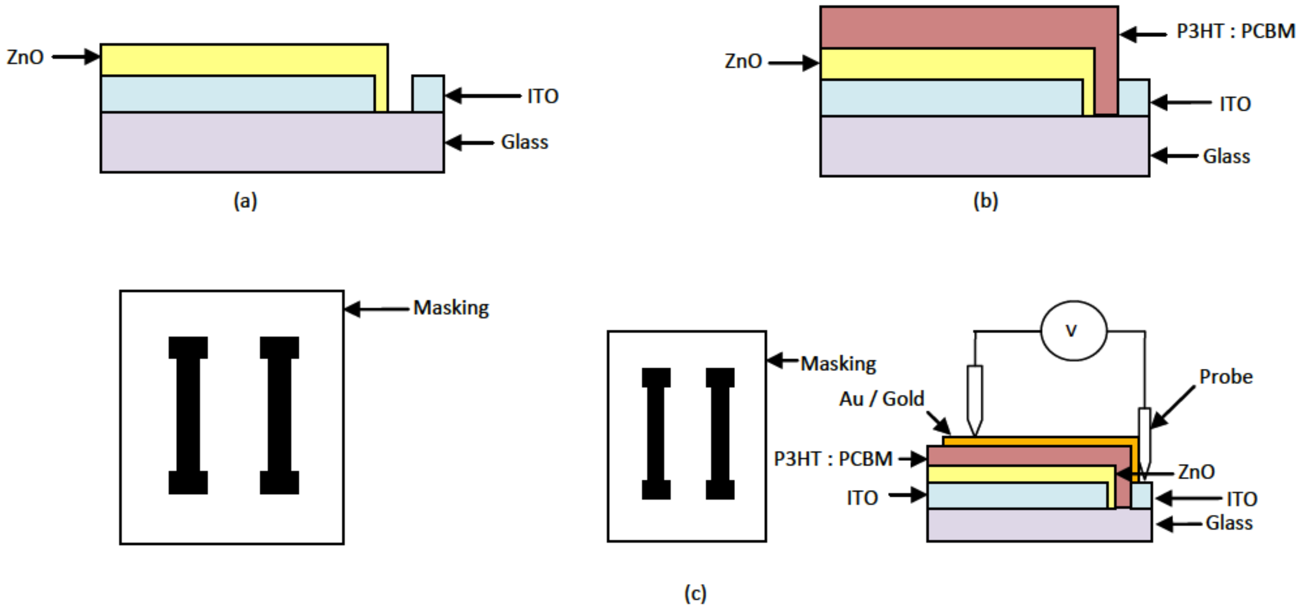


Figure 1: The configuration; (**a**) ZnO layer; (**b**) polymer layer (P3HT:PCBM); (**c**) The electrode masking and *I-V* measurement setup.

electrode was deposited at 40 mA for 200 seconds and the thickness formed was approximate to 100 nm. The metal electrode masking is shown in Figure **1c**.

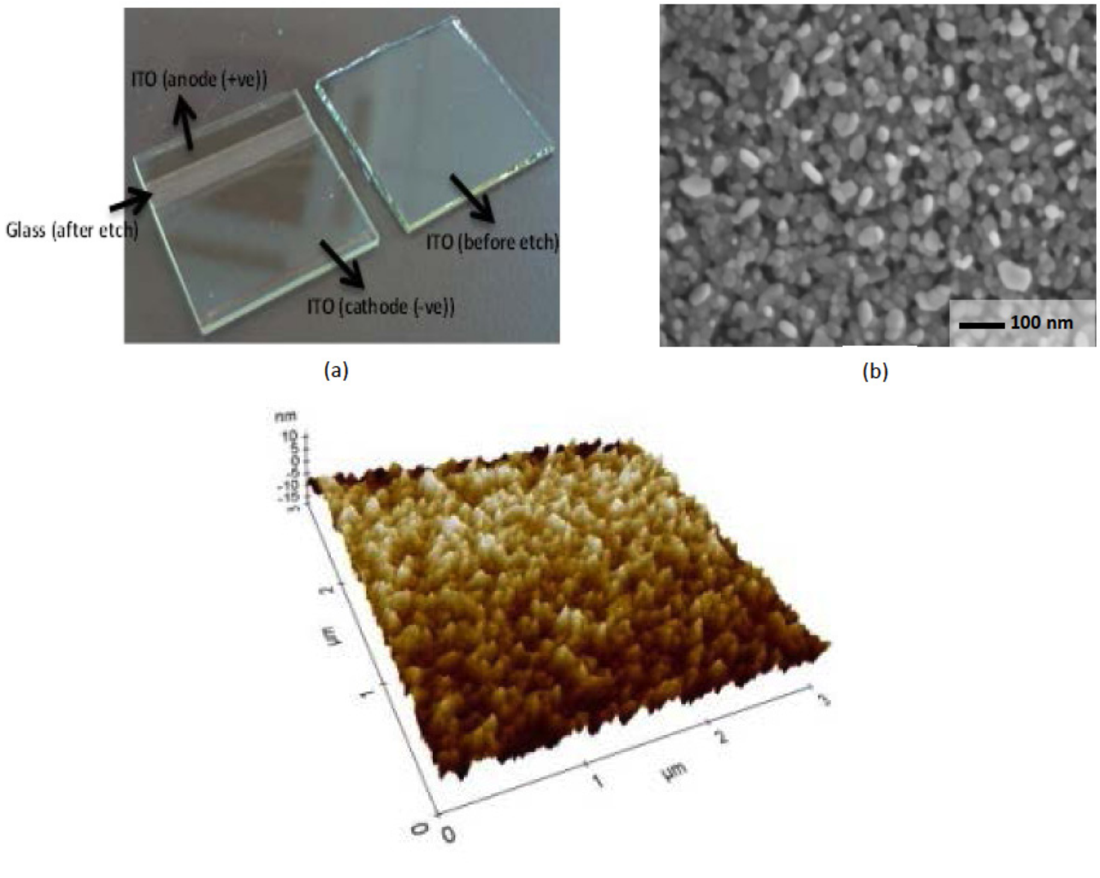
The P3HT:PCBM thin films was characterized into three types of characterization which are thickness analysis, surface topology and electrical properties. The thickness measuring analysis of the polymer layer was done using a surface profiler (KLA Tencor) at scan length and scan speed of 3000 mm^2 and 50 µs, respectively. The morphology of the thin film was observed using an atomic force microscope, AFM (XE-100 Park System). The electrical properties were characterized using *I-V* measurement setup which is shown in Figure **1c**. The sample were masked and coated with gold (Au) using d.c. sputter coater. The probes were placed on the two electrodes which are ITO and gold (Au) surfaces. The characterization of ZnO structures was done using a field emission scanning electron microscopy, FE-SEM (JEOL JSM-7600F).

4. RESULTS AND DISCUSSION

Etching process isolates the ITO coated glass into two parts which are anode and cathode in order to prevent short circuit. Figure **2a** shows the surface of ITO coated glass substrate after etching process. It is seen that the white trench is actually the glass surface where the ITO has been removed through etching process.

Figure **2b** indicates the field emission scanning electron microscope (FESEM) results of ZnO layer at 100,000 magnifications. The image of ZnO particles shows that the diameters of the particles are in the range of 50 nm to 100 nm (considered as nanostructures) [10]. ZnO act as a charge collector where electrons will be collected and accumulated before moving to the ITO electrodes [10].

The thicknesses of the P3HT:PCBM layer are listed in Table **1**. By reducing the coating times, the thicknesses of polymer obtained were differ and labeled by A, B, C and D.



(a)

(b)

(c)

Figure 2: (**a**) Substrate after etch; (**b**) The ZnO layer structures at 100,000 magnifications; (**c**) The morphology of P3HT:PCBM after anneal.

Table 1: Thickness Results

Sample	Coating	Thickness
A	10 times	272.62 nm
B	8 times	209.74 nm
C	4 times	163.57 nm
D	1 times	150 nm

The morphology of the thin film may relate to the performance of organic solar cells. In order to understand the morphological effect before and after applying an annealing or heating to the thin film, we used the atomic force microscopy (AFM) to probe the device surfaces. Figure **2c** shows the AFM results of P3HT:PCBM after annealing. The roughness of the thin film is 6.29 nm. From the results obtained, it shows that the P3HT:PCBM film is stable and uniform. By applying heat energy, the polymer material would expand depending on its thermal expansion coefficient. The surface become smoother and the crystal will be rearranged.

Figure **3a-b** shows the current-voltage (*I-V*) characteristics of organic solar cell using different thickness. Sample A and B which have organic layer thicknesses of 272.62 nm and 209.74 nm indicate an ohmic behaviour showing that, there is a short circuit between Au and ITO.

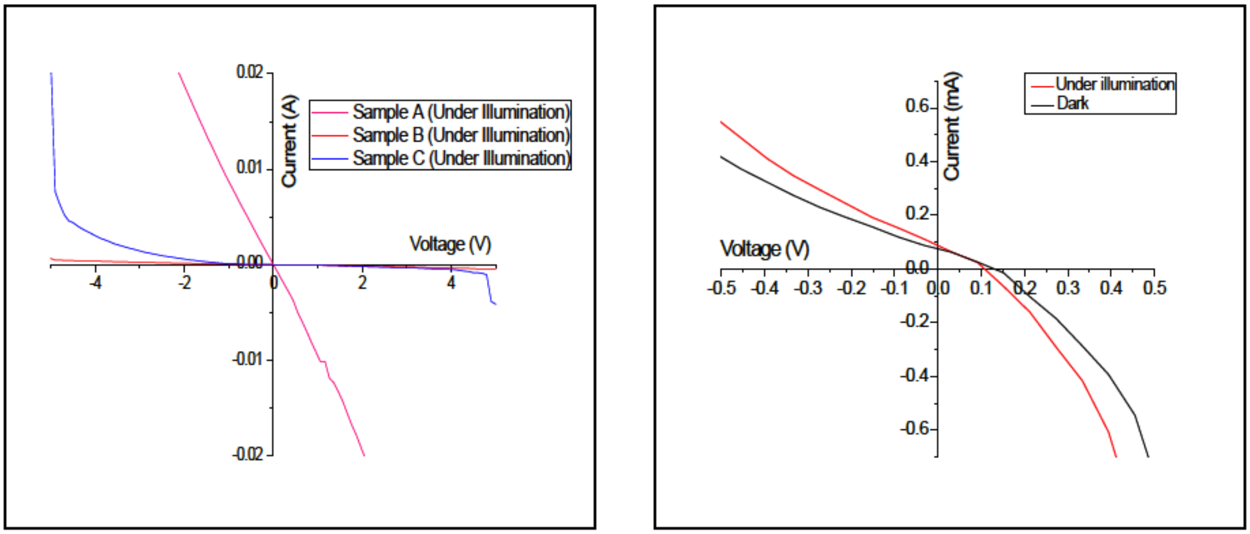
On the other hand, sample C which has organic layer thickness of 163.57 nm shows an open circuit voltage (V_{oc}) which indicates that a solar cell has been formed. However, there is no efficiency. Sample D which has organic layer thickness 150 nm shows a short circuit current density (J_{sc}) of 0.287 mA/cm^2 and open circuit voltage (V_{oc}) of 0.111V.

The efficiency (ɳ) and Fill Factor (FF) of this organic solar cell are 0.0067% and 19.73, respectively. Therefore, we could propose a mechanism explaining the reason of how a solar cell was formed.

The mechanism of the organic solar cell behavior is shown in Figure **4a-c**. Figure **4a** shows the polymer layer deposited using only 1 layer. Since the polymer layer is thin, the exciton will diffuse and has enough life-time to arrive at the metal electrode. Therefore, the solar cell was formed and the efficiency was obtained. Figure **4b** shows a thick polymer layer resulted from 10 times deposition. Since the polymer is easily dissolved in 1-2dichlorobenzene, the resulting film was not uniform and some of the region was etched away during spin coating which forming pin-holes as indicates in Figure **4c**. Pin-hole that occurs on the substrate will cause short circuit between polymer and the substrate resulting an ohmic behavior. This phenomenon is applied to sample A and B. When the coating times were reduced, the formation of pin-hole also reduced. Thus, creating more homogenous thickness film and increasing the possibility of solar cell formation.

5. CONCLUSION

The aim of this study was to examine the effect of ZnO nanostructures for efficient energy conversion in



(a) (b)

Figure 3: *I-V* characteristics of P3HT:PCBM; (**a**) Sample A and B shows an Ohmic curve while sample C shows a Schottky curve; (**b**) Organic solar cell curve.

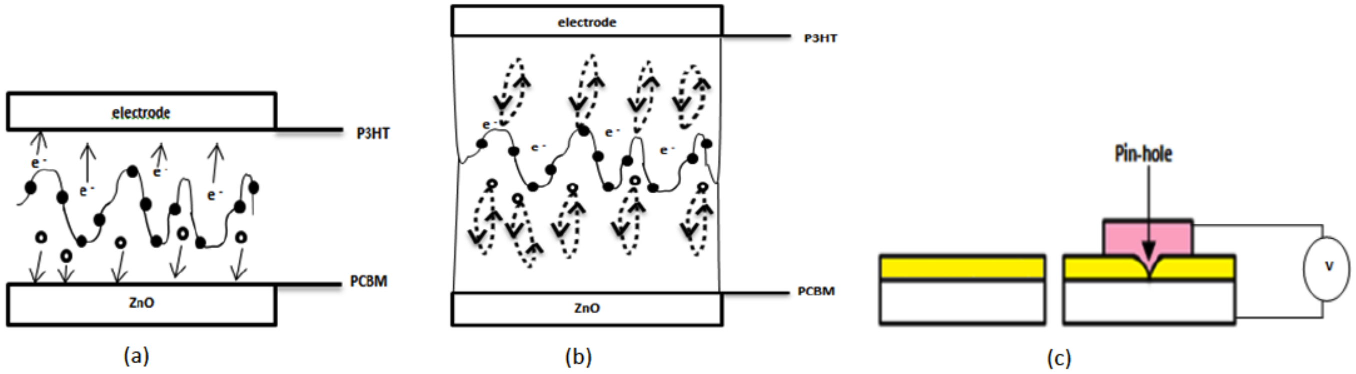


Figure 4: The mechanism of polymer layer; (**a**) Thin polymer layer; (**b**) Thick polymer layer; (**c**) Polymer layer with or without pin-hole.

organic solar cells. We have successfully developed a solution-processed ZnO layer as interlayer for organic solar cells through a simple and low-cost method which is spin coating. The solution-processed ZnO interlayer effectively block holes and collect electrons from the active layer (P3HT:PCBM). It was found that, organic solar cell has been formed and shows the optimum performance with efficiency of 0.0067% and Fill Factor of 19.73. The optimum thickness of the active layer was observed in order to improve the performance of organic solar cells. In conclusion, the effects of ZnO nanostructures were highly influence the stability and efficiency of organic solar cells. This is due to the function of the interlayer to provide a hole blocking capability for efficient electron extraction on the active layer (P3HT:PCBM).

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