



INSTITUTE OF PHYSICS – SRI LANKA

**Research Article****Fabrication of P3HT/PCBM inverted solar cells with ZnO electron transport layer****R. M. G. Wanigasekara, D. G. K. K. Namawardana, W. T. M. A. P. K. Wanninayake, K. M. D. C. Jayathilaka, R. P. Wijesundera\*, W. Siripala***Department of Physics and Electronics, University of Kelaniya, Kelaniya 11600, Sri Lanka***ABSTRACT**

Organic solar cells (OSCs) have gained much popularity among researchers as possible candidate for fulfilment of future energy requirements. Poly(3-hexylthiophene) (P3HT): Phenyl-C61-Butyric Acid Methyl Ester (PC61BM) based bulk heterojunction OSC is one of the most popular types. In this study, inverted P3HT:PCBM OSCs were fabricated on Stainless Steel (SS) substrate with and without ZnO layer in between the SS and active material. In fabrication of the device, ZnO and P3HT:PCBM layers were deposited using spin coating technique while poly-(4,3-ethylene dioxythiophene) (PEDOT): poly(styrenesulfonate) (PSS) layer was deposited using doctor blade method. Finally, gold (Au) front contact was sputter coated. In comparison with the best SS/P3HT:PCBM/PEDOT:PSS/Au device, we could fabricate a SS/ZnO/P3HT:PCBM/PEDOT:PSS/Au device with a 280% increase in power conversion efficiency (PCE). This PCE enhancement is due to the improvement of short wavelength response with the introduction of ZnO to the device.

**Key words:** P3HT, PCBM, Bulk heterojunction, OPV, ZnO

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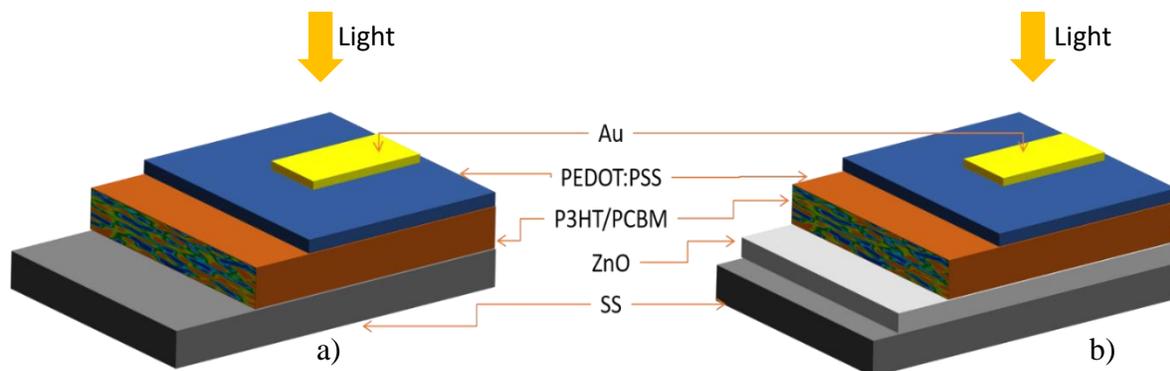


## 1. INTRODUCTION

In the quest to harvest clean energy, solar energy is one of the most promising energy sources due to its free and environmentally friendly nature [1]. Power generation using photovoltaic (PV) systems has increased from 0.26 GW in 2000 [2] to 516 GW in 2018 [3], that is nearly a increment of 2000 folds within just two decades. At present the most used types of photovoltaic (PV) devices are based on inorganic solar cells. However large-scale fabrication process of Silicon (Si) solar cells is associated with a high production cost and environmental pollution [4].

Such drawbacks in the Si solar cell manufacturing have paved the way towards alternative solar cell manufacturing methods. Organic photovoltaics (OPVs) have received more academic and industrial attention in the recent years over the conventional inorganic counterparts, owing to their potential to be low cost, efficient, environmentally friendly and solution processable [5].

Inverted architecture of the solar cell as shown in Figure 1 has gained a considerable attention [6] from researchers because of its stability with compared to the non-inverting organic solar cells. This particular structure avoids the formation of chemically unstable junction between poly-(4,3-ethylene dioxythiophene) (PEDOT):poly(styrenesulfonate) (PSS) PEDOT:PSS and Indium doped Tin Oxide glass (ITO) in the conventional solar cells [7]. And, therefore, it provides more chemically stable architecture to the solar cells. Moreover, mechanical flexibility of the Stainless Steel (SS) substrates over ITO and organic solar cell materials helps to fabricate non-rigid solar cells. Efficiency of these inverted solar cells can be further improved by reducing charge recombination and increasing charge transfer efficiency between the substrate and Poly(3-hexylthiophene (P3HT)/ Phenyl-C61-butyric acid methyl ester (PCBM) blend. Therefore, a thin ZnO layer was coated on the SS substrates to work as an Electron Transport Layer (ETL) [8]. ETLs reduces the surface recombination by decreasing hole mobility and increasing electron mobility through the layer resulting in much higher currents, ultimately increasing the Fill Factor (FF)[9].



**Figure 1:** Inverted architecture of organic solar cells: a) SS/P3HT:PCBM/PEDOT:PSS/Au, and b) ZnO as ETL in SS/ZnO/P3HT:PCBM/PEDOT:PSS/Au

## 2. EXPERIMENTAL METHOD

### 2.1. Materials and Device Fabrication

Regioregular Poly(3-hexylthiophene) (P3HT) (>99%) was purchased from Sigma Aldrich, USA. [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) (>99%) was purchased from Sigma Aldrich, Netherlands. Mono-chloro-benzene (MCB) (>99.5%) was purchased from Sigma Aldrich, Germany. Poly(3,4-ethylenedioxythiophene) and polystyrene sulfonate (PEDOT:PSS) (conductive grade) was purchased from Sigma Aldrich. Zinc acetate dihydrate ( $\text{Zn}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$ ) (<99.5) was purchased from FreyaLab Bulgaria. 304 Grade Stainless steel (SS) was purchased from Sri Lanka. All the materials were used as received.

P3HT:PCBM Organic solar cells (OSCs) were prepared with and without ZnO layer in between the 304 Grade Stainless Steel (SS) substrate and active material. In growth of ZnO, the following procedure was adopted.  $20 \times 25 \text{ mm}^2$  sized polished SS substrates were cleaned ultrasonically with detergent and rinsed in deionized water, acetone, methanol, and isopropyl alcohol respectively, with air drying condition at each step. 1.1 g Zinc acetate dihydrate ( $\text{Zn}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$ ) was dissolved in 10 ml methanol to form a 0.5 M solution and magnetically stirred for 30 minutes at room temperature. The solution was aged 24 hours before the deposition. Aged Zinc acetate solution was spin coated at 3000 rev/min for 30 seconds on clean SS substrates and annealed at  $250 \text{ }^\circ\text{C}$  for 10 minutes, several layers of Zinc acetate were grown on top of each other following the same procedure. Final samples

were annealed at 500 °C for 60 minutes in order to form ZnO. Number of layers were optimised based on photoactive measurements of the final device. Results (not shown) revealed that optimum device can be fabricated with six Zinc acetate layers.

P3HT:PCBM OSCs with ZnO layer in between the SS substrate and active material was fabricated using following steps. 10 mg of P3HT and 10 mg of PCBM were mixed in 1 ml of MCB to form a solution of 20 mg/mL and the solution was magnetically stirred for 12 hours at 55 °C. This solution was spin coated on top of the annealed ZnO coated SS substrates at 3000 rev/min to grow a thin film. The samples were annealed at 140 °C for 30 min. Conductive grade, 1.3 wt.% dispersion of PEDOT:PSS was mixed with ethylene glycol (EG) (10 wt.%) as a dopant. Prepared PEDOT:PSS was blade coated and subsequently annealed at 120 °C for 15 minutes to grow the Hole Transport Layer (HTL). Finally, Gold (Au) spots were deposited on the PEDOT:PSS layer by sputter coating to produce the SS/ZnO/P3HT:PCBM/PEDOT:PSS/Au structure. Also, the reference device was fabricated without ZnO layer. All the above procedure was repeated without coating ZnO layer on SS substrate.

## 2.2. Characterization

Prepared devices were illuminated with ScienceTech SciSun-300 solar simulator at 1.5 AM and Open Circuit Voltage ( $V_{oc}$ ) and Short Circuit Current ( $I_{sc}$ ) were measured using Keithley 2100 multimeter. Light and dark I-V curves were measured using the Gamry Series G Potentiostat/Galvanostat/ZRA. Bulk resistances of the devices were measured using (two wire method) Keithley 2100 multimeter. Spectral responses of the devices were measured using computer controlled ScienceTech 9010 (200 - 1200 nm) monochromator, Stanford Research Systems SR 540 optical chopper and Stanford Research Systems SR830 DSP Lock-in amplifier.

## 3. RESULTS AND DISCUSSION

P3HT:PCBM OSC devices were prepared with and without ZnO layer in between the SS substrate and active material. In growth of ZnO, several layers of Zinc acetate were deposited on top of each other and each layer was annealed at 250 °C for 10 minutes. Finally, samples were annealed at 500 °C for 60 minutes in order to grow ZnO. Number of layers were

optimised based on photoactive measurements of the final device. Results (not shown) revealed that optimum device can be fabricated with six Zinc acetate layers.

Figure 2 shows the dark and light J-V characteristics for the devices of SS/P3HT:PCBM/PEDOT:PSS/Au and SS/ZnO/P3HT:PCBM/PEDOT:PSS/Au. It clearly indicates that the device fabricated with ZnO produces relatively better diode characteristics compared to the device fabricated without ZnO. Photoactive properties of the two devices were shown in the Table 1. SS/P3HT:PCBM/PEDOT:PSS/Au device produced  $V_{oc}$  of 228 mV,  $J_{sc}$  of 4.3 mA/cm<sup>2</sup>, FF of 25% and efficiency of 0.24% while SS/ZnO/P3HT:PCBM/PEDOT:PSS/Au device exhibited  $V_{oc}$  of 349 mV,  $J_{sc}$  of 6.2 mA/cm<sup>2</sup>, FF of 31% and efficiency of 0.67% indicating the enhancement of the photoactive properties with the introduction of ZnO layer. However, both devices produced low efficiencies due to the poor FF. In general, low FF is due to the high series resistance ( $R_s$ ) or low shunt resistance ( $R_{sh}$ ) or both. Therefore, series and shunt resistance of the devices were calculated using J-V characteristics illustrated in Figure 3. Inverse of the gradients of light I-V curves at  $V_{oc}$  and  $I_{sc}$  depict the  $R_{sh}$  and  $R_s$ , respectively. Calculated  $R_s$  and  $R_{sh}$  are shown in the Table 2.  $R_s$ ,  $R_{sh}$  and  $R_s/R_{sh}$  values for devices with and without ZnO layer are 37.82  $\Omega$ , 104.38  $\Omega$  and 0.36, and 52.93  $\Omega$ , 53.53  $\Omega$  and 0.99 for the devices with and without ZnO layer, respectively. Further, increase of  $R_{sh}$  reduces current flowing through the internal loops and increases current flowing to the load causing better FF for the device with ZnO layer. Results reveal that both  $R_s$  and  $R_{sh}$  were improved for the device with ZnO indicating the slight improvement of FF. However, FF is still poor due to the low shunt resistant.

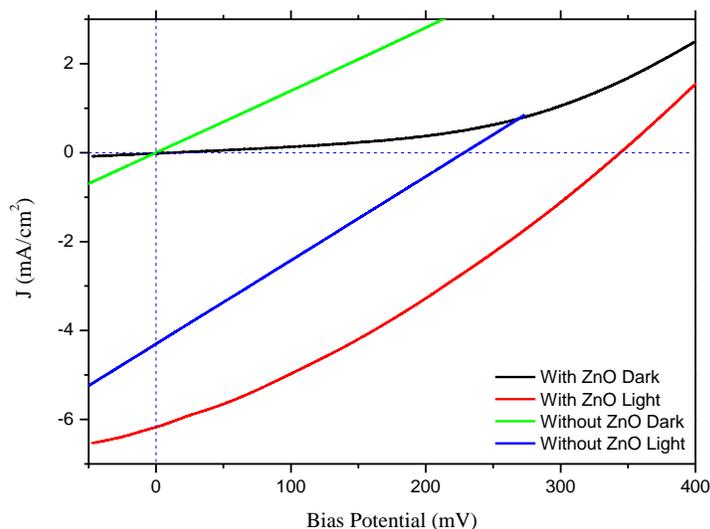


Figure 2: Dark and light J-V characteristics of the devices of SS/P3HT:PCBM/PEDOT:PSS/Au and SS/ZnO/P3HT:PCBM/PEDOT:PSS/Au

Table 1: Photoelectronic properties of the devices of SS/P3HT:PCBM/PEDOT:PSS/Au and SS/ZnO/P3HT:PCBM/PEDOT:PSS/Au

	$V_{oc}$ (mV)	$J_{sc}$ (mA/cm <sup>2</sup> )	Fill factor	PCE
SS/P3HT:PCBM/PEDOT:PSS/Au	228	4.3	25 %	0.24 %
SS/ZnO/P3HT:PCBM/PEDOT:PSS/Au	349	6.2	31 %	0.67 %

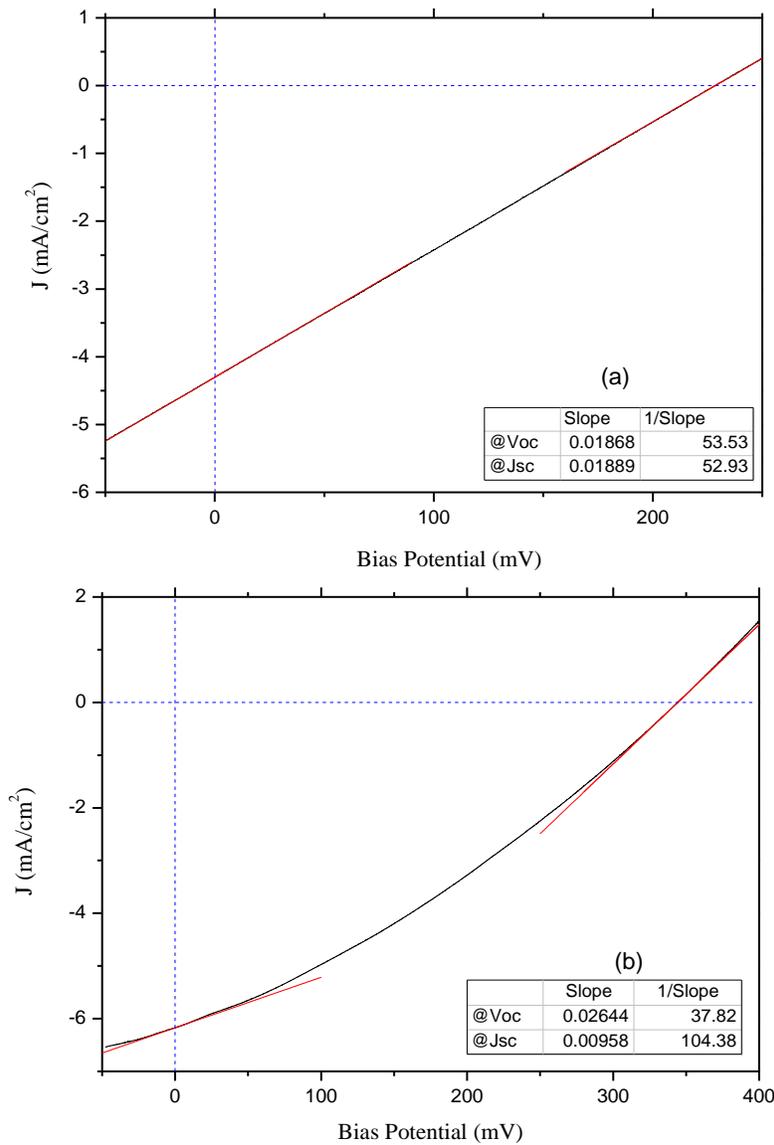
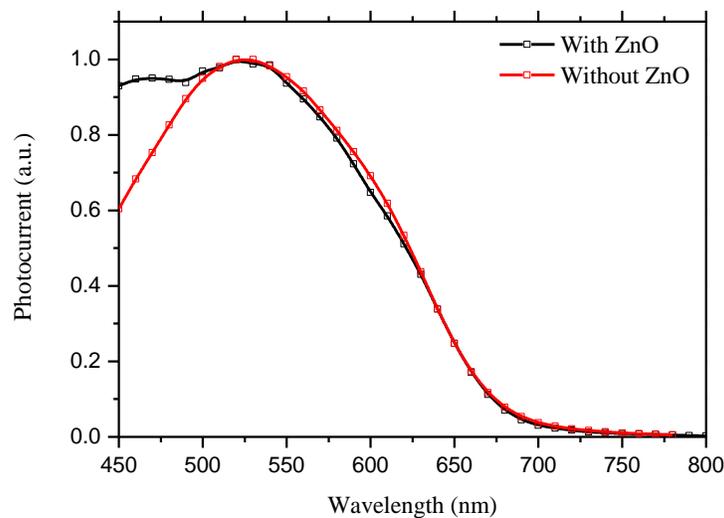


Figure 3:  $R_s$  and  $R_{sh}$  calculations for devices (a) SS/P3HT:PCBM/PEDOT:PSS/Au and (b) SS/ZnO/P3HT:PCBM/PEDOT:PSS/Au

Table 2:  $R_s$  and  $R_{sh}$  values for the devices of SS/P3HT:PCBM/PEDOT:PSS/Au and SS/ZnO/P3HT:PCBM/PEDOT:PSS/Au

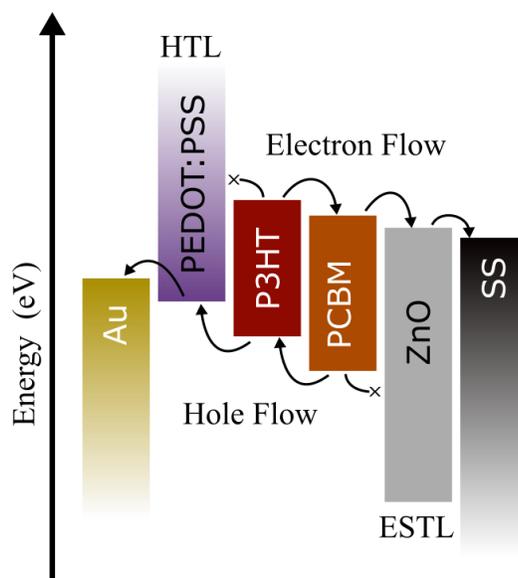
	Without ZnO ESTL	With ZnO ESTL
Series Resistance ( $R_s$ ) ( $\Omega$ )	52.93	37.82
Shunt Resistance ( $R_{sh}$ ) ( $\Omega$ )	53.53	104.38
$R_s / R_{sh}$	0.99	0.36

This enhancement of photoactivity of the device with ZnO was further studied with spectral response measurements. Spectral response spectra are shown in Figure 4. It is clear that, both devices, with and without ZnO have shown responses in the visible wavelengths of the electromagnetic spectrum. But the devices with ZnO produced higher photocurrent for short wavelength region indicating the enhancement of the photoactivity of the device. This increased photon absorption, can be attributed to the reduction of recombination [10] due to the fast transfer of electrons from PCBM layer to SS substrate. This results evidence that ZnO layer attribute as electron transport layer (ETL). Spectral responses of both devices are limited to 700 nm indicating that photon energy higher than 1.77 eV absorbs by the device.



**Figure 4:** Spectral response of the devices SS/P3HT:PCBM/PEDOT:PSS/Au and SS/ZnO/P3HT:PCBM/PEDOT:PSS/Au

The work function of the SS affects the photovoltaic performance of the P3HT:PCBM organic solar cell devices and the maximum performance can be achieved when the work function of the SS is aligned with the LUMO level of PCBM. The role of the electron transport layer is to improve the electron collection efficiency by providing an ohmic contact between SS and PCBM. Since ZnO is a n-type wide band gap semiconductor, its Fermi level is very close to the conduction band [11][12]. Conduction band of the ZnO locates well between the work function of SS and LUMO level of PCBM as shown in Figure 5. Therefore, ZnO makes better band alignment between SS and PCBM causing better transportation of photogenerated electrons to the SS. On the other hand, valence band of ZnO are well below the work function of SS due to the wide band gap nature of the ZnO. It creates a barrier for transportation of photogenerated hole between HOMO level of PCBM and the SS substrate. Since the band alignment of the device with the introduction of ZnO layer, we could fabricate a device with 280% increase in Power Conversion Efficiency (PCE) of the devices.



**Figure 5:** Energy band diagram of SS/ZnO/P3HT:PCBM/PEDOT:PSS/Au device.

#### 4. CONCLUSION

In this study, inverted P3HT/PCBM organic solar cells were fabricated on stainless steel substrate with and without ZnO layer as an ETL. The solar cell structures SS/P3HT:PCBM/PEDOT:PSS/Au exhibited  $V_{oc}$  of 228 mV,  $J_{sc}$  of 4.3 mA/cm<sup>2</sup>, FF of 25% and efficiency of 0.24%. Also, SS/ZnO/P3HT:PCBM/PEDOT:PSS/Au device exhibited  $V_{oc}$  of 349 mV,  $J_{sc}$  of 6.2 mA/cm<sup>2</sup>, FF of 31% and efficiency of 0.67%. Enhancement of the power conversion efficiency of the devices with ZnO is due to the improvement of short wavelength response and high electron transportation suppressing recombination of photogenerated charge carriers.

#### ACKNOWLEDGMENTS

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