

Fabrication of P3HT:PCBM Inverted Organic Solar Cells

D. G. K. K. Namawardana, R. M. Geethanjana Wanigasekara,
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
**palitha@kln.ac.lk*

ABSTRACT

In recent years, polymer based organic solar cells (OSCs) have received more academic and industrial attention as a potential candidate for producing clean and renewable energy. As an alternative for the conventional device structure, OSC devices with inverted structure were fabricated and characterized under top illumination. Regioregular poly (3-hexylthiophene) (P3HT) and phenyl-C61-butyric acid methyl ester (PCBM) were used as electron donor and electron acceptor material respectively for the device fabrication with the structure of SS/P3HT:PCBM/PEDOT:PSS/Au. Performances of fabricated OSC devices were optimized by varying several parameters including the spin rate at which active layer was casted, annealing temperature and duration of annealing the active layer. The best device produced an open-circuit voltage (V_{oc}) of 238 mV and short-circuit current density (J_{sc}) of 4.36 mAcm^{-2} . The maximum power conversion efficiency (PCE) was 0.25% with a fill factor (FF) of 24.86% under 1 sun illumination (AM 1.5G, 1000 Wm^{-2}).

1. INTRODUCTION

Polymer based organic solar cells (OSCs) have become a widely researched topic owing to their potential to be low cost, efficient, environmental friendly and solution processable [1]. Most reported fabrications of OSC devices have been conducted on indium-tin oxide (ITO) coated glass substrates in conventional order [2]. However, to minimize the oxidation and degradation of active material due to the diffusion of oxygen and moisture through low-work-function metal cathodes such as Al, inverted structure of OSC devices with high work function metals (Ag, Au) can be occupied [3]. Furthermore, ITO glass substrates are not ideal for large scale fabrication due to their rigid nature and high production cost as Indium is a scarce and expensive element, therefore metals can be used as substrate [4]. Furthermore, metal substrates possess many advantages over glass substrates including lightweight, high mechanical flexibility, and large-area processability [5].

Inverted structure of OSC consists of a conductive glass or metal substrate as the cathode, an active layer, a hole transport layer (HTL) and a top metal anode [6]. In polymer based OSC devices, most widely studied combination as the active layer is a bulk heterojunction blend of [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) and regioregular poly(3-hexylthiophene) (rr-P3HT) [7]. They currently dominate the research

Fabrication of P3HT:PCBM Inverted Organic Solar Cells

in polymer OSCs achieving efficiencies over 5% [8]. Regioregular P3HT (poly-3-hexylthiophene) act as the electron donor material possessing high hole mobility and absorbing photons at longer wavelengths. PCBM act as the electron acceptor material with a high electron mobility [9]. On active layer there is a conductive polymer layer of Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) which acts as an electron-blocking layer, and also it assists in transporting photo-generated holes to the anode [10]. Therefore, this study will mainly be focused on fabricating an OSC on Stainless Steel (SS) and to demonstrate the optoelectronic properties of the fabricated OSCs.

2. EXPERIMENTAL DETAILS

2.1 Materials

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) polystyrene sulfonate (PEDOT:PSS) (1.3 wt.%, conductive grade) was purchased from Sigma Aldrich, USA. 304 Grade Stainless steel (SS) was purchased from Sri Lanka.

2.2 Fabrication of Devices

The 304 grade polished stainless steel substrates were ultrasonically cleaned stepwise in detergent, DI water, acetone, methanol, 2-propanol and subsequently dried by air flow. Bulk-heterojunction polymer blend was made by mixing regioregular P3HT and PCBM with a weight ratio of 1:1 in chlorobenzene (20 mg/mL) and stirred at 55 °C for 12 h. Then this blend was spin-coated onto pre-cleaned SS substrates and annealed to form the active layer. Conductive grade, 1.3 wt.% dispersion of PEDOT:PSS in H₂O was doped with Ethylene Glycol (EG) to prepare a 10 wt.% solution and stirred at room temperature for 12 h. As a hole-transport-layer (HTL), it was blade-coated on the active layer and the stack was annealed at 120 °C for 10 minutes. Finally, as the top contact of the device, Gold (Au) spots (2×2 mm²) was sputter coated. The cross sectional view of the final device structures (SS Substrate/P3HT:PCBM/PEDOT:PSS/Au) is schematically shown in Fig. 1

Open circuit voltage (V_{oc}), short circuit current (I_{sc}), power conversion efficiency (PCE) and fill factor (FF) of fabricated devices were measured using Keithely 2100 multimeter under 1 sun illumination (AM 1.5G, 1000 Wm⁻²) of Sciencetech Scisun-300 solar simulator. Dark and light I-V characteristics of the devices were obtained using Gamry series G300 potentiostat. Spectral responses of the cells were measured using a computer controlled system consisting of Stanford Research-SR 830 DSP lock-in amplifier, ScienceTech 9010 (200 - 1200 nm) monochromator and a Stanford SR 540 chopper.

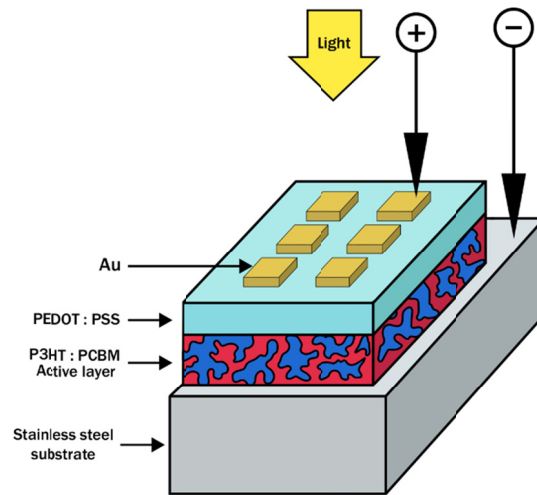


Fig. 1: Schematic diagram of cross section of top illuminated inverted OPV devices on SS substrate

2.3 Device Characterization

3. RESULTS AND DISCUSSION

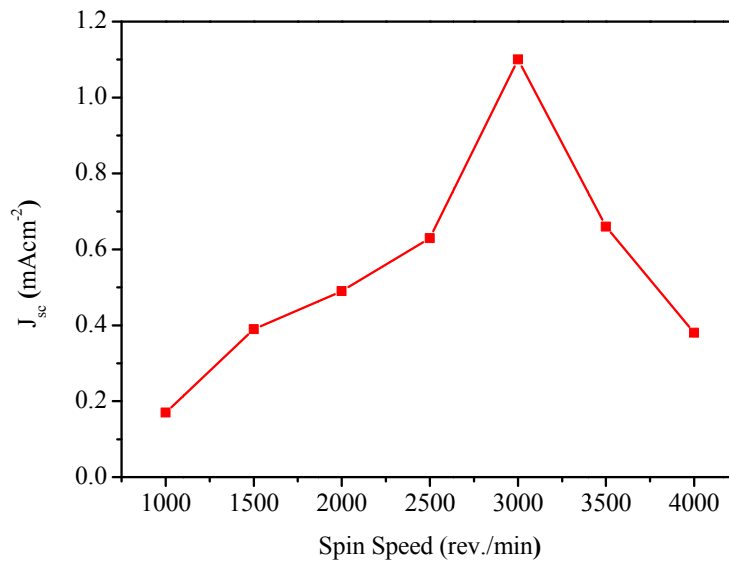


Fig. 2: Variation of J_{sc} with spin speed at which active layer was casted

Table 1: Photoactive performance of OSCs which active layers were deposited with different spin rates (annealed at 140 °C for 30 minutes)

Spin rate (rev./min)	J_{sc} (mAcm ⁻²)	V_{oc} (mV)	FF %	PCE %
1000	0.17	23	25.20	0.005
1500	0.39	74	24.53	0.035
2000	0.49	52	24.82	0.031
2500	0.63	95	23.39	0.070
3000	1.10	165	23.38	0.210
3500	0.66	124	23.58	0.096
4000	0.38	65	24.71	0.030

In optimization of the P3HT:PCBM active layer, three different parameters: the spin speed at which the layer was cast, annealing temperature and duration were varied. Spin speed was varied between 1000 to 4000 rev./min. It mainly effects for the active layer thickness and uniformity of the film. At lower spin speeds, polymer blend did not spread uniformly forming visible changes of the layer thickness and subsequently resulted in low J_{sc} values as depicted in Fig. 2. Layer thickness also plays a crucial role in device performance. Low spin speeds have caused higher film thickness which increase drift lengths exceeding range of excitons. The extended exciton diffusion length results for higher rate of exciton recombination [11]. At very high spin speeds, low J_{sc} values have been resulted due the lower thickness and more pinholes formed in the film. In addition, the thickness of the active layer should be set within the penetration length of the incident light. The indicated low device performance may be due to exceeding the penetration length at high spin speeds. The highest J_{sc} was obtained at the spin speed of 3000 rev./min, indicating the film has become more uniform and reached the optimum level of layer thickness. Table 1 shows photoactive properties of OSCs which active layers were deposited at different spin speeds.

Table 2: Photoactive performance of OSCs with annealing temperature of the active layer (active layer was casted at 3000 rev./min and annealed for 30 minutes)

Annealing Temperature (°C)	J_{sc} (mAcm ⁻²)	V_{oc} (mV)	FF %	PCE %
Non-annealed	0.09	8	24.48	0.009
100	0.42	85	24.64	0.04
120	0.90	91	24.91	0.11
140	1.21	153	24.40	0.22
160	1.09	141	24.71	0.19
180	1.06	110	25.49	0.15
200	0.70	113	25.13	0.09

The effect of annealing temperature on device performance was studied at the temperature range of 100 °C and 200 °C for a fixed time duration of 15 minutes. Photoactive properties of OSCs annealed at different temperatures are shown in Table 2. Also, the annealing duration was varied in the time range between 10 minutes and 120 minutes at a fixed temperature of 140 °C. Table 3 shows the photoactive properties of OSCs annealed at different durations. With compared to the non-annealed reference device, it can be observed that the J_{sc} was significantly enhanced after the annealing treatment. The annealing encourages the P3HT chains to organize and self-assemble into a more regular, crystalline state, resulting in higher charge mobility. Also, the PCBM diffuse and aggregate separately to form larger domains in the thin film. This phase separation between donor and acceptor materials facilitates an efficient exciton dissociation at the donor/acceptor interface leading to higher J_{sc} values. The highest J_{sc} was obtained at 140 °C indicating optimum phase separation to facilitate for the maximum exciton dissociation as shown in Fig. 3. However, at higher temperatures, it can be observed that J_{sc} has gradually decreased. The donor and acceptor materials should be in close proximity in the range of the excitons diffusion length to enable an efficient exciton dissociation at the heterojunction. At higher temperatures, larger phase separated domains are formed exceeding the exciton diffusion length resulting higher rate of exciton recombination and low J_{sc} values [12]. When annealing duration is increased, phase separation between the donor and acceptor materials was enhanced. The highest J_{sc} was obtained from the devices annealed for 60 minutes as shown in Fig. 4. This could be due to the optimum size of the separated domains is reached the maximum exciton dissociation. Further increase of annealing time, J_{sc} starts to decline. Longer annealing time decreases the donor-acceptor interfacial area owing to larger size phase separation, resulting in higher rate of excitons recombination.

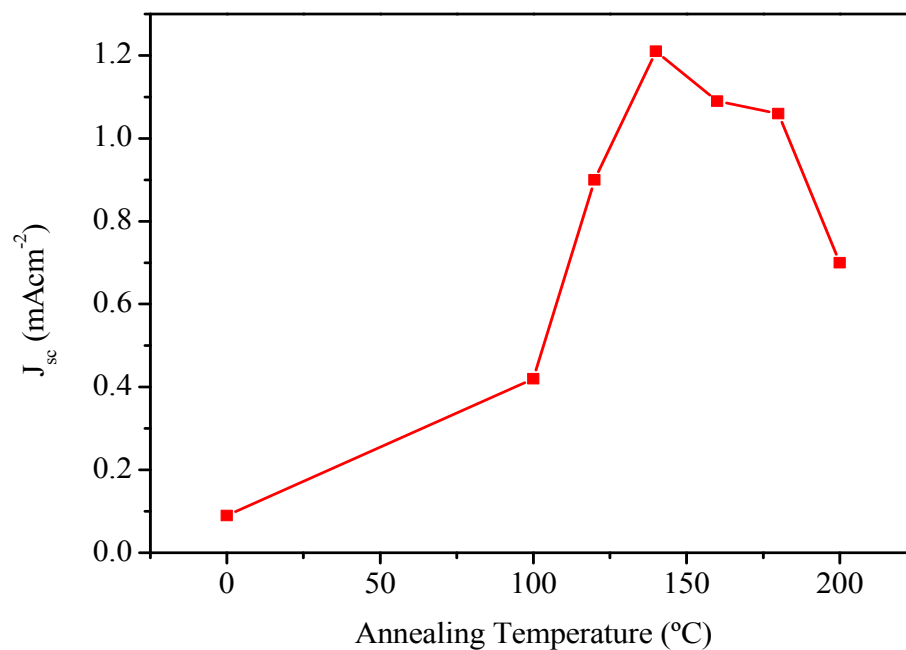


Fig. 3: Variation of J_{sc} with annealing temperature of the active layer

Table 3: Photoactive performance of OSCs with annealing duration of the active layer (active layer was casted at 3000 rev./min and annealed at 140 °C)

Annealing Time (min)	J_{sc} (mAcm ⁻²)	V_{oc} (mV)	FF %	PCE %
Non-annealed	0.09	8	24.48	0.009
15	0.76	108	22.85	0.09
30	1.10	165	23.38	0.21
45	1.25	163	23.40	0.22
60	1.52	213	20.80	0.33
75	1.14	221	22.14	0.27
90	1.02	57	24.92	0.014
105	0.64	69	24.66	0.011
120	0.49	51	24.82	0.031

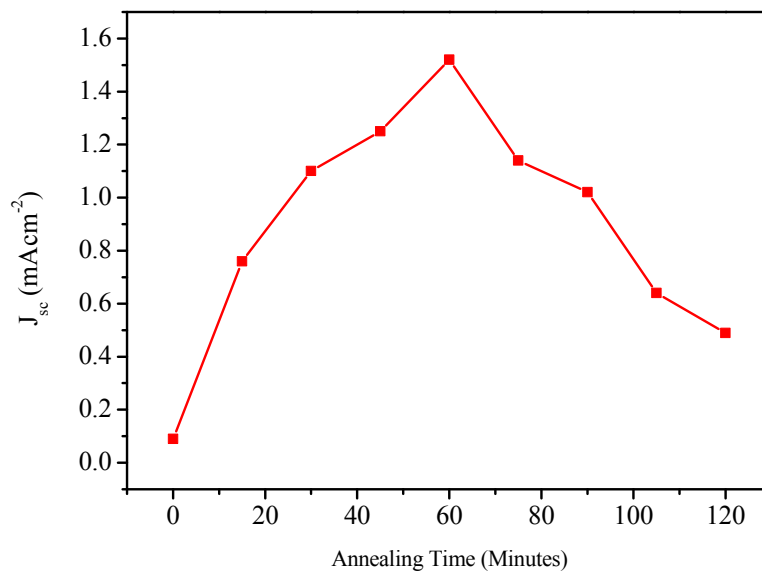


Fig. 4: Variation of J_{sc} with annealing time of the active layer

Fig. 5 shows dark and light I-V characteristics of the best OSC fabricated using optimum conditions. The best device fabricated under the optimized conditions produced open circuit voltage (V_{oc}) of 238 mV and current density (J_{sc}) of 4.36 mAcm⁻² with a fill factor (FF) of 24.86%. The maximum power conversion efficiency (PCE) for the best OSC was calculated and it was 0.24% under 1 sun illumination.

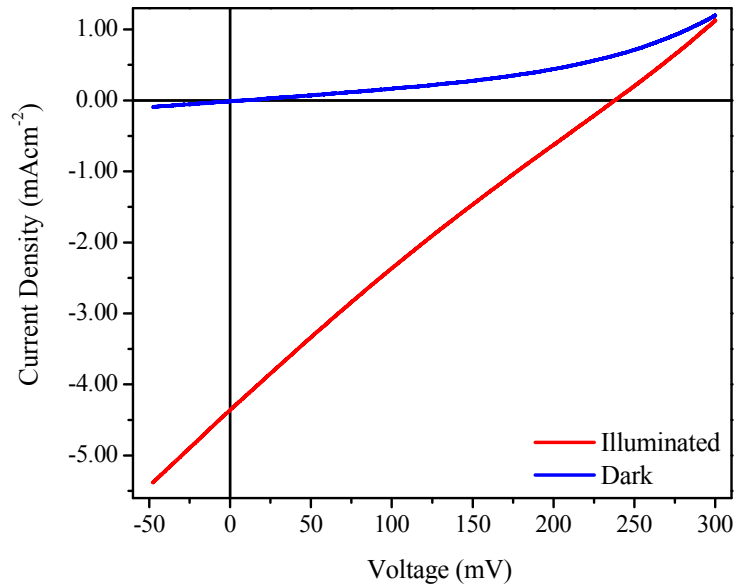


Fig. 5: Dark and light I–V curve of the top illuminated inverted best OSC device

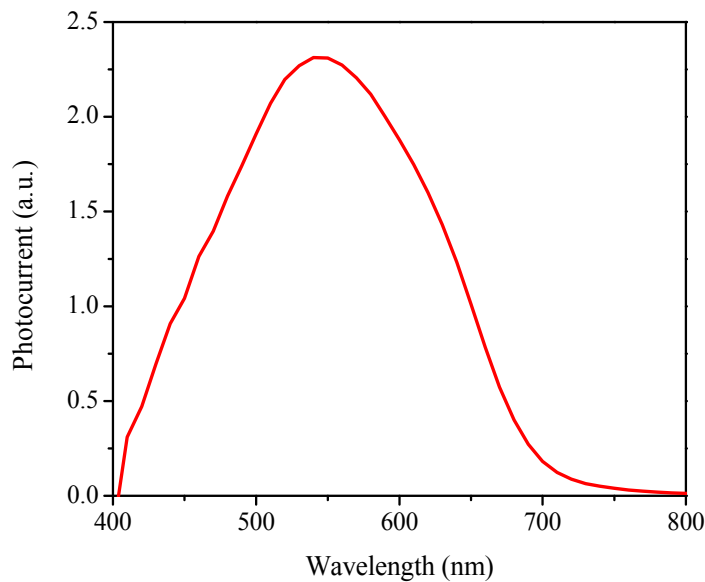


Fig. 6: Spectral response of the best OSC device

Fig. 6 shows the spectral response obtained for the device fabricated at optimum conditions. It can be observed that the device responds to the visible wavelengths of the electromagnetic spectrum. It absorbs more photons in the wavelength range of 500 nm to 600 nm resulting a bell-shaped curve. Further, it indicates that the device absorbs photons with energy higher than 1.77 eV with a band edge at 700 nm to generate electron-hole pairs, thus a photocurrent. Due to the higher energy level difference between HOMO (highest occupied molecular orbitals) and LUMO (lowest unoccupied molecular orbitals) levels of the active material, lower energy photons are not absorbed.

4. CONCLUSION

Fabrication of P3HT:PCBM Inverted Organic Solar Cells

In this study, we have successfully fabricated an inverted P3HT:PCBM organic solar cell device using optimized growth parameters. Results indicated that the spin speed of the active layer formation, annealing temperature, annealing duration of the active layer and doping of PEDOT:PSS solution have significantly effects on the device performance. Optimizing the layer thickness, annealing temperature and annealing duration of the active layer has maximized the donor-acceptor interfacial area and the higher degree of crystallinity. This optimized morphology and phase segregation of active layer has improved the device performance.

5. ACKNOWLEDGMENT

We gratefully acknowledge the financial supports by the National Science Foundation under the research grant NSFPSF/ICRP/2017EA&ICT/02.

6. REFERENCES

- [1]. Li, G., Zhu, R. & Yang, Y. *Polymer solar cells*. Nat. Pho., 6 (2012) 153–161.
- [2]. Zhang, C., You, H., Lin, Z., & Hao, Y., *Inverted Organic Photovoltaic Cells with Solution-Processed Zinc Oxide as Electron Collecting Layer*, Jap. J. App. Phy., 50.10 (2011) 1143.
- [3]. Chen, L. M., Hong, Z. R., Li, G. & Yang, Y., *Recent Progress in Polymer Solar Cells: Manipulation of Polymer:Fullerene Morphology and the Formation of Efficient Inverted Polymer Solar Cells*, Adv. Mater., 21 (2009) 1434–1449.
- [4]. Chang, Y.-M., Chen, C.-P., Ding, J.-M., Leu, C.-Y., Lee, M.-J. & Chen, R.-D., *Top-illuminated organic solar cells fabricated by vacuum-free and all-solution processes*, Sol. Energy Mater. Sol. C., 109 (2013) 91–96.
- [5]. Galagan, Y., Rubingh, J. E., Andriessen, R., Fan, C. C., Blom, P., Veenstra, S. C. and Kroon, J. M., *ITO-free flexible organic solar cells with printed current collecting grids*, Sol. Energy Mater. Sol. C., 95 (2011) 1339–1343.
- [6]. Jenekhe S. A. and Yi, S., *Efficient photovoltaic cells from semiconducting polymer heterojunctions*, App. Phy. Lett., 77 (2000) 2635–2637.
- [7]. Breeze, A. J., Schlesinger, Z., Carter, S. A., Tillmann, H. and Horhold, H.-H., *Improving power efficiencies in polymer-polymer blend photovoltaics*, Sol. Energy Mat. Sol. C., 83 (2004) 263–271.
- [8]. Ma, W., Yang, C., Gong, X., Lee, K. & Heeger, A. J., *Thermally stable, efficient polymer solar cells with nanoscale control of the interpenetrating network morphology*, Adv. Funct. Mater., 15 (2005) 1617–1622.
- [9]. Shrotriya, V., Ouyang, J., Tseng, R. J., Li, G. & Yang, Y., *Absorption Spectra Modification in Poly(3-Hexylthiophene):Methanofullerene Blend Thin Films*, Chem. Phy. Lett., 411 (2005) 138-143.
- [10]. Kumar, V., & Wang, H., *Selection of metal substrates for completely solution-processed inverted organic photovoltaic devices*, Sol. Energy Mater. Sol. C., 113 (2013) 179-185.
- [11]. Kietzke, T., *Recent Advances in Organic Solar Cells*, Adv. OptoElec., 2007 (2008) 1687-1702.
- [12]. Yang, X. N., Loos, J., Veenstra, S. C., Verhees, W. J. H., Wienk, M. M., Kroon, J. M., Michels, M. A. J. & Janssen, R. A. J., *Nanoscale morphology of high-performance polymer solar cells*, Nano Lett., 5 (2005) 579–583.