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journal homepage: www.elsevier.com/locate/orgelEfficient light trapping and interface engineering for performance enhancement in PTB7-Th: PC₇₀BM organic solar cellsKunal Borse¹, Ramakant Sharma¹, H.P. Sagar, P. Anil Reddy, Dipti Gupta*, Aswani Yella*

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ABSTRACT

Inefficient light absorption and poor charge separation are considered as two major bottlenecks for achieving highly efficient bulk heterojunction organic solar cells (BHJ OSCs). In the present study, we have introduced an additional phenyl-C71-butyric acid methyl ester (PC₇₀BM) layer to modify the interface between ZnO based electron transport layer (ETL) and photoactive layer comprised of Poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b; 4,5-b']dithiophene-2,6-diyl-alt-(4-(2-ethylhexyl)-3-fluorothieno[3,4-b]thio-phen-)-2-carb-oxylate-2-6-diyl)] (PTB7-Th):PC₇₀BM. This interface engineering has quenched the electron–hole recombination at the interface and has improved power conversion efficiency (PCE) from 6.65 to 7.74%. Devices were fabricated in an inverted geometry having a structure ITO/ZnO (40 nm)/PC₇₀BM (5 nm)/PTB7-Th:PC₇₀BM (70 nm)/MoO₃ (10 nm)/Ag (100 nm). Additionally, V-grooved textured PDMS films were attached to the backside of OSC substrates which has further improved PCE to 9.12%. Our study suggests that the performance enhancement as observed in OSCs with V-grooved textured PDMS films could be due to increased total optical path length of the incident light within the device.

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1. Introduction

Solution processed bulk heterojunction organic solar cells (OSCs) offers many advantages such as good cost-efficiency balance, short energy payback time and unique form-factor and therefore have attracted a significant attention in recent years [1–5]. However, their power conversion efficiency (PCE) is way behind the other emerging PV technologies [6,7]. To improve the device performance, researchers have adopted two different strategies: (i) to design and develop new donor and/or acceptor molecules and (ii) to optimize various aspects of device engineering processes [8–12]. Both these strategies aims at overcoming the two major impediments restricting the PCE i.e. inefficient light absorption of the donor molecules and inefficient charge collection at the interface at donor/acceptor and/or active layer and transport layer. Over the years, it has been demonstrated that the PCE can be improved by designing new donor polymers from ~3% with poly(3-hexylthiophene) (P3HT): phenyl-C71-butyric acid methyl ester (PC₇₀BM) OSCs to over 10% with Poly[(5,6-difluoro-2,1,3-

benzothiadiazol-4,7-diyl)-alt-(3,3''-di(2-octyldodecyl)-2,2'; 5',2''; 5'',2'''-quaterthiophen-5,5'''-diyl)](PffBT4T-2OD):PC₇₀BM OSCs [11–15]. These recent low bandgap donor molecules have not only shown improved photons harvesting over the wide spectral range but also have demonstrated improved charge mobility as compared to the previously reported donor molecules [11,12]. Thus, a substantial increase in PCE can be achieved by designing and developing new low bandgap donor molecules. However, in the last two decades a very handful of donor molecule seems to be promising and thus making the choices limited [11–13,15,16]. To improve the PCE further by 10–20% of the reference devices using the known donor polymers with the marginal increase in the cost of OSCs, optimization of various aspects of device engineering processes needs to be thought of.

Some of the approaches of device engineering involve use of different combinations of electron and/or hole transport layers, solvent additives, incorporation of metal, dielectric and/or semiconducting nanoparticles (NPs), etc. [17–22]. These modifications have been proved beneficial to enhance the device performance. However, this increase in PCE is limited due to various factors such as poor quality of interface between ETL/HTL and active layer, alteration in the active layer morphology due to incorporation of metal, dielectric and/or semiconducting nanoparticles (NPs). The

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problem of the poor quality of the interface between ETL/HTL and active layer is not that complicated and can be addressed by introducing the interlayer so as to achieve smooth interface [23–25]. But problem of alteration in the active layer morphology due to incorporation of metal, dielectric and/or semiconducting nanoparticles (NPs) and SWCNTs in some cases is somewhat critical. On the one hand introduction of various nanoparticles (NPs) facilitates the trapping of light due to enhanced optical path length [26,27]. In particular, when metal NPs are introduced in active layer, they can additionally offer local surface plasmon resonance, therefore, when an incident light with a similar mode of frequency interacts with the NPs, its energy can be stored in the oscillation mode of the NPs resulting in more absorption and/or scattering [18]. However, most of these NPs are generally synthesized using the chemical routes and have lot of surface defects which acts as a trap centres. Further, if their concentration is increased beyond the optimized concentration, they will occupy more volume fraction of active layer and therefore the probability of scattered photon getting absorbed again gets decreased [19,20]. Both these issues related to incorporation of NPs restrict the improvement in performance. Thus, it is necessary to employ non-destructive efficient light trapping technique which will not alter or modify the active layer and will not have trap centres. Various light trapping techniques were previously used to improve the performance of OSCs. These include use of textured substrates, micro-prisms, diffraction gratings, stress-induced micro-scale wrinkles/folds, or 2D periodic array following laser interference patterns [28–32]. Some of these techniques are quite efficient to improve device performance but are very costly. Recently, Cho et al. has proposed textured plastic films attached to the external surface of the substrates of OSCs as spectrally neutral light trapping schemes [28]. In their study, they have demonstrated that random and V-groove texturing is very efficient to improve the performance of OSCs.

Thus, present study aims to simultaneously address issue of inefficient light absorption and inefficient charge collection. Thus, we have introduced an additional PC₇₀BM layer to modify the interface between ZnO based electron transport layer (ETL) and photoactive layer. The photoactive layer comprised of Poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b; 4,5-b']dithiophene-2,6-diyl-alt-(4-(2-ethylhexyl)-3-fluorothieno[3,4-b]thiophene-)-2-carb-oxylate-2-6-diyl)] (PTB7-Th):PC₇₀BM. Devices were fabricated in an inverted geometry having a structure ITO/ZnO (40 nm)/PC₇₀BM (5 nm)/PTB7-Th:PC₇₀BM (100 nm)/MoO₃ (10 nm)/Ag (100 nm). Additionally, V-grooved textured PDMS films were attached to the backside of OSC substrates. Utilizing the interface modification and textured PDMS films, we have observed an increase in the power conversion efficiencies by ~37%. Our study suggests this performance enhancement after introduction of additional PC₇₀BM layer between ZnO based ETL and photoactive layer is due to improved charge collection and observed improvement in OSCs with V-grooved textured PDMS films could be due to increased total optical path length.

2. Experimental

PTB7-Th (Lumtec), PC₇₀BM (Lumtec, 99.5%), dichlorobenzene (DCB) (Aldrich, 99.9%), dichloromethane (Aldrich, 99.9%), MoO₃ (Alfa Aesar, 99.9995%), 1, 8 diiodooctane (DIO) and Silver (Alfa Aesar, 99.99%) were used as received without further purification.

2.1. Preparation of sol gel ZnO

Sol gel ZnO was prepared by the method reported elsewhere [14]. Briefly, 10 ml of 0.25M solution of Zinc acetate dihydrate (Aldrich, 99.9%) was prepared in 2-methoxy ethanol. Subsequently,

0.25M of ethanolamine was added to the solution and allowed to stir rigorously for 12 h at 70 °C to get a homogeneous, clear and transparent solution. Thereafter solution was aged for 24 h before using it for spin-coating as an electron transport layer.

2.2. Preparation of PDMS textured film

PDMS textured film was prepared by the method reported by Changsoon Cho et al. [28] Back-light enhancement films (BEF, Shinwha Intertek PTX338) used in the LCD industry were employed as masters. At first, PDMS (Sylgard 184, Dow Corning) base and cross linker were mixed in 10:1 wt ratio and allowed to stir for 30 min. This mixture was degassed for 30 min to remove the air bubbles. Textured PDMS films replicating the topology of the masters were then prepared by casting a pre-polymer (Sylgard 184, Dow Corning) on the masters and curing them at 90 °C for ~4 h. The textured PDMS films were peeled off, cleaned with isopropyl alcohol (IPA) to remove any dust particles and dried with nitrogen gun before attaching to the backside of OPV substrates.

2.3. Device fabrication

At first, photoactive blend comprised of PTB7-Th (10 mg) and PC₇₀BM (15 mg) was prepared in 1 ml of DCB with 3% v/v of 1, 8 diiodooctane (DIO) solvent as an additive. The solution was allowed to stir at 70 °C in the dark for at least 12 h. For the device fabrication, ITO coated glass substrates (Luminescence Technology corp. Taiwan, with a sheet resistance of 15 Ωsq⁻¹ and transmittance >85%) were cleaned by process reported elsewhere [14,15]. Thereafter, sol gel ZnO, which was previously synthesized, was spin-coated on pre-cleaned ITO substrates at 2000 rpm for 30 s to obtain a film of ~40 nm. The substrates were then annealed at 200 °C for 15 min to remove excess solvents. Thereafter, substrates were transferred inside nitrogen filled glove box and a photoactive blend was spin-coated at 900 rpm for 120 sec. The films were allowed to get dried for 2 h and then subsequently, the devices were evaporated using the shadow mask by thermal evaporation of 10 nm MoO₃ layer as a hole transport layer and 100 nm Ag electrode as anode. For the devices with the additional PC₇₀BM interlayer, PC₇₀BM solution (10 mg/ml in DCM) was spin-coated on top of the ZnO nanocrystalline thin film at a speed of 1200 rpm for 60 s and annealed at 70 °C for 10 min. The reason for selecting the DCM for making the PC₇₀BM solution is because of its orthogonality with DCB. This is very important to avoid washing out or mixing of underneath PC₇₀BM interlayer during the upper layer (photoactive layer) spin-coating.

2.4. Device characterization and testing

The current density-voltage (J-V) characteristics curves of fabricated devices with and without PC₇₀BM interlayer and/or textured PDMS films were measured using a Keithley 2600 source meter and a Newport solar simulator (model number 91160) shines light with AM 1.5 G spectral distribution, which was calibrated using a certified reference solar cell to an intensity of 1000 W/m². The test cells were masked with a single aperture and care has been taken to exclude all light from entering the cell elsewhere, including shading of the edges of the substrates. The active device area is defined as 4.5 mm² by using a shadow mask. After measurement of the devices, a V-grooved textured PDMS films were attached to the backside of OSC substrates and measurements were taken again. Field Emission Gun-Scanning Electron Microscope (FEG-SEM) images were taken using JEOL JSM-7600F FEG-SEM instrument. The absorption studies were carried out using PerkinElmer Lambda 950 UV/VIS/NIR spectrophotometer.

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