An insight on oxide interlayer in organic solar cells: From light absorption and charge collection perspectives

Zhenghui Wu, Bo Wu, Hoi Lam Tam, Furong Zhu[*]

Department of Physics, Institute of Advanced Materials, and Institute of Research and Continuing Education (Shenzhen), Hong Kong Baptist University, Kowloon Tong, NT, Hong Kong

A B S T R A C T

A comprehensive study of the effect of oxide interlayer on the performance of bulk-heterojunction organic solar cells (OSCs), based on poly[[4,8-bis[(2-ethylhexyl)oxy] benzo [1,2-b:4,5-b'] dithiophene-2,6- diyl] [3-fluoro-2-[(2-ethylhexyl)carbonyl] thieno [3,4-b] thiophenediyl]] (PTB7): [6,6]-phenyl C71 butyric acid methyl ester ($PC_{70}BM$) blend system, is carried out by optical simulation, interfacial exciton dissociation and charge collection analyses. It is found that a PTB7:$PC_{70}BM$ blend layer thickness optimized for maximum light absorption in OSCs does not generally give rise to the highest power conversion efficiency (*PCE*). OSCs, e.g., based on PTB7:$PC_{70}BM$ blend system, can benefit from the oxide interlayer in two ways, (1) to enhance the built-in potential for reducing recombination loss of the photo-generated charges, and (2) to improve charge collection by removal of unfavorable interfacial exciton dissociation. The combined effects result in ~20% improvement in *PCE* over an optimized control cell, having an identical layer configuration without an oxide interlayer.

1. Introduction

Power conversion efficiency (PCE) of >10% for both single junction and tandem organic solar cells (OSCs) has been demonstrated recently [1,2] through continued progresses made in both new material development and device innovation. However, the performance of OSCs still faces a major challenge to overcome the mismatch between optical absorption length and charge transport scale, caused by the low charge mobility in organic materials. High performing OSCs require a balance between charge transport and optical absorption in selecting the most suitable active layer in a narrow thickness range from 75 to 300 nm. It has been revealed that the unbalanced charge mobility in the photoactive layer, due to oxygen-induced charge traps, is one of the degradation mechanisms [3]. The degradation caused by the interfacial passivation could be avoided by the removal of the low work function cathode [4]. Different approaches have been proposed to enhance the performance of OSCs, e.g., optimizing the nanoscale morphology of organic blend layer to benefit the charge transport [5], incorporating photonic structures in the active layer to achieve broadband absorption enhancement via the optical coupling effect [6], and interposing an oxide optical spacer between the active layer and the electrode [7—10]. The application of metal oxides in OSCs and the impact of the properties of metal oxide/organic hetero-interfaces on cell performance have attracted a lot of attentions. For example, the use of a titanium suboxide [8] or ZnO interlayer [9] between the active layer and the reflective electrode in OSCs has been shown to increase the absorption in the active layer. The enhancement in the photocurrent generation due to the ZnO spacer is found to be more beneficial in OSCs with a thin active layer (<60 nm), but has less effect in device with a thicker layer (>90 nm) [10]. The ZnO layer also serves as a hole blocking layer to reduce the recombination rate [11]. Despite numerous reports about the improvement on OSCs due to the incorporation of the oxide spacer, mechanisms of improving cell performance due to oxide interlayer in OSCs are still inconclusive and controversial. Inganäs et al. [12] reported that no optical beneficial effect can be expected by interposing an optical spacer layer in OSCs with an already optimized active layer thickness. In a recent work, we found that the insertion of a ZnO interlayer between the active layer and the metal contact enables to eliminate the unfavorable exciton dissociation that would otherwise occur at the organic/metal interface, thereby improving the charge collection efficiency [13]. This suggests that the removal of the unfavorable interfacial

exciton dissociation is a perquisite for high performing OSCs.

In addition to the absorption enhancement, it is also important to understand the effect of oxide interlayer on charge collection properties at the organic/cathode interface. The organic/oxide hetero-interfaces have a crucial impact on interfacial exciton dynamics, interfacial charge trapping behavior and the overall device performance. The complexity of physics operating in these OSCs offers a major driving force for new developments. In this work, a systematic study on the effect of ZnO interlayer on OSCs, based on poly[[4,8-bis[(2-ethylhexyl)oxy] benzo [1,2-b:4,5-b'] dithiophene-2,6- diyl] [3-fluoro-2-[(2-ethylhexyl)carbonyl] thieno [3,4-b] thiophenediyl]] (PTB7): [6,6]-phenyl C71 butyric acid methyl ester (PC$_{70}$BM) blend system, was carried out. The absorption enhancement in OSCs due to the presence of a ZnO interlayer between the organic active layer and metal contact is analyzed using optical admittance analysis. Effect of metal oxide/organic hetero-interfaces on the charge recombination and exciton dissociation dynamics at organic/electrode interface in OSCs was analyzed using light intensity dependent current density−voltage (J−V) characteristics and transient photocurrent (TPC) measurements. Our results showed a 20% power conversion efficiency (PCE) improvement in OSCs, realizing through a simultaneous enhancement in light absorption and effective charge collection.

2. Experimental section

ITO/glass substrates with a sheet resistance of 10 Ω/square were used for the OSC fabrication. They were cleaned in ultrasonic bath sequentially with detergent, deionized water, acetone and isopropanol for 20 min each, followed by the *in situ* oxygen plasma treatment prior to the cell fabrication. The PTB7 (1 Material):PC$_{70}$BM (Nano C) blended in a weight ratio of 1:1.5 was fully dissolved in chlorobenzene (CB) (Sigma−Aldrich, 99.8%) with 3% 1, 8-Diiodooctane (DIO) (Sigma−Aldrich) at 60°C before use. A set of structurally identical OSCs with different active layer thicknesses ranging from 60 to 130 nm was then fabricated on PEDOT:PSS-covered ITO/glass substrates by spin-coating inside a N$_2$-purged glove-box with O$_2$ and H$_2$O levels <0.1 ppm. ZnO NPs were synthesized following the procedure described by Hermann-Jens [14]. A 10 nm thick ZnO interlayer was deposited on the active layer by spin-coating inside the glove-box. The samples were then transferred to the adjacent vacuum system with a base pressure of <5.0 × 10^{-4} Pa for forming a 100 nm thick Al top contact, evaporated at a rate of 1 Å/s. OSCs were transferred back to the glove-box for J−V characteristic measurement under an air mass (AM) 1.5G irradiation of 100 mW/cm^2. The intensity of the solar simulator was calibrated using a silicon reference cell with a KG-5 filter.

The transient photocurrent in the devices, e.g., ITO/PEDOT:PSS/PC$_{70}$BM (400 nm)/ZnO(10 nm)Al (30 nm) and a control sample of ITO/PEDOT:PSS/PC$_{70}$BM (400 nm)/Al (30 nm), was generated using a pulsed Nd:YAG laser with the wavelength of 355 nm and pulse duration of <5 ns, illuminated from a semitransparent top Al cathode side. The devices were connected to the 1 MΩ input terminal of an oscilloscope (Agilent DSO8064A Infiniium Digital Oscilloscope) to measure the transient photovoltage. The corresponding transient photocurrent of the devices was obtained by converting the transient photovoltage to the current using the internal resistor of the functional generator (50 Ω) at different biases.

3. Results and discussions

It is known that the performance of OSCs is dependent on the intensity and incident angle of solar irradiation, varied due to sunrise to sunset during the day. In the simulation, we considered incoming light at normal to the cell to unraveling the fundamental

mechanisms of ZnO-induced performance enhancement of OSCs. From optical point of view, a flat OSC can be considered as a thin film system consisting of m layers. The optical electric field distribution in the cells can be optimized optically with an appropriate choice of the active layer thickness or by insertion of an oxide interlayer between the bulk heterojunction and the metal contact. Under normal incidence, the absorption spectrum of the ith layer, for example the active layer $A_i(\lambda)$, in an m layered thin film solar cell can be calculated by optical admittance method [15,16]:

$$A_i(\lambda) = [1 - R(\lambda)][1 - \psi_i(\lambda)] \prod_{j=1}^{i-1} \psi_j(\lambda), \qquad (1)$$

where ψ_j is the ratio of the time averaged numerical magnitude of the Poynting's vector at the jth and (j-1)th boundaries, $R(\lambda)$ is the wavelength-dependent reflectance of the cell. Using the flux of the incident solar radiation $F(\lambda)$, e.g., AM1.5G measured in the units of W/m^2·nm, the integrated absorbance of the active layer, defined as $\overline{A}_i$ which is proportional to the short circuit current density (J_{SC}) of the cell, can be calculated as [15,16]:

$$\overline{A}_i = \frac{\int A_i(\lambda)\, F(\lambda)\, d\lambda}{\int F(\lambda)\, d\lambda}. \qquad (2)$$

Equation (2) allows evaluating the optimal active layer, e.g., PTB7:PC$_{70}$BM, thickness in OSCs through maximizing its integrated absorptance. Essentially, the optical phenomena in thin film OSCs have a profound impact on light absorption in the active layer. This procedure takes into account the interference effects and allows us to optimize light absorption enhancement in the active layer, thereby improving J_{SC} and PCE. Light absorption in different types of OSCs under normal incidence was calculated in the wavelength range from 380 to 780 nm. The thickness of the organic photoactive layer was varied over the range from 40 to 240 nm. This region is comparable in thickness to the active layer in OSCs made with different organic photoactive materials.

To understand the effect of the ZnO interlayer on absorption enhancement in the OSCs, the integrated absorbance of the active layer in OSCs of ITO/PEDOT:PSS (40 nm)/PTB7:PC$_{70}$BM/Al (100 nm) (control cell) and that of the structurally identical cells with a ZnO interlayer inserted between the active layer and the metal contact: ITO/PEDOT:PSS (40 nm)/PTB7:PC$_{70}$BM/ZnO/Al (100 nm), was calculated using eqs. (1) and (2). The wavelength dependent refractive indices of each layer in the OSC system were measured using variable angle spectroscopic ellipsometer [17].

The integrated absorptance of the PTB7:PC$_{70}$BM layer, calculated for the control OSC and the structurally identical cells with different ZnO interlayer thicknesses (10 nm, 20 nm and 30 nm), as a function of its layer thickness ranging from 40 to 240 nm is shown in Fig. 1. It is clear that the integrated absorbance displays an oscillation behavior with increase in the active layer thickness, having a relative absorption maximum occurred at the blend layer thickness of ~105 nm for a control OSC. However, the thickness of the PTB7:PC$_{70}$BM layer corresponding to the absorption maximum in the integrated absorptance becomes thinner, e.g., ~90 nm for OSC with a 10 nm thick ZnO interlayer. A slight decrease in the integrated absorbance is observed when the thickness of the ZnO interlayer further increases from 10 to 30 nm. This suggests that the insertion of an oxide interlayer between the organic active layer and the metal contact does not have an obvious contribution to the absorption enhancement in active layer as compared to that in an optically optimized control cell.

Although a thin oxide interlayer alone cannot account for light