High efficient inverted polymer solar cells by surface treatment of zinc oxide
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1. Introduction

Polymer solar cells (PSC) have been considered as attractive candidate for next generation renewable energy sources due to their potentials such as low material cost, easy processability over large area via roll-to-roll coating process, and unique flexibility [1]. The performance of PSC based on bulk heterojunction (BHJ) structure has been gradually increased by the development of new materials such as low-bandgap donor polymers, high lowest unoccupied molecular orbital (LUMO) level fullerene derivatives, new device structures and processing conditions. Although the efficiency of PSC improved above 7% in single active layer normal type device configuration of glass substrate/Indium Tin Oxide (ITO) anode electrode/ poly-3,4-ethyleneoxythiophene: poly-4-styrenesulfonate (PEDOT:PSS) hole transport layer/BHJ active layer/LiF/Al cathode electrode, this normal type has some problems in device stability because of using PEDOT:PSS and Al. The PEDOT:PSS has an acidic and hygroscopic properties which affect the degradation of ITO electrode, and low-work function Al electrode is easily oxidized under air, oxygen or humidity.

In contrast, inverted type PSCs have advantages over these problems by changing configuration of glass substrate/ITO/electron transport layer (ETL)/active layer/hole transport layer/Ag, where ETL and HTL is usually metal oxide of ZnO, TiOx, and MoO_3, V_2O_5, respectively. In that case, ETL has important role of lowering the work function of ITO from 4.6~4.8 eV to 4.2~4.3 eV (the LUMO level of fullerene acceptor). The widely used solution processed sol-gel ZnO ETL, however, has still limitations of surface defects and energy level mismatch leading to high charge recombination and non-ohmic contacts causing low fill factor (FF), and low current density (J_{sc}). Hence, several studies have been conducted to improve interfacial properties between ZnO ETL and active layer in inverted PSCs [2].

Here, we demonstrated useful and effective method of surface treatment by self assembled monolayer (SAM) of two benzoic acid derivatives in PSCs with thieno[3,4-b]-thiophene/benzodithiophene copolymer (PTB7): [6,6]-phenyl C_{71}-butyric acid methyl ester ($PC_{71}BM$) active layer.

2. Experiment
2.1 Device fabrication

The inverted device structure was ITO/ZnO/SAM/PTB7:$PC_{71}BM$/MoO_3/Ag. ITO-coated glass substrates (10 Ω/□) were initially cleaned by sequential ultrasonication in acetone, de-ionized water and isopropyl alcohol, followed by drying in a vacuum oven. Next, a UV-O_3 treatment of the ITO substrates was performed during 20 min. A 35 nm ZnO layer was formed by spin-coating of ZnO precursor onto the ITO and baked on a hot plate for 1 hour at 200°C in air. The ZnO precursor was prepared by dissolving zinc acetate dihydrate (Sigma-Aldrich) and ethanolamine (Sigma-Aldrich) in 2-methoxyethanol (Sigma-Aldrich) under vigorous stirring for 12 h to realize a hydrolysis reaction in air. The SAM layer were then deposited on the ZnO surface using a solution containing of SAM molecules, 4-methoxybenzoic acid (mBA, Sigma-Aldrich) and 4'-methoxybiphenyl-4-carboxylic acid ($mBPCA$, Alfa Aesar), as illustrated in Figure 1, with a concentration of 1 mM in 2-methoxyethanol. A solution containing a mixture of PTB7 (1-materials) and $PC_{71}BM$ (Nano-C) at a weight ratio of 1:1.5 in mixed solvent of chlorobenzene/1,8-diiodoctane (97:3% by volume) was spin-coated on the top of the SAMs-modified ZnO with thickness of approximately 80 nm. Finally, MoO_3 (10 nm) and Ag (120 nm) were deposited through a shadow mask by thermal evaporation in a vacuum under 1×10^6 Torr. The active area of device was 5 mm^2.
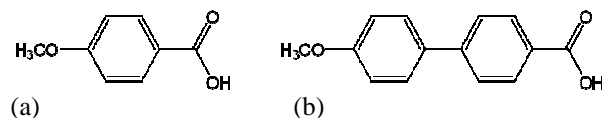

Fig. 1. The chemical structures of (a) mBA and (b) $mBPCA$

2.2. Characterization

Photocurrent density-voltage (J-V) measurement was performed with a Keithley model 2400 Source Meter and a Newport 91192 solar simulator system (equipped with 1KW xenon arc lamp, Oriel). Light intensity was adjusted to simulated AM 1.5 radiation at 100 mW/cm2 with a Radiant Power Energy Meter (model 70260, Oriel). External quantum efficiencies (EQE) were measured using an IPCE G1218a (PV measurement). All measurements were carried out under ambient conditions at room temperature.

3. Results and discussions

The SAM treated inverted PSCs show increased J_{sc}, and thus the enhanced device performance of over 7 %. This increased J_{sc} shows good agreement with the corresponding IPCE spectra.
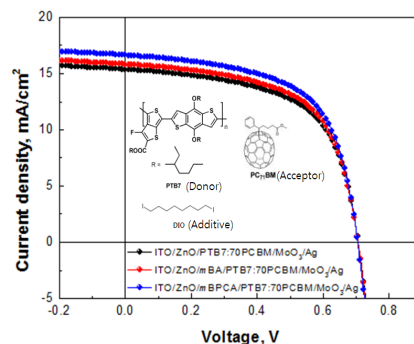

Fig. 2. J-V characterizations of inverted PSCs

The improvements are mainly attributed to the reduced surface trap and dipole moment effect induced by SAM layer. The surface morphology, UV-Vis absorption and device performance properties will be discussed fully.

References

[1] C. J. Brabec, S. Gowrisanker, J. J. Halls, D. Laird, S. Jia, and S. P. Williams, "Polymer–fullerene bulk-heterojunction solar cells". Adv. Mater. 22, 3839 (2010).
[2] H.-L. Yip and Alex K.-Y. Jen, "Recent advances in solution-processed interfacial materials for efficient and stable polymer solar cells". Energy Environ. Sci., 5, 5994 (2012)