Solar Energy Materials & Solar Cells 120 (2014) 744–750

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

High-efficiency inverted tandem polymer solar cells with step-Al-doped MoO_3 interconnection layer

Jian Liu [a,b], Shuyan Shao [a], Gang Fang [a,b], Jiantai Wang [a,b], Bin Meng [a], Zhiyuan Xie [a,*], Lixiang Wang [a]

[a] State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, PR China
[b] University of Chinese Academy of Sciences, Beijing 100039, PR China

ARTICLE INFO

Available online 12 July 2013

Keywords:
Tandem polymer solar cells
Bulk heterojunction
Interconnection layer
Metal oxide
Work function

ABSTRACT

A highly transparent and physically robust step-Al-doped MoO_3 layer was successfully utilized as the interconnection layer (ICL) to fabricate high-efficiency inverted tandem polymer solar cells (PSCs). The inverted tandem cell constructed by the same PCDTBT:$PC_{70}BM$ active layer showed a power conversion efficiency (PCE) of 6.88% with equivalent external quantum efficiency of nearly 80%, implying a high charge-collection efficiency in tandem structure. Incorporation of two sub-cells with complementary absorption spectra leads to further increase of PCE over 7.31%, which is the best results for tandem PSCs with PEDOT:PSS-free interconnection layer.

1. Introduction

Bulk heterojunction (BHJ) polymer solar cells (PSCs) have attracted considerable interest due to their potential to become a new energy source with low-cost, light-weight and mechanical flexibility [1–15]. The power conversion efficiency (PCE) of single-junction polymer:fullerene PSCs has been progressively increased to over 9% with the development of advanced conjugated polymer donor materials, fine-tuning of the active layer morphology and optimization of the cell structure [16–21]. The tandem device architecture is considered to be one of the effective approaches to further boost the PCE of PSCs by extending the spectral coverage to solar light [22–29]. Very recently, a highest PCE of 10.6% was reported for PSCs by using tandem architecture [30]. Apart from the optimal combination of the low and wide band-gap donor polymers, the interconnection layers (ICLs) linking the sub-cells in a tandem structure is crucial to the final photovoltaic performance. An ideal ICL should be not only highly transparent and conductive, but also possess different work functions (WFs) at both sides, enabling energetic matching to the highest occupied molecular orbital (HOMO) level of polymer donor and the lowest unoccupied molecular orbital (LUMO) level of acceptor in sub-cells to lower the interfacial resistance and realize efficient recombination of electrons and holes generated in sub-cells. The ICL should also be robust enough to withstand organic solvents during multi-layer solution processing. Up to now, the commonly used ICL in tandem PSCs is poly(3,4-ethylenedioxythiophene): poly(styrene sulfonate) (PEDOT:PSS)/n-type transition metal oxide (TiO_x or ZnO) nano-crystal bi-layer structure [23,29]. The high conductivity and hydrophilic property of metallic PEDOT:PSS render the ICL very robust and efficient charge recombination layer. However, metallic PEDOT:PSS layer would lead to light attenuation loss in the infrared region [31]. In addition, the incorporation of PEDOT:PSS also raises device instability concerns due to its acidic and hygroscopic nature [32,33]. Transition metal oxides, such as MoO_3 and V_2O_5, have been used to replace the PEDOT:PSS layer in the ICL structure [27,34]. MoO_3 is an excellent hole-collecting material. With MoO_3 as the hole-collecting layer, some ICL structures such as MoO_3/ZnO, MoO_3/TiO*x*, LiF/Al/MoO_3 and MoO_3/Ag/Al/Ca, have been explored to fabricate tandem PSCs [35–39]. Although the cross-linked n-type TiO*x* and ZnO prepared from the sol–gel method can prevent organic solvents from penetrating into the underlying BHJ while spincoating the upper BHJ layer, TiO*x* and ZnO films require high-temperature annealing for completed hydrolysis to realize sufficient conductivity and robustness, which limits the free selection of front sub-cell to optimize the performance of tandem PSCs [34,37]. A combination of MoO_3 and low WF metal is also not an ideal ICL in tandem PSC due to possible charge recombination and optical loss induced by the metal layer [38,39].

Herein, we report an efficient MoO_3-based ICL in inverted tandem structure by using step-Al-doping approach. Al-doping of top half MoO_3 layer can change the high-WF MoO_3 into low-WF MoO_3–Al composite, and thus provides the large WF offset at two sides of MoO_3-based ICL without sacrificing its transparency [40]. More importantly, the MoO_3–Al layer was found to be physically

* Corresponding author. Tel./fax: +86 431 85262819.
E-mail address: xiezy_n@ciac.jl.cn (Z. Xie).

0927-0248/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.solmat.2013.06.034

robust to withstand organic solvents during multi-layer solution processing owing to the formation of Mo–O–Al complex structure. With this step-Al-doped MoO_3 ICL, inverted tandem PSC device constructed by two sub-cells based on a blend of PCDTBT:$PC_{70}BM$ showed a PCE of 6.88% and an equivalent external quantum efficiency (EQE) approaching 80%, implying a high charge-collection efficiency in tandem structure. Tandem PSCs with two sub-cells having complementary absorption spectra were also constructed and a PCE of 7.31% was achieved, which is the best result for tandem PSCs with PEDOT:PSS-free ICL. These results indicate that the step-Al-doped MoO_3 layer is an excellent ICL for tandem PSCs. In addition, an approach was developed to measure the current–voltage (*J–V*) characteristics and EQE spectra of the sub-cells in a tandem structure. Different from the reported method [23,24], the corresponding *J–V* characteristics and EQE spectra of two sub-cells can be extracted regardless of their absorption features.

2. Experimental

2.1. Materials

PCDTBT (molecular weight, Mw=24,000; polydispersity index, PDI=1.8) was synthesized in our laboratory. PDPP3T (Mw=24,000, PDI=3.15) was purchased from Solarmer Material Inc. and $PC_{70}BM$ was purchased from American Dye Source Inc. MoO_3 was purchased from Sigma-Aldrich (99.5%) and used as received.

2.2. Device fabrication and characterization

Inverted tandem polymer solar cells were fabricated on ITO-coated glass substrates. The ITO-coated glass substrates were cleaned with detergent, ultra-sonicated in de-ionized water, acetone, and isopropyl alcohol in sequence, and subsequently dried at 120 °C in an oven overnight. The MoO_3–Al composite cathode buffer layer (10 nm) with 55% Al content in weight percentage was thermally deposited on ITO substrate by co-evaporation in a vacuum chamber under a base pressure of 4×10^{-6} Torr. For the tandem PSCs, a solution containing a mixture of PCDTBT:$PC_{70}BM$ (1:4, w/w) in dichlorobenzene with a PCDTBT concentration of 3.2 or 4.3 mg mL^{-1} was spin-cast on top of the MoO_3–Al composite layer to produce a 65 or 150-nm-thick active layer as the front BHJ. The step-Al-doped MoO_3 ICL was deposited atop the first active layer with two sequential processes: firstly, 10-nm pure MoO_3 without Al-doping was evaporated on top of active layer; secondly, MoO_3 and Al were co-evaporated on 10-nm pure MoO_3 film and the Al doped content was set as 55% in weight percentage by modulating the corresponding evaporation speeds. The thickness of Al-doped MoO_3 film was 10 nm. Then, the rear BHJ layer of the PCDTBT:$PC_{70}BM$ (1:4, w/w; 105 nm) or PDPP3T:$PC_{70}BM$ (1:2, w/w; 120 nm) was deposited on top of the MoO_3-based ICL via spin-coating. The PDPP3T:$PC_{70}BM$ (1:2, w/w) blend was dissolved in a solution mixture of 1,2-dichlorobenzene/chloroform/1, 8-diiodooctane (0.76:0.19:0.05, v/v/v) with PDPP3T concentration of 8 mg mL^{-1}. Finally, a bi-layer structure of MoO_3 (6 nm)/Al (80 nm) was deposited atop the rear BHJ layer via thermal evaporation in a vacuum of 4×10^{-6} Torr to complete the device fabrication. The cell active area was 12 mm^2, which was defined by the overlapping area of the ITO and Al electrodes. An Oriel 150 W solar simulator with AM 1.5G filter was used to provide 100 mW cm^{-2} simulated solar light for illumination of the photovoltaic cells. The light intensity was determined by a calibrated silicon diode with KG-5 visible color filter. Current–voltage traces were obtained with a Keithley 236 source meter. External quantum efficiency measurements were performed under short-circuit conditions with a lock-in amplifier (SR830, Stanford Research System) at a chopping frequency of 280 Hz during illumination with a monochromatic light from a Xenon lamp.

2.3. Thin film characterization

Transmittance and absorption spectra of the samples were measured using a Perkin-Elmer35 UV-visible spectrophotometer. The refractive index (*n* and *k* values) and the thicknesses of the various layers in the device structure were measured using spectroscopic ellipsometry (Horiba Jobin Yvon). UPS measurements were performed on Thermo ESCALAB 250 using He–I (21.2 eV) discharge lamp. A sample bias of −12 V was used in order to separate the sample and the secondary edge for the analyzer.

3. Results and discussion

Fig. 1(a) shows the device configuration of the inverted tandem PSCs. The Al content in MoO_3–Al composite (cathode buffer layer) is 55% in weight percentage. The two sub-cells with identical or complementary BHJ are linked by MoO_3-based ICL with top half doped with 55% Al in weight percentage. In the former case, both of two sub-cells were based on PCDTBT:$PC_{70}BM$ BHJ; in the latter case, a PDPP3T:$PC_{70}BM$ BHJ was used to replace the PCDTBT:$PC_{70}BM$ BHJ in rear sub-cell to extend the absorption spectra coverage [41]. The molecular structures of PCDTBT, PDPP3T and $PC_{70}BM$ are shown in Fig. 1(b). The pure MoO_3 film possesses a high work function of 5.49 eV and upon the coverage of Al-doped MoO_3 film the work function was reduced to 4.07 eV (See Fig. S1 in Supporting Information). Fig. 1(c) illustrates the energy level diagram of the tandem cell structure. The MoO_3–Al composite with low work function is able to form an Ohmic contact with the LUMO of $PC_{70}BM$ as a cathode buffer layer on the ITO electrode. The pure MoO_3 layer with high work function serves as the top anode in combination with Al electrode. The step-Al-doped MoO_3 ICL was used to link the two BHJ layers with the pure MoO_3 side contacting with front sub-cell and the MoO_3–Al side contacting with rear sub-cell. Thus, the HOMO level of polymer donor in front sub-cell is well aligned with the LUMO level of fullerene acceptor in rear sub-cell, enabling the efficient charge recombination in ICL. The effective conductivity of such ICL was measured to be 8.5×10^{-7} S/cm and just brought in an additional series resistance of 2.3 Ω cm^2(see Fig. S2 in Supporting Information). Thus the electron can easily tunnel the ICL with negligible voltage drop.

Fig. 2(a) displays the optical constants (*n* and *k*) of MoO_3 and MoO_3–Al layers measured with the spectroscopic ellipsometry. The extinction coefficient dispersion of MoO_3–Al layer is red-shifted compared to that of MoO_3 layer, possibly due to reduction of effective band gap. The ICL structure of MoO_3(10 nm)/MoO_3–Al (10 nm) exhibits a high transparency of over 95% as shown in Fig. 2(b). Fig. 2(b) shows the absorption of the ITO/MoO_3–Al/PCDTBT:$PC_{70}BM$, ICL/PCDTBT:$PC_{70}BM$ and ITO/MoO_3–Al/PCDTBT:$PC_{70}BM$ ICL/PCDTBT:$PC_{70}BM$ structures. The superposition of the BHJ absorption in sub-cells fits well with the absorption of the tandem structure, indicating that spin-coating the upper BHJ layer did not deteriorate the underlying MoO_3-based ICL and the bottom BHJ layer. Previous work demonstrated that Mo–O–Al complex structure was formed after Al doping [40]. Such complex structure makes the whole layer cross-linked and consequently physically robust to withstand organic solvents. The optical modeling based on the classic transfer matrix method was used to optimize the thickness combinations of two BHJ layers of front and rear sub-cells linked by the MoO_3-based ICL [41]. Fig. 2(c) shows a dependence of simulated short-circuit current (J_{SC}) of the inverted