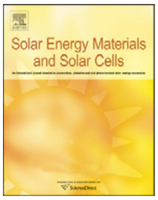
Solar Energy Materials & Solar Cells 93 (2009) 497–500

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

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



Inverted and transparent polymer solar cells prepared with vacuum-free processing

Yinhua Zhou [a,b], Fenghong Li [a], Sophie Barrau [a], Wenjing Tian [b], Olle Inganäs [a,c], Fengling Zhang [a,c,*]

[a] Department of Physics, Chemistry and Biology (IFM), Linköping University, SE-581 83 Linköping, Sweden
[b] State Key Lab for Supramolecular Structure and Materials, Jilin University, 130012 Changchun, China
[c] Center of Organic Electronics, Linköping University, SE-581 83 Linköping, Sweden

ARTICLE INFO

Article history:
Received 29 August 2008
Received in revised form
6 November 2008
Accepted 7 November 2008
Available online 18 December 2008

Keywords:
Inverted polymer solar cells
Vacuum-free processing
PEO
Open-circuit voltage

ABSTRACT

Inverted transparent polymer solar cells were fabricated by sequentially depositing several organic layers from fluids, on ITO/glass substrates. ITO was used as a cathode to collect electrons. The photovoltage of these diodes can be increased by up to 400 mV by inserting a buffer layer of polyethylene oxide between ITO and the active layers, which results in 4-fold enhancement of power conversion efficiency under the illumination of 100 mW/cm^2 simulated AM1.5 solar light. The enhancement of V_{oc} is consistent with the work function change between ITO and ITO/PEO measured by photoelectron spectroscopy. Solar cell production without vacuum processing may lower production costs.

1. Introduction

Polymer solar cells are attractive due to the possibility of printing devices on large areas to decrease cost [1–4]. However, so far most polymer solar cells still involve metal electrode deposition in vacuum by evaporation or sputtering, because the conductivity of electrodes processed from solutions is not high enough to replace metals as electrodes in solar cells [5,6]. Vacuum-deposited electrodes for polymer solar cells require pinhole free organic layers, which increases the cost and limits the size of devices, and complicates the process.

Electrodes used in solar cells must have high conductivity and suitable work function (WF) for efficient charge carrier collection. ITO is commonly used as the anode to collect hole due to its high WF, high conductivity and transparency. A metal, usually Al, is used as a cathode to collect electrons and as a reflector to reflect photons back to the active layers for further absorption. The metal is generally deposited in vacuum. There are efforts to make solar cells without vacuum-deposited electrodes [7,8]. For instance, Gadisa et al. [7] used transparent polymer electrodes in laminated devices and Huang et al. [9] demonstrated laminated solar cells using ITO to replace the metal electrode. However, to lower the WF of ITO, ITO was modified by Cs_2CO_3, which was still deposited in vacuum. We recently reported the use of high-conductivity PEDOT (PH500) replacing ITO as the anode, to collect holes in flexible polymer solar cells built on the plastic substrate polyethylene terephthalate [10,11]. The WF of these electrodes was 5 eV [10]. To avoid deposition of electrodes under vacuum, some conductors with suitable WF are needed to replace the metal as cathode for electron collection. ITO could be used as the cathode to replace metal [12] but the high WF would result in a small open-circuit voltage (V_{oc}) in solar cells. We have demonstrated that PEO from aqueous solution can be used for modifying the active layer/cathode (Al) interface, to increase V_{oc} by ~200 mV in polymer solar cells [13]. Steim et al. [12] also used a related polymer, polyoxyethylene tridecyl ether (PTE), as the interface layer between ITO and TiO_x, which results in the improvement of around 15% in their performance over comparable devices without the organic interfacial layer. Based on these two findings, here we present inverted transparent solar cells based on APFO3:PCBM, processed by sequentially spin-coating organic layers on commercial ITO/glass substrates. We use ITO as the cathode and high-conductivity PEDOT as the anode. The efficiency of these solar cells is significantly increased by adding PEO as a buffer layer to modify the WF of ITO. The simplicity of making solar cells by depositing layers from solutions on commercial electrodes guarantees fast production and cheaper products compared to processes involving vacuum deposition. The transparency of the devices also makes it useful for image detection [14]. The device structure is shown in Fig. 1.

---

[*] Corresponding author. Department of Physics, Chemistry and Biology (IFM), Linköping University, SE-581 83 Linköping, Sweden. Tel.: +46 13 28 1257; fax: +46 13 28 8969.
E-mail address: fenzh@ifm.liu.se (F. Zhang).

0927-0248/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.solmat.2008.11.002

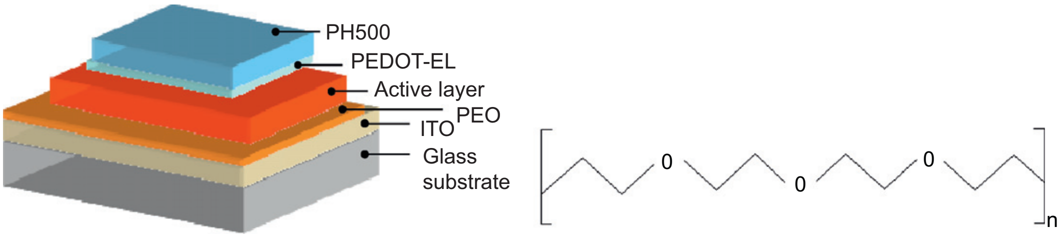


Fig. 1. Device structure of the inverted transparent solar cell (ITO/PEO/APFO3:PCBM/PEDOT-EL/PH500) and the chemical structure of PEO.

2. Experimental

A thin PEO layer was spin-coated on pre-cleaned ITO glass substrate from aqueous solution with the concentration of 1 mg/ml and heated at 70 °C for 10 min on a hot plate. APFO3:PCBM was spin-coated from chloroform solution on the top of PEO, as an active layer with thickness ~90 nm (measured by Veeco Dektak 6 M Surface Profiler). Later, a thin (about 50 nm) low-conductive PEDOT:PSS P VP Al 4083 (PEDOT-EL) layer was spin-coated on the top of the active layer and heated at 80 °C for 30 min on a hot plate followed by a 200 nm high-conductive PEDOT:PSS PH500 spin-coated and heated at 80 °C for 30 min. For comparison, identical layers of APFO3:PCBM/PEDOT-EL/PH500 were also spin-coated directly on an ITO glass substrate without PEO. The area of devices is ≈5–6 mm^2.

The WF of ITO and ITO/PEO was measured by ultraviolet photoelectron spectroscopy (UPS) carried out using a Scienta ESCA 200 spectrometer equipped with a He discharge lamp. The binding energies were obtained referenced to the Fermi level with an error of ±0.05 eV. WF of Au substrates sputtered by Argon gas *in situ* can reach 5.1±0.1 eV. The full-width at half-maximum of the Au $4f_{7/2}$ line is 0.65 eV [15]. The surface morphology of ITO and ITO/PEO was imaged by Dimension 3100 atomic force microscopy (AFM). The current–voltage (*I*–*V*) curves of devices were characterized in the dark and under illumination of AM1.5 with the intensity of 100 mW/cm^2. The photocurrent spectra were recorded by a Keithley 485 pico ammeter under monochromatic illumination. The fabrication and photovoltaic measurements were all conducted in ambient lab environment without any protective atomosphere.

3. Result and disscussion

When using ITO to replace the metal as the cathode, some differences between ITO and metal should be kept in mind. First, ITO is transparent and cannot reflect photons back to the active layer. This will cause lower optical absorption in the active layer, unless external reflectors are used. Second, the WF of ITO is higher than that of Al, which will result in a low built-in potential to extract charge carriers from active layers and low V_{oc}, because the photovoltage is determined by the difference between LUMO of the acceptor (PCBM) and HOMO of the donor (APFO3) [16,17] as well as influenced by the WF difference between two electrodes [18]. Inverted solar cells from solution process using ITO and PEDOT as electrodes were semitransparent, because the two electrodes and the thin active layer were all quite transparent. The advantage of the solar cells with two transparent electrodes is that they could be illuminated from either side, and the drawback is inefficient absorption without the reflector.

Inverted solar cells directly built on ITO by spin-cast APFO3: PCBM, PEDOT(EL) and PEDOT(PH500), without buffer layer modifying the WF of ITO, presented a V_{oc} of 0.26 V as shown in Fig. 2, which was much lower than that (1 V) of normal solar cells (ITO/PEDOT/active layer/LiF/Al) based on the same active layers [19]. V_{oc} is a critical parameter for efficiency, though the photocurrent is reasonable for thin transparent active layers without a mirror. The short-circuit current (J_{sc}) was sensitive to reflection, as shown in Fig. 2, and could be enhanced from 1.1 to 1.3 mA/cm^2 by adding a reflective Al foil or white paper on the backside of solar cells to reflect unabsorbed photons back. Alternatively, no enhancement was obtained by adding black paper on the backside of the solar cells.

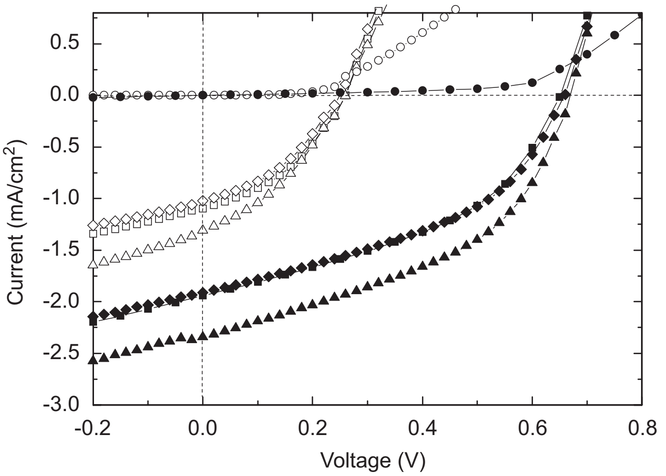


Fig. 2. *J*–*V* curves of devices without PEO (ITO/APFO-3:PCBM/PEDOT-EL/PH500) (open symbols) and with PEO (ITO/PEO/APFO-3:PCBM/PEDOT-EL/PH500) (filled symbols) in dark (circles) and under illumination of AM1.5 100 mW/cm^2, with air (squares), white paper (triangles) and black paper (diamonds) on the backside of the solar cells.

To increase V_{oc}, a thin PEO layer was inserted between ITO and active layers. The *J*–*V* curves of the inverted solar cells with PEO in dark and under AM1.5 100 mW/cm^2 are also shown in Fig. 2. The introduction of the PEO layer enhances the open-circuit voltage (V_{oc}) from 0.26 to 0.66 V, J_{sc} from 1.1 to 1.9 mA/cm^2 and fill factor (FF) from 0.39 to 0.43, which results in the power conversion efficiency (PCE) enhanced from about 0.11% to 0.53%. Obviously, the PEO layer enhanced V_{oc} not only but also J_{sc} and FF, and thus the overall quality of the solar cells. It should be noted that the V_{oc} of 0.66 V *is a* representative here. We fabricated 6 devices with PEO layer. Their V_{oc} ranged in the area of 0.68±0.08 V. The introduction of PEO can enhance the V_{oc} from 0.24±0.04 to 0.68±0.08 V efficiently.

The 400 mV enhancement of V_{oc} in Fig. 2 was consistent with the WF difference between ITO and ITO/PEO. The UPS results of ITO and ITO/PEO (Fig. 3) show that the WF of ITO dropped from 4.4 to 3.9 eV after being covered by a thin buffer layer of PEO. We assume that a dipole of 0.5 eV is induced by the thin insulating polymer, PEO. Similar phenomena have been extensively observed at the metal/thin insulating layer in organic semiconductor devices [20,21].