



Inverted organic solar cells with polymer-modified fluorine-doped tin oxide as the electron-collecting electrode



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ABSTRACT

We report on inverted solar cells using amine-containing polymer (polyethylenimine ethoxylated, PEIE) modified fluorine-doped tin oxide (FTO) as the electron-collecting electrode. PEIE lowers the work function of FTO from 4.6 eV to 3.8 eV, measured by Kelvin probe, sufficiently low for collecting electrons in solar cells. With the FTO/PEIE electrode, inverted solar cells based on poly[(4,8-bis-(2-ethylhexyloxy)-benzo[1,2-b:4,5-b']dithiophene)-2,6-diyl-alt-(4-(2-ethylhexanoyl)-thieno[3,4-b]thiophene)-2,6-diyl];phenyl-C₆₁-butyric acid methyl ester exhibited an open-circuit voltage of 0.70 ± 0.01 V, a short-circuit current density of 15.2 ± 0.2 mA/cm², a fill factor of 0.60 ± 0.01 and a power conversion efficiency of $6.3 \pm 0.2\%$ averaged over 9 devices under 100 mW/cm² AM1.5 illumination, which is comparable to the solar cells fabricated on indium–tin oxide glass substrates. In addition, we found that ultraviolet light-containing illumination can reduce the work function of bare FTO from 4.66 eV to 4.34 eV presumably because of the desorption of oxygen trapped in FTO.

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1. Introduction

Organic solar cells have been attracting considerable attention due to their potential as a future renewable alternative energy source with low-cost fabrication, light weight and good mechanical flexibility [1–3]. So far, organic solar cells with power conversion efficiency (PCE) of above 8% have been reported [4,5]. In these solar cells, indium–tin oxide (ITO) is used as the transparent electrode because it possesses the excellent combination of high electrical conductivity and optical transmittance. Unfortunately, indium is of high price due to its limited supply. For the replacement of ITO, the conducting polymer poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) [6–12], silver nanowires [13–17], carbon nanotubes [18], and graphene [19–22], have been reported as alternative transparent electrodes for organic solar cells.

Fluorine-doped tin oxide (FTO) is another commonly used transparent electrode, having comparable transmittance and sheet resistance to ITO. It is typically processed by spray pyrolysis from solution, a relatively low-cost production, without the need of expensive or rare elements. Commercially, the price of FTO-coated glass substrates is about one-tenth to one-fifth of ITO-coated glass substrates. FTO electrodes have been widely used in dye-sensitized solar cells. However, only a few examples using FTO as the electrode for organic bulk-heterojunction solar cells have been reported [23–25]. One of the

reasons is the rough surface of FTO. Fig. 1a displays an image of the FTO surface by atomic force microscopy (AFM). The average surface root-mean-square (RMS) roughness is 13.6 ± 2.4 nm averaged over five locations on one substrate in an area of $1 \mu\text{m} \times 1 \mu\text{m}$. It is much rougher than the ITO surface with a RMS value of 3.8 ± 0.1 nm averaged over three locations in $1 \mu\text{m} \times 1 \mu\text{m}$. To fabricate organic solar cells in an inverted structure on FTO substrates, a thick layer of low-work function TiO_x (above 100 nm) was required to fully cover its surface for lowering the work function of FTO uniformly and achieve high device yield and reproducibility [24].

Recently, we reported physisorbed amine-containing polymer modifiers that can substantially reduce the work function of a series of conductors [26]. Because of the physisorption of the polymer surface modifiers, it is expected that the FTO surface can be fully modified even with a thin PEIE layer, not dependent on the surface roughness of FTO. Here, one of the polymer surface modifiers, polyethylenimine ethoxylated (PEIE, Fig. 1b), is used to modify FTO, which reduces the work function of FTO from 4.7 eV to 3.8 eV, but does not change the transmittance. Inverted solar cells were fabricated using FTO/PEIE as the electron-collecting electrode and poly[(4,8-bis-(2-ethylhexyloxy)-benzo[1,2-b:4,5-b']dithiophene)-2,6-diyl-alt-(4-(2-ethylhexanoyl)-thieno[3,4-b]thiophene)-2,6-diyl] (PBDTTT-C) [27]; phenyl-C₆₁-butyric acid methyl ester (PCBM) as the photoactive layer. The solar cells with a structure of glass/FTO/PEIE/PBDTTT-C:PCBM/MoO₃/Ag (Fig. 1c) exhibited an open-circuit voltage (V_{OC}) of 0.70 ± 0.01 V, a short-circuit current density (J_{SC}) of 15.2 ± 0.2 mA/cm², a fill factor (FF) of 0.60 ± 0.01 and a PCE of $6.3 \pm 0.2\%$ averaged over 9 devices under 100 mW/cm² AM1.5 illumination.

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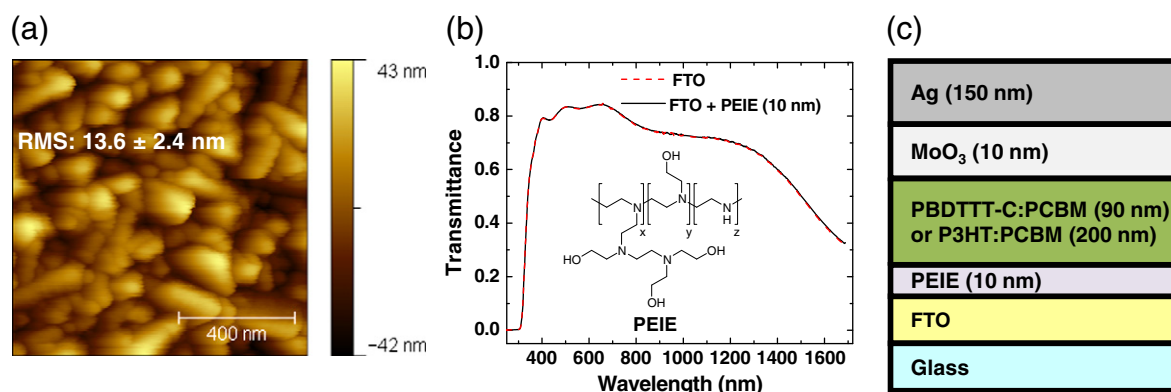


Fig. 1. (a) Image of the surface of FTO glass substrates by atomic force microscopy; (b) Transmittance of FTO glass substrates with and without a layer of PEIE; inset is the chemical structure of PEIE; (c) Structure of the inverted solar cells with FTO/PEIE as the electron-collecting electrode.

2. Experimental details

Glass slides coated with FTO (TEC-15, Hartford Glass Co. Inc.) with a sheet resistance of $15 \Omega/\text{sq}$ were used as the substrates for the inverted solar cells. The substrates were cleaned in an ultrasonic bath of detergent water, rinsed with deionized water, and then cleaned in sequential ultrasonic baths of deionized water, acetone, and isopropanol. Each ultrasonic bath lasted for 20 min. Nitrogen was used to dry the substrates after each of the last three baths. A 300-nm-thick layer of SiO_x was deposited on the cleaned FTO by e-beam deposition (AXXIS, Kurt J. Lesker) to pattern the anode. Next, the substrates were sonicated in isopropanol for 10 min and blown dry with nitrogen. The surface roughness of the FTO samples was measured under atmospheric conditions using AFM (Dimension 3100, Veeco) in tapping mode equipped with a NanoScope III controller. Cantilevers (NSC18/no Al, Mikromasch) made from n-type silicon were used to probe the surface.

PEIE ($M_w = 70,000 \text{ g/mol}$) was diluted into 2-methoxyethanol to a concentration of 0.5 wt.% from a concentration of 35–40 wt.% in H_2O when received from Aldrich. FTO substrates were treated with PEIE by spin coating the solution at a speed of 5000 rpm for 1 min. Then, the samples were annealed at 120°C for 10 min on a hotplate in ambient air. Previously, we have shown that these PEIE layers do not have a uniform thickness [26]. For calibration purposes, spectroscopic ellipsometry (J. A. Woollam Co. M-2000) experiments were carried out on PEIE layers prepared under the same conditions on a silicon wafer. An effective thickness of 12 nm was derived through modeling assuming a layer with uniform thickness (i.e. neglecting surface roughness). The substrates were then transferred into a N_2 -filled glove box. PBDTTT-C (Solarmer) :PCBM (Nano-C) and poly(3-hexylthiophene) (P3HT, Rieke Metal, 4002-E) :PCBM were used as the photoactive layers. PBDTTT-C:PCBM was prepared by spin coating from a solution (1:1.5, w/w, a total concentration of 25 mg/ml) in chlorobenzene:1,8-diiodooctane (97:3, v/v) at a speed of 1000 rpm and an acceleration of 10,000 rpm/s for 20 s. The thickness of the active layer was 90 nm. P3HT:PCBM was prepared by spin coating from a chlorobenzene solution (1:1, w/w, a total concentration of 40 mg/ml) at a speed of 700 rpm and an acceleration of 10,000 rpm/s for 1 min and annealed at 150°C for 10 min. The thickness of the active layer was 200 nm. Samples were transferred to a vacuum thermal evaporation system (SPECTROS, Kurt J. Lesker) and a layer of MoO_3 (10 nm) and a layer of Ag (150 nm) were deposited through a shadow mask at a base pressure of $2.7 \times 10^{-5} \text{ Pa}$. The device area was about 13 mm^2 . For comparison, solar cells with FTO only (without PEIE modification) were also fabricated.

Current density–voltage (J – V) characteristics were measured inside the N_2 -filled glove box by using a source meter (2400, Keithley Instruments, Cleveland, OH) controlled by a LabVIEW program. To test the solar cell properties under illumination, an Oriel lamp with

an intensity of 100 mW/cm^2 was used as the light source. The work function values of FTO samples were measured using a Kelvin probe (Besocke Delta Phi) in air. A highly ordered pyrolytic graphite (HOPG) sample with a WF of 4.5 eV was used as the reference.

3. Results and discussion

Fig. 2a shows the J – V characteristics of devices in the dark and under illumination with the structure of FTO/PBDTTT-C:PCBM/ MoO_3 /Ag (without PEIE modification) and FTO/PEIE/PBDTTT-C:PCBM/ MoO_3 /Ag. The devices without PEIE show poor performance (Table 1): $V_{\text{OC}} = 0.31 \pm 0.02 \text{ V}$, $J_{\text{SC}} = 14.0 \pm 0.3 \text{ mA/cm}^2$, $\text{FF} = 0.37 \pm 0.02$, and $\text{PCE} = 1.6 \pm 0.2\%$, averaged over 4 devices. The poor photovoltaic performance is attributed to the high work function of FTO, 4.66 eV (measured by Kelvin probe in air), which does not facilitate the collection of electrons from the photoactive layer. When FTO was modified by PEIE, the work function was reduced to 3.80 eV, sufficiently low for efficient electron collection. Fig. 2b shows the J – V characteristics in the dark and under AM1.5 100 mW/cm^2 illumination. In the dark the devices show a large rectification ratio of 10^4 at $\pm 1 \text{ V}$, two orders of magnitude larger than the device without PEIE modification. Under illumination, the devices yield a $V_{\text{OC}} = 0.70 \pm 0.01 \text{ V}$, a $J_{\text{SC}} = 15.2 \pm 0.2 \text{ mA/cm}^2$, a $\text{FF} = 0.60 \pm 0.01$, and a $\text{PCE} = 6.3 \pm 0.2\%$, averaged over 9 devices (Table 1). The device yield for the 9 devices is 100%. The rough surface of FTO did not bring leakage current and was not detrimental to the device yield either. The PCE of devices based on FTO is comparable to the performance of devices based on ITO/PEIE that we previously reported with a $V_{\text{OC}} = 0.68 \pm 0.01 \text{ V}$, a $J_{\text{SC}} = 16.1 \pm 0.4 \text{ mA/cm}^2$, a $\text{FF} = 0.61 \pm 0.01$ and a $\text{PCE} = 6.6 \pm 0.2\%$, averaged over 5 devices [26].

For the devices FTO/PBDTTT-C:PCBM/ MoO_3 /Ag (without PEIE modification), we studied the evolution of their J – V characteristics as a function of exposure to light from a solar simulator. As shown in Fig. 3, an S-shape kink is initially observed in the J – V characteristics under illumination for the newly fabricated cells. After exposure to the illumination from a solar simulator, the S-shape kink in the J – V characteristics vanished and the device performance was improved (Fig. 3). After exposure to the illumination for 22 min, device performance was improved and saturated with a $V_{\text{OC}} = 0.52 \text{ V}$, a $J_{\text{SC}} = 13.5 \text{ mA/cm}^2$, a $\text{FF} = 0.53$ and a $\text{PCE} = 3.7\%$. The improvement of device performance after light exposure is mainly attributed to a work function reduction of FTO under ultraviolet (UV) light-containing illumination in an inert atmosphere. We measured the work function of FTO before and after light illumination using Kelvin probe. The work function of cleaned FTO was measured to be $4.66 \pm 0.04 \text{ eV}$ averaged over 3 devices. After illumination through the glass side using a solar simulator in a N_2 -filled glove box, which is the same condition used

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