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The effect of hole transfer layers and anodes on indium-free TiO$_2$/Ag/TiO$_2$ electrode and ITO electrode based P3HT:PCBM organic solar cells

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ABSTRACT

Transparent composite electrodes (TCE), TiO$_2$/Ag/TiO$_2$ (TAgT), have been demonstrated as a promising alternative of indium tin oxide (ITO) in organic solar cell application. TiO$_2$/Ag/TiO$_2$ have been incorporated into bulk heterojunction organic solar cells (OSCs) to replace ITO as the anode. Two different hole transfer layers (HTL), poly(3,4-ethylenedioxythiophene): poly(styrene sulfonate) (PEDOT:PSS) and MoO$_3$, are compared in terms of their compatibility with the TiO$_2$/Ag/TiO$_2$ anode. The MoO$_3$ layer has been shown to be a beneficial HTL for TiO$_2$/Ag/TiO$_2$ based OSC. However, the wettability of MoO$_3$ for polymer blend is not as good as PEDOT:PSS, and results in a relatively thin active layer in OSCs. On the other hand, ITO based OSCs using PEDOT:PSS and MoO$_3$ as the HTL are fabricated as control samples to compare the performance of TAgT and ITO anodes. Results of the investigation shows that the superior electrical property of TAgT anodes contributes to the effective collection of photo-carriers and its lower optical transmittance barely degrades the light absorption in OSCs. In a few words, the higher Haacke figure of merit of TAgT enables better performance of OSCs with MoO$_3$ HTL, in comparison with ITO based OSC.

1. Introduction

An electrode that allows the light transmission and emission as well as electrical conduction is indispensable in organic solar cells (OSCs) and light emitting diodes (LEDs). The electrical and optical properties of that electrode significantly impact the efficiency of OSC and LED devices. Transparent conductive thin films are ideal candidates for that electrode [1–4]. Indium-tin oxide (ITO) is one of the most widely used transparent conductive thin film due to its high optical transmittance and low resistivity [1–5]. However, the rare earth element indium in ITO limits its sustainability and increases its cost. More importantly, ITO is brittle; therefore, the weak mechanical flexibility of ITO is a major concern when employing ITO in flexible devices [2,5,6]. As a means to address these concerns, transparent composite electrodes (TCEs) have been reported as a promising alternative to ITO-based electrodes due their indium-free composition, good mechanical flexibility, low processing temperature, and superior figure of merit (FOM) [1–3,7].

A typical TCE is a three-layer thin-film structure: an intermediate metal layer sandwiched between equivalent top and bottom transparent metal oxide (TMO) layers [1–5,7–16]. The optical properties of TCE can be tailored to different application by varying the thickness and material of each individual layer [17]. Our previous work shows that the optimal materials of TCE for the anode of conventional bulk heterojunction (BHJ) organic solar cells is TiO$_2$/Ag/TiO$_2$ (TAgT) with 42 nm TiO$_2$ top and bottom layer and a 10 nm thick Ag layer [18]. This structure demonstrates a high device-specific Haacke figure of merit of 69.6 $\times$ 10^{-3} sq/Ω; and this is almost twice higher than that of ITO [18]. In addition, the optimized TAgT has been successfully incorporated into OSC devices. The OSC has a structure of anode/MoO$_3$/ P$_3$HT:PC$_{61}$BM/LiF-Al. The TAgT based OSC shows higher power conversion efficiency (PCE) than that of the ITO based OSC reference device [18]. The effect of TAgT and ITO anodes on OSC's performance is compared and studied further in this paper.

Apart from anode, the interface layer between BHJ active layer and electrodes also plays an important role in the performance of OSCs. The interface layer is typically used to: adjust the band alignment between electrode and active layer to form an Ohmic contact, selectively transport only one type of carriers, prevent the chemical reaction between electrode and active layer and act as an optical spacer to adjust incident light distribution [19,20]. The interface layer between cathode and active layers is called the electron transfer layer (ETL); while, the interface layer between the anode and active layers is called hole transfer layer (HTL). The most commonly used ETL is LiF; while, HTL has various types including poly(3,4-ethylenedioxythiophene):poly (styrene sulfonate), (i.e., PEDOT:PSS), semiconducting transition metal

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oxides such as molybdenum oxide (MoO_3), vanadium oxide (V_2O_5), nickel oxide (NiO) and tungsten oxide (WO_3), organic hole-transporting materials such as poly[9,9-dicotylfluorene-*co*-N-[4-(3-methylpropyp)]-diphenyl-amine] (TFB) and 4,4′-bis[(p-trichlorosiylpropylphenyl)phenylamino]biphenyl ($TPDSi_2$) [19–22]. Particularly, PEDOT:PSS is the most widely used HTL materials due to its ease of fabrication; however, PEDOT:PSS etches the anode (ITO and other transparent conductive oxide) due to its acidic nature and results in degradation of the OSC [19–21,23]. To avoid the attack of PEDOT:PSS to anode, MoO_3 is reported as a promising alternative to ITO by many researchers [19–22,24,25]. Firstly, MoO_3 has no chemical reaction with the oxide anode. Due to the high work function of MoO_3, the band bending of the donor's HOMO at MoO_3/organic interface and gaps states created by oxygen vacancy defects in MoO_3 enable and enhance the hole extraction from the donor to anode [24–27]. In this study, both PEDOT:PSS and MoO_3 are employed as HTL to study their compatibility with TAgT as well as their impact on the performance of OSCs. Specially, the effect of HTLs' wettability and their contacts with anode and active layer are studied. To compare the performance of TAgT and ITO anodes, ITO based OSCs using PEDOT:PSS and MoO_3 as HTL are also fabricated and studied as control samples. The impact of anode on performance of OSC are investigated, especially the impact of light transmittance and sheet resistance of anodes on the charge generation and transport.

2. Experiment

2.1. Electrode fabrication

The multilayer structure of TiO_2/Ag/TiO_2 was sputter deposited on glass substrate at room temperature with a base pressure of 1×10^{-6} Torr. According to our previous finding [18], TiO_2 top and bottom layer with a thickness of 42 nm and Ag middle layer with a thickness of 10 nm are optimal for OSC application. The top and bottom TiO_2 layers were deposited by RF sputtering of a TiO_2 target (99.9% purity) with a power of 90 W and Ar pressure of 2.5 mTorr. The middle Ag layer was deposited by DC sputtering of an Ag target (99.9% purity) at Ar pressure of 4 mTorr, and with a power of 235 W.

2.2. OSC fabrication

2.2.1. Reagent and materials

The electrode donor material regioregular poly (3-hexylthiophene) (P_3HT) was from Reike Metals, Inc. The electron acceptor material [6,6]-phenyl C_{61} butyric acid methyl ester (PCBM) and solvent 1,2-dichlorobenzene were from Sigma Aldrich. The hole transfer layer material, poly(3,4-ethylenedioxythiophene):poly (styrenesulfonate) (PEDOT:PSS) with neutral pH value was purchased from Sigma Aldrich as well.

2.2.2. Device fabrication and testing

With the use of ITO and TAgT anodes, two different hole transfer layers, MoO_3 and PEDOT:PSS, were deposited on each type of anodes, respectively. As a result, OSC with four different structures were fabricated: ITO/PEDOT:PSS/P_3HT:PCBM/LiF-Al (ITO + PEDOT:PSS), ITO/MoO_3/P_3HT:PCBM/LiF-Al (ITO + MoO_3), TAgT/PEDOT:PSS/P_3HT:PCBM/LiF-Al (TAgT + PEDOT:PSS), TAgT/MoO_3/P_3HT:PCBM/LiF-Al (TAgT + MoO_3). MoO_3 film with a thickness of 14 nm was thermally evaporated from MoO_3 powder (99.99% purity, Alfa Aesar) on ITO and TAgT anodes, respectively. PEDOT:PSS was spin coated onto ITO and TAgT anodes at 5000 rpm for 60 s, followed by baking on a hot plate at 200 °C for 15 min in nitrogen-filled glove box. The electron donor P_3HT and electron acceptor $PC_{61}BM$ with a weight ratio of 1:0.8 were dissolved in the 1,2-dicholorobenzene to make a solution containing 20 mg/ml P_3HT. The solution was stirred at room temperature for a period of 12 h in a nitrogen-filled glove box. Then the blended solution was spin coated at 600 rpm for 60 s, and then baked at 150 °C

for 30 min in glove box. In the end, the electron transfer layer LiF of 0.7 nm and metal cathode Al of ~80 nm were sequentially deposited by thermal evaporation using a shadow mask that defines an active area of 0.2 cm². The current density-voltage (*J-V*) curve were measured under simulated AM 1.5 global solar irradiation (100 mW/cm²) using a xenon-lamp solar simulator (Spectra Physics, Oriel Instruments, USA).

2.3. Characterization

The work function of ITO and TAgT on glass were measured using Kelvin Probe (McAllister 6500). A highly ordered pyrolytic graphite (HOPG) film with a work function of 4.5 eV was used as the reference sample [28]. Two methods were used to measure the sheet resistance of thin films. One method implemented was a 4-point probe system equipped with a 100 mA Keithley 2700 digital multimeter. Another method was based on the Van Der Pauw method and equations. In this case, the measurement was conducted using Ecopia HMS-3000 system. The thickness of MoO_3 film, and spin-coated active layer (P_3HT:PCBM) were measured by stylus profilometer (Dektak XT). The roughness of PEDOT:PSS and MoO_3 films were inspected by atomic force microscopy (AFM) (Bruker Dimension 3100) with 2 μm × 2 μm scan. At the same time, the cross-section profile of a 1 μm line in the scanning area were inspected to give a direct profile of the surfaces. The light reflectance of OSCs structures (anode/HTL/P_3HT:PCBM/LiF-Al) was measured by Ocean Optics double channel spectrometer (model DS200) in a wavelength range of 300–800 nm. The light absorption were calculated by subtracting light reflectance from 100%. The external quantum efficiency (EQE) in wavelength range of 300–800 nm was evaluated by a QEX10 quantum efficiency measurement system with a xenon arc lamp source and dual-grating monochromator. The internal quantum efficiency (IQE) was calculated by dividing the EQE by the light absorption of the devices.

3. Results and discussion

3.1. Overall performance of four OSC structures

Fig. 1 shows the *J-V* characteristics for several device configurations: *i*) ITO + PEDOT:PSS, *ii*) TAgT + PEDOT:PSS, *iii*) ITO + MoO_3, and *iv*)TAgT + MoO_3. Table 1 lists the device parameters for all these four device configurations. For the TAgT + PEDOT:PSS device, it shows the worst overall performance among all the devices and its bad performance is due to the significantly high R_s. Such high R_s implies that TAgT anode is probably attacked by PEDOT:PSS even with the use of neutral pH PEDOT:PSS as HTL. Hence, PEDOT:PSS is not a suitable HTL for TAgT based OSC. In contrast, with the use of MoO_3 on TAgT anode, all the device parameters are significantly improved and highest power
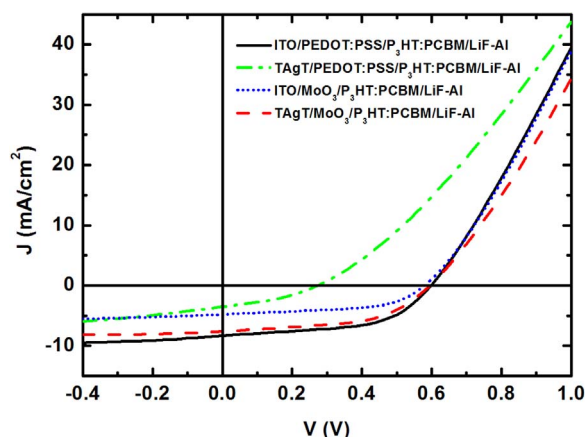

Fig. 1. The *J-V* characteristics under illumination for of Anode/HTL/P_3HT:PCBM/LiF-Al with ITO and TAgT as anodes and MoO_3 and PEDOT:PSS as HTLs.