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Effect of titanium chelate as a function of thickness on the electron mobility and electron transport and collection efficiency

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ABSTRACT

Electron extraction layers (EELs) with shallow lowest unoccupied molecular orbitals (LUMO) featuring good energy level alignment with LUMO of acceptor materials are desirable for high-performance polymer solar cells (PSCs). Here, the use of alcohol-soluble titanium chelate, titanium (IV) oxide bis(2, 4-pentanedionate) (TOPD) as EEL layer and to tune the work function (WF) of EEL is proposed. The enhanced photovoltaic performance can be experimentally explained by the decreased barrier potential between photoactive layer and TOPD/ITO composite electrode from the ultraviolet photoelectron spectroscopy (UPS) curve, and the enhancement of electron mobility and electron transport and collection efficiency from space-charge-limited current (SCLC), time of flight (TOF) curve and the photocurrent density versus effective voltage (J_{ph}-V_{eff}) curve. Simultaneously, the weaker bimolecular recombination between photoactive layer and the TOPD layer were confirmed by the short-circuit current (J_{SC}) value as a function of light intensity. Consequently, the *PCE* of TOPD-based PSCs arrives to 9.16% with 15 nm TOPD layer as EEL, which is higher than the *PCE* of 8.83% for ZnO-based PSCs.

1. Introduction

Polymer solar cells (PSCs) are being extensively investigated due to their advantages – i.e., being light in weight and low-cost energy source. They have attracted more and more attention as renewable energy source in recent years (Dennler et al., 2009; Liu et al., 2011; Pivrikas et al., 2011). Significant efforts are now being focused on how to further enhance their power conversion efficiency (*PCE*), which has recently exceeded 12% with the ternary structure of photoactive layer (Zhao et al., 2016; Li et al., 2016). Inverted PSCs have attracted significant attention since the utilization of metal oxides as HEL (e.g. MoO_3, WO_3 and V_2O_5) and EEL (e.g. ZnO and TiO_2), and high WF metals (e.g. Ag and Au) as anode (Sanchez et al., 2017; Chou et al., 2011). These strategies have led to notably improvement in air stability over regular structured PSC devices (Chao et al., 2013; Chang and Leu, 2012). ZnO nanoparticles have been synthesized following the Pacholski method (Gonzalez-Valls and Lira-Cantu, 2009) and used as EEL material for common inverted PSCs. They have the advantages of low cost and easy to produce. Titanium oxide (TiO_X) is one of the most promising materials for this application (Gregg, 1996; Kim et al., 2006), which transports electrons from the energy level of the lowest unoccupied molecular orbitals (E_{LUMO}) of the acceptor materials to the TiO_X/ITO composite anode. However, the common fabrication method of a TiO_X layer is vacuum deposition, which has the disadvantages of high cost and limited large-scale production, among others. Thus, the design and synthesis of solution-processed TiO_X as an anode buffer layer in PSC devices has attracted the interest of many research groups.

Yongfang et al. reported that inverted PSCs were fabricated with the titanium chelate, titanium di-isopropoxide bis(2,4-pentanedionate) (TIPD) as an EEL by spin-coating a TIPD isopropyl alcohol solution on the top of indium-tin-oxide (ITO) glass, and the isopropoxy groups of TIPD molecules were hydrolyzed and formed Ti═O bonds and a titanium (IV) oxide bis(2, 4-pentanedionate) (TOPD) layer by thermal treatment of the TIPD layer (Tan et al., 2012; Wang et al., 2012; Wang et al., 2013; Yang et al., 2014), which has the advantages of solution processability, stable chemical properties, etc. The chemical structures of TIPD and TOPD are shown in Fig. 1(a) and (b), respectively. In this study, we have introduced an alcohol-soluble titanium chelate, TOPD as EEL to replace ZnO nanoparticles on indium tin oxide (ITO) glass in inverted PSCs with MoO_3/Ag as compsite cathode. A blend of thieno [3,4-b]thiophene/benzodithiophene (PTB7) and [6,6]-phenyl C71-butyric acid methyl ester ($PC_{71}BM$) acts as photoactive layer. The

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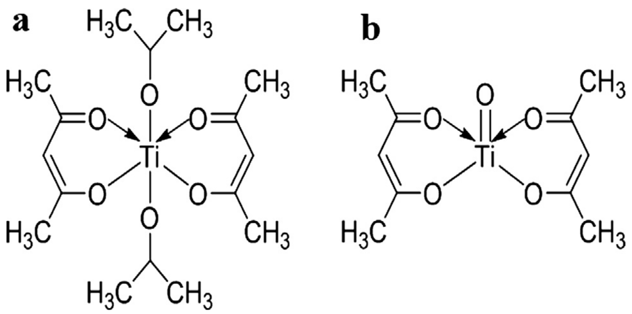

Fig. 1. Chemical structure of (a) TIPD and (b) TOPD.

fabricated PSCs have a device structure of ITO/TOPD/PTB7:$PC_{71}BM$/MoO_3/Ag. Moreover, the TIPD solution and TOPD layer possesses the advantages of low cost, stable chemical characteristics at room temperature, and low annealing temperature (130 °C). Furthermore, for the TOPD layer fabrication, the solution process using isopropanol solvent and water could be carried out with common technologies, such as spin- or spray-coating.

In this work, we focused on: the effect of TOPD layer as a function of thickness on the electron mobility and photocurrent density. (1) the space charge-limited current (SCLC) and time of flight (TOF) were used to investigate the effect of electron mobility; (2) the photocurrent density versus effective voltage (J_{ph} - V_{eff}) curve were measured and to explained the charge carrier transport and collection efficiency and (3) the short-circuit current (J_{SC}) as a function of light intensity were measured and to research the effect of TOPD layer as EEL to replace ZnO on the bimolecular recombination between photoactive layer and EEL.

2. Experiments

2.1. Materials

PTB7 was purchased from One Material Inc. $PC_{71}BM$ was purchased from Nano-C, Inc. TIPD, isopropyl alcohol, *o*-dichlorobenzene (ODCB, anhydrous, 99%) and 1,8-diiodooctane (DIO) were obtained from Sigma-Aldrich. MoO_3 and Ag were obtained from Alfa Aesar. ZnO nanoparticles were synthesized following the Pacholski' method (Gonzalez-Valls and Lira-Cantu, 2009).

2.2. TOPD layer and device preparation and characteristics

The TIPD solution was prepared by adding 0.4 g of TIPD in 10 mL of organic solvent (the ratio of isopropanol solvent and deionized water is 4:1) and stored the solution for 2 h in air. PTB7:$PC_{71}BM$ (1:1.5, wt.%) were dissolved in ODCB solution overnight with a PTB7 concentration of 10 mg mL^{-1}. To obtain better photovoltaic results, 3% (1,8-diiodooctane (DIO)/1,2-dichlorobenzene (DCB), v/v) of DIO is used as an additive in PTB7:$PC_{71}BM$ blend solution. The ITO substrates were ultrasonicated following by washing with isopropyl alcohol, acetone and deionized water for 30 min each. Subsequently, the ITO glass substrates were dried under a stream of nitrogen and heated on a hot stage. UV/ozone treatment of the ITO glasses was carried out for 20 min.

The ZnO layer were fabricated by spin-coating ZnO solution on the ITO electrode and then thermal annealed at 130 °C for 15 min in air. The thickness of ZnO is 20 nm and were acquired by a surface profilometer. The TOPD layer was fabricated by spin-coating the TIPD solution on the ITO electrode and then thermal annealed at 130 °C for 15 min in air. The thickness of TOPD is various according to the experiment requests (the spinning speed is 2500 rpm, 2300 rpm, 2100 rpm, 1900 rpm and 1700 rpm corresponding to the TOPD thickness of 9 nm, 12 nm, 15 nm, 18 nm and 21 nm). After transferring to a nitrogen-filled glove box, the blend of PTB7:$PC_{71}BM$ in ODCB solvent was spin-coated on the top of the TOPD layer and thermally annealed at 130 °C for 15 min to form photoactive layer and the thickness of PTB7:$PC_{71}BM$ is around 90 nm. Finally, MoO_3 layer and Ag anode were prepared by vacuum evaporation method through a shadow mask to define the active area of the devices ($3 \times 3\,mm^2$) under a pressure of $\sim 4 \times 10^{-5}$ Pa. The MoO_3 and Ag were vacuum evaporated to a thicknesses of 15 and 150 nm, respectively. The deposition rate and nominal film thickness were monitored with a quartz crystal thickness monitor (TM-400, Maxtek, USA). The control devices with ZnO (20 nm) as EEL have similar device structure. The current-voltage curves were obtained using a standard source measurement unit (Keithley 2400). The current density-voltage (*J-V*) characteristics and lifetime of the PSCs were measured in a glove box under illumination at 100 mW cm^{-2} using an AM1.5 G solar simulator. The average photovoltaic parameter values are obtained from 5 devices fabricated in parallel.

The space-charge-limited current (SCLC) devices were fabricated according to aforementioned procedure but with different device configurations. ITO/TOPD/PTB7:$PC_{71}BM$/Al for electron-only SCLC devices. The control electron-only SCLC devices have a structure of ITO/ZnO/PTB7:$PC_{71}BM$/Al. In our previous research and the other paper reported (He et al., 2012; Liu et al., 2016), the optimized electron mobility value were obtained based on the Cs_2CO_3 layer as EEL. We will to fabricate the standard electron-only SCLC devices and the device configurations is ITO/Cs_2CO_3/PTB7:$PC_{71}BM$/Al. The dark current of the SCLC devices were measured using an Agilent 4155B semiconductor parameter analyzer. The mobilities were determined by fitting the dark current to the model of a single carrier SCLC with field dependent mobility, which is described as (Matsumoto et al., 1999; Murphy et al., 2013):

$$J_D = \frac{9}{8}\varepsilon_0\varepsilon_r\mu_e\frac{V^2}{L^3}$$

where J_D is the current density, μ_e is the zero-field mobility, ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material, V is the effective voltage and L is the thickness of the active layer. In simulations, ε_r was assumed to be 3, which is a typical value for organic materials. The thickness of the film (L) was measured using a step profiler. The average photovoltaic parameter values are obtained from 5 devices fabricated in parallel.

The time of flight (TOF) devices were fabricated according to the aforementioned procedure but with different device configurations of ITO/PEDOT:PSS/PTB7:$PC_{71}BM$/TOPD/Al. The standard and control TOF devices with the Ca and ZnO as EEL and to replace TOPD layer, the Ca and ZnO layer were fabricated by vacuum evaporation and electron beam evaporation method respectively. The PTB7:$PC_{71}BM$ layer were fabricated by drop wise PTB7:$PC_{71}BM$ blend solution onto an PEDOT:PSS layer and the thickness (d) is 5 µm. The laser power was attenuated so that the amount of extracted charge was small enough to avoid space charge effects but large enough to provide good signal to noise. The illuminated by a wavelength and frequency of 470 nm and 4.7 ns pulse (Nd:YAG laser) through the ITO electrode. The applied electric field (E) is 1.1×10^5 V cm^{-1}. The time-of-flight were obtained from the photocurrent curve. The electron mobility were described as (Arı et al., 2016):

$$\mu = \frac{d}{Et}$$

The samples were stored and measured under vacuum conditions. The average photovoltaic parameter values are obtained from 5 devices fabricated in parallel.

3. Results and discussion

The effects of TOPD as EEL on the photovoltaic performance were studied and the control PSC devices were fabricated using ZnO as EEL. Fig. 2a and Table 1 show the *J-V* curves of ZnO-based PSCs and TOPD-