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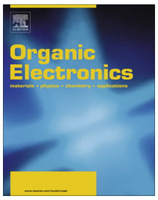

A facile approach to fabricate solution-processable metal oxides for interfacial layer in polymer solar cells

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ABSTRACT

We report a facile approach to prepare metal oxides for the interfacial layer in polymer solar cells (PSCs), in which the precursor solutions were obtained by dissolving commercial metal oxide/hydroxide in ammonia water. This approach can be adopted as a general method to prepare various solution-processable metal oxides for interfacial layers in PSCs, such as MoO_x, VO_x, WO_x and ZnO_x. The photovoltaic performance of PSCs buffered by these metal-oxide layers was studied and the applicability of these interfacial layers was demonstrated both with P3HT and a low band-gap polymer PBDT-T8-TPD.

1. Introduction

In recent years, the interfacial layer at the electrode/active layer interface in polymer solar cell (PSC) has been proven to be critically important for device performance [1,2]. Interfacial layers, such as LiF [3], CsF [4], and Cs_2CO_3 [5], can improve the performance of organic light-emitting device (OLED) by enhancing the carrier injection due to their ability to reduce the energy barrier [6,7]. Furthermore, they have been used in polymer solar cells (PSCs) as buffer layer and consequently these PSCs have shown improved performance due to the promoted extraction of charge carriers at the electrode/active layer interface caused by the reduced energy barrier. It is well known that the energy level alignment of the layers in PSCs is a crucial factor to achieve high device performance [2]. Normally, it is considered that the V_{oc} is determined by the energy level difference between the donor highest occupied molecular orbital (HOMO) and the acceptor lowest unoccupied molecular orbital (LUMO) [8]. In addition, the effective extraction of electrons and holes at the cathode and anode respectively has to be assisted by a suitable energy level offset between the active layer and the two electrodes.

Conventionally, interfacial layers have been prepared by thermal evaporation or sputtering. However, these depositions can cause severe damage to PSCs [9] especially to the underlying organic layers due to the high energy of deposited atoms. Meanwhile, these methods are limited in practical application by the prerequisite of high vacuum, high temperature or high voltage supply, and the deficiency in substrate scale-up in process. Hence in recent years, solution-processing method for fabricating the interfacial layer has becoming desirable technique for thin film PSCs, especially those methods that are carried out at low temperature. As a prototype interfacial material, poly(ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PSS) has been used to modify the indium tin oxide (ITO) anode by a solution process and it was demonstrated that this modification can improve device performance significantly compared to the device

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without buffer layer, with all parameters increased [1]. This improvement was attributed to the contact change from non-Ohmic in the bare ITO case to Ohmic in the PEDOT:PSS-modified ITO case, due to the suitable work function of ITO after modification by PEDOT:PSS. However, these devices, especially the ones with a standard architecture, still suffer from disadvantages such as the acidic and hygroscopic nature [10,11], electrical inhomogeneity [12] and insufficient electron-blocking ability [13] of PEDOT:PSS.

To overcome these problems and explore new novel interfacial materials, effort has been put into solution-processable organic [14–16] and inorganic [17–19] alternatives. Inorganic interfacial materials, particularly model transition metal oxides such as titanium dioxide (TiO_2) [20] and zinc oxide (ZnO) [20–22] (used together with MoO_3 in inverted structure) as well as vanadium oxide (V_2O_5) [18,23,24], molybdenum trioxide (MoO_3) [25–28] and tungsten trioxide (WO_3) [29] have been used to replace the PEDOT:PSS as electrode buffer layer in PSCs by solution-processing deposition and thermal evaporation. Comparable, and in some cases better, device performance by specific material have been achieved owing to their wide range of energy-aligning capabilities and large diversity in physical, chemical and electronic properties [30]. However, all these metal oxides have always been synthesized or prepared by different synthetic methods or procedure and always with different precursors, and also some are deposited by thermal evaporation. In previous reported works, solution processed oxides layers have often been deposited using their corresponding organometallic precursors, for example, vanadium (V) triisopropoxy oxide [23,24] for VO_x, $Mo(CO)_3(EtCN)_3$ [26] or MoO_2(bis(2,4-pentanedionate)$)_2$ [28] for MoO_x, and zinc acetate dehydrate [21] for ZnO_x. However, these organometallic precursors are not easily available due to their complex [26,28] synthesis route and strict storage conditions, and thus more expensive than their commercially available metal oxides or metal hydroxides. Besides organometallic solution precursors, metal oxides interfacial layers in PSCs have also been prepared with nanocrystal dispersions [10,18,27,29]. However, the complex process to prepare the nanoparticles and the shortcoming in morphology control of particle film due to the curvature and agglomerate of particles make it nonideal approach.

In this report, we developed a facile approach to prepare solution-processable model metal oxides for interfacial layer in PSCs. The precursor solutions were prepared by dissolving corresponding commercially available metal oxides in excess of ammonia water, where the dissolving is governed by hydrolysis of oxides and finally forms soluble ammonium-metal salt (e.g. aqueous ammonium molybdate and ammonium tungstate). The solution was then spin coated on substrate, the solvent evaporates and the excess ammonia escapes by annealing. Consequently, metal oxide films were obtained. Besides MoO_3 and WO_3, other popular metal oxide used in PSCs, such as V_2O_5 and ZnO were also prepared by this approach and their applicability has been demonstrated in PSCs based on poly(3-hexylthiophene) (P3HT) and a previous reported polymer PBDT-T8-TPD [31].

2. Experimental section

All the chemicals and solvent were purchased from Sigma–Aldrich and Acros Organics. All the precursor solution of metal oxides can be prepared with the following facile approach, (taking MoO_x as an example), molybdenum oxide (MoO_3, Acros Organics, 99+%, 30 mg) was added in ammonia water (25–28%, 10 ml) and stirred for 4 h at room temperature in the ambient, till a transparent solution was obtained. The VO_x, WO_x and ZnO_x precursor solution were made in a similar way. It should be noted that WO_x requires heating and small amounts of hydrogen peroxide to promote its solubility in ammonia water. Zinc oxide solution was prepared by dissolving zinc hydroxide in ammonia water instead of ZnO, similar to a previous report [22].

PSC devices were fabricated on ITO substrates, which were cleaned by ultrasonic bath in detergent, acetone, deionized water and isopropyl alcohol sequentially, and finally treated by UV/ozone for 15 min. For the standard structured PSCs, a structure of ITO/hole-extracting layer/Polymer:$PC_{61}BM$/LiF/Al was used. The hole-extracting layer MoO_x, VO_x or WO_x was deposited on ITO substrate by spin coating (4000 rpm for 40 s) their corresponding precursor solutions prepared as aforementioned. This is followed by annealing at various temperatures for 10 min in air or N_2 atmosphere. PEDOT:PSS (H.C. Starck, Clevios P VP Al 4083) was spin coated at 4000 rpm for 40 s and annealed at 150 °C for 10 min in air atmosphere. For the inverted structured PSCs, electron-extracting layer ZnO_x and hole-extracting layer MoO_3 (thermal evaperation) were used with a following structure of ITO/ZnO_x/Polymer:$PC_{61}BM$/MoO_3(e)/Al. ZnO_x layers were spin coated at 4000 rpm for 40 s and then thermal annealed at different temperatures in air atmosphere for 10 min. The thickness of MoO_x, VO_x, WO_x and ZnO_x are about 30–40 nm, 5–10 nm, 10–15 nm and 15–20 nm respectively, determined by surface profiler (XP-200, Shanghai). And then the buffer layers coated ITOs were transferred into the N_2 filled glovebox to deposit the active layer materials. P3HT:PCBM blend solution (10:8 mg/ml, *o*-DCB) was spin coated at 600 rpm on the buffer layer coated substrates (with active layer thickness of about 80 nm) and thermal annealed at 120 °C for 10 min. BDT-T12-TPD:PCBM blend solution was prepared by dissolving polymer:$PC_{61}BM$ (7 mg/ml:7 mg/ml) in chloroform and 2% volume DIO filtered with a 0.45 μm PTFE filter. The resulting blend solution was spin coated onto the oxides or PEDOT:PSS layer at 1000 rpm for 40 s (with active layer thickness of about 100 nm).After which, the devices were transferred into the thermal evaporation equipment. 0.8 nm LiF and 100 nm Al for standard structure devices and 8 nm MoO_3(e) and 100 nm Al were thermal evaporated sequentially at a base pressure of 1.5×10^{-6} Torr. The active area was 7.25 mm^2.

The *J–V* characteristics of the devices were measured by using a Keithley 2400 (*I–V*) digital source meter under a simulated AM 1.5 G solar irradiation at 100 mW/cm^2 (Newport, Class AAA solar simulator, 94023A-U). Ultraviolet and X-ray photoelectron spectroscopy (UPS and XPS) were performed by using a Kratos AXIS Ultra-DLD ultrahigh vacuum

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