Organic Electronics 14 (2013) 1305–1312

Contents lists available at SciVerse ScienceDirect

Organic Electronics

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

Buffer and anode-integrated WO_3-doped In_2O_3 electrodes for PEDOT:PSS-free organic photovoltaics

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ARTICLE INFO

Article history:
Received 27 December 2012
Received in revised form 8 February 2013
Accepted 20 February 2013
Available online 6 March 2013

Keywords:
PEDOT:PSS free
WO_3-doped In_2O_3 (IWO)
Organic solar cells
Transparent electrodes

ABSTRACT

We developed PEDOT:PSS-free organic solar cells (OSCs) using WO_3 and In_2O_3 (IWO) mixed electrodes acting as a buffer hole injection layer (HIL) and anode simultaneously. Through the co-sputtering and rapid thermal annealing (RTA) of WO_3 and In_2O_3, we achieved buffer and anode-integrated transparent electrodes with a sheet resistance of 17 Ohm/square, a transmittance of 90.32%, and a work function of 4.83 eV, all of which are comparable to values obtained with a conventional ITO anode. Due to the existence of WO_3 in the In_2O_3 matrix, OSCs fabricated on an IWO electrode with no acidic PEDOT:PSS buffer layer showed a PCE of 2.87%. Therefore, a transparent IWO electrode simultaneously acting as an HIL and anode layer can be considered a promising transparent electrode for cost-efficient and reliable OSCs because it could eliminate the use of acidic PEDOT:PSS buffer layer.

1. Introduction

Organic solar cells (OSCs) based on polymer–fullerene composite active layers have been considered as next generation photovoltaic devices following Si-based photovoltaics due to their low fabrication cost, light weight, and flexibility, as well as the simplicity of the printing-based processes used to manufacture the cells [1–3]. In academic and industrial research, power conversion efficiencies of 3–5% have been easily obtained from bulk heterojunction OSCs with poly 3-hexylthiophene (P3HT) and [6,6]-phenyl C61 butyric acid methyl ester (PCBM) active layers due to the simplicity of both their structure and the fabrication process. In particular, a recent important report on OSCs with a high power conversion efficiency of 9.2% suggests that cost-efficient and high-performance OSCs may be mass-produced in the near future [4]. At present, the majority of research into OSCs has been devoted to the development of new organic active materials or device structures (e.g., tandem or inverted OSCs) to improve the performance of photovoltaics [5,6]. Although the choice of organic active materials and device structure is critical to the performance of an OSC, the importance of a stable transparent anode cannot be ignored because exciton formation and carrier extraction is significantly affected by the transmittance and resistivity of the transparent anode. To enhance the carrier extraction efficiency of conventional indium tin oxide (ITO) anodes, an additional buffer layer such as poly (3,4-ethylene dioxylene thiophene):poly (styrene sulfonic acid) (PEDOT:PSS) or a self-assembled monolayer has been deposited on the ITO anodes [7–9]. However, it is known that the acidic nature of the PEDOT:PSS layer leads to severe etching of the ITO and the diffusion of indium into the organic active layer, which in turn causes degradation of the OSC [10]. To solve the problems associated with acidic PEDOT:PSS, metal

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http://dx.doi.org/10.1016/j.orgel.2013.02.025

oxides such as NiO, V_2O_5, MoO_3, and WO_3 have been introduced as a hole injection layer (HIL) between the organic active layer and ITO anode in order to improve the reliability of OSCs [11–14]. These oxide HILs could assist in hole extraction at the ITO anode and improve OSC performance. In particular, WO_3 has been reported as an effective and stable HIL for OSCs. Choi et al. reported on the merits of an WO_3 HIL, specifically citing its high optical transmittance over a wide solar spectral range and proper energy level alignment for hole-extraction from P3HT [15]. Tao et al. also suggested WO_3 with a high work function of 4.80 eV to efficiently extract holes and suppress electrons from the active layer [16]. Although W-doped indium oxide has been suggested as an alternative to ITO anode for OSCs, a new electrode concept combining a buffer layer and anode for PEDOT:PSS-free OSCs has not yet been reported [17,18]. To simplify the fabrication process and reduce OSC fabrication costs, the development of a multifunctional transparent electrode that simultaneously acts as a buffer HIL and anode layer is imperative.

In this work, we investigated characteristics of WO_3 and In_2O_3 co-sputtered IWO films acting as a buffer HIL and anode simultaneously. Using an optimized IWO anode with a sheet resistance of 17 Ohm/square, a transmittance of 90.32%, and a work function of 4.83 eV, we successfully fabricated the OSC with no acidic PEDOT:PSS buffer layer. Due to the existence of WO_3 in the In_2O_3 matrix, PEDOT:PSS free OSCs fabricated on an IWO electrode showed better performances than PEDOT:OPSS free OSC with conventional ITO anode. This indicates that the IWO electrode could be a promising transparent electrode for cost-efficient and reliable OSCs, because it could eliminate the use of acidic PEDOT:PSS buffer layer, affecting the stability of OSCs.

2. Experimental

An RF/DC magnetron co-sputtering system was employed to deposit a 200 nm-thick IWO thin film on a 15×15 mm^2 glass substrate. A co-sputtering process was carried out using WO_3 and In_2O_3 ceramic targets attached to tilted multi-cathode guns [18]. The IWO films were grown at a constant DC power of 100 W applied to the In_2O_3 target, an RF power of 10 W applied to the WO_3 target, an Ar:O_2 flow ratio of 10:0.1 sccm, and a working pressure of 3 mTorr without substrate heating. During co-sputtering of the WO_3 and In_2O_3 targets, the glass substrate was constantly rotated at a speed of 20 rpm so as to obtain uniformly coated IWO films. After co-sputtering of the IWO films at room temperature, the films were rapid thermal annealed at 600 °C under vacuum ($\sim 10^{-3}$ Torr) for 10 min using a commercial RTA system. The electrical properties of the IWO films as a function of the RTA temperature were analyzed via Hall effect measurements (HL5500PC, Accent optical technology). In addition, the resistivity change in the optimized IWO film was measured using a physical property measurement system (Quantum Design) in the temperature range of 2–300 K so as to investigate the conduction mechanisms of the IWO film. The optical transmittance of the IWO films was measured with a UV/visible spectrometer (UV 540, Unicam) as a function of the RTA temperature. The surface properties of the IWO films were examined by atomic force microscopy (AFM:PUCO Station STD). The microstructure of the IWO films was examined by synchrotron X-ray scattering of the GI-WAXS beam line of the Pohang Light Source (PLS); the wavelength of the incident X-rays was set to 1.243 Å by a double-bounce Si (1 1 1) monochromator. High resolution transmission electron microscopy (HRTEM) was also employed to investigate both the microstructure of rapid thermal annealed IWO films and the interface between the IWO and P3HT:PCBM active layer. In addition, UPS data were obtained for reference ITO and IWO films at room temperature using a modified KRATOS AXIS-165 system so as to examine changes in the work function of the electrodes. For the UPS measurements, a He I (21.2 eV) source was employed and a bias of −10 V was applied to the samples. The base pressure of the analysis chamber was 1×10^{-9} Torr.

To compare the performance of OSCs fabricated on optimized IWO and reference ITO electrodes, we fabricated conventional P3HT:PCBM-based bulk-heterojunction OSCs with and without a PEDOT:PSS HIL. Here, PEDOT:PSS (Clevios PH 510, H.C. Starck) was spin-coated onto the electrode substrates and subsequently annealed at 120 °C for 10 min. A blend solution of 50 mg P3HT (Rieke Metals) and 50 mg PCBM (Nano-C) in 2 mL of o-dichlorobenzene (o-DCB) was spin-coated on the IWO electrode in a nitrogen environment. A solvent annealing treatment was then performed for 120 min while keeping the photoactive films inside a covered glass jar. Each sample was subsequently annealed at 110 °C for 10 min. Finally, a Ca/Al (20/100 nm) cathode with an area of 4.66 mm^2 was deposited on the photoactive layer via thermal evaporation. The cathode layer was patterned by a shadow metal mask. All coating processes on the IWO and ITO electrodes were carried out simultaneously in the same glove box and chamber. The photocurrent density–voltage (J–V) curves of the OSCs fabricated on IWO and ITO electrodes were measured with a Keithley 1200 measurement unit under 100 mW/cm^2 illumination and AM 1.5 G conditions. A reference Si solar cell certified by the International System of Units (SI) (SRC 1000 TC KG5N, VLSI Standards, Inc.) was employed to ensure accurate measurements.

3. Results and discussion

Fig. 1 shows a buffer and anode-integrated transparent anode for PEDOT:PSS-free OSCs was achieved via the co-sputtering of a WO_3 HIL and In_2O_3 anode. Using tilted multi-cathode guns supplied with DC and RF power as shown Fig. 1a, IWO films were sputtered on a glass substrate with dimensions of 1.5×1.5 cm^2. Shown in Fig. 1b is an image of an optimized transparent IWO electrode and PEDOT:PSS-free OSCs fabricated on the buffer and anode-integrated IWO electrode. Because the IWO electrodes were composed of both WO_3 and In_2O_3, conventional bulk heterojunction OSCs can be fabricated without using a PEDOT:PSS HIL. Energy level diagrams for the PEDOT:PSS-free OSC are shown in Fig. 1c. These diagrams were generated based on ultraviolet photoelectron spectroscopy (UPS) data acquired