ITO-free inverted polymer solar cells with ZnO:Al cathodes and stable top anodes

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ABSTRACT

We report on the application of ZnO:Al as the transparent conductive oxide in high performance inverted polymer solar cells. We show that the optimized inverted architecture, which does not contain low work function metals or water-based transport layers, can be employed without sacrificing device efficiency. The widely studied P3HT:PCBM donor–acceptor system was chosen for the active layer. ZnO:Al layers were produced by dc-magnetron sputtering on glass substrates and used as the cathode. The thickness of ZnO:Al was optimized to achieve a low sheet resistance while maintaining high transmission. The resulting ZnO:Al layers were smoother than the reference ITO samples, and the active layers could be processed directly onto ZnO:Al without employing additional buffer layers. The structure of the top anodic contact was also optimized. Initial devices with an Au layer demonstrated poor results, and device performance improved when a MoO_3/Ag anode was used. Control devices in the standard forward structure using commercial ITO coated glass substrates were compared to the ZnO:Al based cells. Higher photocurrents were obtained in the inverted structures than in the ITO-based solar cells due to the higher transmittance of ZnO:Al in the spectral range where the blend absorbs.

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1. Introduction

Polymer–fullerene bulk heterojunction (BHJ) solar cells in the standard architecture are fabricated with *indium tin oxide* (ITO) sputtered on a glass substrate as the semitransparent anode and a low work function metal as the cathode on the top of the stack. The ITO is coated with a solution processed buffer layer, typically *poly(3,4-ethylenedioxythiophene)–poly(styrenesulfonate)* (PEDOT:PSS), which serves as the hole transport layer. The active layer is applied from solution onto the PEDOT:PSS layer, and the cathode is applied as the final fabrication step to close the stack.

From the point of view of stability, cost and performance such a structure involves a few significant drawbacks with regard to the contacts. Firstly, PEDOT:PSS, normally available as a water dispersion, is highly hygroscopic, which makes the ITO/PEDOT:PSS interface very sensitive to ambient air. Furthermore, the acidic character of the PSS component facilitates the chemical

degradation of ITO [1]. The low work function metals employed for the cathode (e.g. Ca, Al) increase the device degradation rate due to the high reactivity of the metal at both the interface with the organic layer and with ambient air [2,3]. Additionally, ITO is a high performance transparent conductive oxide (TCO), but it is expensive due to the scarce reserves of indium in nature, and potentially harmful due to the indium content [4]. ITO-free solar cells employing a metal grid embedded in a PEDOT:PSS layer to form the anode have been demonstrated [5–7] with promising results with respect to the production of high performance flexible solar cells [8] and stable inverted structures [9]. With regard to solar cell performance, the vertical structure of polymer:fullerene active layer in the standard structure of the BHJ has been demonstrated to be suboptimal due to the spontaneous vertical phase separation occurring in spin coated blends leading to a concentration gradient in the active layer with fullerene-rich regions near the substrate side and polymer-rich adjacent to the free surface [10,11], which can reduce both the performance and the reproducibility of the device [12].

An inverted device architecture, in which the negative electrode is at the bottom of the stack, should therefore be beneficial for solar cell stability, cost and performance. *Aluminum doped zinc*
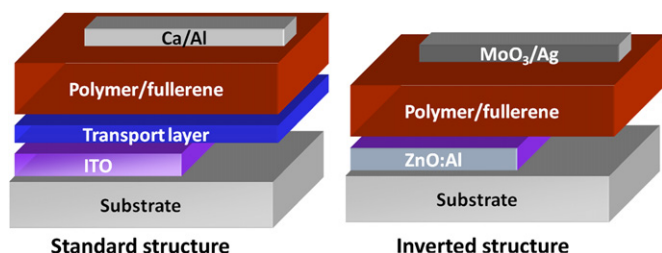
Fig. 1. Standard and inverted solar cell structures. In the standard structure ITO sputtered glass is at the bottom of the stack. ITO is semitransparent and a water-based hole transport layer is applied between the ITO and the active layer. A low work function metal cathode closes the stack at the top. In the inverted structure ZnO:Al sputtered glass is at the bottom device and the ZnO:Al serves as the cathode. The anode is at the top of the stack and a MoO_3 buffer layer is used between the active layer and the Ag contact.

oxide (ZnO:Al) has been demonstrated to be a useful and convenient replacement for ITO in standard small molecule [13] and polymer:fullerene structures [14–16]; however its use in inverted solar cells has been limited likely due to poor performance when compared to standard cell structures. Here we demonstrate that ZnO:Al can be employed to produce high performance inverted solar cells, which do not contain water-based transport layers, heavy elements or low work function metals, and have efficiencies comparable to those of ITO-based structures. The structures of the standard and inverted solar cell architectures are shown in Fig. 1. We optimized the thickness of the ZnO:Al layer to achieve high transmittance while maintaining a low sheet resistance, resulting in very smooth layers. The quality and parameters of the ZnO:Al layer allow for the processing of the active layer directly on top of TCO without the use of any additional buffer layers. This is significant from the point of view of device manufacturing. The structure of the top contact was also investigated, and a 15 nm thick molybdenum oxide (MoO_3) as a buffer layer between the active layer and Ag contact was found to result in the highest device efficiencies. The inverted solar cells showed higher photocurrents than standard ITO-based devices processed from the same active layer materials due to the high transmittance of ZnO:Al in the spectral region where the blend absorbs.

2. Experimental details

ZnO:Al thin films were deposited onto pre-cleaned Corning® glass substrates by dc-magnetron sputtering. ZnO ceramic targets containing 2 wt% Al_2O_3 were used. The temperature of the substrates during deposition was 400 °C. The thickness of the layers was determined with a Veeco Dektak 150 profilometer and by spectroscopic ellipsometry. A four point probing bridge from Jandel Engineering was used to measure the sheet resistance while UV-vis optical characterizations were performed with a Varian Cary 5000 spectrophotometer equipped with an integrating sphere. The surface roughness of the films was measured with Nanosurf Mobile S atomic force microscopy (AFM). The composition of the ZnO:Al films after deposition was analyzed by energy dispersed X-ray spectroscopy (EDX) using an X-Max silicon drift detector from Oxford Instruments. ITO substrates, purchased from PGO (Germany), were also characterized. For the preparation of the inverted solar cells, patterned ZnO:Al coated glass substrates were cleaned in isopropyl alcohol before being transferred to a nitrogen filled glovebox where the other processing steps were performed. The active layer, consisting of a blend, 1:1 in weight ratio, of *poly-3-hexylthiophene* (P3HT, Merck Chemicals ltd, UK) and [6,6]-*phenyl-C61-butyric acid methyl ester* (PCBM, Solenne BV), dissolved in dichlorobenzene, was spun on top of ZnO:Al to obtain

films with a thickness of about 230 nm. The samples were then annealed at 150 °C for 10 min. The anode was thermally evaporated through a shadow mask. MoO_3 and Ag were purchased from Aldrich. The thicknesses of the evaporated layers were determined using a calibrated quartz crystal microbalance during evaporation. The active area of the devices was 0.56 cm^2. Solar cells in the standard forward configuration on commercial ITO substrates with the same active layer thickness and the same active area as those of the inverted cells were prepared as control devices. The layer sequence for the standard devices was glass/ITO/PEDOT:PSS/P3HT:PCBM/Ca/Al. Current–voltage characteristics of all the devices were measured with a Keithley 4200 semiconductor characterization system. The standard reference spectrum AM 1.5G was provided by a P.E.T. class A solar simulator calibrated with a reference silicon solar cell from Fraunhofer ISE (Germany). For each experiment, a batch of 20 substrates was fabricated.

3. Results and discussion

The basic requirements for a TCO to be suitable for electronic applications are high transmittance over a broad spectral range and low sheet resistance. The electrical and optical properties of the ZnO:Al films are determined by the Al content during deposition. Al acts as an n dopant by replacing the Zn atoms in the ZnO structure. The introduction of Al atoms in the ZnO film increases the density of electrons and therefore the conductivity. At the same time, the transmittance in the near-infrared range is reduced. For high doping levels, excess Al forms nonconductive Al_2O_3 clusters, leading to a decrease in conductivity [17]. For this study, the doping concentration was constant, and fixed by the sputtering target composition. From EDX measurements we determined an Al concentration in the films of 0.94% weight by weight (w/w). To optimize the TCO properties, we varied the thickness of the layer. In addition to composition, the deposition temperature of ZnO:Al has a strong impact on the TCO properties. This parameter, however, is beyond the scope of this study and will be the focus of future work. In order to obtain a good trade-off between these two properties, three ZnO:Al batches (A, B, C) with varying thickness were fabricated and characterized. The transmittance of each of the ZnO:Al samples is shown in Fig. 2 together with the respective thickness. The sheet resistance of the layers decreases with increasing layer thickness from 20 to 13 $\Omega/\square$.
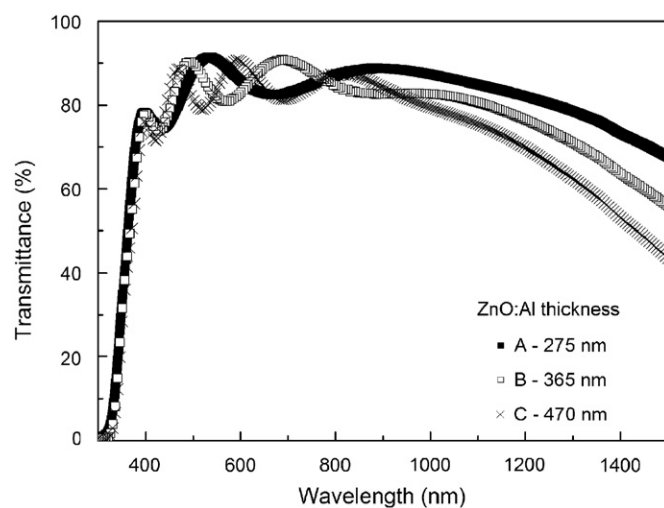

Fig. 2. Transmittance of ZnO:Al layers with thicknesses of 275 nm (closed squares), 365 nm (open squares) and 470 nm (crosses).