Thin Solid Films xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Thin Solid Films

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

High performance inverted polymer solar cells with solution processed metal oxides as electron transport layers: A comparative study

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ARTICLE INFO

Article history:
Received 23 July 2015
Received in revised form 14 December 2015
Accepted 7 January 2016
Available online xxxx

Keywords:
Polymer solar cells
Inverted solar cell architecture
PTB7-Th
Zinc oxide
Aluminum-doped zinc oxide
Titanium oxide
Impedance spectroscopy

ABSTRACT

Transparent metal oxides became an important class of low-temperature solution-processed electron transport layers (ETLs) for inverted polymer solar cells (PSCs) due to their high optical transparency in the visible range, relatively good electrical conductivity and tunable work function. In this work we made a comparative study between the electrical performances of devices realized with various metal oxides as ETLs: ZnO, ZnO:Al and TiO_x. These oxides were prepared by low-temperature solution process techniques and used in PSCs with the configuration glass/Indium tin oxide (ITO)/ETL/photoactive layer/MoO_3/Ag. The photoactive layer was a blend of poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*;4,5-*b*′]dithiophene-2,6-diyl-alt-(4-(2-ethylhexyl)-3-fluorothieno[3,4-*b*]thiophene-)-2-carboxylate-2-6-diyl)] and [6,6]-phenyl C_{71} butyric acid methyl ester. The best power conversion efficiency (9.1%) under simulated AM1.5G illumination of 100 mW/cm^2, was achieved for the PSC fabricated using a ZnO:Al interlayer. In order to elucidate the electrical processes at the interfaces between the ETL and the blend, impedance spectroscopy analysis was carried out. The ZnO:Al PSC shows better charge transfer properties between the active layer and the ITO and longer charge carrier lifetime. These factors contribute to improve the fill factor and increase the current output leading to an higher power conversion efficiency.

1. Introduction

Over the past years, intensive investigations have been carried out in the development of materials for bulk heterojunction polymer solar cells (PSCs) [1–3]. This kind of photovoltaic devices shows promising advantages such as flexibility, light weight, low cost and processability with roll-to-roll printing techniques compared to conventional silicon solar cells [4–7]. In order to compete with these inorganic devices in real-world applications, high power conversion efficiency (PCE) and environmental stability are also important. Actually, PCE surpassing 10% [8,9] and long lifetime [10–12] have been reported but they are not related to the same PSC configuration. The performances and the stability of such devices mainly depend on the photoactive layer (i.e. materials used as electron donor and electron acceptor) and the architecture of the device (i.e. interface materials and contacts) [12,13]. In fact, it has been demonstrated that PSCs, with the so-called inverted device architecture (i.e. a cell where the polarity of the electrodes is reversed compared to the standard configuration), show better photovoltaic performances [14]. In addition, the electrode materials (with higher work function) used in the inverted configuration contribute to improve the stability of the cells [13,15] while the standard device architecture suffers from the degradation of Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) and cathode (Ca/Al) by oxygen and water vapor [16,17].

Transparent metal oxides, such as zinc oxide (ZnO) or titanium oxide (TiO_x) are an important class of low-temperature solution-processed electron transport layers (ETLs) for inverted PSCs due to their high optical transparency in the visible range, relatively good electrical conductivity and tunable work function [18,19]. In addition these materials act also as hole blocking layer because their valence band is much lower than those of the highest occupied molecular orbital of the photoactive polymers and can be solution processed with low temperature treatments. Traces of reactants used to prepare the precursor solution of the metal oxides and still present in the deposited film, can influence the recombination processes at the interface with the blend and can have a great impact on the photovoltaic performance of the devices. The relevance of this issue depends on the photoactive materials employed in the realization of the devices. In fact, it has been shown that these contaminants can have a great impact on the quality of the ZnO film reducing the performance of inverted PSCs based on a blend of poly-3-hexylthiophene (P3HT) and [6,6]-phenyl C_{61} butyric acid methyl ester ([60]PCBM) [20] while it is not critical for devices based on a blend of poly[(4,8-bis-(2-ethylhexyloxy)-benzo[1,2-b;4,5-b′]dithiophene)-2,6-diyl-alt-(4-(2-ethylhexanoyl)-thieno[3,4-

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http://dx.doi.org/10.1016/j.tsf.2016.01.026
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b]thiopene)-2,6-diyl] (PBDTTT-C) and [70]PCBM [21]. Although in the literature studies on performance of different metal oxides as ETLs in P3HT based PSCs are reported [22–24], there is a lack of investigations in device based on the new generation of donor polymers, like copolymers of benzodithiophene and thieno-thiophene units.

In this paper, we realized inverted PSCs using three different metal oxides commonly used as ETLs: ZnO, ZnO:Al and TiO_x. These materials were realized by solution process and with low-temperature treatments. The architecture of all the devices was glass/Indium tin oxide (ITO)/ETL/blend/MoO_3/Ag. The photoactive layer was a blend of poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*;4,5-*b*′]dithiophene-2,6-diyl-alt-(4-(2-ethylhexyl)-3-fluorothieno[3,4-*b*]thiophene-)-2-carboxylate-2-6-diyl)] (PTB7-Th) and [6,6]-phenyl C_{71} butyric acid methyl ester ([70]PCBM). PTB7-Th is a low-bandgap polymer recently used as donor material in PSCs showing PCE greater than 10% using inverted device structure [9]. Solar cells were realized and characterized by external quantum efficiency (EQE) and current–voltage (IV) measurements in dark and under AM1.5G illumination (100 mW/cm^2). In order to elucidate the electrical processes of the PSCs with the different ETLs, we investigated their behavior by impedance spectroscopy (IS). This electric technique is used to check the current response of a device when an AC voltage is applied as a function of the frequency. With this tool it is possible to observe the electric properties of the bulk and the interface usually not detectable with DC methods [25–28].

2. Experimental part

2.1. Materials synthesis and characterization

The ITO coated Corning® Eagle XG glass substrates, were purchased from Delta Technologies, LTD, with a sheet resistance of 10 Ω/square. PTB7-Th and [70]PCBM were purchased from 1-Material and Solenne BV, respectively; 1,2-dichlorobenzene (anhydrous, 99%, DCB), 1,8-diiodooctane (98%, DIO), zinc acetate dihydrate (99.9%), ethanolamine (99.5%), 2-methoxyethanol (99.8%), aluminum nitrate nonahydrate (99.997%) and titanium(IV) isopropoxide (99.9%) were purchased from Sigma-Aldrich. MoO_3 (99.95%) and Ag (99.99%) were purchased from Materion and Umicore. All the chemicals were used as received.

The ZnO precursor was prepared by dissolving 1 g of zinc acetate dihydrate and 0.28 g of ethanolamine in 10 mL of 2-methoxyethanol. The solution was vigorously stirred for 12 h in air for the hydrolysis reaction [21,29]. The ZnO films were obtained by spin coating the solution at 4000 rpm for 60 s on the top of glass or glass/ITO substrates. The films were annealed at 150 °C for 5 min. The thickness of the ZnO films was around 40 nm.

The ZnO:Al precursor was prepared using a similar procedure, by adding 68 mg of aluminum nitrate nonahydrate as dopant source to the ZnO sol ([Al]/[Zn] = 4%) [22]. Then, the solution was stirred for 12 h in air. The corresponding films were prepared as described before for the undoped ZnO. The thickness was around 40 nm.

The TiO_x interlayer material was prepared by diluting 0.5 g of the titanium(IV) isopropoxide in 10 mL of 2-methoxyethanol [30,31]. The TiO_x films were obtained by spin coating the solution, vigorously stirred for about 12 h in air, at 4000 rpm for 60 s on the top of glass or glass/ITO substrates. The film was annealed at 200 °C for 60 min in ambient air. The thickness was around 20 nm.

The film thicknesses were measured by KLA Tencor P-10 surface profiler. UV–VIS optical reflectance and transmittance spectra of layers deposited on glass substrates was carried out using a Perkin-Elmer Lambda 900 spectrophotometer.

2.2. Polymer solar cells realization and characterizations

The architecture of the investigated PSCs was glass/ITO/ETL/PTB7-Th:[70]PCBM/MoO_3/Ag (ETL = ZnO, ZnO:Al, TiO_x), and it is shown in

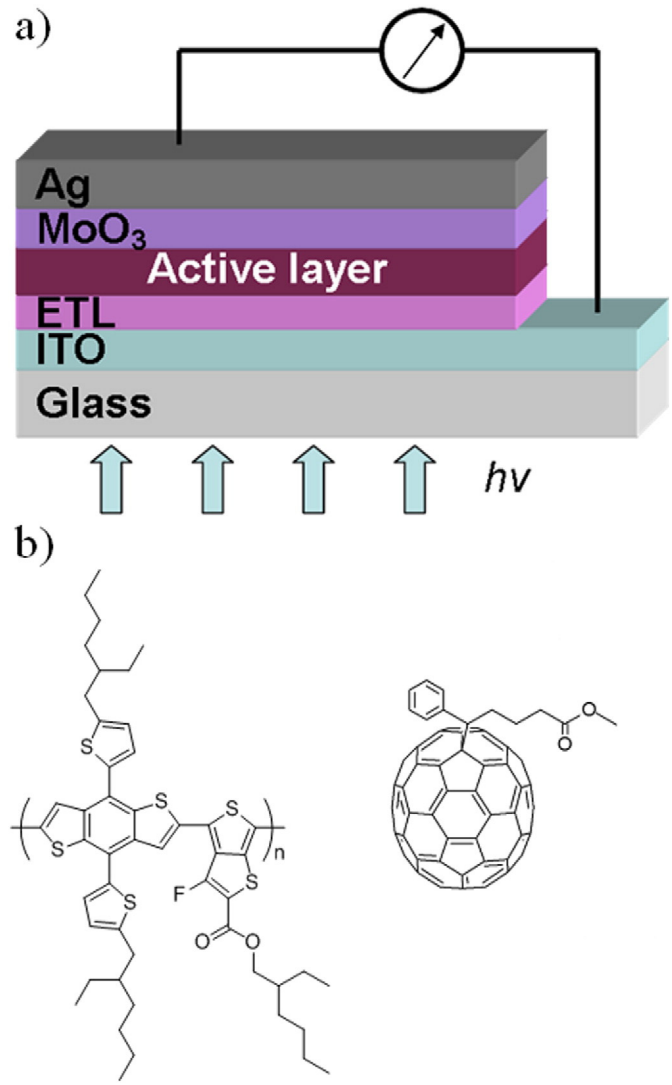

Fig. 1. (a) Device architecture of the investigated inverted polymer solar cells. (b) Chemical structures of PTB7-Th and [70]PCBM (major isomer).

Fig. 1 together with the chemical structure of the materials used to prepare the photoactive layer. The ETL was deposited on patterned glass/ITO substrate as described before. The active layer (90 nm) was realized by dissolving PTB7-Th (15 mg/mL) and [70]PCBM (22.5 mg/mL) in a mixed solvent of DCB:DIO (97:3% by volume) and spin coated on the top of ITO/ETL structure. A 5 nm MoO_3 layer and a 100 nm Ag layer were sequentially thermally evaporated through a shadow mask to form a top anode. The active area of the device was 22 mm^2.

The IV light characteristics of PSCs were performed in a nitrogen-filled glove box (O_2 and H_2O < 1 ppm) at 25 °C with a Keithley 2400 source measure unit (Keithley Instruments Inc., Cleveland, USA). Simulated AM1.5G illumination was provided by a class "AAA" solar simulator (Photo Emission Tech, model CT100AAA, equipped with a 150 W Xenon lamp) and its intensity was calibrated using a mono-Si reference cell with a KG5 filter for 1 sunlight intensity of 100 mW/cm^2. The EQE spectra were measured with a Bentham PVE300 apparatus calibrated with a Si detector. The alternate current measurements were performed by means of HP 4192 A impedance analyzer by applying 0.1 V amplitude voltage and by investigating the frequency range $1 \times 10^2 \div 1 \times 10^7$ Hz. The employed experimental setup allowed to measure the equivalent capacitance and the conductance with resolution of about 0.1 pF and 1×10^{-10} S, respectively. The measurements at different light intensity

Please cite this article as: P. Morvillo, et al., High performance inverted polymer solar cells with solution processed metal oxides as electron transport layers: A comparative study, Thin Solid Films (2016), http://dx.doi.org/10.1016/j.tsf.2016.01.026