Organic Electronics 46 (2017) 218–225

Contents lists available at ScienceDirect

Organic Electronics

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

Spontaneous growth by sol-gel process of low temperature ZnO as cathode buffer layer in flexible inverted organic solar cells

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ARTICLE INFO

Article history:
Received 11 January 2017
Received in revised form
4 April 2017
Accepted 4 April 2017
Available online 17 April 2017

Keywords:
Sol-gel
Zinc oxide
Low-temperature
Inverted polymer solar cells
Flexible device

ABSTRACT

In this study, the sol–gel method was employed to prepare zinc oxide (ZnO) thin films as cathode buffer layers for inverted organic solar cells (IOSCs). We used a low temperature sol-gel process for the synthesis of ZnO thin films, in which the molar ratio of zinc acetate dihydrate (ZAD) to ethanolamine (MEA) was varied; subsequently, using the thin films, we successfully fabricated inverted solar cells on flexible plastic substrates. A ZnO sol–gel was first prepared by dissolving ZAD and MEA in ethylene glycol monomethyl ether (EGME). The molar ratios of ZAD to MEA were set as 1:1.2, 1:1, and 1:0.8, and we investigated the characteristics of the resulting ZnO thin films. We investigated the optical transmittance, surface roughness, and surface morphology of the films. Then, we discussed the reasons about the improvement of the device efficiency. The devices were fabricated using the ZnO thin films as cathode buffer layers. The results indicated that the morphology of the thin films prepared using the ZAD to MEA ratios of 1:1 and 1:0.8 changed to a rippled nanostructure after two-step annealing. The PCE was enhanced because of the higher light absorption in the active layer caused by the nanostructure. The structure of the inverted device was ITO/ZnO/P3HT:$PC_{61}BM$/MoO_3/Ag. The short-circuit current densities (8.59 mA/cm^2 and 8.34 mA/cm^2) of the devices with films prepared using the ZAD to MEA ratios of 1:1 and 1:0.8 ratios, respectively, and annealed at 125 °C were higher than that of the device containing the ZnO thin film that was annealed at 150 °C. Inverted solar cells with ZnO films that were prepared using the ZAD to MEA ratios of 1:1 and 1:0.8 and annealed at 125 °C exhibited PCEs of 3.38% and 3.30%, respectively. More than that, PCEs of the flexible device can reach up to 1.53%.

1. Introduction

Over the past few years, bulk heterojunction polymer solar cells (PSCs) have attracted considerable attention because of their unique properties such as mechanical flexibility, low cost, and large-area fabrication compatibility with roll-to-roll processing [1–3]. Moreover, they have achieved power conversion efficiencies (PCEs) of 9.2 and 10.6% in tandem and as single cells, respectively [4,5]. However, the poor stability and short lifetime of PSC devices are still serious problems that limit their development. Accordingly, the use of an inverted device structure is one approach to alleviate this problem [6].

Inverted polymer solar cells (IPSCs) are devices in which electrons are collected by the top transparent electrode and holes are collected by the bottom electrode. This allows one to use a high-work-function top metal electrode such as gold (Au) or silver (Ag) [7,8], thus eliminating the oxidation problem, and an electron transparent layers (ETL) as the bottom electrode to enhance stability [9–12]. ETLs such as cesium carbonate (Cs_2CO_3) [13], titanium oxide (TiOx) [14,15], or zinc oxides (ZnO) [16–23] eliminate the problem caused by the use of acidic poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) on indium-tin oxide (ITO) substrates. ZnO is usually used because of its high electron mobility, high environmental stability [24], and low light absorption. Hence, it is also extensively used in other organic electronic devices such as organic light-emitting diodes (OLEDs) [25–28] and polymer light-emitting diodes (PLEDs) [29,30]. Currently, sputter deposition (SD) [31,32], atomic layer deposition (ALD) [7,33], electrodeposition [22], colloidal nanoparticles [9], and sol-gel processes [34–42] are the main methods used to prepare ZnO-based thin films for ETLs. The sol-gel method has been extensively investigated as a solution-based thin-film deposition process because it is a low-cost and simple process [43]. Recently, in studies on ZnO annealing

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http://dx.doi.org/10.1016/j.orgel.2017.04.006
1566-1199/

temperatures, the best PCE of 7% was achieved for inverted PSCs realized using ZnO annealed at 150 °C for only 5 min [41]. Comparing the different annealing times of low-temperature-processed ZnO·xH2O devices, the average PCE reached 6.48% with an ambient temperature as low as 80 °C [42]. The PCE was significantly improved from 0.43% for a device using pristine ZnO to 1.14% for another device using ZnO:Cs with a Cs/Zn molar ratio of 0.094 [44]. In this paper, we show that ZnO prepared by the sol-gel techniques, MEA is not only used for catalysts of the zinc oxide film, In addition MEA also is one of the growing ZnO needed, as shown in Reaction formula (1). At higher molar ratios of MEA to ZnO according to the above reaction formula, MEA is not completely reacted; the residual MEA will thus affect the film surface morphology, and the low-temperature-processed ZnO thin films with residual MEA will have poor contact with the active layer, thus reducing the current injection efficiency of the light-absorbing layer. Using a lower molar ratio of MEA to ZnO, the electron transport layer can achieve a higher conversion efficiency at a lower temperature. In addition, the literature points out that the sheet resistance of ITO increases significantly if the annealing temperature exceeds 150 °C [41]. Therefore, in this study, we used annealing temperatures of 150 °C and 125 °C, values that are more in line with the demand for flexible substrates. The process for the precursor formation was very simple, and no other residual organic byproducts were introduced into the final ZnO thin film. Although less the proportion of change will make the film thinner, the thickness of deposited ZnO thin film is enough to act as an electron selective layer of the optimized in flexible inverted PSCs.

$$Zn(CH_3COO)_2 \xrightarrow{EGME} [CH_3COOZn]^+ \xrightarrow{MEA} Zn-O-CH_2-CH_2-NH_2 \xrightarrow{Dry\ in\ air} ZnO \quad (1)$$

2. Experimental section

2.1. Materials

ITO glass with a sheet resistance of 9 Ω/square was purchased from AimCore Technology Co. Ltd. Zinc acetate dihydrate [ZnAc, $Zn(CH_3COO)_2 \cdot 2H_2O$, 99%], 2-methoxyethanol ($CH_3OCH_2CH_2OH$, 99%), and MEA ($NH_2CH_2CH_2OH$, 99%) were purchased from Alfa Aesar. $PC_{61}BM$ and $PC_{71}BM$ were purchased from Nano-C Inc. P3HT and PTB7 were purchased from 1-Material Inc. MoO_3 was purchased from Summit Technology Company (99.9% purity). Silver was purchased from Alfa Aesar (99.9% purity). All the solvents used in this study were purchased from Alfa Aesar. The materials and reagents were used without purification.

2.2. Preparation of ZnO sol-gel thin films

The ZnO sol was made by dissolving zinc acetate dihydrate (0.88 g) in a mixture of 2-methoxyethanol (10 g) and MEA. The molar ratios of zinc acetate to MEA were set at 1:1.2, 1:1, and 1:0.8. The solution was vigorously stirred at 60 °C for 1 h to carry out hydrolysis in air. To yield a stable, clear, and homogeneous sol, the solution was kept at room temperature for approximately 24 h.

2.3. Fabrication of inverted PSCs

To fabricate inverted polymer solar cells, we employed two types of substrates, one flexible, the other rigid. For the flexible ITO-free substrate, a flexible film was employed consisting of a poly(-ethylene naphthalate) (PEN) substrate. We also prepared an ITO/glass electrode substrate. Both types of substrates were cleaned in deionized water, acetone, and isopropanol successively using a sonicator for 10 min. After cleaning, the ITO glass substrates were dried at 130 °C for 10 min in an oven. At first, without using O_2 plasma, a 50-nm-thick ZnO layer was spin coated onto the ITO glass at a speed of 2500 rpm for 30 s and annealed at 125 °C, and 150 °C for 10 min to crystallize the ZnO film, then filtered through 0.45 μm filters.

To fabricate the active layers, P3HT and $PC_{61}BM$ at a weight ratio of 1:1 were co-dissolved in 20 mg/mL of o-dichlorobenzene (ODCB) by magnetic stirring at 40 °C for 24 h. The active layer was prepared from the blended solution of P3HT/$PC_{61}BM$ by spin coating the solution onto the substrates in a glovebox under a N_2 atmosphere at 800 rpm for 40 s to achieve a thickness of 150 nm, then filtered through 0.22 μm filters, and dried in a covered Petri dish for 1 h.

PTB7 and $PC_{71}BM$ at a weight ratio of 1:1.5 were co-dissolved in a 15 mg/mL mixture of chlorobenzene (CB) and 1,8-diiodooctane (97:3% by volume). To form a homogeneous blend, the co-dissolved solution was magnetically stirred at 60 °C for 24 h. The active layer was prepared from the blended solution of PTB7/$PC_{71}BM$ by spin coating the solution at 800 rpm for 40 s to achieve a thickness of 130 nm, then filtered through 0.22 μm filters, and dried at 120 °C for 10 min in a glovebox under N_2 atmosphere. Finally, a thin-hole transport layer of molybdenum oxide (MoO_3) was thermally evaporated ($<8 \times 10^{-6}$ Torr) onto the active layer material, followed by evaporation of the top Ag electrode using a shadow mask.

2.4. Characterization measurements

The film thickness was measured using a Veeco Dektak 150 Alpha Step surface profiler. The transmission spectra of the ZnO thin films on the glass substrates were measured using a Lambda 35 ultraviolet–visible–near-infrared (UV–Vis–NIR) spectrophotometer. The surface morphologies were determined using atomic force microscopy (AFM) (NonoMan NS4+D3100, Digital Instrument). The field emission gun scanning electron microscopy (FEG-SEM) images were obtained using a Hitachi-4700 system. The surface compositions of the ZnO films were examined by X-ray photoelectron spectroscopy (XPS) (JEOL, JAMP-9500F). Current density-voltage characteristics were measured with a Keithley 2400 source meter under AM1.5 global solar illumination (100 mW/cm^2) from a xenon lamp solar simulator (Oriel 91169, NEWPORT). The external quantum efficiency spectra were obtained by illuminating periodically modulated monochromatic light with continuous-wave bias white light on the solar cells.

3. Results and discussion

3.1. Effect of optoelectronic properties on the ZnO films

In this research, ZnO films were applied using the sol-gel process to fabricate inverted organic solar cells. A fixed spinning rate of 2500 rpm was used. The thickness of the film was controlled by adjusting the concentration of the sol-gel. The ratio of the solutes in the sol-gel was also adjusted. The ZnO sol-gel was fabricated using a combination of ZAD and MEA as the solutes. The solvent was ethylene glycol monomethyl ether (EGME). In order to understand the influence of the solutes on the film and its components, ZAD and MEA were combined using molar ratios of 1:1.2, 1:1, and 1:0.8. Then, for each of these solute ratios, several sol-gels were made, each with a different concentration. The device structure of the inverted P3HT:$PC_{61}BM$ and PTB7:$PC_{71}BM$ solar cells is schematically illustrated in Fig. 1(a). The energy level diagram of the inverted solar cell is depicted in Fig. 1(b). The chemical structures and