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Impact of sputtered ZnO interfacial layer on the S-curve in conjugated polymer/fullerene based-inverted organic solar cells

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ABSTRACT

The impact of crystalline structure changes of sputtered ZnO interfacial layer on performances of inverted organic solar cells (OSCs) has been investigated. We find that the structural modification of the ZnO cathode interfacial layer, obtained by thermal annealing, plays a crucial role in the origin and solving of the S-curve in conjugated polymer/fullerene photovoltaics. Our results show that the crystallization (i.e. crystallites size) of poly(3-hexylthiophene) (P3HT) evolves as a function of that of ZnO according to the annealing temperature. This evolution can directly impact the interfacial orientation and organization of the chains of P3HT at the ZnO buried interface. Such an ordered profile favors the vertical phase segregation and raises the carrier mobility, which explains the disappearance of the S-shape observed in current density-voltage device characteristics for annealing temperatures above 200 °C. These results adequately address recent research and provide an important insight into the interfacial layers of inverted OSCs.

1. Introduction

Organic solar cells (OSCs) with inverted structure are among the most promising organic based systems used to convert solar energy into electric power [1]. They have shown a stability improvement while keeping comparable photovoltaic performances with respect to conventional structures [2,3]. Recent studies reported that inverted structures enable power conversion efficiency of about 4% using the P3HT and [6,6]-phenyl C_{61}-butyric acid methylester (PCBM) blends and more than 7% with more advanced donor materials [4]. Among the many advantages, the inverted device is less sensitive to oxygen by using higher work function metals (such as Ag, Au) for the top electrode [5], prevents the use of poly(3,4- ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) as acidic hole-transporting layer with indium-tin oxide (ITO) [6], and shows better interactions with the organic active layers [7]. Such progress could not have been achieved without efforts on the interface engineering on buffer layers. Indeed, the interfacial films employed in the inverted structure play a central role in terms of efficiency, robustness and stability of the OSCs [8,9]. This is particularly relevant for the cathode interfacial layer that is sandwiched between the transparent electrode, often made of ITO, and the active layer such as P3HT:PCBM. The cathode interfacial layer consists of a thin film of n-type semiconducting metal oxide that should present unique properties such as near-UV emission, chemical stability, optical transparency, and electric conductivity [10,11]. In the field of OSCs, ZnO seems best-suited interface material in the inverted structure devices over TiO_x [12] or alternative metal oxides such as Cs_2CO_3 and Al_2O_3 [13]. It has been shown that ZnO, due to its band structure, is well suited to be associated with P3HT:PCBM in OSCs. The ZnO interfacial layer can facilitate the electron transfer since the conduction-band edge of ZnO (−4.4 eV) is located between the conduction-band edge of ITO (−4.7 eV) and the lowest unoccupied molecular orbital (LUMO) energy level of acceptor molecules (−3.7 eV) (Fig. 1a). ZnO is also reported to form an ohmic contact with P3HT:PCBM in inverted structures [14,15]. Note that ZnO provides also interface solutions for recent materials used in advanced organic solar cells, as aliphatic-amine polymers for “universal” electrodes [16] and small molecules for photoactive layers [17]. All these properties make ZnO an ideal cathode interfacial material for inverted OSCs. To prepare high quality ZnO thin films on large-area flexible substrates, ZnO is often deposited by wet processes such as sol-gel or from colloidal nanoparticles [18,19]. However, these methods require more efforts to provide stable and high quality homogenous thin films with reproducible properties [20]. Among alternative fabrication methods, dry processes such as sputtering [21], atomic layer deposition (ALD) [22] or plasma enhanced chemical vapor deposition (PECVD) [23] are potentially interesting to obtain high quality ZnO films. Sputtering technique caught more

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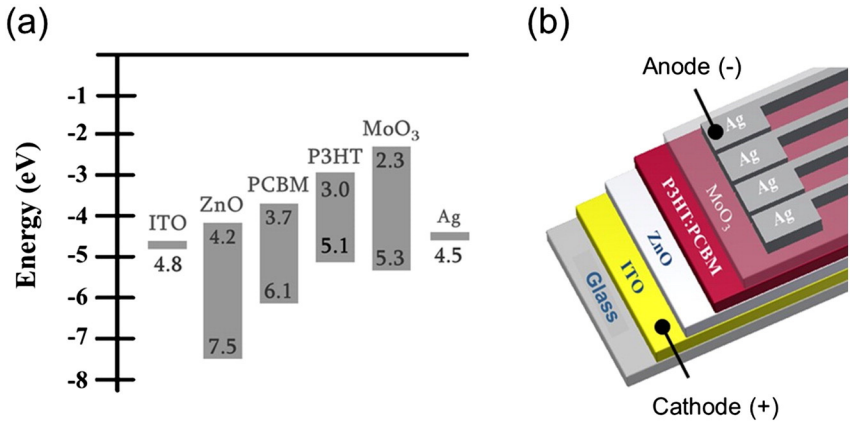

Fig. 1. Inverted organic solar cell. (a) Energy-level diagram of ITO, ZnO, PCBM, P3HT, MoO_3 and Ag. (b) Device structure.

attention lately [24]. It can be operated at low temperature [25], and used to deposit dense, uniform, homogeneous and reproducible ZnO films with well-defined *c*-axis orientation even when deposited on amorphous rigid substrates [26]. Sputtering is also compatible with roll-to-roll processing [27,28].

The role of ZnO layer deposited by sputtering technique has been recently investigated on the performances of inverted OSCs [29]. However, such studies remain limited. Most of the researches including the correlation between crystallinity, stoichiometry, and surface morphology of ZnO films on one hand, and the photovoltaic performances on the other hand, have been made on ZnO interfacial layer formed by sol-gel solution. For instance, Ma et al. investigated the importance of the surface morphology of the ZnO interfacial layer formed by sol-gel solution on the photovoltaic performance parameters of the inverted OSCs based on poly[2,3-bis-(3-octyloxyphenyl)quinoxaline-5,8-diyl-alt-thiophene-2,5-diyl] (TQ1):$PC_{71}BM$ [30]. They claimed that the surface roughness determines the surface energy of ZnO films and thus the donor/acceptor interfacial area of the active layer deposited atop. Liang et al. made similar observations showing that the surface morphology plays an important role in the contact quality between the ZnO and P3HT:PCBM layers [31]. On the other hand, Ka et al. used low thermal annealing (TA) to induce an improvement of the energy-level alignment arising from the crystallinity of aqueous solution-processed ZnO films, which leads to interesting performances of OSCs [32]. Note that the most common way to tune the structural properties of ZnO thin films is to perform thermal annealing (TA) [33]. TA improves the photovoltaic performances in OSCs by optimizing the electric properties (carrier concentration, mobility, conductivity) of the interfacial film, which are significantly influenced by its crystallinity and stoichiometry.

Interestingly, none of the recent researches investigated the details of ZnO film property in terms of interfacial effects. Recent work demonstrated that the molecular order of conjugated polymer/fullerene photovoltaics directly impacts the performance of OSCs. Dhar et al. showed that the underlying substrate influences the orientation of the conjugated backbone of regioregular P3HT (rrP3HT) at buried interfaces and how this molecular organization changes upon thermal annealing [34]. As found by Finck et al., these effects can lead to the disappearance of S-shaped *J-V* curves in OSCs composed of P3HT:PCBM films [35]. These developments must be adequately addressed in current researches of performances in inverted OSCs using sputtered ZnO films as cathode interface.

In this work, we put forward the benefits of the sputtering technique to tune the surface properties of ZnO interfacial film used as cathode layer for improving the photovoltaic performances of inverted OSCs. Especially, we analyze the potential impact of the ZnO morphology change on S-shape in *J-V* cell characteristics. We first grow ZnO on glass/ITO substrates using radio frequency (rf) magnetron sputtering at room temperature. Then, we performed TA processes in a wide range of temperatures (140 to 500 °C) to create different structural and morphological properties of the sputtered ZnO films. Our results highlight that, by increasing the temperature, the structural changes of the ZnO layer play a significant role by inducing better interfacial molecular order of P3HT at the interface with ZnO. Such an ordered profile certainly favors the vertical phase segregation and raises the carrier mobility, which explains the disappearance of the S-shape in *J-V* device characteristics for TA above a temperature of 200 °C. We found that no studies have pointed out this correlation before. To be consistent with our results, we also emphasized the particular effect of defects such as oxygen vacancies on the increase of the OSCs performances.

2. Experimental details

2.1. Material and device elaboration

We elaborated inverted OSCs with P3HT:PCBM layers sandwiched between ZnO cathode and MoO_3 anode interfacial layers, as shown in Fig. 1b. ITO and Ag are used as cathode and anode electrodes, respectively. The ITO-coated glass substrates from Präzisions Glass & Optik GmbH, Germany (CEC20S, $\leq$20 Ω/sq., 20 × 20 mm^2) were cleaned in an ultrasonic bath with acetone, isopropyl alcohol and deionized water, in the order described here. Substrates were treated under UV/ozone for 30 min to remove organic impurities. Then, 54 nm-thick ZnO (99.999% from Neyco Co.) was deposited by rf sputtering using Ar plasma. The rf power and Ar pressure were maintained at 100 W and about 106.66×10^{-2} Pa, respectively. The substrate temperature was kept below 40 °C during ZnO deposition. Prior to ZnO deposition, a pre-sputtering was performed for 10 min in order to clean the target surface. The post-annealing of ZnO-deposited ITO glass was performed at various temperatures from 140 to 500 °C in ambient for 60 min. The as-prepared sample was used as a reference for comparison. The photoactive layer was deposited by spin-coating in air from a P3HT:PCBM solution (1:1 weight ratio in dichlorobenzene) to form a 120 nm thick layer. P3HT (98.5% regioregular from Sigma Aldrich GmbH) and PCBM ($PC_{61}BM$) (from Nano-C Inc.) were used as received without further purification. Subsequently, the photoactive layer was annealed at 140 °C for 15 min in N_2 atmosphere. Finally, MoO_3 (99.99% from Sigma-Aldrich GmbH) and Ag were deposited through a shadow mask by thermal evaporation in vacuum of about 266.64×10^{-6} Pa. The thicknesses of MoO_3 and Ag are estimated to 5 and 120 nm, respectively. The device active area was about 9 mm^2.

2.2. Device characterization

Atomic force microscopy (AFM) images were obtained in tapping mode on a Nanoscope Dimension 3100 from Veeco Instruments. The structural properties of the films were analyzed in the 4°–38° 2θ range