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Metal oxide buffer layer for improving performance of polymer solar cells

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ABSTRACT

We report the application of aluminum doped ZnO (ZnO:Al) layer as a buffer on ITO glass for fabrication of non-inverted polymer solar cells. The ZnO:Al thin film was deposited using DC magnetron sputtering, with the thickness being varied from 23 to 100 nm. The devices showed most discernible improvements in their efficiencies when a thin layer of ZnO:Al film of thickness ~40 nm was introduced. The observed enhancement in short circuit current density and open circuit voltage is likely attributed to the role of the ZnO:Al film as an optical tuner and an interfacial diffusion barrier. The result suggests that a metal oxide layer inserted between ITO and polymer layers can be a route for improving both efficiency and stability of polymer solar cells.

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1. Introduction

Polymer bulk heterojunction solar cells attract great interest due to the cost effectiveness of their solution and low temperature processing. Power conversion efficiencies (PCE) over 5–6% have been achieved on the systems like regioregular poly(3-hexylthiophene):[6,6]-phenyl C61-butyric acid methyl ester (P3HT:PCBM) based solar cells through a careful control of the blend layer morphology [1–3]. However, the performance is still insufficient for their practical applications. Continuous efforts are directed toward the efficiency improvement, like exploration or utilization of low band-gap materials [4–6] and development of tandem structures [7,8]. Moreover, an increased attention is being given to degradation of organic solar cells since this remains a critical barrier to commercialization. The degradation is attributed to susceptible reactions of the organic and the electrode materials with oxygen and water, interfacial indium diffusion, and morphological evolutions with thermal or UV irradiations [9,10].

It is ideal to find strategies that could both improve efficiency and reduce degradation of the devices. Among previous efforts, insertion of a metal oxide between the absorber and the cathode as an optical spacer was used to enhance device efficiency [11,12]. The spacer is considered to shift the maximum of the electromagnetic field of an incident light into the device active layer for enhanced solar energy harvesting [11]. ZnO has been demonstrated to be

one of effective materials for the spacer in that it is highly transparent, conductive when doped, and easily prepared by versatile methods [13,14]. On the other hand, ZnO has been researched as a barrier layer in inorganic thin film solar cells to improve device stability [15,16]. Because of its unique properties, in this work, aluminum doped ZnO was introduced between ITO and poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) for preparation of non-inverted polymer solar cells. This work is aimed at investigating potential effects of such a ZnO layer introduction on the efficiency and stability of these devices.

2. Experiments

ZnO:Al films were deposited on clean ITO glass by DC magnetron sputtering from an Al (2 wt.%) doped ZnO target. The 2% Al doping makes the target conductive thereby reducing the charging of the target surface during DC magnetron sputtering. The deposition was done under the following conditions: a base pressure of 9.3×10^{-5} Pa, power of 100 W, an ultra-pure Ar working pressure of 0.16 Pa, and a distance between the target and the substrate of about 15 cm. There was no intentional heating of the substrate and the temperature of the samples was around room temperature during the deposition as short as ~1 min.

The polymer solar cell comprises of an active layer of P3HT:PCBM blend sandwiched between transparent conductive coating covered glass as anode and top metal film as cathode. ITO glasses with and without ZnO:Al buffer layers were used for fabrication of the polymer solar cells under identical processing conditions in ambient air. Three batches of devices were fabricated

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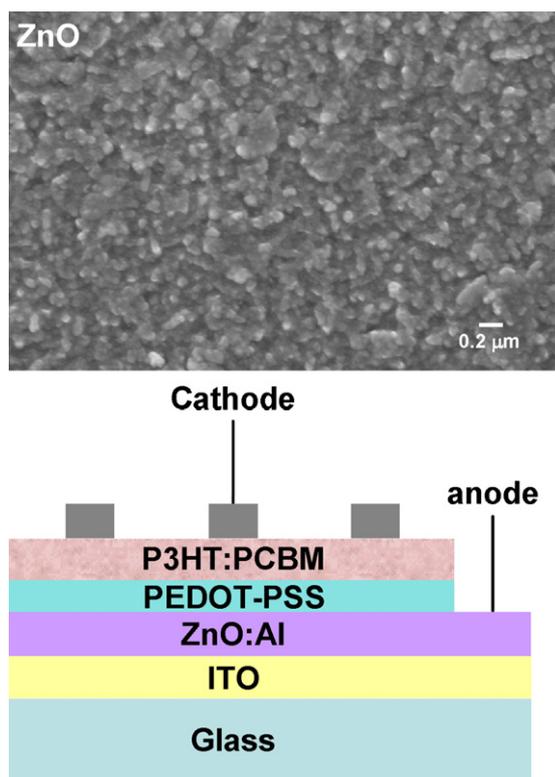


Fig. 1. (a) SEM image of the top view of the sputter-deposited ZnO:Al film and (b) schematic diagram of the polymer solar cell structure.

with the ZnO:Al layer of different thickness, which are 0 (ITO), 50, 75 and 100 nm for batch 1, 0, 50, and 75 nm for batch 2, and 0, 23, 42 and 60 nm for batch 3. The substrates were ultrasonically cleaned in de-ionized water, acetone, and isopropanol followed by drying with N_2 . A thin layer of PEDOT:PSS (Baytron P) was spin coated on the substrates at 3000 rpm, then baked on a hotplate at $230^\circ C$ for 15 min. Regioregular-P3HT:PCBM solution of 1:0.6 weight-ratio was prepared by adding PCBM (American Dye Source) to a solution of P3HT (Rieke Metals) in 1,2-dichlorobenzene (DCB) (17 mg/ml) and subsequently stirring the blend at $45^\circ C$ for 36 h. P3HT:PCBM active layers were spin coated in air from the blend solution at a speed of 1600 rpm for 60 s on the surfaces of PEDOT-PSS coated substrates. Each sample was then immediately placed in a glass Petri dish for the residual DCB to evaporate for ~ 15 min as a solvent annealing step. The resulting active layer thickness was about 100 nm as determined by Alpha step profilometer. Next, an aluminum layer (~ 100 nm) was thermally evaporated on the P3HT:PCBM surface in an evaporation chamber (base vacuum $< 10^{-7}$ Torr), followed by thermal annealing of the completed device on a hotplate at a temperature of $150^\circ C$ for 5 min in air. The devices, with an active area of 15.21 mm^2 , were measured for (I - V) characteristics in air under simulated illumination at AM 1.5G and 100 mW/cm^2 with a Keithley 2400 source meter. A Varian Cary 50 UV-vis spectrophotometer was employed to acquire transmittance and absorbance spectra of the substrates and devices. Zeiss Supra 55 field emission scanning electron microscopy (SEM), set at 10.0 kV, was utilized to examine the surface characteristics of the ZnO:Al film.

3. Results and discussion

The ZnO:Al films were sputter-deposited onto ITO glasses with thicknesses up to 100 nm in this study. Fig. 1 shows a SEM image of the film top view and the schematic diagram of the device struc-

ture with the ZnO:Al film inserted. The film appears to be uniform and comprising of grains, which are multicrystalline and of (002) preferred orientation determined by X-ray diffraction, as reported by the authors elsewhere [17].

Transmittance spectra of the ITO glasses with and without ZnO:Al layers (for batch 1) are presented in Fig. 2a. They clearly show interference fringes [18], which shifted in the peak positions with the ZnO:Al thickness changing from ~ 0 to 100 nm. The substrates with the ZnO:Al films have similar red-shifted transmission edges (near UV wavelength region) and reduced average values ($\sim 80\%$) across 450–800 nm wavelengths compared to that with the bare ITO film. Fig. 2b exhibits absorbance spectra of these substrates with coatings of PEDOT-PSS and P3HT:PCBM on the top surfaces. The spectra show no apparent shape variation or shift with the ZnO:Al thickness change, similar to those of comparable cases incorporating different thicknesses of TiO_x or active layers [19,20]. However, according to the optical theory (see more descriptions below), the absorption should vary with the ZnO:Al thickness due to the interference effects in the thin multilayer systems, where each layer, except the thick glass slab, has a coherent thickness with the electromagnetic wavelengths of the incident light [21,22].

The reason for no apparent observance of the ZnO:Al thickness effects on the absorption spectra may lie in the fact that the data were collected in a transmission mode and a reflection component is included in the data, i.e. $A = 1 - T - R$, where A , T and R denote absorption, transmission and reflection. Sylvester-Hvid et al. alternatively performed reflection mode measurements for their sample structure using an aluminum coating on the top of P3HT-PCBM as a back reflection mirror for the data collection and derived net absorption spectra via $A = 1 - R$ equation. As a result, they were able to see a distinct absorption spectral fingerprint for each specific active layer thickness used in their multilayer systems [20], consistent with the optical modeling predictions by them and others

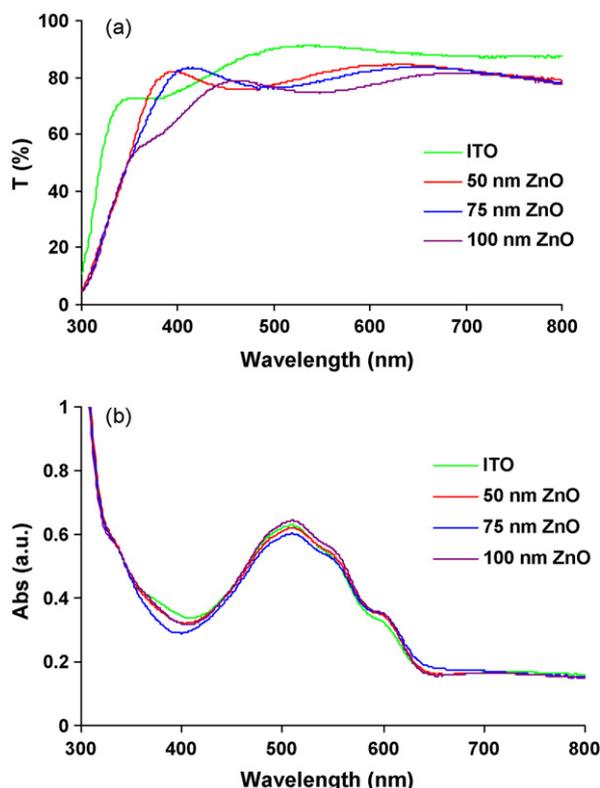


Fig. 2. (a) Transmittance spectra of the ZnO:Al buffered and non-buffered ITO glasses and (b) absorbance spectra of these substrates coated with a stack of PEDOT-PSS and P3HT:PCBM, with ZnO:Al thickness varying from 50 to 100 nm.

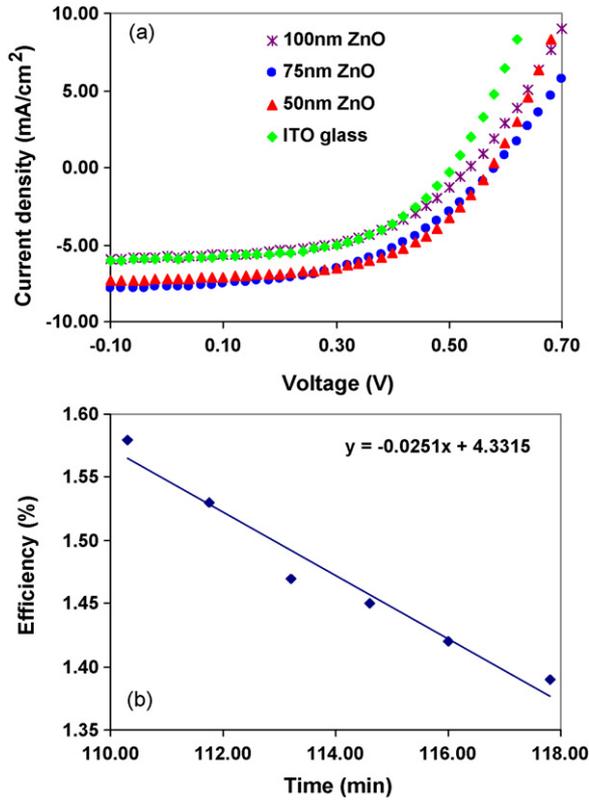


Fig. 3. (a) Current density–voltage (J – V) curves of the P3HT:PCBM solar cell devices with and without ZnO:Al buffer layers of varied thickness as indicated in the figure under 100 mW/cm^2 AM 1.5 irradiation and (b) efficiency decay versus time from the ITO-only film device in (a).

[23,24]. The reason for being able to observe the ZnO:Al thickness effects on the transmittance spectra in this work, recorded in the transmission mode, is that the substrates are transparent or the absorption A is basically zero at wavelengths longer than their transmission edges, reducing the optical relationship to $T = 1 - R$.

Plotted in Fig. 3a is the current density – voltage (J – V) characteristics of batch 1 solar cells under simulated sunlight. The device with insertion of a relatively thin ($\sim 50 \text{ nm}$) buffer layer of ZnO:Al showed the best performance over others as detailed in Table 1. It is important to indicate that these results were collected at different times of the devices staying in ambient air after their removal from Al deposition vacuum chamber. For example the 100 nm-ZnO:Al film device and the ITO-only film device were in air for ~ 31 and 110 min, respectively, before tests. Taking this into account, we performed multiple tests on each device with a dark interval between two subsequent test points. As shown in Fig. 3b for the ITO-only film device, the efficiency linearly decreases during the test because of both chemical and UV induced degradations [9,10]. Based on the assumption that the linear decay and rate hold for the device degradation behavior, the efficiency of the device with zero test delay time in air was extrapolated. By doing so for each

Table 1
Device performance of batch 1 polymer solar cells with and without ZnO:Al buffer layers.

ZnO:Al thickness (nm)	J_{sc} (mA/cm 2)	V_{oc} (V)	FF (%)	PCE (%)	Test delay time (min)
0	5.89	0.51	52.6	1.58	110.3
50	7.21	0.57	54	2.22	89.6
75	7.69	0.59	46.9	2.13	71.3
100	5.79	0.53	50.9	1.56	30.9

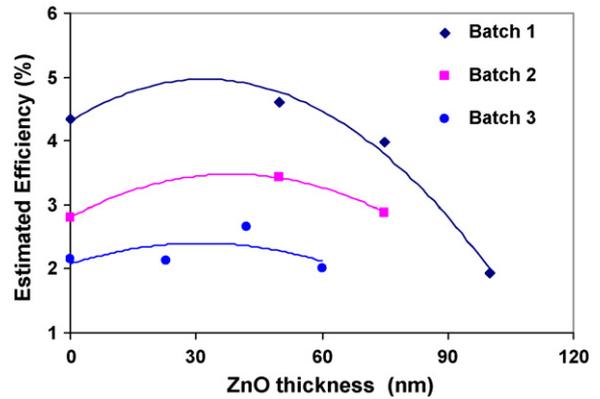


Fig. 4. ZnO:Al thickness dependence of degradation-subtracted power conversion efficiency for the three batches of the devices. The dashed lines are curve fittings for guides to eyes.

of the devices, we obtained the dependence of the efficiency on ZnO:Al thickness for this batch of devices under nearly the same conditions (batch 1 curve in Fig. 4), although there may be some overestimations in the interpolation due to using convoluted rates of UV and chemical degradations during the tests. It is noticed that the introduction of a thin layer of ZnO:Al film, $\sim 40 \text{ nm}$ according to the curve fitting, improved the device performance most prominently over the bare ITO layer, while the thicker ZnO:Al films (e.g. 100 nm) are detrimental to the device performances. This was confirmed by similar trends obtained from two additional batches of devices (with ZnO:Al thickness of 0, 50 and 75 nm in batch 2 and 0, 23, 42 and 60 nm in batch 3) constructed from the same stock solution of P3HT–PCBM prepared. The shift in efficiency of the three fitted curves may be related to different overestimations for the three batches of devices.

To understand these results, electronic and optical properties of the devices were examined. Table 1 indicates that the improvement in the performance of the device with the thinner (50 nm) ZnO:Al layer arises from the higher short circuit current density (J_{sc}) and open circuit voltage (V_{oc}), plus a better fill factor. Such trends were also observed from the data (not presented) of other batches of devices. This improvement could be associated with an enhancement in charge collection or photon absorption. The insertion of the ZnO:Al layer between the ITO and PEDOT-PSS is not supposed to facilitate hole collection, instead it blocks hole-transport as ZnO:Al is an electron selective material [14]. This is evidenced from the reduction in the fill factor of the devices with an increase in ZnO:Al thickness as seen in Table 1. For example, fill factors were 54% in comparison to 50.9% for the 50 nm- and 100 nm-ZnO:Al film devices, respectively. Therefore, the reason appears related to enhanced light absorption.

According to the optical theory [21,22], when a light is normally incident on a multilayer system like a thin film solar cell, the electromagnetic waves undergo Fresnel reflection and transmission at the interfaces between the multi layers, while within each layer the waves may have some phase shift and decay. The electric field distribution within the layers is determined by the interference of forward and backward propagation waves, which is dependent on the thickness and the optical constants (refractive index and extinction coefficient) of all the thin layers in the system. Therefore, changes in these layers or an insertion of a new layer should affect the field distribution and thus the matching of the resultant absorption profile with the solar spectrum in the solar cells.

Both calculations using the one-dimensional transfer matrix method and experimental results have shown increased light absorptions within thin multilayer solar cells with a logical variation in the thickness of the different thin layers [11,20,23–26].

For example, for organic solar cells, a wavy enhancement in the absorption and thus photocurrent with increasing the active layer thickness has been observed [11,24]. However, the benefit in the absorption with using larger resonant thicknesses for the organic absorbers tends to be offset by limited charge carrier mobility and thus more unbalanced charge transport in the thicker layers. Therefore, thinner rather than thicker absorbers are generally used. In this case, inserting a transparent optical spacer between the active layer and the metal cathode in organic solar cells has been found to be an appropriate method to shift thinner absorbers used into the more desirable spatial distribution regions of the electric fields for enhanced light absorption, depending on all the other relevant layers in the systems [11,19]. In the present work, the above demonstrated thickness effects of the ZnO:Al layer (introduced between the ITO and the PEDOT-PSS) on the optical spectra is an indication of electrical field redistributions in the devices, while the observed higher value in J_{sc} from the 50 nm ZnO:Al layer device is consistent with or verifies such a field redistribution. Moreover, the optimal ZnO:Al thickness of ~ 40 – 50 nm, obtained experimentally in this work, is comparable to those of ZnO:Al used as an optical spacer in the solar cells using different active layer thicknesses or materials, since the both ZnO:Al layers function in the multi-layer systems based on interference effects for the absorption and solar spectrum matching [11,12]. Thus, the performance improvement in the thinner ZnO:Al layer devices is likely associated with an enhanced optical absorption. Correspondingly, the efficiency drop in the thicker (e.g. 100 nm) ZnO:Al film devices results from a reduced optical absorption along with an increased hole-blocking effect of the thicker buffers.

In addition, the ZnO:Al layer may play more roles than just affecting the photon absorption or carrier concentration. According to de Jong et al. [10], one of the degradation mechanisms for polymer solar cells is the interfacial diffusion of indium into PEDOT-PSS in the presence of especially moisture and UV light. ZnO:Al situated between them should serve as a diffusion barrier layer for indium. A relevant example is that little or no inter-diffusion at ZnO/Cu(In, Ga)Se₂ (CIGS) interface was found [15] and nowadays ZnO is widely used as a barrier material in CIGS solar cells to improve efficiencies. Suppression of indium diffusion and etching in polymer solar cells means a reduction of device degradation. Thus, it would be expected that the diffusion barrier effect would increase with the metal oxide thickness investigated here. This agrees with the observed efficiency enhancement with the buffer thicknesses up to ~ 40 – 50 nm. However, the performance is dominated by a reduced light absorption plus an increased hole-blocking effect at the thicker ZnO:Al buffers as mentioned above (Fig. 4). Similar to the results reported here, ZnO:Al has been applied to inorganic thin film a-Si:H solar cells as an indium diffusion barrier covering the ITO glass to improve device stability [16].

The above result illustrates that a thin layer of ZnO:Al as a buffer on ITO improves the performance of non-inverted polymer solar cells even though it is an electron selective material and not suitable for such an application. If a hole-selective metal oxide is chosen as a buffer on the ITO to favor hole-transport with an appropriate energy level alignment, a further improvement in polymer solar cells can be expected. Optimizing the layer thickness to maximize the solar spectrum absorption via optical interference effects plus employing the layer as a potential diffusion barrier or a stabilizer could provide great benefits.

4. Conclusion

The introduction of a ZnO:Al film into regular bulk heterojunction polymer solar cells as a buffer on ITO glass is reported. The films were sputter-deposited with thicknesses less than 100 nm. The devices showed the most observable improvement in power conversion efficiency over the ITO-only devices when the ZnO:Al thickness was ~ 40 – 50 nm, while a thicker layer was found to be detrimental. The performance improvement was believed to come from the inserted ZnO:Al layer as an optical tuner via interference effects and an indium diffusion barrier. The result suggests that it is possible to further improve both efficiency and stability of non-inverted polymer solar cells by employing a hole-selective metal oxide as a buffer on ITO.

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