Enhanced Power Conversion Efficiency of Inverted Organic Solar Cells with a Ga-Doped ZnO Nanostructured Thin Film Prepared Using Aqueous Solution


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A dramatic increase in the power conversion efficiency (PCE) of inverted organic solar cells (IOSCs) is realized by a gallium (Ga)-doped zinc oxide (GZO) buffer layer acting as an electron-transport layer. The GZO nanostructured thin-film buffer layer was synthesized via an aqueous solution method at 90 °C. Both an increase of electrical conductivity and a smooth surface morphology were realized by Ga doping. The PCE of a GZO-based IOSC was improved by about 110% at simulated air mass 1.5 global full-sun illumination compared with that of undoped zinc oxide-based IOSCs. The increase of the short-circuit current in GZO-based IOSCs is due to the higher electron conductivity and favorable surface morphology of the buffer layer through Ga-doping, resulting in the dramatic enhancement of the PCE.

1. Introduction

Solution-processed organic solar cells (OSCs) are of great interest due to their low cost, large size, and easily printable fabrication methods. However, the short exciton diffusion length and inefficient exciton dissociation in a polymeric matrix result in a low quantum efficiency (QE), limiting the applications of OSCs. A major breakthrough was achieved through the bulk heterojunction (BHJ) concept based on a polymer:fullerene structure where the nanoscale phase separation creates donor/acceptor interfaces for effective exciton dissociation via efficient charge transfer from donor to acceptor. Despite the high attainable QE, the overall power conversion efficiency (PCE) is still low due to the interior charge-transport properties.

So far, studies regarding the realization of highly efficient BHJ solar cells have focused on the solvent selection, annealing control, and work function engineering. Plasma treatment or BHJ solar cells have focused on the solvent selection, annealing control, and work function engineering. Nevertheless, it has been studied that doping has a large effect on the surface morphologies of as-grown thin films. However, studies have rarely reported on the effect of doping on solar power performance. Herein, we report a dramatic increase in the PCE of inverted organic solar cells (IOSCs) by a gallium (Ga)-doped zinc oxide (GZO) buffer layer acting as an electron-transport layer. This method involves the growth of GZO nanostructured thin films by a simple aqueous solution route, at the low temperature of 90 °C. This is a simple and effective process for improving the PCE of IOSCs. Compared with undoped zinc oxide (UZO)-based IOSCs, the PCE of the IOSCs with the GZO buffer layer was increased by about 110% at simulated air mass (AM) 1.5 global full-sun (1.5G, 100 mW/cm²) illumination.

2. Experimental Section

The UZO and GZO thin films were synthesized using a two-step solution process. The first step for both the UZO and the GZO buffer layers is seed layer preparation. The seed layer for UZO was prepared on an indium tin oxide/glass substrate by dip-coating into 0.05 M zinc acetate (Zn(C₂H₃O₂)₂) dissolved in ethanol and a solution of 50 mM zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O) and zinc acetate in a mass ratio of 1:9 was dissolved in ethanol, leading to an n-type doping. The second step in the synthesis is the main growth of the each layer. A UZO layer was formed in a solution of 50 mM zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O) and 50 mM hexamethylenetetramine (C₆H₁₂N₄) dissolved in ethanol/DI water (vol % = 1:1) at 90 °C for 3 h. A GZO buffer layer was synthesized in the solution in which Ga nitrate (10% of zinc nitrate hexahydrate in a mass ratio) was added into the solution for the main growth of a UZO layer. This solution-based fabrication process for a buffer layer provides many promising advantages, such as low cost, low temperature, and damage-free.

To produce inverted IOSCs based on UZO and GZO buffer layers, a polymer blend of poly(3-hexylthiophene) (P3HT):(6,6)-phenyl C₆H₁₂, butyric acid methyl ester (PCBM) (1:1 vol % in chlorobenzene) was spin-coated onto both buffer layers at 2000 rpm for 120 s and was dried in covered glass Petri dishes (solvent annealing), and thermal annealing at 150 °C for 10 min was then carried out. Molybdenum oxide (MoO₃) as an electron-blocking layer and a gold (Au) anode were subsequently deposited by thermal evaporation. Ga doping to ZnO was confirmed using X-ray photoelectron spectroscopy (XPS) and synchrotron X-ray diffraction (XRD) measurements. Morpholog-
ologies of UZO and GZO thin films prepared using the solution method were examined by atomic force microscopy (AFM) measurements. Contact angles for each sample of UZO and GZO were also measured by water contact angle measurements. For the characterizations of IOSCs, current density–voltage ($J$–$V$) measurements were carried out by using a solar simulator under an irradiation intensity of air mass AM 1.5G (100 mW/cm$^2$). We obtained our results from over 50 IOSCs for UZO and GZO, respectively.

3. Results and Discussion

A field emission scanning electron microscopy (FE-SEM) image in Figure 1a shows the typical surface morphology of the grown GZO nanostructured thin film. The GZO thin film comprising dense nanorod arrays with a c-axis preferred orientation was grown in aqueous solution. Although the thin film has a vertically textured morphology, it was found that the vertically aligned nanorods are also laterally connected to one another. A cross-sectional FE-SEM image and a schematic illustration of our inverted IOSC structure using the GZO are revealed in Figure 1b,c, respectively. The total thickness of our inverted IOSC was about 850 nm, and the thickness of the GZO layers was about 270 nm. The polymer layer was 180 nm thick. The structural dimensions of the UZO-based IOSCs were the same as those of the GZO-based IOSCs.

The doping of Ga into ZnO was examined using XPS and synchrotron XRD measurements. The XPS survey for the Ga element in the GZO thin film is shown in Figure 2a. The two peaks at 1117.4 and 1144.4 eV are ascribed to the electronic states of Ga 2p$_{3/2}$ and Ga 2p$_{1/2}$, respectively; that energy gap is consistent with the value for the element, about 27 eV. The Ga 2p$_{3/2}$ peaks of the UZO and GZO thin films are shown in Figure 2b. In the GZO thin film, a broad peak assigned to the electronic state of Ga 2p$_{1/2}$ is clearly observed, whereas in the UZO thin film, no peak related to the Ga element is detected. The clear appearance of the Ga-related peak in the GZO sample indicates that Ga atoms were doped effectively into the ZnO lattices.$^{15,16}$

Figure 3 shows (002) diffraction peaks of the UZO and GZO thin films in the power diffraction profiles from a synchrotron X-ray source. The scans were taken along the surface normal direction, $Q = 4\pi \sin(\theta/2)/\lambda$, in reciprocal space. The (002) peak position (2.415 Å$^{-1}$) of the GZO thin film was slightly shifted to a higher $Q$ value compared with that (2.412 Å$^{-1}$) of the UZO thin film. This shift means that there is tensile stress in the plane of the GZO thin film as compared with the UZO thin film, which may originate from the difference of the radii of $\text{Ga}^{3+}$ (0.062 nm) and $\text{Zn}^{2+}$ (0.074 nm). The replacement of $\text{Zn}^{2+}$ with $\text{Ga}^{3+}$ decreases the c-axis lattice parameter, resulting in an increase of the diffraction angle.$^{17,18}$ In addition, we could not observe any pure Ga or $\text{Ga}_2\text{O}_3$-related diffraction peaks in the high-resolution synchrotron XRD measurements.

AFM measurements reveal that root-mean-square (rms) roughness values of UZO and GZO surfaces were 10.7 and 4.6 nm, respectively (Figure 4). The rms roughness and the grain size of the grown thin films are decreased upon addition of Ga (see Figure 4), showing good agreement with the previous reports.$^{10,11}$ To understand the surface property of the UZO and GZO thin films, we also measured the contact angles (CAs) via water contact angle measurements. As shown in the insets of Figure 4, the CAs for the UZO and GZO thin films were 87.9° and 69.9°, respectively, demonstrating a higher hydrophlicity on GZO than on UZO.

To compare the solar power performances of IOSCs based on UZO and GZO, current density–voltage ($J$–$V$) measure-ments were carried out by using a solar simulator under standard AM 1.5G solar illumination. Figure 5 shows $J$–$V$ curves for IOSCs with UZO or GZO buffer layers acting as the electron-transport layer under AM 1.5G irradiation. The GZO-based IOSC averagely exhibited an open-circuit voltage ($V_{oc}$) of 0.42 V, a short-circuit current ($J_{sc}$) of 11.7 mA/cm$^2$, a fill factor (FF) of 39.7%, and a PCE of 1.95%, whereas the UZO-based IOSC showed $V_{oc}$ of 0.41 V, $J_{sc}$ of 6.3 mA/cm$^2$, the FF of 35.7%, and the PCE of 0.92%. These data demonstrate that the PCE can be enhanced more than about 2 times by doping Ga into ZnO. The significant enhancement of the PCE in GZO-based IOSCs could be attributed to the improved $\sigma$ of...
the GZO buffer layer as compared with that of the UZO buffer layer, thus enhancing the $J_{sc}$.

The thickness of ZnO thin films in our devices is about 270 nm, which is much thicker than that in the previous work, resulting in a decrease of the PCE due to deterioration of the transparency. We can further improve the PCEs of our IOSCs with either UZO or GZO by controlling thicknesses of a nanostructured ZnO layer. However, it is out of the scope of this work. We believe that the current PCEs (1.95% for GZO-based IOSCs and 0.92% for UZO-based IOSCs) are enough to evaluate our results for Ga-doping effects to the buffer layer in IOSCs.

In Hall-effect measurements based on the Van der Pauw configuration, the $\sigma$ of the as-grown UZO and GZO thin films were measured as $3.4 \times 10^{-3}$ (Ω cm)$^{-1}$ and $7.2 \times 10^{-3}$ (Ω cm)$^{-1}$, respectively. At the initial stage of ZnO growth, nanorods are formed by the fastest growth along the $c$ axis due to the high $c$-axis polar nature of ZnO. However, the preferred $c$-axis growth gradually saturates at a critical growth time. From this time, the growth of side facets of the nanorods proceeds, resulting in thin-film formation by the combination of individual rods. Thus, it can be suggested that the relatively much lower conductivity values of the UZO and GZO thin films obtained by the Hall measurements in this work compared with those of ZnO thin films synthesized by other methods, such as sputtering, are due to hindrance of the electron transport in a lateral direction at the boundaries among the individual nanorods even though they are laterally connected to one another. However, the electron transport along a vertical path into the thin film is more important for obtaining a large $J_{sc}$ than that in a lateral path.

Because the series resistance ($R_s$, Ω cm$^2$) of an IOSC is strongly affected by the conductivity of the functional layers and their contact resistances, higher conductivity generally leads to a lower $R_s$. The $J_{sc}$ of an IOSC can be expressed as

$$J_{sc} = \frac{(V_{\text{dark}} - V_{oc})}{R_s}$$

where $V_{\text{dark}}$ is the intersection between the $x$ axis and the $J$-$V$ curve shifted by the $J_{sc}$. A low $R_s$ can then generate the improved $J_{sc}$ of an IOSC. Furthermore, a bimolecular recombination can also be reduced through decrease of the $R_s$, resulting in enhancing the $J_{sc}$. It was found that the $R_s$ of IOSCs with UZO and GZO thin films were 5.31 and 3.41 Ω cm$^2$, respectively, as determined by performing a mathematical simulation of the $J$-$V$ curves in the dark shown in Figure 6 on the basis of eq 2

$$J(V) = J_0 \{\exp[(V - JR_s)/nKT] - 1\} + (V - JR_s)/R_p - J_{sc}$$

where $J_0$ (mA/cm$^2$) is the reverse bias dark current and $R_p$ (Ω cm$^2$) is the parallel resistance. Thus, on the basis of the
enhancement factors of $\eta$ \((7.2 \times 10^{-3} \text{ from } 3.4 \times 10^{-3} (\text{cm}^2) \text{ cm}^{-1})\), $R_\eta$ \((3.41 \text{ from } 5.31 \text{ cm}^2)\), and $J_{sc}$ \((11.7 \text{ from } 6.3 \text{ mA/cm}^2)\) after Ga-doping, we suggest that the increase of the $J_{sc}$ in a GZO-based IOSC is due to the higher conductivity of the GZO buffer layer, which decreases the $R_\eta$ of devices, resulting in significant enhancement of the PCE.

As demonstrated in previous studies,7,8 the $J_{sc}$ is also strongly dependent on the morphology of the polymer. As shown in Figure 4, the CAs \((69.9^\circ \text{ for } \text{GZO and } 87.9^\circ \text{ for } \text{UZO})\) were affected by doping Ga into ZnO, which means that the surface energies of the films are different.24–26 When a P3HT:PCBM polymer blend is spin-coated onto a buffer layer, the morphology of the polymer blend and the adhesion of interface between the polymer blend and the buffer layer are significantly changed by the surface energy of the buffer layer. In other words, the crystallinity of P3HT, the nanoscale phase separation of donor/acceptor, and improvement of the interface area for the electron conduction path are greatly affected by the wettability of the buffer layer.27,28 Consequently, it can be proposed that the effective charge-carrier extraction and suitable phase segregation on a GZO-based IOISC yielded an improved $J_{sc}$, resulting in the dramatic enhancement of the PCE. Our results in this work suggest that such a doping approach can provide an excellent solution to enhance the PCE of IOSCs.

4. Conclusions

We have demonstrated a significant enhancement of the PCE in GZO-based IOSCs as compared with UZO-based IOSCs. XPS and synchrotron XRD results clearly showed that Ga atoms had been doped effectively into the ZnO lattices, resulting in the higher conductivity of GZO nanostructured thin films and thus mainly improving the $J_{sc}$. The rms roughness values and the grain sizes of the GZO thin films were less than those of the UZO thin films, and the water CA of GZO thin films exhibited a greater hydrophilicity than did that of the UZO thin films. Thus, it is suggested that the dramatic enhancement of the PCE of the GZO-based IOSCs is due to the higher electron conductivity and the favorable surface morphology of the grown GZO thin film.

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References and Notes