

Enhancement of the power conversion efficiency of inverted organic photovoltaic cells with a nanoscale Ga-doped ZnO electron buffer layer

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Inverted organic photovoltaic (OPV) cells containing various concentration of Ga-doped ZnO (GZO) as an electron buffer layer (EBL) were deposited by using a solution-process to enhance their power conversion efficiency (PCE). Atomic force microscopy (AFM) images showed that the measured root mean square roughnesses of 0, 5, and 10% GZO EBL were approximately 11.2, 2.3, and 4.6 nm, respectively, and that the 5% GZO EBL have very smooth surface morphology. The optical transmittance of the 5% GZO thin films in the wavelength range between 300 and 800 nm is 88% higher than those of GZO EBLs. X-ray photoelectron spectroscopy (XPS) measurement was investigated to confirm the valence state of Zn, Ga, and O in the GZO EBL. Current density-voltage (J-V) results showed the highest PCE of the device of the fabricated inverted OPV cells utilizing 5% GZO with 2.61%. The enhancement in the PCE of inverted OPV cells were attributed to an enhancement of the surface smoothness and the modification of the work function of the GZO EBL.

Key words: Organic photovoltaics, Inverted structure, Electron buffer layer, Ga-doped ZnO, Solution-process.

Introduction

Organic photovoltaic devices (OPVs) have been considered as one of the most promising candidates for harnessing solar energy sources due to their high-mechanical flexibility and light weight [1-4]. Recent progress in polymer chemistry and device processing have lead to OPVs with impressive power conversion efficiencies (PCEs) exceeding 8% [5]. The conventional device structure of OPVs, which comprises a bottom ITO anode modified by poly (3, 4-ethylenedioxythiophene)-poly (styrene sulfonate) (PEDOT:PSS), a photoactive layer, and a low work-function metal cathode, has several drawbacks in terms of achieving long-term stability [6]. The drawback of the conventional OPVs is its low stability due to easy photodegradation of various interfaces involved in the device [7, 8]. OPVs with an inverted structure have been suggested in order to overcome these drawbacks, where the charge collection of electrodes is reversed. Such inverted OPVs have shown an enhanced stabilities and PCEs [9, 10]. Among the n-type electron transport oxides, Zinc oxide (ZnO) is the considered as most promising material due to high electron mobility, high degree of transparency in the visible wavelength range, and low work function [11]. ZnO films doped with impurities showed better stabilities compared to those of the undoped ZnO films [12-15]. However, investigations on the enhancement of the PCEs for the OPVs with a Ga-doped ZnO

(GZO) electron buffer layer (EBL) formed by using a solution process have not been clarified yet.

This paper reports data for the enhancement of the power conversion efficiency of inverted organic photovoltaic cells with a GZO EBL. Different concentrations of GZO solutions by using a solution process were deposited to optimize device performances. Atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), and optical transmittance measurements were carried out in order to investigate the surface, electronic, and optical properties of the GZO films. Current density-voltage (J-V) measurements were performed to investigate the device characteristics of the inverted OPV devices with a GZO interlayer. The PCEs of the OPV cells with various surface roughness GZO interlayer were compared with those without a GZO interlayer.

Experimental Details

The inverted OPV cells with a GZO EBL were formed on indium-tin-oxide (ITO)-coated glass substrates. The sheet resistance of the ITO substrates was approximately 10 Ω /sq. After the surfaces of the chemically-cleaned ITO substrates had been treated with an ultraviolet-ozone cleaner, the substrates were introduced into a glove box with a high-purity N_2 atmosphere. In this study, the three different concentration of 0, 5, and 10% Ga-doped ZnO EBL were prepared utilizing zinc acetate ($Zn(C_2H_3O_2)_2$) and gallium nitrate ($Ga(NO_3)_3$) as starting precursors. A 0.1-M ZnO solution containing 0, 5, and 10% of Ga was prepared by using zinc acetate ($Zn(C_2H_3O_2)_2$) and gallium nitrate ($Ga(NO_3)_3$) sources, 10 ml of 2-methoxyethanol ($C_3H_8O_2$), and 0.5 ml of

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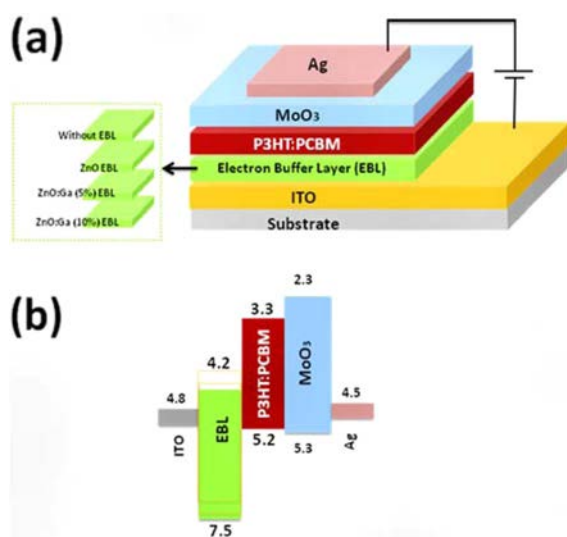


Fig. 1. Schematic diagrams of the (a) structure and the (b) corresponding energy band of an inverted OPV cell with a Ga-doped ZnO electron buffer layer.

monoethanolamine (C_2H_7NO) were used as a solvent stabilizer [16]. The GZO interlayer was spin-coated onto the ITO-coated glass substrates at 3000 rpm for 31 s in a glove box under a high-purity N_2 atmosphere and was annealed at $120^\circ C$ for 15 min. A poly(3-hexylthiophen) : fullerene derivative, [6,6]-phenyl-C61-butyric acid methyl ester (P3HT : PCBM) active layer (1 : 0.8 by weight) was spin-coated on the EBL and annealed at $145^\circ C$ for 10 min. The organic solar cell was completed by deposition of MoO_3 and Ag top contacts with a thickness of 10 and 100 nm, under a system pressure of 2×10^{-6} Torr. Schematic diagrams of the structure and the corresponding energy band of an inverted OPV with a device structure of the ITO/GZO/P3HT : PCBM/ MoO_3 /Ag used in this study are shown in Fig. 1.

The AFM measurements were performed by using an XE-100 atomic force microscope system. X-ray photoelectron spectroscopy (XPS) measurements were performed by using a Thermo Electron (U.K.) model equipped with an Mg $K\alpha$ X-ray as an excitation source. The optical transmittance spectra were measured by using a SHIMADZU UV-2401PC spectrophotometer. The J-V curves were measured in the dark and under illumination by using a Keithley 2400 source meter. The photovoltaic characteristics were measured by using a Xenon lamp under AM 1.5 simulated illumination at an intensity of 100 mW/cm^2 .

Result and Discussions

AFM measurements were performed to investigate the effects of the surface morphology of OPV cells containing various GZO EBL as shown in Fig. 2. Overall surface morphological characteristic appears similar, while the measured root mean square roughnesses of 0,

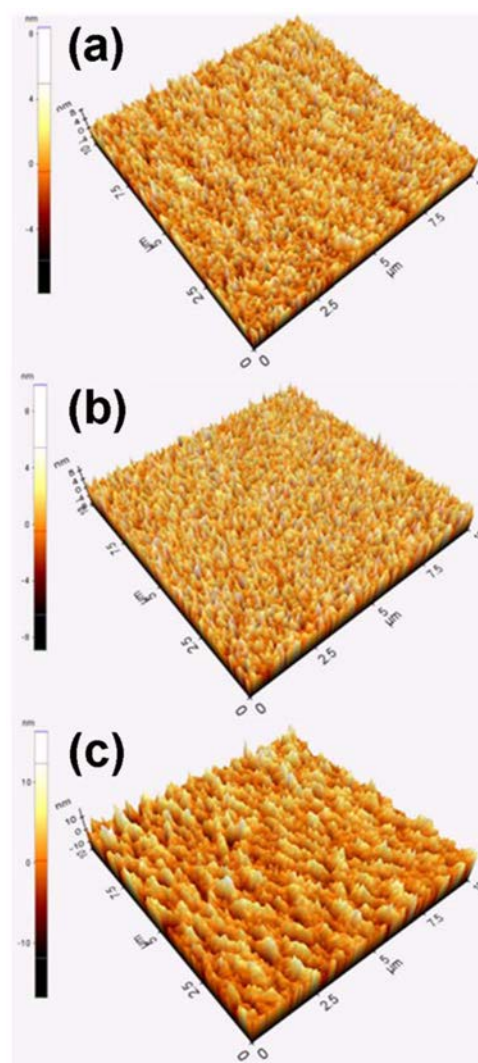


Fig. 2. Atomic force microscope profile images of Ga-doped ZnO thin films with Ga concentration of (a) 0, (b) 5, and (c) 10%.

5, and 10% GZO EBL were approximately 11.2, 2.3, and 4.6 nm, respectively. AFM images of 5% GZO EBL showed a very smooth surface morphology.

XPS measurements were performed to determine the chemical composition and the valence state of the GZO thin films. Figure 3 shows the XPS spectra of the Zn 2p, Ga 2p and O 1s for the GZO thin films. Figure 3(a) shows the binding energy peaks located at 1021.8 and 1045.1 eV are attributed to the spin-orbital splitting of the Zn $2p_{3/2}$ and $2p_{1/2}$, which are in good agreement with those of reported ZnO [17]. Figure 3(b) shows the binding energy peaks located at 1118.5 eV are attributed to Ga^{3+} ions that substituted Zn^{2+} ions [18]. The peaks located at 532.6 eV are assigned to the O^{2-} ions surrounded by Zn or Ga in the ZnO. Figure 4 shows the optical transmittance of the 5% GZO thin films in the wavelength range between 300 and 800 nm is 88% higher than those of GZO EBLs.

Figure 5 shows the J-V curves under simulated AM 1.5 (100 mW/cm^2) conditions for device. The PCE, fill

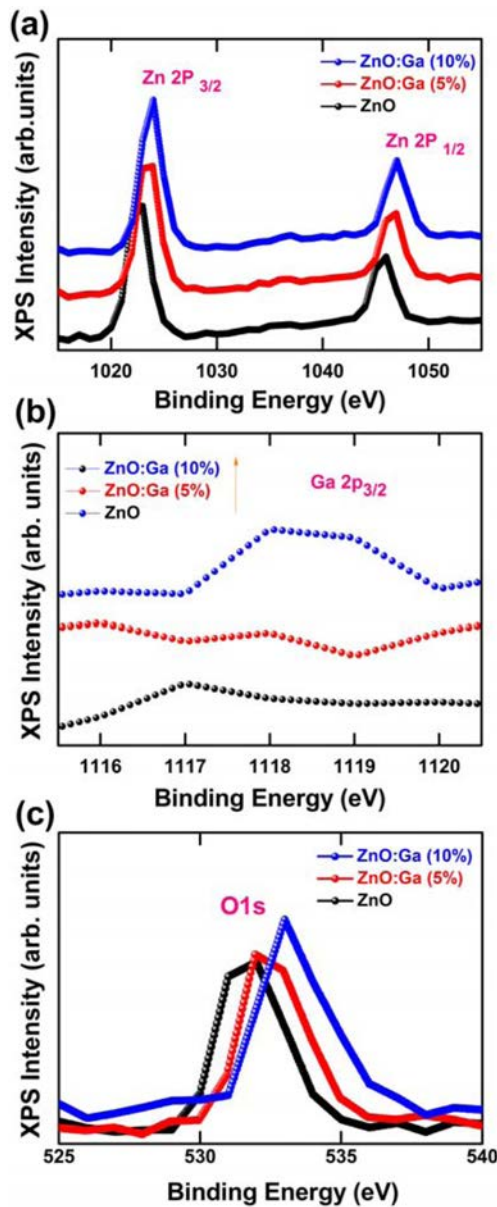


Fig. 3. X-ray photoelectron spectroscopy spectra of various Ga-doped ZnO thin films: (a) Zn 2p, (b) O 1s, and (c) Ga 2p core spectra.

factor (FF), a short-circuit current density (J_{sc}), and open circuit voltage (V_{oc}) of the OPVs with various concentration of GZO EBL are summarized in Table 1. OPV cells with 5% of GZO EBL yields a V_{oc} of 0.64 V, J_{sc} of 7.06 mA/cm², a FF of 0.57, and an efficiency of 2.61%. For comparison, we have also fabricated an OPV device without EBL and measured the J-V curves. Since ZnO has high electron mobility, it can help charge collection and transport [19]. The electron remained at the lowest unoccupied molecular orbital level of PCBM can be easily transferred to the conduction band of ZnO [20]. The charge recombination and charge transport in the photoactive layer depends on the internal electric field, caused by the use of electrodes with different work functions, towards the cathode where they are

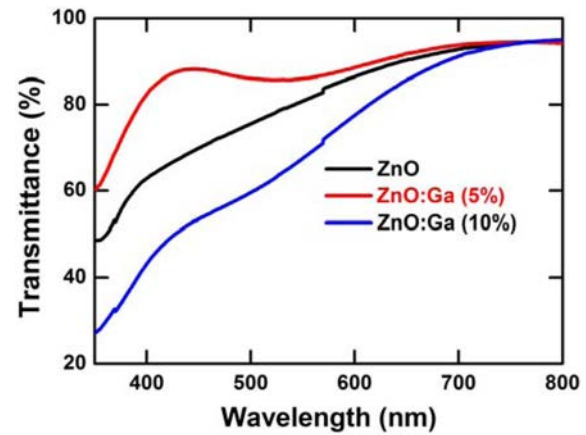


Fig. 4. Optical transmittances of the Ga-doped ZnO electron buffer layers with Ga concentrations of (a) 0, (b) 5, and (c) 10%.

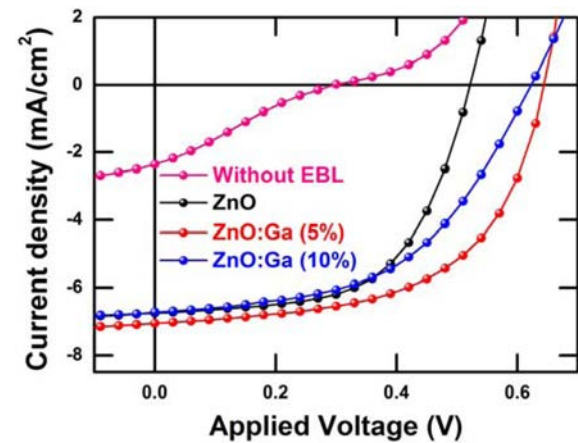


Fig. 5. Current density-voltage curves of the inverted OPV cells with various Ga-doped ZnO electron buffer layers under an AM 1.5 illumination power density of 100 mW/cm².

Table 1. Device performances of inverted OPV cells utilizing various concentrations of Ga-doped ZnO electron buffer layers.

Electron Buffer layer (EBL)	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)
Without EBL	2.36	0.30	0.24	0.17
ZnO	6.75	0.59	0.59	2.07
ZnO : Ga (5%)	7.06	0.64	0.57	2.61
ZnO : Ga (10%)	6.72	0.61	0.51	2.14

collected by the electrodes and driven into the external circuit [4]. Thus from the results we conclude that the increased efficiency are mainly due to the surface roughness and the work function of the OPV cells utilizing a nanoscale Ga-doped ZnO as an EBL [21].

Conclusions

OPV devices with a structure of ITO/GZO/P3 HT : PCBM/MoO₃/Ag containing GZO interlayers as

EBLs were fabricated. AFM images showed the 5% GZO thin films with very smooth surface morphology than those of other GZO EBL. XPS measurement showed the presence of a nanoscale Ga in ZnO EBL. J-V results showed the highest PCE of the device of the fabricated inverted OPV cells utilizing 5% GZO with 2.61%. The enhancement in the PCE of inverted OPV cells were attributed to the surface roughness and the modification of work function due to the GZO EBL.

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