OPTOELECTRONICS LETTERS Vol.12 No.2, 1 March 2016

Al-doping effects on the photovoltaic performance of inverted polymer solar cells*

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(Received 6 January 2016)

The properties of Al-doped ZnO (AZO) play an important role in the photovoltaic performance of inverted polymer solar cells (PSCs), which is used as electron transport and hole blocking buffer layers. In this work, we study the effects of Al-doping level in AZO on device performance in detail. Results indicate that the device performance intensely depends on the Al-doping level. The AZO thin films with Al-doping atomic percentage of 1.0% possess the best conductivity. The resulting solar cells show the enhanced short current density and the fill factor (*FF*) simultaneously, and the power conversion efficiency (*PCE*) is improved by 74%, which are attributed to the reduced carrier recombination and the optimized charge transport and extraction between AZO and the active layer.

Document code: A **Article ID:** 1673-1905(2016)02-0106-4

DOI 10.1007/s11801-016-6003-8

Polymer solar cells (PSCs) have attracted increasing attention for solar energy conversion[1-3]. ZnO has been used as electron transport layer (ETL) in inverted PSCs, since the conduction band minimum of ZnO well matches with the lowest unoccupied molecular orbital (LUMO) levels of fullerene[4-9]. Doped-ZnO thin films, such as In-doped ZnO, Ga-doped ZnO, Al-doped ZnO (AZO), with high electrical conductivity and high transparency simultaneously, have been used in PSCs for cathode[10] as well as ETL[11-16]. The relationship between AZO and device performance has been studied, including Al-doping amount, nanostructured AZO ETL and a surface modified AZO[17].

However, the results of device performance as a function of Al dopant amount are still controversial[8,14,15]. To date, the influence of the Al-doped amount on the PSCs performance has not been fully understood. In this work, we make a systematic study on that. The results show that the Al-doping amount of AZO buffer layers plays a crucial role in the performance of PSCs.

The AZO films were performed using a precursor solution consisting of zinc acetate ($Zn(CH_3CO_2)_2\bullet 2H_2O$) and aluminum nitrate ($Al(NO_3)_3\bullet 9H_2O$) in ethanol[18]. The concentration of Al dopant was varied as 0, 0.5%, 1.0%, 1.5% and 2.0% (atomic percentage, the same below). After spin-coating the sol-gel solution on the cleaned ITO-glass, the samples were annealed at 300 °C for 50 min to obtain AZO films.

The P3HT: PCBM blend (containing 20 mg·mL^{-1} P3HT and 16 mg·mL^{-1} PCBM) was spin-coated on AZO thin film to form an active layer with thickness of about 200 nm. After being annealed at 120 °C for 10 min in air, a 3 nm thick MoO_3 film and a 70 nm thick Ag film were thermally evaporated in sequence at 10^{-4} Pa through a shadow mask.

The electrical conductivity was measured by photo-dark conductivity (PDC-40A). The transmittance spectra of the AZO-coated substrates were measured by a Cary spectrophotometer (Cary 5 000UV-VIS). The current density-voltage (*J-V*) characteristics of PSCs were measured with a Keithley 4 200 sourcemeter at the illumination of an AM 1.5G (100 mW·cm^{-2}) solar simulator.

Fig.1 illustrates the effects of the Al-doping amount on the electrical properties of the AZO buffer layers. Due to the existence of oxygen molecules near the ZnO surface area, the intrinsic ZnO film shows an extremely low conductivity[18]. The conductivity of AZO film increases to 2.92×10^{-3} S·cm^{-1} when Al concentration increases from 0 to 1.0%, while further increase of the doping amount leads to a decreased conductivity of AZO films. It is found that the substitution of Zn^{2+} by Al^{3+} could take place when a small number of Al atoms are introduced into the film, because the ionic radius of Al^{3+} is smaller than that of Zn^{2+}. The carrier concentration increases

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* This work has been supported by the National Natural Science Foundation of China (No.61377031), and the Scientific Research Foundation of Zhejiang Ocean University (No.Q1444).

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correspondingly with the doping amount due to one free electron is produced from the substitution. The increased conductivity indicates an effective replacement of the dopant (Al) atoms in Zn sites of the ZnO structure[19]. However, with further increasing the Al amount, the excess Al atoms can not contribute to the free electrons. The formation of neutral defects and the scatting of the carriers from the segregation of Al at the grain boundaries will give rise to the decreased conductivity[20].

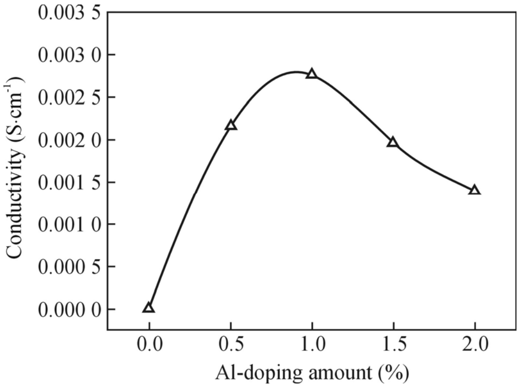


Fig.1 Conductivity of AZO buffer layer as a function of Al-doping amount

The transmittance spectra of the AZO-coated substrates with various doping levels are plotted in Fig.2. All the films exhibit a transmission over 85% in the visible range. The transmission of the films decreases slightly around 400 nm when the Al-doping level increases. It may be related to the increase of grain boundary scattering from the increased carrier concentration[21].

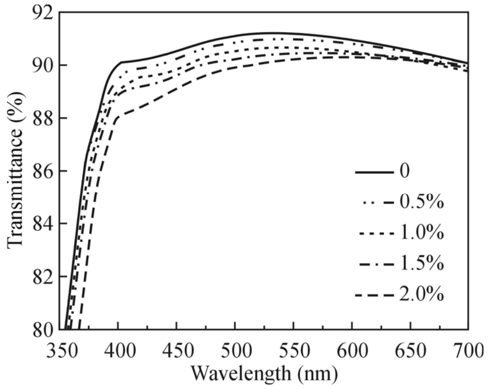
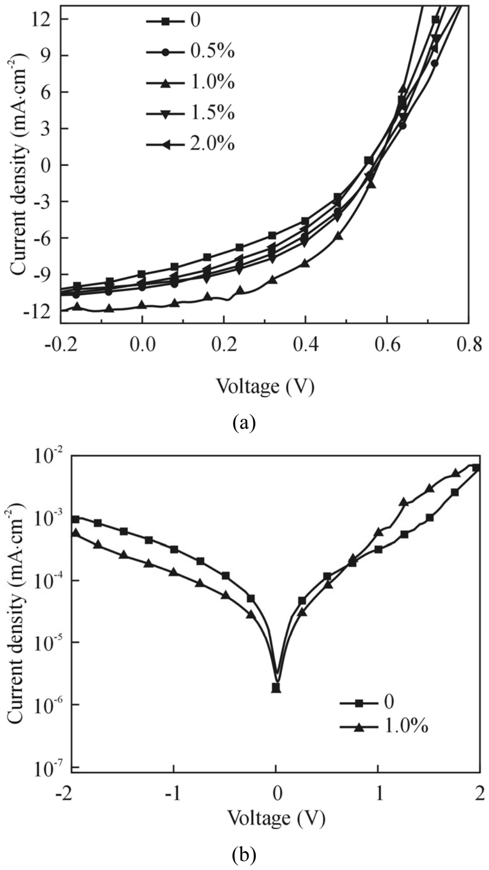


Fig.2 The transmittance spectra of AZO layers with different Al-doping amounts

The surface morphologies of AZO layers can be seen in our previous work[22]. The average grain size increases at first with Al content ranging from 0.5% to 1.0%, then decreases and remains unchanged, thus obtaining a uniform and smooth film when the Al content increases to 2.0%. Grains show a decrease in size with further increasing the Al-doping content[23].

The current density-voltage (*J*-*V*) curves of the devices are presented in Fig.3(a). The extracted performance parameters with respect to the variation of Al-doping amount are summarized in Tab.1. The device based on the intrinsic ZnO layer shows a short-circuit current density (J_{sc}) of 8.79 mA·cm^{-2} and a fill factor (*FF*) of 38.7%. They both increase sharply, from 9.86 mA·cm^{-2} to 11.61 mA·cm^{-2} for J_{sc}, from 42.8% to 50.1% for *FF*, with increasing Al-doping amount from 0.5% to 1.0%. Therefore, the efficiency of inverted solar cells increases from 1.86% to 3.25%. It is clear in Fig.4 that the major improvement of the device performance is realized. However, with further increasing the Al-doping level to 2.0%, the device power conversion efficiency (*PCE*) will decrease to 2.17%.



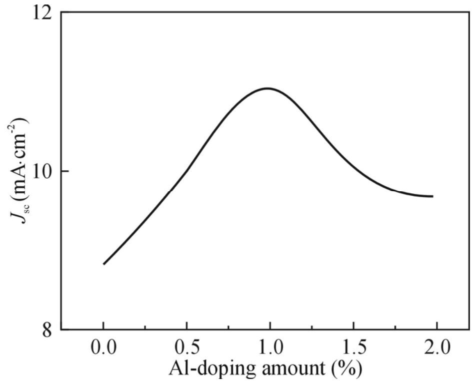
(a)

(b)

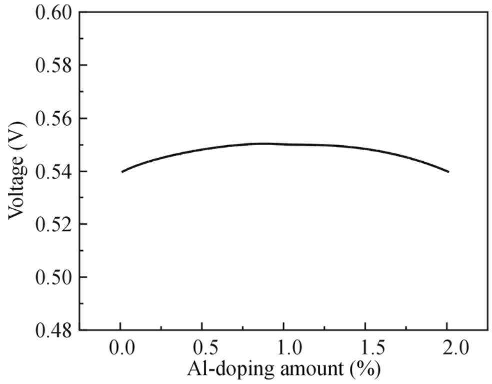
Fig.3 Current density-voltage characteristics of devices (a) at AM 1.5G (100 mW·cm^{-2}) illumination and (b) in the dark

Tab.1 *J-V* characteristics of inverted solar cells with the AZO buffer layers prepared by different Al-doping levels

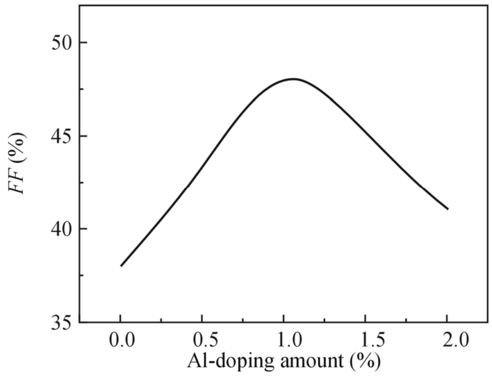
Device	Doping level (%)	Conductivity (S·cm^{-1})	J_{sc} (mA·cm^{-2})	V_{oc} (V)	*FF* (%)	*PCE* (%)	R_s (Ω·cm^2)	R_{sh} (Ω·cm^2)
A	0	4.03×10^{-6}	8.79	0.546	38.7	1.86	31.76	125.73
B	0.5	2.01×10^{-3}	9.86	0.556	42.8	2.35	24.74	251.06
C	1.0	2.92×10^{-3}	11.61	0.557	50.1	3.25	18.86	478.19
D	1.5	1.54×10^{-3}	9.77	0.559	45.6	2.49	21.49	242.26
E	2.0	1.39×10^{-3}	9.64	0.543	41.6	2.17	23.30	235.59



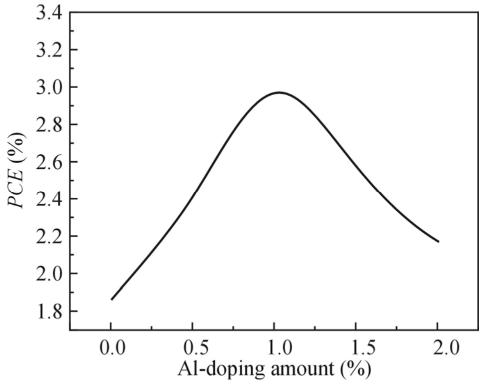
(a) Short current density



(b) Voltage



(c) Fill factor



(d) Power conversion efficiency

Fig.4 The device performance with different Al-doping amounts

The device performance is strongly related to the electronic properties of the interfacial material. The conductivity of AZO buffer layer increases with the Al-doping amount increasing from 0 to 1.0%, resulting in a decrease in surface contact resistance and a lower charge recombination. As shown in Fig.3(b), the lower leakage current of 1.0% Al-doped device suggests that the built-in potential (V_{bi}) increases, which strongly influences the charge transport and extraction. Therefore, J_{sc} and *FF* increase simultaneously with the conductivity of AZO buffer layer increasing from 4.03×10^{-6} S·cm^{-1} to 2.92×10^{-3} S·cm^{-1}. The surface morphology of AZO buffer layer is also influenced by the Al-doping level. The better surface quality of the buffer layer is critical for improving device's *PCE*, which can be seen in terms of series resistance (R_s) and shunt resistance (R_{sh}) of the PSCs[6]. The R_s decreases from 31.76 Ω·cm^2 to 18.86 Ω·cm^2, while the R_{sh} increases from 125.73 Ω·cm^2 to 478.19 Ω·cm^2 when the Al-doping concentration increases from 0 to 1.0% (as shown in Tab.1). As the contact resistance and the charge recombination in the interface are the main reasons for increasing R_s and decreasing R_{sh}, respectively, the better contact quality of the AZO/P3HT: PCBM interface will contribute to reduce charge recombination and enhance device performance. There is a slight decrease in transmittance and conductivity of AZO buffer layer with further increasing Al-doping amount from 1.0% to 2.0%, since high carrier densities would give rise to exciton quenching and carrier recombination at the local active layer area[24]. Therefore, enhanced R_s and shrunk R_{sh} can lead to a reduced *PCE* of 2.17%.

It has been reported that the device open-circuit voltage V_{oc} increases with the increase of Al-doping amount, due to the Fermi energy shift of AZO film[14]. However, the V_{oc} in our experiment almost keeps invariable (see Fig.4). According to the previous reports, the V_{oc} of bulk heterojunction (BHJ) solar cell is related to the difference between the highest occupied molecular orbital (HOMO) level of the donor material P3HT and the LUMO level of the acceptor compound PCBM. Moreover, the V_{oc} is not influenced by the work function of the electrode, indicating the establishment of Ohmic contact between the active layer and the both electrodes. Therefore, the almost unchanged V_{oc} of the devices in a series of experiments suggests that the effect of Fermi energy shift caused by Al-doping amount from 0 to 2.0% on the device performance can be ignored.

The Al-doping amount plays a significant role in the AZO thin films and the device photovoltaic performance. The experimental results indicate that doping Al with amount from 0.5% to 1.0% can significantly optimize the conductivity properties of AZO layers. The device with 1.0% Al-doping amount shows an improved *PCE* by 74% over the intrinsic ZnO device.

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