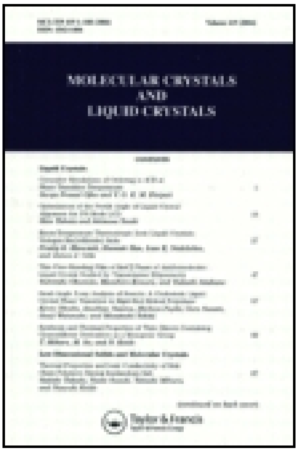

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Effect of Sol-Gel Prepared ZnO Electron Selective Layer on the Performance of Inverted Organic Solar Cells

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ZnO buffer layer was prepared as electron selective layers (ESL) for photo-induced electron transport and hole blocking in inverted organic solar cells (IOSCs) by sol-gel process. The effects of thickness and surface roughness of ZnO ESL on the performance of IOSCs were investigated. Power Conversion Efficiency (PCE) of the IOSC strongly varied as a function of ZnO film thickness and surface roughness, in particular, when the film thickness was <70 nm, increase in the surface roughness enhanced photovoltaic performances. It is demonstrated that optimization of the electrode thickness and roughness is essential for obtaining better performance of organic photovoltaic cells.

Keywords Film thickness; inverted organic solar cells; surface roughness; ZnO sol-gel

Introduction

Organic solar cells (OSCs) have been attracting much attention due to their low cost as well as potential applications in flexible energy conversion devices, converting the solar light directly to electricity [1–3]. OSCs with power conversion efficiency (PCE) of 5–6% have been recently developed by several research groups [4–6]. Inert environments such as Ar and/or N_2 atmosphere are required for the fabrication of OSCs, because conventional OSCs using low-work-function metals such as Al can easily be oxidized in air. In order to improve the stability of OSCs, inverted structures of OSCs have been used. In contrast to the conventional structure, in which holes are injected into the transparent conducting electrode (TCE), electrons are directed

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towards TCE. Inorganic semiconducting materials such as TiO_2 [8,9] or ZnO [10–13] deposited on the Indium Tin Oxide (ITO) electrode can be used as buffer layer for accepting electrons, which can also significantly increase the stability of inverted OSCs (IOSCs) [14–18].

ZnO is one of the most widely used functional materials with a wide and direct band gap, a large exciton binding energy of 60 meV, and thermal stability [19]. ZnO has been extensively used as TCE in solar cell, chemical and gas sensors, field-effect transistor, and light emitting diodes [20–22]. Techniques for deposition of ZnO films have been studied, which include sputtering [23], spray pyrolysis [24], chemical vapor deposition [25] and sol-gel method [26]. Among these methods, sol-gel method has been widely used because of its low cost and simplicity.

In the present study, we fabricated IOSCs with ZnO buffer layers via sol-gel method. By using various concentrations of zinc acetate for preparing sol-gel solutions, ZnO film structures with various thickness and surface roughness could be achieved. Relationship between roughness and thickness of ZnO layer and the photovoltaic performances of IOSC with ZnO buffer layers were tackled.

Experimental

ZnO Electron Selective Layers (ESL) Prepared by Sol-Gel Method

For the preparation of ZnO sol-gel solutions with different concentrations, various amounts of zinc acetate [$Zn(CH_3COO)_2 \cdot 2H_2O$] were dissolved in 2-methoxyethanol solution containing ethanolamine as a stabilizer. The solutions were kept at 60°C for 1 hour under ambient conditions with vigorous stirring. ITO was used as substrate, on which ZnO was deposited using spin coating. The resistance of the substrate was $10\,\Omega/\square$. Prior to the spin coating (1000 rpm/min for 60 sec), the substrates were cleaned using ultra-sonication with ethanol, acetone, and de-ionized water for 10 min. After spin coating, the samples were annealed at 300°C for 10 min in air to remove the remaining solvent.

Fabrications of Inverted Organic Solar Cells

Inverted organic solar cells were composed of a stack of Ag (electrode), poly(4-styrene sulfonate)-doped poly(3,4-ethylenedioxythiophene (PEDOT:PSS, hole transport layer), Active layer (P3HT:PCBM), and ZnO/ITO coated glasses. Poly(3-hexylthiophene) (P3HT) and (6,6)-phenyl C61 butyric acid methyl ester (PCBM) were purchased from Rieke Metals, Inc. and sigma-aldrich, respectively. A mixture of P3HT and PCBM with a weight ratio of 30 mg/ml:21 mg/ml was dissolved in 1,2-dichlorobenzene under vigorous stirring overnight. Then, this solution was spin coated with a rate of 600 rpm for 60 sec on ZnO films deposited on ITO. In addition, PEDOT:PSS solution was spin coated with 5000 rpm, and the resulting structure was annealed at 150°C for 10 min under atmospheric pressure. Ag metal as the back electrode was deposited under vacuum conditions with a base pressure of 3.0×10^{-6} torr on the PEDOT:PSS film. Finally, the device was heated at 150°C for 5 min. The active area of the solar cell was $0.38\,cm^2$. It is worth emphasizing that all the preparation was performed in ambient conditions except for the electrode evaporation.

The structures of ZnO thin films were analyzed by field emission scanning electron microscopy (FE-SEM; JEOL 6000) and atomic force microscopy (AFM, Vecco; MMAFM-2), and their optical properties were measured using UV/Vis transmittance spectrometer (Verian Cary 5000), respectively. The performances of the solar cells were tested using a solar simulator illuminated with a photointensity of AM 1.5, 100 mW/cm^2.

Results and Discussion

Effect of ZnO Sol-Gel Concentrations

The cross section images of FE-SEM of ZnO thin films prepared with sol-gel methods based on four different molarities of zinc acetate (0.1, 0.5, 0.75, 1.5 M) are shown in Figure 1. The dense and uniform ZnO films were obtained by spin coating. The thickness of ZnO thin films were estimated to be approximately 20 nm, 50 nm, 70 nm and 200 nm for four different samples, respectively, as shown in Figures 1(a), 1(b), 1(c) and 1(d).

Figure 2 shows the UV/Vis transmittance spectra of the spin coated ZnO buffer layers on ITO in the wavelength range of 300 nm and 800 nm. All the ZnO films are highly transparent in the UV-Vis region of 400 nm to 800 nm and a sharp fall in transmittance is observed below 400 nm due to band gap absorption [27]. For all ZnO films studied here, more the 85% transparency in the visible regions of 500 nm to 600 nm could be obtained. It can be seen that optical transmittance is almost independent of the ZnO film thickness in the visible range.

AFM images of the ZnO buffer layers with different thicknesses deposited on ITO glasses are shown in Figure 3. With increasing film thickness, roughness mean square (RMS) is also increased. The RMS of ZnO films were estimated to 0.97 nm, 2.77 nm, 3.20 nm and 7.11 nm, as shown in Figures 3(a), 3(b), 3(c) and 3(d), respectively. As the concentration of ZnO sol-gel solution was varied,

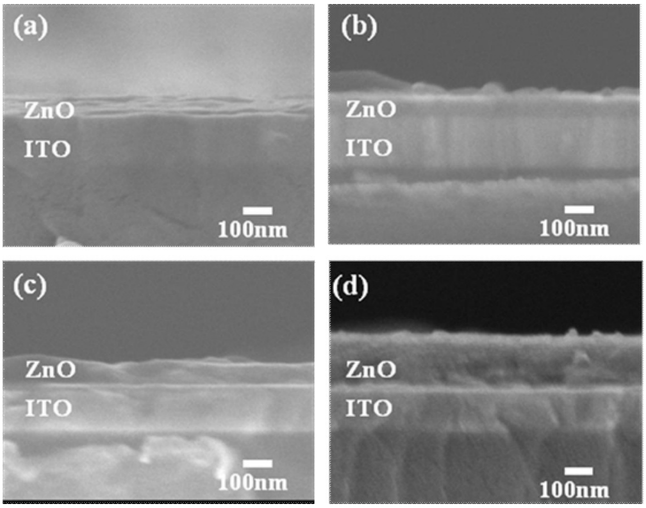

Figure 1. FE-SEM images of the side views of ZnO buffer layers obtained by different concentrations of zinc acetate (a) 0.1 M, (b) 0.5 M, (c) 0.75 M and (d) 1.5 M.

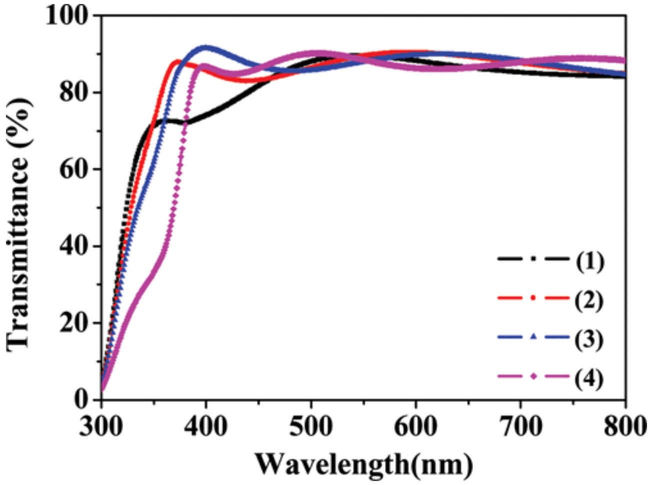

Figure 2. The UV/Vis transmittance spectra of ZnO films obtained by different concentrations of zinc acetate (a) 0.1 M, (b) 0.5 M, (c) 0.75 M and (d) 1.5 M.

both thickness and surface roughness of ZnO films prepared by these sol-gel solutions were altered.

As prepared device structure by cross-sectional FE-SEM and the photovoltaic performances of IOSCs based on without ZnO buffer layer and four different ZnO buffer layers in Figures 1–3 are displayed in Figure 4 and Table 1. The IOSCs

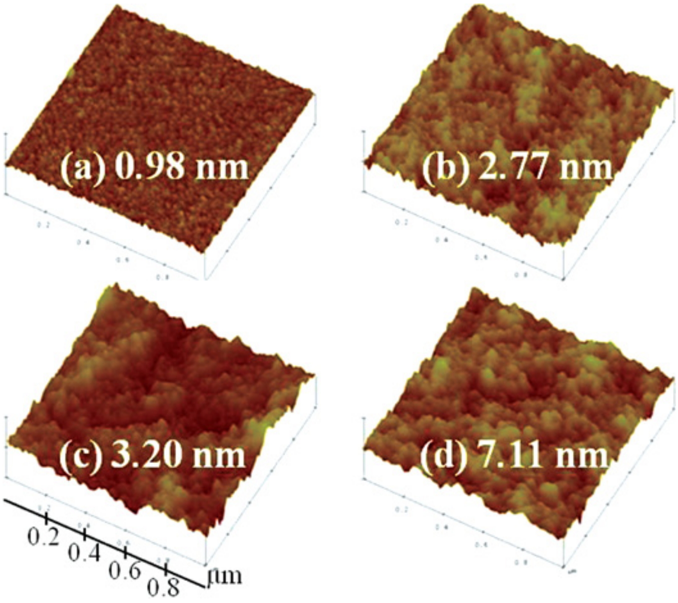

Figure 3. AFM images of ZnO films obtained by different concentrations of zinc acetate (a) 0.1 M, (b) 0.5 M, (c) 0.75 M, and (d) 1.5 M.

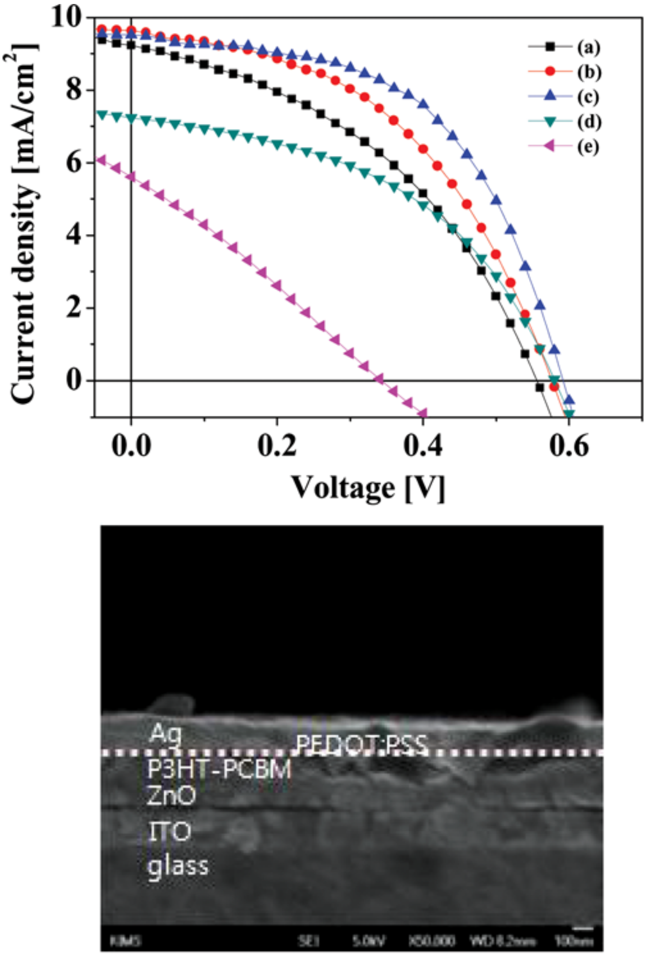

Figure 4. J-V characteristics of the photovoltaic devices with various ZnO films shown in Figures 1–3 and without ZnO films for comparison under 100 mW/cm^2 AM 1.5 G irradiation. Cross section image of the complete solar cell obtained by FE-SEM is shown on the right side.

Table 1. Summary of power conversion efficiency (PCE), fill factor (FF), open-circuit voltage (Voc), short-circuit current (Jsc), and series resistance (Rs) of the IOSCs with various ZnO films shown in Figures 1–3 and without ZnO films

	PCE (%)	FF (%)	Voc (V)	Jsc (mA/cm^2)	Rs ($\Omega \cdot$ cm^2)
(a) 0.1 M	2.13	41	0.55	9.22	6.38
(b) 0.5 M	2.57	46	0.57	9.62	5.76
(c) 0.75 M	3.03	53	0.59	9.51	4.79
(d) 1.5 M	1.09	38	0.54	5.24	9.89
(e) w/o ZnO	0.53	27	0.34	5.60	–

without ZnO buffer layer shows very low performance than that with ZnO buffer layers which means that ZnO buffer layer acts as an electron selective and hole blocking layers reduction electron-hole recombination in here. With increasing thickness of the ZnO film from 20 to 70 nm, a significant improvement in power conversion efficiency (PCE), fill-factor and open-circuit voltage could be observed. When the film thickness was further increased to 200 nm, a decrease in photovoltaic performance could be found. Our result implies that tuning of the ZnO buffer layer structures via sol-gel method can improve photovoltaic performance of the IOSCs. The PCE, fill-factor and open-circuit voltage of IOSCs should be influenced by both the thickness and surface rough ness of ZnO buffer layer. Increase in the surface roughness could enhance contact area between active and buffer layer, thus improving photovoltaic performance. On the other hand, when the ZnO buffer layer becomes too thick, a high intrinsic resistance increasing the series resistance, Rs, and reducing the charge carrier transport ability can decrease the photovoltaic performance of the device.

Conclusions

ZnO film was used as ESL in IOSCs. Various ZnO structures were obtained using different zinc acetate concentrations in ZnO sol-gel solutions. We show that performance of IOSC is dependent of both ZnO film thickness and surface roughness. With increasing film thickness and roughness, photovoltaic performance initially increased, most likely due to the fact that increase in the surface area enhanced contact area between active layer and ZnO. When the film thickness became too thick (200 nm), the photovoltaic performance was reduced. We show that control of ZnO film thickness and surface roughness is essential for obtaining best performance IOSCs.

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