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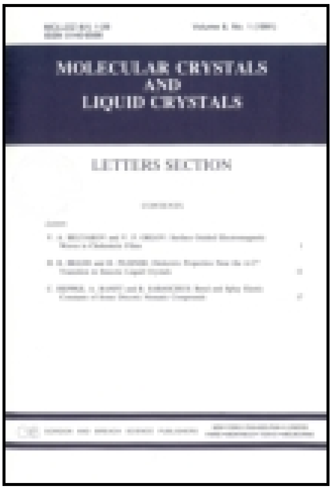

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ITO/AZO Double-Layered Transparent Conducting Oxide Films for Organic Photovoltaic Cells

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ITO/AZO Double-Layered Transparent Conducting Oxide Films for Organic Photovoltaic Cells

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We investigated the electrical and optical properties of single-layered films of indium tin oxide (ITO) and aluminum-doped zinc oxide (AZO) as well as of double-layered ITO/AZO films. These transparent conducting oxide (TCO) films were deposited by sputtering. The ITO/AZO film (500/250 nm thick) had a transmittance slightly higher than that of the ITO film in the visible region, and exhibited slightly lower resistivity than that of the ITO film. These results suggested that photoelectric devices based on double-layered TCO films could be expected to exhibit higher photocurrents. To determine whether this was the case, we used the double-layered ITO/AZO film as the anode electrode in an organic photovoltaic (OPV) cell. The cell was found to exhibit better device performance than that of an OPV cell based on the single-layered ITO film.

Keywords Transparent conductive oxide (TCO); Al-doped zinc oxide (AZO)/indium-tin-oxide (ITO) bilayer; double-layered TCO; organic photovoltaic cell

Introduction

Transparent conducting oxide (TCO) films are used widely in flat-panel displays [1], organic photovoltaic (OPV) cells [2], organic light emitting diodes [3], and smart windows [4]. Indium tin oxide (ITO) is the most commonly used material for fabricating transparent

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electrodes, owing to its outstanding optical and electrical properties [3, 4]. Generally, as the thickness of an ITO film is increased, its carrier mobility improves but its transmittance decreases. Cui et al. have reported that the transmittance of ITO films can be controlled by controlling the oxygen partial pressure during film deposition [5]. Aluminum-doped zinc oxide (AZO) is receiving increasing attention as an alternative material to ITO, as it can be synthesized from abundant, inexpensive, and nontoxic materials. In addition, it exhibits excellent transmittance and a tunable work function, which can be controlled by controlling the doping concentration of aluminum [6]. However, AZO has a few drawbacks. It is not very stable and readily undergoes surface degradation [7]. In addition, its electrical resistivity is higher than that of ITO. Recently, multilayered films of TCOs, such as those having two or three layers, have been investigated in order to simultaneously achieve excellent conductivity and high transparency [8–12]. Multilayered TCO films are attractive because it is possible to tune their electrical and optical properties by adjusting the thicknesses of the individual layers [11].

In this study, we investigated the electrical and optical characteristics of double-layered and single-layered TCO films, namely, of ITO/AZO, ITO, and AZO films, deposited by sputtering. We also fabricated and characterized OPV cells using these films as substrates, and compared the characteristics of these devices.

Experimental

TCO Films Preparation

First, an AZO film was deposited on a chemically cleaned glass substrate (Eagle XG) using a ZnO target 4 inches in diameter and doped with 2 wt% Al_2O_3 (purity 99.99%). A sputtering system (SNTEK, Inc.) was employed for the purpose. The base pressure was $\sim 10^{-7}$ Torr, and the target-to-substrate distance was less than ~20 cm. During deposition, the substrate was rotated at a speed of ~6 rpm. The radiofrequency (RF) sputtering power and annealing temperature of the substrate were 300 W and ~220 °C, respectively. The ITO film was deposited with a direct current (DC) power unit and using an In_2O_3 target containing 10 wt% SnO_2. The deposition rates of the AZO and ITO films were kept constant at 8.3 nm/min and 16.7 nm/min, respectively.

The optical characteristics of the TCO films were determined using an ultraviolet (UV) spectrophotometer (Optizen 2120UV Plus, Mecasys Co., Ltd) over wavelengths of 300–1100 nm. The electrical properties were evaluated using a Hall measurement system (Van der Pauw HMS-5000, Ecopia Corp.) at room temperature. The sheet resistances of the TCO films were measured with a CMT-SERIES four-probe-type resistance meter.

OPV Cells Fabrication

To fabricate the bulk heterojunction (BHJ) OPV cells, first, the TCO-coated glass substrates were cleaned sequentially in detergent, deionized water, acetone, and isopropyl alcohol. Each rinsing step was performed in an ultrasonic bath for 15 min. Then, the cleaned TCO substrates were dried in an electric oven at 100°C for 10 h. Next, poly(3-hexylthiophene-2,5-diyl) (P3HT) (Rieke Metals, Inc.) and phenyl-C61-butyric acid methyl ester (PCBM) (EM Index, Inc.) (weight ratio of 1:0.8) were dissolved in chlorobenzene (CB) in a concentration of 18 mg/mL and stirred at 40°C for 12 h. The stirred P3HT:PCBM blend solution was

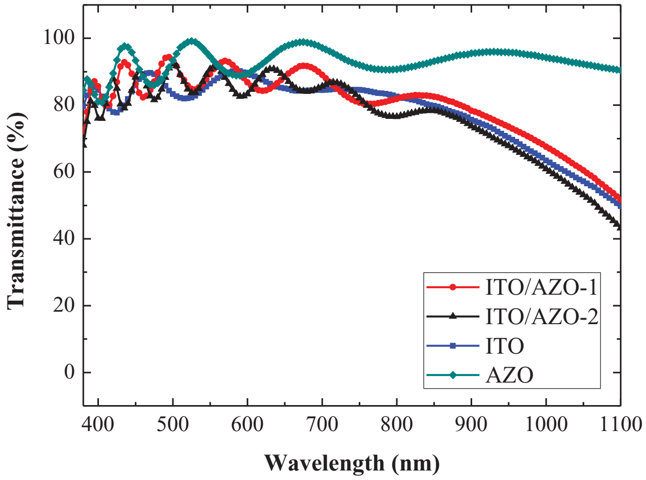

Figure 1. Comparison of optical transmittance spectra for various TCO films.

filtered using a 0.45 μm filter. The TCO-coated glass substrates were treated with an UV-ozone cleaner for 10 min. The TCO-coated glass substrates were then coated with a thin layer of poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) (Heraeus Cleavious P) by spin coating and baked at 140°C for 10 min in ambient air and then in an Ar gas atmosphere. The thickness of the PEDOT:PSS coating was approximately 30–40 nm. A layer of the P3HT:PCBM blend solution was then spin coated (800 rpm, 15 s) on top of the PEDOT:PSS layer in an Ar atmosphere (<0.1 ppm oxygen and moisture) in a glove box, and the substrate was annealed at 120°C for 1 min. The thickness of the thus-formed active layer was ~100 nm. Ca/Al were deposited at $\sim 10^{-7}$ Torr by thermal evaporation. The last step in the fabrication of the OPV cells was the annealing of the samples at 150°C for 30 min. The active area of the OPV cells was 100 mm^2. The current density-voltage (*J-V)* curves of the OPV cells were measured using a Keithley 236 source meter under simulated AM 1.5G irradiation from a solar simulator with an ozone-free xenon lamp (Newport Co. Inc.); the intensity of the radiation was 100 mW/cm^2. The external quantum efficiencies of the OPV cells were measured using a photomodulation spectroscopy system with a 100 W halogen lamp, a monochromator, an optical chopper, and a lock-in amplifier. We used a standard sample to calibrate the Si photodiode.

Results and Discussion

An ITO film, an AZO film, and two double-layered ITO/AZO films of the following thicknesses were prepared: ITO (500 nm), AZO (500 nm), ITO (500 nm)/AZO (250 nm) (labeled as ITO/AZO-1) and ITO (500 nm)/AZO (500 nm) (labeled as ITO/AZO-2). As noted previously, the deposition rates for the AZO and ITO layers were 8.3 nm/min and 16.7 nm/min, respectively. It can be seen from the optical transmittance spectra of the films (Fig. 1) that, in the 400–800 mm region, the ITO film had an average transmittance of 85% while the AZO film had an average transmittance of 93%. Further, the ITO/AZO-1 film had a higher transmittance (87%) than that of the ITO film. Finally, the ITO/AZO-2 film (83%) exhibited a transmittance slightly lower than that of the ITO film. The lower transmittance of the ITO/AZO-2 film may due to the increased thickness of its AZO layer compared to

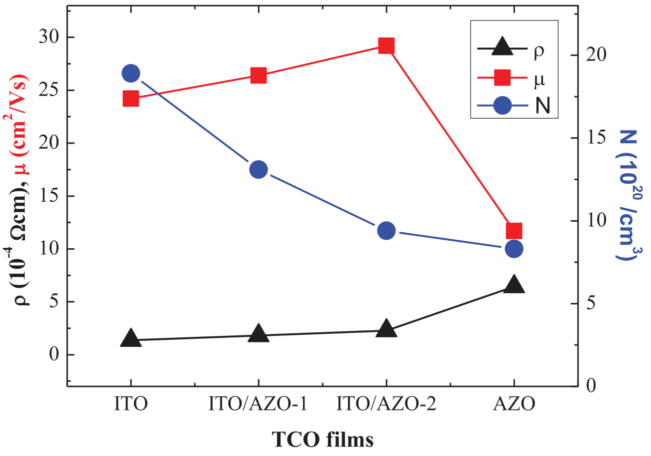

Figure 2. Resistivity ρ (triangles), mobility μ (squares) and charge carrier concentration N (circles) of various TCO films. The lines are to guide the eye.

that of the ITO/AZO-1 film. For wavelengths greater than 800 nm, the transmittance of the AZO film was significantly higher than those of the ITO and ITO/AZO films; this was owing to the low concentration of charge carriers in the AZO film [13–15].

In general, the electrical conductivity, σ, of a TCO film is given by the following equation:

$$\sigma = 1/\rho = q\mu N \tag{1}$$

where ρ is the resistivity, q is the electronic charge, μ is the mobility, and N is the charge carrier concentration.

Typically, as the charge carrier concentration of a TCO film increases, its transmittance decreases if the absorption of free carriers is also increased. The carrier mobility of the film is reduced owing to carrier scattering, which is increased by the presence of ionized impurities [8]. Therefore, to improve the conductivity of TCO films, their carrier mobility needs to be increased by subjecting the films to heat treatments.

By measuring the carrier mobility, electrical conductivity, and charge carrier concentration (Fig. 2) of the four fabricated samples, we could characterize their electrical properties.

The sheet resistances of the ITO, AZO, ITO/AZO-1, and ITO/AZO-2 films were 3.5 Ω/□, 17.4 Ω/□, 3.1 Ω/□, and 2.7 Ω/□, respectively. The ITO film was found to have a mobility of 24 cm^2/V·s. In addition, it exhibited the highest charge carrier concentration (18.9 × $10^{20}/\text{cm}^3$), and the lowest resistivity (1.4 × 10^{-4} Ω·cm) of all the films. On the other hand, the AZO film had the lowest mobility (12 cm^2/V·s), the lowest charge carrier concentration (8.3 × $10^{20}/\text{cm}^3$), and the highest resistivity (6.4 × 10^{-4} Ω·cm). The ITO/AZO-1 film exhibited a mobility of 26 cm^2/V·s, a charge carrier concentration of 13.1 × $10^{20}/\text{cm}^3$, and a resistivity of 1.8 × 10^{-4} Ω·cm; these values were comparable to those of the ITO film. Finally, the ITO/AZO-2 film exhibited the highest mobility (29 cm^2/V·s). Its charge carrier concentration was 9.4 × 10^{20} /cm^3 and resistivity was 2.3 × 10^{-4} Ω·cm. These results are summarized in Table 1.

In order to ensure that a photoelectric device has high efficiency, the TCO film substrate used in the device should simultaneously exhibit high transmittance and low resistivity. Our

Table 1. Electrical properties of various TCO films prepared by sputtering method

TCO film	Thickness (nm)	Treatment (°C)	Charge carrier concentration (10^{20} cm^{-3})	Resistivity (10^{-4} Ω·cm)	Mobility (cm^2/V·s)	R_{sh} (Ω/□)
ITO/AZO-1	500/250	220	13.1	1.8	27.3	3.1
ITO/AZO-2	500/500		9.4	2.3	30.5	2.7
ITO	500		18.9	1.4	23.5	3.5
AZO	500		8.3	6.4	11.7	17.4

results showed that the AZO film had the necessary high transmittance, but showed low mobility and high resistivity; however, the ITO/AZO films exhibited high transmittance as well as low resistivity. Therefore, we fabricated OPV cells using the double-layered ITO/AZO films as substrates and compared the device performance of the cell with those of an OPV cell based on the ITO film.

OPV cells with a regular configuration were fabricated using a blend of P3HT and PCBM on the glass substrates coated with the ITO and the double-layered ITO/AZO films. The structures and energy diagrams of the devices are shown in Fig. 3.

The *J-V* curves of the OPV cells are shown in Fig. 4(a). The structure of the OPV cells was glass/TCO/PEDOT:PSS/P3HT:PCBM/Ca/Al, as shown in Fig. 3(a). The area of the active layer was 1.0 cm^2. The device with the ITO/AZO-1 film had a higher power conversion efficiency (PCE) than that of the device with the ITO film. This was owing to the low sheet resistance and high transmittance of the ITO/AZO-1 film. The cell based on

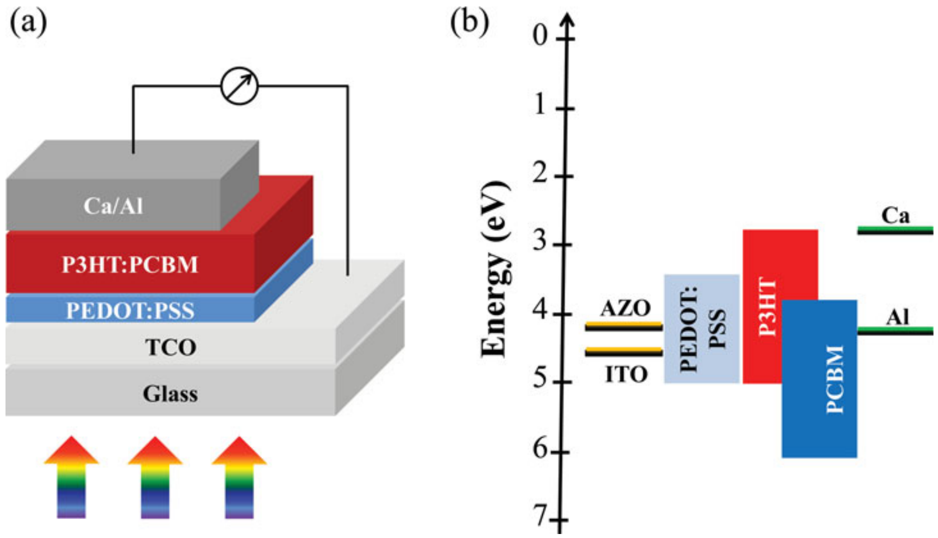

Figure 3. OPV devices based on P3HT blended with PCBM were fabricated on ITO and ITO/AZO double layered TCO coated films with regular configuration (a); the corresponding device structure and the energy diagram are shown in (b).

Table 2. Summary of device performance of OPV cells using ITO and double-layer TCO films

Device	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	PCE (%)
ITO/AZO-1 (500/250 nm)	0.62	7.60	0.62	2.91
ITO/AZO-2 (500/500 nm)	0.61	7.24	0.61	2.69
ITO(500 nm)	0.62	7.37	0.62	2.83

the ITO/AZO-2 film showed a relatively low short circuit current density, J_{sc}. Table 2 lists the values of the various device performance parameters of the fabricated OPV cells.

Figure 4(b) shows the external quantum efficiency (EQE) spectrum of each device.

The J_{sc} values obtained from the *J-V* curves were within 5% of the J_{sc} values obtained by integrating the corresponding external quantum efficiency spectrum. As can be seen in Fig. 4(b), all the devices exhibited a photoresponse in the 350–650 nm region. The EQE spectrum of the device with the ITO/AZO-1 film exhibited peaks at 480 nm and 550 nm; however, the EQE spectra of the devices with the ITO/AZO-2 and ITO films consisted of broad optical absorption peaks in the 450–550 nm region. For wavelengths lower than 440 nm, the device with the ITO/AZO-2 film had a significantly lower EQE value than those of the devices with the ITO/AZO-1 and ITO films. These results were in keeping with those shown in Fig. 1. The device with the ITO/AZO-1 film showed an average EQE of 44.1% in the 400–650 nm region. In addition, its highest EQE value was the highest, ~60.0% at 480 nm, while its J_{sc} was 7.29 mA/cm^2. The device with the ITO film exhibited a slightly lower EQE value (42.0% on average in the 400–650 nm region) than that of the device with the ITO/AZO-1 film.

Therefore, the device with the ITO/AZO-1 thin film exhibited relatively high PCE value due to high photo current, even though the electric conductivity was slightly lower that of the device with the single-layered ITO coating. These results suggest that the optical transmittance of the double-layered films had a significant effect on device efficiency and contributed to the increase in the photocurrent generated.

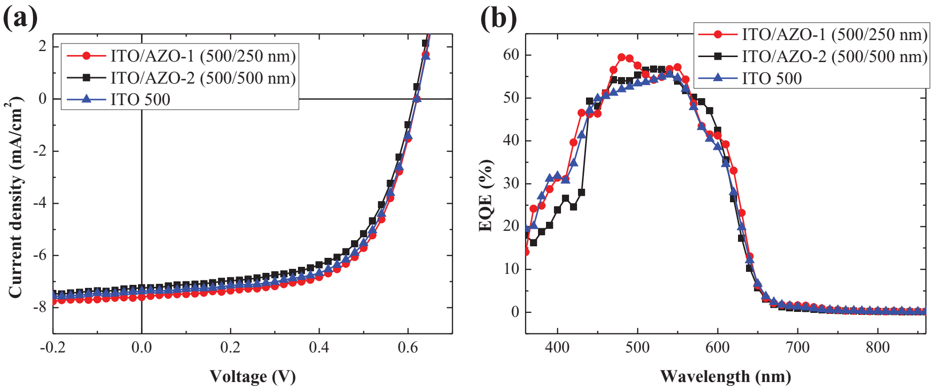

Figure 4. Characteristics of *J-V* curves of 1×1 cm^2 sized OPV cells using ITO and double-layer AZO/TIO films (a), and the corresponding external quantum efficiency spectra (b).

Conclusions

To summarize, double-layer TCO films, that is, ITO/AZO films, were successfully deposited on a glass substrate by the sputtering technique. The ITO/AZO-1 film, in which the ITO and AZO films had thicknesses of 500 nm and 250 nm, respectively, exhibited a transmittance slightly higher (87% on average) than that of the single-layered ITO film (85% on average) in the 400–800 nm region. The ITO/AZO-1 film showed an electrical resistivity (1.8×10^{-4} $\Omega\cdot$cm) that was low and comparable to that of the single-layered ITO film. The OPV cells based on the ITO/AZO films exhibited better electrical performance than did the device fabricated using the ITO film. The OPV cell with the ITO/AZO-1 film among the devices showed the higher PCE due to the high short circuit current density. This suggests that double-layered ITO/AZO substrates have low resistivity and high transmittance and are suitable for use in photodevices.

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