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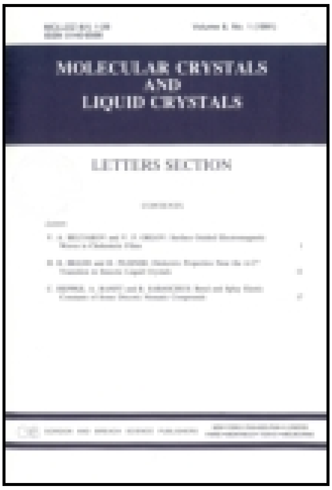

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# Remarkable Improvement of Organic Solar Cells Lifetime with Zn-doped $In_2O_3$ Electrode as UV-blocking TCO

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*We have studied the lifetime improvement of organic solar cells (OSCs) based on the conjugated polymer:fullerene blends using an ultra-violet (UV) blocking transparent conducting oxide (TCO). Without additional passivation films/layers or changing of structure, the performance of the OSC using UV blocking TCO was comparatively stable under the strong UV exposure. When 30 mW/cm$^2$ of UV was irradiated for 300 seconds, the $V_{OC}$ and FF of the OSC without UV blocking TCO decreased to 87% and 64%, respectively. As a result, power conversion efficiency (PCE) decreased to 54%. However, the $V_{OC}$ and FF of OSC with UV blocking TCO slightly decreased to 96% and 87%, respectively.*

**Keywords** Organic solar cells (OSCs); polymer; ultra-violet (UV) blocking; transparent conducting oxide (TCO); stability

## Introduction

Recently, various types of solar cells that can be used as substitutes for fossil energy have been under a research, including silicon based solar cells [1], compound semiconductor solar cells [2], dye-sensitized solar cells (DSSCs) [3, 4], and organic solar cells (OSCs) [5–7]. Among them, OSCs have attracted great attention due to their advantages such as easy fabrication, cost effectiveness, light weight, and flexibility which allows for an application to a variety of devices [8–10]. However, its low conversion efficiency and short lifetime limit its feasibility for a commercial use. The efficiency of OSCs increases significantly with the introduction of the bulk hetero-junction (BHJ) concept which consists of an interpenetrating network of electron donor and acceptor materials and crystallization of active layer through thermal / solvent annealing [11–13]. Besides the necessity for high efficiency, stability is another important issue for the application of the conjugated polymer:fullerene based OSCs to practical products as OSCs especially exhibit weakness against oxygen, humidity, and UV. Therefore, protecting OSCs from oxygen, humidity, and UV exposure is an absolute necessity to achieve a long lifetime [14–20]. For the purpose of UV protection, additional

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UV absorption film or UV blocking layer was used as the common method to protect from UV in order to improve the lifetime of OSCs [21–23].

In this study, we presented the improvement of organic solar cells lifetime with Zn-doped $In_2O_3$ electrode as UV-blocking TCO. We used Zn-doped $In_2O_3$ (IZO) as an UV blocking TCO because it has good electrical and optical properties even when deposited at room temperature and makes the OSCs flexible. In the study, we controlled RF power, working pressure, and deposition time to optimize UV blocking TCO according to OSC operation. Optimized UV blocking TCO was applied to OSCs and the performance was compared with ITO devices which is a non-UV blocking TCO. The OSCs with UV blocking TCO or non -UV blocking TCO were evaluated during the UV irradiation. The performance degradation was observed by the current density-voltage (J-V) characteristics.

## Experiment

### *Fabrication of UV Blocking TCO*

The IZO, the UV blocking TCO, was deposited on glass to optimize the condition of UV blocking TCO at room temperature by RF magnetron sputter from an $In_2O_3$:ZnO (90:10 w%) alloy target (99.99% purity, from LTS research laboratories, Inc.) with 3 inch diameter and 0.25 inch thickness. The substrate was cleaned using acetone, methanol, and deionized water (D.I water) and dried in an oven at 150°C for 10 minutes. In the deposition system, base pressure of $\sim 1 \times 10^{-6}$ Torr and Ar plasma with Ar 40 sccm flow were maintained. RF power, working pressure and deposition time were varied from 40 to 80 W, 3 to 11 mTorr and 10 to 50 min. Optical and electrical properties were measured according to various deposition conditions. Lastly, the UV blocking TCO in optimizing condition was applied to OSCs.

### *Fabrication of UV Blocking TCO*

In this experiment, we fabricated OSCs with UV blocking TCO and non-UV blocking agent. The OSCs were composed of poly(3-hexylthiophene-2,5-diyl) (P3HT, Sigma Aldrich) as a donor and phenyl-C71-butyric-acid menthyl ester (PCBM, American Dye Source Inc.) as an acceptor. The OSCs fabrication was processed by spin-coating method. Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS, Clevios PH1000) was spin coated on the TCO with 4000 rpm with condition of 25 nm thickness and heated at 150°C for 10 minutes. P3HT and PCBM were prepared a day before in dichlorobenzene (30 mg/ml) and deposited on the PEDOT:PSS layer. Finally, an Al cathode was evaporated on the active layer and annealed at 150°C for 10 minutes. The active area of the OSC, defined by the shadow mask, was 0.09 $cm^2$. The structure of the OSC device with UV blocking TCO is presented in Fig. 1 compared with the OSC with non UV blocking TCO and a passivation film.

## Measurements

The optical and electrical properties were measured to determine the availability of UV blocking TCO as OSCs anode. The optical transmission spectra were measured in the wavelength range from 250 to 800 nm by using a UV-Vis spectroscope (CM-3700d, Konica Minolta). The electrical resistivity of the TCO was obtained using a resistance measurement

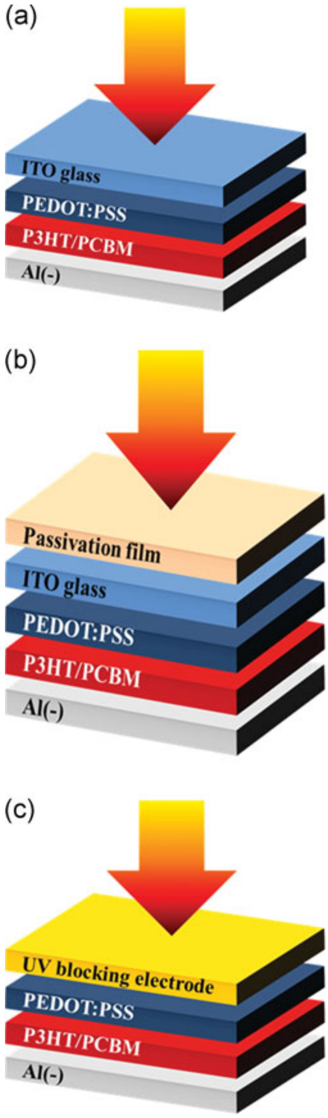

**Figure 1.** The structure of photovoltaic cell fabricated in this study; (a) conventional OSC, (b) with UV passivation film, and (c) with UV blocking TCO.

system (CMT-SR100N). For the characteristics of the OSCs, J-V curve were measured using a source meter (Keithley 2400; Keithley Instruments Inc., Cleveland, OH) and solar simulator (Newport Corp.). It was calibrated to obtain an AM 1.5G spectrum using a reference cell (VLSI standard). In order to observe the degradation of the OSCs performance by the UV, 365 nm UV source (SP-9, Ushio Inc.) was used with the power of 30 mW/cm$^2$ for 300 seconds, increasing 60 seconds of exposure time. In addition to controlling the experimental variables, chemical stability of IZO and PEDOT:PSS were confirmed by the X-ray photoelectron spectroscope (XPS, ThermoFisher).

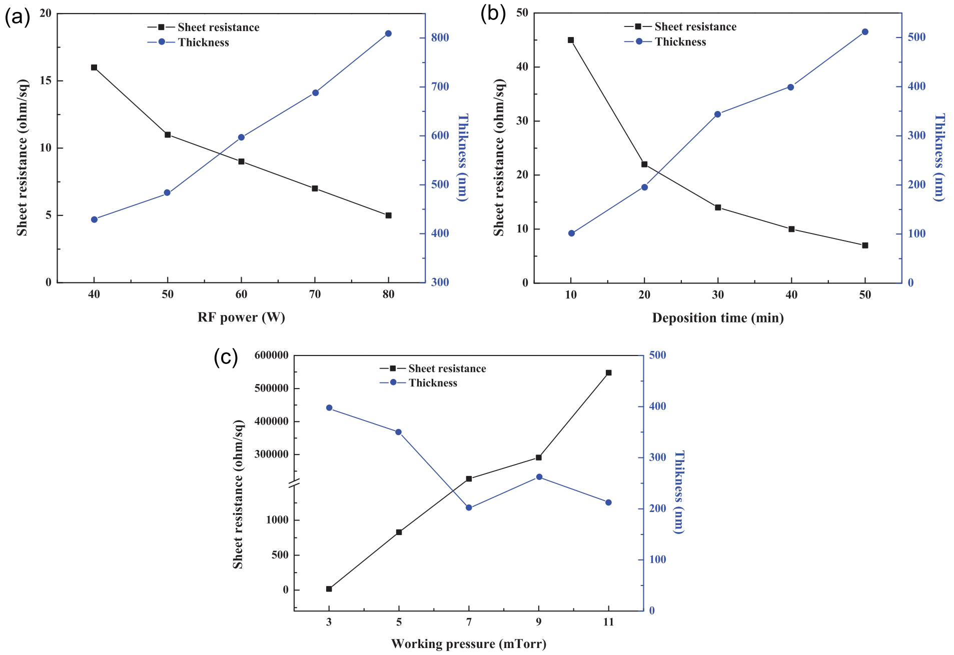

**Figure 2.** Sheet resistance and thickness of UV blocking TCO as a function of deposition condition; (a) deposition time, (b) RF power and (c) working pressure.

## Results and Discussion

The most important characteristic of the electrode is the electrical property. Fig. 2 shows the sheet resistance and thickness of IZO TCO as a function of deposition condition. The deposition conditions gave a direct impact on the thickness of TCO and the sheet resistances exhibited a tendency of inverse proportion with thickness. The thickness increased as a function of increase in deposition time (Fig. 2(a)). As shown in Fig. 2(b), high RF power improved plasma density and Ar ion to hit the target while sputtered IZO particles and rate of deposition. Lastly, we expected the working pressure to remain the same as RF power increases, but, despite its slight reduction, thickness resistance increased rapidly (Fig. 2(c)). It is because of the increased chamber pressure causing the mean free path of the particles to decrease and the inter-particle collisions that occur, which degrade the quality of the film. High resistance of TCO suggests that, as the plasma density increases, Ar ion sputtering gas contains a small amount of oxygen radical that made the oxygen-rich IZO a thin film with high resistance [24, 25].

Figure 3(a) shows the transmittance of the IZO TCO at various deposition times. The transmittance of TCO was dependent on the thickness of TCO and the sheet resistance of TCO was in inverse proportion to thickness of that. As the deposition time increased, interference of light in visible region was raised, but on the average, the transmittance of TCO retained more than 75%. In terms of the efficiency of solar cells, light absorption of the active layer is a very important issue and good electrical properties are also required. In order to optimize the UV blocking TCO, we considered both properties of sheet resistance and transmittance for thickness. The optimized UV blocking TCO has sheet resistance of less than 10 Ω/□ and the transmittance of UV blocking TCO is shown in Fig. 3(b) with

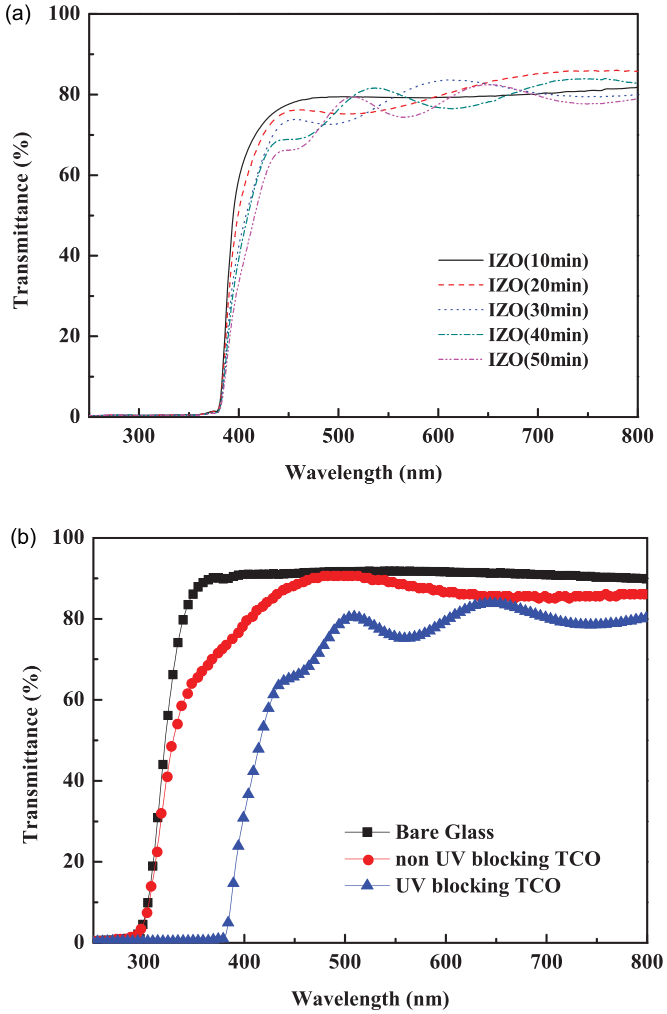

**Figure 3.** (a) Transmittance of the IZO TCO with various deposition time and (b) comparison of transmittance of UV blocking TCO and non-UV blocking TCO.

non-UV blocking TCO. The resistance is almost zero in the UV range of ∼370 nm for the UV blocking TCO, but it decreases with the increase in layer thickness in the visible range.

Before the fabrication of OSC with UV blocking TCO, we investigated chemical stability between IZO TCO and PEDOT:PSS to confirm whether the degradation of OSC is caused only by UV. Because IZO TCO is easy to etch with acid [23] and PEDOT:PSS is a weak acid solution [26], the chemical stability between both materials is an important factor. Hence, we checked the IZO damage according to the PEDOT:PSS solution temperatures 25, 50, and 75°C during 10 minutes to consider the effect of applied heat on the production process. Fig. 4(a) shows the elemental ratio (Zn/In) and sheet resistance of IZO TCO as a function of temperature and Fig. 4(b) is the IZO TCO composition measured by XPS at the temperature of 75°C. The elemental ratio was maintained until 50°C, but it was reduced as the solution temperature reached 50°C and the TCO lost its electrical properties at 75°C.

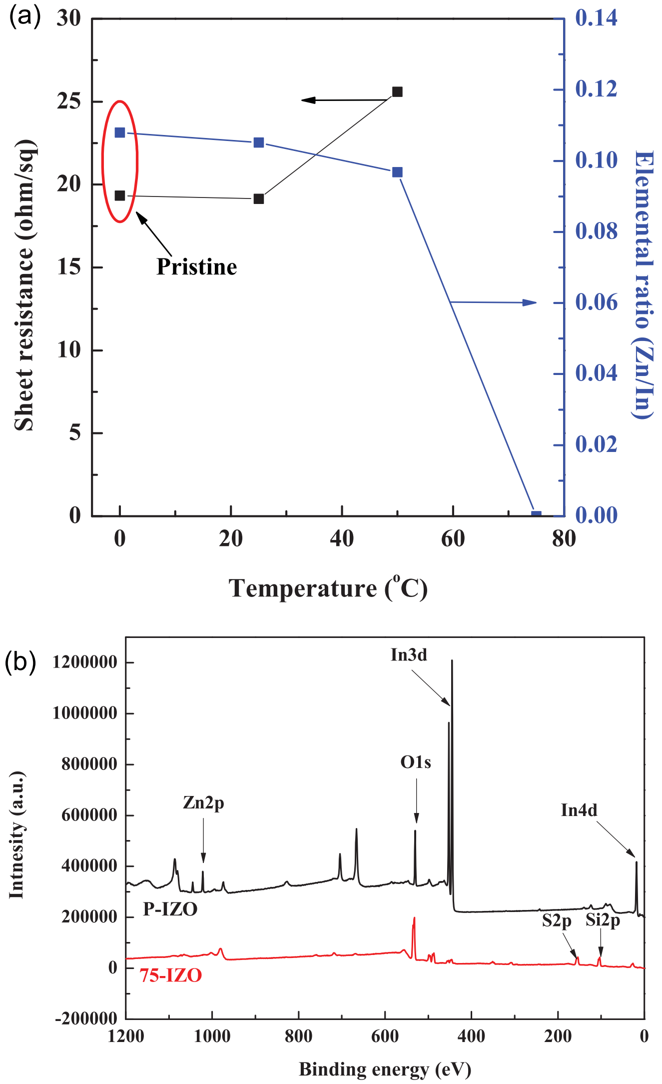

**Figure 4.** Chemical composition of IZO TCO; (a) elemental ratio (Zn/In) and sheet resistance and (b) XPS result of IZO TCO composition.

Fig. 4(b) shows Zn component did not remain on the substrate. As a result of the findings, we confirmed that the fabrication of OSCs with IZO UV blocking TCO with PEDOT:PSS is available since we fabricated OSCs with PEDOT:PSS temperature of 25°C.

OSCs were manufactured with UV blocking TCO, as mentioned in manufacture part above. In order to observe the degradation of the OSC performance, we fabricated two types of OSC devices with UV blocking TCO and non-UV blocking TCO. The performance degradation of the devices was investigated under 30 mW/cm$^2$ of UV intensity for 300 seconds. As shown in Fig. 5(a), the $V_{OC}$ and FF of OSC with non-UV blocking TCO decreased when the UV was illuminated; the $V_{OC}$ and FF varied from 0.615 to 0.535 V and from 0.486 to 0.31, respectively. The $J_{SC}$ was negligibly changed during the UV illumination

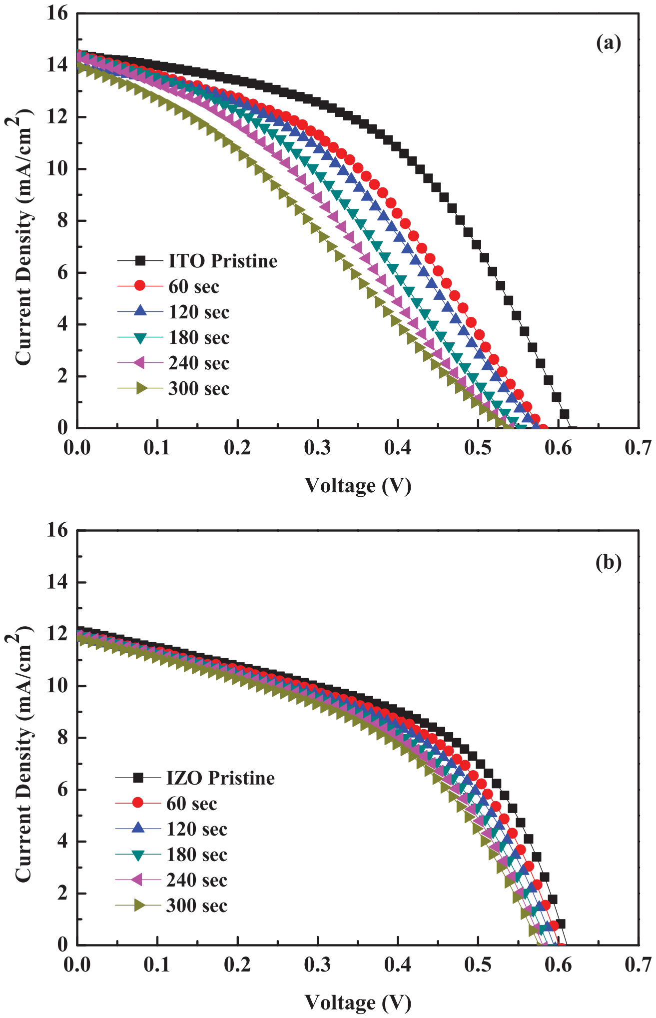

**Figure 5.** J-V characteristics of the OSC with; (a) non-UV blocking TCO and (b) UV blocking TCO.

for 300 seconds. Consequently, the power conversion efficiency was decreased to 2.3% compared to 4.32% of the pristine OSC device. For the OSC with UV blocking TCO, as shown in Fig. 5(b), $V_{OC}$ and FF decreased slightly from 0.641 to 0.616 V and from 0.517 to 0.451, respectively. The power conversion efficiency showed a decrease of 20% compared to that in the OSC with the non-UV blocking TCO which showed a decrease of 46%. Fig. 6 shows the normalized cell parameters for the devices. It should be noted that the $V_{OC}$, FF, and PCE decreased linearly as the UV was illuminated on the OSC for 300 seconds and that $J_{SC}$ was negligibly changed. Among these parameters, FF has the greatest impact on the power conversion efficiency and the degradation in FF is very significant compared to $V_{OC}$ and $J_{SC}$. Such result is because the defects created during illumination and P3HT, the polymer used in the OSC, can degrade in the thin film structure containing the molecular oxygen when it is irradiated [27], despite of the relatively low transmittance in the visible spectrum OSC with UV blocking TCO which has relatively improved stability. This result

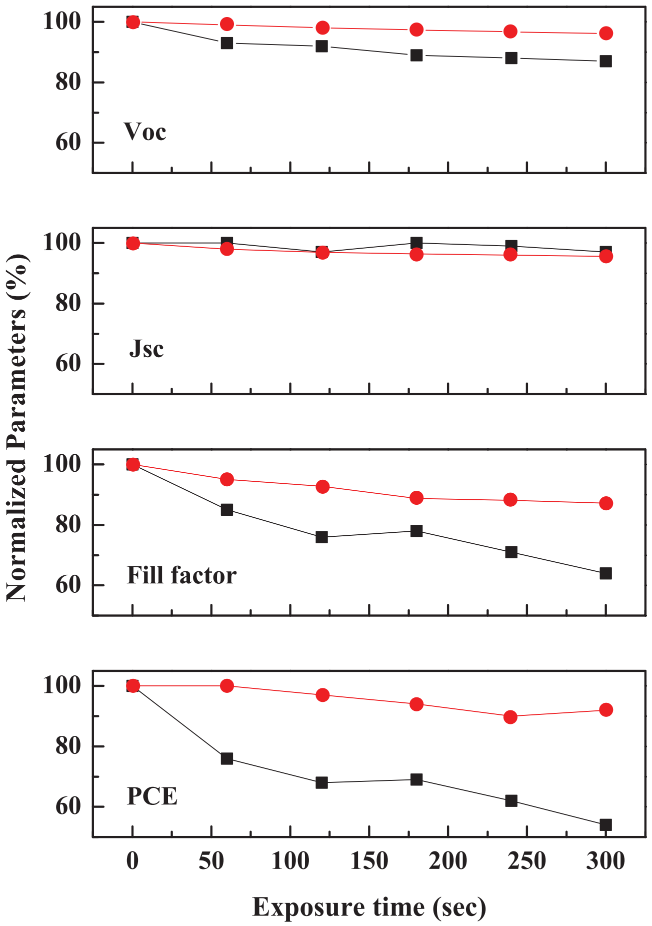

**Figure 6.** Normalized cell parameters according to the UV illumination time. (Black square: non-UV blocking TCO, red circle: UV blocking TCO).

showed that, though the relatively low efficiency, the UV blocking TCO is possible to improve the lifetime of OSC.

## Conclusions

In this study, we made an attempt at improving the lifetime of OSCs by UV protection. Without adding a passivation film/layer, we utilized conventional transparent electrode as an UV blocking TCO by controlling the deposition condition. The optimized conditions to deposit UV blocking TCO were obtained 40 W of power, 3 mTorr of working pressure and 40 sccm of Ar during 50 min with 10 w% Zn-doped $In_2O_3$ target. The UV blocking TCO was chemically stable during the fabrication process. When 30 mW/cm$^2$ of UV was illuminated on the OSC device fabricated with UV blocking TCO, the PCE decreased to 20% and PCE of OSC with non-UV blocking TCO decreased to 46% compared to the pristine devices. These results demonstrated the possibility of IZO TCO as an UV blocking TCO.

## Funding

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