Effect of pentacene/Ag anode buffer and UV-ozone treatment on durability of small-molecule organic solar cells

S Inagaki, S Sueoka and K Harafuji
Department of Electrical and Electronic Engineering, Ritsumeikan University, Kusatsu, Shiga 525-8577, Japan

Abstract. Three surface modifications of indium tin oxide (ITO) are experimentally investigated to improve the performance of small-molecule organic solar cells (OSCs) with an ITO/anode buffer layer (ABL)/copper phthalocyanine (CuPc)/fullerene/bathocuproine/Ag structure. An ultrathin Ag ABL and ultraviolet (UV)-ozone treatment of ITO independently improve the durability of OSCs against illumination stress. The thin pentacene ABL provides good ohmic contact between the ITO and the CuPc layer, thereby producing a large short-circuit current. The combined use of the abovementioned three modifications collectively achieves both better initial performance and durability against illumination stress.

1. Introduction
Organic solar cells (OSCs) are considered to be promising candidates for renewable energy applications because they possess several desirable properties such as flexibility, low cost, large size, and ease of fabrication. OSCs, however, still have two major disadvantages: low power-conversion efficiency ($\eta_p$) and a short lifetime. Several degradation mechanisms that contribute to the short lifetime of OSCs have been reported. In the course of OSC degradation, the current–voltage ($J–V$) characteristics frequently become distorted from an exponential diode curve to a curve with an S-shaped kink in the positive-bias region. This leads to decreases in the fill factor (FF) and in $\eta_p$ [1]. Several theoretical models have been proposed to explain the mechanisms responsible for the S-shaped kink in the curve, e.g., charge accumulation induced by the cathode buffer layer [2] and charge blocking originating from the presence of strong interface dipoles [3].

The effects of three types of stress, i.e., illumination, air exposure, and electrical stress, on device performances have been systematically examined in CuPc/fullerene ($C_{60}$) OSCs [4]. Understanding the degradation mechanisms resulting from illumination stress is of primary importance because OSCs generate power by receiving light energy. In pentacene/$C_{60}$ OSCs exposed to constant solar illumination, differences in the temporal changes in the $J–V$ characteristics are clearly present between devices kept in air, under vacuum, and under vacuum with an ultraviolet (UV) filter [5]. Under UV radiation, reorganization of pentacene near the indium tin oxide (ITO) substrate is considered to generate a gap that leads to a reduction in contact quality between ITO and pentacene. The interface conditions between ITO and the donor layer certainly play a decisive role in achieving durability under illumination.

One promising method for improving durability is the introduction of a thin layer of inorganic and organic materials between the ITO anode and the donor layer, called an anode buffer layer (ABL). The stability of OSCs under irradiation by light is reported to be markedly enhanced by insertion of a
MoO₃ ABL [6]. Organic ABLs also play various roles in OSC improvement, such as modification of the molecular orientation of donor, which enhances charge transport, adjustment of the work function (WF), and reduction of the potential-barrier height of hole transport. The S-shaped kink is suppressed under illumination upon insertion of a set of ultrathin Ag and thin pentacene layers [1]. Furthermore, UV-ozone treatment of the ITO surface is a useful technique for optimizing the surface conditions. This treatment eliminates organic contaminants, tunes the anode WF, and increases the hole-transport efficiency [7].

Although several surface modifications of ITO have been proposed to improve OSC performance, only few systematic studies have investigated the durability of OSCs against illumination. This study investigates the effects of two types of ABLs: ultrathin Ag and thin pentacene layers. Moreover, against illumination, the effect of UV-ozone treatment on the durability of small-molecule OSCs with an ITO/anode buffer/CuPc/C₆₀/bathocuproine (BCP)/Ag structure is investigated.

2. Experimental method

Figure 1 shows the schematic structures of three types of organic solar cells: Devices A–C. All three devices comprise a 20-nm-thick CuPc layer as the donor, a 40-nm-thick C₆₀ layer as the acceptor, and a 10-nm-thick BCP layer as the cathode buffer layer. Device A is a standard device. Device B has an additional ABL of a 3-nm-thick pentacene layer. Device C has an ABL composed of a 0.5-nm-thick Ag layer and 3-nm-thick pentacene layer. CuPc is purified three times via thermal gradient sublimation before use. The other organic materials are used as-purchased.

![Figure 1. Schematic structures of three types of organic solar cells.](image)

An ITO substrate with a thickness of 1600 Å is cleaned three times using ultrasonic treatment in detergent, deionized water, acetone, and ethanol, in this order, for 5 min each. Subsequently, a 10-min UV-ozone treatment is performed on the ITO surface with an intensity of 13.5 mW/cm². Organic materials comprising CuPc, C₆₀, and BCP are evaporated onto the ITO substrate at a rate of 0.5 Å/s under a pressure of less than 1.0 × 10⁻³ Pa. Pentacene is evaporated at a rate of 0.2 Å/s, the Ag cathode material is evaporated at a rate of 1.0 Å/s, and the ultrathin Ag anode buffer is evaporated onto the ITO substrate at a rate of 0.1 Å/s. The top Ag electrode is thermally evaporated via a 6 mm² stainless-steel mask with an active area of 2.4 × 2.5 mm².

The J–V measurements are performed using xenon lamp illumination at an intensity of 100 mW/cm² and an air mass 1.5 global spectrum (AM1.5G). All measurements are performed in air at room temperature. Repetitive illumination through the bottom ITO electrode is imposed on the device. Repetitive illumination refers to 100 cycles, each comprising 3 s of illumination and subsequent darkness maintained for 12 s. The repetition period, T, is 15 s. Device parameters are monitored as a function of the number of illumination cycles.

3. Experimental results and discussion

Table 1 summarizes the experimental results for the initial device parameters. Here, J∞ is the short-circuit current density and V∞ is the open-circuit voltage. Devices B and C with pentacene as an anode buffer have larger values of J∞ compared with Device A with no pentacene; this results in an increase in ηp. The effect of UV-ozone treatment on the initial performance is unclear.
Table 1. Initial device parameters for Devices A–C with and without UV-ozone treatment.

| Device | UV exposure time (min) | $J_{sc}$ (mA/cm²) | $V_{oc}$ (V) | $FF$ | $\eta_p$ (%) |
|--------|-----------------------|-------------------|-------------|------|-------------|
| A      | 0                     | 4.2               | 0.44        | 0.59 | 1.1         |
|        | 10                    | 4.2               | 0.44        | 0.57 | 1.0         |
| B      | 0                     | 4.8               | 0.46        | 0.58 | 1.3         |
|        | 10                    | 4.5               | 0.45        | 0.59 | 1.2         |
| C      | 0                     | 4.4               | 0.46        | 0.56 | 1.2         |
|        | 10                    | 4.4               | 0.43        | 0.54 | 1.0         |

Figures 2(a) and 2(b) show the $J$–$V$ dynamics for the 1st, 50th, and 100th cycles and changes in $J_{sc}$, $V_{oc}$, $FF$, and $\eta_p$ for Device A without UV-ozone treatment, respectively. The $J$–$V$ curve becomes sharply S-shaped during the 100th cycle. In addition, the decrease in the gradient of the $J$–$V$ curve in the first and fourth quadrants is substantial. This decreasing gradient indicates an increase in series resistance, $R_s$, at the ITO/CuPc interface. With increasing number of cycles, $\eta_p$ decreases significantly, accompanied by a large decrease in $FF$. After the 100th cycle, $FF$ and $\eta_p$ decrease by 40% and 50%, respectively, relative to their initial values, while $J_{sc}$ and $V_{oc}$ decrease by only 8% and 9%, respectively.

![Figure 2](image1.png)

**Figure 2.** Experimental results for Device A without UV-ozone treatment. (a) $J$–$V$ dynamics and (b) changes in $J_{sc}$, $V_{oc}$, $FF$, and $\eta_p$ as a function of the number of illumination cycles.

Figures 3(a)–(c) depict the $J$–$V$ dynamics for Device B without and with UV-ozone treatment, and Device C without UV-ozone treatment, respectively. The $J$–$V$ curve for Device B without UV-ozone treatment becomes sharply S-shaped during the 100th cycle. Conversely, the $J$–$V$ curve for Device B with UV-ozone treatment does not show the S-shaped kink; however, the gradient of the $J$–$V$ curve in the first and fourth quadrants decreases slightly with increasing number of cycles. The $J$–$V$ curve for the first cycle for Device C without UV treatment is almost coincident with that for the 100th cycle; i.e., only slight degradation occurs after 100 cycles.

![Figure 3](image2.png)

**Figure 3.** Experimental results of $J$–$V$ dynamics. (a) Device B without UV, (b) Device B with UV, and (c) Device C without UV.
Figure 4 shows the experimental results for Device C with UV-ozone treatment, with the $J$–$V$ dynamics depicted in Figure 4(a). The $J$–$V$ curve for the first cycle is almost completely coincident with that for the 100th cycle. Figure 4(b) shows the changes in $J_{sc}$, $V_{oc}$, $FF$, and $\eta_p$. The graph demonstrates that $\eta_p$ decreases by only 7% at the 100th cycle, accompanied by a slight decrease in $V_{oc}$ and $FF$. Moreover, $J_{sc}$ remains very close to its initial value even during the 100th cycle.

Figure 4. Experimental results for Device C with UV-ozone treatment. (a) $J$–$V$ dynamics, and (b) changes in $J_{sc}$, $V_{oc}$, $FF$, and $\eta_p$ as a function of the number of cycles.

A separate atomic force microscopy analysis of a 2-nm-thick CuPc on ITO indicates that the heat generated by the UV component of illumination possibly causes a change in the CuPc crystal structure near the ITO/CuPc interface; this deteriorates the quality of the electrical contact. The present study demonstrates that two types of surface modifications on ITO, i.e., an ultrathin Ag layer and UV-ozone treatment, independently and collectively improve the durability of OSCs against illumination stress. The thin pentacene layer itself does not lead to any durability improvement but its combined use with the Ag layer and UV-ozone treatment yields better initial device performance. Using scanning electron microscopy, we separately observed that the Ag layer was discretely deposited onto ITO. Resonant light absorption in Ag clusters may accumulate trapped electrons near the interface, reduce the barrier height of hole transport, and suppress the S-shaped kink. The UV-ozone treatment creates hydrophilic conditions with the OH functional groups on ITO [8]. The attraction between H atoms from the OH functional groups and \pi electrons from the CuPc molecules might prevent disorder in the CuPc crystals during illumination.

4. Conclusion

The thin pentacene layer on ITO provides good ohmic contact at the ITO/CuPc interface, thereby resulting in a large short-circuit current. An ultrathin Ag layer and UV-ozone treatment of ITO independently and collectively improve the durability against illumination stress.

References
[1] Oida T and Harafuji K 2013 Japan. J. Appl. Phys. 52 011601
[2] Wang J C, Ren X C, Shi S Q, Leung C W, Chan P K L 2011 Org. Electron. 12 880
[3] Kumar A, Sista S, Yang Y 2009 J. Appl. Phys. 105 094512
[4] Harafuji K, Sato H, Matsuura T, Omoto Y, Kaji T, Hiramoto M 2014 Japan. J. Appl. Phys. 53 122303
[5] Sullivan P, Jones T S 2008 Org. Electron. 9 656
[6] Kanai Y, Matsushima T, Murata H 2009 Thin Solid Films 518 537
[7] Sugiyama K, Ishii H, Ouchi Y, Seki K 2000 J. Appl. Phys. 87 295
[8] Farina F E and Harafuji K 2015 KJF Int. Conf. on Organic Materials for Electronics and Photonics (Jeju).