

Current-voltage characteristics of organic photovoltaic cells following deposition of cathode electrode

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The current-voltage characteristics of benzoporphine-fullerene solar cells were measured subsequent to the deposition of Al as a cathode material. Even in vacuum, a shift in the open circuit voltage was observed at 20 min after Al deposition. Moreover, the displacement of inert gases (N₂ or Ar) in the evaporation chamber enhanced the photovoltaic parameters. The power conversion efficiency was increased by 24% over the initial characteristics (from 1.04% to 1.29%), which indicates that the structure of the organic-metal interface changed rapidly after Al deposition, even if the process was performed in an air-free glovebox. © 2010 American Institute of Physics. [doi:10.1063/1.3516469]

Organic photovoltaic (OPV) cells are expected to be the next-generation solar energy conversion devices that promise to be light, flexible, and printable. Control of the charge transport at the heterointerfaces of multilayered OPV structures is one of the most important issues for the improvement of OPV cells.¹⁻⁹ It has been reported that the insertion of buffer layers between the organic layer and the electrodes improves the device performance.²⁻⁹ For example, the insertion of a LiF layer that is several angstrom thick between the organic layer and the Al electrode is one of the most effective ways to improve performance.⁸ However, the detailed effects and mechanism of the improvement of parameters are still not entirely clear. In addition, heterointerfaces can be easily affected by external factors over time,¹⁰⁻¹² which makes evaluation even more difficult. In order to clarify the heterointerface phenomena, it is necessary to evaluate OPV cells soon after the formation of the interface (vacuum deposition of a metal electrode). In this study, we report on the time-dependent changes of the current-voltage (*J-V*) characteristics from immediately after Al cathode deposition until the time when the device is exposed to N₂ gas at atmospheric pressure.

The OPV cell configuration used was indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS)/tetrabenzoporphyrin (BP)/[6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM)/Al. The BP/PCBM materials were selected because they have both high stability and high power conversion efficiency (PCE) of 5%–7% with an optimized device structure. The fabrication process of OPV cells utilizing BP/PCBM has already been reported in detail;¹³ therefore, only a brief outline of the fabrication process is described here. The p-i-n junction photovoltaic layers (100 nm) were fabricated on ITO (200 nm)/glass substrates coated with PEDOT:PSS (20 nm). Each p-, i-, and n-layer was stacked by repeat of spin-coating and heating at 250 °C. The device was then transferred into a chamber for Al deposition. In order to evaluate the photovoltaic parameters of the devices immediately after Al deposi-

tion, the solar simulator and measurement system were attached to the evaporation chamber (Fig. 1). A measurement probe was contacted to the ITO electrode and another one was contacted to the area that was to be deposited with Al to allow measurement soon after Al deposition. Prior to evacuation, the evaporation chamber was displaced with an inert gas at least several times to prevent residual gases, such as oxygen. An Al layer (100 nm) was deposited through a shadow mask in 3×10^{-4} Pa. The effective area of the devices was 0.06 cm². The *J-V* characteristics were then measured using a Keithley 2400 source measurement unit under vacuum or atmospheric pressure with 80 mW/cm² light illumination.

Figure 2(a) shows the *J-V* characteristics measured just after Al deposition (dashed line) and following 30 min (solid line). Although the characteristics have almost the same PCE of approximately 1%, each OPV parameter [open circuit voltage (*V*_{OC}), short current density (*J*_{SC}), and fill factor (FF)] was shifted slightly, as shown in Table I.

*V*_{OC} increased from 0.42 to 0.45 V, while *J*_{SC} and FF decreased from 4.23 to 4.10 mA/cm² and from 0.47 to 0.45 for 30 min, respectively. The time-dependent changes of each OPV parameter are shown in Fig. 2(b). The parameter shifts were reproducible and were not due to thermal effects

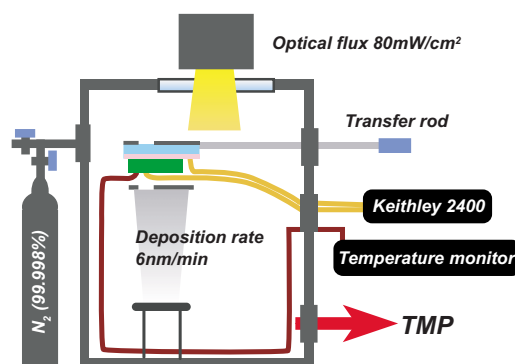


FIG. 1. (Color online) Schematic representation of the deposition and measurement setup.

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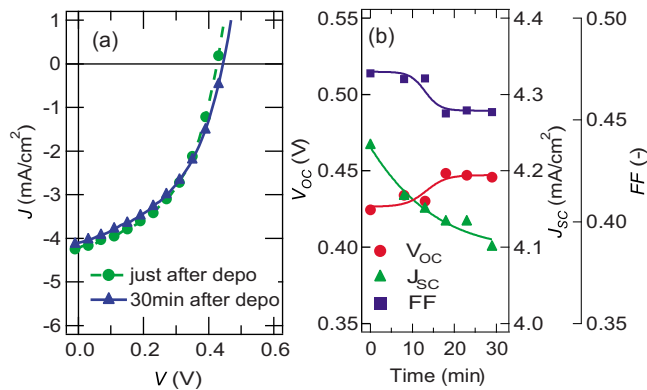


FIG. 2. (Color online) (a) J - V characteristics of the OPV cell under 80 mW/cm² light (dotted line) just after Al deposition and (solid line) following 30 min after Al deposition. (b) Behavior of the photovoltaic parameters: V_{OC} (●), J_{SC} (▲), and FF (■).

by Al deposition because the temperature change of the OPV cells was maintained at less than ± 1 °C. The origin of the parameter shifts is not clear but appears to be related to the relaxation phenomenon at the organic-inorganic interface. From the experimental results, this relaxation phenomenon reached the steady state approximately 20 min after Al deposition. Hereafter, this relaxation phenomenon is referred to as the aging effect. The detail of such aging effect is now under investigation.

Figure 3(a) shows the J - V characteristics before (30 min after Al deposition; dashed line) and 30 min after displacement of N₂ (99.998%) gas into the vacuum chamber (solid line) to atmospheric pressure. The OPV performance was clearly improved by the introduction of N₂ gas. The time-dependent changes of each OPV parameter are shown in Fig. 3(b). Here, the finished time of N₂ displacement is redefined as 0 min. Large shifts were observed in all parameters, but such shifts became saturated for 30 min after the N₂ displacement. V_{OC} changed from 0.45 to 0.52 V and the increase of V_{OC} reached 0.10 V in the total procedure. J_{SC} and FF also increased from 4.10 to 4.30 mA/cm² and from 0.45 to 0.46, respectively. The resulting PCE was increased by 24% from the first characterization, as shown in Table I. J_{SC} and FF exhibited different trends under N₂ gas atmosphere compared with that under vacuum, which implies a different mechanism under each condition. UV-vis spectrum and x-ray diffraction analysis were carried out on the device before and after Al evaporation. However, no change was observed in each data (not shown). These results indicate that the change of J - V characteristics is not due to the effect of the bulk condition but due to the interfacial condition.

The results could be explained by the formation of AlO_x at the organic-inorganic interface. We assume that the formation of AlO_x is caused not by oxygen included in the organic layer (internal oxidation), but by oxygen from the introduced

TABLE I. The photovoltaic parameters during the procedure.

	V_{OC} (V)	J_{SC} (mA/cm ²)	FF	η (%)
3×10^{-4} Pa	0.42	4.23	0.47	1.04
(30 min)	0.45	4.10	0.45	1.04
Introduction of N ₂ gas				
1×10^5 Pa	0.52	4.30	0.46	1.29

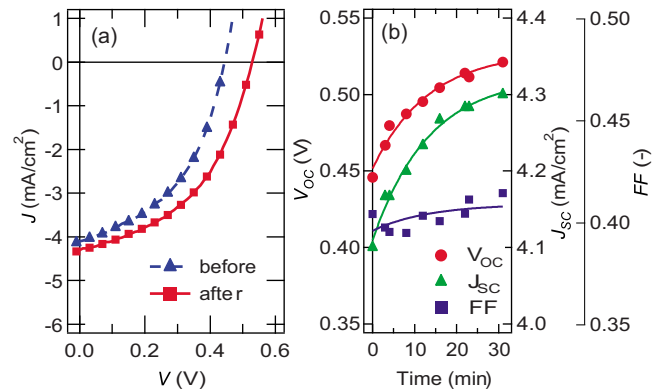


FIG. 3. (Color online) (a) J - V characteristics of the OPV cell under 80 mW/cm² light (dotted line) before (at 30 min after Al deposition) and (solid line) 30 min after the introduction of N₂ gas. (b) Behavior of photovoltaic parameters: V_{OC} (●), J_{SC} (▲), and FF (■).

dry N₂ gas (external oxidation), because if the formation of AlO_x is caused by internal factors, similar shifts (increased J_{SC} and FF) should be observed even under vacuum. To ensure the effect of external oxidation on each OPV parameter, the J - V characteristics were also investigated after the introduction of an inert gas with different purity (Ar: 98.000%). The amount of V_{OC} shift was the same as that in the N₂ procedure, but the speed of shift in V_{OC} was dependent on the purity of the inert gas. In the case of N₂ gas (99.998%), it took 30 min to reach the saturated value. On the other hand, it took only 10 min in the Ar procedure. Thus, low degree of purity accelerated the oxidation of Al. Surprisingly, our results indicated that very slight amount of impurities affect the characteristics of OPV cells.

The most striking result in this experiment is the widely shift in V_{OC} . To clarify the effect of AlO_x on V_{OC} , the J - V characteristics were investigated in the dark. Figure 4 shows the J - V characteristics measured in the dark before and after the introduction of dry N₂ gas into the vacuum chamber. In order to better visualize the changes, the current density is displayed with a logarithmic scale. Dry N₂ gas causes a lowering of the current density within the overall range and the shoulder at low bias is diminished from 0 to 0.3 V. The J - V characteristics in the dark were then analyzed using the following equation:

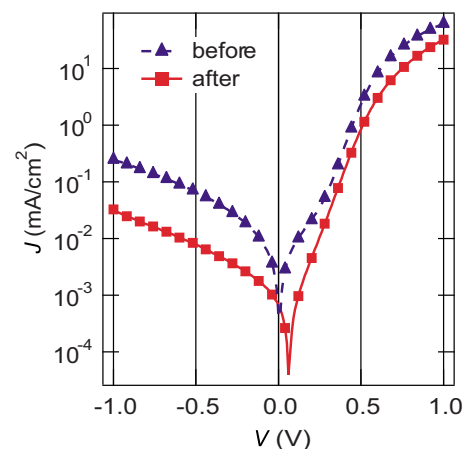


FIG. 4. (Color online) J - V characteristics of the OPV cell in the dark (dotted line) before (at 30 min after Al deposition) and (solid line) 30 min after the introduction of N₂ gas.

$$i = i_0 \left[\exp\left(\frac{qV}{n_d k T_b}\right) - 1 \right], \quad (1)$$

where i_0 is the reverse saturated current, n_d is the diode factor, T_b is the device temperature, q denotes the elementary charge, k represents the Boltzmann constant, and V is the applied voltage.¹⁴ It follows that the lowering of current density and diminishment of the shoulder at low bias caused the decrease of the i_0 and n_d values, respectively. V_{OC} is expressed in the following equation using i_0 and n_d .¹⁵

$$V_{OC} \approx \frac{n_d k T_b}{q} \ln\left(\frac{i_{ph}}{i_0}\right), \quad (2)$$

where i_{ph} is the photocurrent. This formula indicates that the widely V_{OC} shift in this experiment was due to the lowering of i_0 induced by high rectification. It is well known that the interface sensitively affects the OPV performances. For example, buffer layer acts as a dipole moment (LiF),^{8,16} a exciton blocking layer [bathocuproine (BCP)],¹⁷ and a lowering of the work function [tris(8-hydroxyquinolinato) aluminum (Alq3)].¹⁸ To reveal the mechanism of V_{OC} shift, we plan to evaluate i_0 and n_d for the device with such buffer layers (LiF, BCP, and Alq3).

To conclude, the rapid change in the inner structure of OPV cells was revealed, even under vacuum. V_{OC} increased and J_{SC} and FF decreased 30 min after Al deposition (aging effect). On the other hand, all of the OPV parameters (V_{OC} , J_{SC} , and FF) increased by the introduction of N_2 gas. The reason for this change is not yet fully understood, but it can be well explained by the formation of AlO_x . The formation of AlO_x is caused by the reaction of oxygen with the intro-

duced dry N_2 gas (with purity of 99.998%), which implies that very slight impurities in the inert gas can affect the characteristics of OPV cells.

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