Photocarrier Generation in Organic Thin Film Solar Cells

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1. Introduction

Organic solar cells have many advantages such as low material cost, easy fabricating process, light and flexible structure. They can be classified into dye-sensitized solar cell [1, 2] and organic thin film solar cells [3 - 5]. The dye-sensitized solar cells are reported to show efficiency as high as 10%. However, they have the structural drawback in that they usually contain liquid electrolytes. Organic thin film solar cells, which are inherently all-solid devices, have had a problem of low energy conversion efficiency. Although their efficiency has gradually been improved by the introduction of new structures, such as bulk-heterojunction structure made of a conducting polymer and C₆₀ derivatives [4] and multilayer structure consists of low molecular weight materials [5], the efficiency is still not high enough for practical applications. The problem of the thin film solar cells lies mostly in their low photocurrent density.

In order to find approaches to increasing the efficiency of the solar cells, it is crucial to obtain the insights into the mechanisms of the organic thin film solar cells. Hence, we studied the mechanism of photocarrier generation in the organic thin film solar cells with the simplest structure, i.e, ITO/Cu-phthalocyanine (CuPc)/a perylene derivative (PV) or C_{60}/Ag , which were reported by Tang [3].

2. Experimental

Fig.1 shows the typical structure of the organic thin film solar cells we employed in the present study. A PE-DOT/PSS layer (about 100 nm) was deposited by spin-coating an aqueous solution of PEDOT/PSS on the precleaned ITO (Indium Tin Oxide) substrate in order to modify the ITO surface. CuPc (30 nm) and PV (or C₆₀, 60 nm) were vacuum deposited onto the PEDOT layer under high vacuum (10⁻⁶ Torr). Then a metal electrode (40 nm) was vacuum deposited in another chamber.

Current-voltage (I-V) characteristics were measured under illumination with a solar simulator (AM1.5, 100mW/cm²) through the ITO side. Action spectra of the photocurrent were measured with monochromatic light from the white light of 500 W Xenon lamp combined with a monochromator and a light chopper (frequency: 400 Hz). The photocurrent signal was amplified with a lock-in amplifier. Impedance spectroscopy measurements were performed with an impedance analyzer. All the measurements were performed in a vacuum at room temperature.

3. Results and Discussion

Fig.2 shows the action spectra measured for the device with the structure of ITO/PEDOT:PSS/CuPc(30nm)/PV (60nm)/Ag at different potentials. For comparison, the absorption spectra of CuPc and PV are shown by curves (a) and (b). Under reverse biases, the action spectra were similar to the summation of the absorption spectra of both layers, as shown in curve (c). This result indicates that both of the excitons formed in the CuPc and PV layers contribute to the photocurrent. Under forward biases, the photocurrent action spectra changed drastically, which were affected by the filter effect of the CuPc layer, as seen in curve (d). This result indicates that the photocurrent under the forward biases is chiefly generated by the photoexcitation of the PV layer [6]. The same phenomenon was observed when C₆₀ was used in place of PV.

Fig.3 shows the capacitance-voltage (C-V) characteristic of the device consisting of CuPc(30nm) and PV(60nm). The capacitance of the cell under forward bias was larger than that under reverse bias. This suggests that holes enter into the CuPc layer and were accumulated near the CuPc/PV junction under forward bias.

From the analysis of the photocurrent action spectra and C-V characteristic, it is suggested that the photocurrent observed under the forward biases is caused chiefly by the photoexcitation of PV or C_{60} and that the PV or C_{60} in the excited state reacts with to the holes accumulated in CuPc

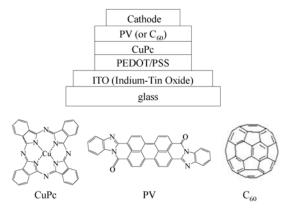


Fig. 1 Typical structure of an Organic Thin Film Solar Cell

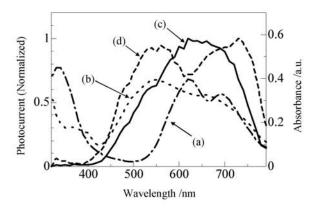


Fig.2 Absorption spectra of (a) CuPc and (b) PV films and action spectra for the device with a CuPc/PV junction measured under (c) reverse and (d) forward biases.

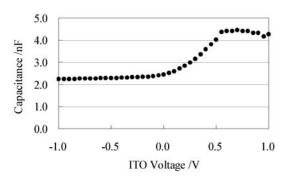


Fig.3 C-V characteristic of the device with the structure of ITO/PEDOT:PSS/CuPc(30nm)/PV (60nm)/Ag (active cell area: 4mm²). The modulation frequency was 1000Hz.

near the CuPc/PV (or C_{60}) interface, leaving a hole in the PV or C_{60} layer, as shown in Fig. 4(b). Since the positive charge in CuPc will be supplied from the ITO electrode, the photocurrent in the forward direction flows continually.

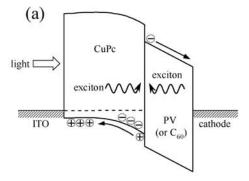
Although the forward photocurrent cannot be utilized for the output from the solar cells, such a spectral analysis will be a useful method for deepening the on understanding of the charge distribution and charge separation process in the organic layers.

4. Conclusions

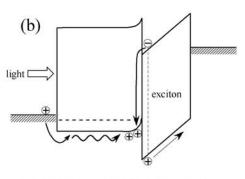
Organic solar cells with an organic/organic heterojunction showed photocurrents not only under the reverse bias but also under the forward bias. The photocurrent under the reverse bias is attributed to the carrier separation from the excitions at the heterojunction. On the other hand, the photocurrent under the forward bias is attributed to the electron transfer from the PV (or C_{60}) exciton to the positive charge accumulated in the CuPc layer near the junction.

Acknowledgements

This work was supported by a Grant-in Aid for Scientific



 $CuPc + PV + exciton \rightarrow CuPc^+ + PV^-$



 $CuPc^+ + PV^*(exciton) \rightarrow CuPc + PV^+$

Fig. 4 A model for photocarrier generation in the device with a CuPc/PV (or C_{60}) junction under (a) short-circuit condition and (b) forward bias.

Research on Priority Arias (417) from the Ministry of Education, Culture, Sports, Science and Technology of the Japanese Government. One of the authors T.Osasa express his special thanks for the center of excellence (21COE) program "Creation of Integrated EcoChemistry" of Osaka University.

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