Formation of bulk-heterojunction structure in organic bilayer solar cells by heat treatment

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1. Introduction

Organic thin-film solar cells have attracted much attention because of their potential for low-cost fabrication. Their easy production by printing or vacuum-sublimation methods, which enable low-cost and large-scale fabrication, is one of the advantages of these devices. Due to these fabrication methods, organic thin-film devices can be fabricated on plastic sheets.

Organic solar cells with a flat bilayer structure [1] generate charge carriers from the excitons at the interface between the two organic layers consisting of electron-donor and electron-acceptor compounds. However, the diffusion length of excitons in Cu-phthalocyanine (electron donor) and perylene derivative (electron acceptor) layers, which are typical materials for the devices, is only about 10 nm [2]. This poses a serious problem of low photocurrent densities in these devices. To overcome this problem, a "bulk-heterojunction" structure has been proposed [3]. This structure is considered to be effective to enlarge the contact area between the two layers and to generate charge carriers. Normally, this structure is formed by mixing soluble fullerene derivative with conducting polymer. However, the simple mixing of two components does not necessarily means the formation of separated paths for holes and electrons to the electrodes, which is indispensable for the generation of photocurrent. The content of the fullerene derivative in the polymer is usually high. This is probably because such a large amount of fullerene compound is necessary to form the carrier path.

We have demonstrated that the bulk-heterojunction structure can be generated in organic solar cells with small-molecules by applying heat treatment to some kinds of organic layers. The structure was formed by the infiltration of low-melting molecules into the layer of high-melting molecules. As a result, photocurrent of the cell was greatly improved. Here, we report the effect of morphological changes of organic bilayers on the solar cell properties.

2. Experimental

Typical structure of organic thin film solar cells we employed in the present study is shown in Fig. 1. A PEDOT/PSS layer (30 nm) was formed by spin-coating an aqueous solution of PEDOT/PSS on the precleaned ITO (Indium Tin Oxide) substrate. Then, N,N'- diphenyl-N,N'bis(3-methylphenyl)-1,1'-deiphenyl-4,4'-diamine (TPD, 30 nm) and C_{60} (60 nm) layers were vacuum deposited onto the PEDOT layer under high vacuum (10⁻⁶ Torr). After depositing these organic layers, the substrate was heated at several temperatures for 15 minutes in the air. Finally, Ag electrodes were vacuum-deposited across the ITO electrodes at right angles.

Current-voltage (I–V) characteristics of the solar cells were measured in vacuum with a source meter (KEITHLEY, SMU 2400) under simulated AM1.5 radiation light (100 mW/cm²) at room temperature. Surface morphology of the organic film was observed with an optical microscope (OLYMPUS, BX-51). Cross-sectional microstructure of organic layers was observed with a Scanning Electron Microscope (HITACHI, S-5200).

3. Results and Discussion

One of the essential parameters determining the energy conversion efficiency of solar cells is open-circuit voltage (V_{oc}). In general, V_{oc} of organic solar cells with small-molecules is about 0.5 V. However, we have found that V_{oc} of as high as 0.8 V is obtained by the solar cell consisting of TPD and C₆₀. On the other hand, this cell shows low photocurrent density of about 1.0 mA/cm² under AM 1.5, 100 mW/cm² irradiated light, and as a result, the energy conversion efficiency on this cell is low (about 0.4 %).

After the application of heat treatment, the photocurrent of the cells consisting of TPD and C_{60} was greatly improved. The increase of photocurrent was observed when the films were treated at temperatures between 120 and 160



Fig. 1 Typical structure of an organic thin film solar cell.



Fig.2 I-V characteristics of organic solar cells with TPD/C₆₀ junction under AM1.5, 100 mW/cm² simulated light. Organic layers were heated with different temperatures for 15 minutes in the air.

°C. Fill factor (F.F) was also improved by the heat treatment. On the other hand, V_{oc} was lowered by the heat treatment, especially when the temperature was higher than 140 °C. The best performance of the cells was obtained by heat treatment at 140 °C and the efficiency was 1.1 % (Fig. 2). Such an improvement in the performance by the heat treatment was unique to the combination of TPD (or other aromatic amines) and C₆₀. No improvements in the performance were observed in the cells consisting of Cu-phthalocyanine (CuPc) and C₆₀, or in the cell consisting of TPD and a perylene derivative (PV).

Optical microscopy shows that embossed structures with a height of several hundred nanometers for the TPD/C₆₀ treated at temperatures above 120 °C, as shown in Fig. 3. The temperature at which embossed structures appeared was nearly the same as the temperature at which the photocurrent of the cells started to increase. To elucidate the microstructure of the organic layers, cross-sectional SEM pictures of organic layers after heat treatment were taken (Fig. 4). From this picture, TPD and C₆₀ layers were shown to diffuse each other near the interface between these layers. Hence, the increased photocurrent is attributed to the formation of a kind of the bulk-heterojunction structure, which has been reported for polymer-based solar cells [3] or p-i-n solar cells made by co-deposition of electron-donor and electron-acceptor compounds [4].

4. Conclusions

Photocurrent of organic bilayer solar cells made of stacked TPD and C_{60} layers was greatly improved by the application of heat treatment, leading a maximum energy conversion efficiency of 1.1 % under AM 1.5, 100mW/cm² simulated solar light. After heat treatment of organic layers above 120 °C, TPD and C_{60} layers diffused each other and formed the bulk-heterojunction structure. This morphological change is attributed to the increased photocurrent and energy conversion efficiency.

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Fig. 3 Optical microscopic image of the surface of the organic layer (a) and those after heat treatment at 80 $^{\circ}$ C (b), 120 $^{\circ}$ C (c) and 140 $^{\circ}$ C (d).



Fig. 4 Cross-sectional SEM image of a sample with a structure of glass/ITO/PEDOT:PSS(30 nm)/TPD(100 nm)/C₆₀(100 nm). The sample was heated at 140 °C for 15 minutes in the air after deposition.

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