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Improved Characteristics in Organic Thin-Film Solar Cells Based on Conducting Polymer : Fullerene Composites

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Since the discovery of the suppression of photoluminescence [1], photoinduced electron transfer [2] and enhancement of photoconductivity [3] in a composite of conducting polymer and C₆₀, the application of a conducting polymer-fullerene system to an organic thin-film solar cell has attracted much interest. Photovoltaic cells using organic semiconductors, such as polymers and small-molecular-weight materials with an extended π -conjugation, have been investigated actively.

For effective dissociations of excitons, a p/n small-molecule layered cell [4], conducting polymer-C₆₀ composite [3,5] and layered [6,7] cells using two organic semiconductors were reported. The dissociations of excitons are enhanced by transferring the positive or negative charges of excitons generated by photoabsorption in an organic semiconductor to the other semiconductor at the interface between a donor and an acceptor. However, there is the restriction of the contact area of the donor/acceptor interface in the layered cell, and the electron transfer by the isolated dispersion of C₆₀ is restricted in the conducting polymer-C₆₀ composite cell. It is significant to enhance both the efficiency of the carrier generation involved with exciton dissociation at the donor/acceptor interface with a large contact area and the efficiency of the carrier transfer to positive and negative electrodes.

Therefore, an interpenetrating network in the polymer devices and a codeposited layer in the small molecule devices were developed for organic photovoltaic devices [8,9], and recently, we have developed a newly method for the fabrication of the donor-acceptor interpenetrating condition [10-12]. Semilayered structures using a weakly dissoluble combination of a solvent and an underlayer material, which maintain the bilayer structure and interpenetrate at the interface of the donor and acceptor layers, were fabricated. In these cells, high external quantum efficiencies (EQEs) were obtained because of the efficient exciton dissociation at the interpenetrating interface and the efficient carrier transport by each continuous pathway between the fullerene molecules for electrons and between the conducting polymers for holes.

In this paper, we report on the improvement of characteristics of photovoltaic cells based on conducting polymer and fullerene composites. The absorption spectra of the composite films changed remarkably before

and after annealing, and the photovoltaic properties of the cells with large amount of fullerenes in the composite films were enhanced by the annealing at optimum temperature.

The molecular structures of regioregular poly(3-hexylthiophene) (PAT6) and {6}-1-(3-(methoxycarbonyl)propyl)-[5]-1-phenyl-[5,6]-C61 (PCBM) and the photovoltaic cell structure of ITO/poly(3,4-ethylene dioxothiophene):poly(styrenesulfonate) (PEDOT:PSS)/PAT6:PCBM/Al used in this study are shown in Fig. 1. The PEDOT:PSS layer was fabricated by spin-coating onto an ITO-coated quartz substrate with a sheet resistance of $10 \Omega/\square$, then the film was dried for 5 minutes at 100°C in an oven. A composite solution of PAT6:PCBM was spin-coated onto the PEDOT:PSS layer in Ar atmosphere. As a counterelectrode to the ITO electrode, a Al layer was deposited by thermal evaporation through a shadow mask onto the PAT6:PCBM layer at a pressure of approximately 10^{-4} Pa, and the cell was annealed on a hot plate. The active area of each photovoltaic cell was $2 \times 2 \text{ mm}^2$. In this cell, the ITO and Al electrodes collected holes and electrons, respectively.

The absorption spectra of the composite thin films spin-coated on quartz substrates were measured using a Shimadzu UV-3150 spectrophotometer.

The current-voltage characteristics were measured with a high-voltage-source measurement unit (Keithley 237) under irradiation of a white light (AM1.5 , $100 \text{ mW}/\text{cm}^2$). From the current-voltage characteristics under irradiation, the fill factor (FF) and energy conversion efficiency (η_e) were estimated using the following definitions: $\text{FF} = I_{\text{max}} V_{\text{max}} / I_{\text{sc}} V_{\text{oc}}$, $\eta_e = I_{\text{sc}} V_{\text{oc}} \text{FF} / P_{\text{in}}$, where I_{max} and V_{max} are the current and voltage for the maximum output power, I_{sc} is the short-circuit current, V_{oc} is the open-circuit voltage, and P_{in} is the intensity of the incident light.

The EQE spectra were measured under the short-circuit condition using an electrometer (Keithley 617S). The spectral responses of the cells were corrected by measuring the calibration spectrum of a UV-enhanced Si photodiode placed at the sample position. The EQE was estimated using the following definition: $\text{EQE} (\%) = I_{\text{sc}} \times 1240 \times 100 / (\lambda (\text{nm}) \times P_{\text{in}})$, where λ is the wavelength of incident light. For all photovoltaic cells, the incident light was irradiated from the ITO electrode side and the measurement was carried out in vacuum.

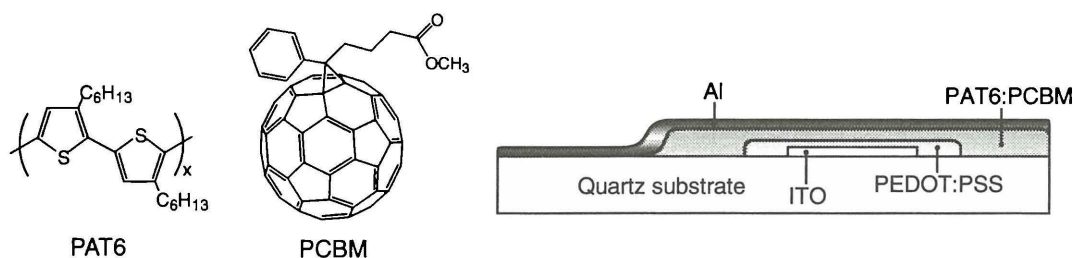


Fig. 1. Molecular structures of PAT6 and PCBM and the photovoltaic cell structure of ITO/PEDOT:PSS/PAT6:PCBM/Al.

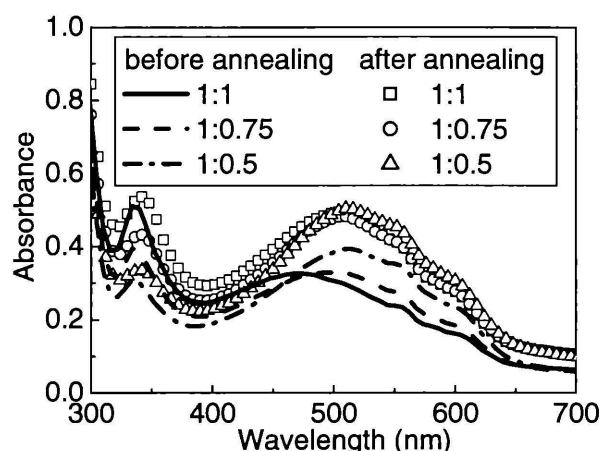


Fig. 2. Absorption spectra of the PAT6:PCBM composite thin films before and after annealing at 150 °C for 5 minutes.

Figure 2 shows the absorption spectra of the PAT6:PCBM composite thin films before and after annealing at 150 °C for 5 minutes on hot plate in Ar atmosphere. In here, the composite ratios of the two materials were 1:1, 1:0.75 and 1:0.5 by weight for PAT6:PCBM. The absorption peaks at the wavelength of around 340 nm related to PCBM were not changed before and after annealing. On the other hand, the absorption intensities were enhanced in the wavelength longer than 400 nm. Especially, the changes of the absorption spectra of the composite films with high concentration of PCBM were remarkable, and the wavelengths of the absorption peaks were red-shifted.

The EQE spectra of the photovoltaic cells with PAT6:PCBM composite ratio of 1:0.75 before and after annealing at 125 and 150 °C for 5 minutes are shown in Fig. 3. The EQE of the cell after annealing at 125 °C was enhanced at whole wavelength range. This enhancement could be explained by the efficient transport of electrons on PCBM network. After the annealing, the phase segregation between the conducting polymers and the fullerenes through the aggregation or the crystallization is progressed in the composite layer. The phase

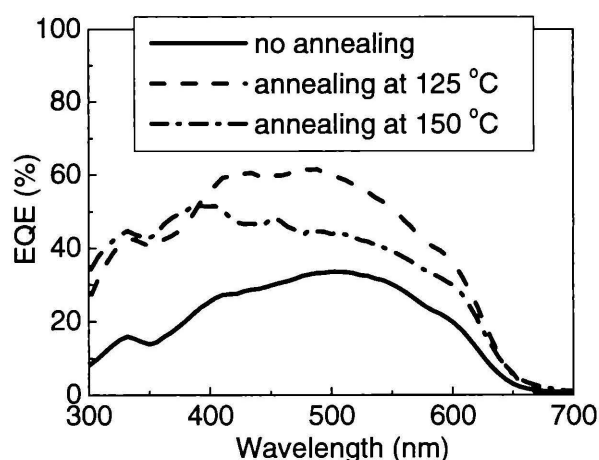


Fig. 3. EQE spectra of the photovoltaic cells with PAT6:PCBM composite ratio of 1:0.75 before and after annealing at 125 and 150 °C for 5 minutes.

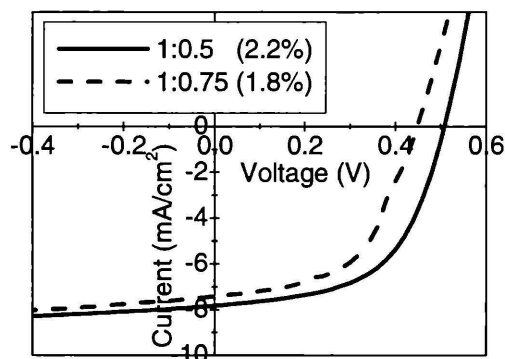


Fig. 4. Current-voltage characteristics of the photovoltaic cells under white light (AM1.5, 100 mW/cm²).

segregated bi-continuous network enhanced the efficiency of transport of the electrons between fullerene molecules and the holes between conducting polymers.

Figure 4 shows the current-voltage characteristics of the photovoltaic cells under white light (AM1.5, 100 mW/cm²). The energy conversion efficiency (η_e) of 2.2% was obtained in the cell with composite ratio of 1:0.5; V_{oc} : 0.51 V, I_{sc} : 7.82 mA/cm² and FF: 0.56.

In conclusion, photovoltaic cells consisting of the conducting polymer and fullerene composite were examined. Significant changes in absorption spectra of the composite films with large amount of fullerenes before and after annealing were observed and photovoltaic properties of the cells were enhanced by the annealing at optimum temperature.

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