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Morphology of F8T2/PC₇₁BM Blend Film as Investigated by Scanning Transmission X-ray Microscope (STXM)

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Clarification of the morphology of bulk heterojunction (BHJ) is indispensable for true comprehension of the organic solar cells. Here, we performed scanning transmission X-ray microscopy (STXM) for a poly-(9,9-dioctylfluorene-co-bithiophene) (F8T2)/[6,6]-phenyl C71-butyric acid methyl ester (PC₇₁BM) blend film annealed at various temperatures (T_{an}). We found that the fullerene concentration within the polymer-rich domain decreases with T_{an} while the domain size (~230 nm) is essentially unchanged. We will discuss the interrelation between the film morphology and the photovoltaic performance.

Keywords organic photovoltaic cell; scanning transmission X-ray microscope; domain size; fullerene mixing

Introduction

Scanning transmission X-ray microscope (STXM) around the carbon K-edge is a powerful tool to reveal the molecular mixing [1–6] within the nano-domains in the BHJ organic solar cells. For example, Collins *et al.*[3] revealed that

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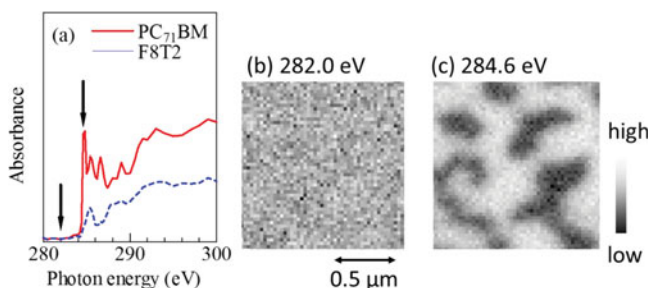


Figure 1. (a) X-ray absorption spectra around the carbon K-edge of PC₇₁BM (solid curve) and F8T2 (broken curve). X-ray absorption images of F8T2/PC₇₁BM blend film annealed at 240°C at (b) 282.0 and (c) 284.6 eV. The brightness represents the absorbance.

a poly-[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-bA] dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b] thiophenediyl] (PTB7)/ PC₇₁BM blend film consists of a pure fullerene domain and a mixed domain of PTB7/PC₇₁BM (70 : 30 wt %).

In order to investigate the intra-domain structure, however, one had to enlarge the domain size by thermal annealing and/or chemical admixture because the spatial resolution of STXM is low (\sim several tens nm).

Among the donor polymers, F8T2 belongs to the class of liquid-crystalline semi-conducting polymers. Significantly, the F8T2/PC₇₁BM blend films form periodic large domains (\sim several hundreds nm).[7] The F8T2/PC₇₁BM solar cell shows a power conversion efficiency (PCE) of 2.23%.[8] Yasuda *et al.*[7] systematically investigated the photovoltaic properties of F8T2/PC₇₁BM (33 : 67 wt. %) solar cells with respect to the annealing temperature (T_{an}): PCE decreases from the optimal value ($=2.28\%$) at $T_{\text{an}} = 80^\circ\text{C}$ to 0.81% at 240°C . Yonezawa *et al.*[9] investigated the charge formation dynamics of F8T2/PC₇₁BM blend film by means of femtosecond time-resolved spectroscopy. Recently, Moritomo *et al.*[10] performed STXM investigation of the PCE-optimized F8T2/PC₇₁BM solar cell, and revealed molecular mixing of the donor- and fullerene-rich domains: the donor - and fullerene -rich domains contain 33 and 71 wt.% PC₇₁BM, respectively.

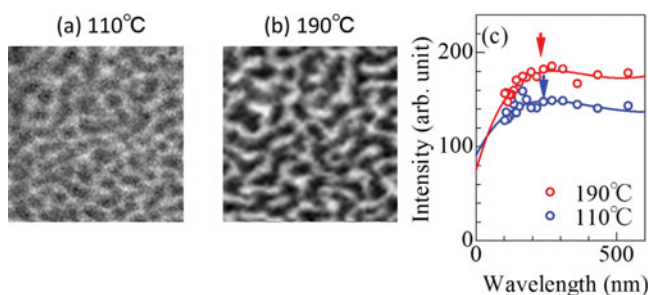


Figure 2. X-ray transmission images of F8T2/PC₇₁BM blend film annealed at (a) 110°C and (b) 190°C at 284.4 eV. The brightness represents the transmission. (c) Intensity of the Fourier transformation of (a) and (b) against the wavelength. The curve is merely the guide to the eyes. Downward arrows represent the length scale (L).

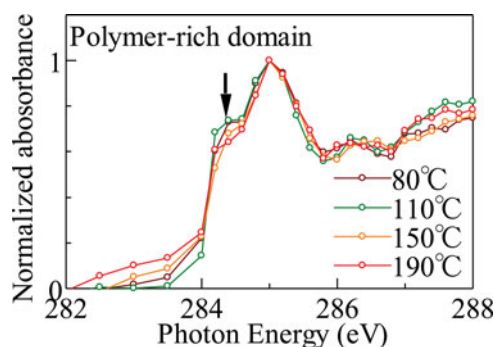


Figure 3. Carbon K-edge absorption spectra in the polymer-rich domain against T_{an} . The spectra are normalized at 285.0 eV. A downward arrow indicates the first π -resonance of fullerene carbon.

In this paper, we performed STXM investigation of F8T2/PC₇₁BM blend films against T_{an} ($= 80, 150, 110, 190$ and 240°C). Our investigation revealed that the fullerene concentration within the polymer-rich domain decreases with T_{an} while the domain size (~ 230 nm)

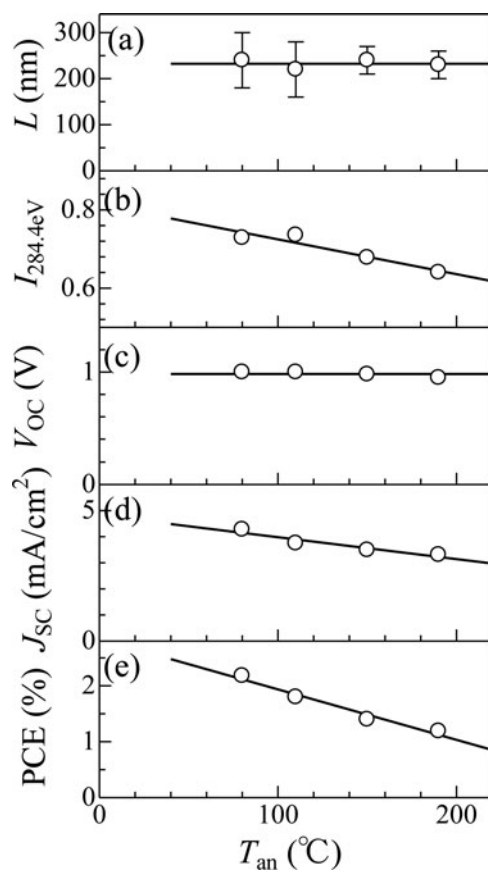


Figure 4. (a) L , (b) $I_{284.4\text{eV}}$, (c) open circuit voltage (V_{oc}), (d) short-circuit current (J_{sc}), and (e) PCE of F8T2/PC₇₁BM solar cell against T_{an} . Solid straight lines are results of least-squares fittings. (c) V_{oc} , and (d) J_{sc} , and (e) PCE are cited from Ref.[7].

is essentially unchanged. Thus, STXM is a powerful tool to reveal the film morphology of organic solar cells.

Experimental Procedure

For the STXM measurements, the F8T2/PC₇₁BM blend films were transferred to a SiN membrane.[11] A bilayer film [poly(sodium 4-styrenesulfonate) (PSS) / blend film] on the glass substrate was prepared by successive spin-coating of an aqueous solution of PSS and an *o*-dichlorobenzene solution of F8T2/PC₇₁BM (33 : 67 wt. %). Then, the bilayer film was cut into 1 × 1 mm² pieces, and the substrate was immersed for several minutes in distilled water to etch away the PSS film. Thus, we obtained small F8T2/PC₇₁BM films floating on the distilled water. A piece of the floating film was scooped up with the SiN membrane (50 nm in thickness and 500 × 500 μm² in area). The thicknesses of the F8T2/PC₇₁BM blend films were ~70 nm after annealing for 10 min at respective temperature ($T_{\text{an}} = 80, 150, 110, 190$ and 240°C).

The STXM measurements were performed using the compact-STXM installed at the BL-13A beamline[12–15] of the Photon Factory (PF), KEK. The details of the compact-STXM are described in the literature.[16] The four-way aperture slit is placed at the focal point of the mirror and provides a virtual source point for illuminating the Fresnel zone plate (FZP). The FZP is placed at 1 m from the aperture slit. The spatial resolution of the compact STXM was several tens nm.

Results

Figure 1(a) shows X-ray absorption spectra around the carbon K-edge of PC₇₁BM (solid curve) and F8T2 (broken curve). The absorption spectrum of PC₇₁BM shows three characteristic peaks at 284.5, 285.5, and 286.7 eV in the π -resonance region. On the other hand, the absorption spectrum of F8T2 shows a rather broad peak at 285.5 eV. Figures 1(b) and (c) show X-ray absorption images of the F8T2/PC₇₁BM blend film annealed at 240°C. In the blend film at $T_{\text{an}} = 240^\circ\text{C}$, the F8T2 and PC₇₁BM domains are known to be macroscopically separated.[10] At the first π -resonance of fullerene carbon [(b) 284.6 eV], the X-ray absorption image exhibits clear bright and dark contrast. The bright and dark regions are assigned to the fullerene and polymer domains, respectively. Thus, the STXM image at the fullerene π -resonance can be regarded as “fullerene image”.

Figures 2(a) and (b) show the fullerene images of F8T2/PC₇₁BM blend film annealed at (a) 110°C and (b) 190°C. Note that the bright region corresponds the polymer-rich domain. In order to evaluate the length scale of the fullerene image, we performed two-dimensional Fourier transformation. In Fig. 2(c), we plotted the intensity of the Fourier transformation against the wavelength. We define the peak position as length scale (L), as indicated by downward arrows.

Figure 3 shows carbon K-edge absorption spectra in the polymer-rich domain against T_{an} . The spectral feature is characteristic to the F8T2 polymer [Fig. 1(a)] except for the shoulder structure at 284.4 eV. The structure is ascribed to the first π -resonance of fullerene carbon. Importantly, the relative intensities ($I_{284.4\text{eV}}$) of the fullerene peak at 284.4 eV systematically decreases with T_{an} . This indicates that the fullerene concentration in the polymer-rich domain decreases with T_{an} . The decrease in the fullerene mixing is reasonable, because the thermal annealing at higher T_{an} accelerates the phase-separation into more pure domains.

Discussion

We plotted in Fig. 4 (a) L , (b) $I_{284.4\text{eV}}$, (c) V_{oc} , (d) J_{sc} , and PCE of the F8T2/PC₇₁BM solar cell against T_{an} . The annealing process significantly alters the photovoltaic performance of the F8T2/PC₇₁BM cells: J_{sc} and PCE steeply decreases with T_{an} while V_{oc} is nearly unchanged. In other words, the annealing procedure at higher T_{an} suppresses the carrier formation at the molecular interface and/or carrier transfer to the collector electrodes. Looking at (a), we found that the domain size is nearly independent of T_{an} . This indicates that the T_{an} -dependent photovoltaic properties cannot be ascribed to the domain size effects in our F8T2/PC₇₁BM system. Looking at (b), we found that the fullerene concentration decreases with T_{an} . We consider that the mixed fullerene within the polymer-rich domain works as a reaction site for the charge separation, because the domain size (~ 230 nm) of our F8T2/PC₇₁BM system is too large for exciton to reach the domain boundary. Then, the reduction of the fullerene concentration suppresses the carrier formation efficiency within the macroscopic polymer domains, even though the domain purification may be advantageous for the carrier transfer efficiency.

Conclusion

We performed STXM investigation of F8T2/PC₇₁BM blend films against T_{an} . We found that the fullerene concentration within the polymer-rich domain decreases with T_{an} while the domain size (~ 230 nm) is essentially unchanged. We ascribed the decrease in J_{sc} and PCE with T_{an} to suppression of the carrier formation efficiency within the macroscopic polymer domains.

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