Scanning Transmission X-Ray Microscopic Investigation of Bulk-heterojunction Organic Solar Cell

Organic solar cells (OSCs) with a bulk-heterojunction (BHJ) are promising energy conversion devices, because they are flexible and environment-friendly, and can be fabricated by a low-cost roll-to-roll process. Using scanning transmission X-ray microscopy (STXM), we investigated the fullerene mixing ($\Phi_{Fullerene}$) of the active layer in OSCs based on films of poly-(9,9-dioctylfluorene-co-bithiophene) (F8T2) / [6,6]-phenyl C_{71}-butyric acid methyl ester (PC$_{71}$BM) blend annealed at various temperatures (T_{an}). We found that the $\Phi_{Fullerene}$ value in the polymer matrix decreases with increase in T_{an}, which suppresses the power conversion efficiency (PCE) of OCS.

The bulk-heterojunction (BHJ) active layer of organic solar cell (OSC) is easily fabricated by thermal annealing after spin-coating of the organic solvent of donor (D) polymer and acceptor (A) fullerene. The active layer consists of phase-separated nano-size domains of the polymer and fullerene. The power conversion efficiency (PCE) is optimized by chemical admixture into the solvent and/or the annealing temperature (T_{an}) via modification of the morphology of the active layer. The energy conversion process of the OSC is realized by the combination of the carrier formation and transfer processes. In the former process, the photo-created exciton migrates to the D/A interface and separates into an electron and hole pair. The nano-size structure is essential for efficient carrier formation, because the length of exciton migration is ~3 nm. In the latter process, the carriers transfer to the collector electrode and are collected as photocurrent. Thus, it is essential to clarify the film morphology in order to truly understand the OSC device.

Scanning transmission X-ray microscopy (STXM) around the carbon K-edge is a powerful tool to clarify

the molecular mixing as well as the domain structure in the BHJ active layer [1, 2], because it can distinguish the fullerene carbon from the polymer carbon. Collins et al. [1] revealed the fullerene mixing ($\Phi_{Fullerene}$) in the polymer matrix of PTB7/PC$_{71}$BM blend film. Due to the low spatial resolution (~ several tens of nm) of STXM, however, the domain size had to be enlarged by chemical admixture [1] or high-temperature annealing [2]. Here, we selected the F8T2/PC$_{71}$BM system, because the blend films form periodic large domains (~ several hundreds of nm) independent of T_{an}. We clarify the interrelation between $\Phi_{Fullerene}$ and T_{an}, and discuss the effect of molecular mixing on photovoltaic performance.

Figure 1 shows an STXM image of the F8T2/PC$_{71}$BM blend films annealed at T_{an} = 190°C at 284.4 eV. The photon energy (284.4 eV) was at the π^*-resonance absorption of the fullerene framework [1, 3, 4]. Therefore, the bright regions correspond to the fullerene-rich domains, while the dark regions the polymer-rich domains. The length scale (~ 230 nm) of the fullerene domain was evaluated by two-dimensional Fourier transformation.
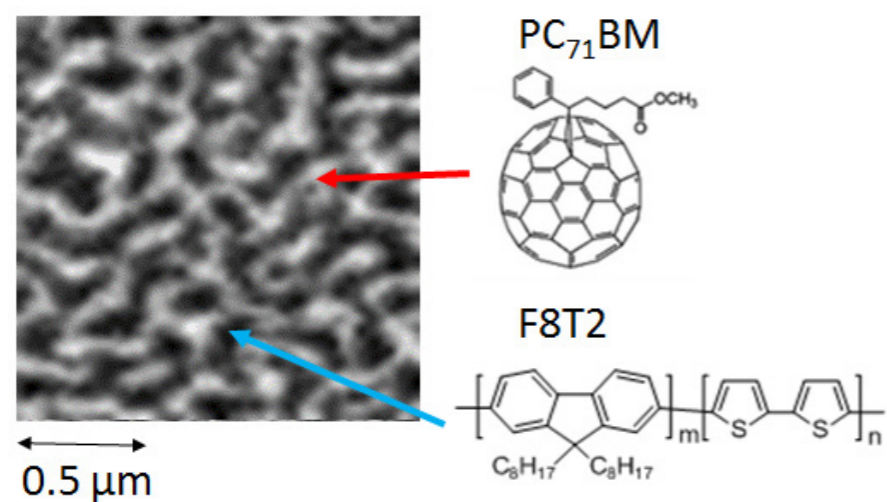

Figure 1: STXM image of F8T2/PC$_{71}$BM blend films at 284.4 eV. The bright regions correspond to the PC$_{71}$BM-rich domains, while the dark regions the F8T2-rich domains.
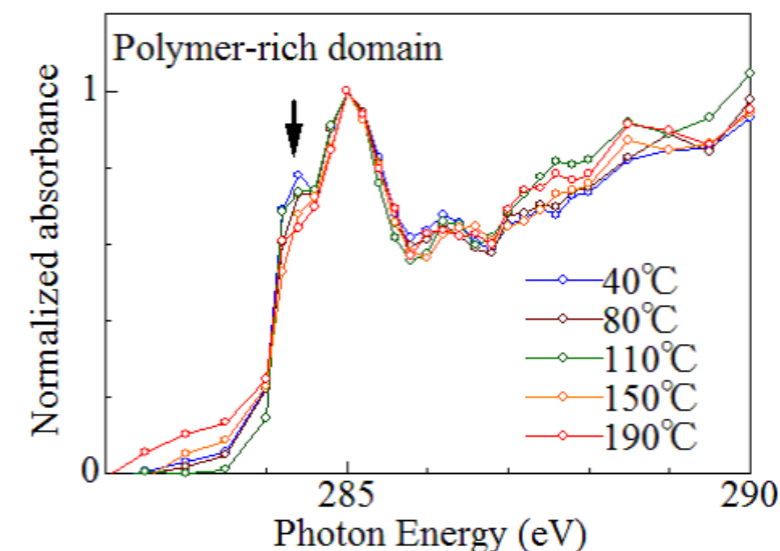

Figure 2: Carbon K-edge absorption spectra in the polymer-rich domain against T_{an}. The spectra are normalized at 285.0 eV. A downward arrow indicates the first π-resonance of fullerene carbon. The data were replotted from Ref. [4].

Figure 2 shows carbon K-edge absorption spectra in the polymer-rich domain against T_{an}. The spectral feature is characteristic to the F8T2 polymer [3] except for the shoulder structure at 284.4 eV. The structure is ascribed to the first π-resonance of fullerene carbon. Importantly, the relative intensity of the fullerene peak at 284.4 eV systematically decreases with T_{an}. This indicates that the $\Phi_{Fullerene}$ value in the polymer-rich domain decreases with increase in T_{an}. The decrease in $\Phi_{Fullerene}$ is reasonable, because the thermal annealing at higher T_{an} accelerates the phase-separation into more pure domains.

The reduction of $\Phi_{Fullerene}$ causes the suppression of the PCE of the OSC. Yasuda et al. [5] systematically investigated the photovoltaic properties of the OSCs based on films of F8T2/PC$_{71}$BM (33 : 67 wt.%) blend annealed at various T_{an}. They found that the PCE systematically decreases from the optimal value (= 2.28%) at T_{an} = 80°C to 0.81% at 240°C. Thus, the annealing process at higher temperature deteriorates the photovoltaic performance. We evaluated the length scales of the fullerene domain against T_{an} by two-dimensional Fourier transformation. We found that the domain size (~ 230 nm) is nearly independent of T_{an}. This indicates that the T_{an} dependence of the PCE cannot be ascribed to the domain size effects in our F8T2/PC$_{71}$BM system. As seen in Fig. 2, the $\Phi_{Fullerene}$ value in the polymer-rich domain decreases with increase in 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/PC$_{71}$BM system is too large for excitons to reach the domain boundary. Therefore, the reduction of $\Phi_{Fullerene}$ suppresses the efficiency of carrier formation within the polymer domains, even though domain purification may be advantageous for carrier transfer efficiency.

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Y. Moritomo[1], T. Yasuda[2], K. Yonezawa[1], T. Sakurai[1], Y. Takeichi[3], H. Suga[4], Y. Takahashi[3, 5], N. Inami[3], K. Mase[3], and K. Ono[3] ([1]Univ. of Tsukuba, [2]NIMS, [3]KEK-IMSS-PF, [4]Hiroshima Univ., [5]The Univ. of Tokyo)