Quantitative Evaluation of Molecular Diffusion in Organic Planar Heterojunctions by Time-of-Flight Secondary Ion Mass Spectroscopy

Kyohei Nakano, † Takahiro Shibamon, § and Keisuke Tajima*†,§

†RIKEN Center for Emergent Matter Science (CEMS), 2-1 Hirosawa, Wako, Saitama 351-0198, Japan
‡TORAY Research Center, Inc., 3-3-7, Sonoyama, Otsu, Shiga 520-8567, Japan
§Precurorsry Research for Embryonic Science and Technology (PRESTO), Japan Science and Technology Agency, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

ABSTRACT: Understanding molecular diffusion across the interfaces in planar heterojunctions is fundamentally important to improving the performance and stability of organic electronic devices. In this study, we quantitatively evaluated the diffusion of [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) across the interface of planar heterojunctions into the polymer layers by time-of-flight secondary ion mass spectroscopy. Careful calibration allowed the concentration of PCBM to be determined in the polymer layer at concentrations as low as 0.01 wt %. We found that approximately 1 wt % PCBM was present in the poly(3-hexylthiophene) layer in the planar heterojunction with no thermal treatments, indicating that a small amount of PCBM diffused into the polymer layer even at room temperature. The diffusion behavior depended strongly on the crystallinity of the PCBM layer and the properties of the polymer layers such as glass transition temperature. Further analysis suggested that the diffusion of PCBM into the polymer layers was also related to the interface free energy between the layers.

INTRODUCTION

Planar heterojunction (PHJ) structures consisting of stacked layers of organic semiconducting materials are used for various organic optoelectronic devices. Multilayered PHJs are widely used in organic light-emitting diodes (OLEDs) to control the charge transport and light-emitting positions precisely.1−3 PHJs are also used in organic photovoltaics (OPVs) as model systems for mixed bulk heterojunction (BHJ) structures because PHJs can eliminate the complicated effects of the mixing morphology in BHJs and reveal the correlation between the material properties and the device performance more directly.4−7 PHJs with electron donor and acceptor materials have been used to investigate the electronic structure near the interface by photoelectron spectroscopy8−10 and the charge generation process by ultrafast spectroscopy11 and to evaluate exciton diffusion length in materials by interference fluorescence quenching.12−14 PHJs have been also used to elucidate the mixing behavior of the semiconducting materials by observing the evolution of the mixed structures during the thermal treatment of PHJs.15−22

It is often assumed that PHJs have a smooth interface and that each layer consists of the pure materials. Experimentally, however, it is difficult to construct well-defined PHJ structures without intermixing of the materials at the interfaces. Preparation of PHJs by vacuum deposition or sequential spin-coating can cause the intermixing of two molecules near the interface or even the diffusion of the molecules into the whole layer.23−29 We previously showed that the contact film transfer (CFT) method can be used to construct the well-defined PHJ structures.30,31 X-ray reflectivity (XRR) and the depth profiles obtained by X-ray photoelectron spectroscopy (XPS) indicated that the interface is flat and there is no substantial intermixing at the interfaces of PHJs made by the CFT method.32 We observed the effects of the interfacial modifications in PHJs, such as the introduction of dipole moments and energetic cascade structures on their photovoltaic performance, which suggests that the surface structures of the films are maintained at the interface of PHJs during CFT.33−35 However, this does not mean that each layer is pure because neither XRR nor depth profiles of XPS can detect the molecular diffusion of less than several percent. A low level of molecular diffusion can affect the photophysical properties of the organic electronics, such as quenching of the excitons and charge recombination. However, such small amount of diffused molecules in PHJs for OLEDs or OPVs has never been quantified.

To quantify the small amount of diffused molecules in PHJs, secondary ion mass spectroscopy (SIMS) is a powerful tool for analyzing the components of the organic thin films with high sensitivity. Dynamic (D)-SIMS has been used to investigate [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) diffusion into polymer layers by thermal annealing.15,16,36 In D-SIMS measurements, owing to the high primary ion intensity, organic...
molecules are decomposed to atomic fragments; hence, it is often necessary to label the target molecules with deuterium. In contrast, static time-of-flight (ToF)-SIMS can ionize target molecules with less decomposition because the amount of the primary ion is much smaller than that of D-SIMS. ToF-SIMS can analyze film surfaces without the deuteration of the materials because the assignment of the mass spectra to the targeted molecules is straightforward. Combined with Ar cluster ion as an etching source, ToF-SIMS can produce reliable depth profiles of the molecules, with little damage to the organic materials. The disadvantage of ToF-SIMS is its difficulty in quantification, mainly due to the dependence of the secondary ionization efficiency on the materials. The quantitative analysis of the low-level molecular diffusion occurring at a low temperature have not been investigated by ToF-SIMS in the bilayer structures.

In this study, we systematically carried out quantitative analysis of PCBM diffusion into various polymer films at room temperature. Sample structures of PCBM/polymer PHJs were used, where // denotes the interface prepared by the CFT method (Figure 1a) and the concentration of PCBM in the polymer layer was evaluated by ToF-SIMS measurements. Careful calibration of the sensitivity allowed the concentration of PCBM to be determined in the polymer layer in PHJs at concentrations as low as 0.01 wt %. The diffusion behavior of PCBM was discussed on the basis of the crystallinity of each organic layer and the polymer properties.

## RESULTS AND DISCUSSION

To calibrate PCBM concentration to the signal intensity of ToF-SIMS, we performed measurements on the mixed thin films of PCBM and the polymers with various PCBM concentrations prepared on a Si/SiO₂ substrate. Figure 2a
shows depth profiles of the PCBM signal intensity in the mass spectra for the mixed films of PCBM and poly(3-hexylthiophene) (P3HT) (see the Experimental Section for the details of ToF-SIMS measurements). The sum of the intensities of the negatively charged molecular peaks of C$_{60}$ and PCBM was used as the PCBM signal intensity. A representative mass spectrum is shown in Figure S1. To eliminate the variation of the primary ion-source intensity in each measurement, PCBM signal intensities were normalized by those of Si$_2$O$_2^-$ derived from the Si/SiO$_2$ substrate (gray lines in Figure 2a). The PCBM signal intensity clearly depended on its concentration in the mixed film. Figure 2b shows the calibration line using the average PCBM signal intensity in 10−50 sputtering cycles. Below 5 wt % PCBM concentration, the signal intensity had a linear relation with the concentration, indicating that the signal intensity can be converted to PCBM concentration in this range. In contrast, the pristine PCBM film (PCBM concentration of 100 wt %) showed a signal intensity much smaller than expected from the straight calibration line. The intensity was even smaller than that of with the calibration line using the average PCBM signal intensity in the Si/SiO$_2$/PCBM (amorphous or crystal)//P3HT structure. That for a pristine PCBM thin film is also shown for comparison.

The depth profiles of PCBM signal intensity in the PHJ samples are shown in Figure 3b. We prepared two samples of Si/SiO$_2$/PCBM (amorphous or crystallized)//P3HT. The thickness of the PCBM and P3HT layers were approximately 30 and 40 nm, respectively. The profile of pristine PCBM is also shown for comparison. The regions with <180, 180−260, and >260 sputtering cycles correspond to the P3HT and PCBM layers and Si substrate, respectively, determined by the point with the half intensity of the corresponding signals. We did not convert the sputtering cycles into film thickness because the etching rate of each layer may be different. PCBM mass spectrum was observed in the P3HT layer of the PHJ samples, indicating that PCBM diffuses into the polymer layer upon contact, even at room temperature. The PCBM signal intensity from the P3HT layer was much lower in the crystallized PCBM//P3HT sample than in the amorphous PCBM//P3HT sample. This result is consistent with previous reports that the crystallization of the PCBM thin film suppresses the diffusion of PCBM into the polymer layer during thermal treatment.

The PCBM concentrations in the P3HT layers with the crystalline and the amorphous PCBM were 0.89−1.4 wt % and 2.0−2.5 wt %, respectively, for 10−100 sputtering cycles. This diffusion of a small amount of PCBM into the polymer layers at room temperature has not been reported previously, probably due to the lack of a quantitative analytical method. PCBM was uniformly distributed in the P3HT layer, or the concentration was slightly higher in the region close to the surface. Near the interface between crystalline PCBM and P3HT (150−180 sputtering cycles), the signal intensity of PCBM appeared as a peak. There are two possible reasons for this: the PCBM concentration was high near the interface, or this was an artifact arising from the existence of the P3HT/PCBM interface. The PCBM signal intensity deviated from the linear scale at high concentrations owing to the matrix effect (Figure 2b). A similar effect could play a role at the interfacial region even if there is no intermixing of the materials at the interface. In the case of a noncrystalline PCBM sample, the doubled signal intensity of PCBM in the bulk P3HT layer may obscure the interfacial phenomena due to the limited depth resolution of ToF-SIMS measurement (~9 nm; see Figure S4), leading to the monotonic decrease of PCBM intensity at the interface. At this stage, it is difficult to obtain an exact picture of the molecular distribution near the heterointerface using ToF-SIMS measurement.
Figure 4a shows depth profiles of PCBM concentration in four polymers: P3HT, regiorandom P3HT (ran-P3HT), PTB7, and polystyrene (PS). PCBM layers were crystallized by thermal treatment in all of the PHJ samples before making contact. The calculated PCBM concentrations in the polymer layers after calibration are listed in Table 1. The calibration contact. The calculated PCBM concentrations in the polymer thermal treatment in all of the PHJ samples before making and polystyrene (PS). PCBM layers were crystallized by four polymers: P3HT, regiorandom P3HT (ran-P3HT), PTB7, weakly crystalline region near the grain boundaries of P3HT.15

We did not test the PHJ of amorphous PCBM and ran-P3HT, which is predicted to exhibit higher PCBM diffusion because the exciton quenching because the exciton diffusion transition in differential scanning calorimetry measurements59 and UV–visible spectroscopy.60 Because Tg of ran-P3HT (∼3 to 4 °C) is lower than that of P3HT,61,62 the difference in Tg may explain the order of PCBM diffusion for at least three polymers (ran-P3HT > P3HT > PS). The interface free energy and crystallinity and the local mobility of the polymer side chains can provide qualitative guidelines for predicting the diffusion behavior at the interfaces in PHJs, although it is still not clear which factor is determining at the room temperature.

Finally, we consider the possible effects of the PCBM diffusion in PHJs on the organic electronic devices. A concentration of PCBM of around 1 wt % corresponds to a molecular density of \(6.6 \times 10^{18}\) cm\(^{-3}\). Assuming a uniform distribution of molecules, the average intermolecular distance was estimated as 5.3 nm. This density is well above the level that affects the exciton quenching because the exciton diffusion length of the semiconducting polymers is typically in the range

**Table 1. Summary of PCBM Concentration in the Different Polymer Layers, Contact Angle with Water of the Polymer Layers, and Interface Free Energy between PCBM and the Polymer Layers Calculated Using Contact Angle**

| PCBM concentration (wt %) | water contact angle (deg) | interface free energy (mJ/m²) |
|---------------------------|---------------------------|-----------------------------|
| P3HT                      | 0.89–1.4                  | 106.3 (0.4)                 | 4.42                       |
| ran-P3HT                  | 5.6–6.1                   | 105.8 (0.2)                 | 4.26                       |
| PTB7                      | 1.2–1.4                   | 98.2 (0.4)                  | 2.22                       |
| PS                        | <0.01                     | 88.4 (1.8)                  | 0.53                       |

*Numbers in parentheses are standard deviations of the four measured values.

Figure 4b shows depth profiles of PCBM-normalized signal intensity for crystalline PCBM//P3HT, ran-P3HT, PTB7, or PS. (b) Depth profile of the crystalline PCBM//PS sample on a logarithmic scale.
of 2–10 nm. This means that we must be careful about the molecular diffusion to obtain the exciton diffusion length by using the PHJ structure and the interfacial quenching model, which may explain the large variation in calculated exciton length.83 The concentration of 1 wt % is too low to form interconnected domains for electron transport, but after the photoinduced electron transfer, the diffused PCBM could cause charge recombination with the holes in the polymer layer. The diffused PCBM may exist locally in the less crystalline domains of the polymer layers. In this case, the effects of the diffused PCBM could be smaller than those expected from the uniform distribution.

**CONCLUSIONS**

In conclusion, we quantitatively determined the amount of PCBM in the range of several weight percent to approximately 0.01 wt % in PHJs with various polymer layers by ToF-SIMS. We found that even in the combination of the crystallized PCBM and crystalline P3HT, approximately 1 wt % PCBM diffused into the P3HT layer at room temperature, which has been overlooked thus far. The lower $T_d$ of the polymers and the higher interface free energy of the contact may facilitate the diffusion. This study provides important insight into PHJ structures where the purity of the layers can affect the interpretation of the measurements and the performance of the organic optoelectronic devices.

**EXPERIMENTAL SECTION**

**Materials.** ran-P3HT ($M_w$: 60 000–95 000; Rieke Metals), regioregular P3HT (lisicon SP001, Merck), PTB7 (1-Material), PS ($M_w$: 5000, TOSOH), and PC$_{61}$BM (purity: 99.5%; Solenne) were purchased from commercial suppliers and used as received.

**Sample Preparation.** Si/SiO$_2$ (300 nm) substrate with a mirror surface was cleaned by sequential ultrasonication in detergent solution, water, 2-propanol, and acetone, followed by mirror surface was cleaned by sequential ultrasonication in detergent solution, water, 2-propanol, and acetone, followed by annealing of the PCBM film. Thermal annealing of the PCBM film was carried out in a N$_2$-filled glovebox. Aqueous poly(sodium 4-styrenesulfonate) (PSS; 30 mg/mL; $M_w$: 70 000; Aldrich) was spin-coated onto a precleaned glass substrate at 3000 rpm for 30 s. A solution of the polymers (10 mg/mL in chlorobenzene) was spin-coated onto the glass/PSS substrate at 1000 rpm for 30 s. The glass/PSS/polymer substrate was gently placed upside down on the Si/SiO$_2$/PC$_{61}$BM substrate, and one drop of water was placed on the edge of the two substrates. Water selectively penetrated into and dissolved the PSS layer, allowing the polymer layer to be transferred onto the PC$_{61}$BM substrate. Figure S3 shows the CFT method.

**Measurements.** The primary ion source of ToF-SIMS (TOF-SIMS 5, ION-TOF) was Bi$_3^{+*}$ (30 kV), with a 5.5 ns pulse width. The negative secondary ion from an area of 300 × 300 μm$^2$ was detected. Sputtering was done with an Ar gas cluster ion beam with an acceleration voltage of 10 kV was applied in front of the detector for improved high mass sensitivity. The water contact angle was measured with a contact angle meter (DMe-201, KYOWA). The contact angle was calculated by using the 0/2 method with a 1.5 μL pure water droplet.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b01524.

Mass spectrum of PCBM, calibration lines for the quantifications, detailed information of the film transfer process, and depth profile for PCBM/P3HT film (PDF)

**AUTHOR INFORMATION**

*Corresponding Author*

E-mail: keisuke.tajima@riken.jp.

**ORCID**

Kyohei Nakano: 0000-0003-2493-2817
Keisuke Tajima: 0000-0003-1590-2640

**Notes**

The authors declare no competing financial interest.

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