



Annealing-induced phase separation in small-molecular bulk heterojunctions

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ARTICLE INFO

Article history:

Received 19 July 2014

Received in revised form 2 August 2014

Accepted 5 August 2014

Available online 22 August 2014

Keywords:

Bulk heterojunction

Donor–acceptor interface

Thermal annealing

Phase separation

Self-organization

ABSTRACT

Morphology optimization of donor–acceptor bulk heterojunctions at microscopic scale is critical for improving performance of organic photovoltaic devices. Here, effects of thermal annealing on phase separation processes in small-molecular bulk heterojunctions with different geometrical structures (i.e., PTCDA, TiOPc, CuPc and C₆₀) are investigated with ultraviolet and X-ray photoemission spectroscopies. It was identified that post-annealing treatment caused the different degrees of vertical diffusions at the bulk heterojunctions, leading to non-uniform composition distributions. Variations in phase separations are mainly due to the differences in surface energy of the involved materials, which play a crucial role in the intermolecular interactions and the molecular diffusion. Low-surface-energy materials were found to segregate preferentially on the surface for minimizing total energy of the systems.

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1. Introduction

In recent years, organic photovoltaic (OPV) devices have attracted growing attention because of their promising advantages of high-efficiency solar-energy conversion, light weight, ease of processing, and compatibility with flexible substrates [1–6]. Power conversion efficiency of OPV devices has been rapidly improved via applications of new photovoltaic materials and novel device architectures [1–7]. The state-of-the-art OPV device is based on the organic donor–acceptor bulk heterojunction (BHJ) formed either by blending conjugated polymers with soluble fullerene derivatives or by co-depositing small-molecular donor and acceptor materials [4,8,9]. An interpenetrating network of the donor–acceptor BHJ

sandwiched between the anode and cathode offers large interfacial area for efficient exciton dissociation and excellent charge transport, leading to high device efficiency [1,4]. Therefore, control of the BHJ morphology at microscopic scale plays a decisive role for improving performance of OPV devices.

Many studies have shown that the organic BHJ morphology depends critically on the processing conditions as well as subsequent annealing treatments, which changes the molecular self-organization and promote the formation of a nanoscale phase-separated morphology with crystalline donor and acceptor domains of different compositions [10]. Particularly, annealing process has become the most commonly used method for performance improvement, since it can dramatically improve crystallinities and thus carrier mobilities of the organic domains. Particularly, vertical phase separation in the BHJ films has been observed in several polymer blend systems, showing a vertical distribution of the donor and acceptor

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molecules [11–13]. For example, spin-coated polymeric BHJ of poly(3-hexylthiophene):[6,6]-phenyl-C₆₀-butyric acid methyl ester (P3HT:PCBM) blend was examined with variable-angle spectroscopic ellipsometry and X-ray photoemission spectroscopy (XPS) to show a vertical composition profile with PCBM-rich near the substrate side to P3HT-rich adjacent to the free (air) surface [12,13]. It is also noteworthy that a suitable degree of the phase separation is beneficial to charge transportation and collection. Random distribution of donor and acceptor materials in a BHJ can lead to charge trapping sites in the conducting pathways to the electrodes [14]. A bicontinuous pathway in phase-separated BHJs must be formed for the photogenerated holes and electrons to reach their respective contacts for efficient charge collection. The morphology as well as the structural properties of organic BHJs are herein decisive for performance optimization.

Although phase separation has been well-understood in several polymer blend systems, only few pertinent studies have been conducted on the BHJs using mixtures of vacuum-deposited small-molecular materials [14–18]. Moreover, available data on the morphological changes of small-molecular BHJs are often limited to the results of lateral microscopic imaging of the treated films [14–16]. Our previous work have demonstrated that vertical phase separation occurs after annealing in copper phthalocyanine (CuPc):fullerene (C₆₀ or C₇₀) mixed films with a concentration gradient varying from CuPc rich near the surface to fullerene-rich adjacent to the substrate interface [17,18]. Clearly, a detailed understanding of the mechanism controlling the intermolecular rearrangement and phase separation is indispensable for further exploiting and optimizing the performance of OPV devices based on small-molecular BHJs. In this paper, the mechanisms of annealing-induced phase separation in homogeneous mixtures of two small-molecular components with different molecular geometries have been investigated via photoemission spectroscopy, which offers a powerful tool for determining the electronic structures and material composition in the BHJs. The present work focuses on the prototypical donor–acceptor pairs formed among 3,4,9,10-perylene-tetracarboxylic dianhydride (PTCDA), titanium oxide phthalocyanine (TiOPc), CuPc, and C₆₀. It was observed that thermal annealing treatment causes non-uniformity in composition distributions, which is highly dependent on the molecular pairs. Morphology variations are mainly attributed to surface energy effects on the intermolecular interactions, leading to the different degrees of the vertical diffusions during the annealing-induced self-organization.

2. Experiment

Preparation and characterization of small-molecular BHJ films were performed *in situ* in a KRATOS AXIS ULTRA-DLD ultrahigh vacuum (UHV) surface analysis system, consisting of a fast load lock (base pressure <1 × 10⁻⁸ Torr), an evaporation chamber (<5 × 10⁻¹⁰ Torr), a multiport carousel chamber (<5 × 10⁻¹⁰ Torr) and an analysis chamber (<3 × 10⁻¹⁰ Torr). Indium tin oxide (ITO) coated glass with a sheet resistance of 20 Ω sq⁻¹

was used as the substrate, which was *ex situ* cleaned by subsequent ultrasonic treatment in Decon 90, acetone, ethanol, de-ionized water, for 20 min each, and then treated by UV–ozone for 20 min. All employed materials were purified before loading into the UHV chamber by thermal gradient sublimation. Prior to film deposition, all the organic materials were fully outgassed to minimize contamination during film deposition. Organic materials were *in situ* thermally deposited onto the ITO–glass substrates at room temperature with a growth rate of 1–2 Å s⁻¹ at a pressure of ~2 × 10⁻⁹ Torr. BHJ films, i.e., PTCDA:C₆₀, TiOPc:C₆₀ and CuPc:C₆₀, were formed by co-depositing donor and acceptor materials from two separated Ta boats. Nominal film thickness and deposition rate were monitored *in situ* with a quartz crystal microbalance. The annealing procedure with a temperature ramp rate of ~10 °C min⁻¹ was also carried out in the evaporation chamber with a heating stage. After each deposition or annealing step, samples were transferred to the analysis chamber without breaking vacuum for ultraviolet and X-ray photoelectron spectroscopy (UPS and XPS) measurements. UPS measurements were performed to characterize the valence states and vacuum level (VL) by using the HeI excitation line (21.2 eV) from a Helium discharge lamp with a total instrumental energy resolution of 100 meV, and samples were negatively biased to enable observation of secondary electron cutoffs. XPS measurements using a monochromatic Al K α source (1486.6 eV) were carried out to characterize the core levels of the components. All the spectra were obtained at room temperature. The binding energy scale was calibrated by determining the Au4f_{7/2} peak position and Fermi level (E_F) edge of the Au film, which was cleaned by Ar⁺ ion sputtering. E_F is referred as the zero binding energy in all the UPS and XPS spectra.

3. Results and discussion

Fig. 1 shows UPS spectra of a 10 nm-thick TiOPc:C₆₀ mixed film (1:1 by weight) after thermal annealing treatment at different temperatures for 30 min, respectively. For comparison, the spectra of neat TiOPc and C₆₀ films after annealing at 150 °C are also shown in Fig. 1. UPS signals of the as-grown TiOPc:C₆₀ film show features originated from the TiOPc and the C₆₀ components, which are in good agreement with previous report [19]. It is evident that the characteristic features of C₆₀ to the TiOPc:C₆₀ mixture are gradually attenuated with increasing annealing temperature, as compared with UPS spectra of neat TiOPc and C₆₀ at 150 °C shown in Fig. 1b. To distinguish accurately the spectral contributions of TiOPc and C₆₀ to that of the TiOPc:C₆₀ mixture, the highest occupied molecular orbital (HOMO) regions of UPS spectra of the as-grown and 150 °C-annealed TiOPc:C₆₀ mixed layers (Fig. 1c) are fitted with the spectral line shapes of neat TiOPc and C₆₀ in Fig. 1b, which are, to a large extent, deconvoluted into the superimposed spectra of TiOPc (thin solid line) and C₆₀ (thin dashed line) with different spectral intensities. It is interesting to note that the relative spectral contributions of TiOPc and C₆₀ (hereafter referred as *I*_{TiOPc/C60}) in the

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