CONTROLLING THE SURFACE COMPOSITION OF PCBM IN P3HT/PCBM BLEND FILMS BY USING MIXED SOLVENTS WITH DIFFERENT EVAPORATION RATES

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Abstract The surface composition of poly(3-hexylthiophene-2,5-diyl) and fullerene derivative [6,6]-phenyl-C61-butyric acid methyl ester (P3HT/PCBM) blend films could be changed by controlling the film formation process via using mixed solvents with different evaporation rates. The second solvent, with a higher boiling point than that of the first solvent and much better solubility for PCBM than P3HT, is chosen to mix with the first solvent with a lower boiling point and good solubility for both PCBM and P3HT. The slow evaporation rate of the second solvent provides enough time for PCBM to diffuse upwards during the solvent evaporation. Thus, the weight ratio of PCBM and P3HT \( m_{PCBM}/m_{P3HT} \) at surface of the blend films was varied from ca. 0.1 to ca. 0.72, i.e., it increases about seven times by changing from single solvent to mixed solvents. Meanwhile, the mixed solvents were in favor to form P3HT nanofiber network and enhance phase separation of P3HT/PCBM blend films. As a result, the power conversion efficiency of the device from mixed solvents with slow evaporation process was about 1.5 times of the one from single solvents.

Keywords: P3HT; PCBM; Surface composition; Mixed solvents; Slow evaporation.

INTRODUCTION

Polymer and small molecule blend films have attracted much attention because of their application in many fields such as organic electronics and photovoltaics\(^1\), coatings\(^2\) and adhesives\(^3\). Many different structures have been reported in the literature for different blend systems and different methods with both lateral and vertical segregation on the nano- to micrometer scale. Actually, vertical segregation is common for polymer and small molecule blend films. There are two driving forces can cause vertical segregation, one is surface energy and the other is entropic-push. If there is very different surface energies of the two materials, the one with the high surface energy will segregate at the substrate interface\(^4\). If the two components aremiscible, entropy drives small molecules to segregate at the substrate interface\(^5\).

Polymer and fullerene or fullerene-derivative mixtures are one of the most promising materials in terms of efficiency and stability in polymer solar cells. Among them, regioregular poly(3-hexylthiophene-2,5-diyl) (rr-P3HT) and fullerene derivative [6,6]-phenyl-C61-butyric acid methyl ester (C61-PCBM) are respectively one of the most important donor and acceptor materials. Recently, some groups have found that P3HT is enriched at the cathode interface and PCBM enriches at the anode interface of as spun films, due to the different surface energies of the two materials (\( \gamma_{PCBM} = 37.8 \text{ mN/m}^2 \), \( \gamma_{P3HT} = 26.9 \text{ mN/m}^2 \)). ToF-SIMS\(^6\), \(^7\), XPS\(^8\), VASE\(^9\) and

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\* This work was financially supported by the National Natural Science Foundation of China (Nos. 20621401, 20834005, 51073151), and the Ministry of Science and Technology of China (No. 2009CB623604).

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Received August 27, 2012; Revised November 8, 2012; Accepted November 14, 2012
doi: 10.1007/s10118-013-1295-7
neutron reflectivity\cite{10, 11} are used to characterize the surface or vertical structure of P3HT/PCBM blend films. A surface layer is relatively depleted in PCBM, while it is relatively rich in PCBM at the substrate interface. It is the inverted not the normal device architecture that is beneficial. It is surface-segregated PCBM not P3HT that can serve as a hole-blocking layer at the Al interface to reduce the electron extraction\cite{12} and enhance the internal quantum efficiency\cite{13}.

The adverse surface-segregation can be suppressed by the way of traditional treatment, for example, thermal annealing and solvent vapor annealing\cite{13}, but the effect is not notable. Other two approaches have been widely investigated\cite{14}. One is controlling the total energies, introduction of some acceptor materials with low surface energy\cite{15, 16} or surface treatment reducing the differences between interface energies\cite{17−19}. The other is controlling the kinetics of the process during the film formation\cite{20}. Actually, crystallization-induced vertical stratified structures can be constructed based on double-crystalline polymer systems\cite{21, 22}. Unfortunately, this method was not suitable in P3HT/PCBM blend films. In addition, the grads structure of bi-layer film has also been employed to obtain suitable vertical structure\cite{23−26}.

However, little is known about the kinetics during the film formation. Time-resolved small-angle light scattering and light reflectivity\cite{27, 28} had revealed the structure evolution of a blend of two polymers during the spin-coating process. First vertical stratification formed, and then the interface between the stratified layers becomes unstable, leading to the final phase-separated thin film. It showed that desirable morphologies could be achieved by designing rational processing conditions. In this paper, mixed solvents with different evaporation rates, are applied to change the surface composition of P3HT/PCBM blend films. The second solvent, with a higher boiling point than that of the first solvent and much better solubility for PCBM than P3HT, carries PCBM molecules upwards after the first solvent evaporate. The slow evaporation process of film formation provides enough time for PCBM to diffuse upwards with the second solvent evaporation.

EXPERIMENTAL

Materials
Regioregular HT-HT P3HT (> 98.5%; HT: head-to-tail; \(M_n = 68 \text{ kDa}\)) was purchased from Sigma-Aldrich Co. Ltd. PCBM with purity of 99% was purchased from Solenne Co. and used as received. Chlorobenzene (Beijing Chemical, China), acetophenone (Beijing Chemical, China) and chloronaphthalene (Sigma-Aldrich) were also used as received. Tetralin (Beijing Chemical, China) was purified before use.

Sample Preparation and Photovoltaic Devices
The solution used in this study for spin-coating active layer was prepared as following: P3HT and PCBM (1:1, \(W/W\)) were dissolved in chlorobenzene to make total 20 mg mL\(^{-1}\) solution, followed by blending with the second solvent (tetralin, acetophenone or chloronaphthalene). The volume ratio of chlorobenzene and second solvent is 1:0.05. This solution was stirred for 12 h at room temperature in dark. The slow evaporated films were spin coated at 500 r/min and 10 s, and the fast evaporated ones were at 2000 r/min 30 s, and then placed on horizontal plate until the films were dried. The films were placed in vacuum more than 12 h after being dried.

The photovoltaic devices were prepared on glass/ITO substrates. The substrates were cleaned by ultrasonic treatment in detergent and deionized water, and then etched by oxygen plasma for 2.5 min. 45-nm-thick poly(ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, Baytron P4083) was deposited by spin-coating (2500 r/min and 60 s) and then dried for at 120 °C for 40 min. The solution of P3HT and PCBM was spin-coated as described above. Finally, the samples were transferred into an evaporator, 1-nm-thick LiF and 80-nm-thick Al electrodes were deposited by evaporation, respectively. The active surface area of typical device is 0.12 cm\(^2\).

Characterization
The surface composition was measured by X-ray photoelectron spectroscopy. XPS experiments with argon sputtering were measured with a VG ESCALAB MK II instrument at room temperature by using an Al K\(\alpha\) monochrom (\(h\nu = 1486.6 \text{ eV}\)) at 14 kV and 20 mA. The sample analysis chamber of the XPS instrument was