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Effects of film treatment on the performance of poly(3-hexylthiophene)/soluble fullerene-based organic solar cells

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Abstract

This work investigates the correlations between the morphological characteristics of the active layers, comprised of poly(3-hexylthiophene) and [6,6]-phenyl-C_{61}-butyric acid methyl ester, and the photovoltaic performance of polymer-based solar cells. The active layers were deposited by spin-coating the polymer solutions under various conditions and, then, characterized by atomic force microscopy, X-ray diffraction, UV/Vis and Raman spectroscopy. Results of this study indicate that solar cells employing the slow-solvent-vapor-treatment blend films as the active layers exhibit the enhanced power conversion efficiency (3.0%), short-circuit (8.71 mA/cm^2) current and fill factor (0.59) than that of as-cast and fast-thermal-annealing blend films.

Keywords: Polymer solar cells; Heterojunction; P3HT; PCBM; Solvent treatment

1. Introduction

Poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) bulk heterojunctions have recently become the favorite materials in the handy, versatile, and low-cost manufacturing of plastic solar cells [1–3]. Accordingly, interest has been growing in the elaboration of different methods for *in-* and *ex-situ* modification of the initial P3HT:PCBM blend, to improve the working parameters of the completed devices [4–9]. The photovoltaic activity of the P3HT:PCBM layers may be increased markedly by varying the film composition, thickness and/or growth conditions, including the processing solvents and annealing temperatures [4–9]. Nevertheless, due to the natural complexity of donor–acceptor bulk heterojunctions, which are disordered interpenetrating polymeric networks, the origin of the modified cell efficiencies is not completely clear. In this work, the P3HT:PCBM-based solar cells are fabricated with a varying film treatment condition, [4,10,11] and the morphological changes of the active layers were monitored using various instruments. The devices cooperated with the slow-solvent-vapor-treatment active layers present a power conversion efficiency (η) of 3.0%, resulting from the favorable transformation of the morphologies in the blend P3HT:PCBM films.

2. Experimental details

2.1. Device fabrication

The solar cells were fabricated in a standard arrangement by sandwiching the blend film of 1:1 wt/wt P3HT:PCBM between a transparent anode and metal cathode. The anode was

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comprised of the indium–tin–oxide (ITO) covered glass substrate (RITEK Corp., 15 Ω/□) with a spin-coated poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) layer (Baytron P, Bayer AG, Germany). Calcium (Ca) (40 nm) and Aluminum (Al) (100 nm) were thermally deposited onto the surface of the P3HT:PCBM film inside a vacuum chamber (4.0×10^{-8} Pa) as the device cathode. All the procedures are implemented inside a nitrogen-filled glove box except for casting the PEDOT:PSS layer. The thicknesses of the P3HT:PCBM layers of all studied samples were maintained approximately 250 nm, as determined by a Woollam M-2000U ellipsometer. The measurement of the thickness is also made by a Tencor Alpha-step 500 surface profiler. The variations of the thickness are around 10–20%. The active area of the device was 0.06 cm^2. Prior to device fabrication, the ITO/glass substrates were sequentially cleaned by ultrasonic treatment in detergent, de-ionized water, acetone and isopropyl alcohol.

Regioregular P3HT (98.5% electronic grade, Rieke Metals, Inc.) was first blended with PCBM (synthesized based on the literature) [12] and then dissolved in chlorobenzene to yield a P3HT:PCBM (30:30 mg/ml) solution. The blend solution was stirred for at least 48 h at 40 °C in a nitrogen-filled glove box. The active layer was obtained by spin-coating the solution at 1500 rpm for 60 s. The studied samples were then transferred to the Petri glass dishes that had been filled with a saturated vapor of chlorobenzene and maintained wet for 20 min, to ensure that the growth of the films was in the slow regime. Finally, the films were thermally annealed at 110 °C for 10 min. These samples are called “slow-solvent-vapor-treatment” devices [13]. To form “fast-thermal-annealing” samples, the films were spin-coated at 1500 rpm, and then immediately annealed at 110 °C for 10 min. Additionally, the films obtained by spin-coating without subsequent treatment (“as-cast”) were used as a reference in comparative experiments. In this work we focused on the effect of solvent-vapor-treatment during the annealing of P3HT:PCBM films, but not on the fabrication of devices with top competitive efficiency or fill factor. To investigate this effect in sufficient details, the prototype of one of the simplest and most studied devices was chosen. The preparation procedure was similar to those described in many other works during last decade, which is thought to render ease of the comparison.

2.2. Characterization

Device characteristics were measured in a nitrogen-filled glove box using a Keithley 2400 sourcemeter under the AM 1.5G-filtered irradiation (100 mW/cm^2) from an Oriel 96000 150 W Solar Simulator. The spectra-mismatch factor of the simulated solar irradiance is corrected by the approach, recently reported by Shrotriya et al., using a Schott visible-color glass-filtered (KG5 color filter) Si diode (Hamamatsu S1133) [14]. A Shimadzu Multispec-1500 spectrometer was used to perform the optical absorption spectroscopy in the ultraviolet/visible (UV/Vis) range and a Jobin Yvon LABRAM-HR spectrometer was employed to obtain Raman spectra (a 532 nm solid state laser was used, with the device resolution set to 0.5 cm^{-1}). Atomic force microscopic (AFM) images (in typing mode) were measured using a Digital Instrument Nanoscope IIIa microscope. X-ray diffraction (XRD) measurements were made by a Siemen D5000 diffractometer (Cu Kα = 1.542 Å) in $\theta/2\theta$ mode.

3. Results and discussion

3.1. AFM measurements

Fig. 1 presents AFM images (heights) of the surface of P3HT:PCBM films obtained in the taping mode. The figures clearly reveal the different surface topographies of fast-thermal-annealing (top) and slow-solvent-vapor-treatment (bottom) films. The morphology of the fast-thermal-annealing film exhibits a rather planar, uniform relief without distinct features, which would be randomly distributed whiskers and some small-sized clusters (diameter < 20 nm). AFM images in the phase contrast mode did not present additional details. For the slow-solvent-vapor-treatment film, the rougher surface morphology suggests the formation of the inter-penetrating P3HT:PCBM molecular network. The corresponding root-mean-square roughness of the fast-thermal-annealing and slow-solvent-vapor-treatment layers was around 1.0 and 1.4 nm, respectively. The aggregated structure corresponds to a nano-to-micron scale ordering in the slow-solvent-vapor-treatment films, in which the effect is consistent with results presented in the literature for variously annealed P3HT:PCBM films [10,11,15,16].

3.2. XRD measurements

Fig. 2 display the XRD spectra of as-cast, fast-thermal-annealing, and slow-solvent-vapor-treatment P3HT:PCBM

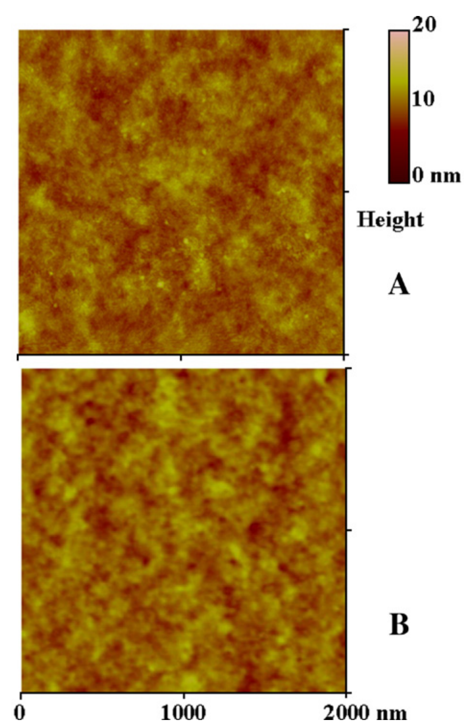

Fig. 1. AFM images (height) of the surface of the P3HT:PCBM active layer (A) fast-thermal-annealing and (B) slow-solvent-vapor-treatment.