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Letter

Enhanced thermal stability of organic solar cells on nano structured electrode by simple acid etching

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ABSTRACT

The long-term thermal stability of organic photovoltaic device has been emerged as a crucial characteristic to satisfy the demand of industry requiring lifespan of 20 year. In this paper, etched indium–tin-oxide (ITO) nanoelectrodes are employed to enhance the thermal stability and power conversion efficiency in poly(3hexylthiophene):methanofullerene bulk-heterojunction solar cells. A simple etching process for the ITO electrode was carried out using a hydrochloric acid solvent in order to significantly increase the roughness of the ITO surface. This nanostructured ITO not only induced efficient light harvesting, but also acted as a barrier that suppressed the PCBM phase separation, resulting in the lifespan increased from 33 h to 77 h during thermal annealing.

1. Introduction

Organic photovoltaic (OPV) devices using conducting polymers as the active layer are one of the most promising future class of solar cells due to their low-cost, lightweight, flexibility and low-temperature processing [1,2]. High device power conversion efficiency (PCE), long-term stability and large-area fabrication are essential to realize their practical commercialization. Among these requirements, long-term stability has received little attention as compared to PCE and large-area fabrication, although, arguably, it is the most important in organic based solar cell system [3].

As in other systems, the stability of OPVs can be classified into ambient stability or thermal stability. It is well known that oxygen and water molecules in the air easily degrade the solar cell as they react with the conducting polymer at room temperature, resulting in a reduction of PCE. Fortunately, the ambient stability issue can be resolved by encapsulating the OPV cells with polymers, which prevent the penetration of oxygen and water molecules to the active layer [4]. However, in contrast, much work is still needed to improve the thermal stability of OPVs at high temperatures for their practical applications. The performance deterioration mainly arises from macro-phase segregation in the active layer, especially at high temperatures, as the OPV devices are exposed to sunlight for long periods of time [5].

In order to improve the thermal stability of OPV devices, several efforts have been conducted in previous works, which include the structural design of thermally stable active materials, photo-crosslinkable conjugated polymers and use of suitable compatibilizer [6–8]. The first method involved the structural design of donor (P3HT-b-P3TODT) and acceptor (bis-PCBA) materials to improve the ordering of the active layer structure [6]. The second method used photo-crosslinkable conjugated polymers (TPD-Br) to prevent PCBM diffusion into the film [7]. Finally, a proper compatibilizer (P3HT-C_{60}) was utilized as a means to

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reduce the interfacial tension between the two dissimilar components in bulk heterojunction (BHJ) solar cells [8].

In this letter, we suggest a new and simple method to enhance the long-term thermal stability and efficiency of P3HT:PCBM photovoltaic device by using acid etched ITO electrodes with highly roughened surfaces. The surface of the ITO electrodes was wet-etched using hydrochloric acid at room temperature, generating the rough ITO surface. Successive improvement of efficiency from 3.21% to 3.53% was achieved on the etched ITO substrates, corresponding to an increased short-circuit current density. More importantly, the thermal stability of OPV devices were enhanced by a factor of two, increasing the lifespan from 33 h to 77 h during thermal annealing the as roughened surface suppressed the separation of PCBM crystals in the active layer.

2. Experimental details

Fig. 1 shows a schematic fabrication flow of the etching process for OPVs: indium tin oxide (ITO)-coated glass substrates were ultrasonicated in a detergent solution for 30 min, followed by drying with nitrogen gas. The substrate was put flatly in the hydrochloric acid etching solution for 7.5 min. Then, the substrate was rinsed in DI water. Subsequently, the etched ITO glass was ultrasonicated in acetone and isopropyl alcohol, following by drying in an oven at 60 °C for 12 h. The etched ITO glass was exposed to oxygen plasma for 5 min before depositing the hole transfer layer poly (3,4-ethylene dioxythiophene):poly(styrene sufonate) (PEDOT:PSS) (500). The PEDOT:PSS was spin-coated on the etched ITO glass at 3000 rpm and thermally annealed in a glove box at 140 °C for 10 min. P3HT (10 mg/ml, purchased from Rieke Met. Inc.) with PCBM (8 mg/ml, Nano-C) dissolved in chlorobenzene was spincoated at 700 rpm on the PEDOT:PSS layer as the active layer. Finally, 120 nm Al electrodes were deposited on the active layer to complete the device. Thermal annealing was carried out at 150 °C in a glove box. A solar simulator (Newport) with a 300 W Xenon lamp and air mass 1.5 global (AM1.5G) filter was used to evaluate the performance of the solar cell. The light intensity emanating from this source was calibrated by using a silicon photovoltaic reference cell (Bunkou Keiki Co., BS-520). Current–voltage (I–V) curves, determined by using a Keithley 236 source measurement unit, were obtained under 1 sun (100 mW cm^{-2}) light intensity conditions. The fabricated solar cell area was approximately 10.2 mm^2. Sample thicknesses were measured by using an Alpha-step IQ (KLA Tencor) profilometer. The surface morphology and the roughness of the blend films were determined by atomic force microscopy (AFM, dynamic contact mode, SII Nano Technology, SPA400). Optical microscopy was obtained by using LV100-POL microscope (Nikon).

3. Results and discussion

In order to investigate the variation of surface morphology during each step, atomic force microscopy studies were conducted for four different substrate surfaces: (i) as-prepared ITO, (ii) chemically etched ITO, (iii) PEDOT:PSS coated on as-prepared ITO and (iv) PEDOT:PSS on the etched ITO (Fig. 2). The surface of as-prepared ITO is highly smooth with an RMS value of 4.06 nm (Fig. 2a). After etching the as-prepared ITO for 7.5 min, the ITO surface became considerably rough with an RMS value of 14.17 nm (Fig. 2b). It should be noted that we tested the surface morphologies as a function of etching time (Fig. S1). It was found that 7.5 min was an optimum etching time to achieve the highest efficiency and long-time stability of the OPVs. Although a longer etching time of 10 min induced much rougher surfaces, with an RMS of 17.56 nm, excessive etching reduced the conductivity of ITO film, resulting in the degradation of the efficiency (Fig. S2). The surface of the PEDOT:PSS coated on as-prepared ITO is highly smooth with an RMS value of 2.68 nm (Fig. 2c). After spin-coating PEDOT:PSS layer on the etched ITO, the rough surface was retained to a good degree by the bottom ITO electrode, with an RMS value of around 8.63 nm (Fig. 2d). In summary, the irregular pattern from the etched ITO surface also forms on the PEDOT:PSS bottom surface.

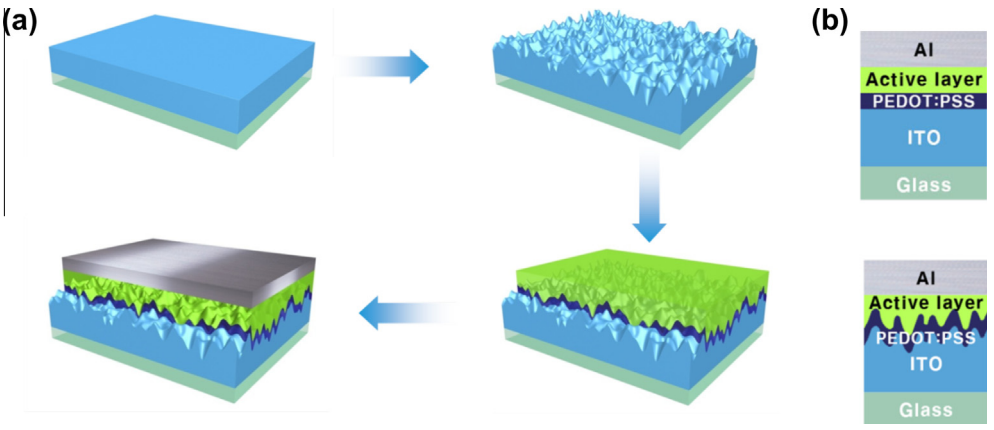

Fig. 1. (a) Schematic of the fabrication flow for P3HT:PCBM solar cells based on etched ITO nanoelectrode. (b) Schematic diagram of conventional and etched ITO nanoelectrode based OPV devices, respectively.