Organic Electronics 14 (2013) 2192–2197

Contents lists available at SciVerse ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel

Thermal annealing effect on internal electrical polarization in organic solar cells

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ARTICLE INFO

Article history:
Available online 31 May 2013

Keywords:
Organic solar cells
Electrical polarization
Photocurrent
Donor:acceptor interfaces
Charge transport

ABSTRACT

This article reports experimental studies on internal electrical polarization effects by using optical absorption and photoexcitation assisted capacitance–voltage (*C–V*) measurements based on morphological development in the standard P3HT:PCBM solar cell. We observe that morphological development can increase absorption intensity upon thermal annealing. The increase of absorption intensity essentially reflects an enhancement of absorption coefficient of local donor and acceptor structures. We attribute the enhancement of absorption coefficient to the well-known morphological developments: increased polymer crystallinity and molecular aggregations caused by thermal annealing. Furthermore, the enhancement in absorption coefficient indicates stronger electrical polarizations in the P3HT:PCBM film. The *C–V* studies find that increasing local electrical polarizations can lead to an enhancement on the generation of charge carriers at donor:acceptor interfaces and the transport of generated charge carriers to respective electrode interfaces in the P3HT:PCBM device. Our experimental findings suggest that local electrical polarizations play an important role in the development of photovoltaic processes in organic solar cells.

1. Introduction

Organic bulk-heterojunction solar cells have become an attractive component in photovoltaic devices based on facile tuning of materials parameters, possible fabrication of using printing technique, and mechanically flexible properties [1–6]. Essentially, the morphological development of donor and acceptor interpenetrating networks is a critical issue in controlling internal photovoltaic processes [7–12]. It is noted that the morphological development of donor and acceptor structures is intimately coupled with local electrical polarizations when the donor and acceptor are in excited states [13–15]. Specifically, the local electrical polarizations of donor and acceptor structures can be inevitably changed due to the Coulomb interactions at the interfaces of excited donor:acceptor when donor and acceptor structures are developed into interpenetrating networks. It is further noted that the change of local electrical polarizations can affect light absorption, charge dissociation, and charge transport at donor:acceptor interfaces in the development of photovoltaic functions [16–20]. In this work, we study electrical polarization effects upon morphological development through thermal annealing based on ITO/PEDOT/P3HT:PCBM/Al device by using optical absorption and photoexcitation assisted capacitance–voltage (*C–V*) measurements. Our intention is to elucidate the effects of local electrical polarizations on internal photovoltaic processes in organic bulk-heterojunction solar cells.

2. Experimental section

We use poly(3-hexylthiophene) (P3HT) (purchased from Nanostructured Carbon) as electron donor and

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http://dx.doi.org/10.1016/j.orgel.2013.05.016

1-(3-methyloxycarbonyl)propyl-1-phenyl [6,6] C61 (PCBM) (purchased from Luminescence Technology) as the acceptor to fabricate organic bulk-heterojunction solar cells with device architecture of ITO/PEDOT/P3HT:PCBM/Al. The P3HT:PCBM weight ratio was prepared to be 1:0.8 in ortho-dichlorobenzene (ODCB) solution. The photovoltaic films were spin cast with the thickness of 150 nm on precleaned indium tin oxide (ITO) substrates coated with 40 nm thin layer of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (Baytron P AI4083). Then 100 nm thick aluminum (Al) electrode was deposited onto the photovoltaic film under the vacuum of 2×10^{-6} Torr. The finished devices are annealed at 150 °C for 10 min in nitrogen gas. For obtaining the absorption spectra, the P3HT:PCBM photovoltaic films were spin cast on the quartz substrates, and a UV-3600 UV–VIS–NIR spectrophotometer was used to measure optical absorption. The photocurrent–voltage characteristics were recorded by using Keithley 2400 source meter under illumination of AM 1.5G 100 mW/cm^2 from Newport solar simulator. The photoexcitation assisted *C–V* measurements were performed by using a dielectric spectrometer (Agilent, 4294A) with alternating voltage of 50 mV at 1 kHz. All measurements were performed at room temperature in inert atmosphere.

3. Results and discussion

Fig. 1a shows the optical absorption for the P3HT:PCBM blend film measured before and after annealing. We can see that thermal annealing leads to an increase on absorption intensity in the range from 450 nm to 550 nm. The calculation indicates that the optical absorption intensity is increased by 4.35% upon thermal annealing. Because the P3HT:PCBM film thickness maintains un-changed during the thermal annealing, the increase of absorption intensity indeed reflects an enhancement on absorption coefficient of P3HT:PCBM film. We know that absorption coefficient is defined as the probability that an incident photon can be absorbed by a given molecule. This probability is determined by the interaction between incident photon (electromagnetic field) and induced electrical dipole. A stronger electrical polarization can lead to a larger electrical dipole. The enhancement in absorption coefficient can thus suggest a stronger electrical polarization in the P3HT:PCBM film. Morphological studies have shown that thermal annealing can increase the crystallinity of the P3HT structure and the aggregations of PCBM molecules [21–23]. This can lead to an enhancement on photovoltaic performance in the ITO/PEDOT/P3HT:PCBM/Al device (Fig. 1b). We should note that the polymer crystallinity and molecular aggregations can increase inter-chain and inter-molecular Coulomb interactions in excited states under photoexcitation. Consequently, the Coulomb interaction between P3HT and PCBM structures at the donor:acceptor interfaces can be increased upon morphological development of donor and acceptor interpenetrating networks. In principle, developing donor and acceptor interpenetrating morphologies can inevitably modify the local polarizations, changing photovoltaic functions in organic solar cells.

Fig. 2 schematically shows the development of electrical polarizations in bulk photovoltaic film and electrode interfaces in dark and under photoexcitation conditions. Due to work function difference, ITO (hole collecting electrode) and Al (electron collecting electrode) become negative and positive surfaces, respectively, caused by the charge tunneling through photovoltaic film between two electrodes under dark condition (Fig. 2a). The negative ITO and positive Al surface carry charge carriers: $-Q_e$ and $+Q_e$, respectively. More importantly, the difference in work function between anode and cathode generates a built-in electric field across a photovoltaic film in an organic solar cell. Essentially, the local P3HT and PCBM structures become electrically polarized in excited states under the influence of built-in electric field. It is noted that the electrical polarizations in P3HT and PCBM structures do not generate net charge carriers but can dominantly determine the absorption coefficient of photovoltaic P3HT:PCBM film by interacting with an incident electromagnetic wave. Therefore, measurement of absorption coefficient can elucidate internal electrical polarization in an organic solar cell. On the other hand, the electrical polarization can lead to net charges, namely surface charges (Q_s) on the surfaces of a photovoltaic film under dark condition (Fig. 2b). Obviously, changing local electrical polarizations can modify the density of surface charges. Clearly, the surface charges Q_s and electrode charges Q_e have opposite signs. The effective charges Q_{eff} at organic/electrode interfaces can be given by:

$$Q_{\text{eff}} = Q_e - Q_s \tag{1}$$

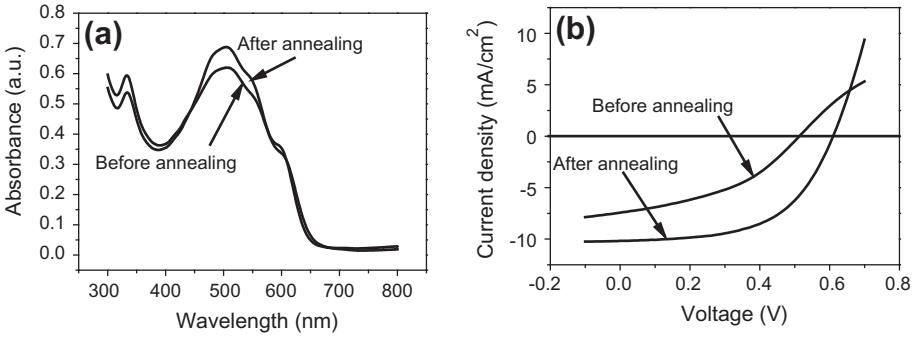

Fig. 1. (a) UV–VIS absorption spectra of P3HT:PCBM film before and after annealing. (b) Current–voltage (*I–V*) characteristics. The measurements were performed on ITO/PEDOT/P3HT:PCBM/Al device before and after annealing.