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Probing the annealing induced molecular ordering in bulk heterojunction polymer solar cells using in-situ Raman spectroscopy

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ABSTRACT

We have carried out temperature dependent *in-situ* Raman as well as optical microscopy of poly(3-hexylthiophene) and [6,6]-phenyl-C_{71} butyric acid methyl ester (P3HT:PCBM) films to investigate the structural and morphological evolution during heating and cooling cycles of thermal annealing. The full-width half-maximum of symmetric C=C stretching mode, C=C/C–C intensity ratio and Raman shift of C=C mode of P3HT measured during heating upto 130 °C as well as subsequent cooling revealed that: (i) molecular disorder in P3HT chains increase during heating cycle and (ii) on cooling the molecular ordering enhances rapidly at ~100 °C. However, heating to higher temperatures (> 150 °C) leads to the formation of PCBM aggregates. The mechanism of morphology evolution in P3HT:PCBM films envisaged through *in-situ* Raman and optical microscopy has been confirmed by other *ex-situ* techniques, such as, atomic force microscopy, scanning electron microscopy, UV–vis spectroscopy and X-ray elemental mapping. A correlation between the morphological evolution and various photovoltaic parameters of the fabricated P3HT:PCBM solar cells has been established.

1. Introduction

Bulk-heterojunction polymer solar cells based on conjugated polymer–fullerene blends are widely studied owing to their low-cost, flexibility, ease of material synthesis and manufacturing advantages [1–5].The most successful bulk-heterojunction polymer solar cells are based on poly(3-hexylthiophene) (P3HT) that acts as an electron donor and phenyl-C_{61}-butyric acid methyl ester (PCBM) that acts an electron acceptor[6–8]. In these P3HT:PCBM solar cells the energy-conversion process involves (i) creation of excitons upon light absorption which are dissociated into free charges at the donor/acceptor interface and (ii) transport of free charge carriers to the respective electrodes. One of the primary factors limiting the efficiency of these solar cells is the exciton dissociation at the donor–acceptor interface, which is mainly governed by the local morphology and distribution of P3HT and PCBM phases in the film[9]. In general high efficiency can be obtained if: (i) the active layer is phase separated to form bulk-heterojunctions with interpenetrating P3HT and PCBM domains having a size equal to that of exciton diffusion length (~10 nm); and (ii) a very high interfacial area between P3HT and PCBM phases. However, achieving such morphology is difficult in reality as the structure and morphology depends upon interplay between various complex thermodynamic and kinetic factors [10]. Experimentally, the efficiencies of bulk heterojunction P3HT:PCBM based solar cells have been reported in the range of 2–5% [1], whereas the theoretically predicted value is as high as 8% [11,12]. Thus there is a great experimental interest in the investigation of the structural and morphological evolution of P3HT:PCBM films so that solar cells fabricated using them has high efficiencies. In order to control the structure and morphology of P3HT:PCBM films different approaches such as thermal annealing [13,14], solvent annealing[15], electrical field annealing [16] and nano-patterning [17] have been employed. Among these, thermal annealing is widely employed owing to its simplicity and effectiveness in controlling the morphology via de-mixing of PCBM and stacking of P3HT in coplanar conjugated segments. Experimental results show that the highest efficiency is obtained when the active layer is annealed at a temperature in the range of 120–150 °C [9,18]. As of now it is not fully understood that how annealing processes affects the ordering of molecules, morphology and domain size of each component in the P3HT:PCBM films. In order to gain an insight into the annealing induced structural and morphological changes, various *in-situ* characterizations such as grazing-angle X-ray diffraction, near-field spectroscopy, photoluminescence (PL), Raman spectroscopy, and synchrotron X-ray

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reflectivity have been carried out [19–22]. These *in-situ* studies provide time dependent information on structural and morphological evolution that cannot be obtained by *ex-situ* techniques. For instance, the *in-situ* photoluminescence (PL) of P3HT:PCBM films during solvent annealing revealed that suppression of PL occurs mostly in the first minute, which is responsible for de-mixing of PCBM and stacking of P3HT in coplanar conjugated segments [21]. A combination of *in-situ* current–voltage measurements and grazing-incidence X-ray scattering of P3HT:PCBM bulk heterojunction active layer at elevated temperatures revealed a strong correlation between the photo-conversion efficiency and molecular ordering [19,23] In-situ monitoring of the photovoltaic and transport properties of P3HT:PCBM based solar cells during thermal annealing revealed that the photovoltaic parameters improve significantly only during first few minutes of the thermal annealing [24]. *In-situ* Raman spectroscopy—a powerful inelastic light scattering based technique that is capable of monitoring the nanoscale changes in the polymer structure through the measurement of vibrational modes—has not extensively been used for the investigation of structural/morphological changes during thermal annealing of P3HT:PCBM films.

In this paper, we report a systematic study on the temperature dependent *in-situ* resonant Raman and optical microscopy of P3HT:PCBM films. For this purpose, P3HT:PCBM films were deposited on ITO substrates and *in-situ* spectra/image were recorded during both heating as well as cooling cycles. The structural and morphology evolution of P3HT:PCBM films envisaged through *in-situ* resonant Raman and optical microscopy was further confirmed by other *ex-situ* techniques such as, atomic force microscopy, scanning electron microscopy, UV–vis spectroscopy and X-ray elemental mapping. These results also establish a direct correlation between the molecular ordering of P3HT and the efficiency of P3HT:PCBM solar cells.

2. Experimental

2.1. Materials

Regioregular P3HT (with $M_n = 65$ K g/mol with polydispersity of 2, 99.995% trace metals basis) and [6,6]-phenyl-C_{71} butyric acid methyl ester ($PC_{71}BM$) (hereafter mentioned as PCBM) were purchased from Sigma Aldrich and used as received without any further purification. Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS, PH1000) was obtained from Ossila Limited, England. Indium tin oxide (ITO) coated glass substrates with a sheet resistance of $10\,\Omega\,sq^{-1}$ were used for solar cell fabrication. Anhydrous 1,2-dichlorobenzene and all solvents were purchased from Sigma Aldrich and used as received.

2.2. Fabrication of P3HT:PCBM solar cells

ITO substrates were cut into required dimensions and subsequently cleaned using detergent, de-ionized water, acetone and 2-propanol. Polymer solar cells were fabricated with a device architecture of ITO/PEDOT:PSS/P3HT:PCBM/Al. For this, hole transport PEDOT:PSS layer (thickness: 50 nm) was deposited onto clean ITO substrates by spin coating, which were then transferred to glove box (MB 20G, MBraun Inc. Germany) having moisture and oxygen < 0.1 ppm. These samples were then annealed at 130 °C for 30 min. A mixture of P3HT and PCBM (with 1:1 W/W, 20 mg/ml) were dissolved in 1,2-dichlorobenzene solvent by continuous stirring for 24 h and later filtered through 0.45 μm syringe filters. An active layer P3HT:PCBM (thickness:100 nm) layer was deposited by spin coating the filtered solution onto PEDOT:PSS coated ITO substrates. These samples were annealed at various temperatures between 25 °C and 180 °C for 30 min. The solar cell configuration was established by thermal deposition of Al under a base vacuum of $\sim 10^{-6}$ Torr through a shadow mask to obtain an active area of 6 mm^2. These solar cells were encapsulated using UV curable epoxy inside the glove box and taken out for the photovoltaic characterization. The photovoltaic parameters of the devices were measured using a solar simulator (Sciencetech, Canada) under 1sun (AM 1.5G), 100 mW/cm^2 illumination.

2.3. In-situ and ex-situ characterization

For in-situ Raman and optical microscopy measurements, P3HT:PCBM films (thickness: 100 nm) were deposited on clean ITO substrates by spin coating. The temperature dependent Raman spectra and optical images were recorded simultaneously by placing the P3HT:PCBM films on the heating stage (Linkam THMS 600) of micro-Raman spectrometer Jobin-Yvon (LabRAM HR800). The films were heated to different temperatures (110–180 °C) under inert atmosphere at a rate of 10 °C/min and the spectra were recorded during both heating and cooling cycles. This heating stage has an accuracy and stability of ±0.1 °C. The spectra were collected in the 180° backscattering geometry with a spectral resolution of 1 cm^{-1} using the Ar^+ laser (514 nm) as an excitation source. The laser intensity and acquisition time was controlled in such a manner that the sample does not undergo a photo-degradation. The laser beam was focused onto the sample using 50× objective lens and the laser spot size was ~5 μm. The obtained spectra were fitted using a Lorentzian function to determine the peak position, band width and intensity ratio with Labspec 5 software. UV–vis spectra were recorded using UV–vis spectrophotometer (V-800, Jasco). Atomic force microscopy images were obtained in contact mode using scanning probe microscope (NTMDT). The morphology of the films were also imaged using scanning electron microscope (TECSCAN, Model:VEGA MV2300T/40) and the uniformity of the composition was examined by reordering the elemental X-ray analysis (Oxford, INCA X-Act analyzer).

3. Results and discussion

3.1. Photovoltaic characterization

Fig. 1 shows the current–voltage (*J–V*) characteristics of as-deposited and thermally annealed (75 °C, 110 °C, 130 °C, 150 °C, and 180 °C for 30 min) P3HT:PCBM bulk-heterojunction solar cells, which were measured under AM 1.5G, 1sun illumination. From these

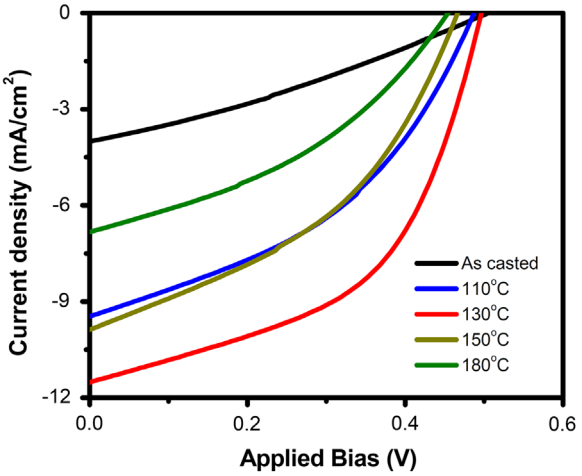

Fig. 1. *J–V* characteristics of as-deposited and thermally annealed (at various temperatures) P3HT:PCBM bulk-heterojunction solar cells.