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Effect of thermal annealing on the structural, optical and dielectrical properties of P3HT:$PC_{70}BM$ nanocomposites

Walid Aloui[a,*], Tham Adhikari[b], Jean-Michel Nunzi[b,c], Abdelaziz Bouazizi[a]

[a] Laboratory of Condensed Matter and Nanosciences, Faculty of Sciences of Monastir, Avenue of the Environment, 5019 Monastir, Tunisia
[b] Department of Chemistry, Queen's University, Kingston, ON K7L 3N6, Canada
[c] Department of Physics, Engineering Physics and Astronomy, Queen's University, Kingston, ON K7L 3N6, Canada

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ABSTRACT

The effect of thermal annealing on the optical, structural and the dielectric properties of P3HT:$PC_{70}BM$ blended films were investigated. By means of atomic force microscopy, we observed the morphology evolution of the annealed P3HT:$PC_{70}BM$ nanocomposites. Raman spectroscopy showed a substantial ordering in the polymer film after annealing. The absorption spectra of the annealed P3HT:$PC_{70}BM$ films were improved and red shifted than un-annealed samples. The results indicate that the P3HT in the nanocomposite becomes an ordered structure with annealing. The ordered P3HT facilitates the charge transport. From the photoluminescence measurements, the formation of polymer crystallites was observed upon annealing. Thus, the device efficiency reaches 2.2% after annealing at 150 °C. Impedance spectroscopy shows the classical complex plan curves; the low frequency is related to the effective lifetime of charge carriers and the high frequency corresponds to the diffusion time of these carriers. Global mobilities are in the range $3.8–4.6 \times 10^{-3}\ cm^2\ V^{-1}\ s^{-1}$.

1. Introduction

In last few years, organic photovoltaic solar cells (OPV) on conjugated polymers and fullerenes nanocomposite have grown in popularity as a promising alternative source of energy due to their ease of processing, flexibility, low cost and light weight [1]. The P3HT: PCBM nanocomposite is the most successful and popular materials; the efficiency of the solar cells is increasing and reported the highest efficiency up to 11% [2]. In organic photovoltaic solar cells, the nanocomposite morphology plays a key role in determining the efficiency of charge carrier generation and collection at electrodes. In particular, polymer: fullerene nanocomposite must form phase separated morphology on the order of exciton diffusion length while retaining bi-continuous percolation paths for the charge carriers [3–6]. The P3HT: PCBM nanocomposite is a model material combination which is well-studied and understood relative to other OPV blended materials. The morphology of this particular nanocomposite develops distinct molecularly ordered phases when subjected to solvent [7,8] or thermal processing [9–12]. Both annealing processes enable material reorganization and redistribution at the surface and within the bulk film resulting in increased crystallinity [10]. Thermal processing studies are valuable for OPV because they can provide an overview of the fundamental of the devices and materials as well as practical information on the device performance in real conditions [13–18]. Thermal annealing has been shown to be a critical step in the blend of P3HT: PCBM solar cells [19,20]. The electrical characterization is a common method for understanding the charge transport mechanisms. Impedance Spectroscopy has been successfully used in organic material to obtain valuable information about the device performance such as chemical treatments, bias voltage, illumination intensity [21,22]. It is also a precious tool to observe bulk and interfacial electrical properties that cannot be observed in direct current regime. Moreover, it permits the determination of several electronic parameters such as the effective lifetime of the electrons for the recombination process [23] and the global mobility [24]. Indeed, in this technique, we apply a small sinusoidal voltage superposed on a bias voltage affecting the space charge region. However, the effect of thermal treatment on the dielectric properties has remained poorly investigated. It is the interaction of the collective dynamical properties of the polymer chains and the fullerene molecules that make the dielectric study interesting. The fundamental question is how the interactions between the different components of the nanocomposite changes as the state varied with temperature.

* Corresponding author.
E-mail address: alouiwalid26@yahoo.fr (W. Aloui).

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In this paper, we elaborate OPV cells with P3HT: $PC_{70}BM$ active layer. All measurements were performed in an ambient atmosphere. We present the obtained results related to the optical, structural and dielectric properties of P3HT: $PC_{70}BM$ blends as function of annealing temperature.

2. Materials and methods

Regioregular P3HT was used as electron donating material while a soluble fullerene derivative ($PC_{70}BM$) was used as an acceptor material and the (PEDOT: PSS) was used as hole transporting material. Those products are purchased from Sigma Aldrich. The Indium tin oxide ITO substrates were sonicated in fresh 10% NaOH solution, rinsed thoroughly in water and dried under N_2 flow. A thick PEDOT: PSS hole transporting layer was subsequently spin coated onto the treated ITO substrate, which was annealed in a hot plate at 110 °C for 10 min. To prepare the nanocomposite layer, we dissolved a weight ratio of 1:1 (P3HT: $PC_{70}BM$) in dichlorobenzene. The blend solution was spin coated at 1500 rpm for 20s onto the PEDOT: PSS barrier layer to prepare four devices (samples: (a)–(d)). ITO/PEDOT:PSS/P3HT:$PC_{70}BM$ devices prepared in the same batch were annealed at different temperatures: sample (a) without annealing, sample (b) annealed at 110 °C, sample (c) annealed at 130 °C and sample (d) annealed at 150 °C for 10 min. The metal top electrode (Al) was deposited by thermal evaporation under 10^{-6} mbar vacuum.

3. Results and discussion

3.1. Atomic force microscopy

In order to investigate the effect of thermal annealing on the morphology of P3HT: PC70BM nanocomposites, AFM images were taken. The AFM images of the nanocomposites before and after thermal annealing are shown in Fig. 1. The surface of the film shows an inhomogeneous dispersion of some aggregates mainly due to inter-chain interactions. No phase separation has been observed in the morphology. Indeed, in fundamental state some conjugations of the polymer stack with each other leading to the overlap between the π orbital [25,26]. However, the presence of fullerene molecules in the polymer matrix makes difficult the relocation of these orbital. Therefore, a low aggregation occurred in the nanocomposite that has not undergone a thermal annealing. Observing the AFM image of the surface of the annealed nanocomposites, it is clearly seen that the temperature promotes the phase separation as the temperature increases the dispersion of $PC_{70}BM$ molecules. It results in homogeneous surface. This is due to the increase in the interaction after thermal annealing beyond the glass transition temperature ($T_g = 65 - 80$ °C). The thermal treatment beyond the glass transition provides a reorganization of the polymer chains into a thermodynamically conformation more favorable and increases the interchain interactions. Otherwise, the thermal annealing increases the P3HT crystallinity and leads to the phase separation of the nanocomposite to train a bi-continuous morphology [27]. Further, annealing at high temperatures (150 °C) leads an increase of the density of the $PC_{70}BM$ aggregates forming the percolation paths. At 150 °C, it appears that the aggregates are homogeneously dispersed and the phase separation significantly changes.

3.2. Raman spectroscopy

Fig. 2 compares the Raman spectra of the films of P3HT: $PC_{70}BM$ deposited on a glass substrate without annealing and after thermal annealing at 110, 130 and 150 °C. These spectra have the expected vibration frequencies [28]. The peak at 1450 cm^{-1} is attributed to the symmetric stretching deformation at C=C bond. The peak at 1375 cm^{-1} is associated at the C—C stretching deformation in the aromatic thiophene ring [29,30]. In order to extract additional information from the Raman spectra, we examined the 1350–1500 cm^{-1} region before and after thermal annealing. It is observed that the Raman intensity of the symmetric mode C=C and the C—C mode increases with the annealing temperature suggesting the occurrence of a large order in the polymeric film after annealing. No shift is observed in the C=C peak after annealing. This usually indicates an increase in the crystallinity of the P3HT polymer and an extension of the conjugation length along the polymer backbone [31]. This observation is in good agreement with the morphological studies.

3.3. UV–vis spectroscopy

Fig. 3 shows the absorption spectra of P3HT: PC70BM nanocomposites before and after thermal annealing. The absorption spectrum is composed by an apparent vibronic shoulder near the wavelengths of 510, 550 and 615 nm, characteristics of the π-π* transition of the P3HT polymer. Due to thermal annealing, there is an expansion of the absorption band and an increase of the absorption peaks. As demonstrated by the morphological analysis, the thermal annealing beyond T_g causes an increase in the conjugation length of the polymers. These spectra show that the intensity of the vibronic shoulders at 615 nm gradually increases with the annealing temperature until reaching a maximum intensity at an annealing temperature of 150 °C, indicating an increase in the P3HT crystallinity. We also note that at 150 °C, a shift towards higher wavelengths is observed. This suggests that the polymer structure is reorganized. This shift can be interpreted by the decrease of the interaction between the P3HT and $PC_{70}BM$ after annealing. This is correlated with the structural and morphological results highlighting the crystallinity order at high annealing temperature.

3.4. Photoluminescence spectroscopy

The photoluminescence (PL) measurements (Fig. 4) provide an additional evidence of the highest crystallinity order due to thermal annealing. Indeed, the increase of the PL intensity is supported by the change in the phase separation initiated by the aggregation of PCBM molecules as it has been observed by AFM. Although the generation rate of excitons tend to increase with thermal annealing, their cleavage may be hindered due to the PCBM diffusion creating a phases separation greater than the diffusion length of excitons [32]. The efficiency of electron transfer depends obviously on the average distance between the conjugated polymer and fullerene molecules. However, Malgas et al. [33] have shown that a total extinction is observed for the nanocomposite P3HT: PCBM (1:1) without thermal annealing. It is further noticed that the concentration of PC70BM in the film does not change during the annealing. It is concluded that the variation of the PL intensity derived from the phase separation initiated by the thermal treatment. In addition, the reorganization of the polymer is strongly indicated by the red shift in the PL spectrum of the annealed sample [29].

3.5. Effect of annealing temperature on the electrical properties

Fig. 5 shows the J–V characteristics of ITO/PEDOT:PSS/P3HT: $PC_{70}BM$/Al devices under illumination. As annealing temperature increases, the photovoltaic parameters improve significantly. The short-circuit current density (J_{sc}) and the power conversion efficiency (η) increase from 1.75 to 3.35 mA/cm^2 and from 0.8 to 2.2%, respectively.