Effect of annealing of poly(3-hexylthiophene)/fullerene bulk heterojunction composites on structural and optical properties

Uladzimir Zhokhavets [a,*], Tobias Erb [a], Harald Hoppe [b], Gerhard Gobsch [a], N. Serdar Sariciftci [b]

[a] Institute of Physics, Ilmenau Technical University, PO Box 100565, D-98693 Ilmenau, Germany
[b] Linz Institute for Organic Solar Cells (LIOS), Physical Chemistry, Johannes Kepler University Linz, Altenbergerstr.69, A-4040 Linz, Austria

Abstract

Composite films of P3HT/PCBM-(poly[3-2,5-diyl]/[6,6]-phenyl C_{61} butyric acid methyl ester) are widely used as an active layer in plastic solar cells. We have studied the influence of thermal annealing on nano-structural and optical properties of thin spin-coated P3HT/PCBM-films. Their structural properties were studied by X-ray diffraction in grazing incidence geometry. It was found that the crystallinity of the investigated films is drastically increased upon annealing. Furthermore, the anisotropic dielectric function of such films was determined by spectroscopic ellipsometry. Significant changes were observed both in parallel and perpendicular components of the dielectric function after annealing. These changes were attributed to the formation of crystalline domains upon annealing.
© 2005 Elsevier B.V. All rights reserved.

1. Introduction

Poly[3-hexylthiophene-2,5-diyl]/[6,6]-phenyl C_{61} butyric acid methyl ester (P3HT/PCBM) composites are currently the best performing material system for application in bulk heterojunction polymer/fullerene plastic solar cells [1–3]. Due to the strong impact of annealing on morphological and optical properties of such photoactive blends, these parameters are of current research interest [3–5]. In particular, the origin of the enhanced optical absorption in the lower photon energy region ($\hbar\omega = 2.0 - 3.0$ eV) needs to be understood. The significance of the increase in optical absorption on the achievable photocurrent of P3HT/PCBM solar cells upon annealing has been investigated earlier [4].

Besides an increase in optical absorption improvements of the transport properties have been reported [2,3]. It was suggested, that the improved transport characteristics are due to the formation of percolating pathways of the fullerene phase during the annealing [3]. The present work focuses on the changes in the polymer domain morphology, in particular its crystallinity, domain size and orientation.

In this work, the structural properties of thin P3HT/PCBM-films were studied by X-ray diffraction (XRD). The size and orientation of polymer crystallites within the films were determined. In addition, the optical properties of these films were investigated by measuring the anisotropic dielectric function using spectroscopic ellipsometry and by photoluminescence measurements. A clear correlation between optical and structural properties was found.

2. Experimental details

Thin P3HT/PCBM composite films were prepared under ambient conditions. The photoactive blend films were prepared by spin casting from 1.1 wt.% chlorobenzene solution of the blended materials onto silicon substrates. The solution was stirred overnight under slightly elevated (50 °C) temperature, without any sonication or filtering. The mass fraction of PCBM was 67%. The spin casting procedure included 40 s of 1500 rpm followed by 20 s of 2000 rpm. A part of the samples was annealed on a hot plate at 150 °C for 3 min under argon atmosphere. The film

thickness was nearly 50 nm for both annealed and not annealed films.

XRD measurements were performed with a Philips X'Pert-Pro diffractometer. The thin films were studied in grazing-incidence diffraction geometry in order to increase the XRD beam path in the film and thus to maximize the signal-to-noise ratio. The radiation was a monochromatized Cu K_α beam with wavelength $\lambda = 0.154056$ nm. The angle between film surface and incident beam was fixed at 0.3°. The experimental resolution and the integration time per step were 0.05° and 180 s, respectively. The detector scans in a plane defined by incidence beam and the surface normal.

Ellipsometric data were obtained by means of a J. A. Woollam Co. VASE® variable angle spectroscopic ellipsometer with rotating analyser in the spectral range $\hbar\omega = 1.5–4.0$ eV in steps of 0.02 eV. The measurements were performed at several angles of incidence in the range of 60–75° at room temperature in air. In order to determine the anisotropic dielectric function of the films, a multiple-sample analysis was applied as described elsewhere [6–8].

Photoluminescence spectra were obtained by illumination of the samples with a 2.5 mW semiconductor GaN-Laser operating at a wavelength of 408 nm. The photoluminescence signal of the samples was analyzed using a single-grating monochromator with an attached N_2-cooled CCD-array.

3. Results and discussion

The diffractograms of both untreated and annealed P3HT/PCBM-films are shown in Fig. 1. The annealed sample shows a single peak at $2\theta = 5.24°$. The corresponding lattice constant d can be calculated using Bragg's law

$$2d\sin(\Theta) = n\lambda, \qquad (1)$$

where $\lambda = 0.154056$ nm is the wavelength of incident beam, 2θ is the angle between incident and scattered X-ray wave vectors and n is the interference order. Applying (1), we obtain $d = (1.68 \pm 0.03)$ nm. Comparing this value with data from literature [9–11], it can be concluded, that the detected peak
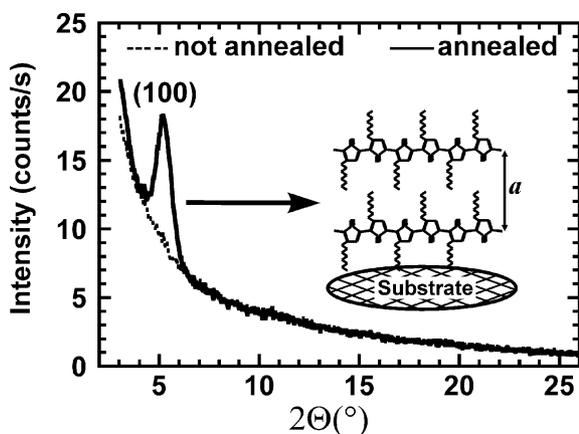

Fig. 1. Diffractogram of the untreated (dashed line) and the annealed (solid line) P3HT/PCBM-films. The orientation of the crystalline P3HT-domains with respect to the substrate is shown in the inset.
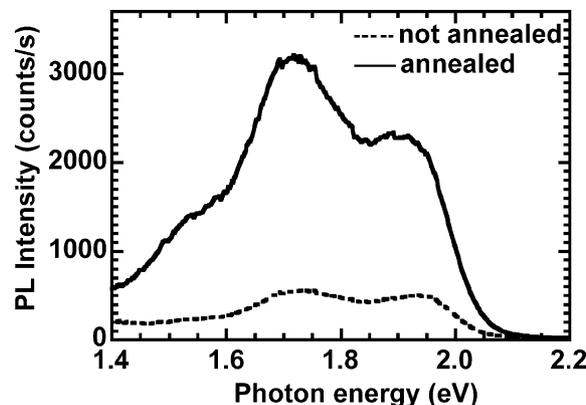

Fig. 2. Photoluminescence spectra of untreated (dashed line) and the annealed (solid line) P3HT/PCBM-films. A considerable increase of the structure and some red-shift is observed, typical for crystalline ordering of the conjugated polymer.

originates from polymer crystallites with a-axis orientation (backbone parallel and side-chains perpendicular to the substrate, as shown in the inset in Fig. 1). We assume that the symmetric sidechain substitution together with high regioregularity enable the crystallisation of P3HT. No crystallites with b-(backbone and sidechains parallel to the substrate) or c-axis (backbone perpendicular to the substrate) orientation (lattice constants $b = 0.383$ nm and $c = 0.385$ nm, respectively [8–10]) were detected. The reason for a-axis orientation of P3HT crystallites is not completely understood. We suppose that the a-axis orientation of the P3HT-crystallites is forced by interaction between the hydrophobic P3HT sidechains and the hydrophilic SiO_2 substrate. The a-axis orientation of the P3HT molecule is energetically favourable, because the contact area between the P3HT sidechains and the Si substrate is lower in this case as compared to b-axis orientation (i. e. polymer backbone and sidechains parallel to the substrate). This interface layer could induce the same orientation throughout the film [8].

In the case of the untreated sample, no diffraction peaks were observed at all. Thus, this sample was found to be amorphous within the limits of our sensitivity.

In the case of the annealed sample, the size of the polymer crystallites L can be obtained applying the Scherrer formula

$$L \sim \frac{0.9\lambda}{\Delta_{2\theta}\cos(\theta)}, \qquad (2)$$

where $\Delta_{2\theta}$ is the full width half maximum of the peak. Using (2), one obtains a lower limit for the crystallite size $L = 9.2$ nm. It should be pointed out, that the obtained value corresponds to the domain size along the a-axis. The domain size along the b- and c-axes cannot be estimated from our measurements, because the corresponding peaks are absent in the diffractogram. The width of the diffraction peak and therefore the crystallite size are nearly constant for the annealed films with different thicknesses.

Photoluminescence measurements on the same samples (Fig. 2) provide further evidence of the formation of polymer crystallites. The photoluminescence of the annealed sample is several times higher than that of the untreated one. That means

that the photoinduced electron transfer from the polythiophene becomes less efficient upon annealing. The effciency of electron transfer depends obviously on the mean distance between conjugated polymer and fullerene molecules. If the distance between polymer and fullerene becomes comparable with the exciton diffusion length (~10 nm), some excitons cannot reach the neighbouring fullerene molecule and recombine radiatively, giving rise to photoluminescence signal. Since the concentration of the PCBM in the film does not change upon annealing, we conclude, that the change of the photoluminescnece intensity originates from a phase separation and thus changes in the morphology of the active layer. Furthermore, in agreement with the crystallization process, a polymer aggregate formation is strongly indicated by the observation of a characteristic red shift in the PL spectrum of the annealed sample [12].

It should be pointed out, that in our measurements diffraction peaks caused by PCBM crystallites were not detected. In [13], pure PCBM powder was studied by XRD. A distinct diffraction pattern with characteristic narrow peaks was measured [13]. These peaks, however, are absent in the diffractogram of both as cast and annealed P3HT/PCBM thin films (Fig. 1). Thus, the PCBM is not crystalline in our P3HT/PCBM films within the limit of our sensitivity. The reason for this lies probably in the short annealing time (3 min in our case) in comparison to the typical time needed for formation of large PCBM crystallites, which is between 20 min and several hours [14,15].

It was shown, that the degree of alignment of the polymer chains parallel to the substrate can be characterized by the optical anisotropy A, which we define as a quotient of the maxima of the parallel and perpendicular components of the imaginary part of dielectric function, i. e. $A = \frac{\varepsilon_{2\parallel}^{max}}{\varepsilon_{2\perp}^{max}}$ [7,16]. This is because the lowest energy optical transition ($\pi - \pi^*$) is excited by an electric field that is oriented parallel to the polymer backbone [17], and hence, the absorption strength of the polymer is maximal parallel to the polymer backbone. As it follows from the XRD-measurements, the annealing induces the formation of polymer crystallites with pronounced a-axis orientation. Consequently, the optical anisotropy A should increase upon annealing.

The determined imaginary part of the anisotropic dielectric function ε_2 of the samples is shown in Fig. 3. In the UV spectral region $\hbar\omega > 3.2 eV$, the dielectric function of the films is nearly isotropic, i.e. $\varepsilon_{2\parallel} \approx \varepsilon_{2\perp}$. This is because the optical absorption in this energy region is mainly determined by the optical transition of the PCBM at 3.67 eV, which is isotropic. There are only minor changes in the amplitude of the PCBM-peak at 3.67 eV between the untreated and the annealed samples.

In the visible region $\hbar\omega < 3.2$ eV, however, the changes of the dielectric function are much stronger. The following three important differences between the dielectric function of the annealed and the untreated film are observed in the low photon energy region:

1. The local maximum of the imaginary part of the dielectric function ε_2 is shifted to lower photon energies. This is true for both parallel and perpendicular components of ε_2.
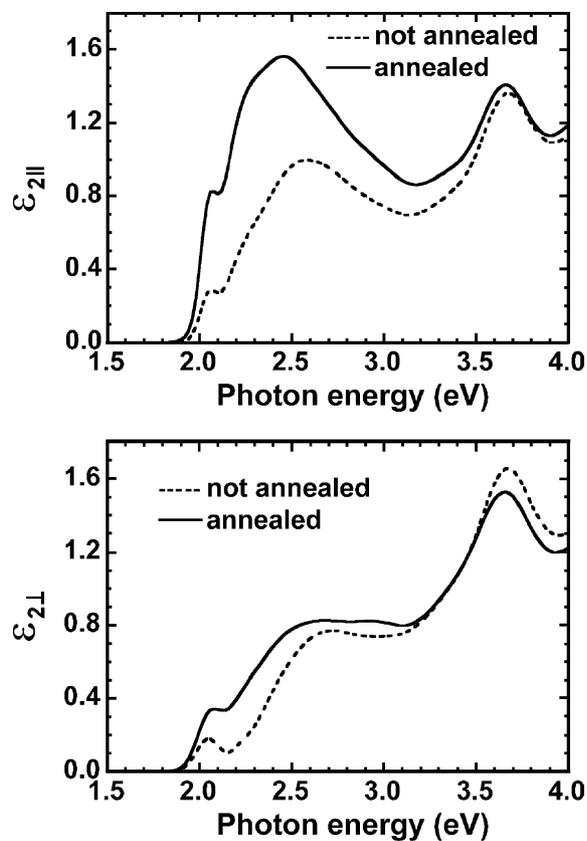

Fig. 3. Parallel (upper panel) and perpendicular (lower panel) components of the imaginary part of the anisotropic dielectric function of the untreated (dashed line) and the annealed (solid line) P3HT/PCBM-films.

2. Both parallel and perpendicular components of ε_2 are increased upon annealing.
3. The optical anisotropy is increased upon annealing (from $A = 0.99/0.77 = 1.29$ for the untreated to $A = 1.56/0.82 = 1.90$ for the annealed film).

It has been shown [18,19], that both absorption and emission maxima of conjugated polymers are shifted towards lower photon energies with increasing conjugation length. Therefore the first phenomenon is obviously caused by increasing of the mean conjugation length upon annealing. The increase of the mean conjugation length is in a good agreement with XRD-measurements performed on the same films (see Fig. 1). From XRD-measurements, the formation of polymer crystallites was concluded. The conjugation length in crystallites is larger because the polymer molecules within such crystallites are well oriented and there are less structural defects like chain kinks, which limit the conjugation length. Thus, the mean conjugation length for annealed samples should be larger, resulting in the observed shift of the absorption and the emission (see Fig. 2) maxima to the lower photon energies. The increase of the mean conjugation length upon annealing gives also rise to the improved optical absorption.

The increase in optical anisotropy is in agreement with the formation of the polymer crystallites. From the XRD-measurements it follows that such crystallites have a pronounced a-axis orientation (polymer backbone parallel to the substrate). Thus

the polymer chains become more parallel oriented to the substrate resulting in a higher optical anisotropy [8].

A question arises what is the origin of the improved solar cell performance after annealing [2]. Photoluminescence measurements show that the photoinduced electron transfer becomes less effective upon annealing (Fig. 2). On the other hand, annealing leads to an improvement of the optical absorption in visible region (Fig. 3). Since the polythiophene molecules are better ordered in the case of annealed polythiophene/fullerene films, it is reasonable to assume, that the hole mobility is higher for the annealed sample. We conclude that increase of optical absorption together with improved hole transport properties overcompensate the less efficient photoinduced electron transfer and lead to the observed improvement of P3HT/PCBM solar cell efficiency.

4. Conclusion

In conclusion, we have studied structural and optical properties of both untreated and annealed P3HT/PCBM composite films. The untreated P3HT/PCBM-films were found to be non-crystalline whereas the annealed ones were partially crystalline. In the case of the annealed film a crystallite size of 9.2 nm was obtained from analysis of the X-ray diffraction pattern. Only the polymer domains with a-axis orientation (polymer backbone parallel and side-chain perpendicular to the substrate) were observed. The photoluminescence measurements confirm the formation of the polymer crystallites upon annealing. Further on, the anisotropic dielectric function of the films was determined by spectroscopic ellipsometry. An enhanced optical anisotropy, increased absorption in low photon energy region and a red shift of the absorption were found for annealed P3HT/PCBM-films. These changes were explained in terms of the formation of polymer crystallites upon annealing.

Acknowledgment

References

[1] P. Schilinsky, C. Waldauf, C.J. Brabec, Appl. Phys. Lett. 81 (2002) 3885.
[2] F. Padinger, R.S. Rittberger, N.S. Sariciftci, Adv. Funct. Mater. 13 (2003) 85.
[3] D. Chirvase, J. Parisi, J.C. Hummelen, V. Dyakonov, Nanotechnology 15 (2004) 1317.
[4] H. Hoppe, N. Arnold, D. Meissner, N.S. Sariciftci, Thin Solid Films 451 (2004) 589.
[5] X.N. Yang, J. Loos, S.C. Veenstra, W.J.H. Verhees, M.M. Wienk, J.M. Kroon, M.A.J. Michels, R.A.J. Janssen, Nano Lett. 5 (2005) 579.
[6] M. Tammer, P. Monkman, Adv. Mater. 14 (2002) 210.
[7] J. Sturm, S. Tasch, A. Niko, G. Leising, E. Toussaere, J. Zyss, T.C. Kowalczyk, K.D. Singer, U. Scherf, J. Huber, Thin Solid Films 298 (1997) 138.
[8] U. Zhokhavets, G. Gobsch, H. Hoppe, N.S. Sariciftci, Synth. Met. 143 (2004) 113.
[9] T.J. Prosa, M.J. Winokur, Macromolecules 25 (1992) 4364.
[10] K.E. Aasmundtveit, E.J. Samuelsen, M. Guldstein, C. Steinsland, O. Flornes, C. Fagermo, T.M. Seeberg, L.A.A. Pettersson, O. Inganäs, R. Feidenhans'l, S. Ferrer, Macromolecules 33 (2000) 3120.
[11] T. Erb, S. Raleva, U. Zhokhavets, G. Gobsch, B. Stuhn, M. Spode, O. Ambacher, Thin Solid Films 450 (2004) 97.
[12] P.J. Brown, D.S. Thomas, A. Kohler, J.S. Wilson, J.-S. Kim, C.M. Ramsdale, H. Sirringhaus, R.H. Friend, Phys. Rev., B 67 (2003) 064203.
[13] T. Erb, U. Zhokhavets, G. Gobsch, S. Raleva, B. Stühn, P. Schilinsky, C. Waldauf, C. Brabec, Adv. Funct. Mater. 15 (2005) 1193.
[14] X. Yang, J.K.J. van Duren, R.A.J. Janssen, M.A.J. Michels, J. Loos, Macromolecules 37 (2004) 2151.
[15] H. Hoppe, M. Niggemann, C. Winder, J. Kraut, R. Hiesgen, A. Hinsch, D. Meissner, N.S. Sariciftci, Adv. Funct. Mater. 14 (2004) 1005.
[16] D. McBranch, I.H. Campbell, D.L. Smith, J.P. Ferraris, Appl. Phys. Lett. 66 (1995) 1175.
[17] D. Comoretto, G. Dellepiane, F. Marabelli, J. Cornil, D.A. Santos, J.L. Bredas, D. Moses, Phys. Rev., B 62 (2000) 10173.
[18] Y. Kanemitsu, K. Suzuki, Y. Masumoto, Y. Tomiuchi, Y. Shiraisi, M. Kuroda, Phys. Rev., B 50 (1994) 2301.
[19] G. Padmanaban, S. Ramakrishnan, J. Am. Chem. Soc. 122 (2000) 2244.