

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

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## Abstract

Composite films of P3HT/PCBM-(poly[3-2,5-diyl]/[6,6]-phenyl C<sub>61</sub> 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.

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## 1. Introduction

Poly[3-hexylthiophene-2,5-diyl]/[6,6]-phenyl C<sub>61</sub> 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 ( $\hbar\omega=2.0\text{--}3.0$  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

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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 $\alpha$  beam with wavelength  $\lambda=0.154056$  nm. The angle between film surface and incident beam was fixed at  $0.3^\circ$ . The experimental resolution and the integration time per step were  $0.05^\circ$  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<sup>®</sup> variable angle spectroscopic ellipsometer with rotating analyser in the spectral range  $\hbar\omega=1.5\text{--}4.0$  eV in steps of 0.02 eV. The measurements were performed at several angles of incidence in the range of  $60\text{--}75^\circ$  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<sub>2</sub>-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  $2\theta=5.24^\circ$ . The corresponding lattice constant  $d$  can be calculated using Bragg's law

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

where  $\lambda=0.154056$  nm is the wavelength of incident beam,  $2\theta$  is the angle between incident and scattered X-ray wave vectors and  $n$  is the interference order. Applying (1), we obtain  $d=(1.68\pm0.03)$  nm. Comparing this value with data from literature [9–11], it can be concluded, that the detected peak

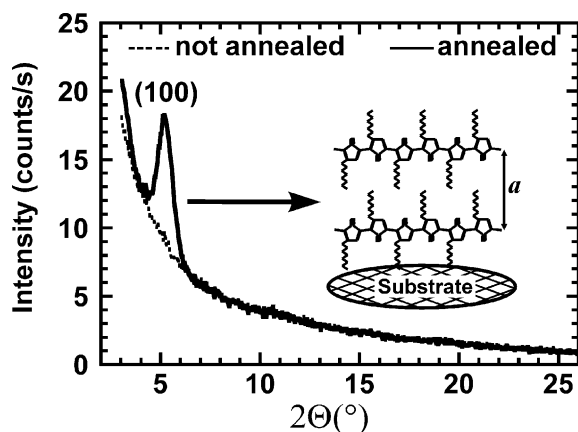


Fig. 1. Diffractogram of the untreated (dashed line) and the annealed (solid line) P3HT/PCBM-films. The orientation of the crystalline P3HT-domains with respect to the substrate is shown in the inset.

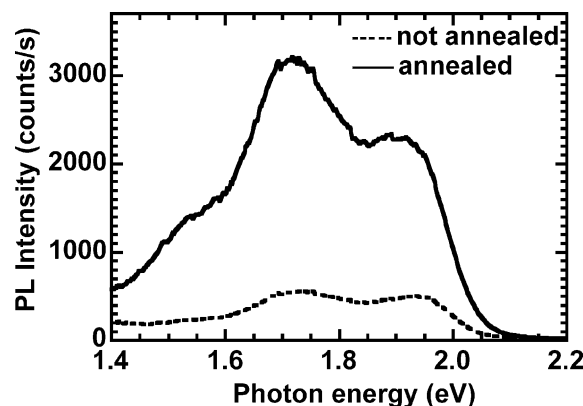


Fig. 2. Photoluminescence spectra of untreated (dashed line) and the annealed (solid line) P3HT/PCBM-films. A considerable increase of the structure and some red-shift is observed, typical for crystalline ordering of the conjugated polymer.

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<sub>2</sub> 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

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

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

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