Anisotropic optical properties of thin poly(3-octylthiophene)-films as a function of preparation conditions

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

[a] *Institute of Physics, Ilmenau Technical University, Weimarer Street 32, P.O. Box 100565, D-98693 Ilmenau, Germany*
[b] *Linz Institute of Organic Solar Cells (LIOS), Johannes Kepler University Linz, Altenbergerstr. 69, A-4040 Linz, Austria*

Abstract

We have determined the anisotropic dielectric function of thin spin-coated as well as drop-cast poly(3-octylthiophene)-films from near-normal reflectance and transmittance data and from spectroscopic ellipsometry. The influence of the growth parameters (i.e. spin frequency, concentration of the polymer in solvent, type of solvent) and of the substrate on the anisotropic dielectric function of the films was studied. The determined anisotropic dielectric functions were used to investigate the orientation of the polymer chains within these films. For the spin-coated films we found, that the optical anisotropy increases with increasing spin frequency and decreasing polymer concentration in the solution, indicating that polymer chains become more aligned parallel to the substrate. The drop-cast films were found to be even more anisotropic. In addition, the anisotropy increases considerably if the property of the Si substrate is changed from hydrophilic to hydrophobic (done by HF-treatment). Summing up, all results are discussed in dependence of the film thickness as the decisive parameter for the anisotropy.
© 2003 Elsevier B.V. All rights reserved.

Keywords: Conjugated polymers; Optical anisotropy; Dielectric function; Morphology; Thin film

1. Introduction

Conjugated polymers are promising materials for application in electronic and optoelectronic devices such as field-effect transistors, organic light-emitting diodes or organic solar cells. The great advantage of the polymeric electronics compared with crystalline semiconductor based solid-state ones lies in the potential of producing devices with simple, low-temperature and low-cost polymer processing technologies like spin-coating, printing and producing roll-to-roll [1–3].

At present, most of the polymer organic devices are produced using the spin-coating technique. However, to design highly efficient devices, some structural order in such layers is desired. In particular, the orientation and the interchain packing of the polymer chains are of great importance. A clear correlation between the orientation of the polymer chains and the anisotropic conductivity was demonstrated [4–6]. In all cases, the highest conductivity was observed in the direction of the polymer main chain. For example,

the preferable orientation of the polymer chains parallel to the film surface results in an improved in-plane electron mobility and in a poor (several orders of magnitude lower) out-of-plane mobility [5,6]. Therefore, such an arrangement is desired for field-effect transistors in a planar configuration, but it is less favourable for optoelectronic devices like solar cells and light-emitting diodes, where high electron mobility perpendicular to the electrodes (out-of-plain) is needed. Thus, the optimisation of the organic devices requires a detailed knowledge of the morphology of the active layer.

For spin-coated films of some conjugated polymers, uniaxial optical anisotropy with the optical axis perpendicular to the surface was reported [7–13]. This phenomenon was related to the preferable orientation of the polymer chains parallel to the substrate. This assumption was also confirmed by X-ray diffraction measurements on thin spin-coated poly(3-alkylthiophene) films [14,15]. The degree of the optical anisotropy depends on the angular distribution of the chains, i.e. the higher optical anisotropy corresponds to the better alignment of the chains parallel to the substrate.

In spite of the importance of this finding, the anisotropic dielectric function of most conjugated polymers were not reported up to now. To our knowledge, the influence of the

* Corresponding author. Tel.: +49-3677-693168;
fax: +49-3677-693173.
E-mail address: uladzimir.zhokhavets@tu-ilmenau.de (U. Zhokhavets).

growth parameters such as the spin frequency, the concentration of the polymer in the solvent and the type of solvent on the optical anisotropy of the polymer films was not reported yet.

In this paper we present a systematic study of the optical properties of thin spin-coated and drop-cast P3OT films depending on the spin frequency, the concentration of the polymer in the solvent, the type of the solvent and the type of the substrate. The dielectric functions of these films were obtained by means of spectroscopic ellipsometry and reflectance/transmittance measurements. The analysis of structural properties of the films was based on the investigation of the imaginary part of the anisotropic dielectric functions.

2. Experimental

The films of regioregular poly(3-octylthiophene) with ∼99% head-to-tail couplings were spin-coated or drop-cast on silicon and glass substrates. For the determination of their dielectric functions, spectroscopic ellipsometry and reflectance/transmittance data were used. The absolute near-normal transmission and reflection spectra of the samples were taken with a spectrophotometer Cary 3G (Varian). As spectral range $\hbar\omega = 1.5$–3.5 eV was used. A dielectric function was then fitted to the reflectance and transmittance data with the commercial software SCOUT (M. Theiss, Hardware and Software, D-52078 Aachen, Germany).

It should be pointed out, that due to the near-normal incidence of the light beam, mainly the in-plane component of the dielectric function was tested. Consequently, no out-of-plane component of the dielectric function was determined by reflectance/transmittance measurements separately.

Ellipsometric data were obtained by means of a Woollam variable angle spectroscopic ellipsometer (VASE) with rotating analyser (RAE) in the spectral range $\hbar\omega = 1.5$–3.5 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. Because of the oblique angle of incidence, both in-plane and out-of-plane components of the dielectric function could be determined. For the analysis of the ellipsometric spectra the Woollam WVASE software was used. In order to determine the anisotropic dielectric function of the films, we have analysed the ellipsometric data with an optical one-layer model. The model parameters are the ordinary and extraordinary components of the DF and the layer thickness. In order to determine the film characteristics, the model parameters were varied to obtain the best fit between experimental data and those calculated by the model. To prevent a strong parameter correlation, a multiple sample analysis was applied [13,16]. In multiple sample analysis, several films of the same material are simultaneously analysed assuming the same dielectric function for all films, while the film thickness is allowed to be different for each sample. In

our case we analysed simultaneously three samples prepared from the same concentration of the solvent, but using slightly different spin frequencies, which results in slightly different film thickness. The fitted anisotropic dielectric function was then equalized to the dielectric function of the sample with the mean spin frequency.

Because of the relatively small differences between the optical properties of the chosen three samples, the multiple sample analysis can be applied in our case. Nevertheless, the results of multiple sample analysis were carefully proved by reflectance/transmittance measurements, which provide both the film thickness and the parallel component of the DF. The results of the reflectance/transmittance measurements were found to be in a rather good agreement with those of ellipsometric multiple sample analysis. Additionally, the AFM pictures of scratched samples were taken to determine the film thickness. The good agreement of the film thickness provided by these three methods indicates the reliability of our results.

3. Results and discussion

In order to investigate the influence of the preparation conditions on the optical properties of the spin-coated films, we have studied the P3OT-films at Si and glass substrates, prepared by different spin frequencies and polymer concentrations in the solution. The solvents used were chlorobenzene and toluene. The spin frequency was varied from 500 to 6000 rpm, and the polymer concentration from 0.7 to 2.0%.

The real ε_1 and imaginary ε_2 part of DF of the films on Si substrates prepared by different spin frequencies (750–4000 rpm) and fixed polymer concentration (1.1%) are shown on Fig. 1.

It has been shown [4,7], that the imaginary part of the DF ε_2 (which is proportional to the absorption coefficient) indicates the degree of optical anisotropy of the investigated material and therefore characterizes the degree of alignment of the polymer chains in the film. This is because the lowest energy optical transition (π) is excited due to an electric field that is parallel to the conjugated main chain (polymer backbone) [7,11] and hence the absorption of the polymer is the strongest parallel to the polymer backbone. The absorption of light polarized perpendicular to the main chain direction occurs in ultraviolet region of the spectrum [17–19] and is very weak in visible region. Therefore it has been neglected in our study. If now the absorption in the plane of the film becomes stronger, more polymer backbones are aligned parallel to it. The real part of the DF ε_1 will not be discussed in further considerations. In our study we use the quotient of the maxima of the parallel and perpendicular components of the imaginary part of DF

$$A = \frac{\varepsilon_{2\parallel}^{\mathrm{max}}}{\varepsilon_{2\perp}^{\mathrm{max}}}$$
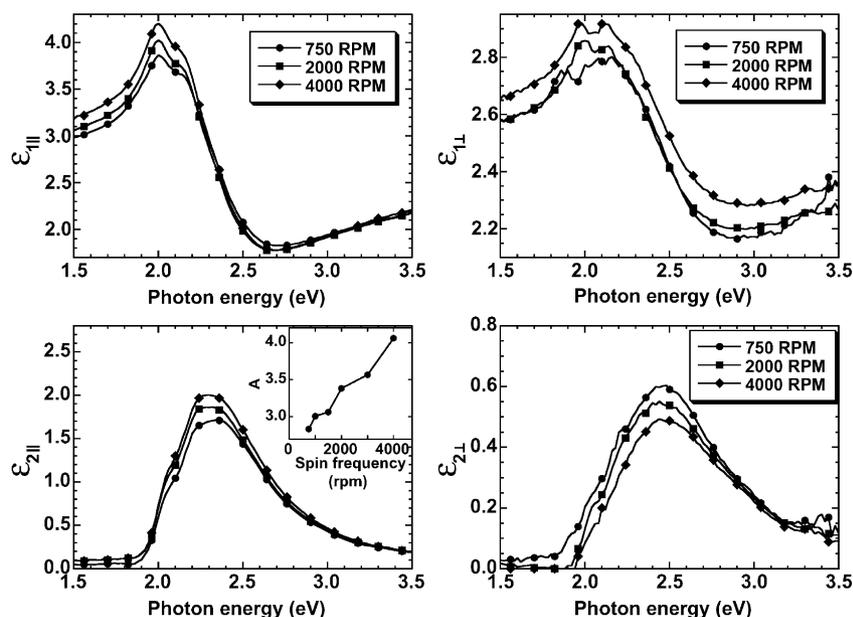
Fig. 1. Real ε_1 and imaginary ε_2 parts of the parallel (left) and perpendicular (right) components of the anisotropic DF of spin-coated P3OT films prepared by different spin frequencies and fixed polymer concentration of 1.1% in chlorobenzene.

for a qualitative analysis of the optical and structural anisotropy. The parameter A equals infinity if all of the chains are lying parallel to the substrate and it is unity for an isotropic film. We believe that this simple parameter is sufficient to describe the investigated phenomena because the shapes of the parallel and perpendicular components of the DF change only slightly between the samples investigated.

With increased spin frequency, the parallel component of the DF increases and the perpendicular one decreases; the anisotropy parameter A grows from 2.85 (spin frequency 750 rpm) to 4.08 (spin frequency 4000 rpm). This means on average the films become more aligned with increased spin frequency.

The same behaviour can be observed for films prepared by fixed spin frequency (1500 rpm) but various polymer concentrations (0.7, 1.1, 1.5, 2.0%; see Fig. 2). The anisotropy parameter A grows from 2.37 (polymer concentration 2.0%) to 4.05 (polymer concentration 0.7%).

To investigate the influence of the substrate on the optical properties of the spin-coated films, the P3OT films were spin-coated onto both Si and glass substrates. In addition, some Si-substrates were treated with HF prior to spin-coating of the polymer films. It is known, that such a treatment changes the surface properties of the Si to be hydrophobic, whereas the untreated Si is hydrophilic. The determined DF of the P3OT-films deposited onto hydrophilic and hydrophobic Si substrates are shown on Fig. 3.

The anisotropy of the film deposited on hydrophilic Si is comparable to the spin-coated films on glass. However, the films deposited on hydrophobic substrates are more anisotropic (the anisotropy parameter A changes from 2.30 to 2.97). The origin of this phenomenon is discussed below.

For comparison, we have plotted the anisotropy parameter A for all spin-coated samples in dependence on the film thickness, which was also obtained from spectroscopic ellipsometry (see Fig. 4). The anisotropy of the spin-coated films increases with decreased film thickness, and depends not
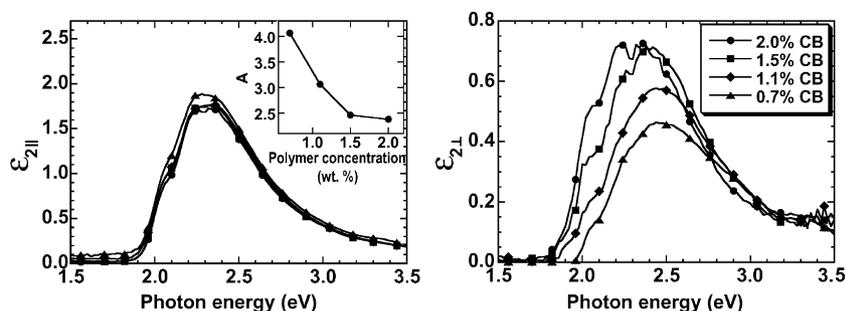

Fig. 2. Imaginary part of the parallel (left) and perpendicular (right) components of the anisotropic DF of spin-coated P3OT films prepared from chlorobenzene solutions of different polymer concentrations and fixed spin frequency 1500 rpm.
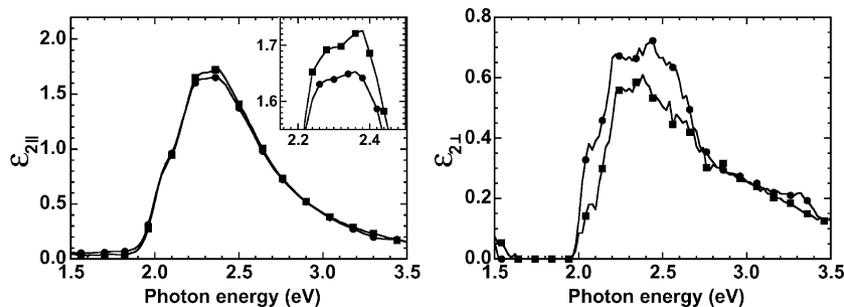
Fig. 3. Imaginary part of the parallel (left) and perpendicular (right) components of the anisotropic DF of spin-coated P3OT films prepared on untreated Si (●) and HF treated (■) Si substrates. The spin frequency was 650 rpm and the polymer concentration in chlorobenzene was 1.1% for both samples.

strongly on the spin frequency and polymer concentration. At a given film thickness, the variation of spin frequency and polymer concentration induces a change in anisotropy of maximum 15% (see Fig. 4). There is also no strong dependence on the solvent type. There are no significant differences between samples deposed on Si and glass substrates with exception of the film deposed on HF-treated (hydrophobic) Si substrates, as it was discussed above. It can be concluded, that the film thickness is the decisive parameter for the optical anisotropy of spin-coated films, as all the data points fall unto some kind of "master curve".

In addition, we have measured drop-cast films deposited on untreated Si and glass substrates. The results are shown on Fig. 5. A decrease of the anisotropy with a film thickness is also observed. On the same figure, the "master curve" for spin-coated films taken from Fig. 4 is also shown for comparison. All measured drop-cast films are more anisotropic than spin-coated films of comparable film thickness.

Our results can be understood by the assumption [15], that the film begins to solidify at the substrate and that the polymers form to some extend little crystallites by parallel

alignment of the polymer main and side chains [14,15]. For the first layers of the polymer film the interaction between the polymer and the substrate is significant. Depending on the interaction the alignment of the main chain will be more or less parallel to the substrate. This can explain the observed differences in the anisotropy between the films deposited on the HF-treated silicon and the non-treated silicon substrates. The interaction of the polymer chain with the hydrophobic surface is enhanced as compared to the hydrophilic one.

Further on, the deposition time (i.e. the time of evaporation of the solvent) is the other important parameter that determines the properties of the films. For drop-cast films, the deposition time is significantly larger (∼30 s and more), and the polymer molecules have more time to settle and align. Therefore the obtained order of the polymer within these films is better than in the spin-coated ones. For the spin-coated films, the deposition time is (with just a few seconds) lower. In summary the product of the deposition time and the interaction strength between substrate and polymer yields the extend of optical anisotropy within the polymer films.

The differences in the deposition time and the interaction on the glass and silicon substrates seem not to differ very
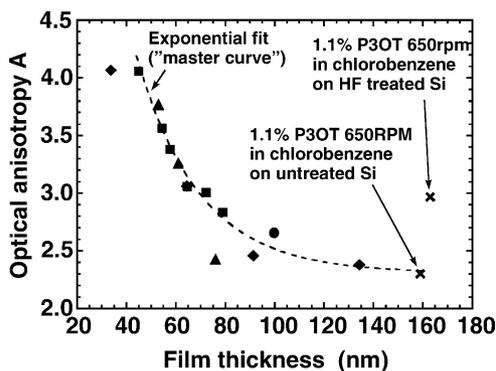

Fig. 4. Anisotropy parameter *A* of spin-coated P3OT-films prepared by: various spin frequencies (750, 1000, 1500, 2000, 3000, 4000 rpm) on untreated Si substrates from 1.1% chlorobenzol solution (■); various polymer concentrations (0.7, 1.1, 1.5, 2.0%) on untreated Si substrates from chlorobenzene solution by 1500 rpm (◆); various spin frequencies (2000, 3000, 4000 rpm) on glass substrates from 1.5% chlorobenzol solution (▲); 1500 rpm on Si substrate from 1.1% toluene solution (●). The experimental points fall closely on a single "master curve", an exponential decay.
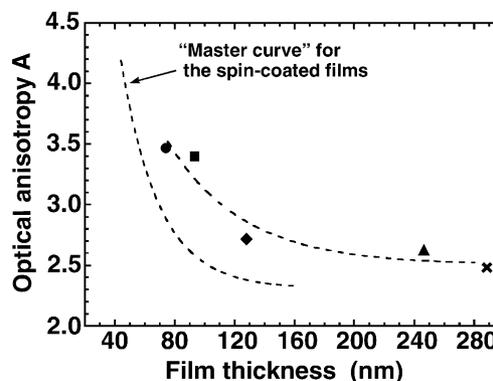

Fig. 5. Anisotropy parameter *A* of drop-cast P3OT-films prepared from: 0.7% chlorobenzene solution on glass (●); 0.7% chlorobenzene solution on untreated Si (■); 1.1% toluene solution on untreated Si (◆); 1.5% chlorobenzene solution on glass (▲); 1.5% chlorobenzene solution on untreated Si (✖). The "master curve" for spin-coated films (cp. Fig. 4) is also shown for comparison.

much for the spin cast films. This can be an explanation for that the relation between the anisotropy and the film thickness falls on one curve for the different preparation conditions used to produce these films. The shape of the curve suggests an exponential drop off of the anisotropy with film thickness (see fit in Figs. 4 and 5. The characteristic length for the decay is on the order of a few tens of nanometers. The function used to fit the data in Figs. 4 and 5 is

$$y = y_0 + A_1 \exp\left[-\frac{x}{t_1}\right]$$

This suggests, that within the first layers of the film the ordering of the polymer molecules seems to be the highest, driven by the short-range interaction between substrate and polymer. Hence we expect the polymer to form crystallites directly at the substrate polymer interface. After this initially strongly ordered layer the order of the polymer drops off exponentially with a characteristic length (t_1), which can be understood as a correlation length for the main chain direction, similar to the behaviour of nematic liquid crystals in the isotropic phase [20].

4. Conclusions

In conclusion, we have studied the optical anisotropy and the degree of uniaxial orientation of thin spin-coated and drop-cast poly(3-octylthiophene)-films depending on the preparation conditions (i.e. spin frequency, polymer concentration in the solvent, type of solvent), preparation method (spin-coating and drop-casting), type of substrate (glass and Si substrates) and substrate treatment (hydrophilic and hydrophobic). For the spin-coated films, the film thickness was found to be the decisive parameter for the optical anisotropy. The orientation of the spin-coated films on Si substrates can be improved by treatment with HF acid, changing the Si surface from hydrophilic to hydrophobic. The drop-cast films were found to be more anisotropic than spin-coated ones. The obtained results were explained by the assumption, that the film begins to solidify at the substrate, and that the polymer–substrate interaction as well as the formation time of the film determine the overall anisotropy.

References

[1] G. Hadziioanou, P.F. van Hutten, Semiconducting Polymers, Wiley-VCH Verlag GmbH, Weinheim, 2000.
[2] S.E. Shaheen, C.J. Brabec, N.S. Sariciftci, F. Padinger, T. Fromherz, J.C. Hummelen, Appl. Phys. Lett. 78 (2001) 841.
[3] P. Fournet, J.N. Coleman, B. Lahr, W.J. Blau, D.F. O'Brien, H.-H. Horhold, J. Appl. Phys. 90 (2001) 969.
[4] H. Sirringhaus, R.J. Wilson, R.H. Friend, M. Inbasekaran, W. Wu, E.P. Woo, M. Grell, D.D.C. Bradley, Appl. Phys. Lett. 77 (2000) 406.
[5] P. Gattinger, H. Rengel, D. Neher, M. Gurka, M. Buck, A.M. van de Craats, J.M. Warman, J. Phys. Chem. B 103 (1999) 3179.
[6] E. Punkka, M.F. Rubner, Synth. Met. 41–43 (1991) 1509.
[7] D. McBranch, I.H. Campbell, D.L. Smith, J.P. Ferraris, Appl. Phys. Lett. 66 (1995) 1175.
[8] 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.
[9] L.A.A. Pettersson, F. Carlsson, O. Inganas, H. Arwin, Thin Solid Films 313–314 (1998) 356.
[10] R.W. Gymer, R.H. Friend, H. Ahmed, P.L. Burn, A.M. Kraft, A.B. Holmes, Synth. Met. 55–57 (1993) 3683.
[11] M. Tammer, P. Monkman, Adv. Mater. 14 (2002) 210.
[12] C.M. Ramsdale, N.C. Greenham, Adv. Mater. 14 (2002) 212.
[13] U. Zhokhavets, R. Goldhahn, G. Gobsch, W. Schliefke, Synth. Met. 138 (2003) 491.
[14] H.J. Fell, E.J. Samuelsen, J. Als-Nielsen, G. Grubel, J. Mardalen, Solid State Commun. 94 (1995) 843.
[15] K.E. Aasmundtveit, E.J. Samuelsen, M. Guldstein, C. Steinsland, O. Flornes, C. Fagermo, T.M. Seeberg, L.A.A. Pettersson, O. Inganas, R. Feidenhans'l, S. Ferrer, Macromolecules 33 (2000) 3120.
[16] C.M. Herzinger, B. Johs, W.A. McGahan, J.A. Woollam, W. Paulson, J. Appl. Phys. 83 (1998) 3323.
[17] E.K. Miller, G.S. Maskel, C.Y. Yang, A.J. Heeger, Phys. Rev. B 60 (1999) 8028.
[18] F.C. Krebs, S.V. Hoffmann, M. Jorgensen, Synth. Met. 9563 (2002) 1–4.
[19] E.K. Miller, D. Yoshida, C.Y. Yang, A.J. Heeger, Phys. Rev. B 59 (1999) 4661.
[20] Iam-Choon Khoo, Liquid Crystals, Wiley/Interscience, New York, 1995 (Chapter 2.1).