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A systematic study of the anisotropic optical properties of thin poly(3-octylthiophene)-films in dependence on growth parameters

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Abstract

Poly(3-octylthiophene) (P3OT) is a promising candidate for plastic solar cells. We have determined the anisotropic dielectric function (DF) of thin spin-coated and drop-cast P3OT-films deposited on Si and glass substrates from both near-normal reflectance and transmittance spectroscopy and from variable angle spectroscopic ellipsometry. The influence of the deposition parameters (such as spin frequency, concentration of the polymer in solvent, type of solvent, type of substrate) on the anisotropic DF of the film was investigated. The anisotropy of the DF can be related to the orientation of the polymer chains in the film. The optical anisotropy of spin-coated films increases with increasing spin frequency and decreasing polymer concentration in the solvent, indicating that polymer chains become more aligned parallel to the substrate. The drop-cast films were also found to be anisotropic. In addition, the anisotropy increases considerably if the property of the Si substrate is changed from hydrophilic to hydrophobic (by treatment with hydrofluoric acid). With increasing film thickness the optical anisotropy decreases. Summing up, all results are discussed in dependence of the film thickness as the decisive parameter.
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1. Introduction

Polyalkylthiophenes are promising materials for application in polymer electronic devices like field-effect transistors, light-emitting diodes or solar cells [1–3].

At present, most of the polymer devices are produced using the spin-coating technique. The spin-coated films of conjugated polymers show a pronounced optical anisotropy with the optical axis perpendicular to the film plane [4–10]. This phenomenon originates from the preferable orientation of the polymer chains parallel to the substrate, as it was determined from X-ray measurements [11–14]. The more aligned polymer films show a higher optical anisotropy than the less aligned ones. On the other hand, charge carriers are transported primarily along the polymer backbone [15–17]. The interchain hopping is assumed to be a less effective mechanism of charge transport. Therefore, such an orientation of the polymer chains should lead to a highly anisotropic conductivity with the in-plane conductivity several orders of magnitude larger than the out-of-plane one. The high in-plane mobility is required for field-effect transistors. However, for devices like solar cells and light emitting diodes, where the current passes perpendicular to the electrodes, such orientation of the polymer chains is unfavourable. Therefore, the detailed knowledge about the film morphology is required to design highly efficient devices.

We have studied the optical properties of thin spin-coated and drop-cast poly(3-octylthiophene) (P3OT)-films in dependence of the spin frequency, the concentration of the polymer in the solvent, the type of the solvent and the type of the substrate. The dielectric function (DF) of these films is 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 DFs.

2. Experimental details

For the determination of the DF, spectroscopic ellipsometry and reflectance/transmittance data were used.

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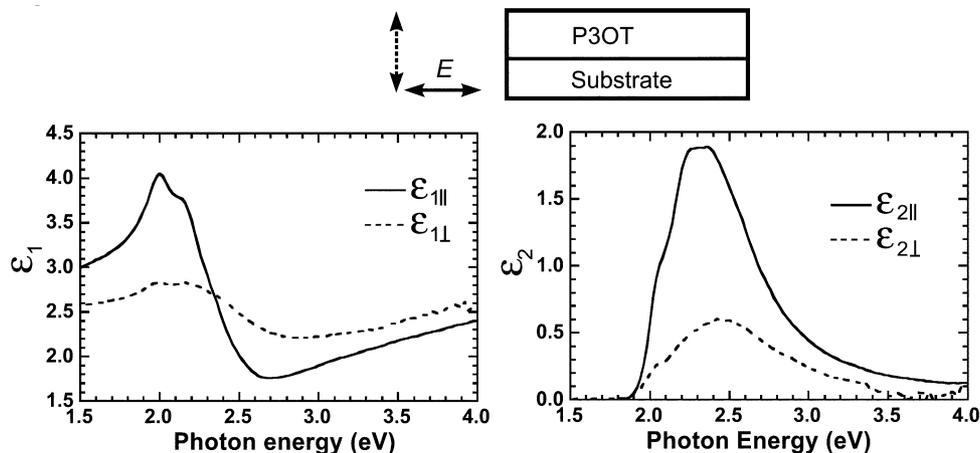*E-mail address:* gerhard.gobsch@tu-ilmenau.de (G. Gobsch).

Fig. 1. Real ε_1 and imaginary ε_2 parts of the parallel (solid line) and perpendicular (dashed line) components of the anisotropic DF of spin-coated P3OT-films prepared by 3000 rpm from a 1.5% chlorobenzene solution (film thickness 61 nm).

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 DF was then fitted to the reflectance and transmittance data with the commercial software SCOUT (M. Theiss, Hard- 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 DF was tested. Consequently, no out-of-plane component of the DF could be determined separately by reflectance/transmittance measurements.

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 DF could be determined. For the analysis of the ellipsometric spectra the Woollam WVASE software was used. The anisotropic DF of the films and the film thickness were obtained from multiple sample analysis as described in Refs. [6,8,10]. The results obtained by 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 very good agreement with those of ellipsometric multiple sample analysis. Additionally, 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

A typical anisotropic DF of thin spin-coated P3OT-film is presented in Fig. 1. The parallel/perpendicular component of the DF corresponds to the light polarized parallel/perpendicular to the substrate. In the transparent region where $\varepsilon_2 = 0$ ($\hbar\omega = 1.5$–3.5 eV), the real part of the DF ε_1 is related to the refraction index n of the polymer film by $\varepsilon_1 = n^2$. In our consideration we use the imaginary part of the anisotropic DF which is proportional to the absorption coefficient α

$$\varepsilon_2 = \frac{\alpha}{\omega} nc, \tag{1}$$

with n as refractive index and c as light velocity, which can be used to characterize the orientation of the polymer chains [4,8]. This is because the lowest energy optical transition (π–π^*) is excited due to an electric field which is polarized parallel to the conjugated main chain (polymer backbone) [18] and hence, the absorption of the polymer is the strongest for electric field parallel to the polymer backbone (Fig. 2). For example, the preferred orientation of the polymer molecules parallel to the substrate leads to an enhanced absorption of light polarized parallel to the substrate (and leads therefore to the increase of $\varepsilon_{2\parallel}$), and reduced absorption of light polarized perpendicular to the substrate (decrease of $\varepsilon_{2\perp}$). Thus, the ratio

$$A = \frac{\varepsilon_{2\parallel}^{max}}{\varepsilon_{2\perp}^{max}} \tag{2}$$

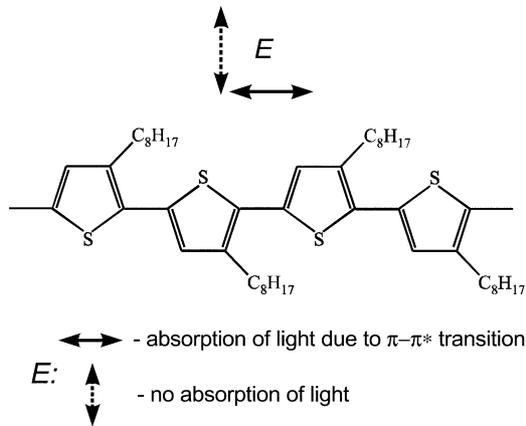has been used to characterize the strength of the optical anisotropy and the degree of alignment of the polymer

Fig. 2. Chemical structure of P3OT. *E* is the vector of electric field. The lowest in energy $\pi-\pi^*$ transition is polarized parallel to the polymer backbone. No absorption occurs for the light polarized perpendicular to the main chain (in the spectral range considered here).

chains in the film. The parameter *A* equals infinity if all of the chains are lying parallel to the substrate, and it is unity for a completely 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.

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 750 to 4000 rpm, and the polymer concentration from 0.7 to 2.0%.

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 (Fig. 3).

With increasing spin frequency (see Fig. 3, squares) the anisotropy parameter *A* grows from 2.85 (spin frequency 750 rpm, corresponding film thickness 77 nm) to 4.05 (spin frequency 4000 rpm, film thickness 44 nm). The same behaviour can be observed for films prepared by fixed spin frequency (1500 rpm) but with various polymer concentrations (0.7, 1.1, 1.5 and 2.0% (by weight); see Fig. 3, diamonds). The anisotropy parameter *A* grows from 2.37 (polymer concentration 2.0%, film thickness 134 nm) to 4.08 (polymer concentration 0.7%, film thickness 33 nm). This means that on average the films become more aligned with increasing spin frequency (or with decreasing polymer concentration).

To investigate the influence of the substrate on the optical properties of the spin-coated films, the P3OT-films were spin-coated on both Si and glass substrates.

In addition, some Si-substrates were treated by hydrofluoric acid (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 (see, e.g. Ref. [19]). The determined anisotropy parameter *A* of the films deposited onto hydrophilic and hydrophobic Si substrates is also shown on Fig. 3 (cross).

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.

There is a tendency common for all spin-coated films that should be mentioned: the anisotropy of the spin-coated films decreases with increasing film thickness. Furthermore, the anisotropy depends not 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 at a maximum of 15% (Fig. 3). In addition, we have not observed a strong dependence on the solvent type. There are no significant differences between samples deposited 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
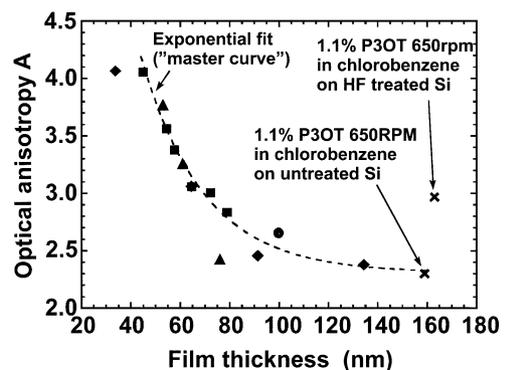

Fig. 3. Anisotropy parameter *A* of spin-coated P3OT-films prepared by: various spin frequencies (750, 1000, 1500, 2000, 3000, 4000 rpm) on untreated Si substrates from 1.1% chlorbenzol solution (■); various polymer concentrations (0.7, 1.1, 1.5, 2.0%) on untreated Si substrates from chlorobenzene solution by 1500 rpm (♦); various spin frequencies (2000, 3000, 4000 rpm) on glass substrates from 1.5% chlorbenzol solution (▲); 1500 rpm on Si substrate from 1.1% toluene solution (●). The experimental points fall closely on a single 'master curve', an exponential decay.
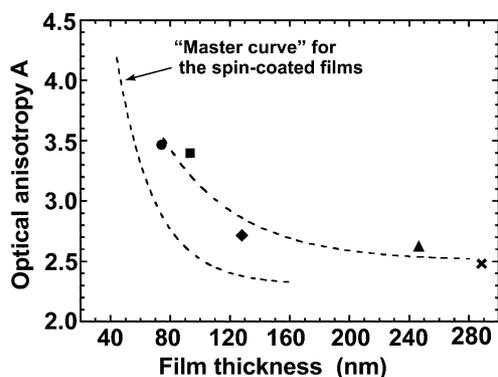
Fig. 4. Anisotropy parameter A of drop-cast P3OT-films prepared from: 0.7% chlorobenzene solution on glass (●); 0.7% chlorobenzene solution on untreated Si (■); 1.1% toluene solution on untreated Si (♦); 1.5% chlorobenzene solution on glass (▲); 1.5% chlorobenzene solution on untreated Si (×). The 'master curve' for spin-coated films (in this figure) is also shown for comparison.

shown on Fig. 4. A decrease of the anisotropy with film thickness is also observed. In 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 the polymers form little crystallites to some extend by parallel alignment of the polymer main and side chains [15,14]. 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 for 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. For the spin-coated films, the deposition time is (with just a few seconds) lower. Therefore, the obtained order of the polymer within the drop-cast films is better than in the spin-coated ones. 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.

4. Conclusions

In conclusion, we have studied the optical anisotropy and the degree of uniaxial orientation of thin spin-coated and drop-cast P3OT-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.

Acknowledgments

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