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Characterization of optical anisotropy in oriented poly(ethylene terephthalate) films using reflectance difference spectroscopy

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Abstract

We present a new method for the characterization of molecular orientation in polymer materials based on the determination of the optical anisotropy by reflectance difference spectroscopy (RDS). Data interpretation is quite straightforward even in the case of thin transparent films, as shown for the example of biaxially oriented poly(ethylene terephthalate) (PET). A comparison with birefringence data obtained by spectroscopic ellipsometry (SE) demonstrates the superior measurement precision and robustness of RDS. Using azimuth dependent RDS, the position of the optical eigenaxes in the film plane can be established, which are found to coincide with the crystalline orientation determined by wide-angle X-ray scattering.

Keywords: Reflectance difference spectroscopy; Poly(ethylene terephthalate); Oriented polymers

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1. Introduction

Many polymer processing methods such as fiber spinning, blow moulding (bottles) or roll drawing (films) introduce molecular orientation, thus leading to specific (generally anisotropic) material properties [1,2]. For most applications, this effect is highly desirable, as parameters like the elastic modulus or the yield strength depend on the molecular orientation and can be tailored during the production process. In order to understand these effects, a detailed characterization of both the degree of orientation and its principal direction is required. Various methods have been reported to provide insight on different aspects of orientation in amorphous and semi-crystalline polymers. These include infrared spectroscopy [3], X-ray diffraction [4] or nuclear magnetic resonance [5]. A simple, yet efficient approach is the measurement of optical birefringence [2], which gives an averaged information on the orientation in amorphous and crystalline phases in semi-crystalline polymers. The full determination of the birefringence, however, requires the measurement of the refractive indices along the optical eigenaxes of the material, which can be a tedious task, especially for thin films.

We present a new approach for the determination of molecular orientation in polymers based on reflectance difference spectroscopy (RDS) using biaxially oriented poly(ethylene terephthalate) (PET) films as an example. The results obtained by RDS are compared to the birefringence deduced from spectroscopic ellipsometry (SE) measurements on the one hand and to crystalline orientation data obtained by wide-angle X-ray scattering (WAXS) measurements on the other hand.

2. Experiment

The main experimental technique used in this study is reflectance difference spectroscopy (RDS). RDS is a non-destructive optical method, which measures the normalized reflectance difference (RD) $\Delta r/r$ of light polarized along two perpendicular directions of the surface in normal incidence geometry:

$$\frac{\Delta r}{r} = 2\left(\frac{r_1 - r_2}{r_1 + r_2}\right) \tag{1}$$

Here r_1 and r_2 denote the complex reflectivities along the two orthogonal in-plane polarization axes of the incident light

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beam. Due to the normalization, $\Delta r/r$ is independent of intensity fluctuations of the light source and the detection efficiencies.

The optical setup of the RD spectrometer [6] is schematically depicted in Fig. 1. The incident light beam, generated by a 75 W Xe short arc lamp, is first linearly polarized by a Rochon prism. A photoelastic modulator (PEM) whose fast axis is rotated by +45° with respect to the initial polarization direction then introduces a periodic phase shift between the two orthogonal amplitude components of the form $\delta(t) = A \sin \omega t$, where A is the modulation amplitude and ω the modulation frequency, usually around 50 kHz. After near-normal incidence reflection from the sample, the polarization state of the reflected light beam is analyzed by a second polarizer (analyzer), also oriented at +45°. Finally, a monochromator and a photomultiplier are used to collect photons as a function of their energy in a range between 1.5 and 5.5 eV.

The resulting intensity at the detector can be described by a series of harmonics

$$I(t) = I_0 + I_\omega \sin \omega t + I_{2\omega} \sin 2\omega t + \ldots \tag{2}$$

where I_0 is the dc component of the signal, and I_ω and $I_{2\omega}$ denote the ac components at the fundamental excitation frequency of the PEM and at the first harmonic, respectively. It can be shown that the real and imaginary parts of $\Delta r/r$ are proportional to the ac/dc ratios of the signal at these two frequencies: [6]

$$\mathrm{Re}\left(\frac{\Delta r}{r}\right) \approx \frac{I_{2\omega}}{I_0}, \qquad \mathrm{Im}\left(\frac{\Delta r}{r}\right) \approx \frac{I_\omega}{I_0} \tag{3}$$

A more detailed description of the spectrometer and the signal analysis can be found in Refs. [6] and [7].

Due to the normal incidence geometry, RDS is only sensitive to in-plane optical anisotropies. In isotropic materials, such an anisotropy can only arise from the sample surface due to the lower symmetry compared to the bulk. RDS is thus an extremely sensitive optical probe of the electronic and structural properties of the surface, and has been used extensively to study semiconductor and metal surfaces [7].

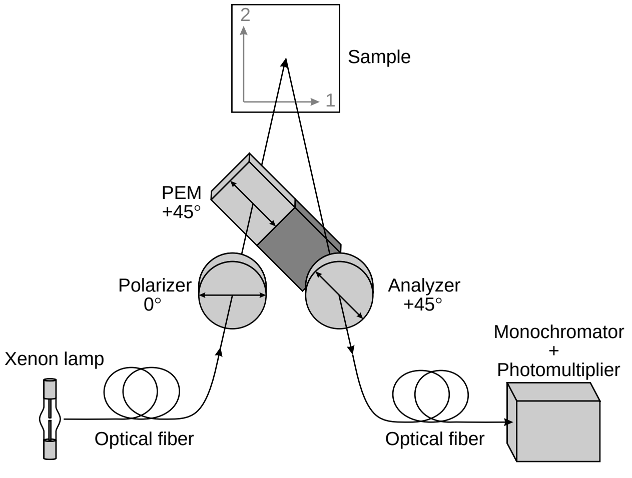

Fig. 1. Schematic setup of the RD spectrometer.

In the case of polymers, however, the reflectance difference is caused by anisotropic bulk properties in the form of birefringence (Δn)

$$\frac{\Delta r}{r} = \frac{2\Delta n}{\bar{n}^2 - 1} \tag{4}$$

where $\Delta n = n_1 - n_2$ and the average refractive index $\bar{n} = (n_1 + n_2)/2$, with n_1 and n_2 denoting the complex refractive indices along two optical eigenaxes of the sample.

This birefringence is in turn a result of the molecular orientation in the material and it has been shown that it provides averaged information about the orientation in crystalline and amorphous phases in semi-crystalline polymers [1,2,8]

$$\Delta n = x_\mathrm{c} \Delta n_\mathrm{c} + x_\mathrm{a} \Delta n_\mathrm{a} \tag{5}$$

where x_c and $x_\mathrm{a} = 1 - x_\mathrm{c}$ are the volume fractions of the crystalline and amorphous phases, and Δn_c and Δn_a are the corresponding birefringences. Form birefringence can also be present in polymers, but usually accounts for only a small amount (a few percent) of the total birefringence [1], so it is neglected here. Substituting $\Delta n_i = \Delta n_i^{\max} \langle P_2(\cos\theta)\rangle_i$ yields [1]

$$\Delta n = x_\mathrm{c} \Delta n_\mathrm{c}^{\max} \langle P_2(\cos\theta)\rangle_\mathrm{c} + x_\mathrm{a} \Delta n_\mathrm{a}^{\max} \langle P_2(\cos\theta)\rangle_\mathrm{a} \tag{6}$$

where $\Delta n_i^{\max}$ is the maximum birefringence for fully oriented material of phase i and $\langle P_2(\cos\theta)\rangle$ is the average value of the second-order Legendre polynomial of the orientation distribution function of phase i. As the RDS signal is proportional to the birefringence, it can in principle be used for the determination of orientation functions in polymers given that some parameters like crystallinity and maximum birefringence are known. For measurements of thin films, RDS is restricted to the measurement of the molecular orientation in the film plane.

The key advantage of RDS compared to other optical techniques like ellipsometry, attenuated total reflectivity (ATR) or Abbe refractometry is that one single measurement is enough to obtain directly Δn, whereas all other techniques require at least two measurements for n_1 and n_2. Other strong points are its high sensitivity to optical anisotropies ($\Delta r/r$ values as low as 10^{-4} are readily detected), its high time resolution (≈ 10 ms), and the capability to perform spectroscopic measurements. Furthermore, the experimental setup is fairly simple and the only requirement is to have a direct optical access to the sample along the surface normal, regardless of the environment. The characterization of small samples, such as thin fibres, seems difficult due to the rather large diameter of the light beam (usually on the order of several mm), however, RDS has been integrated in a confocal microscope to achieve lateral resolutions of <1 μm [9].

Refractive index data were acquired using a spectroscopic phase-modulated ellipsometer (UVISEL by ISA Jobin Yvon) [10], operating in a photon energy range of 1.5–5.2 eV. Spectra with a resolution of 10 meV were recorded at an incidence angle of 61°, near the Brewster angle for PET, to ensure maximum sensitivity. Due to the fact that ellipsometry is mainly sensitive to the optical properties of the sample along the plane of incidence, n_1 and n_2 were determined by two separate measurements along the optical eigenaxes of the sample.

To correlate structural and optical properties, the samples were additionally characterized by wide-angle X-ray scattering (WAXS) using an area detector. The measurements were performed in transmission mode, ensuring that the bulk properties were measured. WAXS patterns provide information, among others, on the orientation of crystalline domains in the polymer. This allows the determination of the orientation function $\langle P_2(\cos\theta)\rangle_c$ in Eq. (6) from the WAXS patterns [4].

The samples were industrially produced biaxially oriented transparent PET films with thicknesses of 12 and 50 μm. In order to avoid interference effects in the optical measurements, the backsides of some samples were mechanically roughened. A subsequent cleaning step with isopropanol was introduced to remove dust and surface contaminations. No influence of the cleaning process on the optical properties was observed.

3. Results and discussion

Fig. 2 shows complex refractive index data of two PET samples (12 and 50 μm) with rough backsides as determined by SE. The two spectra were recorded with the plane of incidence parallel to either of the optical eigenaxes of the sample surface, which were determined by rotating the sample around its surface normal and finding the minima and maxima of n. The presence of birefringence is obvious and can be seen by the offset between the two curves throughout the measured spectral range. The sample is transparent for photon energies between 1.5 and 4 eV, where Δn takes typical values of 0.07 for the 12 μm film and 0.12 for the 50 μm film.

Above the absorption edge, a broad feature at 5.1 eV appears in the bottom panel (k) of Fig. 2. This feature was reported to correspond to a transition involving molecular orbitals of the benzene rings [11]. Additionally, two low-intensity peaks can be identified around 4.1 and 4.3 eV, which were previously attributed to the same electronic transition in the carbonyl group [11]. The splitting is a result of the different molecular configurations. Considering that the strength of the 4.1 eV transition depends more strongly on the rotation angle, it was assigned to the carbonyl transition in crystalline areas, where almost all molecules adopt a *trans* conformation. Correspondingly, the more isotropic 4.3 eV transition originates from molecules in the amorphous areas of the material, where the majority (75–90%) of the PET molecules are in the *gauche* conformation [2].

To determine the refractive indices and the birefringence by SE, two independent measurements along the optical eigenaxes are required. The RDS signal, however, is already proportional to the birefringence (Eq. (4)), which means that one single measurement is enough to determine Δn. Fig. 3 shows a typical RDS spectrum obtained from a 50 μm thick PET film with roughened backside. In the transparent spectral region, the RDS signal is constant and $\mathrm{Re}(\Delta r/r)\approx\Delta n$ because $k=0$. Similar to the SE measurements, the absorption edge is visible at 4 eV and accompanied by a nonzero imaginary part of the RDS signal at higher energies. The penetration depth of light at a photon energy of 5 eV is on the order of 20–40 nm, which means that in this case the RDS signal originates from the sample surface. RDS can thus be either bulk or surface sensitive for PET, depending on the chosen wavelength range. Also shown in Fig. 3 is a calculation of the RDS signal using the refractive indices given in Fig. 2. The calculation is based on the reflection matrix method as described, e.g. in chapter 4.7 of Ref. [12] assuming a two-phase model (isotropic ambient—biaxially anisotropic semi-infinite substrate). The measured and calculated RDS signals correspond nicely up to ca. 4.4 eV, above which the experimental error of the ellipsometry

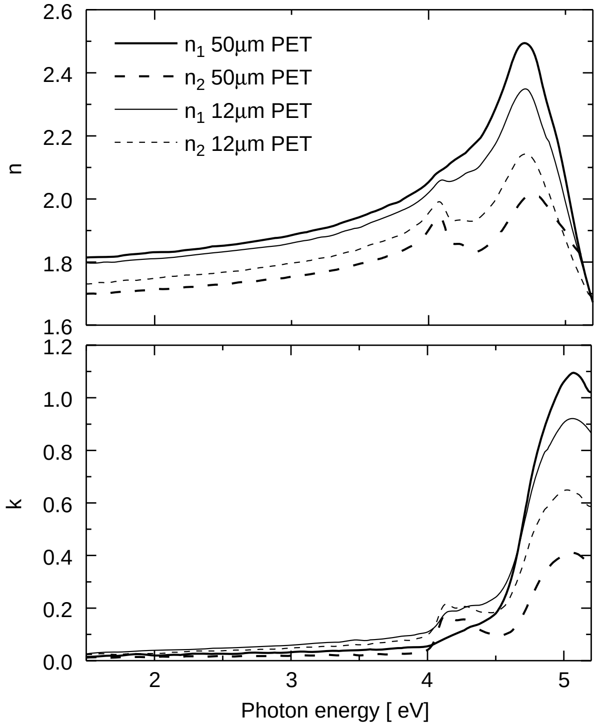

Fig. 2. Real (top) and imaginary (bottom) parts of the principal in-plane complex refractive indices ($n+ik$) of 12 μm (thin lines) and 50 μm PET films (thick lines) as determined by spectroscopic ellipsometry.

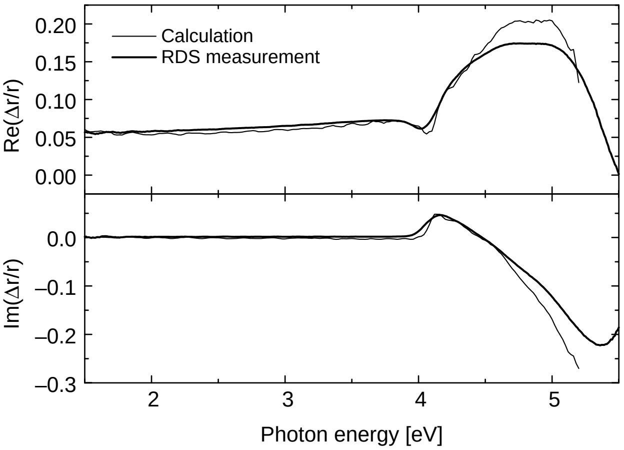

Fig. 3. RDS measurement (thick line) of a 50 μm thick PET film with rough backside and model calculation (thin line) using the refractive index data from Fig. 2.

measurements leads to a slight overestimation of the birefringence and to an increased noise level compared to the RDS measurement. The precision of RDS measurements is usually on the order of 10^{-4} in $\Delta r/r$ and thus also in Δn, which is considerably better than the precision in Δn calculated from ellipsometry data.

The results presented above were obtained from samples with a rough backside. In most practical cases, however, thin PET films have flat surfaces on both sides, which leads to interference effects in the transparent spectral range for small film thicknesses. This is illustrated in Fig. 4, where an RDS measurement in the transparent range (1.5–4 eV) of a 12 μm thick PET film is shown. Also given is the result of a reflection matrix calculation assuming a three-phase-model (isotropic ambient—biaxially anisotropic film—isotropic ambient) [12]. Strong interference fringes in $\mathrm{Re}(\Delta r/r)$ and $\mathrm{Im}(\Delta r/r)$ can be found throughout the spectrum. The real part of the RDS signal is dominated by fast oscillations whose frequency is proportional to the optical thickness $n \cdot d$ of the film, where n denotes the average refractive index and d the film thickness. Due to the fact that the film thickness deviates by $\pm 1\%$ from the nominal thickness (as specified by the manufacturer), the light beam, whose diameter is on the order of a few mm, averages over an ensemble of thicknesses resulting in a modulation of the interference fringes by a damped oscillation with a longer period. This was also accounted for in the calculation using a linear distribution of thicknesses of 12 μm ± 120 nm. The fine oscillations get less pronounced as the photon energy increases due to the onset of absorption in the film. In the calculation, k was assumed to be zero in the displayed range and, therefore, the calculated amplitudes are not sufficiently damped. The imaginary part of $\Delta r/r$ is mainly governed by a slow oscillation, whose period is proportional to $\Delta n \cdot d$. As a consequence, even if the birefringence cannot be read directly from the RDS spectrum like in the interference-free case, it can be reliably calculated from the oscillation frequency of $\mathrm{Im}(\Delta r/r)$ if the thickness of the film is known. The so calculated value of Δn corresponds to the one determined by measurements on samples with a rough backside (cf. Fig. 3).

So far, we have seen that the size of the optical anisotropy in the film can be analyzed in detail using RDS. It is, however, also possible to determine the position of the orientation axes in the plane of the film using a technique called azimuth dependent RDS (ADRDS) [13]. ADRDS is based on the fact that upon a rotation of the sample around its surface normal, i.e. by varying the azimuthal angle ϕ, the RDS signal is modulated as $\cos 2\phi$. If the in-plane optical eigenaxes of the sample are not aligned with respect to the polarization of the incident light beam, off-diagonal elements in the reflection Jones matrix of the sample appear and give rise to this modulation. Due to symmetry reasons, the modulation period is 180° and the maxima and minima of $\Delta r/r$ correspond to the angular position of the in-plane optical eigenaxes of the sample. For sufficiently thick transparent films, however, the beams reflected from the front and back sides of the sample become incoherent, which leads to a modulation period of 90° [13]. These effects can be excluded either by an appropriate choice of the photon energy (i.e. above the absorption edge) or by roughening the back surface of the sample.

Fig. 5 shows the results of an ADRDS measurement at 4.05 eV on a 50 μm PET film where the sample was rotated in 5° steps. 0° corresponds to a direction parallel to the machine direction (MD) and 90° denotes the transverse direction (TD) of the film. As expected, the modulation period is 180° and the exact positions of the maxima and minima were determined by fitting a cosine function to the data with the phase shift ϕ_0 and the maximum RD value as adjustable parameters. The maximum anisotropy was found at an angle of $\phi_0 = 18°$, which means that the optical eigenaxes are rotated by 18° with respect to the machine and transverse directions, respectively. The position of the optical eigenaxes relative to the reference coordinate system of the original PET sheet is illustrated in the inset in Fig. 5.

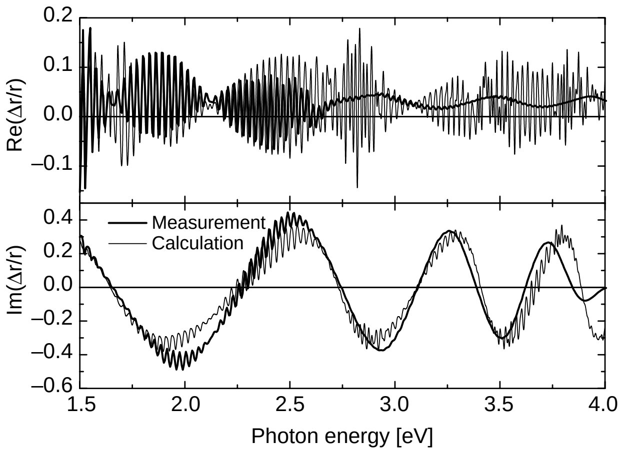

Fig. 4. RDS measurement (thick line) of a 12 μm thick PET film with parallel flat surfaces and calculation using a three-phase model including surface roughness (thin line).

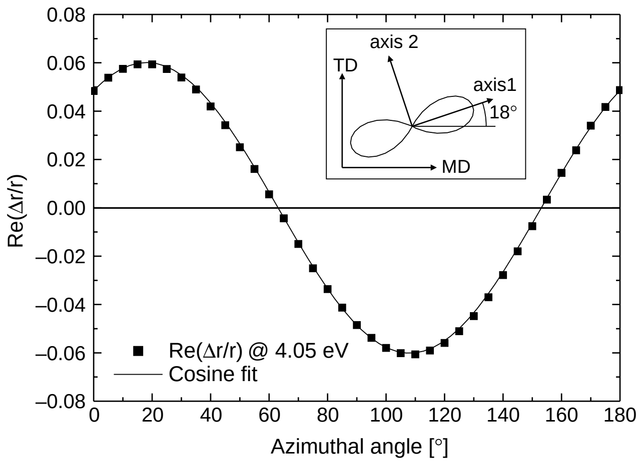

Fig. 5. Azimuth dependent RDS signal of a 50 μm PET film (squares) recorded at 4.05 eV and cosine fit (solid line). The inset visualizes the position of the optical eigenaxes with respect to the machine (MD) and transverse (TD) directions using a polar plot of the same data.

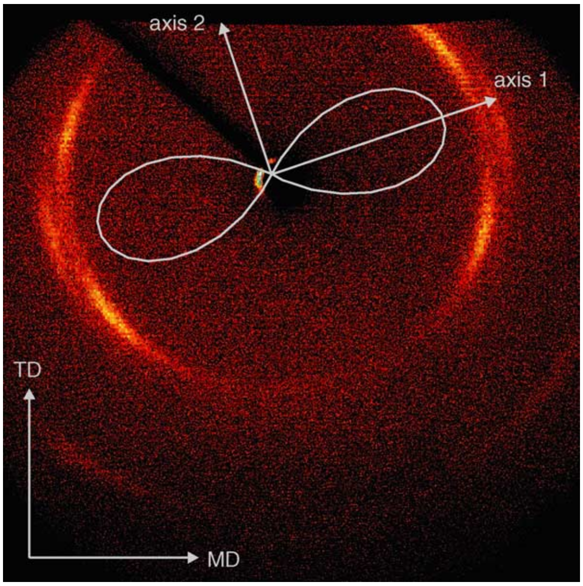

Fig. 6. Wide-angle X-ray scattering pattern of a 50 μm PET film and polar plot of the ADRDS measurement of Fig. 5.

In order to correlate the observed optical anisotropy to the structural properties of the sample, wide-angle X-ray scattering measurements were performed. The WAXS pattern of a 50 μm PET film shown in Fig. 6 reveals the same twofold symmetry as the RDS measurements. The image also shows that the crystalline domains are tilted with respect to the machine direction, whose angle is given by the position of the pattern's symmetry axes. The comparison to the ADRDS data, which is also shown in the figure as a polar plot, yields a similar angle of $\approx 18°$ for both methods. The birefringence is thus mainly determined by the orientation of the crystallites, which is also supported by the fact that the WAXS pattern does not show a continuous ring due to scattering from the amorphous phase, i.e. the degree of crystallinity is very high.

4. Summary

We have presented a new approach to the determination of molecular orientation in polymer films using reflectance difference spectroscopy. We show that a single measurement in normal reflection geometry is enough to obtain precise values for Δn. The data are consistent with spectroscopic ellipsometry measurements, where the two in-plane refractive indices can be determined independently. Furthermore, azimuthal dependent measurements provide information on the angular position of the optical eigenaxes in the film plane, which coincide with the crystalline axes as derived from the WAXS data.

The application of RDS appears attractive in the light of possible in situ experiments due to the fast data acquisition rates that can be achieved. Such measurements could also be performed during mechanical deformation or during the deposition of metal layers on polymer films.

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References

[1] Bower DI. An introduction to polymer physics. Cambridge: Cambridge University Press; 2002.
[2] Ward IM. Adv Polym Sci 1985;66:81.
[3] Jarvis DA, Hutchinson IJ, Bower DI, Ward IM. Polymer 1980;21:41.
[4] Balta-Calleja F, Vonk C. X-ray scattering of synthetic polymers. Polymer Science Library. Elsevier: Amsterdam; 1989.
[5] Clayden NJ, Eaves JG, Croot L. Polymer 1997;38(1):159.
[6] Acher O, Drevillon B. Rev Sci Instrum 1992;63:5332.
[7] Weightman P, Martin DS, Cole RJ, Farrell T. Rep Prog Phys 2005;68:1251.
[8] Lapersonne P, Tassin JF, Monnerie L. Polymer 1994;35(10):2192.
[9] Koopmans B, Richards B, Santos P, Eberl K, Cardona M. Appl Phys Lett 1996;69(6):782.
[10] Acher O, Bigan E, Drevillon B. Rev Sci Instrum 1989;60:65.
[11] Gioti M, Laskarakis A, Logothetidis S. Thin Solid Films 2004;455–456:283.
[12] Azzam RMA, Bashara NM. Ellipsometry and polarized light. Amsterdam: North Holland Publishing; 1977.
[13] Macdonald BF, Law JS, Cole RJ. J Appl Phys 2003;93(6):3320.