

# Variable Angle Spectroscopic Ellipsometry Study of Poly(3,4-ethylenedioxythiophene):Polystyrene Sulfonate Thin Films in Contact with Air

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**Abstract**—Thin films of conducting polymer complex poly(3,4-ethylenedioxythiophene) : polystyrene sulfonate (PEDOT:PSS) are studied by means of varied angle spectroscopic ellipsometry (VASE) in the wavelength range 370-880 nm, at five different angles of incidence (AOI). The goal is to simultaneously determine the film thicknesses and its dielectric function. Samples of varied film thickness are prepared by spin coating the aqueous suspension onto Si/SiO<sub>2</sub> wafers at different spin rates, and subsequent annealing at 170 °C. The measured spectra at constant angles of incidence are fitted by applying Fresnel's equations for a stratified optical layers model (SLM) which postulates several optical layers with well defined optical interfaces, in combination with the dielectric function  $\tilde{\epsilon}(\lambda)$ . Different possibilities for data fitting are critically assessed, pointing to some pitfalls in the VASE data analysis and interpretation. Two methods which involve the assessment of a theoretical Lorentz-Drude (LD) dielectric function were compared: one in which a unique function is assumed for all of the prepared samples (i.e. film thicknesses), while in the other, a variation of the dielectric function was permitted. The validation criteria include comparisons with the experimental film thickness measured by means of the atomic force microscope, the quasi-experimental dielectric function fitted independently for each wavelength, and the literature value of the main optical transition energy calculated by quantum mechanical modelling. In the limit of the studied system and model, all of these comparisons point to the necessity of simultaneously fitting the VASE data measured for films of varied thickness, in which case both the thickness and the dielectric function may be determined.

**Index Terms**—ellipsometry, spectroscopic, PEDOT, conducting, polymer, film

## I. INTRODUCTION

The conducting polymer complex poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) is a widely used thin film material in the field of organic

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electronics [1], [2], as well as in several other fields [3]. The conduction mechanism of PEDOT in PEDOT:PSS films relies on the fact that it is an electron-deficient (oxidized)  $\pi$ -conjugated polymer. Thus, in its conductive state, PEDOT is doped with holes and behaves as a p-type semiconductor. Meanwhile, the negatively charged PSS electrostatically stabilizes the doping state of PEDOT and makes it dispersible in aqueous medium [4]. Such PEDOT:PSS suspensions are technologically easily processable and mostly used in the form of thin (semi)conducting films, deposited on surfaces by various techniques (casting, spin-coating, ink-jet and roll-to-roll printing etc.). The conductivity of those films as function of chemical environment and in relation with different applications, presents their mostly studied property [1], [5]–[7]. Another attractive field of implementation is that of light emitting and harvesting devices, which rely on the optoelectronic properties of the film, and where there is still an insufficient level of both theoretical understanding and experimental information. Several available experimental studies focused on the electrochromism of electropolymerized PEDOT [8]–[10], and some on the dielectric function of a PEDOT:PSS film [6], [7]. Since the latter function presents a very important feature for the optoelectronic properties of a film material, the methods for its experimental assessment deserve special attention.

Optoelectronic properties of a conducting or semiconducting material, including conductivity and the intensity of optical absorption and reflection, are derived from the *dielectric function* [11], [12]. The latter is a complex function for semitransparent materials, where the real part is related to the speed of light, while the imaginary part is related to the intensity of light absorption within a material. The electronic conductivity of a material is directly proportional to the free charge carrier density (either electrons or holes) which is detectable in the near infrared region of the dielectric function as the Drude "tail" [13]. Meanwhile, the density and symmetry of the electronic states entering the transition moment (subject

to selection rules), determine the optical absorption detectable in the ultraviolet and visible (UV-VIS) region [14]. In the case of PEDOT, the electronic states include the valence band (VB), conduction band (CB) and two types of intra-gap phonon-electron coupled states known as polarons and bipolarons [15]. The latter states are the most important for an ample conductivity of PEDOT, and their concentration depends on the doping state which is mainly regulated by the oxidation state.

In general, for most conducting and semi-conducting materials, the dielectric constant is actually not a constant, but a function of the wavelength of the incident electromagnetic radiation to which the material is exposed. This gives rise to different absorption and reflection of light depending on the wavelength, which may be measured with spectroscopic techniques. While the standard transmission spectrophotometry may be implemented for measuring the imaginary part of the dielectric function, the experimental determination of both the real and imaginary parts is possible by applying the spectroscopic ellipsometry techniques. Once the dielectric function is determined, it can be related to the conductivity of the material by invoking the laws of electrodynamics [16].

In the present paper, the dielectric function of a PEDOT:PSS film is experimentally determined from the spectroscopic ellipsometry measurements at varied angles of incidence (i.e. Variable angle spectroscopic ellipsometry, VASE). In addition to the dielectric function, this technique is sensitive to the thickness of the film, which on one hand suggests a possibility of simultaneous film thickness determination. However, since the interpretation of the spectroscopic ellipsometry data depends on the optical model of the sample and calibration with respect to film thickness is not possible (in contrast to standard spectrophotometry), caution is necessary. The optical model often involves a relatively large number of parameters, whereby the determination of both thickness and dielectric function becomes questionable. The aim of the present work is to test several approaches for fitting VASE data measured for a PEDOT:PSS thin film, in order to assess their applicability for simultaneous determination of the dielectric function and film thickness. For this task, it was necessary to perform VASE measurements for samples of varied thickness, which was independently determined from the atomic force microscope (AFM) scans. This work presents a part of a wider effort to establish and validate methods for studying the electrodynamic behavior of such films in the working conditions for organic bioelectronic devices [17]–[19].

### Ellipsometry

In standard ellipsometry and reflectometry, the change in the polarization state of monochromatic light upon reflection from a thin semi-transparent film, expressed as the ellipsometric angles  $\Psi$  and  $\Delta$ , is measured [11], [12], [20]. The ellipsometric angles are related to the film thickness via the Fresnel's equations, which involve the complex refractive index ( $\tilde{n} = n + ik$ ) or equivalently the complex dielectric constant ( $\tilde{\epsilon} = \tilde{n}^2 = \epsilon_1 + i\epsilon_2$ ), the thickness  $d$  and the

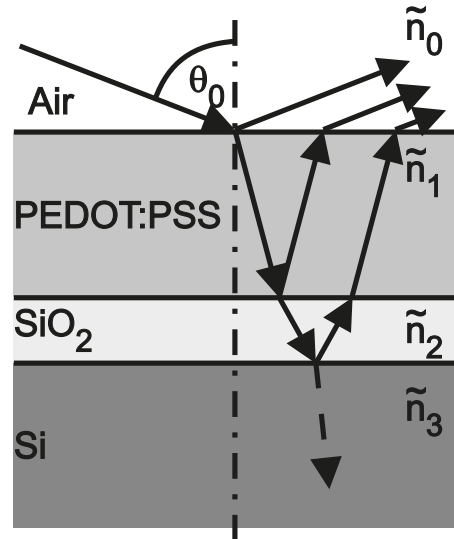


Fig. 1. Stratified layers model for the Si/SiO<sub>2</sub> substrate with the deposited PEDOT:PSS film

angle of incidence (AOI)  $\theta_0$ . The optical model consists of a stack of  $m$  optically homogeneous layers with sharp phase boundaries identified with an abrupt change of the refractive index (stratified layers model, SLM), as depicted in Fig. 1. The Fresnel's reflection coefficients for an optical interface between two infinite homogeneous optical materials, are defined as:

$$\rho_{\sigma, \tilde{n}_j, \tilde{n}_{j+1}} = \frac{\tilde{n}_j \cos \theta_j - \tilde{n}_{j+1} \cos \theta_{j+1}}{\tilde{n}_j \cos \theta_j + \tilde{n}_{j+1} \cos \theta_{j+1}} \quad (1a)$$

$$\rho_{\pi, \tilde{n}_j, \tilde{n}_{j+1}} = \frac{\tilde{n}_{j+1} \cos \theta_j - \tilde{n}_j \cos \theta_{j+1}}{\tilde{n}_{j+1} \cos \theta_j + \tilde{n}_j \cos \theta_{j+1}} \quad (1b)$$

where subscripts  $\sigma$  and  $\pi$  denote Fresnel's reflection coefficients for the  $\sigma$ - and  $\pi$ -components of the elliptically polarized light, reflecting from an interface between the two optical media with refractive indexes  $\tilde{n}_j$  and  $\tilde{n}_{j+1}$ , while  $\theta_j$  and  $\theta_{j+1}$  denote the angles of the incident and refracted beam, respectively, to the surface normal. Thus,  $\theta_j$  and  $\theta_{j+1}$  are related through Snell's law

$$\tilde{n}_j \sin \theta_j = \tilde{n}_{j+1} \sin \theta_{j+1}. \quad (2)$$

For a semi-transparent thin film with a refractive index  $\tilde{n}_1$ , deposited on a semi-transparent but infinite substrate with a refractive index  $\tilde{n}_s$ , and in contact with a medium with a refractive index  $\tilde{n}_0$  (with reference to Fig. 1,  $\tilde{n}_s$  would replace  $\tilde{n}_2$  and  $\tilde{n}_3$  as the refractive index of a single "effective" optical medium), Fresnel's coefficients are a property of the studied materials (medium, thin film, substrate). Their relationship with the ellipsometric angles  $\Psi$  and  $\Delta$ , as a property of the measured EM radiation and the angle of incidence, is defined through the total reflection ratios for the  $\sigma$ - and  $\pi$ -parallel components:

$$P_\sigma = \frac{\rho_{\sigma, \tilde{n}_0, \tilde{n}_1} + \rho_{\sigma, \tilde{n}_1, \tilde{n}_s} e^{-i2\beta}}{1 + \rho_{\sigma, \tilde{n}_0, \tilde{n}_1} \rho_{\sigma, \tilde{n}_1, \tilde{n}_s} e^{-i2\beta}} \quad (3a)$$

$$P_\pi = \frac{\rho_{\pi, \tilde{n}_0, \tilde{n}_1} + \rho_{\pi, \tilde{n}_1, \tilde{n}_s} e^{-i2\beta}}{1 + \rho_{\pi, \tilde{n}_0, \tilde{n}_1} \rho_{\pi, \tilde{n}_1, \tilde{n}_s} e^{-i2\beta}} \quad (3b)$$

where  $\beta = 2\pi d/\lambda$ . The ellipsometric angles  $\Psi$  and  $\Delta$  are related to  $P_\sigma$  and  $P_\pi$  through the general ellipsometry equation:

$$P = \frac{P_\pi}{P_\sigma} = \tan(\Psi) e^{i\Delta}. \quad (4)$$

Eqns. 1 - 4 form a closed set which, for a system composed of three phases separated by two optical interfaces, can be solved analytically (for instance, see [20] p. 35). The general solution for a larger number of layers (four in the present case, cf. Fig. 1) is more complicated and involves formulation of the total reflection ratio in terms of transfer matrix expansion (for a very concise explanation, see for instance Appendix in [21]), which can be solved computationally.

Thus, for calculating  $\Psi$  and  $\Delta$  starting from an optical model, a certain stack of semi-transparent optical layers deposited on a substrate first needs to be postulated. If the thicknesses and complex refractive indexes for all the layers except for the film are known, the thickness and the complex refractive index of the film can be numerically fitted from the experimental VASE spectra  $\Psi(\theta_0, \lambda)$  and  $\Delta(\theta_0, \lambda)$ .

#### Spectroscopic ellipsometry - the dielectric function

Both the optical and electronic properties of a material depend on the wavelength of the incident EM radiation, and are mutually related through the complex refractive index dispersion [ $\tilde{n}(\lambda) = n(\lambda) + ik(\lambda)$ ] or equivalently complex dielectric function [ $\tilde{\epsilon}(\lambda) = \tilde{n}^2(\lambda) = \epsilon_1(\lambda) + i\epsilon_2(\lambda)$ ]. For materials which absorb light in addition to reflection and refraction, the dielectric function is complex ( $\epsilon_2 > 0$ ). Then, according to classical electrodynamics, the electromagnetic radiation can interact with electrons in the material according to a forced and damped harmonic oscillator model, also known as the Lorentz oscillator [11], [12], [20]. If there is more than one type of electronic transitions present in the material, the dielectric function according to this model can be written as

$$\tilde{\epsilon} = \epsilon_\infty + \sum_j \frac{A_j}{E_{0,j}^2 - E^2 - i\Gamma_j E} \quad (5)$$

where  $E$  is the energy of the incoming photons,  $E_{0,j}$  is the resonant energy of the electrons,  $A_j$  is called the oscillator strength and is proportional to the density of electrons in the state  $j$ , while  $\Gamma_j$  is the damping frequency which can be identified with the inverse mean free time for scattered electrons,  $\Gamma \equiv 1/\tau$ . By applying Planck's law, all the energies in the above expression can be substituted by frequencies. Thus for example  $E_{0,j}$ , which represents the elastic potential energy of electrons bound in chemical bonds of a material as defined by Hooke's law, can be substituted by the resonant frequency ( $\omega_{0,j} = E_{0,j}/\hbar$ ). A special case of the general Lorentz

oscillator model equation (cf. eq. 5) is the *Lorentz-Drude* (LD) model, where the resonant energy is set to zero for one of the oscillators, and which represents the dielectric function of free electrons modelled as electron (Fermi) gas. The strength of a Lorentz oscillator is given as  $A = \hbar^2 e^2 N_e / \epsilon_0 m_e$ , where  $N_e$  denotes the number of electrons involved in the optical transition. For the Drude oscillator, the resting mass of electron  $m_e$  is replaced by the effective mass  $m^*$  of a hole or electron, and the latter is empirical (for some conducting polymers, a ratio  $m^*/m_e \approx 10^{-2}$  was estimated from quantum mechanical modelling [22]). Eq. 5 is written for an optically isotropic medium (film), while in the case of anisotropy,  $\tilde{\epsilon}(\lambda)$  has to be separately written for each optical axis. In the latter case, the Fresnel's reflection coefficients also depend on the direction in the laboratory coordinate system. It is worth noting that a generalization and extension of the Drude term in above theoretical dielectric function were proposed for fitting the experimental spectroscopic and conductivity data of the solid state semiconductors and (semi)conducting polymers (particularly in the THz frequency range) [23]–[25], however the discussion in the present case is narrowed to the above simple form which applies to the wavelength range studied in this work.

#### Variable angle spectroscopic ellipsometry (VASE)

The dielectric function for a thin film can be determined from spectroscopic ellipsometry data [11], [12], by numerically fitting  $\Psi$  and  $\Delta$  measured at varied wavelength, with the values calculated by introducing a model dielectric function for the film, into Fresnel's equations (1). Another possibility is to fit  $\epsilon_1(\lambda)$  and  $\epsilon_2(\lambda)$  as parameters, from the data measured at varied AOI. The latter is known as the "wavelength-by-wavelength" (WbW) fitting. If the dielectric function is *a priori* known, the film thickness can be fitted from Fresnel's equations, which is frequently used in the case of thin solid state films. On the other hand, if the film thickness is reliably known, the parameters of the dielectric function can be obtained by fitting. However, if both are not known *a priori*, the fitting of both  $\tilde{\epsilon}(\lambda)$  and  $d$  will rarely be accurate. In that case, it can be helpful to perform the spectroscopic ellipsometry measurements at varied angles of incidence (VASE), and simultaneously fit the  $\Psi$  and  $\Delta$  spectra measured at different AOI.

#### EXPERIMENTAL PART

The high-conductivity grade PEDOT:PSS (Orgacon HIL-1005) was purchased as aqueous suspension (1.1 % w/w) from Sigma Aldrich, filtered (Chromafil Xtra CA-20/25 cellulose acetate filters, 0.2  $\mu\text{m}$ ) and spin-coated onto silicon substrates (1 cm x 1 cm) at 2000, 3000, 4000, 5000 rpm, by using a computer-controlled spin-coater (SC100, Metallic Nova, Croatia). The sheet resistance of the product, as reported by the manufacturer, is 50-120  $\Omega/\text{sq}$ , and the pH around 2. After spin-coating, the films were dried and annealed for 20 min. at 170  $^\circ\text{C}$  on a hot plate.

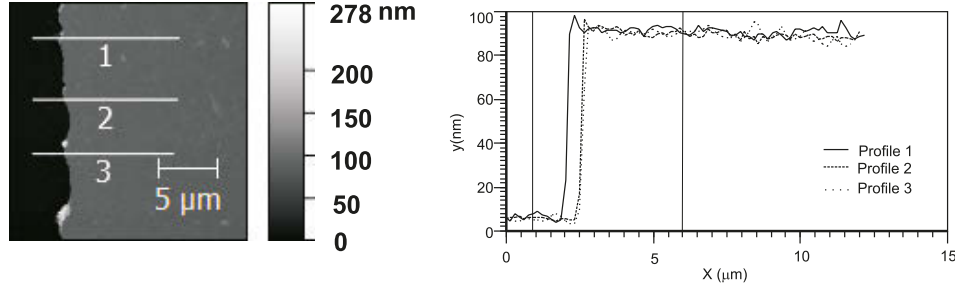


Fig. 2. Scanning atomic force micrograph of the PEDOT:PSS film spin-coated at the Si/SiO<sub>2</sub> wafer at spinning rate of 2000 rpm (left), and the corresponding height profile diagram, determined along the three lines indicated in the micrograph.

AFM measurements were performed with a Bruker Dimension Icon instrument. A step was created in all the samples by scratching the film with a sharp tweezer. Tapping mode AFM scans were performed across the step, at three different spots on the film surface, with the scanned area of  $20 \times 20 \mu\text{m}^2$ . The height profile images obtained from the scan were processed by using the Gwyddion 2.44 software. A flattening procedure was performed to remove the so called "bow/tilt" artefact in the height profile image. Three line profiles were extracted per scan, from which an average thickness was calculated.

The VASE measurements were performed with the Accurion EP4 spectroscopic imaging ellipsometer, at room conditions (297.15 K, in absence of humidity control). The computer-controlled instrument applies the nulling method for determining the ellipsometric angles  $\Psi$  and  $\Delta$  (nulling ellipsometry). The sample was first aligned perpendicular to the goniometer axis and the optical plane defined by the incoming light beam and the axis of the reflected beam, by using an in-built alignment sensor. For all the measurements, the 5x optical objective was used at the detector arm. After a perfect alignment, a spectroscopic ellipsometry experiment was performed, in which the spectra were measured in the wavelength range of 360-880 nm. Twenty points were accumulated for each spectrum, at five angles of incidence (AOI = 45°, 50°, 55°, 60°, 65°). The measurement was performed in two zones of polarizer and analyzer positions separated by 180°, from which  $\Psi$  and  $\Delta$  were calculated as average. All the model fittings were performed by using the Accurion EP4 Model software.

Another set of experiments was performed with the same samples as above, in which AOI was varied in the range 45° – 65° with a step of 1°. The acquisition of  $\Psi$  and  $\Delta$  was done for 20 different wavelengths in the same range as above. This was necessary in order to collect sufficient data for comparing the theoretical dielectric function fitted from  $\Psi(\lambda)$  and  $\Delta(\lambda)$  spectra, with the quasi-experimental dielectric function obtained by applying the wavelength-by-wavelength (WbW) fitting method (see below).

### Data fitting methods

The  $\Psi$  and  $\Delta$  spectra, measured by VASE for PEDOT:PSS thin films of varied thickness at a Si/SiO<sub>2</sub> substrate, in the visible range of incident radiation, are fitted and analyzed in terms of the stratified optical layers model (cf. Fig. 1). For the substrate, the dielectric functions of crystalline Si(1,0,0) and amorphous SiO<sub>2</sub> were used as cited in [26]. For the film, both the parameters of the Lorentz-Drude model dielectric function, as well as the film thickness, were fitted as unknown parameters. The film thickness obtained from fitting was compared to the values measured with the scanning atomic force microscope (AFM), as one of the criteria for evaluating the quality of the fitted dielectric function.

Fitting a model dielectric function and the film thickness from the raw VASE data [ $\Psi(\lambda, \theta_0)$ ,  $\Delta(\lambda, \theta_0)$ ] is in principle ambiguous. As will be discussed, if all of the parameters involved in the Fresnel's equations are fitted (the dielectric function parameters and film thickness), their mutual dependence will cause poor statistical determination. This is a very common problem of parameter cross-correlations when fitting functions involving (too) many parameters (also known as *overfitting*). In this case a reduction of the model, fixing some of the parameters, or simultaneous data fitting for experiments selectively designed in order to better express some of the parameters (as for example film thickness in the present case), is necessary. This also invokes validation of the data fitting methods prior to presenting and discussing the results.

The experimental ellipsometric spectra measured at varied angle of incidence (VASE spectra) of the spin-coated PEDOT:PSS films, were fitted with the stratified layers model as described in Fig. 1, in combination either with an isotropic LD dielectric function for the film, or a "quasi-experimental" isotropic dielectric function obtained by applying the WbW method. Thus in the first approach (LD1 and LD2 methods), the complex dielectric function for the film is calculated from the LD model as a sum of a Lorentz oscillator, a Drude oscillator, and a constant term:

$$\tilde{\epsilon} = \epsilon_{\infty} + \frac{A_L}{E_0^2 - E^2 - i\Gamma_L E} + \frac{A_D}{-E^2 - i\Gamma_D E} \quad (6)$$

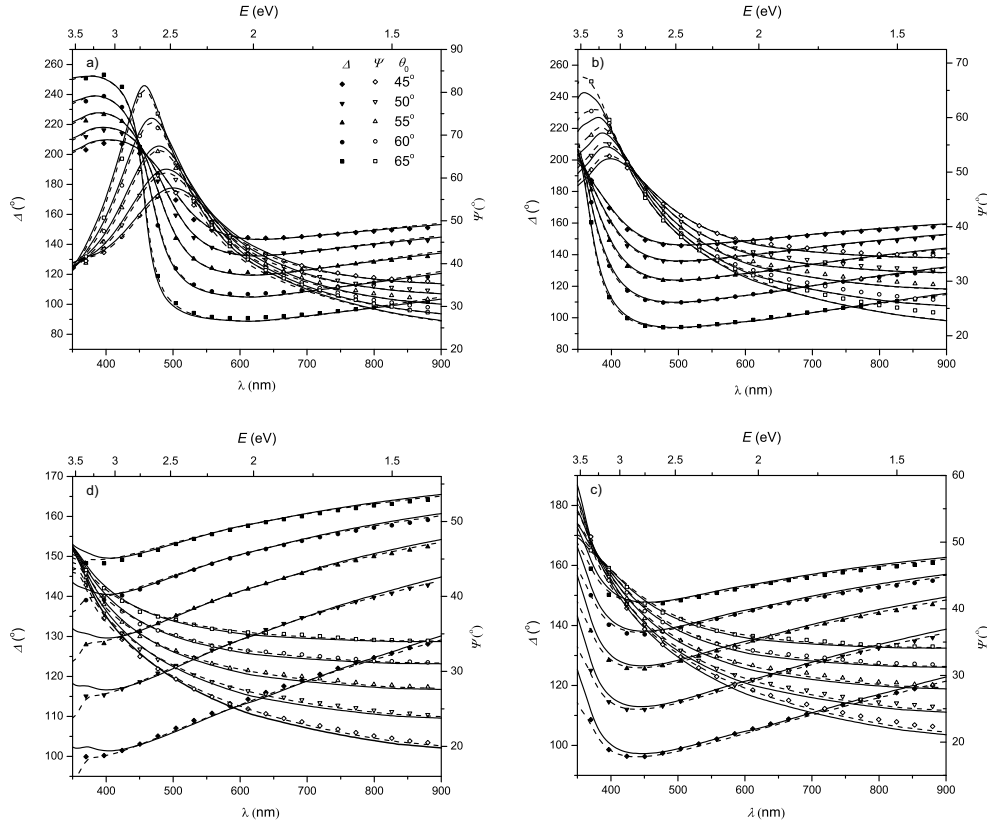


Fig. 3. Experimental VASE spectra ( $T = 297.15\text{K}$ , symbols as indicated in the legend in a), for the studied PEDOT:PSS films on Si/SiO<sub>2</sub>, spin-coated at different spin rates: a) 5000 rpm; b) 4000 rpm; c) 3000 rpm; d) 2000 rpm. Solid and dashed lines represent the best fit functions obtained with the Lorentz-Drude model dielectric function 6, by applying methods LD1 and LD2, respectively.

At the right hand side,  $E = hc/\lambda$  is the independent variable, while all the rest are treated as parameters. Indices L and D denote the parameters for the Lorentz and Drude oscillators, respectively,  $A$  and  $\Gamma$  describe the oscillator strength and damping, respectively,  $E_0$  is the Lorentz oscillator resonant frequency and  $\epsilon_\infty$  is the purely real high-frequency dielectric constant. Since the dielectric function is treated as continuous over the whole wavelength domain, this approach is suitable for fitting  $\Psi(\lambda)$  and  $\Delta(\lambda)$  at fixed AOI. The two approaches denoted as LD1 and LD2 differ in the following: in LD1, a common dielectric function was fitted for all the measured ellipsometric spectra at varied AOI and film thicknesses. This results with a common set of the dielectric function parameters for all the film thicknesses. In another method denoted as LD2, a common dielectric function was fitted for the ellipsometric spectra at varied AOI, however spectra for varied film thickness were fitted separately. This allowed fitting different LD dielectric function parameters for different film thicknesses. Since the described optical models already involve a significant number of parameters (six of them stemming from the LD dielectric function and the thickness), these were tested only as isotropic. As will be shown in the results, the choice of only one Lorentz, and the simplest form of the Drude oscillator in the theoretical dielectric function (cf. eq. 6) is in the present

case justified, since the introduction of additional oscillators or terms would certainly result in overfitting of the ellipsometric data within the available experimental wavelength range.

The WbW method was applied for fitting the  $\Psi(\theta_0)$  and  $\Delta(\theta_0)$  at each measured wavelength. In this method, the film thickness was fixed to the value measured with AFM, while  $\epsilon_1(\lambda)$  and  $\epsilon_2(\lambda)$  were fitted. In this way, best fit values for  $\tilde{\epsilon}$  are obtained independently at each wavelength. The resulting points  $[\epsilon_1, \lambda]$ , and  $[\epsilon_2, \lambda]$  may be regarded as "quasi-experimental". Although not free from assumptions laid down in the SLM, WbW presents the method for fitting VASE data in the case when the dielectric function of the film is not known *a priori*, which is least dependent on the model. As such, it may be used as reference for validation of the LD1 and LD2 model dielectric functions.

## RESULTS AND DISCUSSION

A typical AFM image obtained for the studied samples is presented in Fig. 2, along with the calculated height profile. The experimental values of the film thicknesses determined from the AFM height profiles measured for different applied spin-coating speeds, are tabulated in Table I, right column.

The VASE spectra for the four studied PEDOT:PSS films with different thicknesses are presented in Fig. 3. The solid

TABLE I

PEDOT:PSS FILM THICKNESSES OBTAINED BY FITTING THE LORENTZ-DRUDE MODEL DIELECTRIC FUNCTION TO THE ELLIPSOMETRIC SPECTRA PRESENTED IN FIG. 3, COMPARED WITH THE THICKNESS MEASURED WITH AFM. IN LD1 METHOD, THE ELLIPSOMETRIC SPECTRA MEASURED FOR DIFFERENT FILM THICKNESSES WERE FITTED BY A COMMON DIELECTRIC FUNCTION. IN LD2, SPECTRA AT VARIED AOI WERE FITTED BY A COMMON DIELECTRIC FUNCTION, SEPARATELY FOR EACH THICKNESS.

Spin speed (rpm)	$d$ (LD1) (nm)	$d$ (LD2) (nm)	$d$ (AFM) (nm)
5000	45.3	48.7	42.50 ± 1.93
4000	54.5	58.0	52.36 ± 2.82
3000	65.0	65.1	59.50 ± 2.58
2000	86.6	89.2	87.88 ± 4.20

lines represent the best fit by the LD1 method, where the data for all the studied samples were fitted simultaneously. The thereby obtained film thickness is presented in Table I and compared with the values obtained from the AFM measurements. A relatively good agreement with these values may be observed, corroborating the applicability of the LD1 fitting method. However in overall, the thickness measured with AFM is by 1-5 % smaller than the values determined from the LD1 fits. The fitted LD1 dielectric function parameters (cf. eq. 6) are listed in the top row of Table II. The RMSE calculated for all 800 data points (for each sample and each of the five angles of incidence, a spectrum contains twenty of both  $\Psi$  and  $\Delta$  measurements) equals 1.45 degrees. From this value it is observed that the fits obtained by the LD1 method are indeed good, in spite of a moderate number of fitted parameters. A deviation of the LD1 curves from the measured data points is observed for the two thinner films (cf. Figs. 3 c) and d). This deviation is more pronounced at lower wavelengths for  $\Delta$ , while at higher wavelengths for  $\Psi$ .

The best fit common dielectric function calculated from the fitted parameters of the Lorentz-Drude model (LD1 method) is presented in Fig. 4. The magnitude of the real part of the dielectric function ( $\epsilon_1$ ) is predominately determined by  $\epsilon_\infty$ , but a mild monotonically decreasing trend with increasing wavelength can also be detected. The latter trend occurs due to the Drude oscillator pull. As can be inferred from the comparison of the two oscillator strengths ( $A_L$  vs.  $A_D$ , first row in Table I), the Drude oscillator is much stronger than Lorentz. Thus the imaginary part ( $\epsilon_2$ ) of the LD1 dielectric function exhibits a very weak absorption peak around 2 eV.

The dashed lines in Fig. 3 represent the spectra modelled by applying the LD2 method, thus fitting the dielectric function parameters and thickness, both as characteristic for each sample, and keeping those parameters common for all AOI. The fitted curves almost perfectly coincide with the measured data in the whole range of the studied wavelength (except for the sample prepared at 2000 rpm). This may be also evidenced as low RMSE values for the LD2 fits (cf. Table II lower part), which are lower than in the case of LD1 fit. The fitted film thickness is somewhat greater than the LD1 value, and is by ca 10 % greater than the thickness measured with AFM.

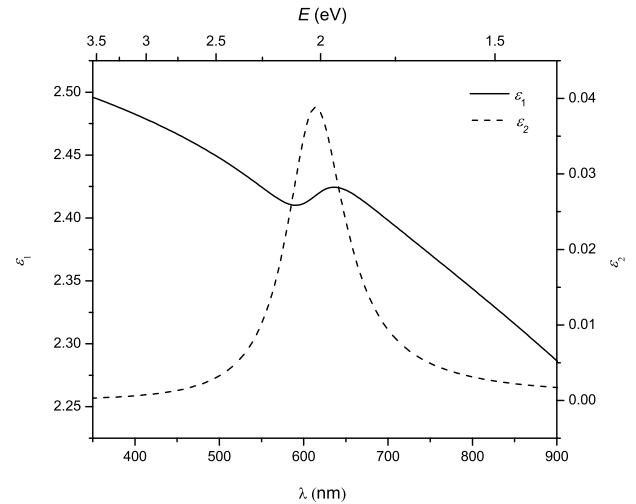


Fig. 4. Best fit common Lorentz-Drude dielectric function (cf. eq. 6) for all the studied films at 297.15 K, obtained by simultaneously fitting all of the measured ellipsometric spectra (method LD1). The corresponding film thicknesses fitted by this method are listed in Table I.

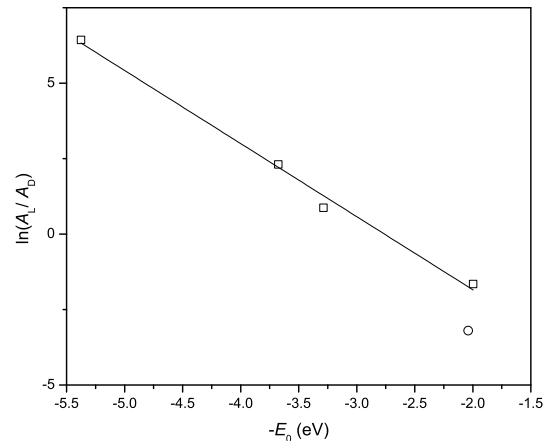


Fig. 5. Correlation between the  $\ln(A_L/A_D)$  and  $E_0$ , obtained from LD2 (squares) and LD1 (circle) methods for samples of varied film thicknesses. The fitted straight line  $y = -2.4212x - 6.6853$ ;  $R^2 = 0.9936$  was calculated only from the LD2 parameters (squares).

When considering the latter as a reference, one has to keep in mind that the AFM micrographs were scanned in a local area of  $400 \mu\text{m}^2$ , while the ellipsometric signal was collected over a much larger area, such that the discrepancies could be caused by a film thickness variation in lateral directions. The values of  $A_L$  and  $A_D$  parameters obtained from these fits (cf. Table II, lower part) are not coherent, whereby a significant variance in the strengths of the two oscillators can be detected. Thus, while the Lorentz oscillator is dominant for the samples

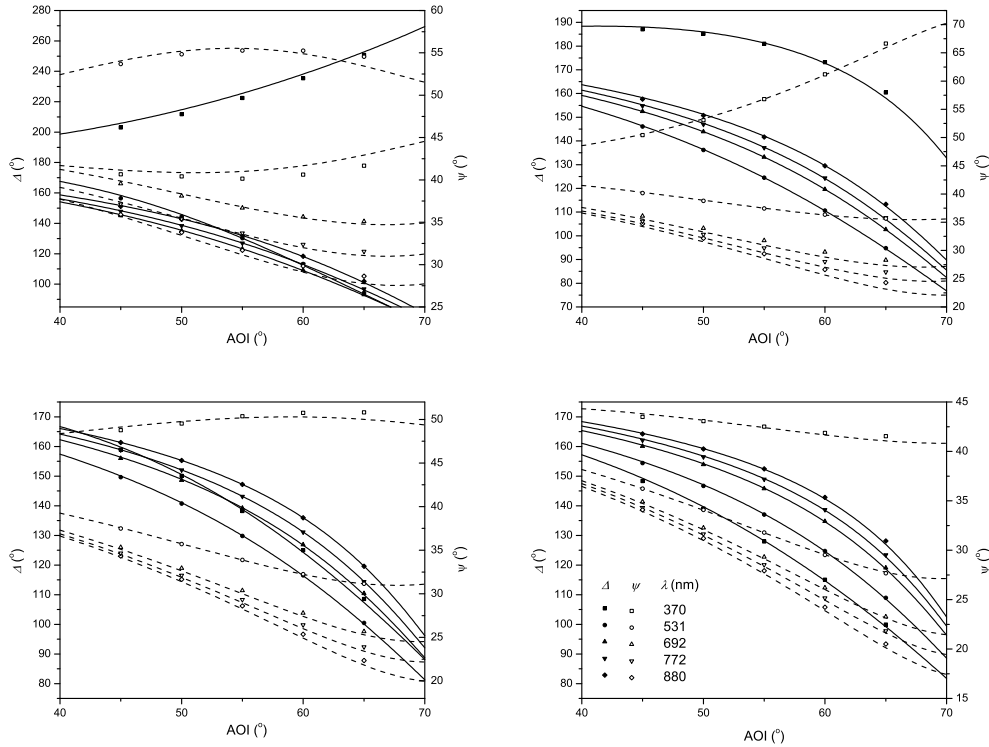


Fig. 6. VASE spectra for five selected wavelengths (see legend), measured at  $T = 297.15\text{K}$  for the PEDOT:PSS films prepared by spin-coating at different spin rates: a) 5000 rpm; b) 4000 rpm; c) 3000 rpm; d) 2000 rpm. The lines present the functions fitted by applying the WbW method (see text).

spun at 5000, 4000, 3000 rpm, the Drude term is stronger for the film spun at 2000 rpm. The values of the Lorentz resonance energy also range from 2.00 eV to 5.37 eV, while the broadening  $\Gamma_L$  is a bit more coherent around 1 eV. By keeping in mind that the fitted dielectric function parameters should exclusively represent properties of the film material and not its thickness, such incoherences should in principle not occur. VASE measurements were repeated for samples spun at 2000 and 5000 rpm, and LD2 fitting of those ellipsometric spectra resulted with parameters that almost perfectly coincide with those presented in Table II. This points to the fact that the observed incoherence in the LD2 parameters is not caused by an unreliable fit, but might represent either a property of the studied films, or a systematic trend inherent to the fitting method or model.

TABLE II  
THE PARAMETERS OF THE LORENTZ-DRUDE DIELECTRIC FUNCTION, OBTAINED FROM LD1 AND LD2 FITS OF THE ELLIPSO-METRIC SPECTRA PRESENTED IN FIG. 3. FOR ALL ENTRIES,  $\Gamma_D = 0.00$ .

Fit type	Spin rate (rpm)	$A_L$ ( $\text{eV}^2$ )	$E_0$ (eV)	$\Gamma_L$ (eV)	$\epsilon_\infty$	$A_D$ ( $\text{eV}^2$ )	RMSE ( $^\circ$ )
LD1	-	0.02	2.04	0.27	2.54	0.49	1.45
LD2	5000	1.46	3.68	1.04	2.11	0.15	0.43
	4000	0.77	3.29	1.24	2.31	0.32	0.66
	3000	5.61	5.37	0.57	2.19	0.01	0.98
	2000	0.16	2.00	0.71	2.53	0.81	1.74

The graph presented in Fig. 5 demonstrates a linear correlation between  $\ln(A_L/A_D)$  and  $E_0$ , observed by applying the LD2 fitting method. Thus the observed cross-correlation of the parameters might lead to a conclusion that for a given film thickness,  $A_L$ ,  $A_D$  and  $E_0$  may mutually adjust such that either Lorentz or Drude oscillator gains more strength, without much affecting the RMSE. Although in the present case,  $A_L$  and  $A_D$  may not be well determined from VASE data fitting, their ratio is determined by  $E_0$ , which is purely a property of the Lorentz term in (6). This provides the LD model parameters mathematical determinability, meaning that by including more data sets measured under different conditions (for example thickness, as is the case in LD1), LD dielectric function becomes progressively better determined in the VASE data. Parameter cross-correlations may not be completely excluded even in the case of LD1 (the correlation matrix for LD1 parameters was inspected and shows cross-correlations up to even 90 % as compared to 99 % in the case of LD2). Thus, the RMSE obtained from fitting should not be considered as a main criterion in model optimization and the dielectric function will be significantly better determined when there is a larger number of VASE data points measured for varied film thickness.

The so far presented results clearly demonstrate an ambiguity in simultaneous fitting the LD dielectric function parameters and film thickness, whereupon the LD1 approach apparently leads to a more reliable fit. This is also evidenced

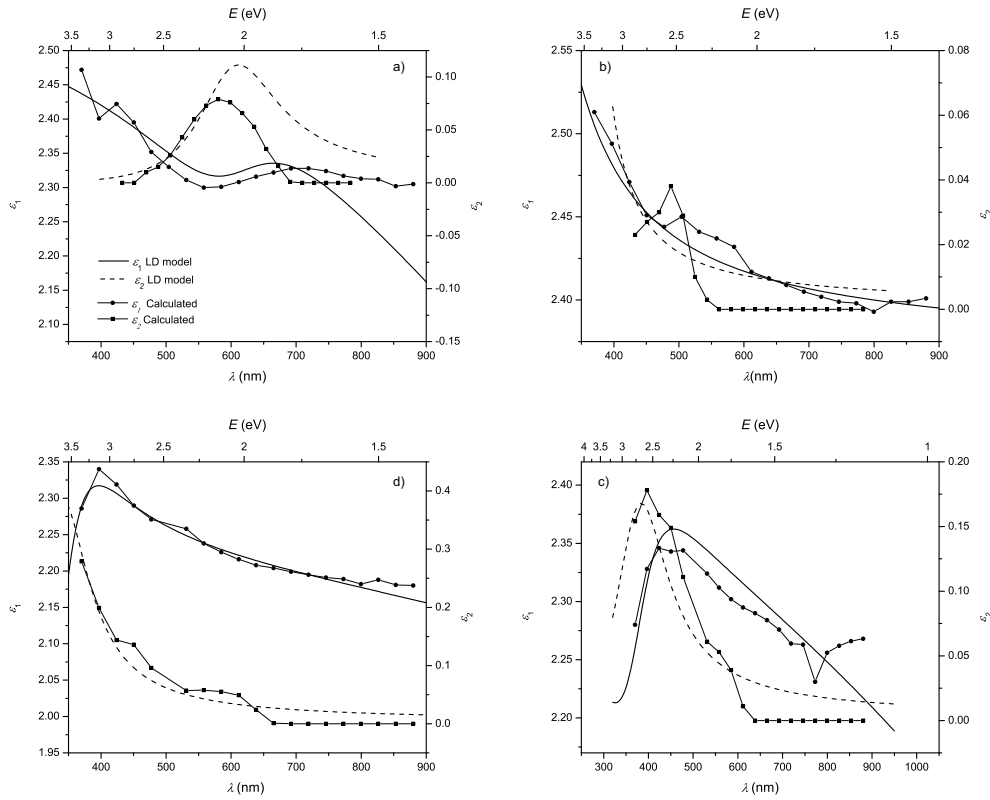


Fig. 7. Dielectric constant fitted independently for constant wavelengths in the VASE spectra (WbW method, symbols connected with lines), compared with the Lorentz-Drude dielectric functions fitted by the LD2 method (curves).

when the fitted  $E_0$  parameter is compared with the expectation value based on theoretical electronic structure of PEDOT [22]. It was found by computational modelling that the main optical transition in oligo- and polythiophenes depends on the chain length (polymerization index) and the oxidation state, and may range from  $\sim 3.0$  eV in the case of a trimer in neutral (unoxidized) state to as low as  $\sim 0.5$  eV for the case of singly oxidized nonamer [14], [27]. When comparing the parameters presented in Table II with these theoretical values, it has to be noted that in the studied samples, the chain length is not known and probably not strictly defined. Moreover the oxidation state of PEDOT was not controlled and the influence of PSS on the electronic density of states of PEDOT should also not be neglected. Nevertheless, we may detect that some of the  $E_0$  values obtained in LD2 fitting are by far too large to be physically meaningful. On the other hand, the value of 2.04 eV obtained from the LD1 fit seems reasonable for the  $\pi \rightarrow \pi^*$  transition in the neutral state. It is interesting to note that a similar value was obtained by the LD2 fitting method only for the thinnest film spun at 2000 rpm. In this case, the ratio of electron to hole density, which may be calculated from the  $A_L/A_D$  ratio, amounts to 0.4 from the LD1 fit, and 2.1 from LD2. This large difference demonstrates the sensitivity of the LD parameters to the density of electronic states in the studied film material.

The VASE ellipsometric angles as function of AOI at a constant wavelength are presented in Fig. 6. For sake of clarity, these graphs include data for only five out of twenty studied wavelengths. A nearly perfect fit of the curves obtained by implementing the WbW fitting method may be detected. The set of dielectric constants obtained in this manner, presented by connected points in Fig. 7, may be considered as the quasi-experimental VASE dielectric function, since  $\epsilon_1$  and  $\epsilon_2$  were fitted as parameters of the SLM, independently for each wavelength. The thickness of the film was kept fixed at the values obtained from the AFM measurements, while  $\epsilon_2$  was constrained to positive values. Under these conditions, some of the  $\epsilon_2$  points coincide with zero, which is a consequence of a low absorbed intensity and points to underdetermination of  $\epsilon_2$  with respect to  $\epsilon_1$ . Surprisingly, the LD2 dielectric functions presented in Fig. 7 show good consistency with the WbW quasi-experimental dielectric functions. This points to a possibility that the LD2 functions do not result from overfitting but are correctly determined as a property of the studied films. In that case a large variation in these functions for the studied samples of varied thicknesses (and possibly oxidation state), deserves further investigation.

## CONCLUSION

The presented results demonstrate successful introduction of a method for simultaneous determination of PEDOT:PSS



film thickness and the dielectric function, by using variable angle spectroscopic ellipsometry (VASE) in the visible spectral range. The method requires postulation of an optical model for the surface (stratified layers model), in combination with an appropriate model for the dielectric function of the studied film. In this respect, an isotropic Lorentz-Drude model function proved to be applicable. The simultaneous determination of the dielectric function parameters and film thickness requires a rigorous and methodical data fitting approach. In order to avoid cross-correlations of the fitted parameters (overfitting), it is recommended to simultaneously fit VASE data measured for samples of varied film thickness, whereupon the RMSE obtained from fitting should not be taken as the sole criterion for selecting the optimal model.

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