SPECTROSCOPIC ELLIPSOMETRY AND REFLECTOMETRY MODEL FOR ORGANIC LAYERS

Katarína Bombarová[1], Juraj Chlpík[1], Július Cirák[1]

[1] Institute of Nuclear and Physical Engineering, Faculty of Electrical Engineering and Information Technology, Slovak University of Technology in Bratislava
Ilkovičova 3, SK-812 19 Bratislava, Slovakia

E-mail: katarina.bombarova@stuba.sk

Received 24 May 2014; accepted 28 May 2014

1. Introduction

Organic materials such as oligothiophenes are suitable for exploring different synthetic, morphological and electronic relationships in organic semiconductors. They are widely used in organic electronics because of their excellent optical, electrochemical properties and the effect of self-organization. Correlation of electrochemical and photophysical properties with the molecular structure is important for rational investigation of novel materials for (opto-)electronic applications, including organic solar cells (OSCS), dye sensitized solar cells (DSSCs), organic light-emitting diodes (OLED) and organic FETs (OFETs) [1].

For determining optical properties of oligothiophene ultrathin films spectroscopic ellipsometry was used. Spectroscopic ellipsometry is a very sensitive method; it enabled to determine thickness and refractive index of oligothiophene films deposited on a silicon substrate by the Languir-Blodgett method as well as by spin coating technique. This work was focused on creating a spectroscopic ellipsometry model for organic materials. The samples were measured by spectroscopic ellipsometry and reflectometry using polarimeter Horiba Jobin-Yvon MM-16. Spectroscopic model based on the Lorentz dispersion was elaborated.

2. Ellipsometry and Reflectometry

Ellipsometry is a nondestrustive optical method used in a wide range of thin layers applications. The basic principle is observation of polarization state changes in the reflected light. After the reflection of light from a layered surface both the amplitude and the phase of *p* and *s* polarization components are changed. Analyzing the data measured, the ellipsometric parameters Δ (phase difference) and ψ (ratio of Fresnel's reflection amplitudes) are extracted using the ellipsometric equation

$$r_p / r_s = \tan\psi \, e^{i\Delta} \qquad (1)$$

where r_p, r_s are complex Fresnel's reflection amplitudes [2].

The values of the ellipsometry parameters depend on thickness and complex material permittivity constant of the layered structure, including a substrate. Because the material constants are dependent on the wavelength of the incident light and considering the fact that light can interfere on the layered structure, the parameters ψ and Δ exhibit spectral dependences.

The measured data are used to construct a model in which each layer refers to a given material. The model uses mathematical relations called a dispersion formula that helps to evaluate thickness and optical properties of the material by adjusting specific fitting parameters. In our analyses we used a model based on the Lorentz dispersion described by the following equation

$$\varepsilon = \varepsilon_\infty + \frac{(\varepsilon_s - \varepsilon_\infty)\omega_t^2}{\omega_t^2 - \omega^2 + i\Gamma_0\omega} \tag{2}$$

where ε_∞ is the high frequency dielectric constant, ε_S ($\varepsilon_S > \varepsilon_\infty$) gives the value of the static dielectric function at zero frequency, ω_t is the resonant frequency of the oscillator whose energy corresponds to the absorption peak, Γ_0 is the broadening of each oscillator also known as the damping factor [3].

In ellipsometry the theoretical model is to be compared with the measured data. The ellipsometry model comprises a multilayer structure consisting of individual material models representing the substrate, all assumed layers (SiO_2, interface layers), and the superimposed material layer under study.

Fig. 1: *Layer structure of ellipsometry model.*

In spectroscopic reflectometry the intensity of reflected light is measured in a broad wavelength range. Non-polarized light at a normal incidence is used. The method is based on the measurement of light intensity before and after reflection from the sample. The ratio of the reflected and incident light intensity is denoted as the absolute reflectance. Generally, it is difficult to measure directly the intensity of light before the incidence. The absolute reflectance of an unknown sample can be calculated from the measurement of the relative intensity of reflected light if the absolute reflectance of the reference sample is known (Si with a native SiO_2 layer). The evaluation of data is also based on the fitting of parametric multilayer model, similarly to the ellipsometry model (Fig.1), to measured reflectance. Illustrations of measured and fitted reflectances are shown in Fig 2.

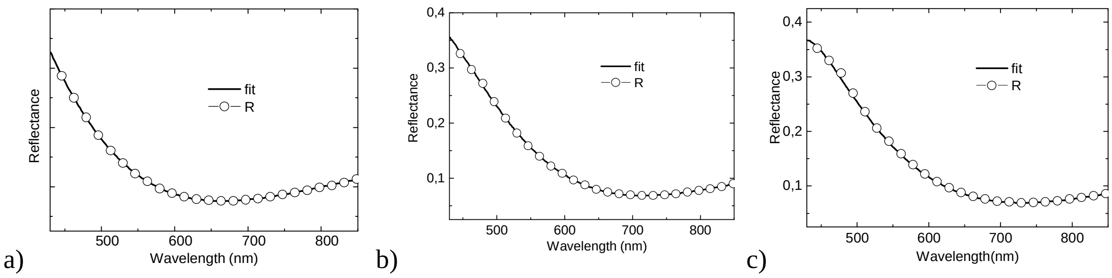

Fig. 2: *Comparison of measured and fitted spectral reflectances of oligothiophene LB monolayer (a), LB multilayer (b), and spin coated layer (c).*

3. Results

All measurements were carried out using spectroscopic polarimeter Horiba Jobin-Yvon MM-16. The spectral range of the device was between 430 nm and 850 nm with a step of 2 nm. The light beam diameter was 1 nm. The experimental data were evaluated by DeltaPsi2 software.

Spin coating is a deposition technique which provides an organic layer of uniform thickness. A small amount of material was added at a center of the rotating substrate. The sample deposited by spin coating (2000 rpm) was prepared at the Institute of Electronics and Photonics FEI STU in Bratislava.

Monomolecular assemblies on substrates, now termed Langmuir-Blodgett (LB) films, exhibit many interesting properties and can perform functions which give them perspectives to impact advanced technologies and molecular electronics in an important way. When using this technique, the organic material was spread on a water surface where it spontaneously forms a monomolecular layer. The material was deposited onto a substrate by slow dipping and withdrawing through the air/water interface. In this way it is possible to prepare a monolayer or by multiple traversals even a multilayer. By contrast with evaporation or sputtering the LB technology is based on a low temperature process which never results in a damage of the substrate surface [4].

Oligothiophene hexamer (OTH) – 3,3‘“‘-bis-decyl[2,2‘;5‘.2“;5“;2‘‘‘;5‘‘‘,2‘‘‘‘,2‘‘‘‘]sexitiophene-5,5‘‘‘‘-didaroxilic acid was synthetized according to the procedure presented in [5].

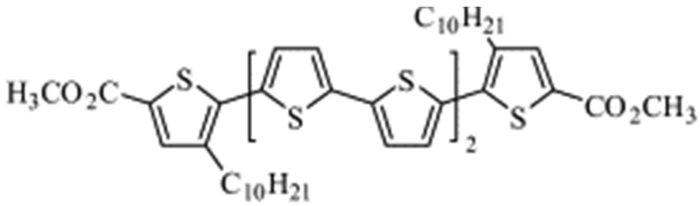

Fig. 3: *Chemical structural formulae of oligothiophene hexamer.*

The samples of organic thin films were prepared on silicon substrates. The main goal of this study was to establish a suitable model for determining thickness and the refractive index of the layers. The material models were based on the Lorentz dispersion. The ellipsometry model involved Si substrate, SiO_2 interlayer and a top layer of oligothiophene (see Fig.1).

We elaborated two ellipsometry models. Each ellipsometry model consists of SiO_2 dispersion interlayer. In the former (Model I) SiO_2 dispersion was theoretically calculated, in the latter (Model II) SiO_2 dispersion was computed from the measured data and taken to the ellipsometry model. The same models were used for ellipsometry and reflectometry data. Both models give similar results, which are listed in Table 1 and Table 2.

Tab. 1: *Thickness of organic layers evaluated from ellipsometry and reflectometry on the basis of Model I.*

thickness nm	monolayer	multilayer	spin coating
ellipsometry	1.17±0.01	11.2±0.45	14.49±0.56
reflectometry	1.56±0.19	12.78±0.05	14.98±0.7

Table 1 shows results from the ellipsometry model in which SiO_2 dispersion was theoretically calculated. The results from the ellipsometry model (Model II) with SiO_2 dispersion computed from measured data are presented in Table 2.

Tab. 2: *Thickness of organic layers evaluated from ellipsometry and reflectometry on the basis of Model II.*

thickness nm	monolayer	multilayer	spin coating
ellipsometry	1.36±0.12	12.99±0.02	14.79±0.02
reflectometry	1.12±0.98	12.21±0.05	14.80±0.05

We analyzed reflectometry and ellipsometry data concurrently by the bound multimodel. It is useful to bind several experimental data types from the same sample or different samples that exhibit at least one common physical property. Combining data provides generally the advantage to reduce strong parameter correlation in the optical data modelling process. Resulting thicknesses are shown in Table 3.

Tab. 3: *Thickness of organic layers evaluated from ellipsometry and reflectometry on the basis of the bound multimodel.*

nm	monolayer	multilayer	spin coating
thickness	1.17±0.01	12.71±0.85	14.53±0.47

Both methods used in this study spectroscopic ellipsometry and reflectometry provide similar results. This is documented in Fig. 4 by a spectral dependence of the index of refraction.

Fig. 4 shows behaviour of the complex refractive index, a real part of the refractive index on the left and the dependence of extinction coefficient on the right side. The absorption spectrum was recorded from the solution of oligothiophene in chloroform whereas the extinction coefficient was evaluated from the data obtained from a layer as deposited on the solid substrate. This fact caused an apparent shift in the peak position by approx. 70 nm towards higher wavelengths.

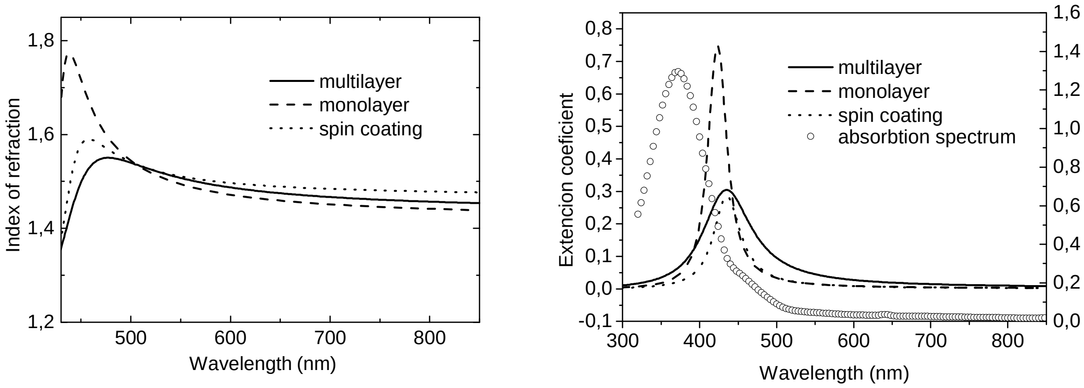

Fig. 4: *Refractive index and extinction coefficient of monolayer, multilayer film and film prepared by spin coating*.

4. Conclusion

In this work oligothiophene samples prepared by the Langmuir-Blodgett and spin coating techniques were analyzed. The samples were measured by spectroscopic ellipsometry and reflectometry. Three types of ellipsometry models were elaborated and compared.

Acknowledgement

This work was supported by the Slovak Research and Development Agency under the contracts No. APVV-0108-11 and APVV-0262-10.

References:

[1] A. S. Sizov at al.: Applied Physics Letter, **103**, (2013).

[2] H. G. Topkind, E. A. Irene: Handbook of ellipsometry, Springer, USA (2005)
[3] H. Fujiwara: Spectroscopic Ellipsometry: Principles and Applications, John Wiley&Sons, Tokyo, Japan (2003).
[4] M. C. Petty: Langmuir-Blodgett films: an introduction, Cambridge University Press, UK (1996)
[5] G. Čík, Z. Végh, F. Šeršeň, J. Krištín, B. Lakatoš, P. Fejdi: *Synth. Met.*, **149**, 31 (2005).