OPTICAL ANALYSIS OF ZnO THIN FILMS USING SPECTROSCOPIC ELLIPSOMETRY AND REFLECTOMETRY

Katarína Bombarová[1], Juraj Chlpík[1,2], Soňa Flickyngerová[3], Ivan Novotný[3], Július Cirák[1]

[1]Institute of Nuclear and Physical Engineering FEI STU in Bratislava,
[2]International Laser Centre Bratislava
[3] Institute of Electronics and Photonics FEI STU in Bratislava FEI STU in Bratislava
E-mail: katarina.bombarova@stuba.sk

Received 12 April 2013; accepted 17 May 2013

1. Introduction

Zinc oxide belongs to a group of transparent conductive oxides (TCO). TCOs are of great interest in optics and optoelectronics. Due to the wide band gap and resulting high transmittance in the visible spectra range in conjunction with relatively low electrical resistivity, TCOs are essential in photonic applications as transparent conductive layers. They are mainly used as top electrodes in solar cells or flat panel displays. It is thermally and chemically stable, low cost non-toxic material.

Numerous advanced applications such as gas sensors, surface acoustic waves components, UV light emitters are based on pure or doped ZnO. Spectral transmittance and reflectance measurements are the most common experimental methods used to obtain important information about the optical properties of ZnO. A good and useful way to obtain the parameters of the layer within one measurement is spectroscopic ellipsometry, as well as reflectometry. Using an appropriate sample model one can obtain the values of many unknown variables by fitting measured data to the model parameters. The complex index of refraction, absorption coefficient, band gap energy, as well as the thickness of the layer can be provided using these methods. Several material models for TCOs exist in spectroscopic ellipsometry. Here, two of them: the Cauchy and the Tauc-Lorenz models are compared. Three types of samples of different ZnO layer thickness are examined. The layers were prepared by HF diode deposition on both corning glass and Si substrate.

2. Spectroscopic ellipsometry

The output of an ellipsometric measurement is a pair of parameters ψ and Δ. Their meaning comes from the ellipsometric equation [1]:

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

where r_p and r_s are the amplitude reflectivities of *p*- and *s*-polarized light, respectively. The values of the ellipsometry parameters depend on thicknesses and complex material permitivities of the layered structure, including a substrate. While the material constants are dependent on the wavelength of incident light and also the light can interfere on the layered structure, the parameters ψ and Δ exhibit spectral dependences.

In ellipsometry the theoretical model is to be compared with the measurement data. The ellipsometry model comprises a multilayer structure consisting of individual material models representing the substrate, assumed layers (SiO_2, interface layers), material layer studied (ZnO) and a possible roughness layer on the top of the structure (Fig. 1).

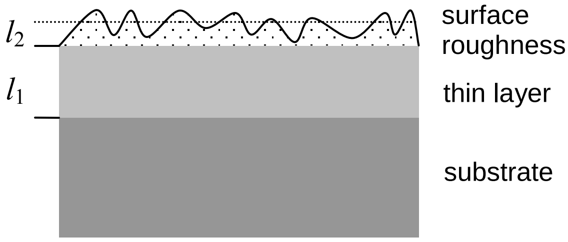

Fig. 1: *Layer structure of ellipsometry model.*

The material model is an analytical dispersion function of complex permittivity or index of refraction. As the simplest approximation, a spectral dependence of the index of refraction in the visible region could be described by the Cauchy model [2]. The Cauchy model describes a dependence of the refraction index and wavelength. It is suitable for determining the index of refraction of non-metal materials (dielectrics and semiconductors) in the visible spectral range. For evaluating an empiric relation dependence of the index of refraction on wavelength is used

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \tag{2}$$

where *A, B, C* are the Cauchy coefficients for a given material. This model is suitable for analysing data from the visible spectral range. Although the model cannot yield the energy gap, it is good for determination of the thickness and the index of refraction in non-absorbing material.

For the determination of the optical energy gap the Tauc-Lorenz model was used [3]:

$$\varepsilon = \varepsilon_1 + i\varepsilon_2 \tag{3}$$

$$\varepsilon_2(E) = \begin{cases} \dfrac{1}{E} \cdot \dfrac{AE_0 C\left(E - E_{\mathrm{g}}\right)^2}{\left(E_2 - E_0^2\right)^2 + C^2 E^2} & E > E_{\mathrm{g}} \\ 0 & E \le E_{\mathrm{g}} \end{cases} \qquad \varepsilon_1(E) = \varepsilon_\infty + \frac{2}{\pi} P \int_{E_{\mathrm{g}}}^{\infty} \frac{\xi \varepsilon_2(\xi)}{\xi^2 - E^2} \mathrm{d}\xi \tag{4}$$

where E_{g} is the band gap energy, E_0 denotes a position of the Lorenz peak, ε_∞ is the high-frequency permittivity, *A*, *C* are appropriate constants and *P* symbol means the Cauchy principal value. The Tauc-Lorenz model is extended the Lorenz model of permittivity, which defines a value of the imaginary part ε_2 equal to zero for the energies smaller than E_{g}. There is no absorption in this region by default. The main advantage of this approximation is relatively small number of parameters [4].

Success of the ellipsometry measurement depends how well the numerical model can be approximated to the reality. Especially the surface roughness brings in difficulties to this approach. Surface defects, impurities or roughness can be modeled by the Effective Mass Approximation (EMA) model [5]. EMA allows to find an effective thickness of the surface roughness layer of the sample. The basis of EMA model is a conception of inhomogeneous material containing inhomogeneities above an atom dimension but below the diffraction limit.

3. Spectroscopic reflectometry

In spectroscopic reflectometry the intensity of reflected light are measured in a broad wavelength range. Non-polarized light at normal incidence is used.

The method is based on the measurement 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. 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 native SiO_2 layer) [6].

The evaluation of data is also based on the fitting of parametric multilayer model, similarly to the ellipsometric model (Fig. 1), to measured reflectances. Illustrations of measured and fitted reflectances are shown in Fig. 2.

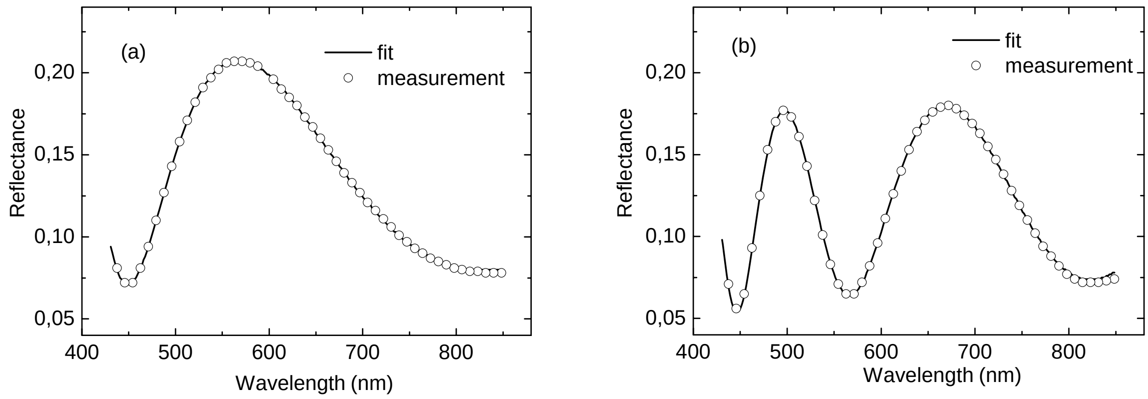

Fig. 2: *Comparison of measured and fitted spectral reflectances of ZnO layers with thickness of (a) 200 nm and (b) 400 nm on glass substrate using the Tauc-Lorenz material model.*

4. Results

ZnO layers were prepared by radio frequency diode sputtering at the Institute of Electronics and Photonics FEI STU in Bratislava by the Perkin-Elmex Randex 2400-8L system. The layers were deposited on silicon substrates with native SiO_2 and also on Corning glass 7059 substrates in Ar atmosphere with pressure of 1.3 Pa. ZnO samles were prepared in three different thicknesses.

Measurements were carried out by polarimeter Horiba Jobin Yvon MM-16 with spectral range 430–850 nm with a resolution of 2 nm. The light beam diameter was 1 mm. Data were analysed by the DeltaPsi2 software.

Tab. 1: *Thickness of ZnO on glass substrate by Cauchy model.*

nm	sample1		sample2		sample3	
	thickness	roughness	thickness	roughness	thickness	roughness
ellipsometry	95	3,4	211	5,67	424	13
reflectometry	103	3,5	208	11,3	415	19,9

Tab. 2: *Thickness of ZnO on Si substrate by Cauchy model.*

nm	sample1		sample2		sample3	
	thickness	roughness	thickness	roughness	thickness	roughness
ellipsometry	107	n.a.	226	11,9	434	20
reflectometry	102	n.a.	228	n.a.	414	20

The measured thickness as well as roughness of the layers obtained using the Cauchy model is summarized in Table 1 and Table 2 for glass and silicon substrates, respectively. Similar results are presented in Table 3 and Table 4 derived using the Tauc-Lorenz model.

Tab. 3: *Thickness of ZnO on glass substrate by Tauc-Lorenz model.*

nm	sample1		sample2		sample3	
	thickness	roughness	thickness	roughness	thickness	roughness
ellipsometry	95	3,6	209	6,2	424	12,9
reflectometry	103	3,5	206	12,2	415	19,8

Tab. 4: *Thickness of ZnO on Si substrate by Tauc-Lorenz model.*

nm	sample1		sample2		sample3	
	thickness	roughness	thickness	roughness	thickness	roughness
ellipsometry	107	n.a.	231	8,7	439	18,9
reflectometry	112,3	n.a.	230	7,5	423	20,6

This approach provides an attractive possibility to investigate surface roughness, the values are also listed in Tables 1–4. One can see a good agreement between the ellipsometry and the reflectometry measurement results.

It is obvious that the surface roughness on glass and silicon substrates is different. It is probably caused by the fact that we did not take into consideration in the ellipsometry model an interlayer between glass and ZnO thin film [7]. The results indicate that surface roughness increases with increasing thickness of the layers. For the further quantitaive analysis a comparison to additional methods (AFM, contact profilometry) would be required.

The values of optical energy gap obtained by the Tauc-Lorenz model are also shown in Table 5.

Tab. 5: *Energy gap of ZnO from Tauc-Lolenz model.*

eV	sample1		sample2		sample3	
	Si	glass	Si	glass	Si	glass
elipsometry	3,20	3,28	3,04	3,30	3,23	3,25
reflectometry	3,29	3,30	3,27	3,29	3,28	3,29

Both methods used in this study spectroscopic ellipsometry and reflectometry provide similar results regarding optical properties of thin ZnO layers. This is documented in Fig 3 by spectral dependence of the index of refraction.

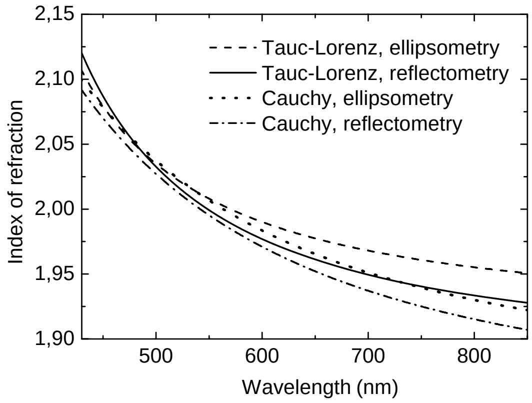

Fig. 3: *Comparison of the results of ellipsometry and reflectometry. Index of refraction of the ZnO layers on glass substrate using the Tauc-Lorenz and the Cauchy model.*

5. Conclusion

Optical properties (refractive index, thickness and optical energy gap) of ZnO layers in the spectral range between 430 nm and 850 nm were obtained using ellipsometry and reflectometry. The Cauchy and Tauc-Lorenz material models were compared. The results of both experimental methods as well as both material models lead to similar values of investigated parameters. The Cauchy model seems to be a good choice if only a real part of the index of refraction is of interest. The Tauc-Lorenz model can be used to evaluate the optical band gap of ZnO layers. Even if the spectral range of measurement does not cover the value of ZnO E_g, it is shown that it can be successfully determined using this approach.

Acknowledgement

This work was financially supported by Slovak Republic grant agency VEGA 1/0879/11.

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

References:

[1] H. Fujiwara: *Spectroscopic Ellipsometry. Principles and Applications*. John Willey & Sons, Tokyo (2003).

[2] Q. H. Li, D. Zhu, W. Liu, Y. Liu, and X. C. Ma: Appl. Surf. Sci., **254,** 2922 (2008).

[3] J. Tauc, R. Grigorovici, and A. Vancu: Phys. Statu. Solidi *B,* **15,** 627 (1966).

[4] G. E. Jellison, F. A. Modine: Appl. Phys. Lett., **69,** 371 (1996).

[5] K. Bombarová, J. Chlpík, S. Flickyngerová, and J. Cirák: *Proc. of the 18th International Conference APCOM,* 280 (2012).

[6] K. Bombarová, *Investigation of optical properties of very thin films*, Diploma Thesis, Comenius University (2010).

[7] N. Ehrmann, R. Reinke-Koch: Thin Solid Films, **519,** 1475 (2010).