MATERIAL MODEL OF ZnO FOR ELLIPSOMETRY MEASUREMENTS

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1. Introduction

ZnO and other transparent conductive oxides (TCO) are of great interest in the fields of microelectronics, photonics and photovoltaic. Due to its transparency and electrical conductivity, ZnO should serve as the transparent top electrode in photovoltaic components.

The measurement of optical parameters of ZnO and TCO in general, is very useful in the process of optoelectrical systems design as well as in the optimization of technology. Unfortunately, relatively complicated dispersion relation does not allow to formulate a general parametric model for this class of materials as in the case of SiO_2. Every technological approach requires an individual specialized material model, if considered to be investigated using ellipsometry.

The complex analysis of the dispersion relation of ZnO could be found in [1]. Authors introduced an ellipsometric material model involving a high interband transition in the UV region, band gap transition in visible range and effect of free carriers in the near infrared region to the complex permittivity of ZnO. Although, their model allows to fit measured data very precisely, its main disadvantage iconsists in a large number of parameters. Too many degrees of freedom leads to considerable large uncertainties of important variables.

In this work, spectroscopic ellipsometry measurements of ZnO layers prepared by magnetron sputtering are presented. The article is a part of a larger work, whose main purpose is to find an optimum material model for reliable and fast measurement of basic optical parameters such as the complex refractive index, energy gap or layer thickness of ZnO layers. We focus on the Tauc-Lorenz material model and comparison with conventional methods of layer thickness and energy of band gap measurements are discussed.

2. Ellipsometry modelling

The main task of spectroscopic ellipsometry data processing is to find the best fit of the model parameters to the measured data. The ellispometry model is usually a multilayer structure consisting of individual material models representing the substrate, assumed layers on the substrate (SiO_2, interface layers), studied material layer (ZnO) and a possible roughness layer at the top of the structure (Fig. 1). As the simplest approximation, spectral dependence of the index of refraction in the visible region could be described by the Cauchy model [2]. Even if, by this empirical approach the band-gap energy cannot be seen directly, this important parameter should be found by the Tauc plot technique [3]. Better, involving also the permittivity for energies above E_g, seems to be the Tauc-Lorenz model approach [4]:

$$\varepsilon = \varepsilon_1 + i\varepsilon_2 \tag{1}$$

$$\varepsilon_2(E) = \begin{cases} \dfrac{1}{E} \cdot \dfrac{AE_0C\left(E - E_\mathrm{g}\right)^2}{\left(E_2 - E_0^2\right)^2 + C^2E^2} & E > E_\mathrm{g} \\ 0 & E \le E_\mathrm{g} \end{cases} \qquad \varepsilon_1(E) = \varepsilon_\infty + \frac{2}{\pi} P \int_{E_\mathrm{g}}^{\infty} \frac{\xi\varepsilon_2(\xi)}{\xi^2 - E^2} \mathrm{d}\xi \tag{2}$$

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 symbol P means the Cauchy principal value of integral. 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.

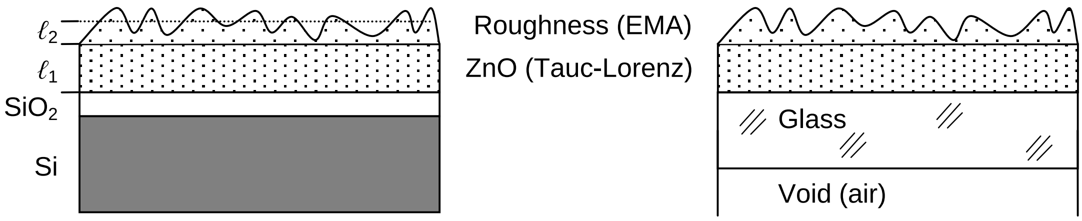

Fig. 1 *Layer structures used in the ellipsometry modeling, SiO_2/Si (Left) and corning glass substrate (Right).*

The surface roughness is represented by EMA (Effective Mass Approximation) [5]. EMA allows to find an effective thickness of the surface roughness layer of the sample.

The material parameters of Si were taken from [6], the natural SiO_2 was measured on a non deposited substrate using the Lorenz model. The corning glass pure substrate was also measured and fitted using the Lorenz model.

All the parameters of the ZnO Tauc-Lorenz layer, as well as its thickness, volume fraction and thickness of the surface roughness layer were fitted. The result vs. ellipsometry measurement of 311 nm ZnO layer is in the Fig. 2. The good agreement of the model with the measured data can bee seen (χ^2 = 0.277).

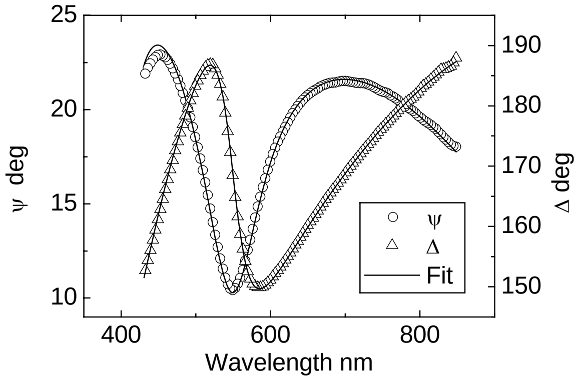

Fig. 2 *Ellipsometry measurement (scatter) and fit (line) of 311 nm ZnO layer on glass substrate. The model matches experimental data with χ^2 = 0.277*

3. Results and discussion

We had two series of ZnO layers dopped by Al (2 %) prepared by magnetron plasma sputtering on two types of substrates: corning glass and Si with a natural SiO_2 layer.

The thin layer samples were prepared by magnetron sputtering at the Institute of Electronics and Photonics FEI STU in Bratislava by the Perkin-Elmer Randex 2400-8L system. Thin ZnO layers were deposited on Si and Corning glass 7059 substrates in Ar atmosphere with the pressure of 1,3 Pa. The three types of samples differ by the time of deposition by a factor of 2.

Ellipsometry measurements were done by Horiba Jobin-Yvon MM-16 spectroscopy ellipsometer. The device enables to measure in the spectral range 430 nm – 850 nm with 2 nm resolution.

The experimental results of the ZnO layers thickness are summarized in the Tab. 1. The height of the edge of etched layer was measured by the contact profilometer. Its accuracy is determined by the quality of etching process and is less than 5 nm. In the ellipsometry results, the total thicknes is defined as the thickness of the bulk ZnO layer plus the effective thickness of the surface roughness layer on the top. Even if the fitting uncertainties are small, they are strongly affected by the volume fraction parameter in the EMA model. The estimation of the real accuracy is still around 5 nm. Thickness of the surface roughness layer is an interesting parameter. Since the surface roughness of ZnO deposited by magnetron sputtering is supposed to be small (less than 1 nm), the ellipsometry fit gives better results when the roughness was taken into account. In the case of 159 nm and 311 nm layer it was more than 30 nm on the Si substrate. For the thinner sample (81 nm) the roughness was at the resolution limit of the ellipsometer.

Tab. 1 *Thicknesses of ZnO layers measured by Profilometry and Ellipsometry*

Sample	Profilometry	Ellipsometry			
		Glass		*Si*	
	Thickness nm	Total nm	Rough layer nm	Total nm	Rough layer nm
1	81	75 ± 2.3	3.0 ± 0.80	73 ± 0.46	0.10 ± 0.14
2	159	157 ± 0.13	13 ± 0.06	154 ± 1.3	31 ± 0.86
3	311	314 ± 0.71	25 ± 0.20	305 ± 2.7	39 ± 1.03

In the Tab 2, there are the band gap energies compared to the values from the Tauc plot of transmission measurement. The transmission measurements were done with the samples on corning glass in the spectral range 250 nm –1100 nm. The results from the Tauc plots are affected by the missing reflectometry measurement, which could cause a systematic error of 10 %.

The values measured by profilometry and transmission analysis were used as the initial values in the ellipsometry fits.

Tab. 2 *Band-gap energy of ZnO layers measured by Tauc plot and Ellipsometry*

Sample	Tauc plot	Ellipsometry	
	E_g eV	*Glass*	*Si*
1	3.35 ± 0.042	3.20 ± 0.15	3.30 ± 1.19
2	3.33 ± 0.034	3.30 ± 0.067	3.51 ± 0.12
3	3.30 ± 0.090	3.50 ± 0.080	3.42 ± 0.090

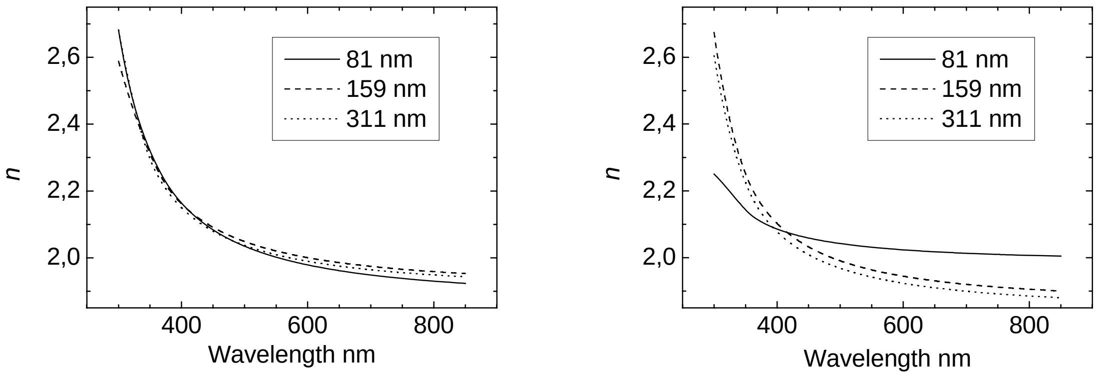

Fig. 3 *Measured and extrapolated indices of refraction of the ZnO layers on Glass substrate (left) and Si substrate (right).*

The indices of refraction of ZnO layers are plotted in the Fig. 3. The thinner layer (81 nm) differs significantly from the others in both the corning glass and the Si substrates. This effect may have two explanations: either the chosen material model is not satisfactory for thinner samples, or the index of refraction really differs for layers thinner than, approximately 100 nm. The results were extrapolated to the vicinity of E_g, since the Horiba Jobin-Yvon MM-16 ellipsometer spectral range starts from 430 nm, which corresponds to 2.88 eV.

4. Conclusion

We have shown that the Tauc-Lorenz model could be useful for qualitative ellipsometry measurements of ZnO. For more detailed investigation of this material, other models, such as the Tanguy should be implemented. Althoug, the Tauc-Lorenz can fit ellipsometry data with quite a good accuracy, it is unsatisfactory when E_g is to be estimated. The Lorenz shape of the imaginary part of permittivity is a feature of amorphous materials. As it is shown in literature, the Gauss or at least the non-Lorenzian broadening of absorption is typical of polycrystalline ZnO [1]. This is caused by a random orientation of domains, crystal disorders, vacancies, and tension at the interface of grains.

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