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Investigation of zinc oxide thin film by spectroscopic ellipsometry

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Abstract. ZnO films were deposited on glass substrates by magnetron RF-sputtering. An accurate determination of the optical constants of these films is extremely important prior to its application in optical devices and spectroscopic ellipsometry provides a reasonably accurate method for the determination of optical constants of thin films. In this study, we present the results gained by analyzing spectroscopic ellipsometry of ZnO thin film combined with comparison of transmission spectroscopy measured on a UV-VIS-NIR spectrophotometer. Ellipsometry data have been fitted with a model including a glass substrate and a ZnO film plus a surface void layer on top. From this fitting the refraction index (n), extinction coefficient (k) and thickniess (d) of the sputtered ZnO films were determined. By using the gained n, k and d values the transmission spectrum was theoretically calculated and compared with the experimentally obtained transmission one. As a result of the combined spectroscopic ellipsometry and transmission analysis, there was the good correlation in comparison.

Keywords: Thin film, ellipsometry, transmission spectrum, refraction index, extinction coefficient.

1. Introduction

Although ellipsometry theory was well-known for a long time ago, until 70s of the XX century ellipsometry has not been commonly used, because of its sophisticated mathematical technique. Since the computer science has strongly developed, ellipsometer systems become popularly used in laboratories for characterisation of materials, and for optic thin films in particular.

The theory for ellipsometric analysis is based on the change in the polarization state of light when the light transmits or reflects from an optic sample. In both the case of a single layer and a multilayer of the thin film which are coated on a glass substrate, after the transmision and/ or reflection through/ from the sample, the light is polarized depending on the thickness and the refraction index of the film. From the ellipsometry spectra of the samples one can find out the optic constants and optical properties of the films.

This work presents new investigation results on zinc oxide (ZnO) thin film deposited on glass substrate by using spectroscopic ellipsometer with a wavelength range from 350 nm to 1100 nm. The

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measured ellipsometric data are fitted with theoretical spectra generated assuming appropriate models regarding the sample structures. The fitting has been done by minimizing the squared difference (χ^2) between the measured and calculated values of the ellipsometric parameters (ψ and Δ) and accurate information has been derived regarding the thickness and optical constants of the different layers.

2. Experimental

ZnO films were deposited on glass substrates by a magnetron Rf-sputtering. A ZnO ceramic target with diameter of 75 mm was used. The sputtering pressure of the Ar/O_2 mixture gases was maintained at $P = 8 \times 10^{-3}$ Torr, the density of the sputtering current was kept at $I \approx 60$ mA/cm^2 with the bias voltage of V = 350 V. The deposition time was of about 70 min and the average deposition rate was evaluated as 1.5 Å/s.

The ellipsometric measurement is normally expressed in terms of a polarization angle Ψ [1, 2], as follows:

$$\tan(\Psi)e^{i\Delta} = \rho = \frac{r_p}{r_s} \quad (1)$$

where ρ is the complex ratio as a function of wavelength, $\Delta = \delta_p - \delta_s$ is the phase difference (as well as an amplitude ratio), r_p and r_s are the complex Fresnel reflection coefficients of the sample, respectively for p- (in the plane of incidence) and s- (perpendicular to the plane of incidence) polarized light, as shown in Fig. 1.

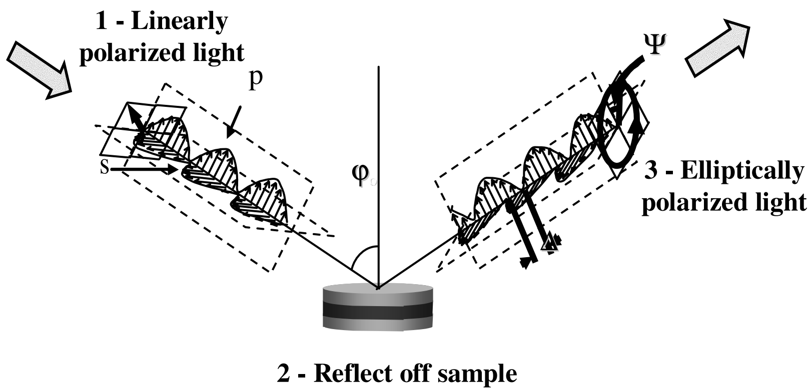


Fig. 1. Schematic diagram of ellipsometer system.

The ellipsometric spectra were measured in a spectroscopic phase modulated ellipsometer (Model UVISEL HR 460, Jobin – Yvon) in the wavelength range from 280 nm to 1700 nm. On this measurement system, the modulated signal to detector takes the general form as follows:

$$I(t) = I[I_o + I_s\sin\delta(t) + I_c\cos\delta(t)] \quad (2)$$

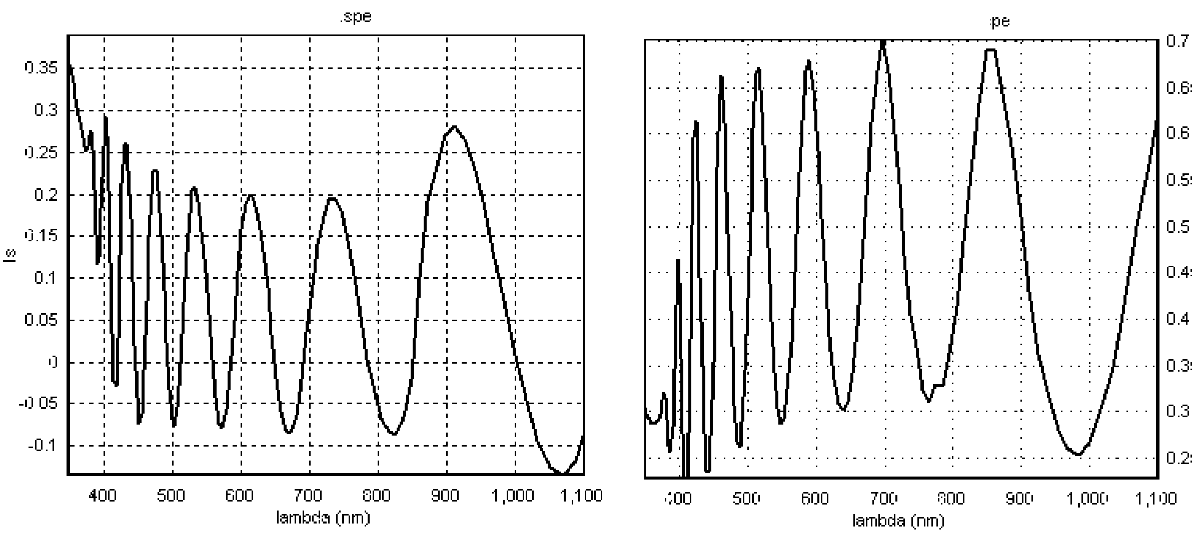
where I_o, I_s, I_c are complicated trigonometry functions related to the measurement conditions (e.g. the angle of polarization mirrors and modulators) and parameters of film (Δ, Ψ). The measurement configuration is chosen for the purpose of simplifying the calculation of trigonometry functions. In the present set of measurement, M = 0°, P = 45°, A = 45°, so that,

$$I_o = 1 \tag{3}$$

$$I_s = \sin 2\Psi \sin\Delta \tag{4}$$

$$I_c = \sin 2\Psi \cos\Delta \tag{5}$$

Ellipsometric data have been analyzed by Delta Psi software (Jobin – Yvon Co.). Fig. 2 shows ellipsometer spectra $I_s(\lambda)$, $I_c(\lambda)$ of a ZnO film. Transmission spectra of the sample were measured on a Jasco. UV-VIS-NIR V530 spectrophotometer, in a wavelength range from 190 nm to 1100 nm (Fig. 3). From the transmission spectra, one can note that the ZnO spectrum quite appears in the same transparent region of the substrate. This means, the glass substrate did not affect to the shape of transmission spectrum of coated ZnO film. From this spectrum one can also determine the optical band gap (E_g) of the zinc oxide film which was found to be $E_g \approx 3.33$ eV.



a. b.

Fig. 2. Polarized spectra of ZnO sample, with $I_s = \sin 2\Psi \sin\Delta$ (a) and $I_c = \sin 2\Psi \cos\Delta$ (b).

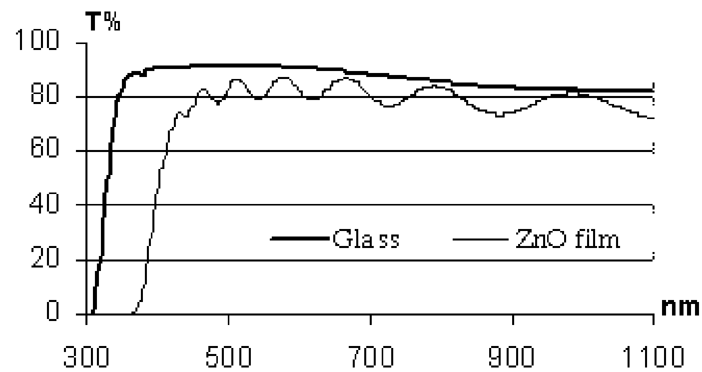


Fig. 3. Transmittance spectra of glass substrate and ZnO film.

3. Results and discussion

3.1. Modeling and fitting I_s, I_c spectra

Ellipsometry does not directly measure film thickness or optical constants; it measures the changes in polarization expressed as Ψ and Δ [4]. To extract useful information about a material structure, it is necessary to perform a model dependent analysis of ellipsometric data.

A model for the optical structure of the sample was designed with initial estimates of the parameters. Initially, we have started with the simplest model; it included a glass substrate and a single film on the surface. By regularly increasing complexity, we have constructed more complicated model, for instant, increasing the amount of possible films or the possible elements exist in film structure, predicting different thicknesses, changing the kind of substrate material. Through these steps, we finally could find out the best model which has the most suitable structure in compare with the real sample. The initial guesses of the model parameters were transformed finally into true parameters of the sample, such as thickness and optical constants.

In the process of fitting parameters of model and sample, by using the Marquardt – Levenberg algorithm [5] one can get the difference between the experimental values (from the measurement) and calculated values (from the model).

The Mean Square Error (MSE) χ^2 is used to qualify the difference between the experimental and predicted data.

$$\chi^2 = \frac{1}{N}\sum_{i=1}^{N}\frac{(\mathrm{Mes}_i - \mathrm{Th}_i)^2}{\sigma_i^2} \qquad (6)$$

where σ_i is the standard deviation of the i^{-th} data point

N is the number of data points

Mes_i is the i^{-th} experimental data point

Th_i is the i^{-th} calculated data point from assumed theoretical model

MSE is different in each model. A smaller MSE implies a better model fit to the data. MSE will exhibit a minimum value when the model matches the experimental data as closely as possible.

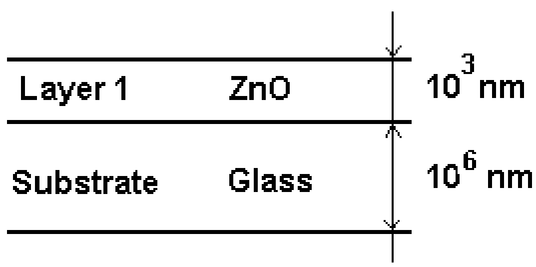
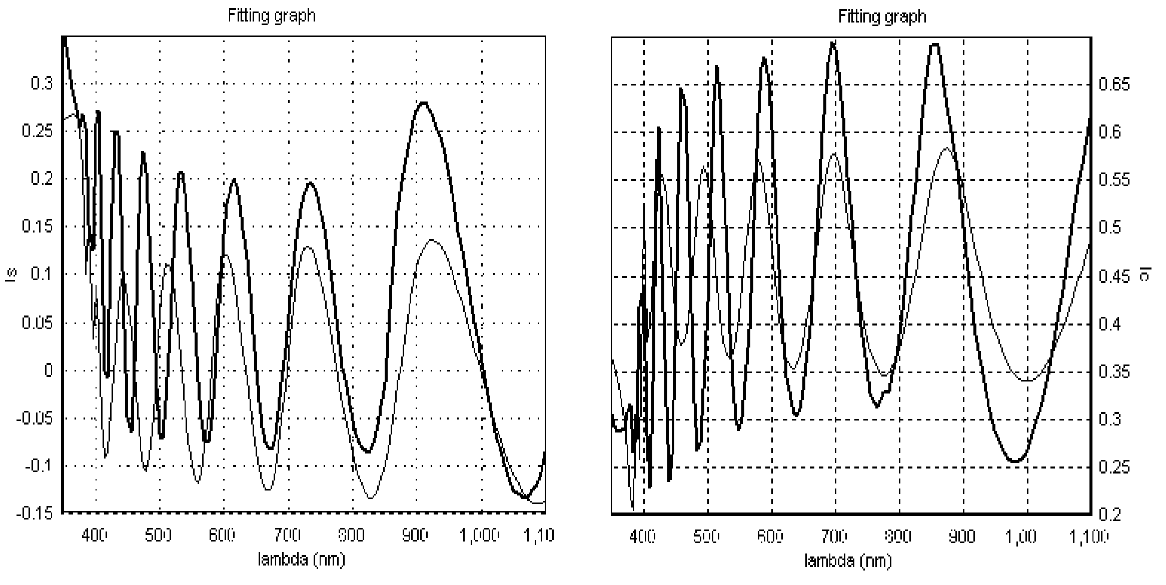


Fig. 4. The first fitting model of ZnO sample.

From the measurement I_s, I_c spectra were plotted as a function of wavelength. Next, a model for the optical structure of the sample have been constructed. This first model included a glass substrate and a single film ZnO on surface with 1000 nm predicted thickness (Fig. 4). The fitting results of model 1 have been presented in Fig. 5 and Table 1. With this model the MSE has been found to be of 133.6, this means that by model 1 there was a big difference between the measured I_s, I_c spectra with the calculated I_s, I_c spectra.



a. b.

Fig. 5. Measured data (dark curve) and simulated data (light curve) of ZnO sample in model 1 for Is (a) and Ic (b). In this case, it was hard to accept this model.

3.2. Comparison of theoretical and experimental transmission spectra

To evaluate the results from analyzing polarized spectra there was a comparison between the calculated transmission spectrum and the experimental transmission spectrum. By applying the algorithm from [6] we have used fitted ellipsometric data (n, k, d) to calculate the transmission spectrum of ZnO sample. After that, we have made a compare between this calculated spectrum and the measured spectrum of ZnO sample. Fig. 6 shows the difference of these two spectra, one is the transmission spectrum calculated from resulting fit parameters, which have gained from analyzing I_s, I_c spectra (calculated spectra), in model 1 and another is the transmission spectrum measured from experiments (measured spectrum).

It shows that the model did not adequately represent the true structure, the model needed to be reformulated.

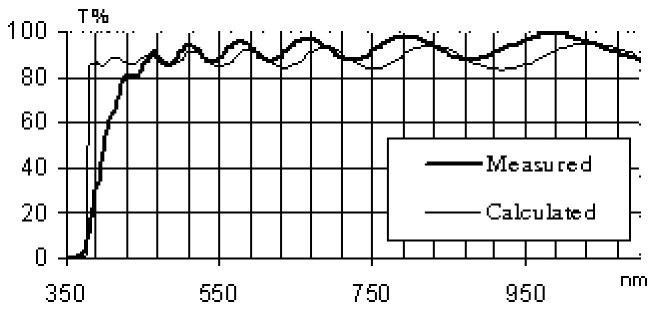


Fig. 6. Measured and calculated transmittance spectra in Model 1.

3.3. Bruggeman effective medium approximation (EMA) model

In the case of composite layers, consisting of more than one material, or material(s) and void, the calculation for the effective optical constants have been done using EMA model, which describes a composite of aggregated phases or random mixture microstructure. Dielectric function ε of the composite is described by the follow equation:

$$\sum_i f_i \left(\frac{\varepsilon_i - \varepsilon}{\varepsilon_i + 2\varepsilon} \right) = 0 \qquad (7)$$

where ε_i is the dielectric function of i^{th} component in the composite.

f_i is the volume fraction for i^{th} component in the composite.

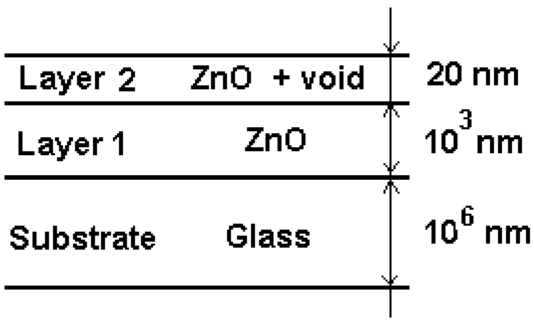
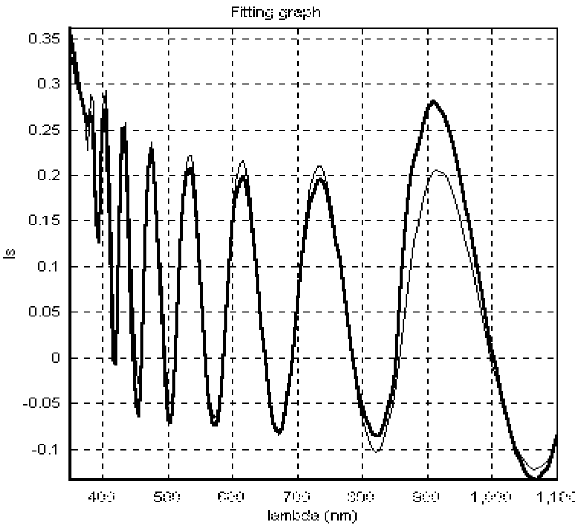
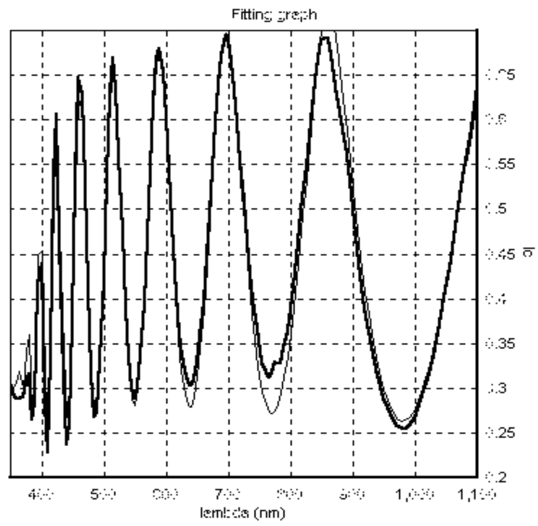


Fig. 7. The second fitting model of ZnO sample.

In the second fitting, we have assumed a new model by adding a surface void layer to the ZnO film, called model 2. To model this additional layer we have used BEMA with a 50 – 50% mixture of ZnO and void, layer thickness has been predicted about 20nm (Fig. 7). The fit results for a more complex model are shown in Fig. 8 and Table 1. And the resulting fit MSE was χ^2 = 7.2; it was reduced by an order of magnitude. Additionally, in model 2 the calculated spectra I_s, I_c were well matched with experimental spectra. This shows that model 2 is much better than model 1 for getting a good agreement in fitting.



a.



b.

Fig. 8. Measured data (dark curve) and simulated data (light curve) of ZnO sample in model 2. for Is (a) and Ic (b). The second model is in good agreement with the experimental data.

Table 1. The resulting fit parameters of constructed models

Model	χ^2	Parameters
1. Without void	133.6	$d_{ZnO(a)}$ = 1168.0 ± 17.8nm
2. Void on top	7.2	$d_{ZnO(a)}$ = 1039.5 ± 45.1nm; $d_{void\ ZnO(a)}$ = 23.2 ± 2.1nm %ZnO void = 65.0 ± 3.4

There was a good match between the calculated and measured transmission spectra (Fig. 9). The minimum and maximum wavelength values of interference fringes were well fit. From that, model 2 and its fit parameters are acceptable, in good agreement with the true structure of the sample.

Besides MSE (χ^2), thickness and mixture ratio, the fitting results also gave the dependence of refractive index n and extinction coefficient k on wavelength of ZnO film, illustrated in Fig. 10.

The ZnO film refractive indices in the wavelength range of 500 nm – 1100 nm were found to be from 1.94 to 1.85. The extinction coefficient *k* equals to zero for wavelengths greater than 500 nm and suddenly increased higher in the range from 350 nm to 500 nm, this corresponds to an absorption edge which the transmission spectrum obtained.

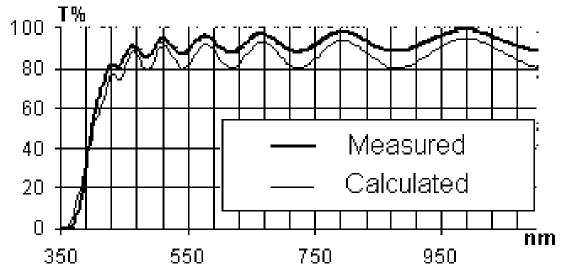


Fig. 9. Measured and calculated transmittance spectra in model 2.

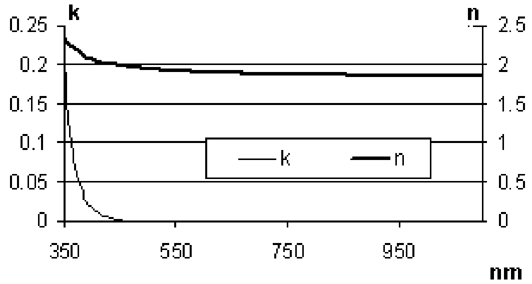


Fig. 10. The wavelength dependence of reflective index *n* and extinction coefficient.

4. Conclusions

ZnO films, deposited on glass substrate by magnetron sputtering process, have been analyzed based on spectroscopic ellipsometry in compare with transmission spectroscopy from a UV-VIS system. Ellipsometry data have been fitted with a model including a glass substrate and a ZnO film plus a surface void layer on top. From this fitting the refraction index (n), extinction coefficient (k) and thickness (d) of the ZnO films were determined. By using the gained n, k and d values the transmission spectrum was theoretically calculated and compared with the experimentally obtained transmission one. As a result of the combined spectroscopic ellipsometry and transmission analysis, there was the good correlation in comparison.

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