CHARACTERIZATION OF SPUTTERED ZnO BLOCKING LAYERS WITH SURFACE PLASMON RESONANCE METHOD

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ABSTRACT
Thickness and dielectric permittivity of nanoscale polycrystalline ZnO films were revealed with a surface plasmon resonance (SPR) method using spectroscopic ellipsometry data [1]. The UV-Vis absorption spectra of the ZnO films were measured, and their bandgaps were evaluated from the fundamental absorption edge. Performed research allowed us to determine the sputtering regimes of nanoscale ZnO films that are promising for use as a blocking layer in a planar perovskite-based solar cells.

1. INTRODUCTION

Zinc oxide is a semiconductor material with the hexagonal wurtzite or cubic zincblende structures. In wurtzite form ZnO crystals have n-type conductivity and a direct band gap in the near-UV spectral region [2, 3]. ZnO is not new to the semiconductor field, but in recent years interest in it has resumed due to new areas of application as an optoelectronic or electronic material. In new applications, the material is often used in the form of thin films. One of the promising fields is using ZnO as a hole-blocking layer in a planar perovskite-based solar cells. The introduction of intrinsic ZnO between the perovskite layer and anode leads to a large reduction of the recombination at this interface [4]. The need to use thin layers increased interest in the study of their optical properties because the nanoscale structures exhibit properties different from the bulk material. The quantum confinement effect has a significant impact on the optical properties of ultrathin ZnO and Al-doped ZnO films, in particular, the excitonic absorption near the absorption band edge [3]. It was reported that quantum confinement effect has a significant influence on the dielectric functions. As compared to bulk ZnO, the ultrathin films exhibit a significant reduction in both real and imaginary parts of the dielectric function, accompanied by the increase in both band gap energy and excitation binding energies [1]. The surface plasmon resonance (SPR) method is one of the most power tools for characterization of ultrathin films, particularly their dielectric properties and thickness [5, 6], that are important parameters for photovoltaic (PV) cells fabrication. A thin and compact layer of required thickness acting as electron-selective contact and hole blocking layer is a crucial component of PV cell [7]. In this work we used SPR method for characterizing thin ZnO blocking layers.

2. EXPERIMENTAL

2.1. Samples preparation

The VST (VST, Israel) Magnetron Sputtering system was used for ZnO films fabrication. The ZnO films of various thickness were deposited on glass substrates in DC regime of sputtering. The power of magnetron source was 100W, the depositions were made at 5 mTorr Argon pressure. The durations of sputtering were 30, 60, 120, 180 s and 10, 20 and 30 min. Between deposition sessions the sputter chamber were vacuumed with turbomolecular pump to residual vacuum not worse than $1*10^{-6}$ Torr.

The glass substrates for SPR measurements before ZnO sputtering were covered with a gold film of a thickness of 48 nm using Agar high resolution sputter coater AGB 7234 (AGAR Scientific, UK). A thickness of the gold film was checked *in situ* (in the process of sputtering) with the quartz resonator method.
At the final stage of preparation procedure all samples were annealed at 250°C under pressure of 2 $*10^{-2}$ Torr for 60 min in vacuum furnace Kejia 1200 (Kejia Furnace, China). After preparation the samples were packed into individual Petri dishes and stored under vacuum in desiccator.

2.2. Characterization methods

Before and after sputtering the part of glass substrates were weighed on the balance XPR 10 (Mettler Toledo, USA) with the accuracy better than 0.04 mg in order to estimate a deposition rate and the thickness of prepared ZnO films by weight. The weighted substrates were captured with 5MP Digital Micposcope (China) and their surface was measured with ImageJ software. Obtained data were used for calculations of thickness.
The XRD measurements of 30 min sputtered samples were carried out with a PANalytical X'Pert Pro (Malvern Panalytical Ltd., UK) diffractometer with $Cu_{K\alpha}$ source.
Magnified, high resolution images of the deposited ZnO films were obtained with scanning electron microscopy (SEM) using a TESCAN MAIA3 device (Czech Republic).
The precise thickness measurements of ultrathin deposited ZnO films were made with SPR method. The Kretschmann configuration SPR setup was compiled by an individual order by the company STANDA (Lithuania). The measurement control, synchronization, and data storage were accomplished by LabView software (USA). Output data were processed by the WinSpall package [8].
UV-Vis absorption spectra of ZnO films were recorded in wavelength interval from 200 to 600 nm with BioMate 3S (Thermo Fisher Scientific, USA) spectrophotometer.

3. RESULTS AND DISCUSSION

3.1. Structure and topology of ZnO films revealed with XRD and SEM methods

The XRD pattern of sputtered ZnO films with deposition time of 30 min is presented in Fig. 1. The XRD analysis indicates that ZnO films were polycrystalline with wurtzite crystal structure with preferential growth of crystallites along [002] orientation (*c*-axis). There were no registered zincblende phase inclusions in ZnO films. The average crystallite size calculated from XRD pattern according to the well-known Scherrer equation was about 10 nm. Obtained results are in a good agreement with literature data [1–3].

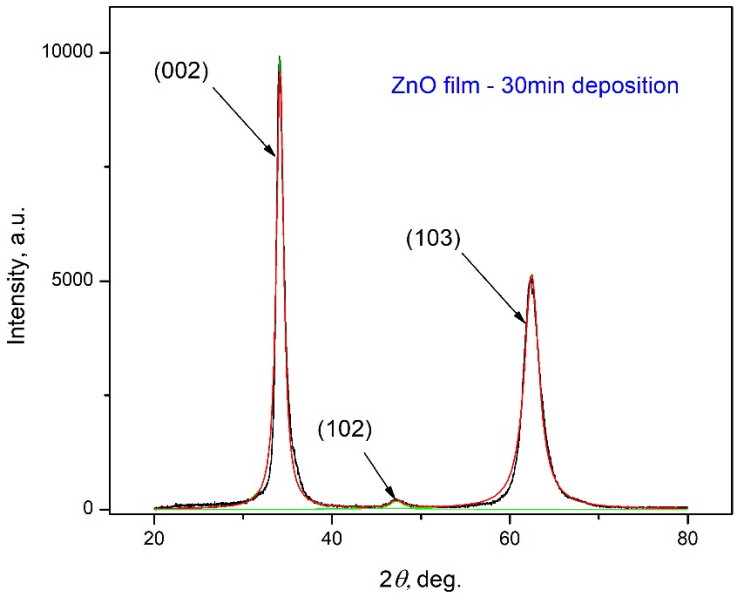

Fig. 1. XRD profile of ZnO film with 30 min sputtering duration.

The topology of prepared films was revealed with SEM. Images of the surface of sputtered layers with different deposition duration are presented in Fig. 2.

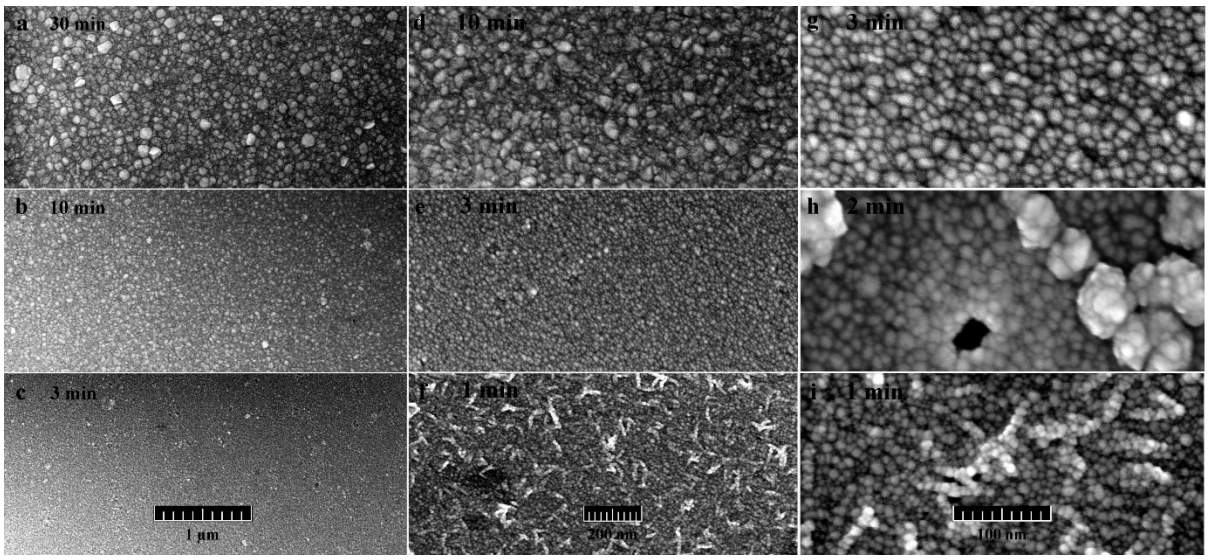

Fig. 2. SEM images of ZnO films with different deposition times.

In Fig. 2, the images located in the same column have the same magnification. It can be seen that the average grain size increases with increasing deposition time from 7 nm for 1 minute of sputtering to 80 nm for 30 minutes. Moreover, at the initial stage of deposition we obtained inhomogeneous films with variety of cavities and other defects, and even at 2 min of deposition time the films had through holes (see Fig. 2h). However, increasing the deposition time to 3 min lead to formation of uniform

homogeneous films with average grain size about 10 nm (see Fig. 2c, e and g). Such pinhole-free layers are perspective candidates for blocking layers of PV cells.

3.2. Application of SPR method for measuring dielectric permittivity and thickness

In order to evaluate deposition rate and estimate the thickness of obtained films with precise weighing (PW) method, relatively thick ZnO films were sputtered on glass substrates with durations of 10, 20 and 30 min. The linear fitting of film's thickness calculated with PW method is presented in Fig. 3.

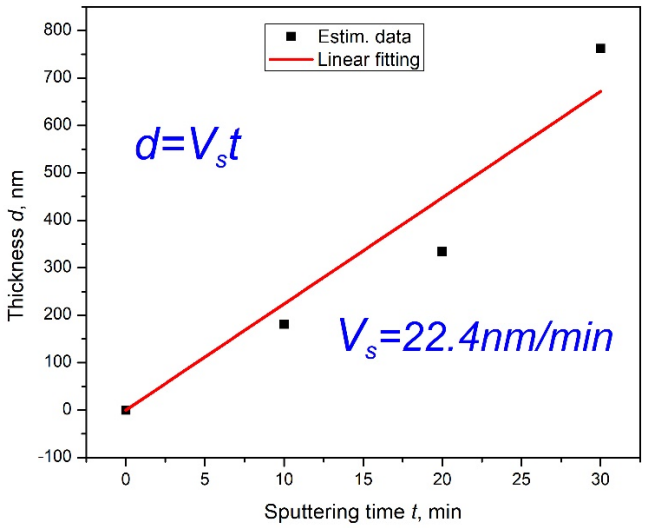

Fig .3. The deposition rate and the thickness of ZnO films estimated with PW method.

The inconsistency between fitting data and experimental results is caused by the fact that at the initial stage of the film formation the growth rate depends on the film thickness. Thereby our fitting provides only a rough estimation of film's thickness for short-time depositions (30, 60, 120 and 180 s) that is critical for correct calculation of optical and electrical properties of ZnO blocking layers.

For the first time the SPR method was applied to precise measurements of thickness of nanoscale ZnO films. The SPR curves were registered for the shot deposition time films (the sputtering times were 30, 60, 120 and 180 s). The mere SPR curve doesn't allow us to determine both refractive index and thickness of the film. In order to evaluate film's thickness, we should have exact information about dielectric permittivity of this film. Not only a deposition rate but also a dielectric permittivity depends on a film thickness in a nanoscale range [1, 9]. To restore the ZnO films thickness from SPR measurements we used the spectroscopic ellipsometry (SE) data [1] for thickness dependence of dielectric permittivity of ZnO sputtered films. It should be noted that according to XRD and SEM data our ZnO films are very similar to that described in [1]. The asymptotic fitting of SE data [1] in nanoscale thickness range is presented in Fig. 4.

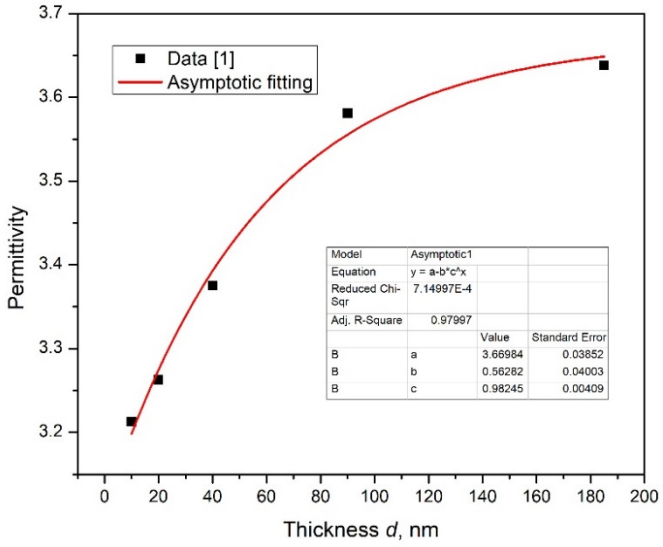

Fig. 4. Thickness dependence of permittivity for nanoscale ZnO films.

Using this approximation dielectric permittivity values were calculated according to thickness estimated with (PW) method. These thickness and permittivity values were further used for SPR curves processing as variable initial parameters. SPR curve approximation with WinSpall software [8] for 60 second sputtered ZnO film is presented in Fig. 5.

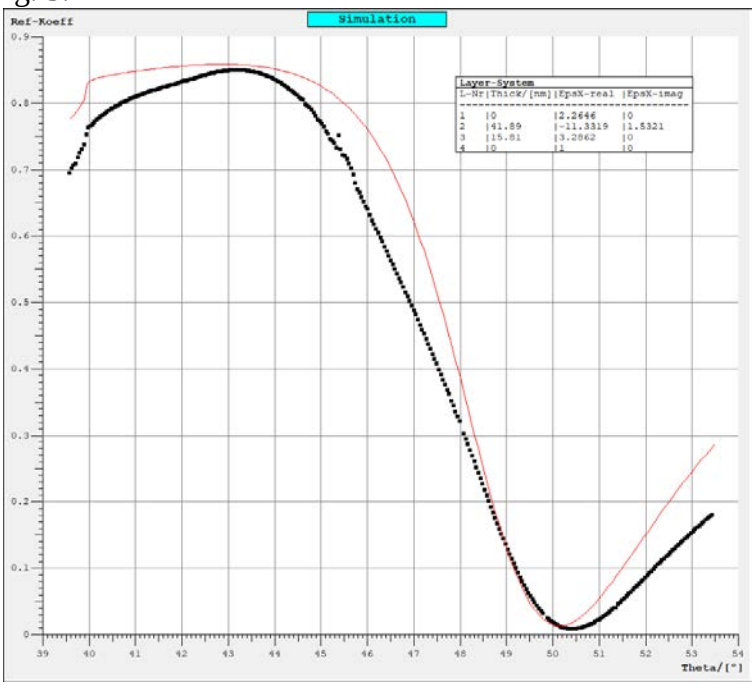

Fig. 5. The processing of SPR curve for ZnO film deposited on a glass substrate for 60 s.

Results of measurements and calculation of thickness and dielectric permittivity with SPR, SE and PW methods for ZnO films with different deposition times are summarized in Table 1.

Table 1. Thickness and dielectric permittivity of ZnO films measured with various methods.

Deposition time, s	Thickness, nm PW (linear approximation)	Permittivity SE (asymptotic approximation)	Thickness, nm SPR	Permittivity SPR
30	11.2	3.21	8.6	3.21
60	22.3	3.29	15.8	3.29
120	44.8	3.41	27.8	3.38
180	67.2	3.5	40.8	3.41

Results of Table 1 confirm that applying the SPR method to thickness measurements allow us to correct obtained data significantly. The thickness values measured by SPR were used further for calculation of optical and electrical parameters of sputtered ZnO films.

3.3. Optical properties of ZnO films

Typical absorption spectra of ZnO films are presented in Fig. 6. Further, absorption coefficient and the bandgap were evaluated using thickness values restored from SPR results.

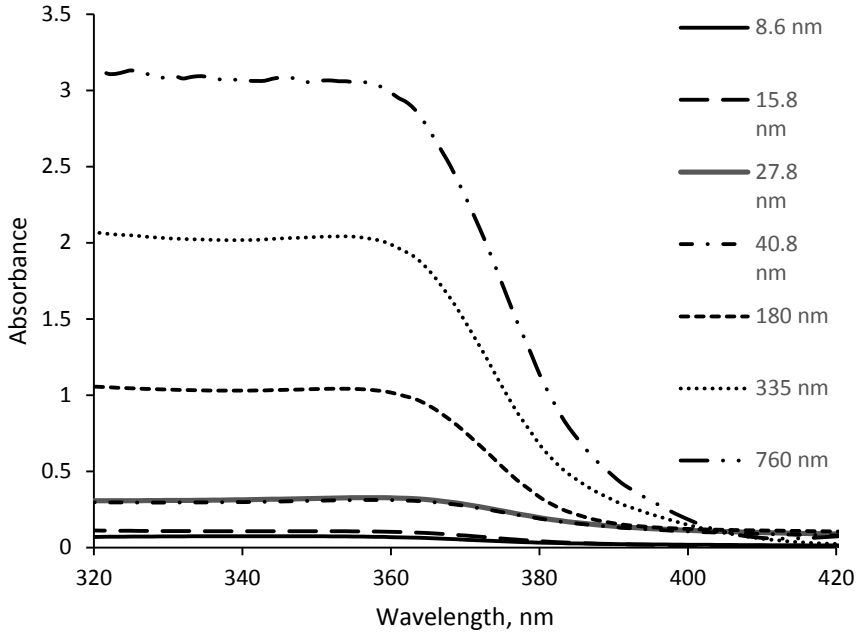

Fig 6. Absorption spectra of ZnO layers, annealed at 250°C in vacuum. Thickness is given in the graph.

The absorption coefficient α can be calculated from the relation

$$2.303A = \alpha d \ ,$$

where A is the absorbance, and d is the thickness of the layer. The dependence of the absorbance of ZnO films on their thickness at the wavelength of 375 nm is presented in Fig. 7. Using linear approximation, we can evaluate the absorption coefficient as $5.6 \cdot 10^4$ cm^{-1}. This value is in accordance with the data presented in previous works [10–12].

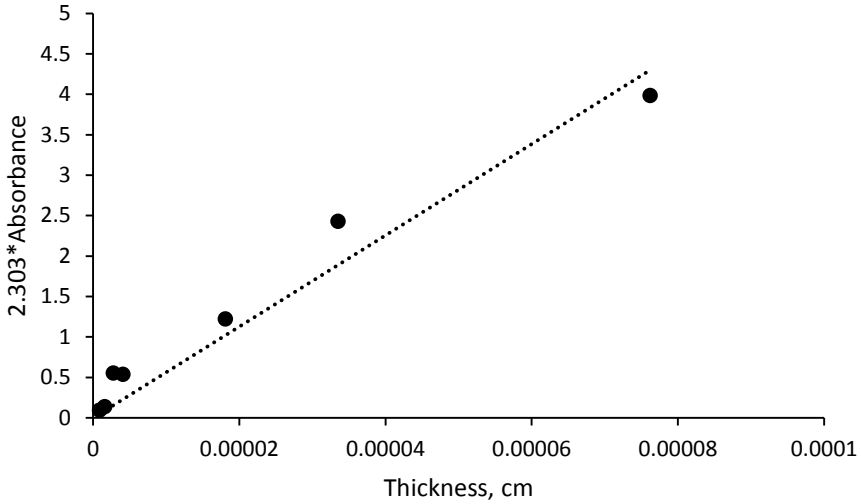

Fig. 7. The dependence of the absorbance of ZnO films on their thickness at the wavelength of 375 nm.

To calculate optical bandgap values, we used the well-known Tauc's method, based on the relation between the optical absorption and the difference between the photon energy and the band gap:

$$\alpha h\nu = A(h\nu - E_g)^n$$

where α is the absorption coefficient, h is Planck's constant, ν is the light frequency, E_g is the bandgap, and A is a constant. The value of the exponent n depends on the kind of the electronic transition. For a direct transition, n = 1/2 or 2/3, and the former value was the method was considered the most appropriate for ZnO thin films since it gives the best linear curve in the band-edge region [13]. Calculated values of bandgap for samples of various thickness and thermal treatment are summarized in Table 2.

Table 2. Values of the optical bandgap for ZnO thin layers.

Thickness, nm	9	16	28	41	180	335	760
Bandgap, eV		3.28*		3.22*	3.28	3.28	3.30
	3.27♦	3.26♦	3.20♦	3.20♦	3.28♦	3.28♦	3.26♦

*Annealed at 200°C ♦Annealed at 250°C

Calculated values of the optical bandgap are slightly smaller than the bulk value of 3.3 eV [14, 15] and in good agreement with previously reported data for ZnO thin films [10, 16].

4. CONCLUSIONS

Nanoscale ZnO films of various thickness were deposited on glass substrates in DC regime with sputtering time varying from 30 s to 30 min. XRD analysis revealed that films were polycrystalline with wurtzite crystal structure and preferential growth of crystallites along *c*-axis. The SEM study showed that at least three minutes deposition time is necessary to form uniform homogeneous films with average grain size about 10 nm. The 3 min deposited pinhole-free ZnO films are supposed to be used as blocking layers for PV cells. For the first time the SPR method was applied for precise measurements of thickness and dielectric permittivity of nanoscale ZnO films based on spectroscopic ellipsometry data [1]. The thickness values measured with

SPR were used for calculation of optical absorption coefficient and bandgap of ZnO films. The obtained values are in good agreement with the published data.

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