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## THE MORPHOLOGY AND STRUCTURE OF ZnO THIN FILMS DEPOSITED BY ALD METHOD

This paper presents research results of zinc oxide thin films deposited on a glass substrate with use of ALD method. Our researches focused on analyzing of the influence of ALD deposition process temperature on the morphology and transparency of thin layers. The morphology was examined using both scanning and transmission electron microscopes. Transparency study was performed by UV-VIS spectroscopy. For our experiments, two sets of the coating have been prepared, differing in temperature and number of cycle used during the preparation process. The first set was deposited in 100 cycles, second one in 500 cycles. Each set of tested coating contained samples prepared at different temperatures.

*Keywords:* ALD, ZnO, SEM, TEM, UV/VIS

### 1. Introduction

The method of atomic layer deposition (ALD) is one of the chemical vapour thin films deposition techniques. It allows performing deposition of thin films using chemical processes [1,2].

One of the most important advantages of ALD method is self-limited layer growth mechanism. The precursor is deposited on the sample surface in the form of a monolayer. Further growth of the film is possible only after adding next dose of precursor portion into the reactor chamber. Each application of the precursor is preceded by purging the chamber with an inert gas (e.g., nitrogen) to remove by-products chemical reactions and the rests of the precursor that was not deposited on the surface of the sample. This growth mechanism allows precise control of the thickness of the deposited layer. During one cycle of ALD process, the growth of material is approx. 0.1 nm thick [1-4].

ALD method can be used in the wide range of temperature settings, starting from 25°C up to 500°C. The ability to use low temperatures settings allows to coat objects made of high temperatures sensitive materials [4-5].

High precision in thickness control of the deposited films at the level of 0.1 nm, high uniformity of formed layers and low amount of surface defects allows using ALD deposition method to produce transparent conductive layers (TCL). Quality of TCL preparation process can be specified by two major parameters of prepared thin films: low electrical resistance and high value of transparency coefficient for wavelengths, especially from the visible light range. These layers are widely used in optoelectronics and photovoltaics [3-6]. The most commonly used materials for this kind of thin films are indium tin oxide (ITO) and fluorine-do-

ped tin oxide (FTO). ITO is characterized by a very high value of transparency coefficient (above 80%) and low resistance (10-4 Ωcm). The transparency coefficient of FTO is approx. 82% and the resistance between 4.0 and 6.0 × 10-4 Ωcm. Due to the high production costs of ITO and FTO, many types of research are carried on to find alternative materials that can replace them [7-10].

An interesting ITO and FTO alternative are other metal oxides, for example, zinc oxide (ZnO). ZnO is characterized by a high value of transparency coefficient and a wide energy gap (3.37 eV). It belongs to the semiconductors group [6,11-12].

The researches of new, efficient TCL materials prepared on non-conductive substrates have an important meaning in develop of surface engineering in the field of modern photovoltaic, especially in case of photovoltaic cells where they can be treated as a hint in future studies.

### 2. Experimental procedure

Experiments results presented in this paper were obtained after analyze of ZnO thin films deposited on a glass substrate by ALD method Two sets of test samples, differing in a number of ALD process cycles, has been used. Each sample set has been prepared at different temperatures: 150, 200 and 350°C (Table 1). Surface layer morphology was analyzed on coatings deposited during 500 ALD cycles. The UV-VIS tests were performed on the coatings deposited during 100 and 500 ALD cycles.

To prepare ZnO thin films, diethylzinc (DEZ) and deionized water were used as precursors. Between each precursor dosing cycle, the reactor chamber was purged with inert gas – nitro-

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TABLE 1

Test samples description and its ALD process parameters

Sample no.	The process temperature [°C]	Number of cycles
1	150	100
2	200	
3	350	
4	150	500
5	200	
6	350	

gen. Each of the precursors was supplied to the chamber in the 0.1-second time frame. The purge time for DEZ was 4.0 seconds and for H<sub>2</sub>O 5.0 seconds.

ALD process precursor's temperatures have been set by choosing temperature value from so-called "growth window", where optimal temperature range for the chemical reactions between certain precursors is indicated [1].

In case of DEZ and H<sub>2</sub>O suggested temperatures begins from 100°C up to 200°C (in some references upper value ends at 250°C) [6,13]. Examined samples: 1 and 2 were prepared in precursor temperatures selected from a range of ALD "growth window" that is 150 and 200°C. Sample 3 preparation temperature was chosen by purpose out the "growth window": 350°C in order to check and present an effect of setting too high deposition process temperature on a morphology of the layer.

Observations of the samples surface morphology were performed in a high-resolution scanning electron microscope ZEISS SUPRA 35 with use of In-Lens detector. This microscope was also equipped with energy-dispersive X-ray detector (EDS) from EDAX. The study was conducted at a beam accelerating voltage from the range of 3÷15 kV.

Surface analyses have been also performed using the transmission electron microscope S/TEM Titan 80-300, operated at 300 kV acceleration voltage. High angle annular dark field (HAADF) and high-resolution transmission electron microscopy (HRTEM) imaging technique was chosen. The diffraction patterns were collected by usage of selected area electron diffraction (SAED) and fast Fourier transformations.

The measurements of transparency of ZnO layers for wavelengths from the visible light range were performed using a UV-VIS spectroscope Evolution 220 from Thermo Scientific.

### 3. Results and discussion

Effect of the influence of the temperature on the surface of the obtained thin layers has been determinate with use of electron scanning microscope. The analyze has been performed on samples prepared in 500 cycles. Thin film surface, prepared at 150°C was characterized by grains of an elongated shape with sizes from 2 to 10 nm (Fig. 1). Similar morphology was found on sample 2 prepared at 200°C, but it case, the grain size was more uniform and in range of about 6 nm (Fig. 2). Layer 3 deposition temperature was set at 350°C. Grains had a spherical

shape and uniform size of about 4 nm (Fig. 3). Crack has been visible on the surface that may cause a decrease of the electrical conductivity of the layer.

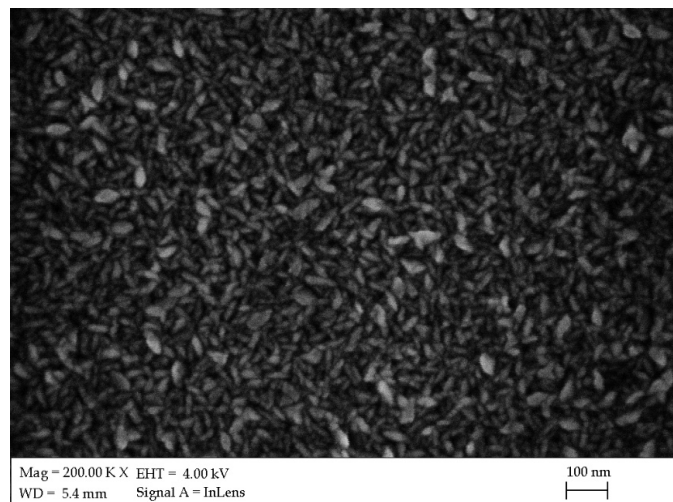


Fig. 1. The morphology of the thin film deposited at 150°C

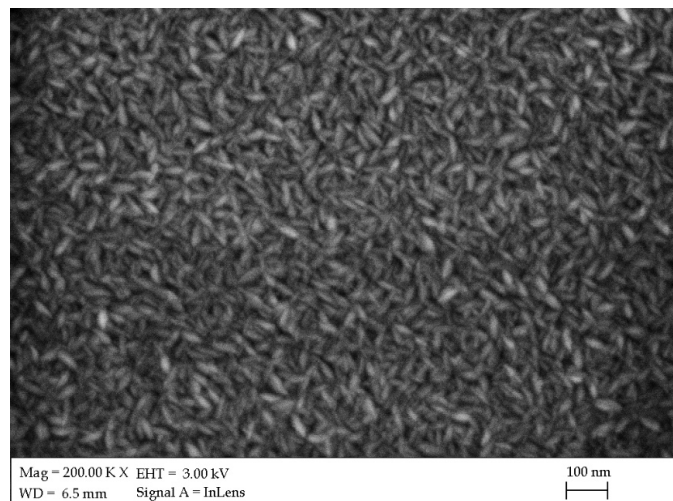


Fig. 2. The morphology of the thin film deposited at 200°C

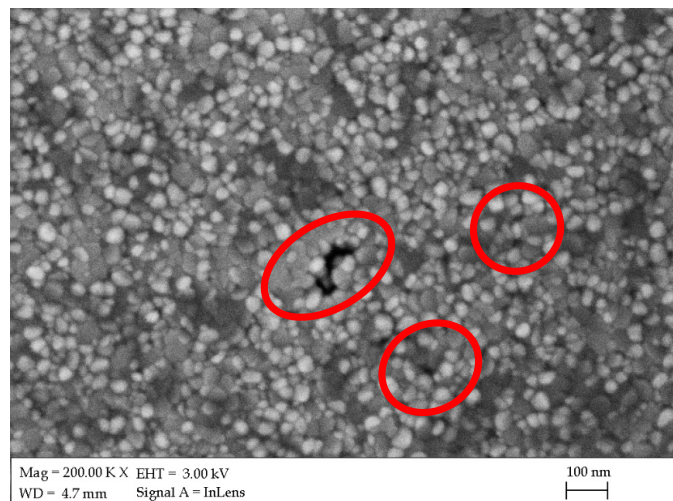


Fig. 3. The morphology of the thin film deposited at 350°C with marked on surface cracks

The confirmation of the chemical composition of ZnO thin film was obtained using the EDS spectrometer. The analyses have been performed in micro areas. This study results confirmed the presence of both: zinc and oxygen in the test sample. In Figure 4 the EDS spectrum where the presence of peaks that are characteristic for zinc (1.01, 8.64 and 9.57 keV) and oxygen (0.52 keV) is shown. There are also visible peaks of silicon (1.74 keV), magnesium (1.25 keV) and calcium (3.69 and 4.01 keV). These elements are part of substrate material on which the layers were deposited.

ZnO thin films transparency coefficients have been measured with use of UV-VIS spectroscopy in the wavelength range from 380 to 780 nm. This test results confirmed that the process temperature and coating thickness have an influence on the transparency of ZnO layers. Measurements results were compared with the transparency coefficient of the uncoated substrate. Transparency of sample 3 (100 cycles, 350°C) was at the level of the uncoated substrate. That might indicate that the temperature of the ALD process was too high and the formed film was very thin (Fig. 5). Samples: 1 (100 cycles, 150°C), 2 (100 cycles, 200°C) and 6 (500 cycles, 350°C) show similar

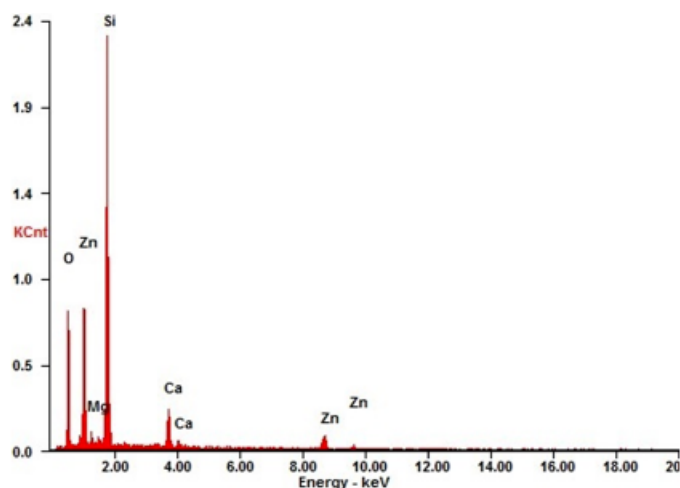


Fig. 4. EDS spectrum for ZnO thin film deposited on the glass

transparency coefficient measurement results for the full analyzed wavelength range with the clear decrease for the shortest wavelength (Figs. 5,6). In case of samples 4 (500 cycles, 200°C) and 5 (500 cycles, 350°C) determined the shape of transparency

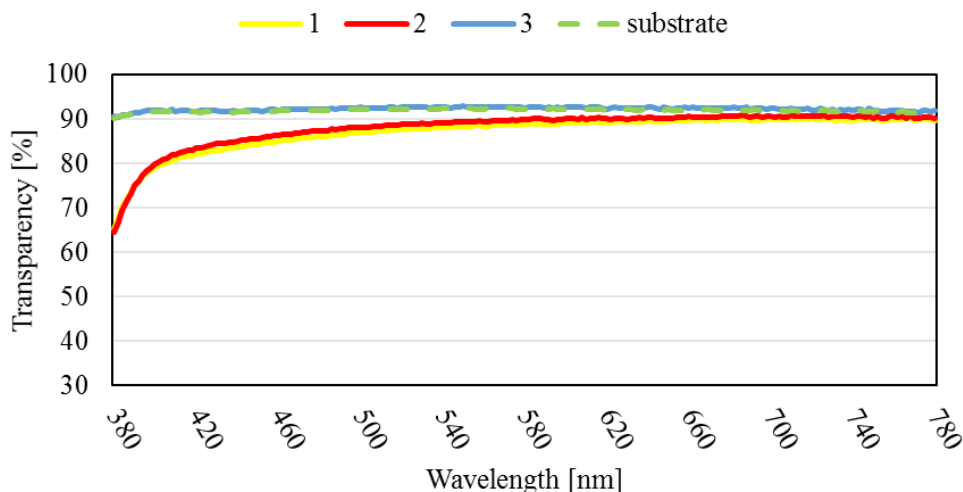


Fig. 5. Transparency of ZnO thin films (samples 1-3) deposited on the glass substrate

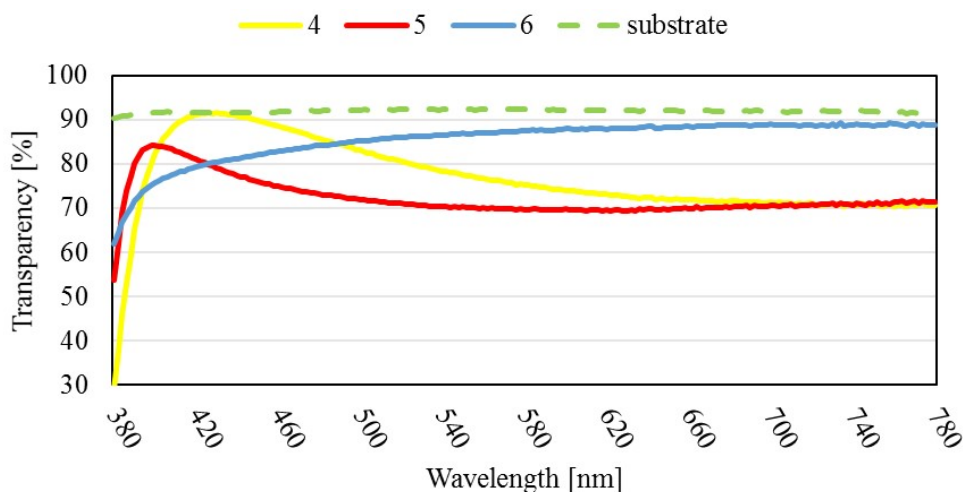


Fig. 6. Transparency of ZnO thin films (samples 4-6) deposited on the glass substrate

characteristic was different compared to other samples. In the range of short wavelengths (below approx. 500 nm), it was dynamically changing. Transparency coefficient was comparable to other tested samples and of course lower than for glass. For wavelengths, longer than 500 nm transparency was much lower than in case of other tested sample, below 85%.

A study performed using a high-resolution transmission electron microscopy allowed to determine the microstructure of the coatings deposited at 150°C (Fig. 7) which was characterized by elongated grains having an average size of 40 nm. In contrast, a coating deposited at 200°C (Fig. 8.) had much greater uniformity; the grains have a spherical shape, and they had the average grain size about 25 nm. On the other hand, HAADF study of coatings deposited at 350 C, allowed determining that

its characterized by the structure of the islands (Fig. 9). Such a structure of the layer probably due to the very high deposition temperature which changed the model of the formation of the layer. This structure provides good transparency of the layer. The results obtained in TEM confirmed the results obtained in a scanning electron microscope.

#### 4. Conclusions

The studies concluded that the ALD process temperature significantly affects the morphology of the surface of the ZnO layers deposited on a glass substrate. Particularly, the temperature settings were affecting such layer properties like the shape

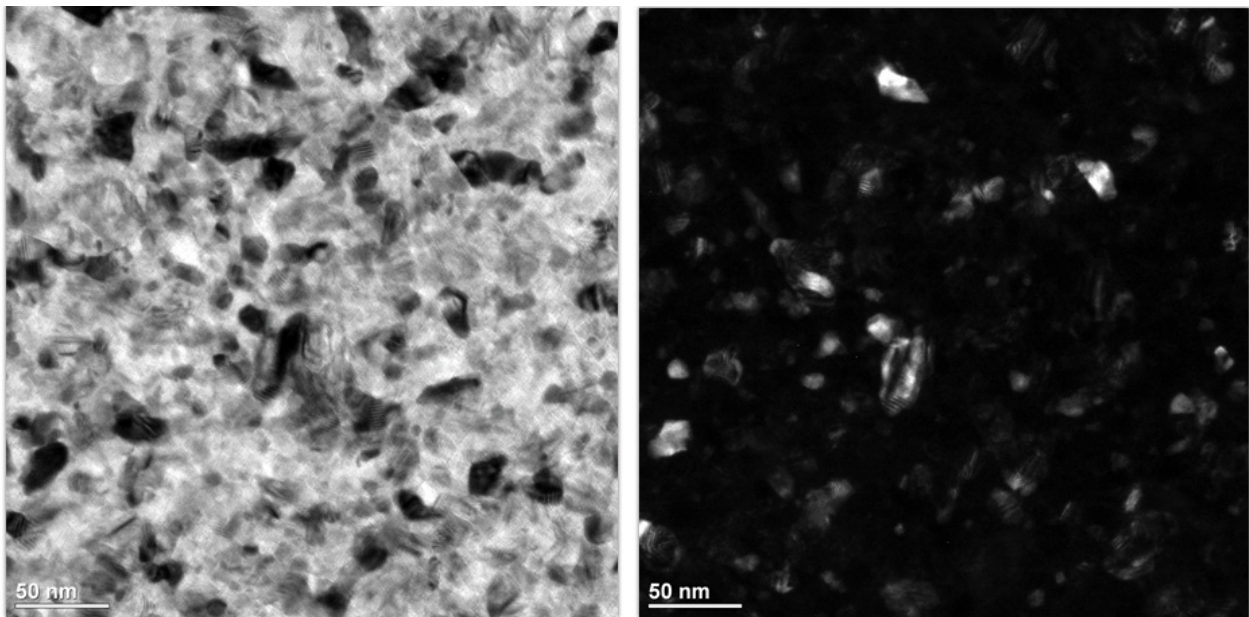


Fig. 7. Bright and dark field TEM image of the thin film deposited at 150°C

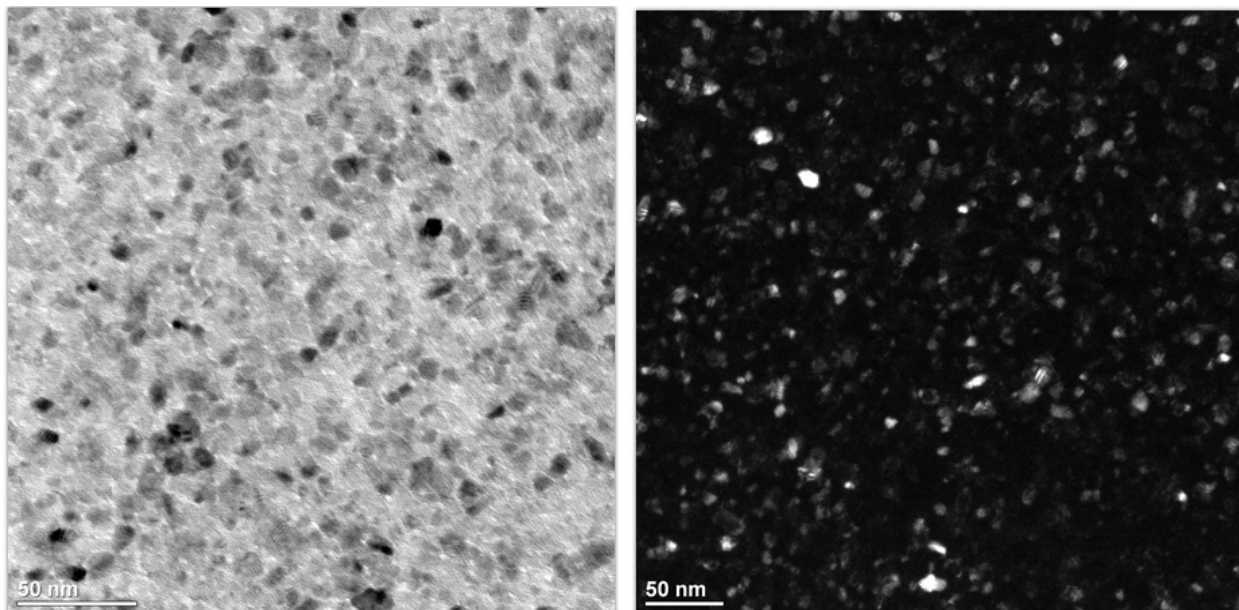


Fig. 8. Bright and dark field TEM image of the thin film deposited at 200°C

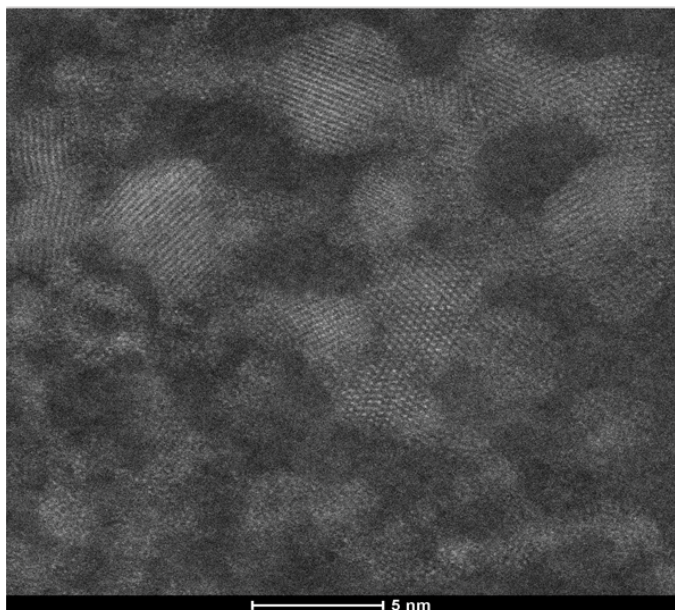


Fig. 9. HAADF image of the thin film deposited at 350°C

and size of grains. The most homogenous structure in respect of grains size was found on samples coated in 200°C and 300°C. However, the surface of second of mentioned samples contained numerous cracks and was much more nonuniform comparing to others tested samples. Those two attributes can have influence on other thin film properties like for example electrical conductivity. On the surface of the sample coated in 150°C, large variety in grain sizes was observed.

The study of chemical composition confirmed the presence of expected elements and didn't show any irregularities in the deposited layers.

The surface morphology of the layers deposited at 350°C showed small cracks and change in the grains growth model which may have an adverse effect on other film properties (e.g., electrical conductivity).

Analysis of transparency showed that transparency coefficient decreases with the increasing number of ALD cycles for a given temperature. This regularity was valid for all temperature settings. Transparency measurements results confirm also that when the number of ALD cycles was increasing, the layer thickness increased simultaneously lowering transparency. The samples deposited at 350°C showed the increase in transparency comparing to the samples deposited at 150 and 200°C with the same number of cycles. This may indicate that the process temperature was too high, resulting in much slower layer growth.

Transparency of the layers deposited in temperatures: 150 and 200°C during 500 cycles showed an increase of transparency coefficient for shorter wavelengths. Further researches will focus on the explanation of this phenomenon. Also, measurement of the thickness of the individual layers must be performed.

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#### REFERENCES

- [1] N. Pinna, M. Knez, Atomic Layer Deposition of Nanostructured Materials, Wiley-VCH, Weinheim, 2012.
- [2] A.C. Jones, M.L. Hitchman, Chemical Vapour Deposition: Precursors, Processes and Applications, Royal Society of Chemistry, Cambridge, UK, 2009.
- [3] P.M. Martin, Handbook of deposition technologies for films and coatings – science, applications and technology, Elsevier Inc., Burlington, USA, 2010.
- [4] H.S. Nalwa, Handbook of thin film materials Vol. 1, Deposition and processing of thin films, Academic Press, San Diego, USA, 2002.
- [5] L.A. Dobrzański, M. Szindler, *Elektronika* **8**, 125 (2012).
- [6] T. Tynell, M. Karppinen, Atomic layer deposition of ZnO, A review, *Semiconductor Science and Technology* **29**, 043001 (2014).
- [7] H.M. Ali, H.A. Mohamed, S.H. Mohamed, *The European Physical Journal Applied Physics* **31**, 87 (2005).
- [8] L. Wei, C. Shuying, *Journal of Semiconductors* **32/1**, 013002 (2011).
- [9] M. Oshima, K. Yoshino, *Japanese Journal of Applied Physics* **50/5S2**, 05FB15 (2011).
- [10] M.M. Ristova, A. Gligorova, I. Nasov, D. Gracin, M. Milun, H. Kostadinova-Boskova, R. Popeski-Dimovski, *Journal of Electronic Materials* **41/11**, 3087 (2012).
- [11] K. Ellmer, A. Klein, B. Rech, *Transparent Conductive Zinc Oxide*, Springer, Berlin 2008.
- [12] R. Escudero, R. Escamilla, *Solid State Communications* **151/2**, 97 (2011).
- [13] A. Illiberi, F. Roozeboom, P. Poodt, *ACS Appl. Mater. Interfaces* **4/1**, 268 (2012).