ZnO THIN FILMS PREPARED BY ATOMIC LAYER DEPOSITION

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Resume

The purpose of this paper is present the influence of deposition conditions of nanometric zinc oxide thin films using atomic layer deposition on the mechanical and optical properties. The influence of the deposition temperature and the number of cycles on the transparency and adhesion of the ZnO, thin films was investigated. In addition, the results of chemical and phase composition analysis of the layers and their topography and structure were discussed. As a substrate for the investigated thin films was used glass. For the preparation of ZnO thin films was used ALD method. Selecting this method is justified by the high quality and good properties of the deposited layers.

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1. Introduction

Zinc oxide belongs to the semiconductor group II-IV type. It is characterized by a wide energy gap of 3.37 eV (at room temperature). Such a wide energy gap makes ZnO completely transparent to the electromagnetic spectrum of visible light. It allows using of ZnO as the transparent conductive layers (TCL). The most commonly used material for such a coating is indium-tin-oxide (ITO). However, due to the high costs of production of ITO, which are mainly generated by the high price of indium, they are sought alternative materials [1 - 5].

Today there are many methods of producing nanometric ZnO conductive layers. One promising method seems to be the atomic layers deposition method - ALD. The main advantages of this method are self-limited growth mechanism and the pulsed nature of the process. The self-limited growth mechanism makes possible to control the thickness of the deposited layer at the nanometer level. Theoretically, during one cycle of the ALD deposited layer obtained a thickness of approx. 0.1 nm. Whereas, pulsed nature of the process allows to use more reactive precursors than is the case in the CVD process.

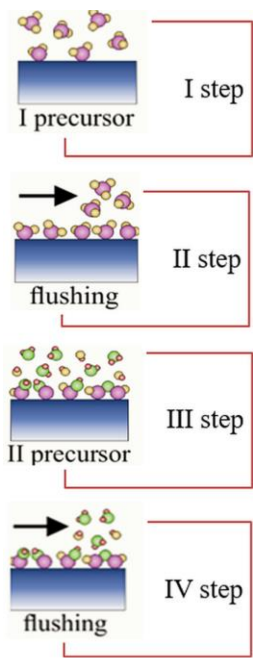

Fig. 1. Schema of the atomic layer deposition process. (full colour version available online)

Fig. 1 shows the schema of ALD process. The thin films were deposited by ALD technique are characterized by high homogeneity and conformality [4 - 10]. This article is a continuation of the tests described in [11].

2. Experimental details

Zinc oxide layer was deposited using ALD method in reactor R-200 from Picosan. As a precursor for zinc was used diethylzinc (DEZ), for oxide was deionized water (H_2O) and nitrogen (N_2) as an inert gas. The dosing time of each precursor was 0.1 s the flushing time was 4 s for DEZ and 5 s for H_2O. The process temperature was 100 to 300° C, depending on the process, and the number of cycles was 200 - 600. ZnO thin films were deposited on a glass substrate and copper ring with a carbon membrane (for transmission electron microscope).

Surface topography and microstructure were observed in a scanning electron microscope Supra 35 from Zeiss and transmission electron microscope Titan 80-300 from FEI.

The chemical composition was checked using energy dispersive X-ray spectroscopy method by Trident XM4 system from EDAX which is part of scanning electron microscope Supra 35 from Zeiss.

X-ray phase analysis was tested by X'Pert Pro diffractometer from Panalytical with a cobalt lamp.

Adhesion was tested using scratch test on the open platform equipped with a Micro-Combi-Tester from CSM. In order to scratch the sample was used a diamond penetrator in the shape of a cone. To evaluate the adhesion of the tested samples was used recording acoustic emission, frictional force and friction coefficient. Scratches were also assessed visually by optical microscopy, which is an integral part of the platform. Measurements were made according with PN-EN 1071-3. The test parameters:

- loading force: 0.03 ÷ 30 N (gradually increasing);
- loading speed: 100 N/min;
- moving speed of table: 10 mm/min;
- length of the scratch: ~3 mm.

Measurements of transparency for ZnO thin films were carried out on a UV-VIS spectrometer Evolution 220 from Thermo Scientific. The test was performed for the wavelength of visible light.

3. Results and discussion

The morphology of the surface of ZnO thin films (Fig. 2) deposited on a glass substrate by ALD is characterized by homogeneity and a nanocrystalline structure. This is confirmed by research carried out using a transmission electron microscope. The thickness of the ZnO thin film is in the range 75 -95 nm depending on the process temperature (Fig. 3).

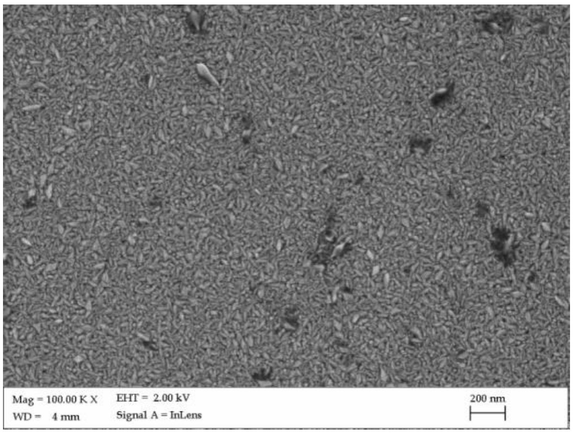

Fig. 2. SEM image of the surface topography ZnO thin film deposited on the glass substrate at 150°C.
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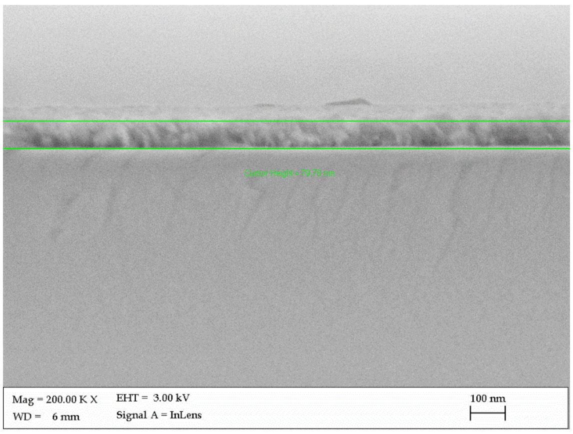

Fig. 3. SEM image of the surface topography ZnO thin film deposited on the glass substrate at 150°C.
(full colour version available online)

Subsequently, for the coating's structure characterization, the TEM microscopes was used. The images presented in Fig. 4 were obtained from selected regions. The bright-field image (Fig. 4a) and dark-field image (Fig. 4b) shows a nanocrystalline character of ZnO films.

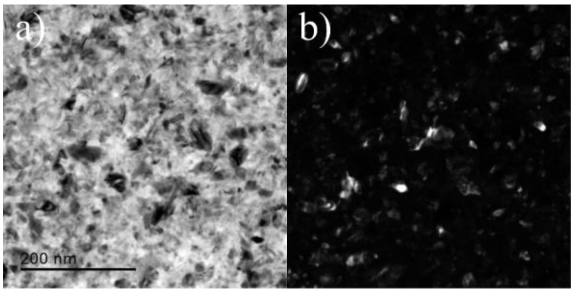

Fig. 4. TEM image of the nanostructured ZnO thin film deposited on a copper ring with a carbon membrane at 150°C; a) bright field image; (b) dark field image.

In order to identify the chemical composition of the deposited thin layers was performed by EDS method. In Fig. 5 shows the EDS spectrum, which confirms the presence of the analyzed coating both zinc (characteristic peaks: 1.012 keV, 8.637 keV and 9.570 keV) and oxygen (0.532 keV). The visible spectrum is only the peaks characteristic of the coating material. The peaks of the substrate material have not been registered because the electron excitation area covered only thin film.

In Fig. 6 are shown the results of X-ray phase analysis obtained by Bragg-Brentano. The results obtained confirm the presence of ZnO phase in the thin film, because occurred the peaks characteristic of this material: 37.061° with index (010), 40.158° (002), 42.349° (011) and 66.798° (110). The peaks were identified using JCPDS files.

To study the adhesion of coated layers scratch test was used. The results are shown in Table 1, Fig. 7. Based on the results, the obtained values for each sample are very close to each other. Also in the case of critical value - LC1 (Table 1), which is a critical parameter of adhesion. Differences between the values for the individual samples are very low. On this basis, it can be concluded that the temperature deposition process of ZnO thin films by ALD method does not have a significant impact on the ZnO thin films adhesion to the substrate made of glass.

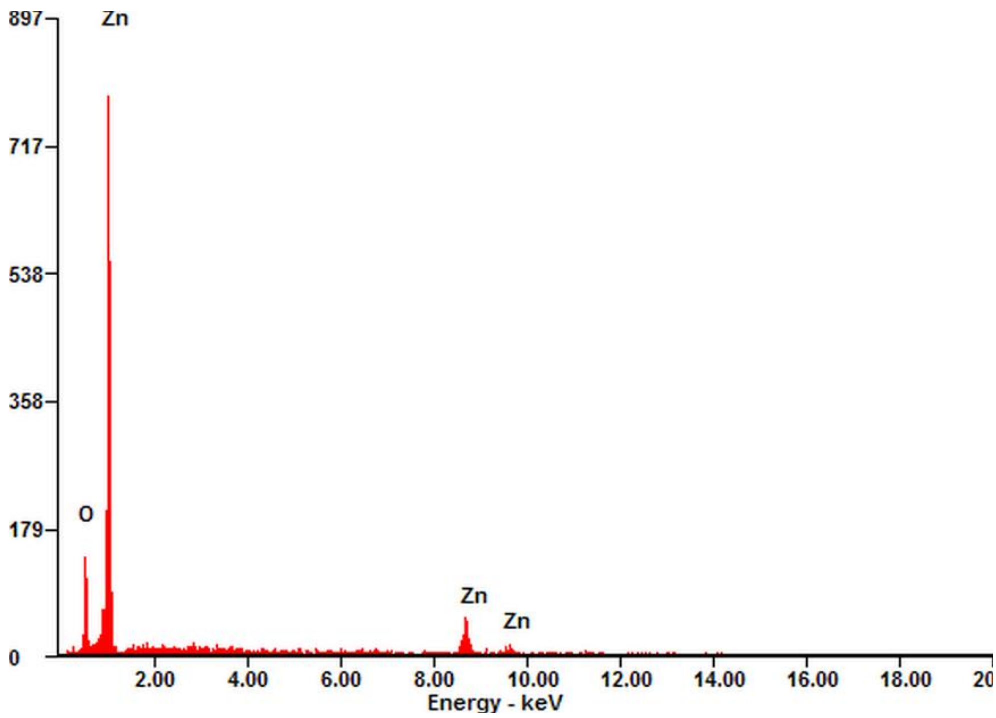

Fig. 5. EDS spectrum of the ZnO coating deposited on glass at 250° C.
(full colour version available online)

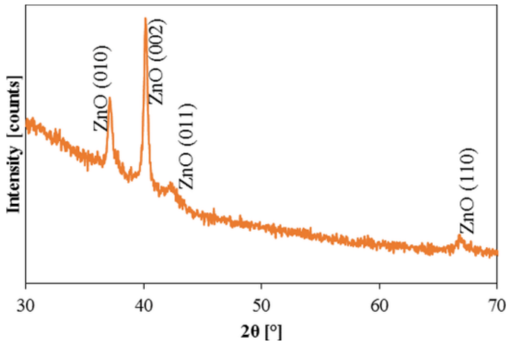

Fig. 6. X-ray diffractometer ZnO thin film deposited on the glass obtained by Bragg-Brentano, the process temperature was 150℃ and number of cycles was 750.
(full colour version available online)

Table 1.
The results of the scratch test of ZnO thin films deposited at a temperature of 100-300°C, 600 cycles.

Sample	Value of indenter load Fn (N)		
	Lc_1	Lc_2	Lc_3
100	3.62	7.87	23.5
150	2.88	7.96	25.2
200	2.50	7.94	25.2
250	2.37	8.09	24.8
300	2.33	7.97	21.6

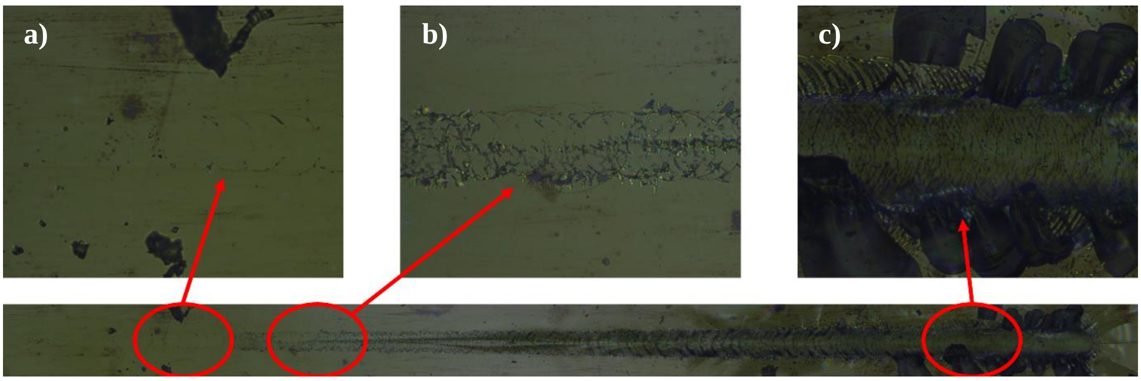

Fig. 7. Types of damage caused during the scratch test: a) the type of Hertz circular cracks (L_{c1} was 4.06 N), b) cracks inside the trace scratches (L_{c2} was 7.68 N), c) cohesive chipping along the edges and inside scratches (L_{c3} was 23.80 N), ZnO thin films deposited at a temperature of 100°C at a number of cycles of 600.
(full colour version available online)

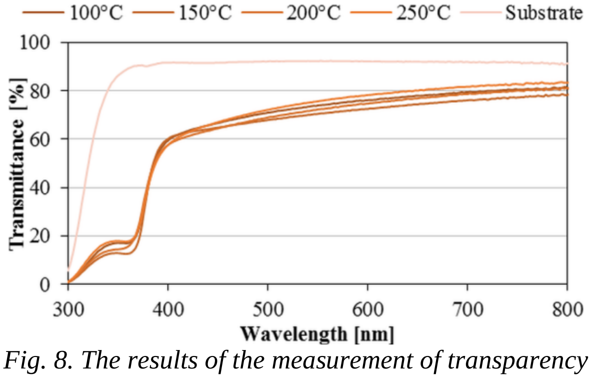

Fig. 8. The results of the measurement of transparency for ZnO thin films deposited at a temperature of 100-250°C at a constant number of cycles of 300.
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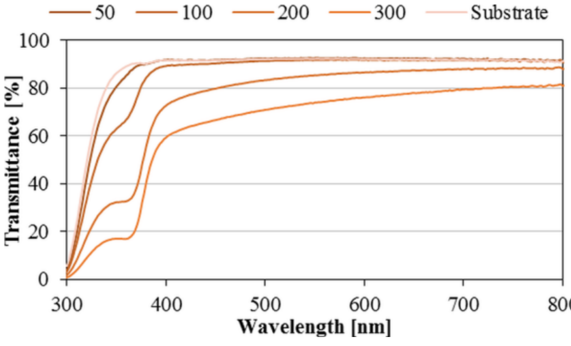

Fig. 9. The results of the measurement of transparency for ZnO thin films deposited at 100°C with the number of times the range of 50-300.
(full colour version available online)

Fig. 8 and 9 shows results of measurements of the transparency of ZnO thin films deposited on the glass substrate depending on the process temperature and the number of cycles. The results were compared with results of the measurement of transparency for a glass substrate. From the obtained results it can be concluded that the deposition temperature has no significant effect on the transparency of the coatings tested (Fig. 8). However, the number of cycles has a significant impact on transparency. If the number of cycles is greater, the thicker layers are deposited and thus lower transparency of produced layers is achieved (Fig. 9).

4. Conclusions

Surface topography and microstructure shows that thin films deposited by ALD are nanocrystalline, homogeneous and uniformity.

Analysis of the chemical composition and phase confirmed the presence of ZnO layers on the surface of the investigated material and showed no evidence of contamination.

Scratch test of ZnO thin film into a glass substrate showed that the temperature of the ALD process hasn't significant effect for adhesion value.

Also, the temperature of the process does not effect on the transparency of thin films investigated. In contrast, the number of ALD cycles, and as a result thickness of ZnO thin films, significantly affects the level of transparency. In addition, all test samples showed a sharp decline in transparency for the near infrared (below 400 nm).

Acknowledgements

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