

## INFLUENCE OF THE PVD PROCESS PARAMETERS ON ZnO: Al THIN FILMS

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### Abstract:

In recent years a growing interest in searching new material for producing Transparent Conductive Layers (TCL) is observed. ZnO:Al thin films are this type material, interesting due to wide range of potential applications where it can be applied like: transparent electrodes, gas sensors, thin film transistors, sensor devices, electroluminescent diodes and others.

The aim of this paper is to discuss influence of the ZnO:Al film deposition parameters of PVD magnetron sputtering method on TCL structure and its chemical composition. It contains description of the ZnO:Al PVD magnetron sputtering deposition method. It discusses results obtained from the analysis of the microstructure of ZnO:Al thin films using a high resolution scanning electron microscope, layers' surface topography determined with atomic force microscope and results of chemical composition analyses.

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### 1. INTRODUCTION

Transparent conductive layers (TCL) are mainly used in electronic devices as components of all types of photovoltaic cells, displays, monitors and other products where it is important to ensure both: the high conductivity of the layer and high transparency. The TCL are thin films, optically transparent and electrical conductive. The most common material used to prepare TCL is indium-tin-oxide (ITO). These layers are characterized by a very high transmittance of visible light (> 85%) and low resistance ( $10^{-4} \Omega \times \text{cm}$ ). Other popular TLC material is the fluorine-doped tin oxide (FTO), characterized by the resistance of  $4 \times 10^{-4} \Omega \times \text{cm}$  and transparency higher than 80%. Currently, researches on new materials that can replace ITO and FTO are carried out. The main reason for this is the high price of base materials, especially of the ITO [1-7].

The interesting alternative material is the zinc oxide (ZnO) thin films. The ZnO has properties typical for the n-type semiconductor. It is characterized by a wide energy gap of 3.37 eV and

transparency higher than 70%. Those two ZnO parameters are the result of the chemical composition change of nonstoichiometric structural defects and electrical properties. In addition, zinc is abundant in nature; consequently, ZnO is relatively cheap [8,9].

The dopant in the metal-doped ZnO (MZO) thin films influences changes in the following properties [10]. The ZnO thin films doped with elements from group III have a high conductivity and n-type semiconductor characteristics [11,12]. It is worth to underline that among all elements of this group, aluminum is cheap, abundant and non-toxic material. The structures shared by the ZnO crystal are wurtzite, zinc blende and rock salt type [13,14].

Chemical composition of TCL should be homogenous and uniformly distributed over the TCL surface. The TCL surface quality is also a crucial parameter. It is required to ensure homogeneity and continuity of the thin film. The TCL layers should be characterized by low porosity and by lack of cracks and holes on the surface. Surface defects can reduce electrical conductivity that is crucial in case of optoelectronic applications [1-9].

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The ZnO:Al thin films can be produced using many different techniques, including chemical and physical processes. Among those methods, the magnetron sputtering, which is a form of physical vapor deposition (PVD) method, is especially interesting, because it can not only be conducted at low temperatures but can also produce high-quality crystalline intrinsic and doped ZnO thin films [15,16].

## 2. MATERIALS AND METHODS

Materials used for the study were two thin films of zinc oxide doped with aluminum and one zinc oxide thin film without dopant, deposited on a glass substrate prepared using physical vapor deposition magnetron sputtering method.

The PVD thin film deposition process is a plasma coating process where atoms are ejected from target material and moved to target surface. The whole process takes place in a vacuum chamber filled with inert gas. After applying high voltage plasma conditions are created. Inert gas atoms become charged ions and because of presents of electric field they are moved with high velocity to the source target. Ions are ejected from sputtering material. Ejected particles are deposited as thin layer on the substrate surface. Magnetron sputtering is one of the forms of the PVD process. Strong magnetic field is created in chamber to control behavior and velocity of charger particles. Due to that, plasma is kept in front of the target material and intensifies the whole deposition process. During the magnetron deposition process, few settings of magnetron sputter can be used. Time of the process can be used to control thickness of the film; temperature can have major influence on thickness and layer structure. The power setting of material targets can affect structure and percentage contribution of used materials in the final thin film [4,15,16].

The deposition conditions are summarized in Tab. 1. Samples 1 and 2 are the ZnO thin films doped with Al. Sample 3 is a reference sample and comprises a thin film ZnO and it was not doped with Al. During the test two ZnO:Al samples (samples 1 and 2) where prepared with different setting of power for Al target. Other magnetron settings where not changed during both preparation processes.

The surface morphology of the deposited layers was mapped with the use of the SUPRA 35 scanning electron microscope (SEM) by ZEISS. In-Lens detector was used to detect the secondary

electrons that later were used to generate images with 3kV accelerate voltage. The chemical composition of samples was analyzed using the energy dispersive X-ray spectroscopy (EDS) technique in the SEM.

**Table 1.** Deposition parameters of ZnO:Al thin films used during tests.

	Sample 1	Sample 2	Sample 3
Power on magnetron ZnO [W]	300	300	300
Power on magnetron Al [W]	250	300	-
Time [s]	3000	3000	3000
Temperature [°C]	200	200	200

The layers' surface topography was determined by measurements performed with an atomic force microscope (AFM) XE-100 by Park System.

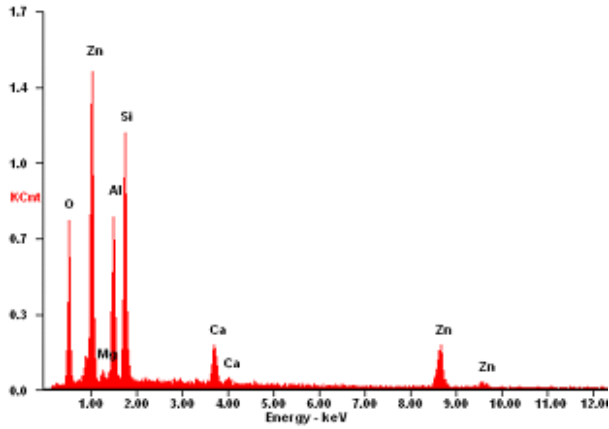
## 3. RESULTS AND DISCUSSION

In the EDS spectra of ZnO:Al (fig. 1a and 1b) are visible peaks which are characteristic for Zn (1.01, 8.64 and 9.57 keV), Al (1.49 keV) and O (0.52 keV). Those EDS spectra contain also peaks of following elements: Mg (1.25 keV), Si (1.74 keV) and Ca (3.69 and 4.01 keV), that are coming from the substrate material. All detected chemical components are desirable. The EDS analysis from fig. 1a and 1b, confirm that tested thin films contained ZnO and Al dopant. Spectrum image from fig. 1c comes from sample 3 where no Al dopant was used.

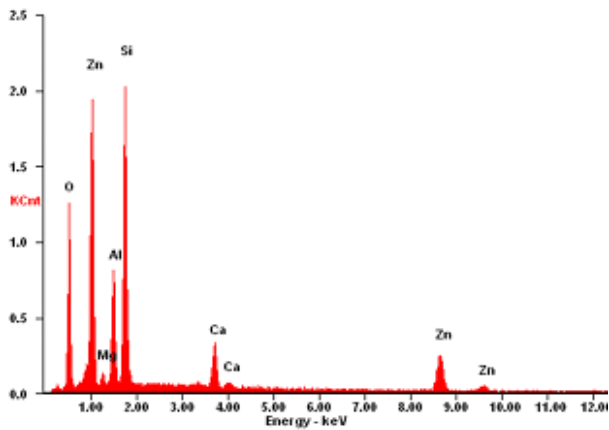
The surface topography was analyzed by the scanning electron microscope (fig. 2).

The TCL thin film surface topography should be homogenous and continuous without cracks or holes in surface. Its porosity should be as low as it is possible. The surface structure should be uniform. Those requirements have been fulfilled in case of sample 3, which is a reference sample in this test. In the case of sample 3, the obtained average grain size was 100 nm (fig. 2c). In the case of samples 1 and 2, the surface structure characteristics differs comparing to sample 3 and unfortunately both results from samples 1 and 2 do not satisfy required good surface quality characteristic for the TCL thin film. Sample 1's (Fig. 2a) morphology is uniform but surface contains minor layer discontinuities, there are visible as small cracks. Its homogeneity and porosity is satisfactory. Sample 1 grains shape is regular and

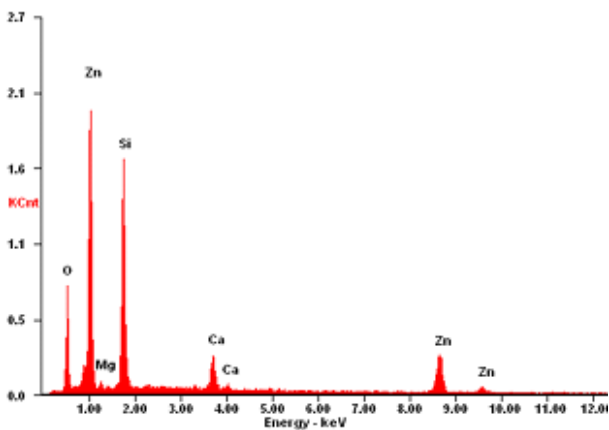
the average grain size is 95 nm. Sample 2 (Fig. 2b) morphology is very diverse and strongly porous. Layer discontinuities in form of holes are clearly visible. Grains shape is irregular. The average grain size is 140 nm. Result from sample 1 is better than result from sample 2, but still not as good as the result from sample 3.



a) sample 1



b) sample 2

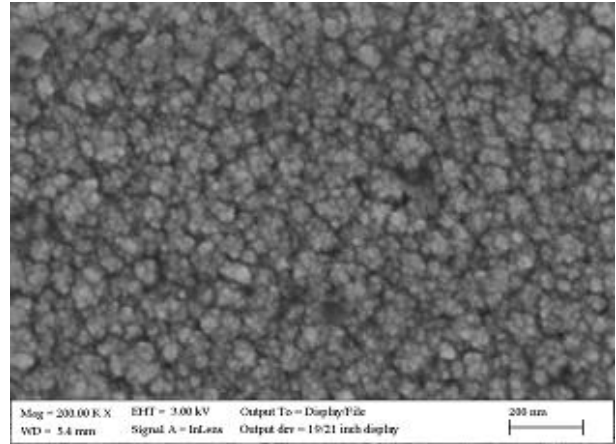


c) sample 3 - reference sample

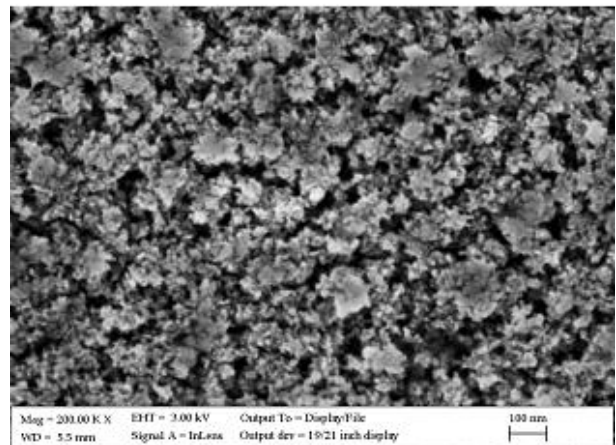
Fig. 1. EDS spectrum of: a) ZnO:Al, b) ZnO:Al, c) ZnO – reference sample

The TCL layers homogeneity and continuity are crucial parameters to ensure good thin film conductivity. Porosity and surface defects are

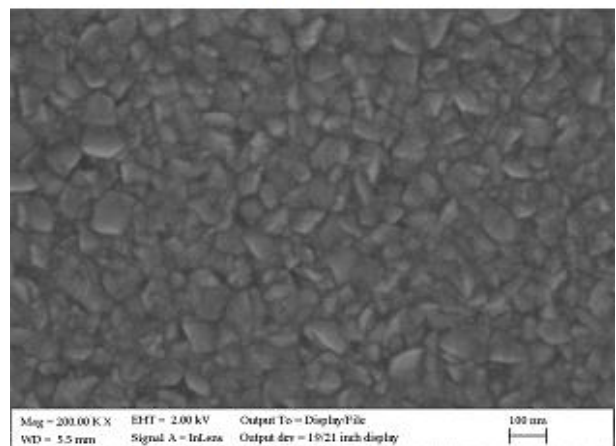
increasing the thin film resistance what reduces the layer's conductivity. For sample 1 and 2, unsatisfactory results regarding continuity, porosity and uniformity can be caused by improper choice of magnetron power settings for the Al target during the magnetron sputtering deposition process. That caused improper thin film growth.



a) sample 1

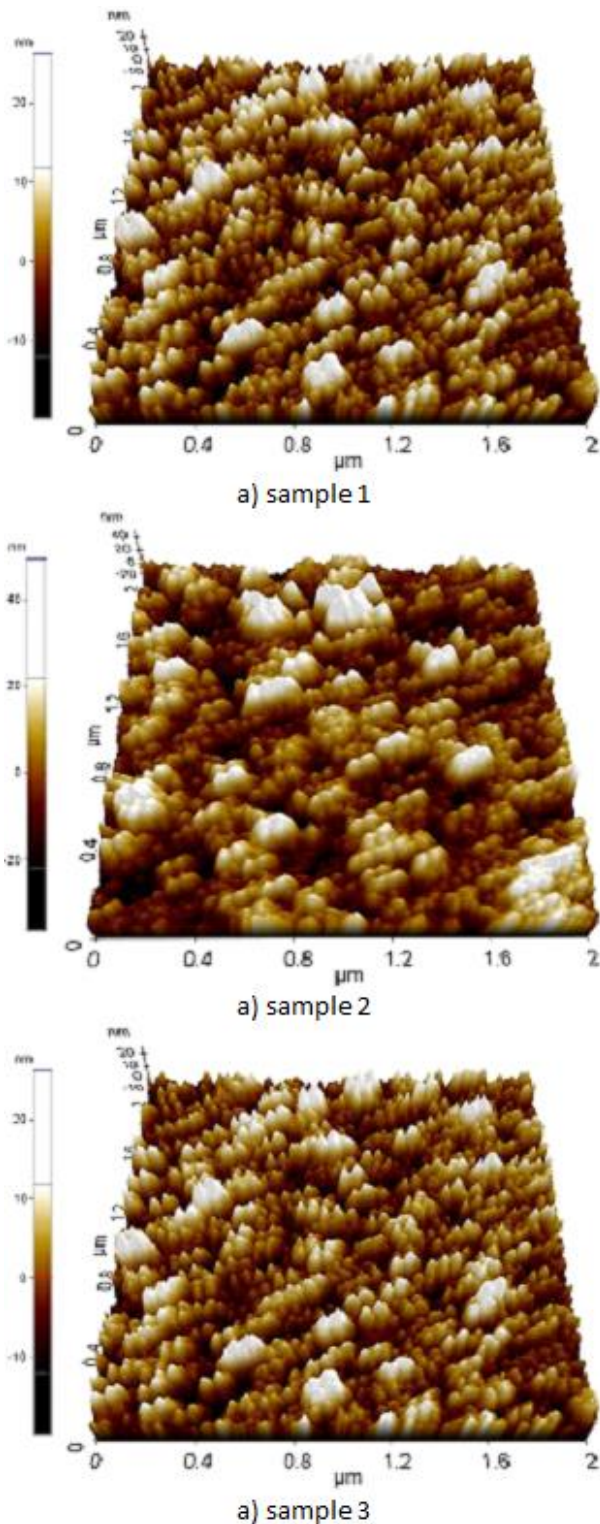


b) sample 2



c) sample 3 - reference sample

Fig. 2. SEM image of the surface topography of: a) ZnO:Al, b) ZnO:Al, c) ZnO – reference sample



**Fig. 3.** AFM image of the surface topography of: a) ZnO:Al, b) ZnO:Al, c) ZnO – reference sample

The study of the surface topography of all tested samples was also performed by atomic force microscope (AFM) set in a non-contact mode (fig. 3 and tab. 2). Area of 2x2  $\mu\text{m}$  square was chosen for investigation. Roughness measurement of reference sample 3, described by the  $R_a$  parameter (arithmetic average) was 3.973 nm (tab. 2). Measured  $R_a$  of sample 1 was 4.815 nm (tab. 2). In the case of sample 2, roughness measurement

showed much higher value of  $R_a$  equal to 8.841 nm (tab. 2). Results from this experiment lead to the conclusion that regarding roughness measurement sample 1 was much more similar to reference sample than sample 2 where result was significantly higher.

The AFM analysis also provided useful information about surface of tested samples (fig. 3). Sample 1 (fig. 3a) and reference sample 3 (fig. 3c) are characterized by fine structure. The grain arrangement in sample 1 and 3 was regular. In the case of sample 2 (fig. 3b) grains uniformity was not regular and it had a coarse structure.

**Table 2.** The roughness parameters of: a) ZnO:Al, b) ZnO:Al, c) ZnO – reference sample

No. sample	Min [nm]	Max [nm]	$R_{pv}$ [nm]	$R_a$ [nm]
1	-19.787	26.146	45.933	4.815
2	-36.185	49.222	85.407	8.841
3	-11.106	20.602	31.708	3.973

Results obtained by the AFM lead to the similar conclusions that were achieved in the SEM surface analysis. The most desirable TCL parameters were exhibit by the sample 1, which was the most similar to the reference sample.

#### 4. CONCLUSION

The surface topography analyses have shown that change of magnetron power settings for doped material significantly influences the structure topography of deposited thin films. Increase of magnetron power on an Al target caused unwanted effects like: higher porosity, lower uniformity and larger number of surface defects on the deposited thin films. Comparable results were obtained after roughness measurements. In the case when the lower magnetron power settings for Al target were chosen, the impact of Al addition on the surface topography was less significant. The EDS analyses confirmed presence of all desired element. Influence of change of magnetron power settings on Al target on EDS results was not noticed in qualitative analyses.

Before the test, it was predictable that change of the magnetron power of Al target would have an influence on prepared TCL structure. The information might be surprising that the second tested Al thin film became useless regarding



possible usage as TCL layer due to its surface defects. That led to the conclusion that proper doper magnetron power selection is very important step during the TCL preparation process and when it is set improperly the TCL layer would not fulfill requirements.

The study that has been performed implied the conclusion that more research work and examination must be performed. Other settings of the dopant magnetron target should be tested, e.g. different magnetron power settings of material targets, time of deposition process and maybe the temperature.

## REFERENCES

- [1] H.M. Ali, H.A. Mohamed, S.H. Mohamed, Enhancement of the optical and electrical properties of ITO thin films deposited by electron beam evaporation technique. The European Physical Journal Applied Physics, 31 (2), 2005: pp.87-93.
- [2] M.S. Farhan, E. Zalnezhad A. R. Bushroa, A.A.D. Sarhan, Electrical and Optical Properties of Indium-tin Oxide (ITO) Films by Ion-Assisted Deposition (IAD) at Room Temperature. International Journal of Precision Engineering and Manufacturing, 14 (8), 2013: pp.1465-1469.
- [3] L. Wei, C. Shuying, Photoelectric properties of ITO thin films deposited by DC magnetron sputtering. Journal of Semiconductors, 32 (1), 2011: pp.013002.
- [4] K. Ellmer, A. Klein, B. Rech, Transparent Conductive Zinc Oxide, Springer, Berlin, 2008.
- [5] M. Oshima, K. Yoshino, Characteristic of low resistivity fluorine-doped SnO<sub>2</sub> thin films grown by spray pyrolysis. Japanese Journal of Applied Physics, 50 (5S2), 2011. pp.05FB15.
- [6] M. M. Ristova, A. Gligorova, I. Nasov, D. Gracin, M. Milun, H. Kostadinova-Boskova, R. Popeski-Dimovski, TiO<sub>2</sub> Coating for SnO<sub>2</sub>:F Films Produced by Filtered Cathodic Arc Evaporation for Improved Resistance to H<sup>+</sup> Radical Exposure. Journal of Electronic Materials, 41 (11), 2012: pp.3087-3094.
- [7] J.C. Manificier, L. Szepessy J.F. Bresse, M, Perotin, R. Stuck, In<sub>2</sub>O<sub>3</sub>:(Sn) and SnO<sub>2</sub>:(F) films - application to solar energy conversion part II - Electrical and optical properties. Materials Research Bulletin, 14 (2), 1979: pp.163-175.
- [8] Zs. Baji, Z. Lábadi, G. Molnár, B. Pécz, K. Vad, Z.E. Horváth, P.J. Szabó, T. Nagata, J. Volk, Highly conductive epitaxial ZnO layers deposited by atomic layer deposition. Thin Solid Films, 562 (-), 2014: pp.485-489.
- [9] R. Escudero, R. Escamilla, Ferromagnetic behavior of high-purity ZnO nanoparticles. Solid State Communications, 151 (2), 2011: pp.97-101.
- [10] S. Nakamura, T. Mukai, M. Snoh, Candela-class high-brightness InGaN/ AlGaN double-heterostructure blue-light-emitting diodes. Applied Physics Letters, 64 (13), 1994: pp.1687-1689.
- [11] D.M. Bagnall, Y.F. Chen, Z. Zhu, T. Yao, S. Koyama, M.Y. Shen, T. Goto, Optically pumped lasing of ZnO at room temperature. Applied Physics Letters, 70 (17), 1997: pp.2230-2232.
- [12] S. Major, K.L. Chopra, Indium-doped zinc oxide films as transparent electrodes for solar cells. Solar Energy Materials, 17 (5), 1988: pp.319-327.
- [13] M. Caglar, S. Ilican, Y. Caglar, F. Yakuphanoglu, The effects of Al doping on the optical constants of ZnO thin films prepared by spray pyrolysis method. Journal of Materials Science. Materials in Electronics, 19 (8), 2008: pp.704-708.
- [14] F. Maldonado, A. Stashans, Al-doped ZnO: Electronic, electrical and structural properties. Journal of Physics and Chemistry of Solids, 71 (5), 2010: pp.784-787.
- [15] É.P. da Silva, M. Chaves, S.F. Durrant, P.N. Lisboa-Filho, J.R.R. Bortoleto, Morphological and electrical evolution of ZnO:Al thin films deposited by RF magnetron sputtering onto glass substrates. Materials Research, 17 (6), 2014: pp.1384-1390.
- [16] H.W. Wu, R.Y. Yang, C.M. Hsiung, C.H. Chu, Characterization of aluminum-doped zinc oxide thin films by RF magnetron sputtering at different substrate temperature and sputtering power. Journal of Materials Science Materials in Electronics, 41 (1), 2013: pp.166-171.

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