# NANOCOMPOSITE STRUCTURE CHANGES IN ZNO-$IN_2O_3$ (ZIO) SYSTEM PREPARED BY SPRAY PYROLYSIS METHOD

## MODIFICĂRI ÎN STRUCTURA NANOCOMPOZITĂ ÎN SISTEMUL ZNO-$IN_2O_3$ (ZIO) PREGĂTIT PRIN METODA SPRAY PIROLISEY

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The electronic properties of transparent conductive oxides (TCO) based on ZITO (ZnO-$In_2O_3$-$SnO_2$) thin films and their perspectives in thermoelectricity were analyzed in our previous works. There within ZIO system the thermoelectric properties of thin films prepared by spray pyrolysis method with different ratio of [Zn]/[In] were studied [1]. The comparison of electrical conductivity of our films with analogous data cited by Hoel in [2] for samples prepared by conventional solid state synthesis find the large enough discrepancy as for values at room temperature and for values under temperature activation. The conductivities of films deposited by our method by 1-2 order of magnitude are less than in [2]. It is obvious that this distinctive feature of studied films is related with thin film's nature (not a bulk sample), low temperature of film's deposition, peculiarities of spray pyrolysis method. Apparently in our technological conditions, the formation of other crystalline phases which were not found in the [2] is probable. The search of actual composition of our thin films by X-ray diffraction (XRD) technique was the aim of further research. This report presents the results obtained during XRD stage of studying of ZIO thin films with various compositions deposited by spray pyrolysis method.

ZIO ($Zn_xInO_{1.5}$) film deposition on polished silicon substrates (1x1 $cm^2$) was performed by the spray pyrolysis method. For this purposes a mixture of 0.2 M water solutions of $InCl_3$ and $ZnCl_2$ according the required composition x was used for deposition of films with thicknesses around of 100 nm at pyrolysis temperature of 450 $^oC$. The value of x was varied within the range 0.125–2 and samples with x= 0.125, 0.25, 0.33, 0.5, 1.0 and 2.0 were prepared. The improved uniformity of the deposited films provided by synchronous rotation of the sample holder and by nozzle swing. Spraying was carried out perpendicular to the sample holder. The average growth rate of the films was in the range of 1–2 nm/s. Several cycles, each lasting no more than 30 s (sprayed solution volume did not exceed 1.5 ml) were used to prevent sufficient holder cooling (<30 °C).

The film thickness was measured by F20 Filmetrics instrument and roughly was monitored by its colour. The surface roughness was measured by atomic force microscopy (AFM) using a Park XE7 instrument. Average surface roughness of deposited ZIO films did not exceed 10 nm. The laser ellipsometry technique was employed for refractive index measurements. These measurements allowed to estimate the effective porosity of our films that was around 20%. The relation between refractive index and porosity, described in [3]. Deposited films were characterized for their structural properties using an EMPYREAN X-ray diffraction system (from Malvern Panalytical) using Cu Kα (λ=1.5405 Å) radiation within a diffraction angle range of 15–70°.

Figure 1 below shows the diffractograms of all deposited films in summarized XRD pattern.

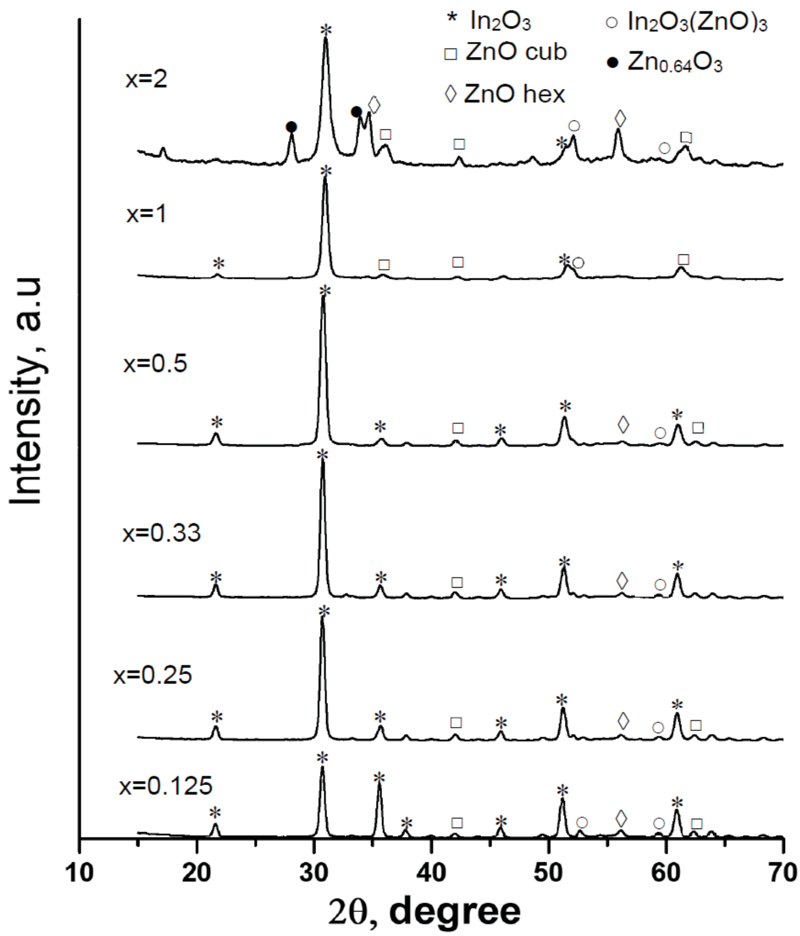


Fig. 1. XRD pattern of ZIO thin films with various composition

Analysis of XRD pattern allows to identify different nanocrystaline phases (from 4 to 5) belonging to diverse compounds and crystallographic syngonies. Such growth formation is already observed with the addition of zinc equal to 0.125. In this case, along with the main most developed cubic $In_2O_3$ phase such compounds as the cubic and hexagonal phases of ZnO, and the $In_2O_3(ZnO)_3$ compounds are found. The lattice structure of $In_2O_3(ZnO)_3$ is composed of alternating octahedral $InO_2^-$ layers and wirtzide-like $InZn_3O_4^+$ slabs and belongs to trigonal symmetry. This phase refers to the homologous series of rather poorly studied compounds having the general formula like $In_2O_3(ZnO)_k$, where k=2-7, 9, 11, 13, 15, 20 [2]. The increase of Zn/In ratio (x= 0–1) in our samples results in gradual size decrease for all nanograins constituted of our films. The grain faceting reconstruction of main phase is also observed. The most pronounced transformations of nanocomposite structure are observed at x=2. They are: a) an appearance of new trigonal phase $Zn_{0.64}O_3$ [4]; b) a significant increase in the mass fraction of zinc-containing compounds, in particular in the form of a new phase, and also for ZnO of hexagonal symmetry; c) further reduction of the grains size for the main phase (up to 10 nm).

We believe that the rise in the proportion of Zn-containing phases and general grain fineness of the obtained nanocomposite is a factor determining the low electrical conductivity of our films compared to the samples obtained by high-temperature synthesis [2]. In the latter compounds, as stated in [5], the source of conduction electrons is not associated with the presence of oxygen vacancies that is usually inherent to the binary metal oxides. Likely this is another reason of low conductivity in our thin films. Obtained results will serve for further studies of thermoelectric phenomena in semiconducting metal oxides which allow to improve their thermoelectric efficiency.

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***References:***

1. KOROTCENKOV, G., BRINZARI, V., HAM, M-H. $In_2O_3$-based thermoelectric materials: the state of art and the role of surface state in the improvement of the efficiency of thermoelectric conversion. In: *Crystals.* 2018, nr. 8(1), pp. 14-50. ISSN 2073-4352.
2. HOEL, C.A., MASON, T.O., GAILLARD, J-F., POEPPELMEIER, K.R. Transparent conducting oxides in ZnO-$In_2O_3$-$SnO_2$ system. In: *Chem. Mater.* 2010, nr. 22, pp. 3569-3579. ISSN 0897-4756.
3. YOLDAS, B. E., PARTLOW, D. P. Formation of broad band antireflective coatings on fused silica for high power applications. In: *Thin Solid Films.* 1985, nr. 129, pp. 1-14. ISSN 0040-6090.

4. Jansen, M., Hoppe, R., Kastner, P. Zur Kenntnis der systeme $Li_2O$/CoO und $Li_2O$/ZnO. In: Zeitschrift fuer Anorganische und Allgemeine Chemie. 1975, nr. 414, pp. 69-75.
5. MORIGA, T., EDWARDS, D.D., MASON, T.O., PALMER, G.B., POEPPELMEIER, K.R., SCHINDLER, J.L., KANNEWURF, C.R., NAKABAYSHI, I. Phase relationship and physical properties of homologous compounds in the zinc oxide-indium oxide system. In: *J. Am. Ceram. Soc.* 1998, nr. 81, pp. 1310-1316. ISSN 1551-2916.