The influence of sintering temperature and Sn\textsuperscript{4+} concentration on electrical and optical properties of ITO nanocrystallites

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Abstract. The indium-tin oxide (ITO) nanocrystallites with different average grain size and Sn\textsuperscript{4+} concentration were synthesized by the modified Pechini method. The X-ray diffraction (XRD) and for the selected samples the transmission electron microscopy (TEM) analysis were done for structure and morphology determination. On the base of obtained powders the ITO layers on glass slides were fabricated by the spin-coating method for comparison of their optical and electrical properties. The influence of Sn\textsuperscript{4+} concentration and sintering temperature on electrical and optical properties of obtained nanocrystalline layers will be discussed in this work.

1. Introduction
The indium-tin oxide is certainly one of the most popular materials in photonics and optoelectronics. Both, transparent, conductive thin films, and semiconductive indium tin oxide nanopowders play an important role in many electronic devices. The main example of ITO-glass slide application are transparent front plate electrodes [1]. Besides at that, indium-tin oxide films and powders could be also applied as solar cells materials [2], conductive pastes [6], anti-static and anti-glare coatings [3-5], heatable glass [7], thermal insulation of windows, etc. [7]. The other applications of ITO thin films are gasses sensors [8,9]. Among the different methods of ITO thin films fabrication [2-4,9-14] recently the most popular are wet chemical deposition processes [10-12] and different sputtering techniques [2,13].

The wet chemical deposition method seems to be very attractive. The method allows to produce coatings of layers on desired shapes and area, to control easily a dopant level and density of the solution. Moreover, the process is easy and does not need of employing any expensive and complicated equipment, comparing to other methods [10]. However, comparing properties of layers obtained by these two methods, one observed that layers fabricated by the wet chemical process were generally characterized by worse transparent and conductive properties than the layers prepared by sputtering [11]. In order to overcome these disadvantages layers could be prepared from the slurries consisted of ITO nanoparticles. The addition of indium tin oxide nanoparticles promotes the crystallization of amorphous ITO gel [11] and at the same time, allowed a preparation of a layer with better electrical conductivity and optical transmission. The influence of Sn\textsuperscript{4+} concentration and average grain size of nanoparticles on properties of the layers is worth examination. On the other side, fabrication of layers with an appropriate amount of nanocrystallites is the simplest way for examination of their electrical and optical properties. In this work, ITO nanoparticles were synthesized by the modified Pechini method [15]. In comparison with other methods of indium-tin oxide nanoparticles fabrication [1,4,6,9,16-19] the modified Pechini method allows to the control the amount of dopant at any range, and average size of nanograins. The structure and morphology of obtained nanoparticles with different Sn\textsuperscript{4+} concentration and synthesized in different temperatures were characterized. The optical and electrical properties of layers fabricated on the base of synthesized...
powders by the spin-coating method [12] were measured and compared. The influence of sintering temperature and Sn⁴⁺ concentration and average grain size of obtained nanopowders on electrical as well as optical properties of fabricated layers will be discussed in this work.

2. Experimental

2.1. Synthesis of ITO nanoparticles

The indium-tin oxide nanoparticles were synthesized in the manner described in our earlier works [20,21]. Two series of samples were obtained. The first one with Sn⁴⁺ concentration at the level of 12% sintered in different temperatures (500 ºC, 600 ºC, 700 ºC, 950 ºC), and the second one synthesized in 800 ºC with different Sn⁴⁺ concentrations (0.5 %, 2 %, 8 %, 12 %, 50 %). As distinct from concentration series synthesized on the base of InCl₃, the temperature series were synthesized on the base of In(NO₃)₃. All samples were sintered for 8 h.

2.2. The structure and morphology characterization

To determine the structure of obtained materials X-ray diffraction measurements were carried out using the XRD-a Stoe Powder Sensitive Detector; filtered by, with? CuKα₁ radiation. Additionally the transmission electron microscopy (Philips CM-20 SuperTwin) was used for determination of morphology selected samples.

2.3. The ITO electrical and optical measurements

In order to determine optical and conductive properties of indium tin oxide nanoparticles thin nano-ITO films were fabricated using the spin-coating method. In the first step slurries consisting of In(NO₃)₃·H₂O, SnCl₂·5H₂O, isopropyl alcohol and ITO nanoparticles were produced. The mass ratio of amount of added nanocrystallites to amount of indium nitride and tin chloride in solution was estimated for 20 wt. %. In the next step the slurries were dropped on rotated (5000 rpm) glass slides. Then the deposition, substrates were dried in 120 ºC for 0.5h and next held in temperature of 500 ºC for 1h. The whole deposition procedure was repeated four times. After that, transmission of obtained layers was measured and compared. The resistances of obtained layers were measured with the four point method using LakeShore 370 AC Resistance Bridge.

3. Results and discussion

3.1. The structure and morphology determination

The XRD patterns for both series (Fig.1 and Fig.2)) confirm that the obtained materials are characterized by patterns typical for Sn:In₂O₃ cubic In₂O₃ phase [JCPDS #06416]. However, it is seen that in high temperature (950 ºC) and for high Sn⁴⁺ concentration (50 %) some peaks corresponding to the tetragonal rutile crystalline phase of cassiterite SnO₂ [JCPDS #411445] also appear. The average grains sizes in the case of samples sintered in different temperatures on the base of In(NO₃)₃ were estimated from the broadening of the diffraction peak using the Scherrer’s formula and presented above the XRD pattern (Fig.1). It is seen that the average grains size increases with sintering temperature. Quite a different situation is observed for samples sintered at 800 ºC with different Sn⁴⁺ concentration (Fig.2). The peaks are thin and sharp. This suggests that average grain size is for sure above 50 nm. To examine a real size and shape of obtained nanocrystallites TEM images were carried out (Fig.3).
Fig.1. The XRD patterns of 12% Sn:In$_2$O$_3$ nanocrystallites sintered at different temperatures

Fig.2. The XRD patterns of ITO nanocrystallites sintered at 800 °C with different Sn$^{4+}$ concentration
Fig. 3. The TEM image of ITO nanopowder with 50 mol % Sn⁺ concentration, sintered at 800 °C

The TEM image shows that sizes of the obtained nanocrystallites are not uniform. The size of most of the nanoparticles is around 50 nm, however a lot of c. a. 20 nm size, strongly aggregated particles are also present in the sample. All particles have unregular, oval shape. Judging from X-ray diffraction pattern (Fig.2.) it is estimated that apart from the ITO phase also another (SnO₂) phase is presented in the sample. Assuming that distinct separation of SnO₂ phase appears around 1070 °C, and that the sample has been sintered at 800 °C it is supposed that the SnO₂ phase has separated in form of smallest nanoparticles.

4.2. Analysis of the layers properties

The comparisons (Fig.4. and Fig.5.) of transmission spectra of ITO layers fabricated on the base of nanoparticles with different Sn⁺ concentration as well as with nanoparticles sintered in different temperatures do not show meaningful differences.

The different situation is observed while comparing conductive properties of the layers. A comparison of resistivity of ITO layers fabricated on the base of nanoparticles with different Sn⁺ concentration (Fig.6) shows the differences between fabricated samples. As it was supposed, the lowest resistivity of the layer has been observed in the layer fabricated on the base of ITO nanoparticles with 12 % Sn⁺ concentration. To this point (12%) resistivity of the layers decreases drastically with Sn⁺ concentration. And for the sample with 50 % Sn⁺ concentration the resistivity is much higher comparing to the optimal sample (12%).

The comparison of resistivity of the layers fabricated on the base of nanoparticles with different average grains size (sintered in different temperatures) (Fig.7) shows that resistivity increases with an average grains size. Moreover, resistivity is in a direct proportion to the average grains size. The explanation of this behavior is following. With decreasing size of nanoparticles the specific surface of nanocrystalline powder increases. That means that a contact surface between each grain also increases and the electrical conductivity of the layer increases accordingly. Additionally, it is known that the main contribution to grains conductivity is that of the grain’s surface. It is obvious that in layers with the smallest grains the ratio of total grains surface to total sample volume is higher comparing to nanopowders with the biggest average grains. This suggests that conductivity of the layer with the smallest grains should be higher comparing to the layer with the biggest grains. The presented results (Fig.7) confirm this hypothesis.
Fig. 4. The transmission spectra of ITO thin films fabricated on the base of nanoparticles with different Sn$^{4+}$ concentration.

Fig. 5. The transmission spectra of ITO thin films fabricated on the base of nanoparticles sintered at different temperatures.
Fig. 6. The resistivity of the ITO layers fabricated on the base of nanoparticles with different Sn$^{4+}$ concentration

Fig. 7. The resistivity of ITO layers fabricated on the base of nanoparticles with different average grains size
4. Conclusions

The ITO nanoparticles were successfully synthesized by the modified Pechini method. However, in samples sintered in the highest temperatures and with the highest Sn\textsuperscript{4+} concentration the separation of SnO\textsubscript{2} cassiterite phase in a form of small nanocrystalline grains is observed. The resistivity of layers fabricated on the base of ITO nanocrystallites increases with the average grains size of ITO nanoparticles. Concerning the results and synthesis method requirements, the optimal average grains size was estimated as 20 nm. The optimal Sn\textsuperscript{4+} concentration in nanocrystallites was determined for 12 %. The influence of average grains size or Sn\textsuperscript{4+} concentration on transmission properties of the fabricated layers was not observed. The properties of ITO layers can be improved by an appropriate post fabrication treatment. The influence of post fabrication treatment of layer properties will be the subject of our future work.

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