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Effect of preparation conditions on physic-chemical properties of tin-doped nanocrystalline indium oxide

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Abstract. In this paper the results of investigation of phase formation and change of concentration of free electrons (Ne) in indium tin oxide system during heat treatment of coprecipitated hydroxides of indium and tin from nitric and hydrochloric solutions and also, for comparison melts of salts nitrates by an alkaline reactant (NH₄OH) are considered. The performed investigation allowed to set the optimal condition of preparation of polycrystalline tin-doped indium oxide with maximal electron concentration.

1. Introduction

There is a growing interest in tin-doped indium oxide (ITO) nanoparticles mostly due to the possibilities of producing highly active catalysts and highly sensitive gas sensors [1].

Tin-doped indium oxide is n-type semiconductor with high electrical conductivity varying in a wide range in dependence on preparation conditions and type of the material (single crystals, ceramics, thin films) [2].

However, it should be noted that most of the publications devoted ITO thin films [3]. And many of the problems of practical use of sol-gel synthesis technology of ITO dispersed materials can not be solved due to the lack of comprehensive studies of the synthesis conditions and the electronic properties of the materials obtained. For example, in work [4] mainly deals with the effects of synthesis temperature and calcinations temperature on morphology and phase structure of ITO particles, but no information about charge carriers concentration. In [5] has information about charge carriers concentration, but examines the impact of her only sintering temperature and Sn concentration.

This work presents the results of study of coprecipitation of hydroxides of indium and tin from nitric or hydrochloric acidic solutions by NH₄OH reactant and following annealing of coprecipitation products, the effect of conditions on the phase composition and major charge carriers concentration (Ne) in prepared nanocrystalline materials. Ne was determined by plasma resonance wavelength from IR-spectra of diffusive reflection [6].

2. Materials and methods

On the basis of EPR, X-ray diffraction and differential thermal analysis the phase formation regularities were established in In-Sn-O system in dependence on starting solutions type, medium pH value, doping addition (tin) concentration, temperature and annealing time. It was shown that independently on used reactants nature the closest interaction of co-precipitating hydroxides takes place in the medium with pH = 6-8 (figure 1).



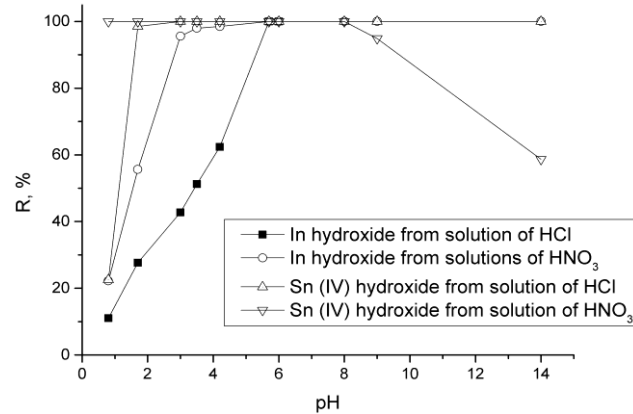


Figure 1. The dependence of a degree sedimentation R on pH of solutions

Co-precipitation products annealing leads to the formation In_2O_3 defect structure of cubic modification with enlarged interplanar distances in comparison to standard values, or two-phase mixture of this phase and tin oxide of tetragonal modification is formed (figure 2, 3, 4).

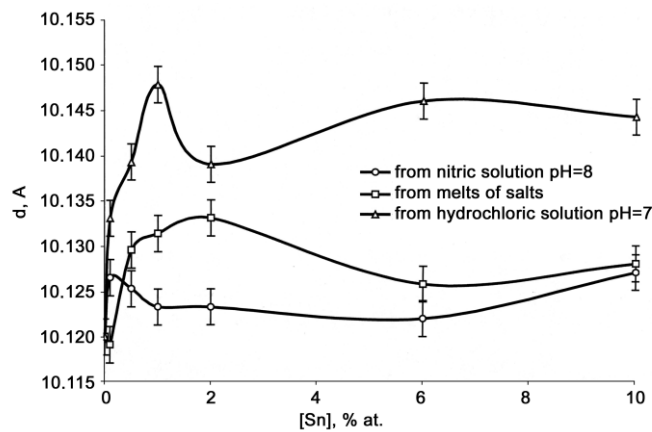


Figure 2. Lattice parameter change in indium oxide as a function of tin content ($T=800\text{ }^\circ\text{C}$)

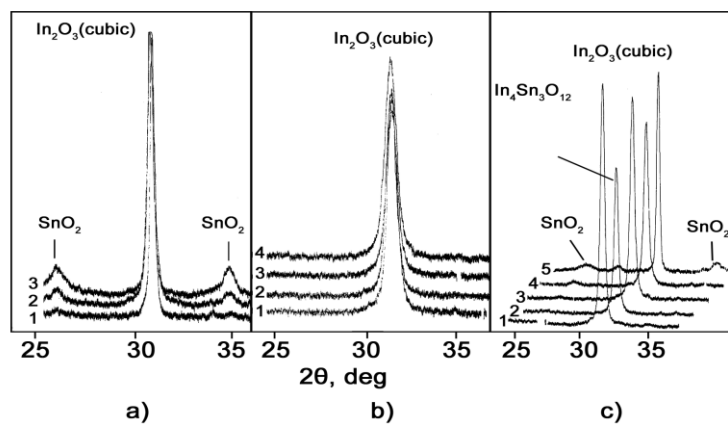


Figure 3. X-ray diffractograms of ITO materials from HCl solutions (a, b) and melts of salts (c) containing 1-1, 2-2, 3-6, 4-10 atom % tin at different temperatures: a, b-900 °C, c-1100 °C

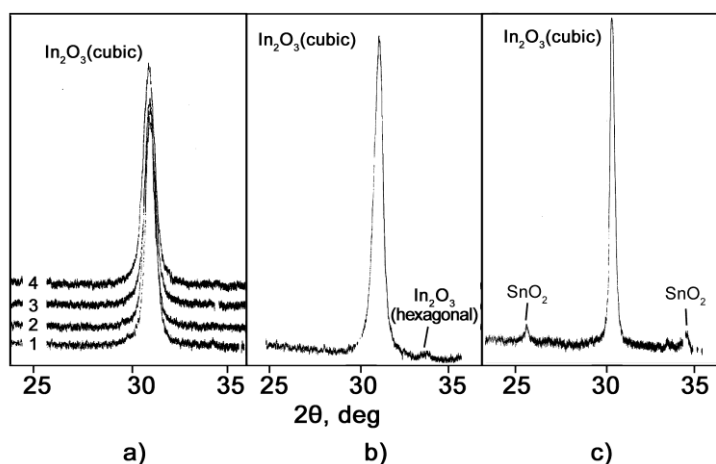


Figure 4. X-ray diffractograms of ITO materials from HNO₃ solutions containing 1-1, 2-2, 3-6, 4-10 atom % tin at different temperatures: a, b- 900 °C, c-1100 °C

3. Results and discussion

The dependence of the change of free electrons concentration on content of tin in indium and tin oxide (ITO) materials was established (table 1, 2).

Table 1. The electron concentration as a function of tin content in ITO materials prepared from different reagents at T = 900 °C and pH = 7.

reagents	C _{Sn} , at. %							
	0.1	0.5	1	2	4	6	10	14
InCl ₃ SnCl ₄ NH ₄ OH	2.6	2.6	2.3	2.2	2.1	2.1	2.1	2.0
In(NO ₃) ₃ Sn(NO ₃) ₂ NH ₄ OH	1.5	1.7	2.1	2.1	2.1	2.1	2.1	2.1
In(NO ₃) ₃ Sn(NO ₃) ₂	0.5	0.9	1.1	1.2	1.2	1.3	1.3	1.4

Table 2. The electron concentration as a function of heat treatment temperature and tin content in ITO materials.

C _{Sn} , at. %	Temperature of heat treatment, °C				
	300	500	700	900	1000
0.1	2.3	1.6	1.6	2.6	2.6
0.1*	1.7	1.5	1.6	2.3	2.6
2.0	1.1	1.2	1.7	2.3	2.4
10.0	0.7	0.9	2.1	2.1	2.1
10.0*	0.8	1.0	2.1	2.1	2.1

Note: * Samples were kept at this temperature for 60 min

The formations of ITO thus, occurs, apparently, at removal of NO₃⁻ ions, which as determine, from IR-spectrum of co-precipitation In(III) and Sn(IV) hydroxides (figure 5), and the products of their thermal decomposition - nitrogen-containing radicals of a different composition, about that the occurrence on curves DTA for nitrate system of several endothermic peaks (figure 6c) testifies. For systems obtained by zol-gel method from hydrochloric and nitric solutions (figure 6a, 6b) the

endothermic peaks on curves DTA relates to evaporation of water and decomposition of indium hydroxides. Endothermic peak on 380 °C (figure 6 b) relates to removal of NO_3^- ions.

According to EPR data the basic intermediate product of thermal decomposition of NO_3^- -ions stabilized in forming structure of an indium oxide are the radicals NO_2 . They formed in the greatest amount after heat treatment at 400 °C. Probably, the formation of nitrogen-containing radicals NO_2 is accompanied by removal of oxygen from the system and, hence, by great deviation from stoichiometry in structure of indium oxide, it results in occurrence of hexagonal modification In_2O_3 at 400 °C. The presence of NO_2 attaches some amorphism to structure of cubic In_2O_3 , it results in low values of Ne (figure 7, 8). The spectrum EPR disappears after heat treatment at 600 °C.

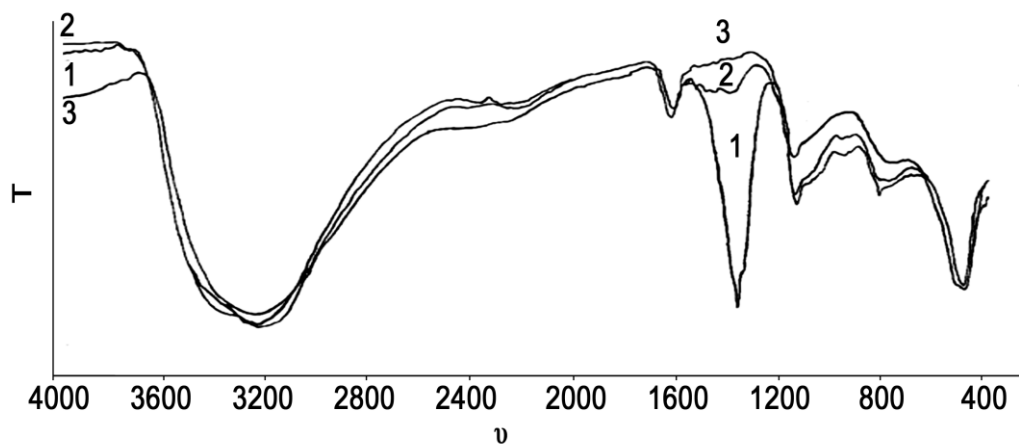


Figure 5. IR absorption spectrum of co-precipitation products from hydrochloric (3) and nitric (1, 2) solutions, where heated at 50 °C, after hot (2) and cold (1) washing procedure

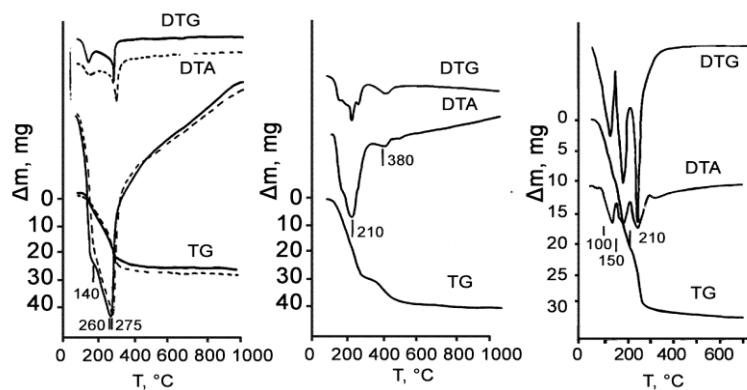


Figure 6. Curves of DTA, TG, DTG for ITO from:
a- hydrochloric solution, b -nitric solution, c - melts of salts

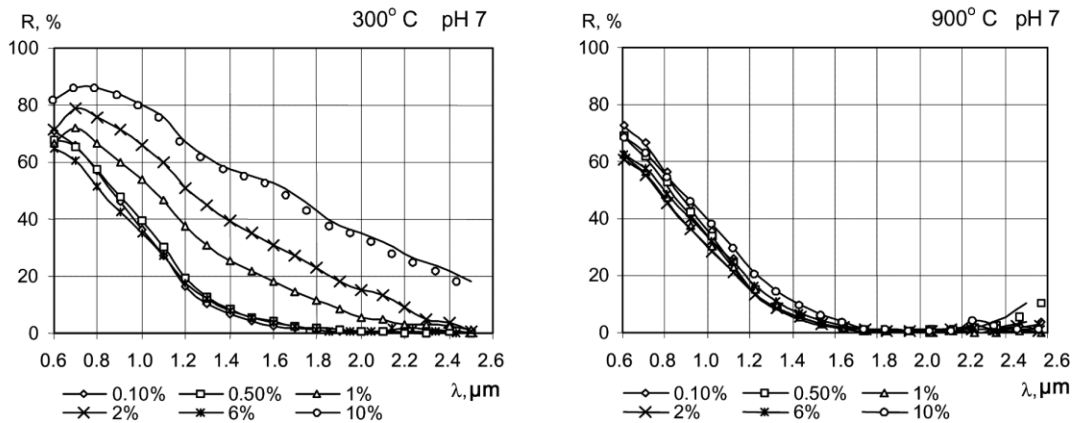


Figure 7. Reflectance spectrum of ITO materials prepared from hydrochloric solutions at different temperature and tin content

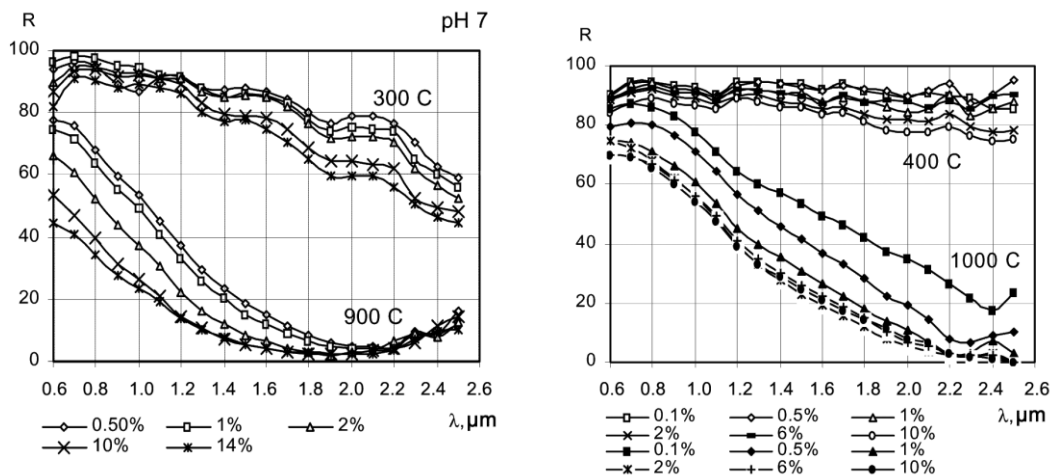


Figure 8. Reflectance spectrum of ITO materials prepared from nitric salts melts (a) and solutions (b) at different temperature and tin content

4. Conclusion

We studied the electronic and spectral properties for ITO material obtained under different conditions of solid phase synthesis. It is shown the upper bounds of mobile electrons concentration are achieved for materials obtained from chloride solutions. At temperatures up to 600 °C a decisive contribution to the concentration of free charge carriers makes oxygen deficiency of the crystal structure of indium oxide doped with tin, while at higher temperatures, is a determining factor is the concentration of the dopant. The ligation efficiency of indium tin oxide, is greatly reduced with increasing tin concentration higher than 1 at. %.

Acknowledgement

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References

- [1] Schmid G, Bumle M, Geerkens M, Heim I, Osemaun C and Sawitowski T 1999 *Chem. Soc. Rev.* **28** 179
- [2] Jikang Y, Wanxia T, Erxin N, Guoyou G, Gang Y, Zhe S, Jinghong D, Jiamin Z, Yichun L and

- Jia-Hong Y 2014 *Adv. Mater. Res.* **833** 61
- [3] Gary C, Goosey, Marti 2009 Materials used in manufacturing electrical and electronic products n *Environmental Science and Technology*, 27 (Electronic Waste Management), 40-74
- [4] Hanafi Z M, Hammad F F and Youssef A M 2009 Preperation and effects of temperature on nanocrystalline ITO particles synthesized by CO-precipitation with different SnO₂ content *Canadian Journal of Pure and Applied Sciences* **3 2** 839-845
- [5] Psuja P, Hreniak D, Strek W 2009 The influence of sintering temperature and Sn⁴⁺ concentration on electrical and optical properties of ITO nanocrystallites, *Journal of Physics: Conference Series* **146** 012012
- [6] Hadj Tahar R B, Ban T, Ohya Y and Takahashi Y1997 *J. Appl. Phys.* **83/4** 2139