Influence of light on electrophysical properties of thin films of mixed zinc and tin oxides

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Abstract. In this work, we studied structural and the electrical properties of thin films of mixed zinc and tin oxides obtained by low-temperature pyrolysis. XRD analysis shows that the obtained films contain phases of zinc oxide and tin dioxide and have nanocrystalline structure with crystallite size about 10-17 nm. A significant effect of daylight on the temperature dependences of the film resistance was established. The temperature dependences of the resistance of ZnO-SnO\textsubscript{2} films, measured in the range from room temperature to 300 °C, show the difference between the heating and cooling curves, that can be explained by two competing processes - thermal activation mechanism of conductivity and adsorption-desorption of oxygen particles on the surface of the oxide film. Using the slope of the linear section on the plots, we calculated the activation energy of conductivity, which amount is 0.7 and 1.1 eV for the samples with the different Zn:Sn ratio.

1. Introduction
Improving the efficiency of converting solar energy into electrical energy is one of the urgent tasks of our time. Currently, silicon-based solar cells are most widely used but materials based on zinc, tin oxides are also used [1]. Indium-tin oxides (ITO) as transparent conductive oxide has some disadvantages for use in electrical devices because of high cost and poor chemical stability. The nanosized films of zinc oxide, as well as films based on it, doped with various compounds, are transparent, have low resistance, are well compatible with other active semiconductor materials, which makes possible to actively use them as electrodes in solar modules [2, 3]. As electrical properties of ZnO strongly depends on stoichiometric and may vary under ambient oxygen [4], doping of ZnO films with various metals (Al, Ga, Sn) is used to improve it. Sn is the most suitable dopant for ZnO because Zn and Sn have similar ionic radii [5].
Two-component oxide system ZnO–SnO₂ has good electrical conductivity, high optical transmittance, good chemical stability. It can be used in a variety of applications such as energy conversion, optical materials, sensors, catalysts, etc [6]. The ZnO–SnO₂ films can be formed by various methods: magnetron sputtering [7], pulsed laser deposition [8], a sol-gel technique [9]. Depending on the synthesis method, the resulting materials may have different physicochemical [10] and electrophysical properties [11], therefore, one of the pressing issues of modern research is the optimal choice of method and conditions for obtaining materials. In the framework of this work, we studied the properties of nanoscale zinc and tin oxides obtained by low-temperature pyrolysis. The chemical pyrolysis is an alternative technique to previously indicated methods with its simplicity and cheapness for the formation of films on large surfaces [12].

2. Experimental

2.1. Films formation
As the main precursors for the preparation of nanosized films of zinc and tin (IV) oxides, tin tetrachloride pentahydrate, zinc nitrate hexahydrate and organic acid were used; the molar ratios of zinc and tin were 99:1, 95:5, 5:95 and 1:99. The resulting compositions of organic salts were dissolved in an organic solvent, applied to purified ceramic alumina-based substrates, and dried in air at 100 °C. For the studied samples, 3 layers of a precursor solution were applied. Heat treatment of materials was carried out at 550 °C for one hour with an average heating rate of 10 deg/min.

2.2. Characterization
The surface morphology of the obtained films was characterized by scanning electron microscope (SEM) Nova Nanolab 600.

Structural properties of the synthesized materials were studied by X-ray diffraction (XRD) using ARL X'TRA diffractometer utilizing CuKα1-radiation with 35 kV and 30 mA.

To study the electrophysical properties of Ni, metal contacts with a thickness of 0.2–0.3 microns were formed on the films surface by vacuum thermal deposition. The temperature dependence of the resistance of the films upon heating to 300 °C and subsequent cooling was measured using Keithley 2450 sourcemeter.

3. Results and discussion
Analysis of microstructure, carried out by SEM (figure 1), exhibits that the film materials obtained by pyrolysis are uniform, dense, distribution occurs over the entire surface. The thickness of the three-layer film is about 90-100 nm.
Figure 1. SEM image film ZnO-SnO$_2$ (99:1 in solution).

XRD analysis (figure 1) confirmed that the obtained films contain phases of zinc oxide and tin dioxide. No additional diffraction peaks were detected in the XRD patterns, indicating that thin films yield pure phase. It was shown, that obtained materials contain single-phase, hexagonal wurtzite structure ZnO according to Crystallography Open Database, COD ID 2300113 [13] (figure 1a) and single-phase tetragonal cassiterite SnO$_2$ structure (figure 1b) according to Crystallography Open Database, COD ID 1521419 [14]. The presence of diffraction peaks along different planes indicates that the films nanocrystalline structure is growing in different directions. It was found that signals on the XRD patterns are expanded, which is typical for nanocrystalline materials.

Figure 2. XRD patterns of ZnO-SnO$_2$ films: (a) 1 – film with Zn:Sn ratio 99:1, 2 – ZnO phase COD ID 2300113; (b) 1 – film with Zn:Sn ratio 1:99, 2 – SnO$_2$ phase COD ID 1521419.

The mean crystallite size $D$ was evaluated according to the broadening of the highest intensity peak diffraction plane using the Scherrer equation [15]

$$D = \frac{k\lambda}{\beta \cos \Theta}$$
where $k$ is the shape factor ($k=0.9$), $\lambda$ is the X-ray wavelength ($\lambda = 0.1540562$ nm), $\beta$ is the full width at the half maximum of the diffraction line and $\Theta$ is the diffraction angle. The values of $\beta$ and $\Theta$ are taken for crystal plane (110) and (101) of the SnO$_2$ cassiterite phase and ZnO wurtzite phase, respectively [16]. According to the Sherrers equation, the particle size is about 10-17 nm.

The resistance dependence of the formed structures on the reverse temperature is shown in figure 3. Those dependences were measured after exposure to daylight and after exposure to darkness for 24 hours.

It can be seen that the effect of light on the film resistance is more pronounced for the sample with a ZnO:SnO$_2$ ratio of 99:1. The nonlinearity of the presented dependences may indicate that the influence of adsorption-desorption processes on the surface of the films is superimposed on the thermal activation mechanism of conductivity.

It is seen that during heating, the resistance of all samples first increases, then, in the temperature range 80-180 $^\circ$C, a change in the nature of the temperature dependence of the resistance is observed - a smooth transition through the maximum occurs. The increase in resistance during heating can be explained by the effect of adsorbed oxygen. Oxygen molecules in the atmosphere are adsorbed on the oxide surface and become negatively charged due to the capture of electrons from the surface ZnO layers [17]. This leads to the formation of a depletion layer in the surface region of the film and a decrease in its conductivity. As the temperature rises, the thermal generation of carriers begins to exert an increasing influence on the resistance of the material, and the character of conductivity changes.

With further heating from 180 to 300 $^\circ$C, a linear section is observed. This region of the temperature dependence of the resistance is well approximated by the Arrhenius equation [18]:

$$\rho = \rho_0 \exp\left(\frac{E_a}{kT}\right),$$

where $\rho_0$ is the preexponential factor, $E_a$ is the activation energy of conductivity and $k$ is Boltzmann constant. The activation energy calculated for samples with Zn:Sn ratio 5:95 and 95:5 is 0.7 eV and for samples with Zn:Sn ratio 1:99 and 99:1 is 1.1 eV. Since for oxide semiconductors, the electrical conductivity is determined by intrinsic defects, primarily oxygen vacancies, this energy corresponds to the levels of these defects in the band gap of the semiconductor.
Figure 3. Resistance (R) dependences on reverse temperature \((1000/T)\) of \(\text{ZnO-SnO}_2\) films with the \(\text{Zn:Sn}\) ratio 1:99 (a), 5:95 (b), 95:5 (c) and 99:1. (1 – after light irradiation, 2 – after dark exposure; (––) – heating, (---) – cooling).

At temperatures below \(180^\circ\text{C}\), the heating and cooling curves do not coincide. This difference in the course of the curves may be due to the lack of desorption of molecular oxygen ions from the surface of the films.

Thus, the change in resistance during heating and cooling is due to two competing processes - thermal generation and electron recombination on the one hand, and their capture by oxygen adsorbed on the surface on the other. Moreover, if in the first case, the equilibrium concentration is established almost instantly, then in the second it depends on the rate of the processes of adsorption and desorption. The difference in the heating and cooling curves in the temperature dependence of the resistance indicates low rates of these processes, comparable with the rates of heating and cooling.

4. Conclusions
The thin films of mixed zinc and tin oxides obtained by low-temperature pyrolysis contain phases of zinc oxide and tin dioxide and have nanocrystalline structure with crystallite size about 10-17 nm. A significant effect of daylight on the temperature dependences of the film resistance has been established. The temperature dependences of the resistance of \(\text{ZnO-SnO}_2\) films, measured in the range from room temperature to \(300^\circ\text{C}\), show the difference between the heating and cooling curves, that can be explained by two competing processes - thermal activation mechanism of conductivity and adsorption-desorption of oxygen particles on the surface of the oxide film. Thus, taking into account the effects found, the synthesized films of zinc and tin oxides can be recommended for use in the functional elements of alternative energy.

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