

## Peculiarities of using nanomaterials based on $\text{SiO}_2\text{-SnO}_2\text{-In}_2\text{O}_3$ as sensitive elements of vacuum sensors

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**Abstract.** Experimental data on the use of nanomaterials based on  $\text{SiO}_2\text{-SnO}_2\text{-In}_2\text{O}_3$  as sensitive elements of vacuum sensors are presented. It is shown that the sensory response of a three-component system under consideration is determined by the mass fraction of indium oxide. It was determined that depending on the content of  $\text{In}_2\text{O}_3$  the nanomaterials under study can be characterized by a decrease and an increase in resistance when the pressure is reduced lower than atmospheric one. The mechanisms that potentially correspond to the observed phenomenon are considered.

Recently, multicomponent systems based on combinations of various wide band gap oxides, such as  $\text{SnO}_2$ ,  $\text{In}_2\text{O}_3$ ,  $\text{ZnO}$ ,  $\text{TiO}_2$ ,  $\text{VO}_2$ , etc., have been of considerable interest for researchers and developers in the field of nanoelectronics [1]. In general, there is a common tendency, according to which the transition from the use of individual oxides to the use of their compound compositions is fixed. It is due to the need for nanomaterials and devices based thereof, having a complex of properties, which is not possible to ensure with the use of the only oxide [2].

For example, for  $\text{SnO}_2$  being widely used in the field of gas sensors, the selective detection of reducing gases or oxidizers, which ensure the preservation of a high sensory response, is still an unsolved problem. At the same time, the known approaches, based on variations of surface morphology and operating temperature of the gas sensitive layer, catalytic additions and creation of conditions for the spillover effect, have a significantly limited range of fundamental and applied applications [3]. In particular, a significant difficulty is the separation of the signal due to the presence of atmospheric humidity and the concentration variation of the controlled reducing gas (for example, ethanol, ammonia vapors, etc.) [4].

There are also significant difficulties in the field of photocatalytic applications that cannot be overcome with the use of individual oxides. For example,  $\text{TiO}_2$  and  $\text{ZnO}$ , being promising materials for photocatalysts, are only effectively activated by UV radiation and have very weak activity in the visible range [5], having a significant fraction of the solar spectrum. In this case, the known ways for expanding the operating wavelength range, based, for example, on the formation of defects in the crystal lattice of titanium dioxide, are inevitably accompanied by the appearance of synergistically interrelated effects, for example, by the rapid degradation of photocatalytic activity.



Similar difficulties arise in a number of other fields, where the use of wide band gap semiconductor oxides is already classical. For example, the creation of high-quality transparent conducting coatings having a high transmittance and a low resistivity is a complex task using only a single-component system. However, it can be easily solved using oxide compositions, as it has been shown, for example, for ITO [6].

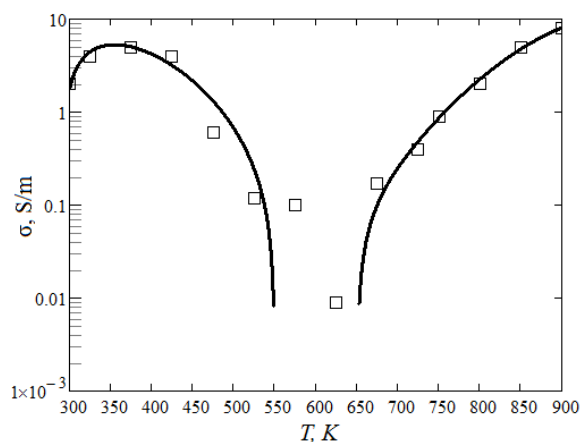
The use of multicomponent systems based on wide band gap oxides allows solving the indicated problems to some extent. For example, in the field of gas sensors, the use of two- and three-component oxide systems allows to significantly improve the selectivity, and to reduce the influence of air humidity [7]. In the field of photocatalytic applications, the use of oxide compositions provides not only an expansion of the operating spectral range, but also increases the activity in the field of UV radiation in a number of cases [8].

As for the issue on measuring the pressure below atmospheric, nanomaterials based on individual ZnO [9] and VO<sub>2</sub> oxides [10], a two-component system of SiO<sub>2</sub>-SnO<sub>2</sub> [11] and a three-component system of SiO<sub>2</sub>-SnO<sub>2</sub>-ZnO [12] have proven to be useful. However, this field of research and development has a number of difficulties, and in general, the peculiarities of using nanomaterials based on wide band gap semiconductor oxides as sensitive elements of vacuum sensors have not been fully studied. In particular, the mechanism of the sensory response of such nanomaterials to variations of the vacuum level is not clear until now, wherein in the majority of works the dominating role of adsorption/desorption of oxygen processes is assumed [13].

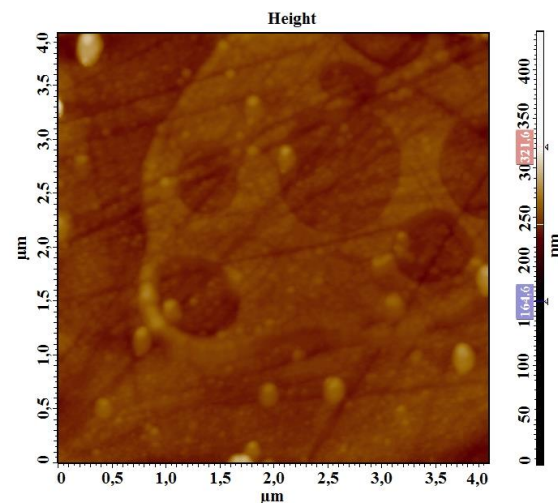
The purpose of this work is to expand the spectrum of materials potentially suitable for measuring the pressure below atmospheric, and to study the three-component system SiO<sub>2</sub>-SnO<sub>2</sub>-In<sub>2</sub>O<sub>3</sub> within the framework of this aspect. Synthesis of the analyzed nanomaterials was carried out in the framework of the sol-gel technology methods using the following precursors: tetraethoxysilane (Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>), tin (II) chloride dehydrate (SnO<sub>2</sub>·2H<sub>2</sub>O), 4,5-aqueous indium nitrate (In(NO<sub>3</sub>)<sub>3</sub>·4,5 H<sub>2</sub>O), wherein hydrochloric acid being used as a catalyst, and ethanol as a solvent. The mass fraction of tin dioxide for all experimental samples was 50 wt. %, and the content of indium oxide varied from 5 to 15 wt. %. Nanomaterials were formed on substrates made of monocrystalline oxidized silicon of 5x5 mm<sup>2</sup>; annealing was carried out at a temperature of 600 °C in the air. Contact pads were made using silver conductive adhesive.

The choice of the three-component system SiO<sub>2</sub>-SnO<sub>2</sub>-In<sub>2</sub>O<sub>3</sub> as an object for investigation is due to the presence of primary experimental data demonstrating the significant contribution of oxygen to the change of its resistance. Figure 1 shows the temperature dependence of the conductivity of the studied nanomaterials, obtained in dry air. The studied samples were placed in a muffle furnace together with silica gel to reduce the effect of water adsorption on their surface; the sample was subjected to temperature control for 10 minutes before each subsequent measurement.

The analysis of the dependence shown in figure 1 shows the presence of a maximum in the low-temperature region of 300–400 K, a deep minimum in the range of 550–650 K, and a sharp increase of conductivity in the high-temperature region of 700–900 K. Such temperature dependence of the conductivity is apparently determined by various forms of oxygen chemisorbed on the surface and in the volume of the three-component system SiO<sub>2</sub>-SnO<sub>2</sub>-In<sub>2</sub>O<sub>3</sub>. In the low-temperature region, oxygen has dominant influence in the form of O<sup>2-</sup>, and in the high-temperature region in the form of O<sup>·</sup>. Simultaneous existence of O<sup>2-</sup> and O<sup>·</sup> corresponds to the minimum of specific conductivity, the contribution from which is summed, and the nanomaterial is maximally depleted by the main charge carriers. The role of indium oxide in the three-component system under consideration is most likely reduced to an increase of the grouping stability of the Lewis type center (a metal ion with chemisorbed oxygen). The introduction of this oxide into a two-component system of SiO<sub>2</sub>-SnO<sub>2</sub> in low concentrations leads to the formation of a solid solution, and the limiting value of the solubility essentially depends on the defectiveness of the initial tin dioxide. There is a segregation of In<sub>2</sub>O<sub>3</sub> in the form of an island structure (figure 2) at its high concentration.



**Figure 1.** Temperature dependence of conductivity of nanomaterials based on  $\text{SiO}_2\text{-SnO}_2\text{-In}_2\text{O}_3$  in dry air.



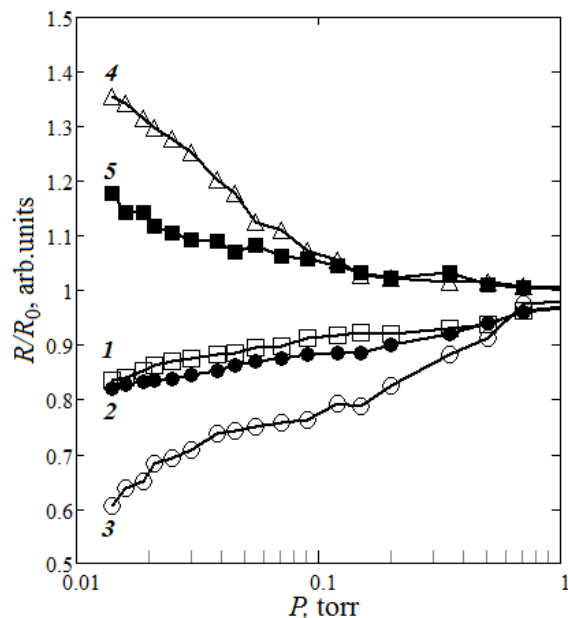
**Figure 2.** An AFM image of the surface morphology of nanomaterials based on  $\text{SiO}_2\text{-SnO}_2\text{-In}_2\text{O}_3$  with a high concentration of indium oxide.

Such a character of the interaction of the investigated nanomaterials with atmospheric oxygen and the concentration features of indium oxide additions determine the sensory response of the system under consideration to a decrease of pressure below atmospheric. Figure 3 shows a relative change in resistance ( $R/R_0$ ) of sensitive elements of vacuum sensors based on nanomaterials of  $\text{SiO}_2\text{-SnO}_2\text{-In}_2\text{O}_3$  composition as a function of pressure. The measurement was carried out using a multimeter Mastech MS8229 when applying constant voltage in 1 B to the sample. The pressure inside the vacuum chamber was fixed by a calibrated gauge thermocouple head. An analysis of the obtained experimental data shows that, depending on  $\text{In}_2\text{O}_3$  content, the decrease (curves 2 and 3), and the increase of resistance with decreasing pressure below atmospheric (curves 4 and 5) can be characteristic for the system under study. In this case, the mass fraction of indium oxide determines not only the form of the presented dependences, but also the value of the sensory response, which can be calculated from the formula:  $S = |1 - R/R_0| \cdot 100\%$ , where  $R_0$  is the initial resistance at the pressure chosen as the reference point;  $R$  is the resistance of the sample for a given value of the measured pressure.

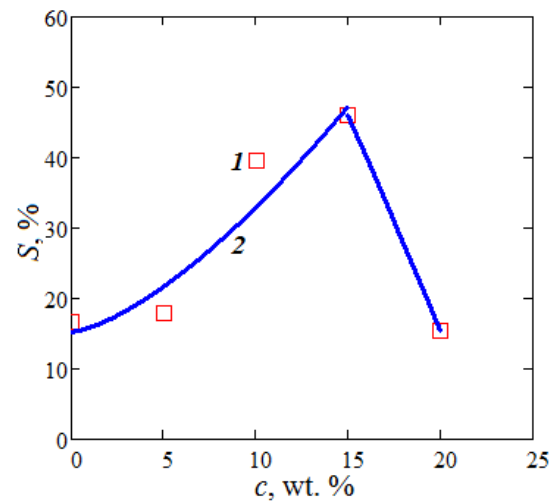
Figure 4 shows the dependence of the sensory response of the sensitive elements of the vacuum sensors based on the three-component oxide system  $\text{SiO}_2\text{-SnO}_2\text{-In}_2\text{O}_3$  on the mass fraction of  $\text{In}_2\text{O}_3$  ( $R_0$  was estimated at a pressure of 0.014 mm Hg, and the initial samples were not subjected to additional heating). The analysis of the presented dependencies shows that the introduction of a small amount of indium oxide into a two-component system based on  $\text{SiO}_2\text{-SnO}_2$  leads to a significant increase of the sensory response of the nanomaterials under study. At the same time, samples containing 15 wt. % of  $\text{In}_2\text{O}_3$  have the maximum sensitivity to the change of pressure. A further increase in the mass fraction of indium oxide leads to a sharp decrease of the sensory response (curve 5 in figure 3). This circumstance has several possible explanations, however, the fundamental role, apparently, is assigned to the structural and morphological changes of the nanomaterials under consideration.

The sensory response of the three-component oxide system  $\text{SiO}_2\text{-SnO}_2\text{-In}_2\text{O}_3$  at low  $\text{In}_2\text{O}_3$  concentrations is explained by the dominant contribution of oxygen in the form of  $\text{O}^{2-}$ , the existence of which on highly defective surfaces is possible over a wide range of temperatures. Decrease of pressure below atmospheric leads to desorption of oxygen from the surface and from the volume of nanomaterials, as a result of which the electrons return to the conduction band, providing a decrease in resistance (curves 2 and 3 in figure 3). A large  $S$  value characteristic for the samples of  $\text{SiO}_2\text{-SnO}_2\text{-In}_2\text{O}_3$  compared to the two-component system based on silicon dioxide-tin dioxide is due to the growth of the stability of the grouping type of the Lewis center.  $\text{In}^{3+}$  cations are stronger Lewis centers than

$\text{Sn}^{4+}$  ions, which determine the increase in the concentration of all forms of the adsorbed oxygen. In this case, the low-temperature form of  $\text{O}^{2-}$  becomes loosely bound, and is easily desorbed as the pressure decreases below atmospheric pressure, which determines the growth of the sensory response.



**Figure 3.** Relative change in resistance of sensitive elements of vacuum sensors based on three-component oxide system  $\text{SiO}_2\text{-SnO}_2\text{-In}_2\text{O}_3$  with different mass fraction of indium oxide: 1 – the sample does not contain  $\text{In}_2\text{O}_3$ ; 2 – 5 wt. %; 3 – 10 wt. %; 4 – 15 wt. %, 5 – 20 wt. % of  $\text{In}_2\text{O}_3$ .



**Figure 4.** Dependence of sensory response of sensitive elements of vacuum sensors based on three-component oxide system  $\text{SiO}_2\text{-SnO}_2\text{-In}_2\text{O}_3$  on the mass fraction of indium oxide: 1 – experimental data; 2 – approximation.

An atypical action of wide band gap semiconductor oxides is characteristic for high concentrations of indium oxide in a three-component system based on  $\text{SiO}_2\text{-SnO}_2\text{-In}_2\text{O}_3$  consisting in the growth of resistance with decreasing ambient pressure. It cannot be explained explicitly from the position of adsorption/desorption of oxygen, and requires consideration of additional mechanisms responsible for the sensory response, for example, the interaction of nanomaterials with atmospheric moisture. An explanation of such mechanisms is the subject of a separate study. It can be assumed that the formation of small  $p$ - $n$  transitions at the  $\text{SnO}_2/\text{In}_2\text{O}_3$  boundary, which arise as a result of the segregation of indium oxide in the form of an island structure, will play a significant role in the observed phenomenon.

Thus, the peculiarities of using nanomaterials based on  $\text{SiO}_2\text{-SnO}_2\text{-In}_2\text{O}_3$  as sensitive elements of vacuum sensors are considered. It is shown that depending on the mass fraction of indium oxide the nanomaterials under study can be characterized both by a decrease and an increase in resistance with decreasing pressure below atmospheric. Proceeding from the formation of a stable grouping of the Lewis type center, the growth of the sensory response of a three-component system with a low content of  $\text{In}_2\text{O}_3$  is explained.

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