Gas-Sensing Properties of Thin Films Grown on the Surface of InP Single Crystals by Thermal Oxidation

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Abstract—Thin nanofilms have been grown on the surface of single-crystal InP wafers using PbO + V_2O_5 mixtures in the gas phase. The oxide mixtures used as chemical stimulators have been shown to accelerate the thermal oxidation of InP. The resultant films exhibit gas-sensing properties for ammonia (concentration of 140 ppm) and carbon monoxide (95 ppm). The highest gas sensitivity is near 1.2 arb. units, at temperatures in the range 200–240°C.

INTRODUCTION

Chemical gas sensors based on nanocrystalline metal oxide semiconductors are currently the most promising solid-state gas detectors because they offer high reliability and are easy to fabricate. Tin dioxide-based gas-sensing films have been manufactured for a rather long time and possess satisfactory characteristics [1–4].

Nevertheless, there is an ongoing search for new materials suitable as basic components of semiconductor gas sensors. At present, research effort is concentrated on oxides such as In_2O_3, ZnO, and Ga_2O_3. In_2O_3 possesses high sensitivity, fast response, a convenient working resistivity range, and a rather low temperature for detection of oxidizing and reducing gases in air. There is ample evidence that the high surface oxygen mobility characteristic of indium oxide plays a decisive role in its exceptional gas-sensing properties. Its gas-sensing response is due to an adsorption competition mechanism: oxygen displacement from the surface and subsequent adsorption of gas molecules of interest on active In_2O_3 centers [5–11]. Not only thin films of undoped indium oxide but also those doped with various metals can be used as a gas-sensing layer, which improves the selectivity and stability of the sensor material.

One way of producing thin semiconductor films on semiconductor surfaces is chemically stimulated thermal oxidation [12]. The use of additional compounds—chemical stimulators—in semiconductor oxidation processes makes it possible to simultaneously accelerate the film growth process on the semiconductor surface and dope the film. This approach to the preparation of thin gas-sensing layers was shown to be very effective in the case of GaAs [13, 14]. The chemically stimulated thermal oxidation of semiconductors with the participation of oxide compounds has a number of advantages: the possibility of doping thin films directly during the film growth process (with variations in both the dopant and doping level); the simple procedure, and, as a consequence, relatively cheap apparatus; and the short time needed for obtaining the desired material.

The purpose of this work was to grow gas-sensing nanofilms on the surface of InP in the presence of a mixture of PbO and V_2O_5 as chemical stimulators.

EXPERIMENTAL

We studied thin films grown on the surface of indium phosphide wafers (FIEO, ⟨100⟩ orientation, 300-K concentration of majority carriers no lower than 5×10^{16} cm^{-3}, intrinsic *n*-type conductivity) in the presence of PbO + V_2O_5 mixtures in the gas phase. InP was oxidized at 500 and 550°C for 10, 20, 30, 40, 50, and 60 min at a constant oxygen flow rate of 30 L/h in a 30-mm-diameter horizontal quartz reactor placed in an MTP-2M-50-500 furnace. Prior to thermal oxidation, the InP wafers were pretreated in an etchant with the composition H_2SO_4 (reagent grade, Russian Federation State Standard GOST 4204-77, 92.80%) : H_2O_2 (extrapure grade, Russian Federation Purity Standard TU 6-02-570-750, 56%) : H_2O = 2 : 1 : 1. The etching time was 10 min. Next, the wafers were rinsed repeatedly in distilled water and dried in air. The temperature in the reactor was maintained constant (±1°C) by a TPM-10 meter/controller. The
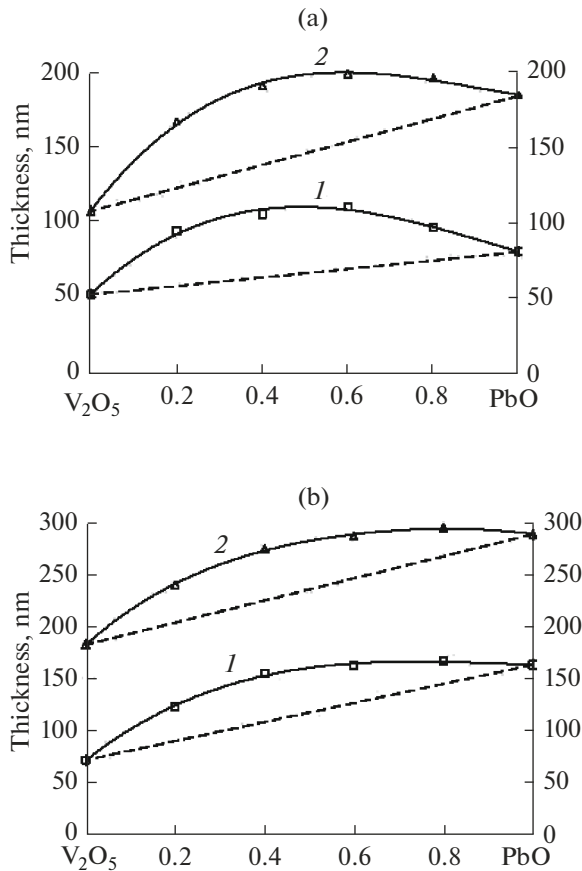
Fig. 1. Composition dependences of the thickness of the oxide layer grown on the surface of InP by oxidation at (a) 500 and (b) 550°C for (*1*) 10 and (*2*) 60 min. The dashed lines represent additive behavior.

Fig. 2. Composition dependences of the relative increase in oxide film thickness on InP at 550°C with respect to stimulator-free thermal oxidation: oxidation time of (*1*) 10 and (*2*) 60 min.

spacing between the surface of the mixture of the chemical stimulators and the semiconductor wafer surface was maintained constant at 10 mm under all thermal oxidation conditions. The thickness of the resultant oxide films was determined using an LEF-754 laser ellipsometer $\lambda = 632.8$ nm) with an absolute uncertainty of ± 1 nm.

The composition and structure of the films growing on the InP surface was determined by infrared (IR) spectroscopy [15] (Vertex 70 spectrophotometer), X-ray microanalysis [16] (JEOL JSM-6510LV equipped with a Bruker energy dispersive X-ray microanalysis system), and atomic force microscopy (AFM) [17] (Solver P47 Pro).

As a working parameter of the semiconductor films, we used their resistivity. On the one hand, this parameter is rather easy to accurately measure. On the other, it is sufficiently informative because it responds to even slight changes in gaseous analyte concentration.

The resistivity of the oxide films was measured by the four probe van der Pauw method using a TsIUS-4 system. Its technical characteristics enabled measure-
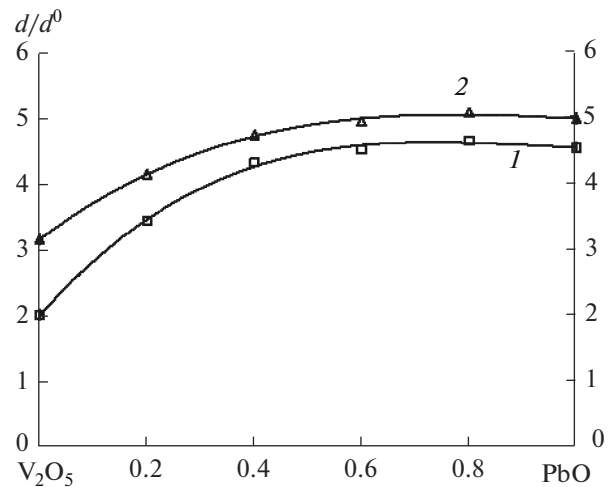
ments in the range $R_s = 10.1$ to 105 $\Omega/\square$ with an accuracy of $\pm 4.5\%$. The gas sensitivity of the films was assessed by a known technique [1], as the ratio of the resistivity of the film in pure air (R_v) to that in the gas mixture under study (R_g): $S_g = \dfrac{R_v}{R_g}$. In our resistivity measurements, the ambient humidity was 55% and the measurements were made in a stationary system. The gaseous analytes were CO (concentration of 95 ppm) and NH_3 (concentration of 140 ppm).

RESULTS AND DISCUSSION

Figure 1 shows composition dependences of the thickness of the oxide film grown on the surface of InP in the presence of mixtures of PbO and V_2O_5 chemical stimulators at different process durations and temperatures, and Fig. 2 shows the relative increase in oxide film thickness (acceleration) achieved with respect to the stimulator-free thermal oxidation of InP. It follows from Figs. 1 and 2 that PbO is a more effective chemical stimulator ($d_{max} = 280$ nm, increase in growth rate by a factor of 4.5 to 5) than is V_2O_5 ($d_{max} = 180$ nm, increase in growth rate by a factor of 2−3). PbO + V_2O_5 mixtures also increase the rate of InP surface oxidation relative to the stimulator-free process, with an essentially constant increase in growth rate in the case of the lead oxide-enriched mixtures, and only at 20% PbO in the mixture of the chemical stimulators does the increase in growth rate begin to drop markedly.

The dashed lines in Fig. 1 represent an additive variation of the oxide film thickness on the InP surface with the composition of the mixture of oxide chemical

Table 1. IR spectroscopy data for the oxide films grown on the surface of InP in the presence of PbO + V_2O_5 mixtures (550°C, 60 min)

Absorption band, cm^{-1}	Compound
430, 440, 620, 630	InP
541, 980	$InPO_4$
538	$Pb(PO_3)_2$
480	VO_2
565	In_2O_3
720	PbO

stimulators. The observed considerable positive deviations from additivity at all oxidation times and temperatures and at all mixture compositions point to particular synergistic effects in the system. Analysis of the present data leads us to the following conclusion: at a given temperature, increasing the oxidation time increases the positive deviation from additivity. At the same time, the data obtained at a given oxidation time and different temperatures demonstrate that, with increasing temperature, the positive deviation from additivity decreases, albeit only slightly.

To find out whether PbO and V_2O_5 become incorporated into the film growing on the InP surface and assess its qualitative and quantitative compositions, the synthesized samples were characterized by IR spectroscopy and X-ray microanalysis. We analyzed the same samples obtained using different mixtures: from 20% PbO + 80% V_2O_5 to 80% PbO + 20% V_2O_5. The oxidation temperature was 550°C and the oxidation time was 60 min. The IR spectroscopy results are summarized in Table 1 and the X-ray microanalysis data are presented in Table 2.

The IR spectra of the films show several characteristic transmission minima. According to previous work [15], the absorption bands at 565, 541, and 980 cm^{-1} correspond to the formation of In_2O_3 and $InPO_4$. Similar bands were observed in the case of stimulator-free oxidation of indium phosphide. In addition, the spectra contain bands characteristic of the oxides used as chemical stimulators and, more importantly, provide evidence for the formation of lead phosphides

(538 cm^{-1}). It is worth noting the absorption bands in the ranges 430–440 and 620–630 cm^{-1}, due to the background of the InP substrate. Thus, the present IR spectroscopy data indicate that the oxides used as chemical stimulators become embedded in the film growing on the InP surface and react with components of the substrate. All the components of the substrate are in an oxidized state, so that the films should be expected to have semiconducting or dielectric properties.

The X-ray microanalysis data support the IR spectroscopy results demonstrating that the chemical stimulators become embedded in the oxide film growing on the surface of InP. Attention should be paid to the considerable oxygen concentration in the films, which also correlates with the IR spectroscopy data showing that all the constituent components of the films are in an oxidized state. The percentage of oxygen in the films was evaluated from the experimentally determined In, P, Pb, and V contents as the balance to 100%. This assumption appears to be justified because the films were produced by oxidation in flowing oxygen. The presence of a considerable amount of phosphorus in the films strongly suggests that the thermal oxidation of InP under the effect of PbO + V_2O_5 mixtures helps to block the phosphorus oxide vaporization process, which should have an advantageous effect on the properties of the growing films. There is a direct correlation between the percentages of the chemical stimulators in the oxide mixtures and those in the films. It also should be noted here that the highest content of the chemical stimulators in the films on the surface of InP does not exceed 3%, which was shown by Lyson-Sypien et al. [18] to be necessary for ensuring gas-sensing properties.

Figure 3 shows AFM images of the films produced by oxidation under the effect of two compositions of PbO + V_2O_5 mixtures (having the highest content of PbO or V_2O_5). There are no drastic differences in structure or surface topography. The roughness height ranges from 15 to 25 nm. The surface is sufficiently uniform and has a grain structure with an average grain size near 40 nm; that is, the films can be thought of as nanostructured. Note also the somewhat larger roughness height and grain size in Fig. 3b, which is, in principle, consistent with the increase in film thick-

Table 2. X-ray microanalysis data for the samples obtained by the thermal oxidation of InP under the effect of PbO + V_2O_5 mixtures (550°C, 60 min, accuracy of ±1 at %; oxygen content found as the balance to 100%)

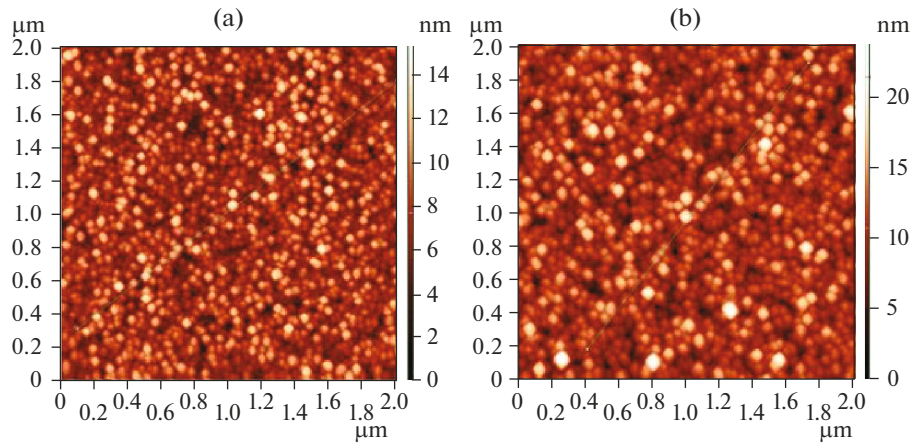| Mixture composition	Elemental composition of the films, at %				
	In	P	Pb	V	O
$(PbO)_{0.2}(V_2O_5)_{0.8}$	34.57	19.05	0.14	0.20	46.04
$(PbO)_{0.4}(V_2O_5)_{0.6}$	37.33	21.22	0.21	0.16	41.08
$(PbO)_{0.6}(V_2O_5)_{0.4}$	23.91	18.22	0.27	0.11	47.49
$(PbO)_{0.8}(V_2O_5)_{0.2}$	34.59	16.50	0.34	0.06	48.51

Fig. 3. AFM images of the films produced on the surface of InP by oxidation under the effect of (a) $(PbO)_{0.2}(V_2O_5)_{0.8}$ and (b) $(PbO)_{0.8}(V_2O_5)_{0.2}$ mixtures ($2 \times 2\ \mu m^2$ scan area).

ness with increasing lead oxide concentration in the mixtures.

Figure 4 shows temperature dependences of the sheet resistance (in the range 20–400°C) in air for the samples prepared by oxidation under the effect of the PbO + V_2O_5 mixtures. For characterization of gas-sensing properties, we chose the samples prepared by the thermal oxidation of InP at 550°C, because this temperature ensured larger oxide film thicknesses, which was expected to facilitate electrical transport measurements.
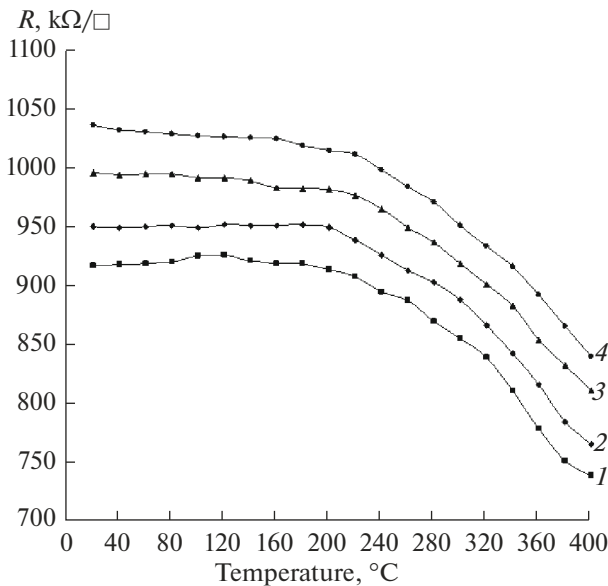
The data in Fig. 4 demonstrate a clear correlation between the composition of the chemical stimulator mixture and the resistance of the oxide film produced on the InP surface by oxidation under the effect of the mixture. The resistance increases with increasing PbO concentration in the films. Increasing the percentage of PbO in the mixture increases not only the thickness of the film on the InP surface but also the total content of the chemical stimulators in the films (Table 2), which is most likely responsible for the growth of high-resistivity films. Moreover, the IR spectroscopy data show that the films contain lead phosphide. Even
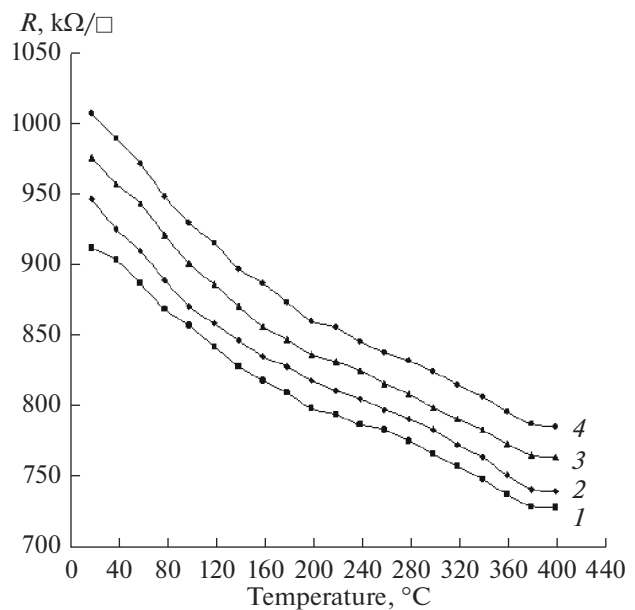

Fig. 4. Temperature dependences of sheet resistance in air for the films produced on the surface of InP by oxidation under the effect of the V_2O_5 + PbO mixtures: (*1*) 80% V_2O_5 + 20% PbO, (*2*) 60% V_2O_5 + 40% PbO, (*3*) 40% V_2O_5 + 60% PbO, (*4*) 20% V_2O_5 + 80% PbO.
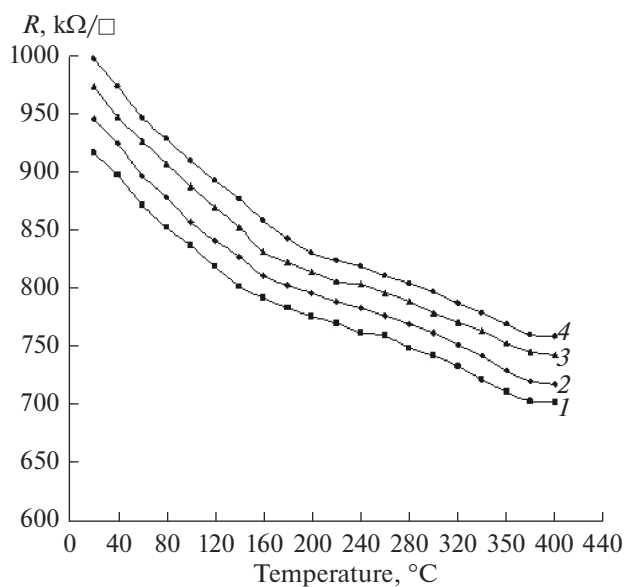
Fig. 5. Temperature dependences of sheet resistance for the films produced on the surface of InP by oxidation under the effect of the V_2O_5 + PbO mixtures and held in an atmosphere with a particular CO concentration: (*1–4*) same as in Fig. 4.

Fig. 6. Temperature dependences of sheet resistance for the films produced on the surface of InP by oxidation under the effect of the V_2O_5 + PbO mixtures and held in an atmosphere with a particular NH_3 concentration: (1–4) same as in Fig. 4.

Fig. 7. Temperature dependences of the sensor signal for the films produced on the surface of InP by oxidation under the effect of the V_2O_5 + PbO mixtures and held in an atmosphere with a particular CO concentration: (1–4) same as in Fig. 4, (4') 20% V_2O_5 + 80% PbO after ten heating–cooling cycles.

though no quantitative data on its concentration in the films were obtained, it is clear that it should increase with increasing lead concentration in the films, which can also cause an increase in resistivity. At the same time, the films retain semiconducting properties, as evidenced by the temperature variation of their resistivity.

Figures 5 and 6 show the measured sheet resistance of the films in the presence of CO and NH_3, and Figs. 7 and 8 show the corresponding sensor signal. The oxide films produced on the surface of InP under the effect of the V_2O_5 + PbO mixtures have a rather high sensitivity to carbon monoxide and ammonia. As follows from the above data, the temperature dependences of the sensor signal have extrema in the temperature range 200–240°C. In this temperature range, the sensor signal increases with increasing PbO concentration in the mixture, shifting to higher temperatures. Note that the peak of the CO sensing signal is located near 200°C, whereas that of the ammonia signal lies near 240°C, which suggests that the films have some selectivity for the gases in question. In all of the samples, the ammonia signal was stronger than the carbon monoxide signal, which was most likely due to the higher ammonia concentration in the mixture studied. To assess the stability of the sensor signal of the thin films grown on the surface of InP in the case of the composition corresponding to the strongest response, we investigated gas-sensing properties after ten heating–cooling cycles (Figs. 7, 8, curves 4'). These results lead us to conclude that the films have rather high stability. The reduction in sensor signal did not exceed 1%.
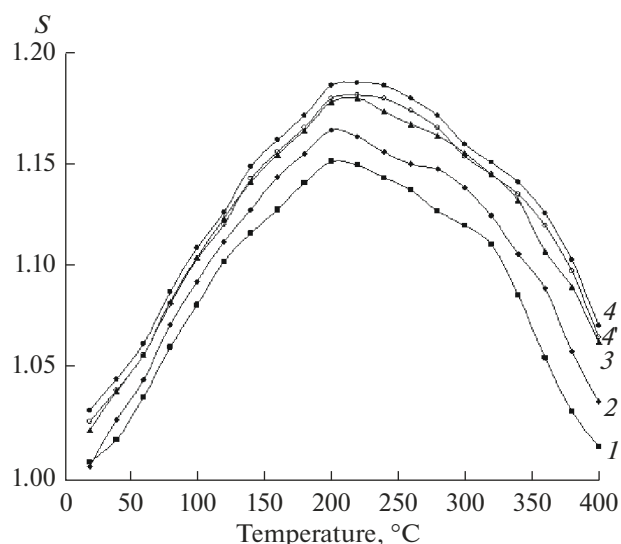
On the whole, the gas-sensing properties of the oxide films grown on the surface of InP are comparable to those of films grown on the surface of GaAs [14], but the response is slightly weaker (1.2 against 1.3). At the same time, such response values were obtained at considerably lower concentrations of the gaseous analytes:
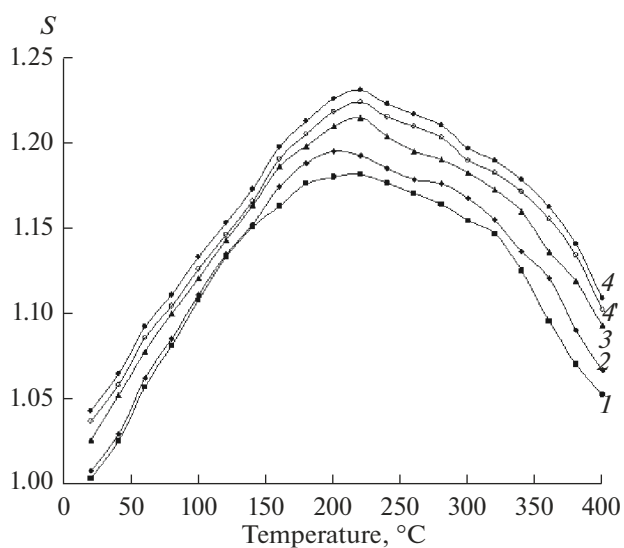

Fig. 8. Temperature dependences of the sensor signal for the films produced on the surface of InP by oxidation under the effect of the V_2O_5 + PbO mixtures and held in an atmosphere with a particular NH_3 concentration: (1–4) same as in Fig. 4, (4') same as in Fig. 7.

95 ppm against 120 ppm of CO and 140 ppm against 170 pm of NH_3.

CONCLUSIONS

Thus, $PbO + V_2O_5$ mixtures are effective chemical stimulators of the thermal oxidation of InP, ensuring an accelerated formation of a surface oxide film having NH_3 and CO sensing properties, with the strongest response to CO at 200°C and to ammonia at 240°C. The sensor responses obtained in this study are comparable to those of films on the surface of GaAs, at considerably lower concentrations of the gaseous analytes.

REFERENCES

1. Rembeza, S.I., Svistova, T.V., Rembeza, E.S., et al., The Microstructure and physical properties of thin SnO_2 films, *Semiconductors,* 2001, vol. 35, no. 7, pp. 762−765.

2. Lekshmy, S.S. and Joy, K., Structural and optoelectronic properties of indium doped SnO_2 thin films deposited by sol gel technique *J. Mater. Sci., Mater. Electron.,* 2014, vol. 25, no. 4, pp. 1664−1672. https://doi.org/10.1007/s10854-014-1781-x

3. Gas'kov, A.M. and Rumyantseva, M.N., Nature of gas sensitivity in nanocrystalline metal oxides, *Russ. J. Appl. Chem.,* 2001, vol. 74, no. 3, pp. 434−439.

4. Ohgaki, T. et al., Synthesizing SnO_2 thin films and characterizing sensing performances, *Sens. Actuators, B,* 2010, vol. 150, no. 1, pp. 99−104. https://doi.org/10.1016/j.snb.2010.07.036

5. Bloor, L.G., Manzi, J., and Binions, R., Tantalum and titanium doped In_2O_3 thin films by aerosol-assisted chemical vapor deposition and their gas sensing properties, *Chem. Mater.,* 2012, vol. 24, no. 15, pp. 2864−2871. https://doi.org/10.1021/cm300596c

6. Han, S.D. et al., Versatile approaches to tune a nanocolumnar structure for optimized electrical properties of In_2O_3 based gas sensor, *Sens. Actuators, B,* 2017, vol. 248, pp. 894−901. https://doi.org/10.1016/j.snb.2017.01.108

7. Miyata, T., Hikosaka, T., and Minami, T., High sensitivity chlorine gas sensors using multicomponent transparent conducting oxide thin films, *Sens. Actuators, B,* 2000, vol. 69, pp. 16−21. https://doi.org/10.1016/S0925-4005(00)00301-4

8. Chuang, M.J., Huang, H.F., Wen, C.H., et al., On the structure and surface chemical composition of indium−tin oxide films prepared by long-throw magnetron sputtering, *Thin Solid Films,* 2010, vol. 518, no. 8, pp. 2290−2294. https://doi.org/10.1016/j.tsf.2008.10.146

9. Elouali, S., Bloor, L.G., Binions, R., et al., Gas sensing with nano-indium oxides (In_2O_3) prepared via continuous hydrothermal flow synthesis, *Langmuir,* 2012, vol. 28, no. 3, pp. 1879−1885. https://doi.org/10.1021/la203565h

10. Singh, N., Yan, C., and Lee, P.S., Room temperature CO gas sensing using Zn-doped In_2O_3 single nanowire field effect transistors, *Sens. Actuators, B,* 2010, vol. 150, pp. 19−24. https://doi.org/10.1016/j.snb.2010.07.051

11. Lee, H., Song, J., Yoon, Y., et al., Enhancement of CO sensitivity of indium oxide-based semiconductor gas sensor through ultra-thin cobalt adsorption, *Sens. Actuators, B,* 2001, vol. 79, pp. 200−205. https://doi.org/10.1016/S0925-4005(01)00876-0

12. Mittova, I.Ya., Influence of the physicochemical nature of chemical stimulators and the way they are introduced into a system on the mechanism of the thermal oxidation of GaAs and InP, *Inorg. Mater.,* 2014, vol. 50, no. 9, pp. 874−881. https://doi.org/10.1134/S0020168514090088

13. Kostryukov, V.F. and Mittova, I.Ya., Ammonia response of thin films grown on GaAs using $PbO + Bi_2O_3$ mixtures, *Inorg. Mater.,* 2015, vol. 51, no. 5, pp. 425−429. https://doi.org/10.1134/S0020168515040056

14. Kostryukov, V.F., Mittova, I.Ya., and Dimitrenko, A.A., Chemically stimulated synthesis of gas-sensing films on the surface of GaAs, *Inorg. Mater.,* 2017, vol. 53, no. 5, pp. 451−456. https://doi.org/10.1134/S0020168517050132

15. Nakamoto, K., *Infrared and Raman Spectra of Inorganic and Coordination Compounds,* New York: Wiley, 1986.

16. Brandon, D. and Kaplan, W., *Microstructural Characterization of Materials,* New York: Wiley, 1999.

17. *Scanning Tunneling Microscopy in Surface Science, Nanoscience and Catalysis,* Bowker, M. and Davies, P.R., Eds., New York: Wiley−VCH, 2010.

18. Lyson-Sypien, B., Czapla, A., Lubecka, M., et al., Nanopowders of chromium doped TiO_2 for gas sensors, *Sens. Actuators, B,* 2012, vol. 175, pp. 163−172. https://doi.org/10.1016/j.snb.2012.02.051

Translated by O. Tsarev