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Chemically Stimulated Synthesis of Gas-Sensing Films on the Surface of GaAs

V. F. Kostryukov, I. Ya. Mittova*, and A. A. Dimitrenko

Voronezh State University, Universitetskaya pl. 1, Voronezh, 394006 Russia

**e-mail: vc@chem.vsu.ru*

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Abstract—Thin nanofilms have been grown on the surface of GaAs via chemically stimulated thermal oxidation. The thickness of the oxide films on the surface of GaAs has been shown to be a nonlinear function of the composition of the mixture of the chemical oxide stimulators. The oxide films obtained, consisting predominantly of Ga_2O_3, contain small amounts (≤3 at %) of Sb_2O_3 and V_2O_5 and exhibit gas-sensing properties in ammonia and carbon monoxide atmospheres, with the highest NH_3 sensitivity of 1.29 in the temperature range 200–240°C and the highest CO sensitivity of 1.26 in the range 180–220°C.

Keywords: semiconductors, gallium arsenide, thermal oxidation, thin films, gas sensitivity

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INTRODUCTION

In recent years, a great deal of attention has been paid to the development of microelectronic primary measuring converters (sensors) of various quantities: temperature, pressure, acceleration, mechanical displacements, magnetic induction, ion concentrations in liquids, humidity, and the chemical composition of gaseous media. A special place among them is occupied by sensors of the chemical composition of gases, which have found a variety of industrial applications [1].

Thin-film sensors have a sensitive layer whose thickness is comparable to the average grain size in the polycrystalline material, as a result of which surface conduction prevails. The key features of such sensors are their high sensitivity, short response time, and low power consumption [2, 3].

One way of producing thin semiconductor films on semiconductor surfaces is chemically stimulated thermal oxidation [4]. If two compounds (for example, oxides) are used simultaneously as chemical stimulators, their combined influence may have a synergistic effect on the thermal oxidation of semiconductors, which will show up as a nonlinear (nonadditive in the general case) dependence of various properties of films (especially of their thickness) on the surface of a semiconductor on the composition of the mixture of chemical stimulators [5]. Thus, there is an extra parameter (in addition to the oxidation temperature and time) which can be varied in order to control the properties of the oxide film growing on the semiconductor surface.

The objectives of this work were to synthesize semiconductor nanofilms on the surface of GaAs in the presence of a mixture of Sb_2O_3 and V_2O_5 as chemical stimulators and investigate their gas-sensing properties.

EXPERIMENTAL

We studied thin films grown using $Sb_2O_3 + V_2O_5$ oxide mixtures on (111)-oriented AGTsCh-1 gallium arsenide substrates with a carrier concentration in the range $(1.5–2.5) \times 10^{18}$ cm^{-3} and resistivity from 0.010 to 0.018 Ω cm. These oxides were previously shown to be active chemical stimulators for the thermal oxidation of GaAs [5], and their combined effect may ensure further increase in the rate of oxide film growth on the surface of GaAs. GaAs was oxidized for 10, 20, 30, and 40 min at 500 and 550°C and 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. The temperature in the reactor was maintained constant (±1°C) by a TRM-10 meter/controller. The separation between the surface of the chemical stimulator mixture and the semiconductor wafer surface was maintained constant at 10 mm. The thickness of the resultant oxide films was determined using an LEF-754 laser ellipsometer (λ = 632.8 nm) with an absolute uncertainty of ±2 nm.

The composition of the films growing on the GaAs surface was determined by infrared (IR) spectroscopy [6] (Vertex 70 spectrophotometer) and X-ray microanalysis [7] (JEOL JSM-6510LV equipped with a Bruker energy dispersive X-ray microanalysis system).

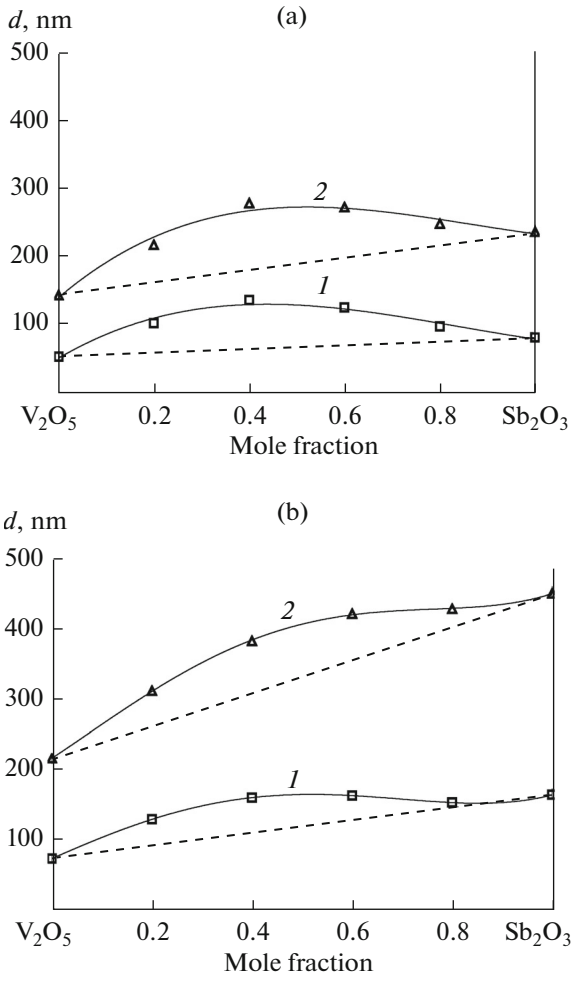

Fig. 1. Composition dependences of the thickness of the oxide film on GaAs after oxidation for (*1*) 10 and (*2*) 40 min at (a) 500 and (b) 550°C. The dashed lines represent additive behavior.

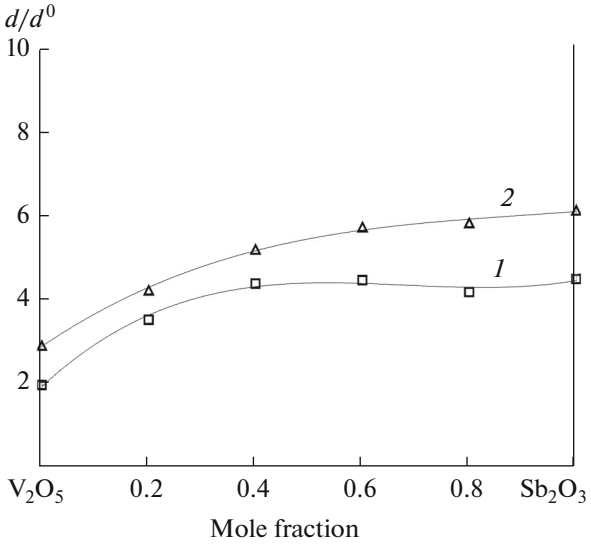

Fig. 2. Composition dependences of the relative increase in oxide film thickness on GaAs at 550°C with respect to stimulator-free thermal oxidation: oxidation time of (*1*) 10 and (*2*) 40 min.

The operation of semiconductor gas sensors is based on the principle that physical parameters of semiconductor materials change when these are brought into contact with a gas. The parameters sensitive to gas adsorption on semiconductor surfaces include the electrical conductance, electron work function, carrier mobility, surface carrier concentration, carrier lifetime, reflectivity, absorption coefficient, and others [8]. These quantities are potential output parameters of gas sensors, but not all of them can be used in practice. In the case of films produced by the thermal oxidation of GaAs using $Sb_2O_3 + V_2O_5$ mixtures, the most informative parameter is electrical conductance (resistance): even slight changes in analyte gas concentration will cause considerable changes in it.

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 measurements in the range $R_s = 10.1$ to 10^5 Ω/□ with an accuracy of ±4.5%. In our resistivity measurements, the ambient humidity was 55% and we used copper contacts. The gas sensitivity of the films was assessed by a known technique [9], as the ratio of the resistivity of the film in pure air (R_v) to that in the gas mixture under study (R_g): $S_g = \frac{R_v}{R_g}$.

RESULTS AND DISCUSSION

Figure 1 shows composition dependences of the thickness of the oxide film on GaAs after oxidation for different times and at different temperatures, and Fig. 2 shows the relative increase in oxide film thickness (acceleration) achieved with respect to the stimulator-free thermal oxidation of GaAs. It is seen that Sb_2O_3 is a more efficient chemical stimulator (d_{max} = 450 nm, increase in growth rate by a factor of 4.5 to 6.1) than is V_2O_5 (d_{max} = 215 nm, increase in growth rate by a factor of 2–3). The mixtures of the oxide stimulators also increase the rate of oxide film growth, and the magnitude of the effect increases smoothly with increasing Sb_2O_3 concentration in the mixtures.

Thus, the addition of Sb_2O_3 to V_2O_5 increases its accelerating effect. In contrast, the addition of V_2O_5 to Sb_2O_3 has a weak effect on the relative increase in film thickness. With increasing oxidation temperature and time, the oxide film thickness increases systematically, and the general character of the dependence on process parameters varies little with increasing oxidation temperature and time.

Table 1. IR spectroscopy results for oxide films grown on the surface of GaAs using $Sb_2O_3 + V_2O_5$ mixtures (550°C, 40 min)

Absorption band, cm^{-1}	Chemical bond
540	Ga–As (substrate background)
420–440, 670	Ga–O
480, 900	As–O
480	V–O
430	Sb–O

It follows from Fig. 1 that, in the case of the combined effect of Sb_2O_3 and V_2O_5, the oxide film thickness on the surface of GaAs is a nonadditive function of the composition of the mixture of the chemical oxide stimulators. We are thus led to conclude that the combined action of Sb_2O_3 and V_2O_5 has a synergistic effect on the thermal oxidation of GaAs, as a result of which the oxide film thickness on the semiconductor surface is a nonlinear function of the composition of the mixture of the chemical oxide stimulators: independent of the oxidation time and temperature and the mixture composition, there is a considerable positive deviation from additive behavior.

Analysis of the present experimental data indicates the following general trends: At a given temperature, the positive deviation from additivity increases with increasing oxidation time. At the same time, if we consider dependences at a constant oxidation time and varied temperature, the positive deviation from additivity decreases with increasing oxidation temperature. An increase in positive deviation from additivity with increasing thermal oxidation time was observed previously for mixtures containing chromium(VI) oxide [10], and one of the mixtures contained, in addition to CrO_3, V_2O_5 as a second component. A decrease in positive deviation from additive behavior with increasing temperature over the entire range of compositions of chemical oxide stimulators has been observed for the first time.

To ascertain whether Sb_2O_3 and V_2O_5 were incorporated into the film growing on the surface of GaAs and determine its qualitative and quantitative compositions, the samples obtained were characterized by IR spectroscopy and X-ray microanalysis (Tables 1, 2). We analyzed the same samples, prepared using oxide mixtures of various compositions: from 20% Sb_2O_3 + 80% V_2O_5 to 80% Sb_2O_3 + 20% V_2O_5. The oxidation temperature was 550°C and the oxidation time was 40 min. The sampling depth in X-ray microanalysis was 1 μm, which far exceeded the film thickness on the surface of GaAs. After measurements, the substrate background was subtracted and the elemental composition of the film was determined. The percentage of oxygen was determined as the balance to 100%, rather than from analytical data.

The spectra of the samples contain several characteristic transmission minima. According to data in the literature [6], the absorption bands at 420–440 and 670 cm^{-1} correspond to Ga–O bonds. Similar bands were observed in the case of the stimulator-free oxidation of gallium arsenide, which points to the formation of Ga_2O_3. The absorption band at $\nu = 900$ cm^{-1} is commonly assigned to As–O bonds, and the absorption band at 430 cm^{-1} corresponds to Sb–O bonds [6]. The absorption band of As–O bonds at 480 cm^{-1} coincides with that of V–O bonds, but as will be shown below the assumption that this frequency corresponds to V–O vibrations appears to be valid. It is worth noting the absorption bands in the 540-cm^{-1} region, which seem to arise from the GaAs substrate background (Ga–As bonds). Thus, the present IR spectroscopy data demonstrate that the chemical oxide stimulators are incorporated into the film growing on the surface of GaAs. All of the components of the film are oxidized, which is of particular importance in the case of arsenic because, being located near the inner interface in films grown via stimulator-free oxidation and being incompletely oxidized, it significantly degrades their properties.

The X-ray microanalysis data confirm the conclusion drawn from the IR spectroscopy results that the

Table 2. X-ray microanalysis results for samples prepared by the thermal oxidation of GaAs using $Sb_2O_3 + V_2O_5$ mixtures (530°C, 40 min)

Mixture composition	Elemental composition of the films, at %				
	Ga	As	Sb	V	O
20% V_2O_5 + 80% Sb_2O_3	39.846	8.761	2.269	0.087	49.037
40% V_2O_5 + 60% Sb_2O_3	38.886	6.912	1.748	0.224	52.230
60% V_2O_5 + 40% Sb_2O_3	39.486	9.567	1.133	0.449	49.365
80% V_2O_5 + 20% Sb_2O_3	38.254	7.290	0.613	0.824	53.019

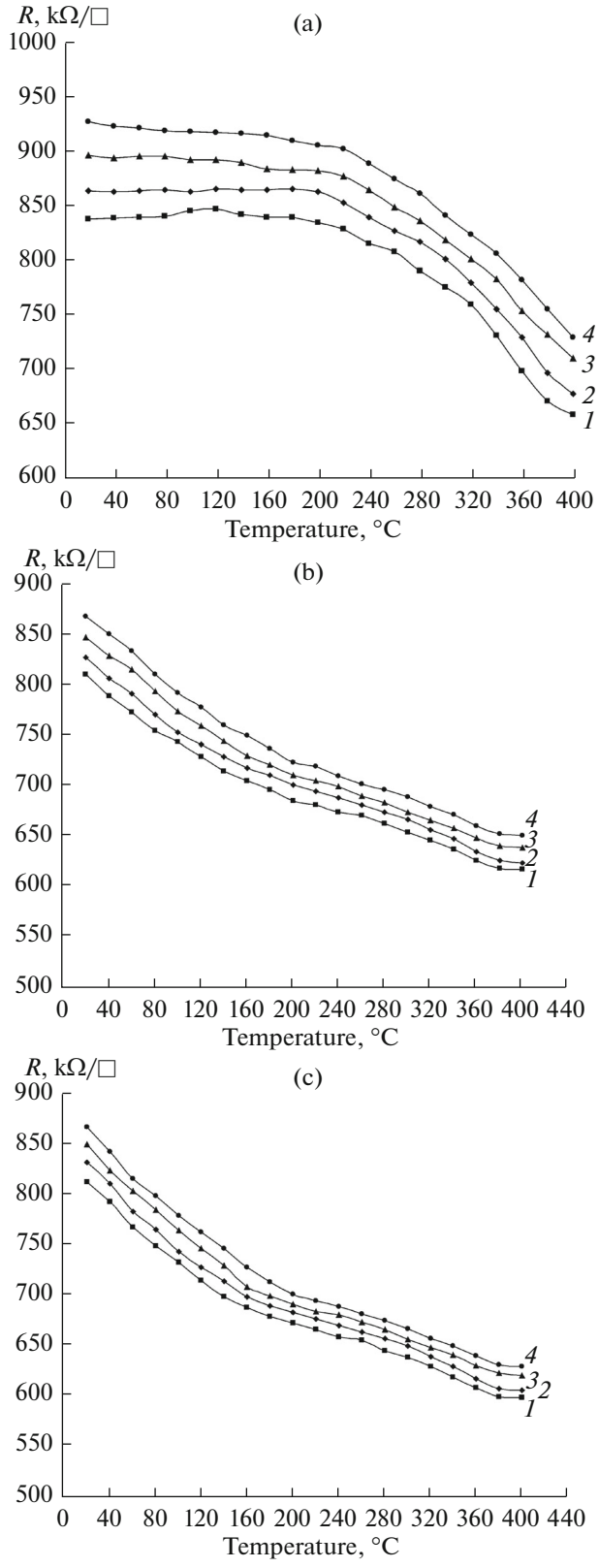

Fig. 3. Temperature dependences of sheet resistance for the films grown on the surface of GaAs using V_2O_5 + Sb_2O_3 mixtures: (a) air, (b) air + CO, (c) air + NH_3; (*1*) 80% V_2O_5 + 20% Sb_2O_3, (*2*) 60% V_2O_5 + 40% Sb_2O_3, (*3*) 40% V_2O_5 + 60% Sb_2O_3, (*4*) 20% V_2O_5 + 80% Sb_2O_3.

vanadium is incorporated into the resulting oxide film on the surface of GaAs. Attention should be paid to the considerable oxygen content of the films, which also correlates with the IR spectroscopic evidence for the formation of oxide films on the surface of GaAs. The chemical stimulators have comparable concentrations in the films, with a slight prevalence of antimony, as would be expected from comparison of the vapor pressures and compositions over Sb_2O_3 and V_2O_5 [11]. At the same time, the ratio of the chemical stimulators in the oxide films differs from that in the starting mixture: all of the films are enriched in antimony. The Sb_2O_3 content of the mixtures ranges from 80 to 20%, whereas that of the oxide films on the surface of GaAs ranges from 96 to 43%. Since Sb_2O_3 is a more efficient chemical stimulator than is V_2O_5 (ensuring a larger increase in oxide film thickness), the increased Sb_2O_3 content of the oxide film on the surface of GaAs is obviously responsible for the positive deviation from additive behavior (Fig. 1). It is also worth noting here that the maximum content of the chemical stimulators in the film on the surface of GaAs does not exceed 3%. As shown by Rekas and Szklarski [12], this is necessary for ensuring gas-sensing properties.

In a previous study [13], thin films grown on the surface of GaAs using PbO + Bi_2O_3 mixtures were shown to possess gas-sensing properties, but the thickness of the films grown in 10–40 min was insufficient for electrical measurements. A longer thermal oxidation time is needed for sensor signal measurements. At the same time, the films grown using the V_2O_5 + Sb_2O_3 mixtures are free from this drawback: their thickness (after oxidation for 40 min) is sufficient for electrical measurements, which is their additional benefit.

Figure 3a shows the temperature dependences (20–400°C) of sheet resistance in air for the samples prepared using V_2O_5 + Sb_2O_3 mixtures. A strong correlation is seen between the composition of the chemical stimulator mixture and the sheet resistance. The resistance increases with increasing Sb_2O_3 concentration in the films. With increasing Sb_2O_3 concentration in the mixtures, the total concentration of the chemical stimulators in the films increases (Table 1), which seems to ensure the growth of high-resistance films. Note also that, with increasing temperature, the resistance of the films decreases, which points to semiconducting properties of the samples obtained. Thus, the use of chemical stimulator mixtures makes it possible, on the one hand, to obtain a positive effect on the rise in the oxide film thickness in comparison with the individual effects of the stimulators and, on the other, to produce films with semiconducting properties, rather than with dielectric properties, which is necessary for subsequent assessment of their gas sensitivity.

The analyte gases were CO and NH_3. Their concentrations were 120 and 170 ppm, respectively. Figures 3b, 3c, and 4 show the temperature dependences

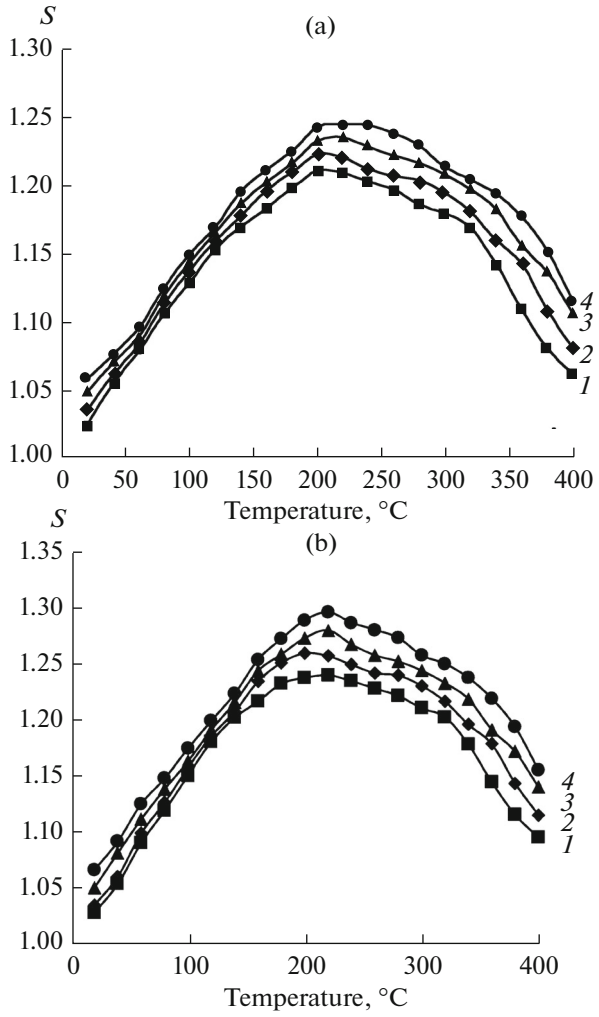

Fig. 4. Temperature dependences of gas sensitivity for the films grown on the surface of GaAs using $V_2O_5 + Sb_2O_3$ mixtures in the presence of (a) CO and (b) NH_3: (*1*) 80% V_2O_5 + 20% Sb_2O_3, (*2*) 60% V_2O_5 + 40% Sb_2O_3, (*3*) 40% V_2O_5 + 60% Sb_2O_3, (*4*) 20% V_2O_5 + 80% Sb_2O_3.

of the resistance and sensor signal for the films in atmospheres containing these gases.

The oxide films grown on the surface of GaAs using $V_2O_5 + Sb_2O_3$ mixtures possess high sensitivity to carbon monoxide and ammonia. A general trend in the present results is that all of the films are more sensitive to ammonia than to carbon monoxide. Note that all the temperature dependences of the sensor signal have extrema, which are located in the temperature range 180–220°C in the case of carbon monoxide and in the range 200–240°C in the case of ammonia. On the one hand, this reduces the energy consumption of potential gas sensors. On the other, this allows molecules adsorbed on the film surface to actively enter into chemical reactions [14]. In the temperature range in question, with increasing Sb_2O_3 concentration in the mixtures the sensor signal rises from 1.21 to 1.24 in the case of carbon monoxide and from 1.24 to 1.29 in the case of ammonia, shifting to higher temperatures. The sensor signal exceeds the minimum necessary level at which a film can be thought of as possessing gas-sensing properties [15], but at the same time it is inferior, albeit only slightly (by a factor of 2), to that of commercial gas-sensing films [16, 17].

CONCLUSIONS

$V_2O_5 + Sb_2O_3$ mixtures are efficient chemical stimulators of the thermal oxidation of GaAs, ensuring a nonadditive positive effect in the dependence of the oxide film thickness on the surface of GaAs on the composition of chemical stimulator mixtures. In the temperature range 20–400°C, the films thus grown exhibit a sensing response to NH_3 and CO, which increases with increasing Sb_2O_3 concentration in the mixture.

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REFERENCES

1. Gopel, W., Solid-state chemical sensors: atomistic models and research trends, *Sens. Actuators,* 1989, vol. 16, pp. 167–193.
2. Rembeza, S.I., Rembeza, E.S., Svistova, T.V, Kosheleva, N.N., and Al Tameemi, V.M.K., Effect of catalytic surface modification on the gas sensitivity of SnO_2 + 3% SiO_2 films, *Semiconductors,* 2015, vol. 49, no. 9, pp. 1237–1241.
3. Vasil'ev, R.B., Ryabova, L.I., Rumyantseva, M.N., and Gas'kov, A.M., Inorganic structures as gas-sensing materials, *Usp. Khim.,* 2004, vol. 73, no. 10, pp. 1019–1038.
4. 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.
5. Mittova, I.Ya., Pshestanchik, V.R., and Kostryukov, V.F., *Nelineinye effekty v protsessakh aktivirovannogo okisleniya GaAs* (Nonlinear Effects in Activated GaAs Oxidation Processes), Voronezh: Voronezh. Gos. Univ., 2008.
6. Nakamoto, K., *Infrared and Raman Spectra of Inorganic and Coordination Compounds,* New York: Wiley, 1986.
7. Brandon, D.D. and Kaplan, W.D., *Microstructural Characterization of Materials,* London: Wiley, 1999.
8. Myasnikov, I.A., Sukharev, V.Ya., Kupriyanov, L.Yu., et al., *Poluprovodnikovye sensory v fiziko-khimicheskikh*

issledovaniyakh (Semiconductor Sensors in Physicochemical Studies), Moscow: Nauka, 1991.

9. Rembeza, S.I., Svistova, T.V., Rembeza, E.S., and Borsyakova, O.I., The microstructure and physical properties of thin SnO_2 films, *Semiconductors,* 2001, vol. 35, no. 7, pp. 762–765.
10. Mittova, I.Ya., Pshestanchik, V.R., Pinyaeva, O.A., Kostryukov, V.F., and Skorokhodova, S.M., Nonadditive effect of oxides in CrO_3–PbO and CrO_3–V_2O_5 compositions as activators of the thermal oxidation of gallium arsenide, *Dokl. Chem.,* 2002, vol. 385, nos. 4–6, pp. 212–214.
11. Kazenas, E.K. and Tsvetkov, Yu.V., *Isparenie oksidov* (Vaporization of Oxides), Moscow: Nauka, 1997.
12. Rekas, M. and Szklarski, Z., Defect chemistry of antimony doped SnO_2 thin films, *Bull. Pol. Acad. Sci., Chem.,* 1996, vol. 44, no. 3, pp. 155–177.
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.
14. 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.
15. Xu, C., Tamaki, J., Miura, N., and Yamazoe, N., Hydrothermal treatment of tin oxide sol solution for preparation of thin-film sensor with enhanced thermal stability and gas sensitivity, *Sens. Actuators,* 2000, vol. 65, pp. 97–100.
16. *Figaro, Inc. Catalog.*
17. *SENSIS-2000 and SENSIS-2003 Gas Sensors Catalog.*

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