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GaAs THERMAL OXIDATION ACTIVATED BY THE COACTION OF P-BLOCK OXIDES

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This study summarizes the results for the investigation of the process of gallium arsenide thermal oxidation processes activated by the coaction of the oxides in Sb_2O_3+Bi_2O_3, Sb_2O_3+PbO and PbO+Bi_2O_3 binary compositions was studied. The analysis of the character and nature of nonlinear effect of various compositions of chemostimulators on the GaAs-supported oxide layer thickness grown on the GaAs surface was performed. It is shown that the actual oxide layer thickness is different from the additive value. The main patterns of the impact for binary compositions of p-element oxides of p-elements on thermal oxidation of gallium arsenide determined by physico-chemical nature of chemostimulators, the nature of their interaction and the method of administration in the system were described.

Keywords: semiconductors, gallium arsenide, thin films, thermal oxidation, nonlinear effects.

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1. Introduction

Good quality of function layers and improvement of properties of the semiconductor/film and film/ambient boundaries are one of the main objectives in forming heterostructures with the set properties in $A^{III}B^{V}$. This is particularly relevant to the binary semiconductors with the volatile GaAs, which have a tendency towards both material and oxide degradation at high temperatures. The nature of the process itself does not allow for good heterostructures formed by the GaAs oxidation, as the parallel oxidation stages are interrelated by the reaction $As_2O_3 + Ga \Rightarrow Ga_2O_3 + As$ [1]. This results in arsenic segregation on the inner boundary, which leads to its degradation. The growing film consists mainly of Ga_2O_3 acting as a semiconductor, and the semiconductor/insulator heterostructure can barely be formed. Therefore, we can define the said reaction as a 'negative feedback channel' between the GaAs oxidation process steps that is determined by thermodynamics.

Applying the present technological solutions of the problem, it is not possible to predict and control these properties. Usually, only one property of the structure is improved (e.g. surface-charge density) and the others remain at a level typical of the oxide layer [2–4]. Furthermore, they are all complicated in practice and can be extremely toxic (e.g., oxidation with the arsenic oxide vapor back pressure, [5]).

Chemostimulated thermal oxidation of semiconductors is one of the solutions to this problem [1]. The suggested approach is based on the idea of the kinetic locking of the 'negative feedback', enhanced by engaging the oxidized semiconductor components in new fast processes with the chemostimulator compositions, i.e. creating 'positive feedback' that enable faster building-up of the target product and modification of its properties. When the chemostimulators are introduced into the reaction zone through the vapor phase (by evaporation), their impact — providing that oxygen can be thermodynamically transferred to the substrate components — is determined by the pressure and composition of the vapor that determines the surface active particles concentration. After the oxygen transfer act, the chemostimulator element is oxidized once again and then continues transferring the oxygen to the substrate components. This chemostimulated semiconductor oxidation process was called redox transit interaction [1]. When the chemostimulator regeneration is complete (the process turns cyclic), it becoming similar to the catalysis [6].

Therefore, the introduction of chemostimulators in GaAs oxidation provides for the new multichannel process with the kinetically conjugated, and adjoint catalytic stages, determined by the chemostimulators and their transformation products, and forming positive feedback between the semiconductor oxidation stages. One chemostimulator may contain two or more active components. Then, the process branches and, as a result, the chemostimulating activity in general increases. The process, however, becomes difficult to control.

When two chemostimulator compositions are used simultaneously, it allows us to manipulate the components of the oxide films growing on the GaAs surface and their properties by regulating the composition components and their quantity.

The purpose of this work was to review and analyze of the main results of the GaAs thermal oxidation process pattern stimulated by the p-block oxide compositions and interpretation of the nonlinear effects of combined effects of chemostimulators.

2. Experimental

We used a polished single-crystal (111)-oriented Sn-doped GaAs wafers (SAGOCh-1 brand). The carrier density was $1.5\cdot10^{18}$ – $2.5\cdot10^{18}$ cm^{-3}; resistivity — 0.010 – 0.018 Ω·cm. The working side of the semiconductor wafer was the ‘gallic’ side. Side A (the gallic one) had numerous etch pits, while there were no such pits on side B (the arsenic one). Immediately before the oxidation process, the samples were put into 49% HF for 10 min., and rinsed with doubly distilled water. Variable binary compositions of antimony (III), bismuth (III) and lead (II) (puriss. p.a.) in increments of 10 mol% were used as chemostimulators. The composition-stimulated GaAs oxidation stimulated by the compositions was carried out in a horizontal quartz reactor (d 30mm) of the MTP-2M-50-500 furnace at 530 °C for 10 – 40 min. The distance from the oxides surface to the working side of the sample was the same all the time (10 mm). The flowing oxygen speed was 30 l/h. The temperature stability (±1 °C) in the reactor was ensured by the TRM-10 sensor unit. A new composition of chemostimulator oxides was prepared for each experiment. The thickness of oxide films was measured each 10 min. using an LEF-754 (λ = 632.8 nm) laser ellipsometer with an accuracy of ±2 nm.

Chemical transformations occurring during GaAs thermal oxidation in the oxides used and their compositions were analyzed by X-ray powder diffractometer DRON-4 (Co K_α-radiation, λ = 1.79021 Å). The composition of the oxide films grown on GaAs surface was determined by IR spectroscopy (IKS, Infralyum FT-02, UR-10), X-ray fluorescence analysis (XRF, VRA–30, Carl Zeiss Yena), electron probe X-ray microanalysis (EPXMA, CamScan), and ultrasoft X-ray emission spectroscopy (USXES, C-500). The composition of vapor from the chemostimulators’ mixture evaporation was studied using mass spectrometry (MS-1301) and Knudsen effusion method.

3. Results and discussion

To determine the difference between the separate and mixture chemostimulator effects, the thickness of the oxide film was plotted as functions of the composition components in Fig. 1. From the plots, we may infer that the nonlinear effect changed qualitatively with the chemostimulator composition and its nature. For the chemostimulator system Sb_2O_3 + Bi_2O_3, a negative anomaly was observed over the entire range of compositions, i.e. the oxides in the composition act like inhibitors. In the presence of the lead oxide, anomalies are of variable sign. The anomaly type, however, varies, depending on the second element introduced. The composition Bi_2O_3 + PbO acts like inhibitor (similar to Sb_2O_3 + Bi_2O_3 system). The composition of PbO + Bi_2O_3, on the contrary, stimulates the latter and enhances its effectiveness. In PbO + Sb_2O_3, the chemostimulators act completely differently: Sb_2O_3 results in the non additive increase in the oxide layer thickness on the GaAs surface, while PbO + Sb_2O_3 inhibits the chemostimulating effect, which was expected, considering their individual chemostimulating effect [7–9].

The observed nonlinear effects develop appropriately as the process continues. For the composition Sb_2O_3 + Bi_2O_3 composition, the negative anomaly increases in absolute magnitude, with the minimum value almost fixed on the composition axis at $\sim$ 40 mol.%. Bi_2O_3, within any oxidation process length. In the other two chemostimulator compositions, the negative anomaly increases both in magnitude and in composition, depending on the oxidation process length. Hence, for a larger range of compositions, the mutual inhibition becomes greater with time. The positive anomaly in such compositions, however, is qualitatively different. For the composition PbO + Sb_2O_3 mixture, it decreases both in magnitude and in the composition range. When GaAs oxidation is activated by PbO + Bi_2O_3, it decreases only in the composition range, while the maximum positive anomaly increases in magnitude.

Hence, introduction of a more active chemostimulator results in nonlinear acceleration of the process, while introduction of a less active oxide — in inhibition as compared to the additive value. The more the chemostimulators differ, the greater the mutual effect. Bismuth oxide, being the least effective, inhibits both PbO and Sb_2O_3, especially the latter. Lead oxide, having medium effectiveness, inhibits Sb_2O_3, but stimulates Bi_2O_3 effect. However, the most active Sb_2O_3 in composition with Bi_2O_3 does not enhance the process and the film thickness on the GaAs surface stays practically unchanged (see Fig. 1a), which can be seen as inhibiting effect in relation to the additive effect.

Nonadditivity of the antimony, lead and bismuth oxide compositions impact on the gallium arsenide thermal oxidation demonstrates, therefore, the mutual influence of the chemostimulators.

To define the process of chemostimulator coactions, we have studied the composition of the obtained films (**USXES, IR spectra**) and the phase composition alterations of the chemostimulators annealed in an oxygen atmosphere at 530 °C for 40 min. (**X-ray powder diffraction**). The composition was determined according to the concentration function extreme points of the films thickness dependencies.

The composition analysis data of the layers obtained by **USXES** is presented in Table 1. We did not study the films for oxygen presence. X-rays penetration was 40 nm. The method showed that the main film component is gallium (as the oxide). After gallium comes arsenic (also as the oxide) with 10 at %. The films obtained using compositions with lead oxide, contain small amounts of lead. The lower the lead oxide content there is in compositions with antimony oxides and bismuth oxides, the less lead there is in the obtained film obtained. However, there were no traces found of either of antimony or bismuth (for the respective compositions) in the films as studied by this method.

The USXES method does not allow us to detect either the presence or absence of antimony in the films. The IR spectra analysis showed that the main component of the films is gallium oxide. In the films obtained using the chemostimulator compositions with antimony and bismuth oxides, there are absorption bands corresponding to Pb–O and Sb–O, while there

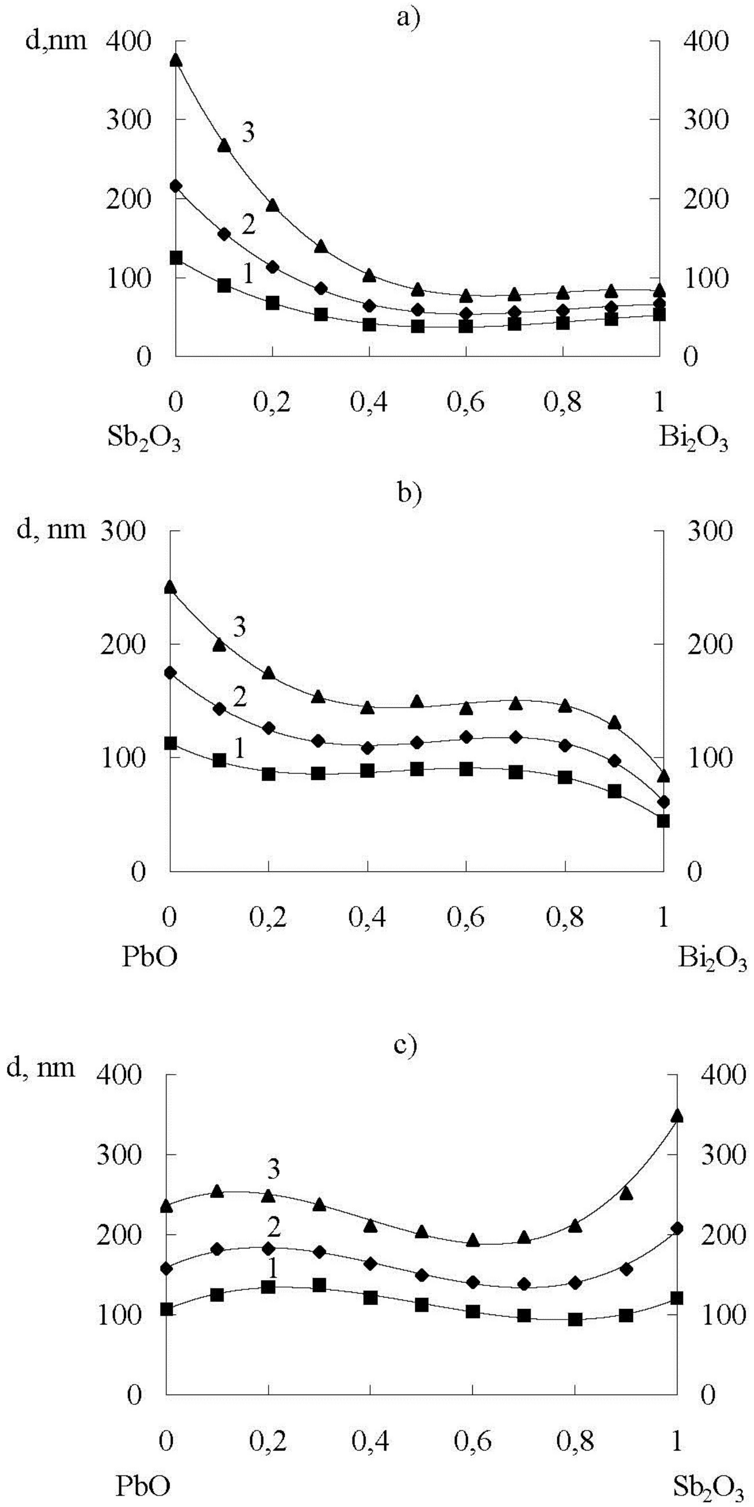

FIG. 1. Oxide film thickness on GaAs surface versus the composition a) Sb_2O_3+Bi_2O_3; b) PbO+Bi_2O_3; c) PbO+Sb_2O_3: 1 – 10 minutes, 2 – 20 minutes, 3 – 40 minutes

Table 1. USXES data for the films obtained by GaAs thermal oxidationstimulated by the coaction of two chemostimulator oxides

Chemostimulator composition, % Bi_2O_3	**Film thickness, nm**	**Composition at %**			
$Sb_2O_3 + Bi_2O_3$					
		Ga	As	Sb	Bi
40	103	58	9	–	
50	85	51	9	–	–
70b	79	47	8	–	–
$PbO + Bi_2O_3$					
Chemostimulator composition, % Bi_2O_3					
		Ga	As	Pb	Bi
30	146	54	10	4	–
50	150	49	12	2	–
80	175	44	12	Traces	–
$PbO + Sb_2O_3$					
Chemostimulator composition, % Sb_2O_3					
		Ga	As	Pb	Sb
20	248	56	9	6	–
50	204	50	8	3	–
70	197	45	8	1	–

are no bismuth traces in the films even when the bismuth oxide concentration in the activator composition is maximum.

The X-ray powder diffraction data given in Table 2 showed that the starting oxides become main elements in chemostimulator compositions and that after annealing Sb_2O_3 transforms into Sb_2O_4. Apart from the bands, however, characteristic of the individual chemostimulators, there are distinct peaks that we could not define. This, nonetheless, allows us to presume that there are intermediate stages, according to the state diagram [10].

Nonlinear dependence of the oxide film thickness on the GaAs surface on the chemostimulator composition, and the X-ray powder diffraction data demonstrate their interactions, which result in the nonlinear effects observed.

The total additive anomaly in general may be caused by the oxides' interaction in the solid (activator sample) and vapor phases and especially on the surface of the sample being oxidized. To solve the problem, the reactor used in the experiment was modified as follows: the weighed batches of individual oxides were placed into a container separated by a partition in order to rule out any contact. This ensured that there would be no interactions in the solid phase. After the process, the oxides from the two parts of the container were studied using X-ray fluorescence analysis that showed that there were no traces of the second oxide found. Thus, the oxides from different parts of the container do not interact in the vapor phase either. The modified container scheme is shown in Fig. 2.

TABLE 2. Interplanar distance (d_{hkl}, Å) defined by the X-ray powder diffraction method for various binary compositions of activator oxides

$Sb_2O_3 + Bi_2O_3$			
Phase	Composition, mol. % Bi_2O_3		
	40	50	70
Sb_2O_4	3.062; 2.936; 2.649; 1.777	3.062; 2.928; 2.642; 1.777	3.062; 2.936; 2.649; 1.777
Bi_2O_3	3.433; 3.298; 3.238; 1.948	3.436; 3.298; 3.238; 1.952	3.436; 3.298; 3.238; 1.948
$PbO + Bi_2O_3$			
Phase	Composition, mol. % Bi_2O_3		
	30	50	80
PbO	2.936; 2.389; 2.024; 1.848	2.928; 2.379; 2.003; 1.858	2.936; 2.389; 1.996; 1.858
Bi_2O_3	3.433; 3.298; 3.238; 1.948	3.436; 3.298; 3.238; 1.952	3.436; 3.298; 3.238; 1.948
Intermediate phase	3.371; 2.227; 1.748; 1.578	3.298; 2.227; 1.740; 1.637	3.371; 2.227; 1.746; 1.624
$PbO + Sb_2O_3$			
Phase	Composition, mol. % Sb_2O_3		
	20	50	70
PbO	2.936; 2.389; 2.024; 1.848	2.928; 2.379; 2.003; 1.858	2.936; 2.389; 1.996; 1.858
Sb_2O_4	3.062; 2.936; 2.649; 1.777	3.062; 2.928; 2.642; 1.777	3.062; 2.936; 2.649; 1.777
Intermediate phase	5.480; 4.548; 1.650; 1.622	5.918; 3.612; 1.753; 1.687	5.818; 4.490; 1.650; 1.574

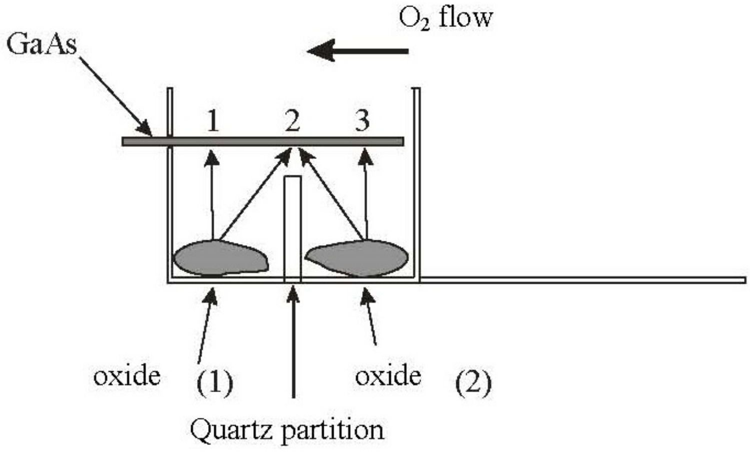

FIG. 2. Spatially separated activators coaction scheme

Due to this spatial separation, three distinct areas (1, 2, 3) appear on the GaAs surface. They are different both in appearance and in the film properties (thickness and composition). Area (1) — the film obtained using practically only the first oxide; (3) — the second; (2) — both oxides acting simultaneously. Oxide films from areas (1) and (3) contain the chemostimulator above which they are placed. The concentration of the second oxide, in these cases, is very low (EPXMA, see below). Consequently, the oxide film thickness in these areas is similar to those obtained using only first or second oxide. In area (2), both chemostimulators are present, and the film thickness is rather different from areas (1) and (3). Thus, the film in area (2) results from simultaneous interaction of chemostimulators separated spatially in the container, but can interact in the vapor phase (through which the interaction of the oxide composition and the oxidized sample is carried out) and on the GaAs surface itself. The following comparison of the spatially separated oxides and the mixture effects will be based on the area (2) data. The nonlinear effect, in this case, results from the mutual influence of the oxides only on the GaAs surface and in the vapor phase. When the oxide film thickness in area (2) is identical to the one grown after the oxide mixture evaporation, it means that the oxides do not interact in the solid phase and the nonlinear effect results completely from the interaction of the activators on GaAs surface and in the vapor phase. When the film thicknesses differ, there is certain interaction in the weighed batch between the activators during the mixture sublimation evaporation. The difference is then equal to the contribution of the interactions in the solid phase to the total nonlinear effect. The contribution may be either positive or negative.

To rule out the interaction on GaAs surface, we carried out a number of experiments, when GaAs had its own pre-grown oxide layer of 50 nm. Thus, the oxide surface took the place of GaAs surface. Here, again, if the pre-oxidized and not pre-oxidized film thickness is the same, then the surface has no influence and the nonlinear effect is caused by the activators' interaction in the vapor phase and in the weighed batches of activators. If they differ, then the activators interact on GaAs surface.

The experiments described, make it possible to determine the contribution from the solid phase interactions and interactions on GaAs surface, and to calculate the contribution of the activator interaction in the vapor phase. To make the discussion more convenient, let the samples with the pre-grown oxide layers be denoted as B-series, the as-received samples — A-series, activator mixture evaporation sublimation in the oxidizing atmosphere — Mode I, spatial separation of the activators – Mode II. We used Sb_2O_3 + Bi_2O_3 composition as a model, as in this system the oxides are the least similar (X-ray powder diffraction), which makes it easier to interpret the results.

The functions obtained are presented in Fig. 3. The given isotherms show the maximum time, since, as stated above, the additive anomaly increases proportionally to the process length.

Clearly, when the activator oxides are introduced separately, there is certain anomaly (curve 2), which proves that the activators interact, despite the spatial separation. Hence, they may interact on the semiconductor surface, or in the vapor phase or in both cases.

In both with the separate and mixture sublimation of the chemostimulators (Modes I and II, Fig. 3. curve 1 and 2) there is a negative anomaly; only with the mixture evaporation is it is much larger. The film thickness grown on GaAs surface with (B-series) and without (A-series) the pre-grown oxide layer depends on the activator composition in the same way both in Mode I (curve 1, 3) and II (curve 2, 4). So, replacing the pure GaAs sample surface by the oxide layer has hardly any effect on the GaAs oxidation process. Hence, there is either no interaction between the activators on the pure surface of the semiconductor in the temperature-time range used, or it is insignificant. These results were quite predictable, considering the fact that even after the preprocessing, GaAs surface is not atomically clean and is always covered

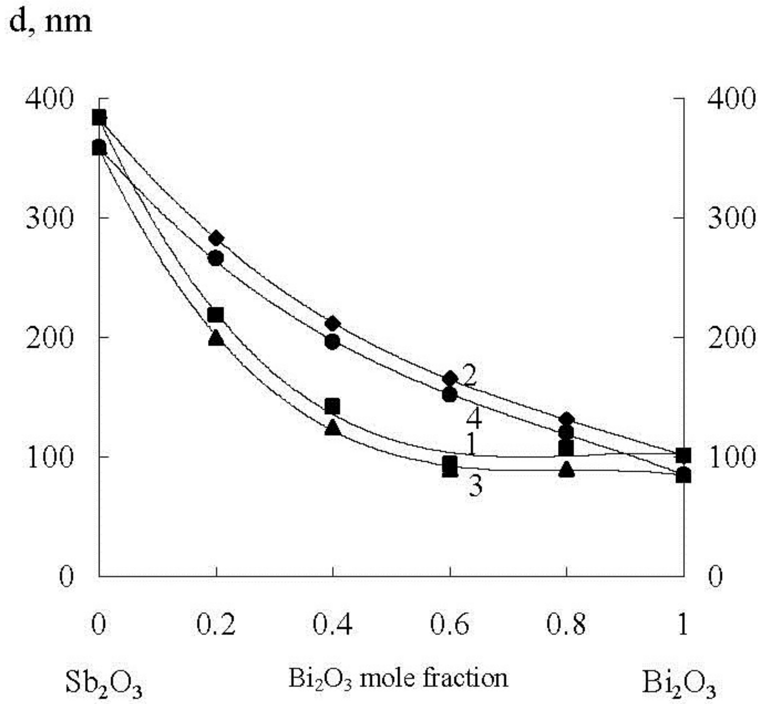

FIG. 3. Oxide film thickness on GaAs surface versus the composition of Sb_2O_3+Bi_2O_3 at 530 °C and an oxidation time of 40 min. 1 – A series, Mode I; 2 – A series, Mode II; 3 – B series, Mode I; 4 – B series, Mode II

by a thin oxide layer. Hence, when the activators are used separately and there is no chance of their interaction in the solid phase (curve 2, 4), the anomalies are caused by the mutual influence of the activators in the vapor phase.

The GaAs samples obtained both with mixture and separate sublimation of antimony and bismuth oxides and oxidized by chemostimulator composition of 60% Sb_2O_3 + 40% Bi_2O_3 for 40 min. were studied using EPXMA. When the chemostimulators are introduced separately, three different areas appear on the sample. That is why we have analyzed three different parts of the wafer corresponding to the said areas (1, 2, 3 in Fig. 2). When the chemostimulators are vaporized from the mixture, there is no such effect. Still, three different areas of the wafer were analyzed. The obtained data (Table 3) shows, that in both cases the main components of the films are As and Ga (the latter prevailing), which, judging by the substantial amount of oxygen, are oxidized (Ga_2O_3, As_2O_3). Such concentration of the chemostimulator in the film (less than 3%) and its oxide nature allow us to suggest using such films as a solid-state component of a gas sensor.

The films contain chemostimulators as well as the substrate components. After the mixture sublimation, they are distributed in the sample in equally low concentrations (see Table 3). After separate sublimation, there is much more antimony in the films than bismuth and it is concentrated largely in area (1) (2.23 at %). In area (2) its concentration becomes approximately three times lower. In area (3), which is above Bi_2O_3, the antimony concentration is even lower ($\sim$ 0.05 at %), but this value, however, is five times higher than the bismuth concentration (0.01 at %). Bismuth is distributed very regularly in the film. Bismuth concentration in the film after separate sublimation is nearly 10 times lower than after mixture sublimation. Thus, after mixture sublimation of antimony and bismuth oxides, the antimony oxide enhances incorporation of the bismuth oxide in the oxide film growing on the surface, while Bi_2O_3 prevents

TABLE 3. EPXMA data for the samples obtained by GaAs thermal oxidation in the presence of a 60% Sb_2O_3 + 40% Bi_2O_3 composition using the mixture activation and spatial separation

Area on the GaAs surface (Fig. 2)	**Film composition**				
	Ga	As	Sb	Bi	O
	at %	at %	at %	at %	at %
Mixture evaporation					
1	21.1	12.5	0.02	0.03	66.35
2	21.3	15.6	0.05	0.04	63.01
3	22.0	17.3	0.09	0.04	60.57
Activating composition – 1.5 : 1					
Film – 1.25 : 1					
Spatial separation					
1	16.2	10.8	2.23	0.01	70.76
2	21.6	19.1	0.67	0.01	58.62
3	23.9	22.4	0.05	0.01	53.64
Activating composition – 1.5 : 1					
Film – 67 : 1					

incorporation of Sb_2O_3 in it. Both the vapor composition and the vapor pressure over antimony and bismuth oxide during their coaction are, therefore, not determined by the additive sum of these values for individual oxides [11].

As we cannot rule out the mutual influence of the chemostimulators in the vapor phase (in this phase the oxides are transferred from the weighed batches of oxides to the surface), the next vital stage was to study the vapor components over the composition. The analysis was carried out using mass spectrometry method (MS-1301). The vapor over the composition of 60% Sb_2O_3 and 40% Bi_2O_3 was analyzed. The mass spectra of the vapor at 690 K has shown $Sb_4O_6^+$ peaks and a small number of SbO^+, $Sb_3O_4^+$ peaks. Antimony oxide activity was about 0.55. Bi^+ ion peaks were registered starting with 730 K. At such temperatures, bismuth concentration in the vapor does not exceed 0.3 %. The pressure and vapor composition data obtained correlates well both with reference data [11] and with EPXMA data concerning the activator incorporation in the film growing on GaAs surface. Antimony oxide activity (0.55) is similar to activator mole fraction in the composition, which, together with X-ray powder diffraction data indicates that the interaction between the activators in the starting weighed sample of oxides is weak.

4. Conclusions

GaAs thermal oxidation activated by chemostimulators demonstrates a nonlinear effect in the dependence of the oxide film thickness on the surface of GaAs from the compositions.

These effects result from the interactions between chemostimulators, which create additional feedback and are localized with comparable impact during the solid and vapor phases. They do not show on the GaAs surface. The study determined the composition of thin films grown on GaAs surfaces from chemostimulator binary compositions, and allows us to suggest their use as solid-state gas sensors.

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