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## The Effect of Certain Complex Chemostimulators and Modifiers on InP Thermal Oxidation

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### Abstract

It is advisable to control characteristics and rate of formation of nanoscale films on InP by introducing chemostimulators, modifiers, or both simultaneously during the thermal oxidation of semiconductors. The chemostimulating effect of the compounds is determined by their transit role as oxygen transmitters or their catalytic function. Modifiers can affect the composition, surface morphology, structure, and properties of the film without changing the film growth rate. The effect of chemostimulators and modifiers on a single process of film synthesis with the desired properties was assumed to be productive.

**Purpose:** Establishment of the effect of certain complex chemostimulators and modifiers on the kinetics, growth mechanism, and properties of complex oxide films on InP in the nanoscale thickness range.

The object of the study was indium phosphide FIE-1A orientation (100). SnO<sub>2</sub>/InP and (40 % Co<sub>3</sub>O<sub>4</sub>+60 % MnO<sub>2</sub>)/InP heterostructures with a layer thickness of ~ 30 nm were formed by magnetron sputtering. Sulphate was deposited through the aerosol phase, followed by air drying and annealing at 200 °C for 30 min for the formation of the Bi<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>/InP heterostructures. SnO<sub>2</sub>/InP and InP samples were thermally oxidized under the influence of AlPO<sub>4</sub> and Bi<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, respectively, introduced into the gas phase in the temperature range 490-570 °C in an oxygen stream for 60 min. The thickness of the films was controlled by laser and spectral ellipsometry and their phase and elemental composition were established by XRD and Auger electron spectroscopy, respectively. For the determination of the electrophysical properties of the films, the contacts were sprayed with aluminium and the resistivity was determined.

The fundamental role of the physicochemical nature of the chemostimulator, its ability to transit interactions and the renewability of oxide forms in the process of InP thermal oxidation was established. The introduction of phosphate groups from AlPO<sub>4</sub> into thermal oxide films, with or without the deposition of SnO<sub>2</sub> on the surface, led to the film resistance similar to that for the oxidation of SnO<sub>2</sub>/InP heterostructures without the additional introduction of phosphates and was 8.5·10<sup>7</sup> Ohm·cm. Bi<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, being a modifier of the composition and properties of the films, did not have a significant chemostimulating effect. Films grown under its influence had a semiconductor characteristics (ρ ~ 10<sup>6</sup> Ohm·cm). The most effective was a 40 % Co<sub>3</sub>O<sub>4</sub>+ 60 % MnO<sub>2</sub> complex chemostimulator, which determined the accelerated (up to 70 %) formation of film by the catalytic-transit mechanism (up to 70 %), being a part of the synthesized films and capable of purposefully modifying their properties by varying the content of components in it (XRD, SE).

**Keywords:** indium phosphide, nanoscale films, chemostimulated oxidation, chemostimulator, modifier, modification of composition and properties.

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## 1. Introduction

Indium phosphide is one of the most important materials of modern semiconductor micro-, nano- and optoelectronics [1,2]. It is used in the production of super high frequency integrated circuits, InP heterostructures are used as photodetectors, in field effect transistors based on Gate stack technology, memory cells, optoelectronic devices, in solar cells, and laser diodes [3–7]. Films grown by InP thermal oxidation could be used in the development of highly efficient and cheap photoconverters of natural and linearly polarized InP-based radiation [8]. However, the InP interface with intrinsic oxide is usually characterized by a rather high density of states, low thermodynamics, and the temporal stability of parameters [9, 10]. It is advisable to control the rate of formation and characteristics of films of the nanoscale thickness range on InP by introducing chemostimulators, modifiers, or both at the same time during the thermal oxidation of these semiconductors [11]. Chemostimulators increase the growth rate of films during thermal oxidation, while suppressing negative reactions and surface degradation [12, 13]; modifiers change the composition, structure, and properties of films [14, 15]. The chemostimulating effect of purposefully selected and introduced compounds is due to their transit role as active oxygen transmitters to semiconductor components or a catalytic function [12]. Modifiers can, without changing the rate of increase in film thickness compared to intrinsic oxidation, affect the film composition, surface morphology, and grain structure, and hence their properties. It is logical to assume that the effect of chemostimulators and modifiers in a single process of film synthesis with the desired properties should be the most productive; however, to control the latter, it is necessary to isolate and separately study the role of such compounds in the InP thermal oxidation process.

The purpose of this study was establishment of the effect of certain binary and complex chemostimulators and modifiers on the kinetics, growth mechanism, and properties of complex oxide films on InP in the nanoscale thickness range.

## 2. Experimental

The objects of the study were thin nanoscale films formed on two-sided polished single-crystal indium phosphide samples FIE-1A orientation (100), doped with tin; the concentration of the main charge carriers at 300 K was not less than  $5 \cdot 10^{16} \text{ cm}^{-3}$ , intrinsic n-type conductivity. The substrates were pre-treated with an etchant of composition  $\text{H}_2\text{SO}_4$  (reagent grade, Russian Federation Purity Standard GOST 4204-77, 92.80 %) :  $\text{H}_2\text{O}_2$  (special purity grade, Russian Federation Purity Standard TU 6-02-570-750, 56 %) :  $\text{H}_2\text{O} = 2:1:1$  for 10 min, then repeatedly washed in distilled water and dried in air.

For the introduction of chemostimulators and modifiers, several approaches were used.  $\text{SnO}_2/\text{InP}$  and (40 %  $\text{Co}_3\text{O}_4$ +60 %  $\text{MnO}_2$ )/InP (molar %) heterostructures with a layer thickness of ~ 30 nm were formed by magnetron sputtering. The deposition was performed in a Covap II vacuum ion sputter, the initial vacuum was  $2 \cdot 10^{-5}$ , and sputtering was carried out in an atmosphere of  $\text{O}_2$ +Ar (purity 99.99 %) at a pressure of  $10^{-3}$  mm Hg. Sn with a purity of 99.99 %, Co with a purity of 99.9 %, and Mn with a purity of 99.9 % were used as the starting material. For the creation of the composition (40 %  $\text{Co}_3\text{O}_4$ +60 %  $\text{MnO}_2$ ) on InP by the magnetron sputtering method, a composite cobalt-manganese target was produced. The composition was selected experimentally taking into account the ratio of areas and sputtering coefficients of the corresponding metals, as well as differences in saturated vapour pressures above the metal surface for cobalt and manganese. Semiconductor substrate during magnetron sputtering was heated to 200 °C for the production of  $\text{SnO}_2$  crystal structure on the InP surface [16].

For the modification of the surface of the semiconductor with bismuth (III) sulphate layers, deposition through the aerosol phase in the established optimal (in terms of modifier layer thickness and reproducibility of results) mode was carried out. The sputtering of the  $\text{Bi}_2(\text{SO}_4)_3$  solution (concentration 0.44 mol/l) was carried out at room temperature substrates using a compressor dispersant, providing an aerosol with a droplet size of the solution up to 4-5  $\mu\text{m}$ . After deposition, the samples were dried in air and annealed in an SNOL muffle furnace at a

temperature of 200 °C for 30 min, thus forming  $\text{Bi}_2(\text{SO}_4)_3/\text{InP}$  heterostructures.

Another approach was the introduction of a chemostimulator or modifier through the gas phase during the oxidation process.  $\text{SnO}_2/\text{InP}$  and  $\text{InP}$  samples were oxidized by  $\text{AlPO}_4$  and  $\text{Bi}_2(\text{SO}_4)_3$  introduced into the gas phase.

Thermal oxidation of all samples was carried out in a MTP-2M-50-500 resistive heating furnace. Temperature adjustment ( $\pm 1^\circ$ ) was carried out using a TPM-10 meter/controller. Thermal oxidation was carried at an oxygen flow rate of 30 l/h. (linear gas flow rate in the reactor was 10 cm/min) for 60 min. In this case,  $\text{SnO}_2/\text{InP}$  heterostructures were oxidized at 530 °C similarly to [16], 40 %  $\text{Co}_3\text{O}_4$ +60 %  $\text{MnO}_2$ )/ $\text{InP}$  heterostructures were oxidized in the temperature range 490-570 °C, and  $\text{Bi}_2(\text{SO}_4)_3/\text{InP}$  – heterostructures were oxidized at 500–550 °C. Samples synthesized by magnetron sputtering were located perpendicular to the oxygen flow. When the oxidation was performed under the action of substances introduced through the gas phase,  $\text{AlPO}_4$  ( $m \sim 0.3$  g) and  $\text{Bi}_2(\text{SO}_4)_3$  ( $m \sim 1$  g) samples were placed in a cylindrical quartz container, covered with the oxidized  $\text{InP}$  sample (at a distance of 10 cm from the surface of the modifiers). Every 10 min, the samples were removed from the reactor and the thickness of the formed films was determined by laser (LE, LEF-754,  $\lambda = 632.8$  nm, absolute error

$\pm 1$  nm) and spectral (SE, Ellipse-1891 spectral ellipsometer, static circuit, range wavelengths of 250–1100 nm) ellipsometry, after oxidation was continued until the process time limit of 60 min was reached.  $\text{AlPO}_4$  powder was synthesized in a similar manner [17]. XRD results showed that all reflections in the diffractogram corresponded to that of an  $\text{AlPO}_4$  powder sample (Fig. 1).

The composition of the films grown by thermal oxidation was determined by the method of X-ray diffraction analysis (XRD) using ARL X'TRA X-ray diffractometer (copper anode, start angle –  $2^\circ$ , final –  $70^\circ$ , step –  $0.05^\circ$ ). X-ray diffraction patterns were recorded in the geometry of a grazing beam (with a fixed position of the arm of the X-ray tube).

The elemental composition of  $\text{Bi}_2(\text{SO}_4)_3/\text{InP}$  oxide films (500 and 525 °C) and thickness distribution of the components were studied by Auger electron spectroscopy (AES) using an ESO-3 spectrometer with a DESA-100 analyser, accuracy  $\pm 10\%$ , using the layer-by-layer etching of films with argon ions.

For the determination of the electrophysical properties, aluminium contacts were magnetronically sputtered on the surface of the synthesized samples through a mask with openings of  $5 \cdot 10^{-3}$   $\text{cm}^2$  in vacuum and the resistivity  $\rho$  (Ohm cm) of the formed structures was determined using an Agilent 344 10A universal multimeter. The thickness of the formed

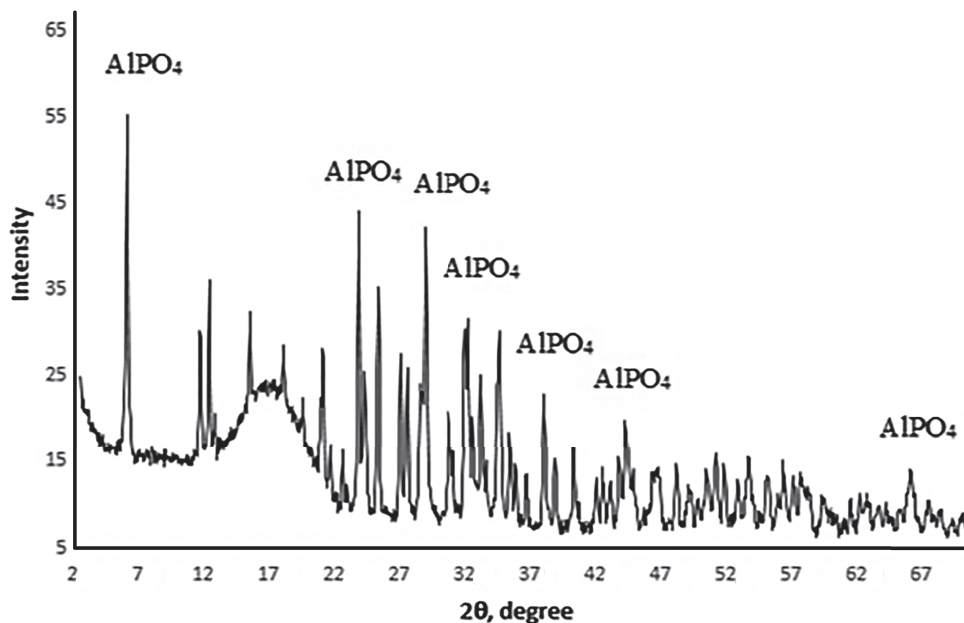


Fig. 1. X-ray diffraction pattern of  $\text{AlPO}_4$

film was taken into account in the process of measuring  $\rho$ .

### 3. Results and discussion

In [16], it was found that the oxide of the p-element of IVA group,  $\text{SnO}_2$ , thermodynamically capable of the transit of oxygen to InP components, in the process of thermal oxidation of this semiconductor plays only a modifying role. Thermal oxidation of  $\text{SnO}_2/\text{InP}$  heterostructures resulted in the formation of nanoscale films, with a higher electrical resistivity ( $\rho = 9 \cdot 10^6 \text{ Ohm}\cdot\text{cm}$ ) than the intrinsic oxide on InP, possessing ohmic conductivity. The achieved semiconductor properties in [16] were explained by the fact that metallic indium is not released during the oxidation of  $\text{SnO}_2/\text{InP}$  heterostructures,  $\text{SnO}_2$  promotes its chemical binding with phosphorus, as a result of which, based on the XRD data, the formation of the corresponding phosphates occurs.

$\text{AlPO}_4$  can serve as a compound playing only a modifying role in the considered process. It contains an “inert” cation, which does not cause either transit or catalytic effects, and a phosphate anion, an increase in the concentration of which in the films on InP, as was shown in [12], improves the electrophysical characteristics of films.

The kinetic curves of InP thermal oxidation under the influence of  $\text{AlPO}_4$  introduced through the gas phase are shown in Fig. 2a. The kinetic parameters of the process, calculated based on the exponential kinetic equation similarly to [15], and the value of the effective activation energy (EAE), determined using the corresponding Arrhenius equation (Fig. 2b) are shown in Table 1.

The values of the relative change in the film thickness over 60 min at temperatures of 475–550 °C as a result of the InP thermal oxidation process with the introduction of  $\text{AlPO}_4$  from the gas phase in comparison with the reference intrinsic oxidation of InP calculated according

to the equation  $b = \frac{\Delta d_{\text{InP}+\text{AlPO}_4}}{\Delta d_{\text{InP}}}$ , did not exceed

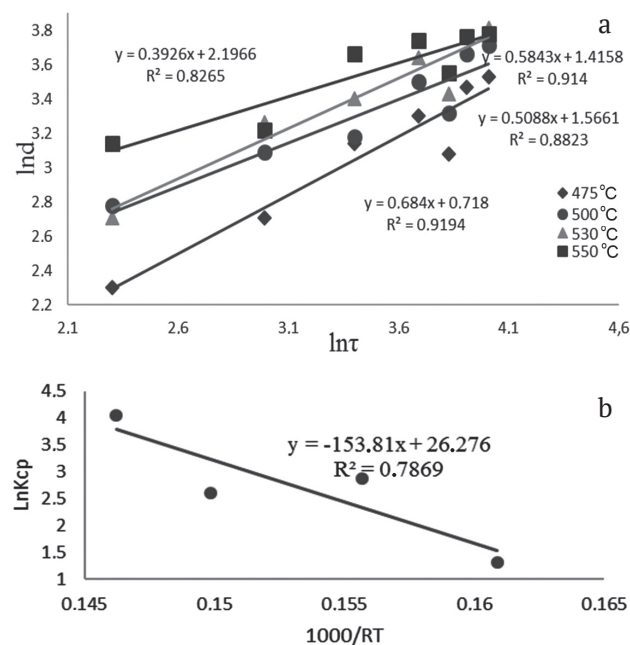
1.23, i.e.  $\text{AlPO}_4$  was not a chemostimulator of the InP thermal oxidation process. However, being part of the growing film,  $\text{AlPO}_4$  could modify its properties. Since, as noted above, the modifying role of the deposited  $\text{SnO}_2$  film was previously established in the thermal oxidation process of InP, the next step was to establish a possible synergy of the action of two modifiers simultaneously introduced by various methods. For this,  $\text{SnO}_2/\text{InP}$  heterostructures, which were formed similarly to [16], were oxidized under the influence of  $\text{AlPO}_4$  instead of a pure InP surface.

The kinetic curves of the oxidation of  $\text{SnO}_2/\text{InP}+\text{AlPO}_4$  and  $\text{SnO}_2/\text{InP}$  samples at a temperature of 530 °C as the most clearly reflecting the process regularities are shown in Fig. 3.

As can be seen from Fig. 3, the effect of  $\text{AlPO}_4$  leads to higher film thickness at the developed stage of the oxidation process due to additional phosphate groups coming from  $\text{AlPO}_4$ , which in turn act as the polyphosphate skeleton of the forming films.

According to the XRD data in Table 2, the introduced aluminium phosphate is included in the film, e.g. the addition of phosphate groups can possess a modifying effect.

However, such a change in composition practically did not change the properties of the films. Electrical resistivity of the  $\text{SnO}_2/\text{InP}+\text{AlPO}_4$ , oxidized at 530 °C for 60 min was  $8.5 \cdot 10^7 \text{ Ohm}\cdot\text{cm}$ , approaching that for  $\text{SnO}_2/\text{InP}$  heterostructure without oxidation –  $7.3 \cdot 10^7 \text{ Ohm}\cdot\text{cm}$  and slightly exceeding the value for  $\text{SnO}_2/\text{InP}$  heterostructure after thermal oxidation in the same mode –



**Fig. 2.** Log plots of kinetic isotherms (a) and Arrhenius plot of the kinetic constant (b) of the process of thermal oxidation of InP with the gas phase of  $\text{AlPO}_4$  at 475–550 °C over 60 min

**Table 1.** Kinetic parameters of the thermal oxidation of InP under the influence of various chemostimulators and modifiers

Kinetic parameters			$n \pm \Delta n, \text{nm}^{1/n} \text{min}^{-1}$	EAE, kJ/mol
	$T, ^\circ\text{C}$	$\ln k_{cp}$		
InP+AlPO <sub>4</sub> <sup>(g)</sup>	475	1.32	0.68±0.142	153
	500	2.88	0.51±0.034	
	530	2.61	0.58±0.042	
	550	4.04	0.39±0.149	
	$n_{av}$		0.54±0.092	
InP+Bi <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> <sup>(g)</sup>	450	2.89	0.44±0.001	187
	475	4.06	0.43±0.001	
	500	5.95	0.36±0.003	
	530	10.51	0.20±0.001	
	550	11.51	0.13±0.001	
	$n_{av}$		0.31±0.002	
Bi <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> /InP	500	38.23	0.11±0.002	459
	530	41.53	0.09±0.001	
	550	42.49	0.09±0.001	
	$n_{av}$		0.09±0.001	
(40 % Co <sub>3</sub> O <sub>4</sub> +60 % MnO <sub>2</sub> )/InP	490	11.09	0.30±0.031	50
	510	11.39	0.25±0.020	
	530	11.89	0.25±0.018	
	550	12.38	0.28±0.005	
	570	12.75	0.27±0.002	
	$n_{av}$		0.27±0.028	

**Table 2.** The identified phases: SnO<sub>2</sub>/InP without thermal oxidation, SnO<sub>2</sub>/InP at 530 °C and SnO<sub>2</sub>/InP with the gas phase of AlPO<sub>4</sub> at 530 °C

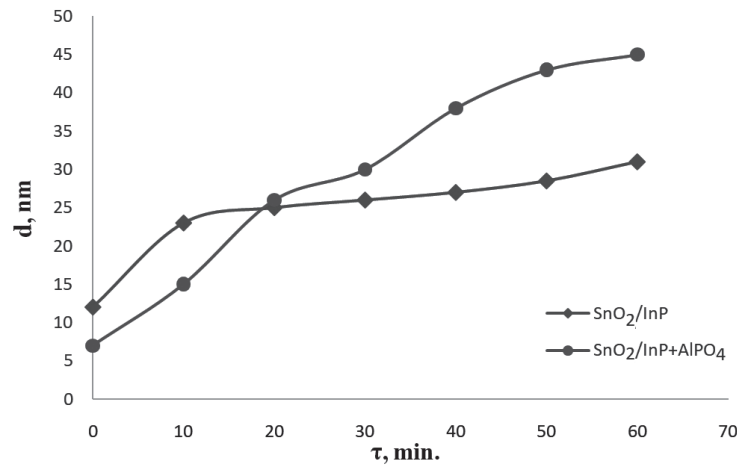
Samples	Interplane distance, $d_{hkl}$	The identified phase
SnO <sub>2</sub> /InP	5.5010; 3.2985	InP
	2.9092; 2.2040; 1.9599	SnO <sub>2</sub>
SnO <sub>2</sub> /InP (530 °C) [6]	5.5524	Sn <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>
	2.9321	In(PO <sub>3</sub> ) <sub>3</sub>
	1.5074	InPO <sub>4</sub>
SnO <sub>2</sub> /InP+AlPO <sub>4</sub> <sup>(g)</sup>	5.3777; 2.5246; 2.9145;	Sn <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>
	3.3849	InP
	1.5798; 1.5570	InPO <sub>4</sub>
	1.5483; 1.5258	AlPO <sub>4</sub>

9.0·10<sup>6</sup> Ohm·cm. Thus, in the absence of a chemostimulating effect, synergistic effects of the studied modifiers have not been achieved.

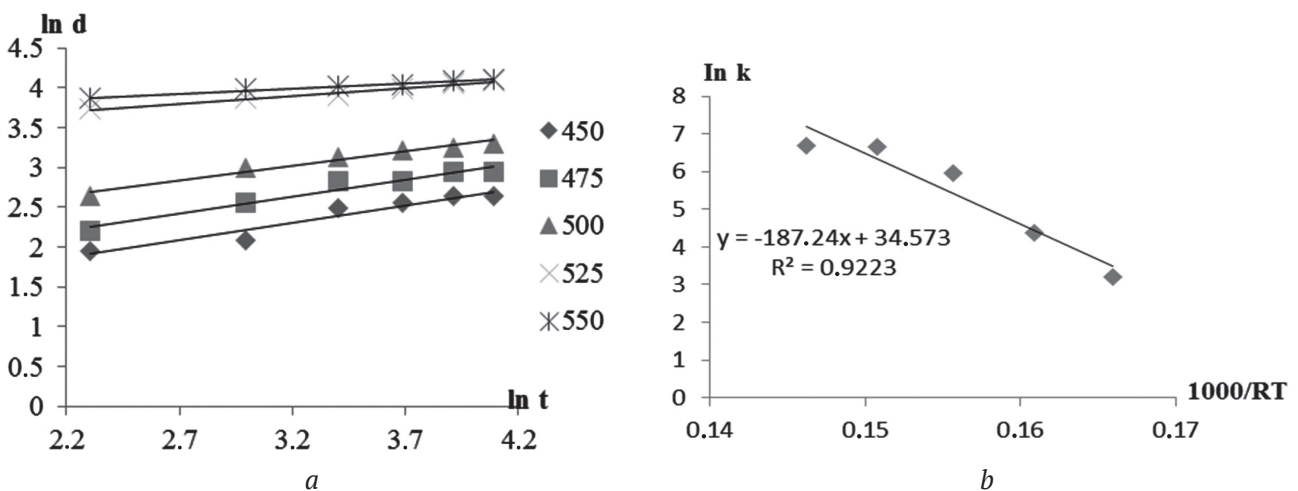
Bi<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> can act as a compound simultaneously providing both a chemostimulating and a modifying effect on the InP thermal oxidation process. Bismuth sulphate contains a transition cation former, the action of which was established for the thermal oxidation of Si, GaAs, and InP [12,18], and the anionic sulphate group, similar in structure to phosphate group [17] and is barely

distinguishable from it by IR spectroscopy [19]. It is known that at InP oxidation temperatures, this compound only partially releases sulphur oxides, mainly preserving the bismuth oxide and sulphate fragments required for our process.

Kinetic isotherms of InP thermal oxidation under the influence of Bi<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> introduced through the gas phase in a process similar to the introduction of AlPO<sub>4</sub> are shown in Fig. 4a, the corresponding Arrhenius plot is demonstrated in Fig. 4b. The kinetic parameters of the process,



**Fig. 3.** Kinetic curves of SnO<sub>2</sub>/InP heterostructures with thermal oxidation with and without the gas phase of AlPO<sub>4</sub> at 530 °C over 60 min



**Fig. 4.** Log plots of kinetic isotherms (a) and Arrhenius plot of the kinetic constant  $\ln k_{av} = f(10^3/RT)$  (b) of the process of thermal oxidation of InP with the gas phase of Bi<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>

calculated according to the aforementioned exponential equation [15], indicate an increase in the contribution of the diffusion component with increasing film thickness (a regular decrease in the exponent n with increasing process parameters) and demonstrate the fact that the solid-phase reaction limited by diffusion in the solid phase is a determining process for InP + Bi<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> in the investigated temperature range of 450–550 °C. The value of EAE was 187 kJ/mol, which, taking into account the error of this calculation (about 10%), can be considered equal to the EAE of the intrinsic oxidation process of indium phosphide, which we determined for InP samples of the same batch (170 kJ/mol) and coinciding with the value obtained previously for intrinsic oxidation of indium phosphide [12].

Based on the values of the acceleration of process calculated using the formula  $b = \frac{\Delta d_{\text{InP+Bi}_2(\text{SO}_4)_3}}{\Delta d_{\text{InP}}}$ ,

the highest effectiveness of the action of the chemostimulator modifier (1.50-1.76 times) occurs at 525 and 550 °C during the first 20 min of the process. With an increase in the oxidation time, the relative increase in the film thickness decreases monotonically, which is typical for a determining diffusion-controlled solid-state process. Under these conditions, the studied process was already approaching the oxidation of the reference sample. The maximum acceleration at the highest temperatures was associated with the increased evaporation of the modifier chemostimulator and an increase in its concentration in the gas phase, which is usually observed in similar processes [14].

For the determination of the dependence of the peculiarities of the action of the chemostimulator modifier on the InP thermal oxidation depending on the way it was introduced into a system, at the next stage InP was thermally oxidized in the presence of  $\text{Bi}_2(\text{SO}_4)_3$  introduced through the aerosol phase, similarly to [11] forming  $\text{Bi}_2(\text{SO}_4)_3/\text{InP}$  heterostructures. Analysis of kinetics of the process (Fig. 5, Table 1) shows the dependence of the revealed patterns on the way chemostimulator-modifier was introduced into the system.

For  $\text{Bi}_2(\text{SO}_4)_3/\text{InP}$  heterostructures very low values  $n$  ( $n_{\text{av}} = 0.09$ ) indicate that diffusion was so significantly decreased that the film thickness remains virtually unchanged. Formally, we can assume that and in this case, the solid-state reaction limited by diffusion in the solid phase was determining, however, a very high EAE value of 459 kJ/mol, indicated a significant contribution of bismuth diffusion into the substrate, which is typical for some chemically stimulated processes with a limited source [12]. Moreover, a value many times higher than the EAE of the intrinsic oxidation of indium phosphide and thermal oxidation of InP in the presence of a chemostimulator modifier  $\text{Bi}_2(\text{SO}_4)_3$  introduced into the system through the gas phase, indicated that the process was constrained in this temperature range. However, it should be noted, that this value is still estimative and preliminary, since it was determined only based on three points. The values of the acceleration process in comparison with the standard were

approximately the same as in the previous case, with the same dynamics of change.

The Auger distribution profiles of components in films synthesized by InP thermal oxidation under the influence of bismuth (III) sulphate introduced through the gas phase in the mode of 500 °C, 60 min (Fig. 6a), showed the presence of bismuth in an amount of about 25 at % over the entire depth of the film. For films synthesized by thermal oxidation of InP under the influence of  $\text{Bi}_2(\text{SO}_4)_3$  introduced through the aerosol phase at 525 °C, 60 min (Fig. 6b), the bismuth content after 5 min of etching was 20 at%. The bismuth content in the film decreased with increasing etching time.

The surface of films formed by thermal oxidation of InP under the influence of  $\text{Bi}_2(\text{SO}_4)_3$ , introduced through the gas and aerosol phases was depleted in the volatile component (phosphorus), however, a second component of the substrate (indium) was present in the surface layer. This confirms the well-known fact of partial evaporation of  $\text{P}_2\text{O}_5$  during the growth of films, the slow formation (although, it was accelerated by a chemostimulator-modifier) of a phosphate skeleton and a high content of  $\text{In}_2\text{O}_3$  in films corresponding to non-strong oxidation conditions [12, 20, 21]. In films synthesized by thermal oxidation of InP under the influence of  $\text{Bi}_2(\text{SO}_4)_3$  introduced through the gas phase (see Fig. 6a), after 20 min of etching, the almost complete disappearance of oxygen and sulphur and a noticeable increase in the phosphorus content was revealed. However, the amount of bismuth remained quite high, which was largely determined

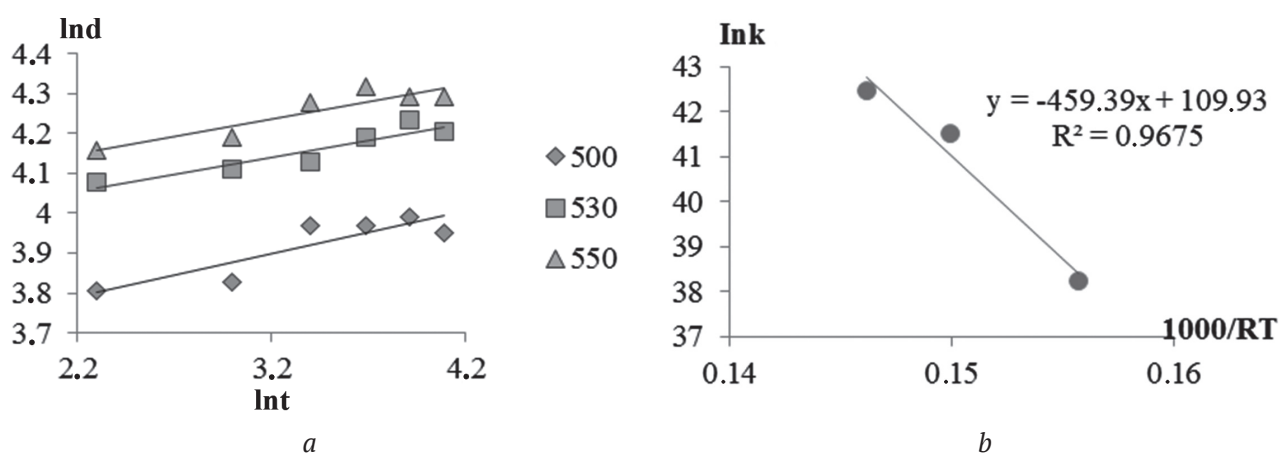
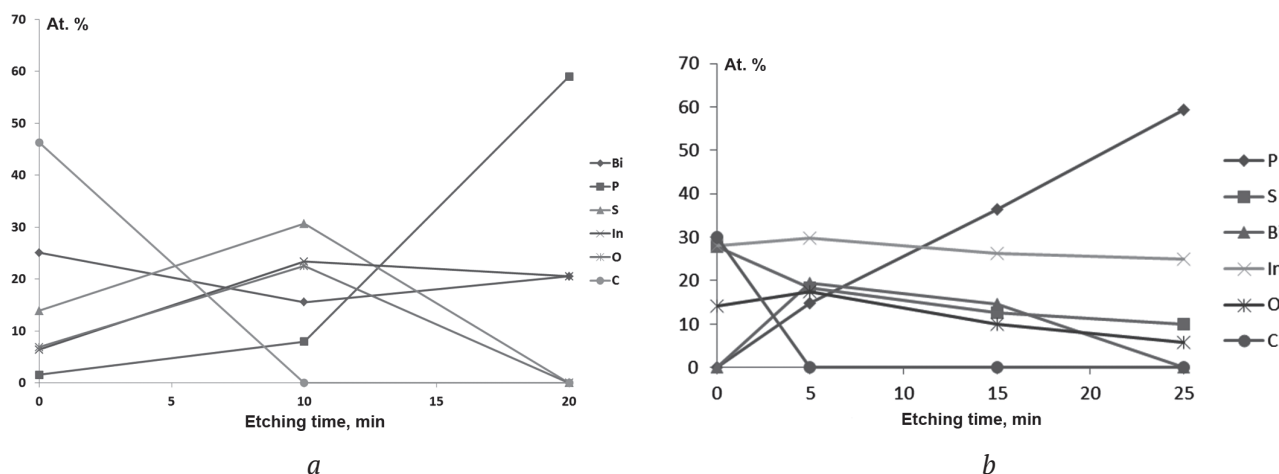


Fig. 5. Log plots of kinetic isotherms (a) and Arrhenius plot of the kinetic constant  $\ln k_{\text{av}} = f(10^5/RT)$  (b) of the process of thermal oxidation of  $\text{Bi}_2(\text{SO}_4)_3/\text{InP}$  heterostructures



**Fig. 6.** Auger profile of thermal oxidation of InP with the  $\text{Bi}_2(\text{SO}_4)_3$  gas phase (at 500 °C during 60 min.) (a) and thermal oxidation of  $\text{Bi}_2(\text{SO}_4)_3/\text{InP}$  heterostructures (at 525 °C, 60 min) (b)

by the constant replenishment of the concentration of the modifier chemostimulator from an endless source in the absence of evaporation of bismuth-containing fragments, in contrast to sulphur-containing fragments. For films, grown by thermal oxidation of  $\text{Bi}_2(\text{SO}_4)_3/\text{InP}$  heterostructures (see Fig. 6b), after 25 min of etching, a noticeable increase in the phosphorus content was observed, bismuth disappeared almost completely, indicating its consumption without replenishment in the case of the final source of the modifier chemostimulator. The amount of sulphur and oxygen was ~ 10 and 6 at%, respectively. The similarity of the distribution profiles of oxygen and sulphur (see Figs. 6a and 6b) indicates that the indium and phosphorus of the substrate can be coordinated not only with oxygen, but also with sulphur. The possibility of such coordination for InP thermal oxidation processes with deposited sulphide layers, sulphur transit, similar to oxygen transit, was demonstrated by us in [12]. Thus, despite the small chemostimulating effect, probably caused by the strength of the binding of bismuth to the sulphate group and a sharp decrease in its capacity as an oxygen transmitter, the role of  $\text{Bi}_2(\text{SO}_4)_3$  as a modifier was obvious. The films grown by both of the above methods had semiconductor properties ( $\rho \sim 10^6 \text{ Ohm}\cdot\text{cm}$ ), in contrast to intrinsic oxide on InP, which is characterized by ohmic conductivity [12, 21].

From all that has been said it follows that the physicochemical nature of the chemostimulator, its ability to transit interactions, and the

renewability of oxide forms play dominant roles. From this point of view, both  $\text{SnO}_2$  and  $\text{Bi}_2(\text{SO}_4)_3$ , being modifiers of the composition and properties of the films, practically do not possess a chemostimulating effect, or the effect was noticeable, but was not very significant. The value of the acceleration of the process compared to the intrinsic oxidation did not even reach two times.

From the point of view of achieving a significant chemostimulating effect while simultaneously modifying the composition and properties of the synthesized films, the use of combinations of oxides with the possibility of synergistic effects was effective. For experimental verification of this position, a composition of 40 %  $\text{Co}_3\text{O}_4$ +60 %  $\text{MnO}_2$  was chosen and magnetronically (see Experimental) deposited on the surface of InP. In terms of its qualitative composition, the sprayed layer corresponded to the specified one (XRD, Fig. 7).

The course of oxidation isotherms of (40 %  $\text{Co}_3\text{O}_4$ +60 %  $\text{MnO}_2$ )/InP heterostructures in the temperature range from 490 to 570 °C is shown in Fig. 8.

The results of processing kinetic data of the oxidation process of heterostructures (40 %  $\text{Co}_3\text{O}_4$ +60 %  $\text{MnO}_2$ )/InP using the formal kinetic equation [15] are presented in Table 1. From the table it follows that  $n_{\text{av}}$  was 0.27, and the EAE was 50 kJ/mol, which was much lower than the EAE of the “reference” systems ( $\text{Co}_3\text{O}_4/\text{InP}$  – 103 kJ/mol,  $\text{MnO}_2/\text{InP}$  – 180 kJ/mol, native InP oxidation was



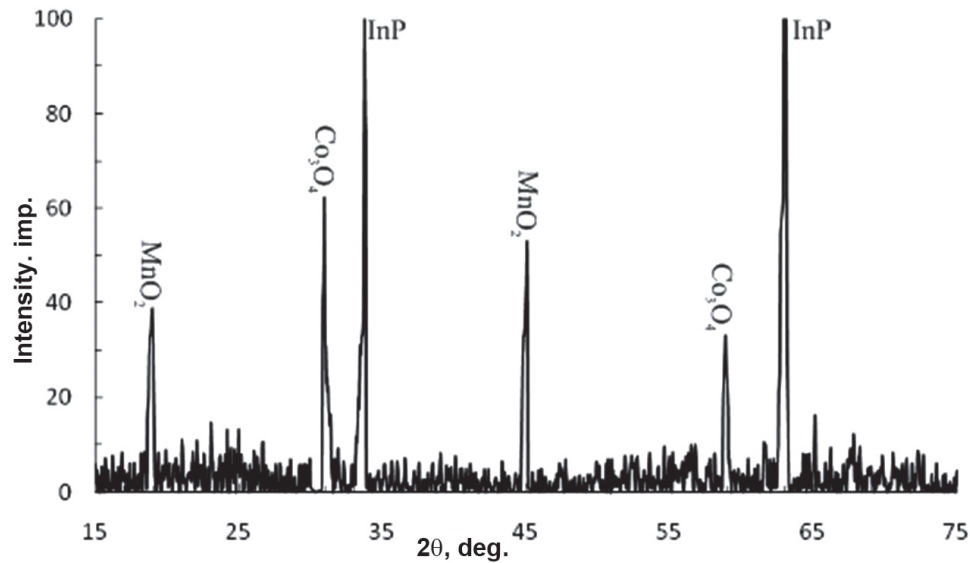


Fig. 7. X-ray diffraction pattern of (40 %  $\text{Co}_3\text{O}_4$ +60 %  $\text{MnO}_2$ )/InP heterostructure without thermal oxidation

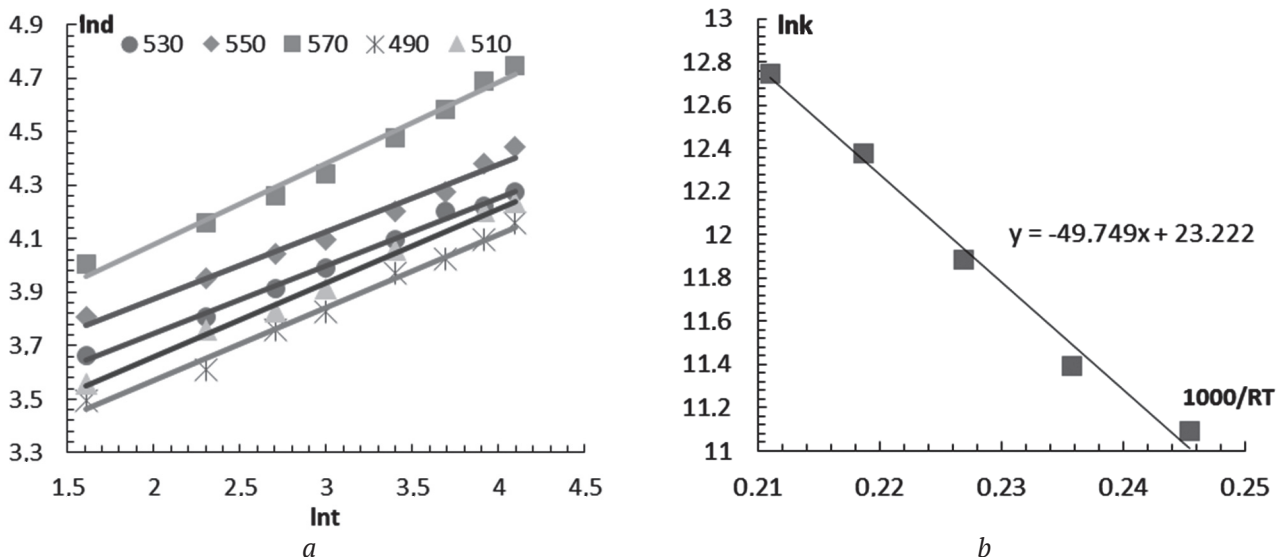


Fig. 8. Log plots of kinetic isotherms (a) and Arrhenius plot of the kinetic constant  $\ln k_{av} = f(10^5/RT)$  (b) of the process of thermal oxidation of (40 %  $\text{Co}_3\text{O}_4$ +60 %  $\text{MnO}_2$ )/InP at 490-570 °C (a)

170 kJ/mol). The determining solid-phase stage was limited by diffusion in the solid phase, but the mechanism of action of the selected complex chemostimulator was close to the catalytic and close to that for  $\text{V}_2\text{O}_5$ /InP heterostructures [12].

The thickness of the formed oxide films turned out to be much higher than expected under the assumption of an independent parallel effect of  $\text{Co}_3\text{O}_4$  and  $\text{MnO}_2$  on the thermal oxidation of InP, which proves the synergy of the combined effects of the chemostimulators of the applied composition.

The relative increase in film thickness compared to intrinsic oxide on indium phosphide

for  $\text{MnO}_2$ /InP,  $\text{Co}_3\text{O}_4$ /InP and (40 %  $\text{Co}_3\text{O}_4$ +60 %  $\text{MnO}_2$ )/InP heterostructures, calculated using

$$b = \frac{\Delta d_{\text{Me}_x\text{O}_y/\text{InP}} - \Delta d_{\text{InP}}}{\Delta d_{\text{InP}}} \cdot 100\%, \quad [13]$$

gradually increased to 60 min, its maximum value was 70 %. Data allowing evaluating the effectiveness of the composition in comparison with individual oxides are shown in Table 3.

$\text{MnO}_2$ /InP heterostructures were characterized by the maximum value of the relative increase in film thickness at the initial stage of the process, in the first 10 min. For  $\text{Co}_3\text{O}_4$ /InP heterostructures the maximum relative increase in film thickness was observed at 30 min. It must be emphasized

**Table 3.** The values of the relative change of the film thickness formed in the process of thermal oxidation of MnO<sub>2</sub>/InP, Co<sub>3</sub>O<sub>4</sub>/InP and (40 % Co<sub>3</sub>O<sub>4</sub>+60 % MnO<sub>2</sub>)/InP in comparison with the thermal oxidation of InP

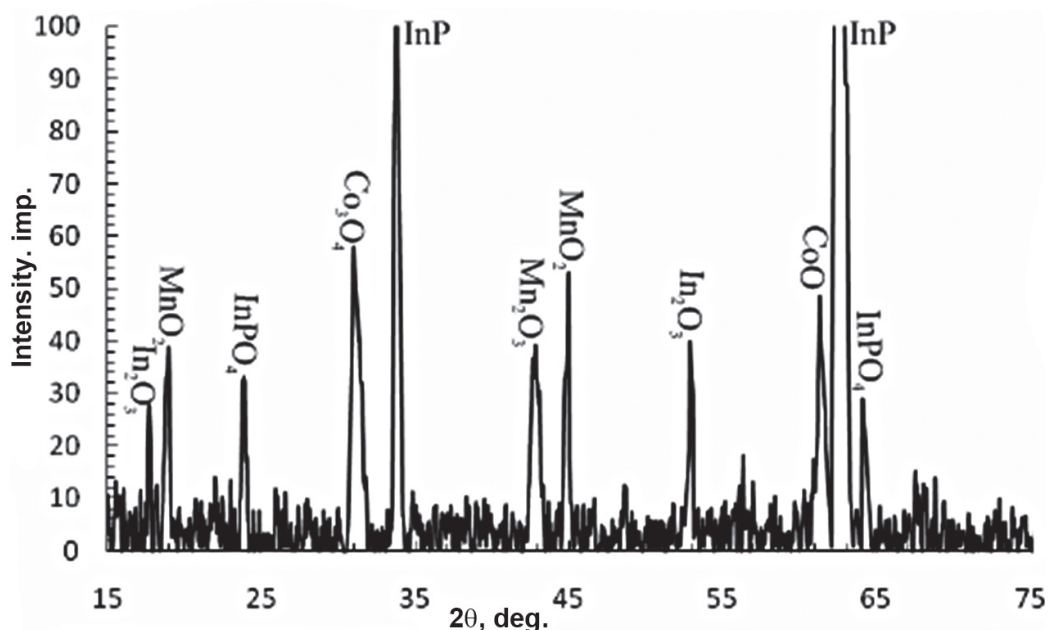
Heterostructure	T, °C	The values of the relative change of the film thickness formed in the process of thermal oxidation, %					
		10, min	20, min	30, min	40, min	50, min	60, min
MnO <sub>2</sub> /InP	530	67	60	56	25	17	11
Co <sub>3</sub> O <sub>4</sub> /InP		37	42	61	50	47	30
(40 % Co <sub>3</sub> O <sub>4</sub> +60 % MnO <sub>2</sub> )/InP		50	25	31	43	56	70

that for the transit mechanism of chemically stimulated oxidation of A<sup>III</sup>B<sup>V</sup> the values of the relative increase in the film thickness decreased during the developed stage of the process passing through the maximum. The relative increase in film thickness during the thermal oxidation of (40 % Co<sub>3</sub>O<sub>4</sub>+60 % MnO<sub>2</sub>)/InP heterostructures had a different dynamics, which, in addition to the low EAE, indicates the large contribution of the catalytic component to transit, e.g. the transit-catalytic mechanism of the process.

According to XRD data, films formed by the oxidation of (40 % Co<sub>3</sub>O<sub>4</sub>+60 % MnO<sub>2</sub>)/InP heterostructures, contained cobalt oxides Co<sub>3</sub>O<sub>4</sub> and CoO, manganese oxides in various oxidation states (MnO<sub>2</sub>; Mn<sub>2</sub>O<sub>3</sub>), In<sub>2</sub>O<sub>3</sub> and InPO<sub>4</sub> (Fig. 9).

From these data it follows that, in addition to chemostimulation, which is reflected in the increase in the rate of film formation (see Table

3), a modification was made by changing their composition. This modification, first, achieved a very low content of unoxidised indium in the films of ~ 0.5 %, according to spectral ellipsometry, while the volume fraction of inclusions of unoxidised indium in films did not exceed 1 %. This means that the intrinsic films on InP, possessing ohmic conductivity, were replaced by semiconductor ones, which is consistent with our previously obtained data [15]. Secondly, there is the possibility to control of the contribution of the catalytic component into the process mechanism and fine adjustment of the properties of semiconductor films by changing the composition of the deposited oxides and taking into account the synergism of their combined effect. Such control is necessary, for example, for target regulation of their sensory response [22]. Third, the additional introduction of an anion



**Fig. 9.** X-ray diffraction pattern of (40 % Co<sub>3</sub>O<sub>4</sub>+60 % MnO<sub>2</sub>)/InP after thermal oxidation at 530 °C over 60 min

former modifier associated with an effective chemostimulator (for example, manganese or cobalt phosphates, or both) to this system will ensure, as we showed in [14], a transition to high-quality dielectric films characterized by high growth rate and acceptable, fairly smooth, surface morphology.

#### 4. Conclusion

Thus, in this study, the fundamental role of the physicochemical nature of the chemostimulator, its ability to transit interaction and the renewability of oxide forms in the process of InP thermal oxidation was established. The introduction of modifying phosphate groups from  $\text{AlPO}_4$  in the thermal oxide films, together with the deposition of  $\text{SnO}_2$  on the surface of without it, led to the resistance of the films, similar to that for the oxidation of  $\text{SnO}_2/\text{InP}$  heterostructures, without additional administration of phosphates. The sophisticated chemostimulator modifier  $\text{Bi}_2(\text{SO}_4)_3$  introduced in the oxidation process both through the gas phase and onto the InP surface, being a modifier of the composition and properties of the films, did not possess a significant chemostimulating effect, which is explained by the limited capabilities of the cation former as a transmitter. The complex 40 %  $\text{Co}_3\text{O}_4$  + 60 %  $\text{MnO}_2$  chemostimulator deposited on the InP surface, determining the accelerated formation of films in comparison with intrinsic oxidation by the transition-catalytic mechanism was the most effective out of the studied chemostimulators. This chemostimulator was the part of the synthesized films, capable of purposefully modifying their properties by varying the content of components in it.

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#### Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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