EFFECT OF OXIDE COMPOSITION (V$_2$O$_5$+Al$_2$O$_3$) VIA GAS PHASE ON THE THERMAL OXIDATION OF InP

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The effect of the oxide-chemostimulator V$_2$O$_5$ and the inert component Al$_2$O$_3$ binary compositions on the thermal oxidation of InP have been studied. The area of negative deviation of nanoscale oxide film thickness on InP from the additive joint effect has been established with a minimum for a composition of 20% Al$_2$O$_3$ + 80% V$_2$O$_5$. A decrease in the transit efficiency effect of V$_2$O$_5$ chemostimulator in composition with Al$_2$O$_3$ has been associated with an intensification of the transformation of V$_2$O$_5$ into V$_2$O$_3$, which is not an oxygen transitor.

Keywords: indium phosphide, thermal oxidation, transitor, chemostimulator, vanadium oxides, nanoscale films.

1. Introduction

Mutual increase or decrease of chemostimulating activity by the cooperative influence of two activator oxides have been observed during A^{III}B^{V} thermal oxidation [1,2]. The phenomenon is due to the chemical interaction of the oxides and products of their transformations while present in the solid and gas phases. Oxides may be introduced through the gas phase or directly deposited on the surface of the semiconductor. The influence of non-chemical factors (size, diffusion, surface, etc.) can be detected when the active oxide is introduced into the system via the gas phase jointly with an inactive oxide, which is inert to both oxidizable semiconductor and the first oxide. A linear relationship between the oxide film thickness on GaAs and the activator oxide's composition was discovered during thermal oxidation processes of GaAs with compositions of a chemostimulating oxide (Sb$_2$O$_3$, Bi$_2$O$_3$, MnO, MnO$_2$, V$_2$O$_5$) and an inert oxide (Al$_2$O$_3$) [3,4]. The realization of such an additive dependence in practice allows one to adjust the chemostimulator concentration and to create nanoscale films doped with precisely controlled gas sensitive properties as shown with the GaAs example [3]. The chemostimulator leads to accelerated oxidation of the semiconductor components on the transit mechanism [5], and the inert oxide can affect both the conversion of oxide-chemostimulator and the above-mentioned non-chemical processes. In addition, one can expect InP to exert an influence on the secondary processes in the resulting film (e.g. formation of phosphate and changing the "polymer" structures [6] of formed phosphates). V$_2$O$_5$ is one of the most interesting chemostimulators, which is capable of having both a transit and catalytic effect on A^{III}B^{V} thermal oxidations. This effect is dependent upon the method of chemostimulator introduction [7–9].

The purpose of this research is to establish the interaction characteristics of oxide compositions V$_2$O$_5$ + Al$_2$O$_3$ and their roles in the processes of the thermal oxidation of InP.

2. Experimental

For these studies, monocrystalline polished FIE-1A (doped by Sn) n-InP(100) wafers were used with a 300 K concentration of majority carriers no lower than 5×10^{16} cm^{-3}. Before thermal oxidation, the wafer surfaces were treated in H$_2$SO$_4$ (reagent grade, Russian State Standard GOST 4204-77, 92.80%): H$_2$O$_2$ (analytical grade, Russian State Standard GOST 177-88, 56%): H$_2$O = 2:1:1 etchant for 10 minutes and then rinsed repeatedly in bi-distilled water. The oxide films were obtained by thermal oxidation in a horizontal quartz reactor with

a diameter of 30 mm (flow system) furnace MTP-2M-50-500, pre-heated to 530 °C operating temperature. The temperature in the reactor was controlled with an accuracy of ± 1 °C (TRM-10). The oxygen flow rate was 30 l/h.

Mixed oxide compositions were made using V_2O_5 and Al_2O_3 (analytical grade, specification TU 6-09-4093-88 and TU 6-09-426-75 respectively) powders with an average particle size of 150–200 μm. After mechanical grinding in an Arden shaker for 15 minutes, each of the powders was passed through a series of sieves with a mesh size of 200 and 150 microns. The mass of each oxide present in a 0.2 g of sample was then calculated using the following formulas:

$$m_{V_2O_5} = \frac{0.2}{\left[\left(\frac{1}{X_{V_2O_5}} - 1\right)\frac{M_{V_2O_5}}{M_{Al_2O_3}}\right] + 1}, \qquad m_{Al_2O_3} = \frac{0.2}{\left[\left(\frac{1}{X_{Al_2O_3}} - 1\right)\frac{M_{Al_2O_3}}{M_{V_2O_5}}\right] + 1},$$

where X is the amount of V_2O_5 and Al_2O_3 in mole %. Samples were thoroughly mixed for at least 3 minutes.

The activator composition was placed in a quartz container, covered by the InP wafer with its working side facing the flow of activator vapor at a distance of 10 mm. The container with the wafer and activator mixture was placed in the work zone of a furnace and kept in an oxygen flow for 10–40 minutes. Oxide composition was changed every 10 minutes, in each experiment a freshly prepared oxides composition was used.

The oxidation conditions were chosen to compare the results with those previously obtained for GaAs with different chemostimulator compositions [3]. The optimal distance between the surface of wafers and the mixed oxides composition was determined empirically by the maximum value of oxidation acceleration when compared with the native InP thermal oxidation and strictly controlled for all experiments.

The thickness of the oxide films were determined after every 10 minutes of oxidation by laser ellipsometer LEF-754 ($\lambda = 632.8$ nm) with an absolute accuracy of ± 1 nm. This methodology (with additional oxidation) allowed measurement of the film thickness on the same sample at different reaction times with a constant temperature and oxides mixture composition. This excluded the uncontrolled errors associated with InP surface treatment (before thermal oxidation) and changes in its properties from sample to sample.

Transformations in the oxides and their compositions was established by X-ray diffraction (XRD, X-ray diffractometer DRON-4, Co-Kα radiation, $\lambda = 1.79021$ Å). The elemental composition of the oxide films on InP and distribution of component thickness was investigated by Auger electron spectroscopy (AES, ESP-3 analyzer DESA-100, an accuracy of $\pm 10\%$). Surface morphology of the samples was measured by scanning tunneling microscopy (STM, complex of nanotechnological equipment "UMKA"), the data were processed using the microscope software. A quantitative analysis of the elemental composition of thin films was performed on CamScan (EPMA, $\pm 0.1\%$).

3. Results and Discussion

The main reason for the nonlinear dependence of the oxide film thickness on the GaAs surface on the composition of the mixture is the pronounced acid-base and redox interactions of the oxides-chemostimulators in both the solid and gas phases [1]. Individual V_2O_5 and Al_2O_3 powders and their compositions were annealed at 530 °C for 10 and 60 mins (conditions corresponding to studied oxidation process of InP) in order to investigate the possibility of any

TABLE 1. X-ray powder diffraction data for individual oxides and their compositions

Sample	Annealing conditions	Identified phases
Al_2O_3	530 °C, 10 minutes	γ-Al_2O_3
V_2O_5	530 °C, 10 minutes	V_2O_5
$(Al_2O_3)_{0.8}(V_2O_5)_{0.2}$	530 °C, 10 minutes	γ-Al_2O_3; V_2O_5
$(Al_2O_3)_{0.2}(V_2O_5)_{0.8}$	530 °C, 10 minutes	γ-Al_2O_3; V_2O_5; V_2O_3; V_6O_{13}
$(Al_2O_3)_{0.5}(V_2O_5)_{0.5}$	530 °C, 10 minutes	γ-Al_2O_3; V_2O_5; V_2O_3
$(Al_2O_3)_{0.5}(V_2O_5)_{0.5}$	530 °C, 60 minutes	γ-Al_2O_3; V_2O_5; V_2O_3
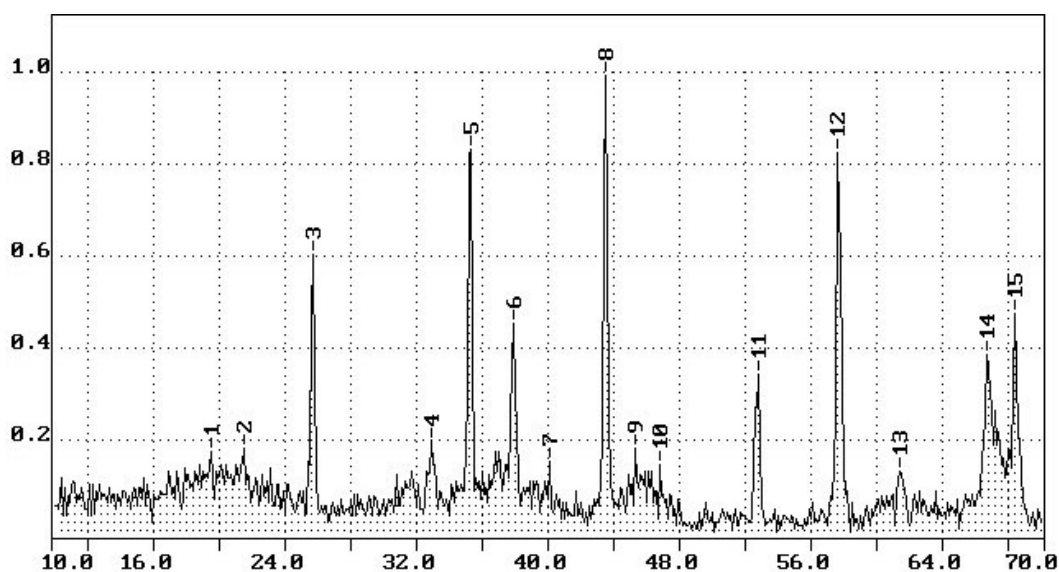
FIG. 1. The XRD pattern of composition 80% V_2O_5 + 20% Al_2O_3 annealed at 530 °C for 10 minutes

additional interactions and transformations. The results of XRD analysis are shown in Tab. 1 and fig. 1.

According to the results of XRD, after 10 minutes of annealing, individual oxides have not changed. The diffractograms of V_2O_5+Al_2O_3 compositions showed peaks corresponding to V_2O_3 (peaks No. 4, 12 and 14, $d = 2.722$, 1.600 and 1.402, respectively), both for 10 min annealing, and for 60 minutes. Consequently, the components of V_2O_5 and Al_2O_3 mixtures react with one another, as shown in the partial conversion of V_2O_5 to V_2O_3.

Although, the joint phase and solid solutions were not detected for these annealing conditions by XRD, however, according to [10], there should be bronze types α ($Al_xV_2O_5$) and ν ($Al_xV_6O_{12}$), solid solution $Al_zV_{2-z}O_4$ and bronze $Al_{0.33}V_2O_5$ phases formed in the Al_2O_3–V_2O_5–V_2O_3 system. The absence of these phases in our systems may be due to insufficient duration and relatively low annealing temperatures.

In reactions performed at 530 °C over 10–40 minutes (fig. 2), it was shown that the oxide film thickness on InP was dependent upon the oxide composition. Furthermore, the addition of small amounts of Al_2O_3 to V_2O_5 resulted in a negative deviation from the additive dependence with a minimum for a composition of 20% Al_2O_3 + 80% V_2O_5. This deviation was reduced with increasing amounts of Al_2O_3 in the composition. Starting from 40% Al_2O_3, there is an additive dependence between the oxide film thickness on InP and the composition

of the oxide mixture. The same relationship was observed with negative deviation from linear dependence of the oxide film thickness for the thermal oxidation of a semiconductor under the influence of 20% Al_2O_3 + 80% MnO_2 composition [4].
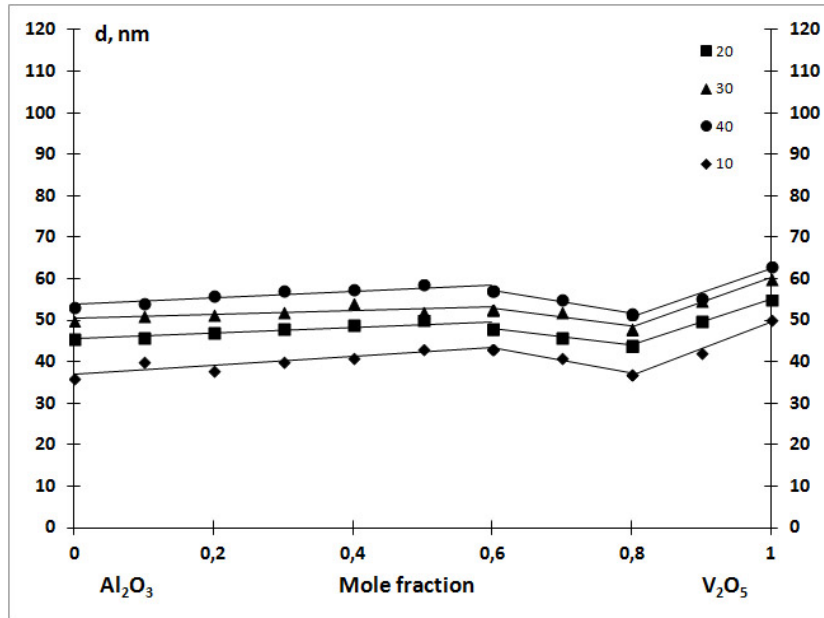

FIG. 2. Plots of the oxide films thickness grown on InP at 530 °C at 10, 20, 30, 40 minutes versus concentration

The relative integral films thickness (dR), defined as the difference between the thickness d of the oxide layer on the InP surface actually achieved under the influence of the oxide composition and the expected thickness calculated by the addition rule, assuming their independent parallel influence. This characteristic, previously introduced for the interpretation of similar processes [11], can quantify characterized non-linear effects during the thermal oxidation of $A^{III}B^V$ semiconductors in the presence of mixed oxide compositions (Fig. 3).

As shown on fig. 3, in a region with up to 40% concentration of Al_2O_3 there is a negative deviation from additive dependence which increases with time. The thickness of the oxide film is increased linearly when the content of Al_2O_3 was higher than 40%. This is evidence of the additive effects of the composition of V_2O_5 + Al_2O_3 upon InP oxidation.

Since the composition of the activator influences the gas-phase InP thermal oxidation, and transitional interactions can occur too, one should consider that a possible decomposition and transformation of the corresponding oxides may occur during the experiments. Mittova et al. found that for equilibrium conditions at 800 K, the percentage of V_4O_{10} did not exceed 0.3% in the vapor phase above the V_2O_5(s) [12]. At 800 K, the vapor over V_4O_8 has a V_4O_{10} content of about 0.06% and it decreased with increasing temperature. Under these experimental conditions, which are far from equilibrium, the chemostimulator in oxide composition can be in different phases . The relative amount of the chemostimulator will depend on the amount of the second component. Transit opportunities for various forms of vanadium oxide during InP thermal oxidation did differ (XRD, table 1). In the first approximation, they can be estimated by changes in the equilibrium values of the Gibbs free energy of oxygen transit reactions at the experimental temperature:
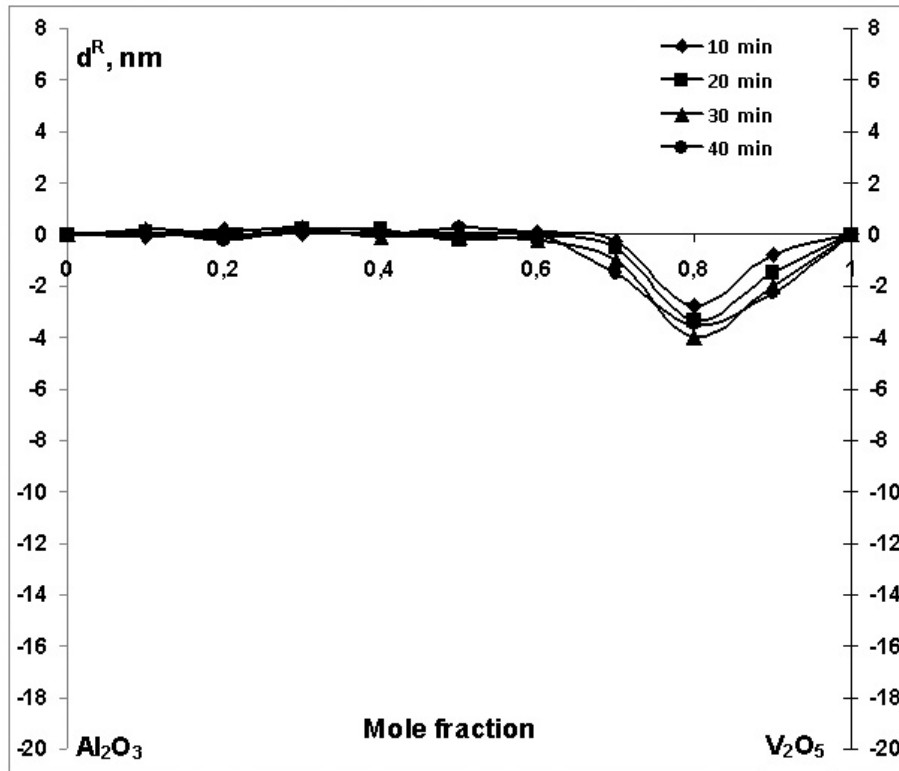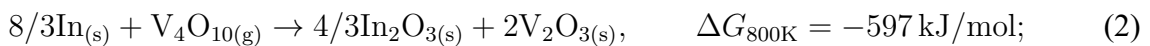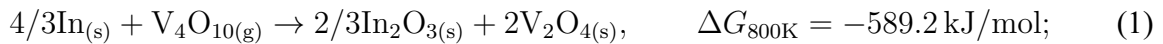
FIG. 3. Relative integral oxide film thickness dR grown on InP at 530 °C at 10, 20, 30, 40 minutes as a function of the $V_2O_5 + Al_2O_3$ composition

$$4/3In_{(s)} + V_4O_{10(g)} \rightarrow 2/3In_2O_{3(s)} + 2V_2O_{4(s)}, \qquad \Delta G_{800K} = -589.2\,kJ/mol; \qquad (1)$$

$$8/3In_{(s)} + V_4O_{10(g)} \rightarrow 4/3In_2O_{3(s)} + 2V_2O_{3(s)}, \qquad \Delta G_{800K} = -597\,kJ/mol; \qquad (2)$$

$$2In_{(s)} + 3/10V_4O_{10(g)} \rightarrow In_2O_{3(s)} + 12/10V_{(s)}, \qquad \Delta G_{800K} = -12.3\,kJ/mol. \qquad (3)$$

Similar reactions for phosphorus are also accompanied by a significant negative change of ΔG, comparable to that of the above.

V_2O_3 produced during the annealing of $V_2O_5 + Al_2O_3$ composition (Table 1), evaporates at temperatures of about 1800 K accordingly to the reaction [4]:

$$V_2O_{3(s)} = VO_{2(g)} + VO_{(g)}. \qquad (4)$$
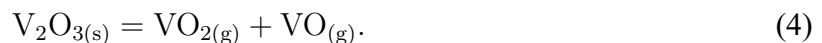
The transfer of oxygen to indium from VO_2 and VO is thermodynamically impossible and therefore, these oxide forms cannot act as an oxygen transistor:

$$2In_{(s)} + 3/2VO_{2(s)} \rightarrow In_2O_{3(s)} + 3V_{(s)}, \qquad \Delta G_{800K} = 793\,kJ/mol, \qquad (5)$$

$$2In_{(s)} + 3VO_{(s)} \rightarrow In_2O_{3(s)} + 3V_{(s)}, \qquad \Delta G_{800K} = 919\,kJ/mol. \qquad (6)$$

The inclusion of these oxides in the film is also not possible because the temperature of InP oxidation was far below the point where V_2O_3 evaporation occurs .

Al_2O_3 does not affect the oxidation process under experimental conditions due to thermodynamic restrictions; it is incapable of transferring oxygen to semiconductor components (its evaporation becomes noticeable only at 2440 K [12]). Aluminum was not detected in the oxide films grown on InP in the presence of $V_2O_5 + Al_2O_3$ compositions (EPMA data).

STM data show a fairly homogeneous surface of oxide films formed on InP in the presence of V$_2$O$_5$ + Al$_2$O$_3$ (height of the relief is in the range of 20–30 nm). The relief of the surface is much more pronounced for films prepared during the thermal oxidation of InP with directly pre-deposited V$_2$O$_5$ nanoislands (order of 60 nm [13]). A slight relief of the film surface in case of exposure to the V$_2$O$_5$ + Al$_2$O$_3$ composition through the gas phase is the result of evaporation of volatile phosphorus oxides during InP thermal oxidation (correlation with the AES data). The height of the surface relief naturally increases with the oxidation time (fig. 4a and 4b).
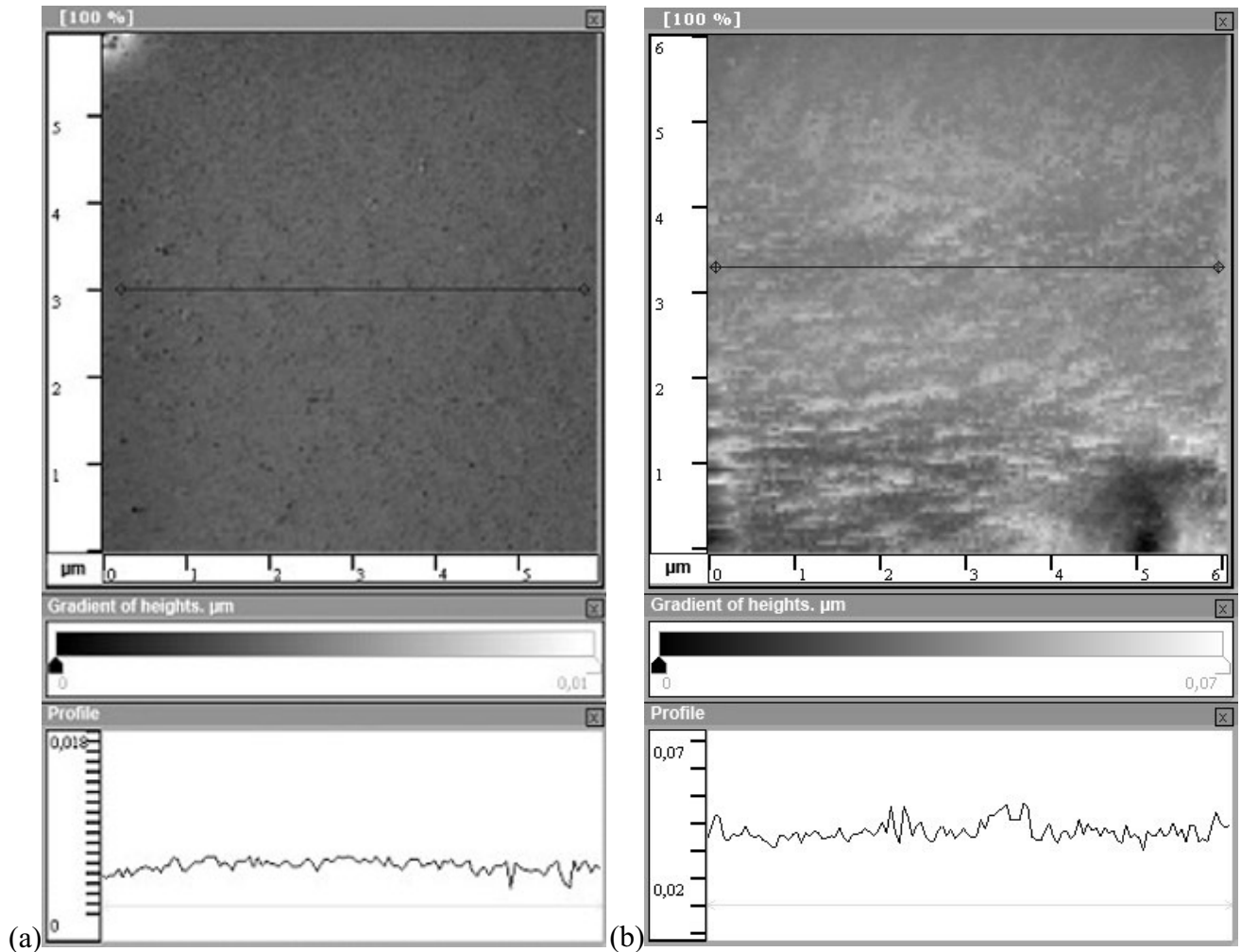

(a) (b)

FIG. 4. STM image and profile of surface of oxide films formed by thermal oxidation of InP in the presence of composition 80% V$_2$O$_5$ + 20% Al$_2$O$_3$ at 530 °C at 10 (*a*) and 40 (*b*) minutes

The kinetic curves "oxide film thickness — oxidation time" were taken at a temperature range of 500–550 °C (fig. 5) in order to establish the mechanism of InP thermal oxidation in the presence of a V$_2$O$_5$ + Al$_2$O$_3$ mixture (60% V$_2$O$_5$ + 40% Al$_2$O$_3$). This composition lies in a linear range, see fig. 3.

By processing the kinetic data using the equation $d = (k\tau)^n$ [14], it was found that the index n was 0.26, and the effective activation energy (EAE) was 219 kJ/mol. This value is between the EAE of InP oxidation with V$_2$O$_5$ introduced via the gas phase (164 kJ/mol) and native InP oxidation (273 kJ/mol). $n < 0.5$, implying that the process of thermal oxidation was
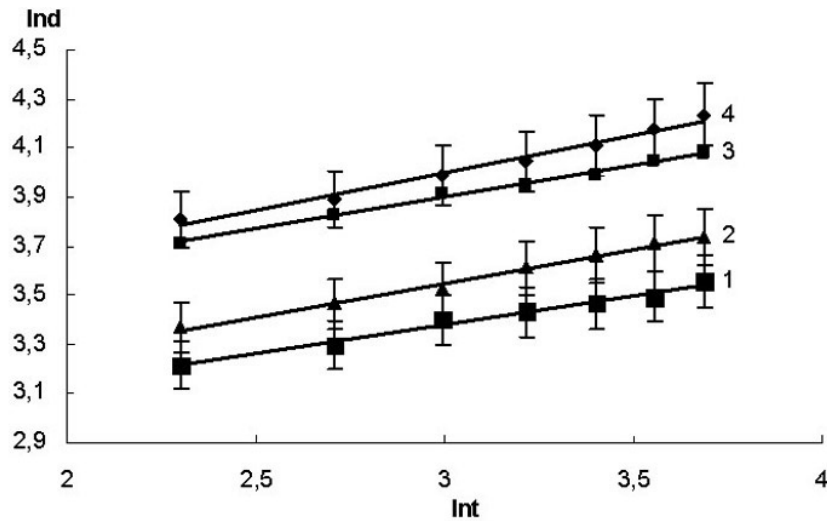
FIG. 5. Log-log plots of the oxide layers thickness vs. time for the thermal oxidation of InP in the presence of 80% V_2O_5 + 20% Al_2O_3 at 500 °C (1), 520 °C (2); 530 °C (3); 550 °C (4)

controlled by diffusion in the solid phase. The relative increase in the film thickness in the presence of a chemostimulator composition compared with its own oxidation, was calculated as:

$$b = \frac{\Delta d_{(V_2O_5+Al_2O_3)-InP} - \Delta d_{InP}}{\Delta d_{InP}} \cdot 100\%,$$

where Δd is the change in the film thickness and is 15–20%. Thus, the transit nature [5] of InP oxidation saved under the influence of V_2O_5 in the gas phase with addition of Al_2O_3.

According to AES data (fig. 6a) indium, phosphorus and oxygen were detected on the surface of the film in the sample oxidized at 530 °C for 40 min in the presence of a composition containing 30% V_2O_5 (linear region, see Fig. 2). For the components of the substrate contained in the oxidized state, the highest oxygen content among of all the elements was at a depth of 15 nm from the surface.

The amount of vanadium was 5–6 atom % in the films on InP, obtained in the presence of the composition with 80% V_2O_5, corresponding to the region of the negative deviation from the additive dependence (fig. 3). Indium and oxygen were present on the surface, however, the presence of phosphorus became noticeable from a depth of 20 nm, which was due to its evaporation, probably in the forms of oxides (fig. 6b). The presence of vanadium in the film, for which there is a negative deviation from the additive d^R dependence, may arise from the inclusion of transit-inactive forms of vanadium (e.g. VO_2) in the growing layers of vanadium oxide. A similar situation was observed for GaAs oxidation in the presence of a similar composition of 80% V_2O_5 + 20% Al_2O_3, where it was shown by XRD that a negative deviation of the oxide film thickness on semiconductor and that VO_2 was present [3]. The absence of aluminum in the films was confirmed by its inertness to InP thermal oxidation.

Negative deviation in the concentration dependence of the relative integrated film thickness on InP (established by the addition of up to 40% Al_2O_3 to V_2O_5) may arise from the change of the temperature range and the nature of chemostimulator's ability to undergo self-transformations. In this case, the dissociation of V_2O_5 to V_2O_3 was facilitated (V_2O_3 is not transistor of oxygen). This weakening of the chemostimulating effectiveness is due to the increased conversion to compounds of lower oxidative activity towards GaAs oxide, as evidenced by Mn_3O_4 in the case of manganese oxides (II) and (IV) in compositions with Al_2O_3 [4]. In
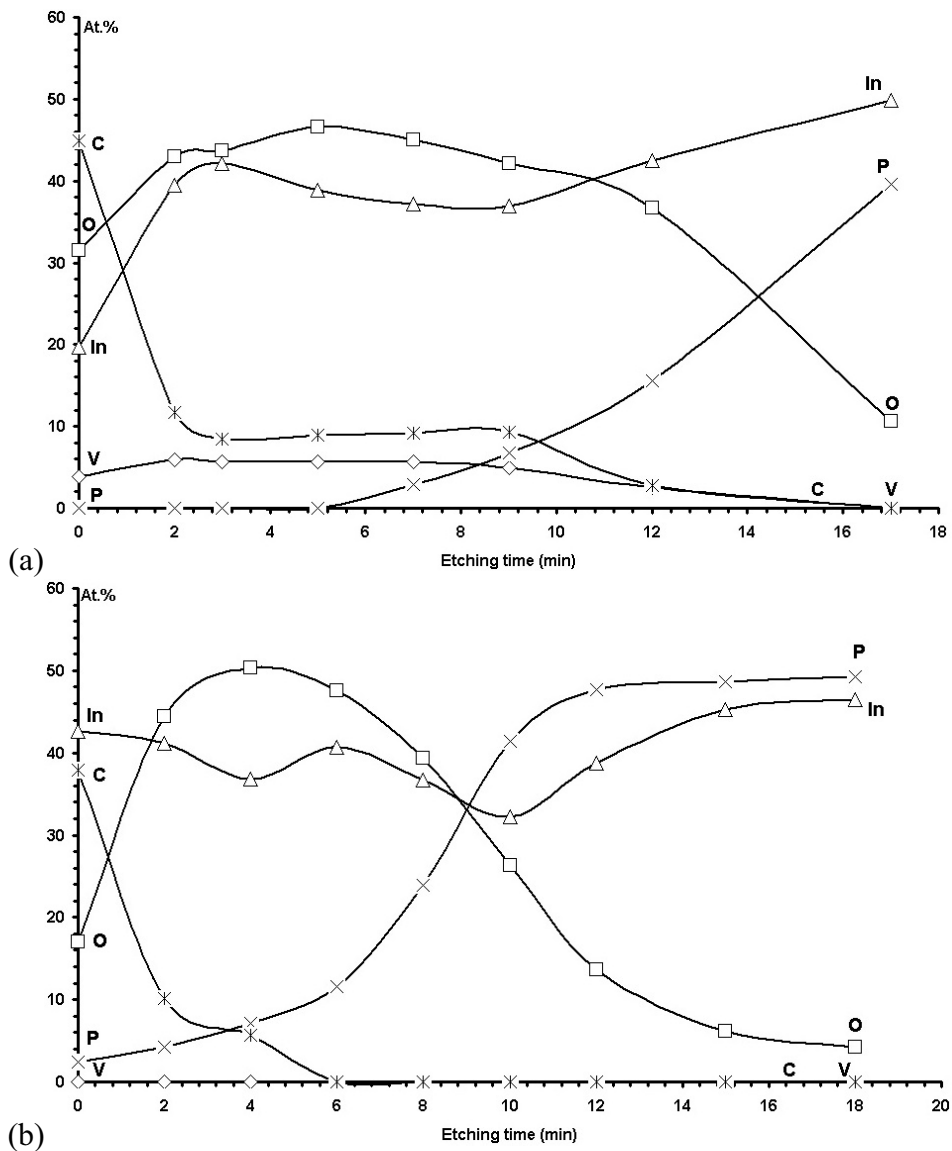
FIG. 6. AES depth profiles, obtained after 40 min of InP oxidation at 530 °C in presence of compositions: (a) −30% V_2O_5 + 70% Al_2O_3; (b) − 80% V_2O_5 + 20% Al_2O_3

addition, the chemostimulating effect of vanadium oxide can be reduced due to possible interactions between Al_2O_3 and V_2O_5, leading to the formation of aluminum vanadate. Although vanadate in an annealed aluminum oxide composition is not found (XRD data), according to [15], incongruent melting of $AlVO_4$ at 760 °C, present in the system $Al_2O_3 - V_2O_5$, can be obtained by heating a mixture of oxides Al_2O_3 and V_2O_5 at 500 °C.

Evidence for a transit mechanism of the process are: oxidation state of indium and phosphorus in the films; the inclusion of vanadium; the relative increase in the film thickness 15% to 20% in the presence of V_2O_5 + Al_2O_3 composition; EAE value close to that of the native oxidation of InP. In the case of the catalytic effect of V_2O_5 on InP thermal oxidation, the EAE was almost an order of magnitude lower in comparison with the value for their native oxidation [16]. The role of Al_2O_3 is to intensify the transition of V_2O_5 into V_2O_3. Al_2O_3 is a non-transistor of oxygen and is not included in the growing film on InP and reduces the chemostimulating effect of vanadium oxide (V).

4.   Conclusions

The influence of the inert component Al_2O_3 on V_2O_5 chemostimulating action during the thermal oxidation of InP in the presence of a mixture of these oxides in the gas phase was identified. Negative deviation from linearity of the nanoscaled oxide film thickness on InP with a minimum 20% Al_2O_3 + 80% V_2O_5 for the composition correlated with the transformation of V_2O_5 into V_2O_3, which does not have the ability to act as an oxygen transit. Thus, Al_2O_3 which is inert to the process of InP oxidation (AES, EPMA) changes the temperature range and the nature of V_2O_5 transformations. This is the ultimate reason for the deviation from linear dependence of the oxide film thickness formed on InP.

Acknowledgments

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