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Combined Influence of Chemostimulator Oxides V_2O_5 and MnO_2 Introduced via the Gas Phase on InP Thermal Oxidation

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Abstract—The effect of combined gas-phase introduction of vanadium(V) and manganese(IV) oxides on thermal oxidation of InP consists in acceleration of the oxide film formation on the InP samples regardless of the chemostimulators mixture composition. The nonlinear oxide film thickness at the InP surface as a function of the chemostimulators mixture composition has been rationalized as a result of mutual influence of V_2O_5 and MnO_2 changing their heat-induced reactivity and evaporation behavior.

Keywords: indium phosphide, vanadium(V) oxide, manganese(IV) oxide, thermal oxidation, ellipsometry

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Studies of combined influence of chemostimulator oxides on thermal oxidation of GaAs [1] including that induced by vanadium(V) and manganese(IV) oxides [2] have shown nonlinear change in the oxide film thickness at the sample surface as a function of the stimulators mixture composition. Magnetron deposition of the chemostimulators (the catalyst oxide V_2O_5 + the transistor oxide PbO) mixture onto the InP surface has revealed the change of catalytic mechanism of the semiconductor oxidation to the transit one; the nonlinear effect of the combined action of the chemostimulators can be used for fine tuning of the composition and properties of the films [3].

We report here on the oxidation of indium phosphide induced with variable-composition mixtures of V_2O_5 and MnO_2 introduced via the gas phase. Fig. 1 displays a representative spectrum of ellipsometry parameters ψ and Δ for the oxide film obtained at the thus treated InP surface.

The spectra interpretation was performed applying several methods; generally, the single-layer model was used. The optical constants of the film were specified proceeding from the expected properties; for instance, the Cauchy equation $n = n_0 + A/\lambda^2$ [4, 5] well described refractive index of dielectrics, whereas the Bruggeman model [5, 6] treated the film as a dielectric matrix with metal inclusions. Then the experimental data were fitted with those equations in order to estimate the fitting parameters n_0 and A, the film thickness d, and the fitting quality.

As described above, the processing of spectral ellipsometry yielded thickness d of the oxide film formed at the InP surface upon thermal oxidation in the presence of V_2O_5 and MnO_2 as a function of the chemostimulators mixture composition (Fig. 2).

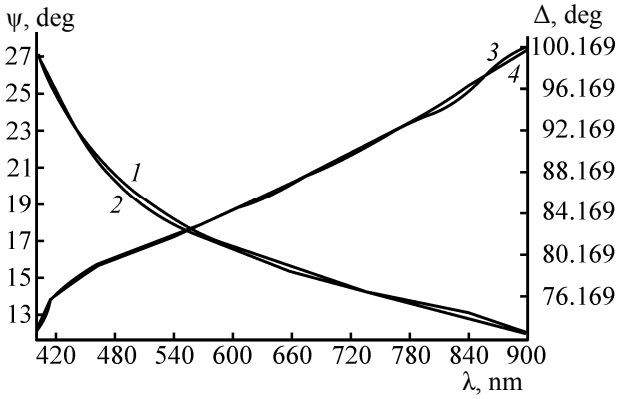

Fig. 1. Spectra of ellipsometry parameters ψ (*1* and *2*) and Δ (*3* and *4*) for the sample formed via thermal oxidation of InP (70%V_2O_5 + 30%MnO_2, 530°C) (*1* and *3*, experimental; *2* and *4*, calculated using the Cauchy model).

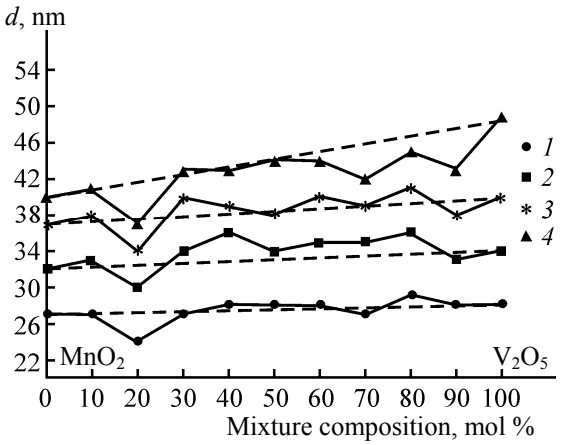

Fig. 2. Thickness *d* of the oxides film grown at InP (530°C, 40 min) as a function of the chemostimulators mixture composition. Oxidation time 10 (*1*), 20 (*2*), 30 (*3*), and 40 min (*4*).

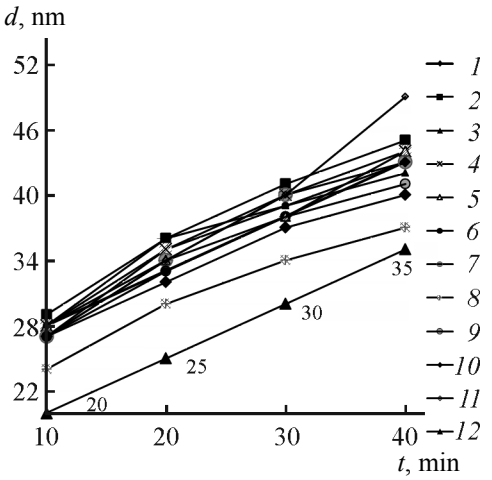

Fig. 3. Kinetics of the oxides film growth upon InP thermal oxidation in the presence of chemostimulators mixture (V_2O_5/MnO_2, mol : mol): 90 : 10 (*1*), 80 : 20 (*2*), 70 : 30 (*3*), 60 : 40 (*4*), 50 : 50 (*5*), 40 : 60 (*6*), 30 : 70 (*7*), 20 : 80 (*8*), 10 : 90 (*9*); in the presence of individual stimulators: 100% MnO_2 (*10*) and 100% V_2O_5 (*11*); and in the absence of any chemostimulator (*12*).

From the plot it is to be seen that the experimentally determined thickness of the oxide film deviated from the additive value based on the data for pure chemostimulators. Hence, the influence of the introduced oxides was nonlinear, the negative deviation from additivity being the highest at 20% of V_2O_5 in the mixture.

In general, the deviation from the additivity was less prominent at low oxidation time (10 min); the longer the oxidation time, the higher was the deviation from the additive behavior. With 30 to 80 mol % of V_2O_5 in the chemostimulators composition, the positive deviation of the film thickness from the additive one was observed, turning into the negative deviation in the final thermal oxidation stage (40 min); the latter was the most prominent in the case of the chemo-stimulators mixture with the highest vanadium(V) oxide fraction.

In the case of the shortest oxidation (10 min), the highest acceleration of the oxide formation was found for the 80 : 20 V_2O_5–MnO_2 mixture (1.45 times thicker oxide film than that in the absence of the chemostimulators); with a longer reaction run the accelerating effect was less prominent at all chemostimulators compositions. In the case of the longest oxidation, the most prominent accelerating effect was observed for pure V_2O_5.

The relatively small acceleration of oxidation as compared to the chemostimulator-free reference is typical of the transit mechanism of the catalysis [7]. Noteworthily, the accelerated formation of the oxide film on the InP surface was observed even in the cases of negative deviation of the film thickness from the additivity (Fig. 3).

Table 1 lists the results of interpretation of X-ray diffraction patterns of the films formed on the InP surface using the ASTM reference base. From the given results it is seen that the films mainly consisted of In_2O_3 and included various oxides of manganese and vanadium as well; the observed InP support phase confirmed the nanometer-scale thickness of the oxides film (Figs. 2 and 3).

The X-ray diffraction results were supported and quantified by local X-ray spectral microanalysis (Table 2).

The results confirmed the presence of small inclusions (no more than 0.3 at %) of vanadium and manganese in the oxide films. The starting support components in the oxidized state (likely, In_2O_3 and P_2O_5) formed the major fraction of the oxides film, thus pointing at a large amount of oxygen in the film. The fractions of vanadium and manganese in the film were clearly correlated with the amounts of the chemostimulators fed into the system (Table 3).

The incorporation of the chemostimulators into the films growing on the InP surface as well as the acceleration of the thermal oxidation in the presence of

Table 1. X-ray analysis: phases identified in the oxide films formed under action of the chemostimuators (under oxygen, 530°C, 40 min)

Chemostimulator	Interplanar distance, Å	Identified phase
V_2O_5	2.9420	InP
	1.9529	In_2O_3
	2.7863	VO_2
	3.5446, 3.4124, 2.3317, 2.0652, 1.7804, 1.6907	V_2O_5
$(V_2O_5)_{0.8} + (MnO_2)_{0.2}$	2.9442, 2.6810	InP
	1.9962	In_2O_3
	3.933	VO_2
	1.9155	V_2O_3
	3.5585	V_2O_5
	3.1081	MnO_2
	3.753	Mn_2O_3
$(V_2O_5)_{0.5} + (MnO_2)_{0.5}$	2.9442, 2.0739	InP
	1.8451	In_2O_3
	1.7162	V_2O_5
	3.0812	Mn_3O_4
$(V_2O_5)_{0.2} + (MnO_2)_{0.8}$	2.9360	InP
	1.7625, 2.1495, 2.0619	In_2O_3
	3.4767, 3.3883	V_2O_5
	1.7949	V_2O_3
	3.0795, 2.7775	Mn_3O_4
	3.6926	Mn_2O_3
	2.8532	MnO_2
MnO_2	2.9410	InP
	2.0739, 1.7714	In_2O_3
	2.8644	MnO_2
	3.7357, 2.7256	Mn_2O_3
	3.0995	Mn_3O_4

the metal oxides evidenced the transit mechanism of the catalyzed films formation.

Table 4 shows the results of processing X-ray diffraction patterns of the chemostimulators compositions treated under conditions corresponding to InP thermal oxidation.

The X-ray diffraction analysis revealed the following process features:

(1) In the case of V_2O_5, addition of MnO_2 led to progressive decrease in the intensity of the signals of vanadium-containing phases. Similarly, the amount of manganese-containing phases decreased upon addition of V_2O_5 to MnO_2.

(2) Amount of VO_2 phase decreased as compared to the case of pure V_2O_5 starting from the $[(V_2O_5)_{0.2} + (MnO_2)_{0.8}]$ composition; however, in the case of the $[(V_2O_5)_{0.9} + (MnO_2)_{0.1}]$ composition, amount of the VO_2 phase was even higher than in the case of pure vanadium(V) oxide. Hence, the addition of manganese(IV) oxide to vanadium(V) oxide accelerated transformations of the latter according to the reactions given below. Further increase of the manganese(IV) oxide fraction suppressed the vanadium(V) oxide transformations.

(3) Intensity of the peak corresponding to the V_2O_3 phase in the case of the composition with the highest vanadium oxide fraction $[(V_2O_5)_{0.9} + (MnO_2)_{0.1}]$ was equal to that in the case of pure vanadium(V) oxide; further increase of manganese(V) oxide fraction led to the decreasing V_2O_3 peak intensity.

(4) Addition of V_2O_5 to MnO_2 resulted in somewhat weakening of the peaks corresponding to the Mn_2O_3 phase; in other words, transformation of MnO_2 into Mn_2O_3 was suppressed. Similar behavior was observed in the case of the $[(V_2O_5)_{0.5} + (MnO_2)_{0.5}]$ composition. Further increase in the V_2O_5 fraction resulted in the growing $MnO_2 \rightarrow Mn_2O_3$ conversion as compared to the pure manganese(IV) oxide.

(5) Relative intensity of the MnO_2 and Mn_2O_3 peaks evidenced significant transformation of MnO_2, whereas in the case of vanadium oxides the VO_2 and V_2O_3 peaks were much weaker than the V_2O_5 one.

The described features of the starting chemostimulators transformations directly influenced the thermal oxidation of InP.

Addition of manganese(IV) oxide to vanadium(V) oxide enhanced transformations of the latter following

Table 2. Local X-ray spectral microanalysis of the oxide films formed under the action of the chemostimuators (under oxygen, 530°C, 40 min)

Sample	Film elemental composition, at %					
	In	P	V	Mn	O	C
100% V_2O_5	32.4188	1.4775	0.1959	–	46.1577	4.7680
80% V_2O_5 + 20% MnO_2	32.7118	19.2135	0.1617	0.0297	43.6268	4.2405
50% V_2O_5 + 50% MnO_2	31.1317	21.6296	0.2066	0.2101	42.1259	4.6862
20% V_2O_5 + 80% MnO_2	32.7139	20.2146	0.0515	0.1507	42.2478	4.6414
10% V_2O_5 + 90% MnO_2	31.9108	18.9865	0.0326	0.1929	44.4454	4.4418
100% MnO_2	36.9286	27.8304	–	0.1857	30.5634	4.4919

the $V_2O_5 \rightarrow VO_2 \rightarrow V_2O_3$ scheme. Since the oxides composition affected the InP thermal oxidation via the gas phase, the features of decomposition and transformation of chemostimulators under the conditions of the experiment should be taken into account. The equilibrium fractions of V_4O_{10} and V_4O_8 in the vapor above $V_2O_{5(s)}$ are below 0.3% and ~0.06%, correspondingly, (800 K), the latter fraction decreasing upon heating [8]. However, the system studied in this work was not equilibrated, and the chemostimulator could exist in a number of forms, their relative amounts being dependent of the presence of the second component.

To generalize, the kinetic study of thermal oxidation of InP assisted by the (V_2O_5 + MnO_2) mixtures of varied composition revealed the accelerating effect of the chemostimulators resulting from the mechanism change from the self-oxidation (in the absence of the chemostimulators) to the transit interaction. The oxides film formed on the InP surface contained the applied chemostimulators, as revealed by X-ray diffraction and local X-ray spectral microanalysis. Addition of the less efficient chemostimulator (MnO_2) to the more efficient one (V_2O_5) resulted in decrease of the formed oxides film, the effect being non-additive (Fig. 2). Generally, the deviation from additivity was negative and depended on the chemostimulators mixture composition and the reaction time. In the early stage of the process the deviation from additivity was minimal, whereas the deviation became progressively prominent with longer oxidation time. The oxides compositions enriched with vanadium oxides were exceptional cases: the deviation from additivity remained minimal throughout the process. In all likelihood, the most efficient form of the chemostimulator (V_2O_5) was transformed into the less active forms in the early stage of the oxidation.

Manganese(IV) oxide is less reactive chemistimulator than vanadium(V) oxide, and the addition of MnO_2 should decrease the oxides film thickness. However, the fraction of vanadium in the films was increased (Table 2); therefore, the negative deviation from the additivity was practically absent after 10 and 20 min of oxidation, whereas at 30–60% of V_2O_5 in the mixture the positive deviation from the additivity was observed (30–40 min oxidation, Fig. 2). When MnO_2 prevailed in the oxides mixture, the amount of chemostimulators in the film decreased, and the negative deviation from the additivity was enhanced.

To conclude, the non-linear dependence of the oxides film thickness on the chemostimulators mixture

Table 3. Ratio of the stimulators in the starting powder mixtures and in the film

Sample	Ratio of the stimulators in the starting powder mixtures	Ratio of the stimulators in the film
100% V_2O_5	1 : 0	1 : 0
80% V_2O_5 + 20% MnO_2	4 : 1	5.4 : 1
50% V_2O_5 + 50% MnO_2	1 : 1	1 : 1
20% V_2O_5 + 80% MnO_2	1 : 4	1 : 3
10% V_2O_5 + 90% MnO_2	1 : 9	1 : 6
100% MnO_2	0 : 1	0 : 1

Table 4. Phases identified by X-ray diffraction analysis of the chemostimulator mixtures kept under oxygen at 530°C during 10 min

Sample	Interplanar distance, Å	Intensity	Identified phase
V_2O_5	5.7316, 4.3616, 4.0724, 3.3997, 2.8744, 2.7607, 2.6842, 2.6119, 2.1869, 1.7841, 1.5624, 1.5178, 1.4908, 1.4136, 1.3057	110, 350, 145, 450, 355, 200, 60, 240, 130, 240, 70, 120, 120, 50, 50	V_2O_5
	1.9955, 1.9169	130, 190	VO_2
	1.6484	100	V_2O_3
$(V_2O_5)_{0.9} + (MnO_2)_{0.1}$	5.7646, 4.3682, 4.0779, 3.4029, 2.8763, 2.7623, 2.6857, 2.6079, 2.1875, 1.5658, 5164, 1.4124, 1.3062	145, 500, 150, 550, 510, 230, 70, 320, 235, 85, 155, 80, 90	V_2O_5
	1.9928, 1.9172	170, 240	VO_2
	2.1475	80	V_2O_3
	1.9045, 1.6501, 1.4922, 1.2723	120, 100, 170, 50	MnO_2
	1.8605, 1.7576	120, 100	Mn_2O_3
$(V_2O_5)_{0.7} + (MnO_2)_{0.3}$	5.7446, 4.3682, 4.0779, 3.4028, 2.8763, 2.7623, 2.6857, 2.6079, 1.7809, 1.5148	85, 230, 90, 25, 220, 120, 40, 100, 90, 55	V_2O_5
	1.9928, 1.9172	55, 75	VO_2
	2.1875	75	V_2O_3
	1.9006, 1.6504, 1.4923	70, 30, 50	MnO_2
	1.8631, 1.7576	40, 40	Mn_2O_3
$(V_2O_5)_{0.5} + (MnO_2)_{0.5}$	5.7587, 4.3772, 4.0996, 3.3997, 2.8810, 2.7667, 2.6119, 1.7808, 1.5149	50, 185, 65, 125, 45, 160, 160, 80, 80	V_2O_5
	1.9987, 1.9197	55, 60	VO_2
	2.1869	50	V_2O_3
	3.1182, 2.4087, 1.8976, 1.6504, 1.5641, 1.4924, 1.3057	40, 40, 45, 20, 20, 30, 30	MnO_2
	1.8603, 1.7575, 1.4153, 1.3372	30, 20, 15, 15	Mn_2O_3
$(V_2O_5)_{0.2} + (MnO_2)_{0.8}$	5.7646, 4.3682, 4.0779, 3.4029, 2.8763, 2.7623, 2.6079, 1.7809	35, 100, 20, 70, 65, 35, 45, 40	V_2O_5
	1.9959, 1.9200	25, 25	VO_2
	2.1875	35	V_2O_3
	3.1129, 2.4006, 1.6268, 1.3078	35, 30, 30, 25	MnO_2
	1.8631	20	Mn_2O_3
MnO_2	4.2478, 3.1094, 2.4042, 1.6211, 1.2051, 1.1408	15, 65, 85, 35, 25, 20	MnO_2
	2.7206, 2.2784, 2.1119, 1.7461, 1.6625, 1.4223	95, 20, 30, 25, 25, 15	Mn_2O_3

composition resulted from the mutual influence of catalysts. The effect was similar to that observed in the study of GeAs oxidation [8] thus revealing its general nature. In particular, the deviations from the additive behavior upon InP oxidation induced by $V_2O_5 + MnO_2$ mixture resulted from the mutual influence of the oxides changing their thermal behavior (the $V_2O_5 \rightarrow VO_2 \rightarrow V_2O_3$ and the $MnO_2 \rightarrow Mn_2O_3$ transformations along with the chemostimulators incorporation in the oxide film formed on the InP surface).

EXPERIMENTAL

The chemostimulators used in this work were powdered polydisperse phases ("analytically pure" grade V_2O_5 and MnO_2). After fractionation through the 150 and 50 μm sieves, the 50–150 μm particles were obtained. The fractionation was necessary because the particles size affects the growing film thickness [9].

The chemostimulators compositions were prepared in the range of 100% V_2O_5 to 100% of MnO_2 with the

10 mol % step. To do so, a mixture of the chemostimulators with the required components ratio was put in a quartz container, the InP specimen serving as the container cap. The distance between the chemostimulators surface and the InP surface was 1 cm in all experiments. The container was installed into a horizontal quartz reactor (30 mm in diameter) preheated to the experiment temperature in a MTP-2M-50-500 furnace. The reactor temperature was kept constant with a TRM-10 flame ionization detector-controller (±1°C).

Thermal oxidation of InP was performed at 530°C under 30 L/h oxygen stream during 10–40 min. The same specimen was oxidized in 10 min steps.

The oxidized InP specimens were studied with an Ellips-1891 spectral ellipsometer (static mode, 250–1100 nm) in order to determine the films thickness [10]. The accuracy of ellipsometry parameters determination was of 0.05º (δΨ) and 0.1° (δΔ). The probe spot size was of 3 × 6 mm.

Composition of the formed films was determined by means of X-ray diffraction analysis (a Thermo-Scientific ARL X'tra diffractometer and the JCPDS – International Center for Diffraction Data reference base [11]) and local X-ray spectral microanalysis (a JEOL-6510LV unit equipped with a Bruker energy-dispersion microanalysis and ESPRIT software).

The interactions between the chemostimulators were studied in the course of the oxides mixtures thermal oxidation; the resulting samples were probed by X-ray diffraction analysis (an EMPYREAN diffractometer, 2θ 20°–80° with scan step of 0.02° and 0.3 min exposition at each step).

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