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Effect of the Procedure of Chemostimulator Application on the Surface Characteristics of V_xO_y/InP Structures in the Process of Their Thermooxidation

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Abstract—Evolution of morphology of surface and the composition of layer near the surface in the process of thermooxidation of V_xO_y/InP formed by soft and hard methods is shown. Dependence of morphology of film surface on the way of application of chemostimulator and the regime of thermooxidation is established. Both methods permit to obtain layers with the sufficiently smooth surface, but while using the hard method nanostuctured films are finally formed.

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Vanadium(V) oxide is the effective chemostimulator of thermooxidation of semiconductors $A^{III}B^{V}$ [1] and depending of the method of its introduction in the system, through the gas phase or directly on the surface of semiconductor, it causes the formation of oxide coating of GaAs and InP by the transition or catalytic mechanism [2, 3]. Methods of application of vanadium(V) oxide on the InP surface may be conventionally divided in two groups. First of them is the group of hard methods when the surface of semiconductor is treated before the beginning of thermooxidation (magnetronic spraying, electric explosion of conductor [3–5]). Another one is the group of soft methods which do not alter the structure and the composition of the surface in the course of formation of chemostimulator layers when application of the vanadium oxide sol or gel with the subsequent annealing is used [6]. Establishing of dependence between the method of application and the characteristic of surface of the V_xO_y/InP structure permits to govern the process of synthesis of objects with the desired characteristics like the composition of films, their thickness, and morphology. Therefore the aim of this work was the establishing of dynamics of alteration of the surface morphology and the composition of the layer near the surface of V_xO_y/InP structures depending on the way of their synthesis and thermooxidation regime.

The magnetronic spraying was chosen as a rigid method, and precipitation of vanadium(V) oxide gel from aerosol, as the soft one. According to the results of the X-ray phase analysis the magnetronically formed layers of nanometer range of thickness consisted of V_2O_5 [3], while the layers obtained by means of soft method after the annealing consisted of a mixture of V_2O_3, VO_2, and V_2O_5 [6].

Scanning tunnel and atomic-force microscopy data show that the surface of V_xO_y/InP structures synthesized by means of soft method is comparatively smooth, the height of contour drop is 10–15 nm. The layers are polycrystalline with the dimensions of separate crystallites about 150 nm.

Table 1. Bond energies and elemental composition of surface of the structures synthesized by soft and hard method after thermooxidation for 60 min at 500°C

Structure	Bond energy, eV				Composition of film, at %			
	In3$d_{5/2}$	O1*s*	P2$p_{3/2}$	V2$p_{3/2}$	In	O	P	V
V_2O_5/InP	444.9	530.3 (I)	133.4	516.0 (I)	25.0	31.7 (I)	4.0	0.5 (I)
rigid method		531.8 (II)		517.3 (II)		30.3 (II)		8.5 (II)
V_xO_y/InP	445.0	530.2 (I)	133.4	515.9 (I)	27.4	22.9 (I)	3.8	0.2 (I)
soft method		532.0 (II)		517.4 (II)		45.2 (II)		0.5 (II)

Greatest non-uniformity of the film contour at 500°C is achieved 30 min after the beginning of thermooxidation, the contour height being ~30 nm. Dimensions of separate crystals reach about 60 nm. Intense interaction of chemostimulator with the components of the substrate and the diffusion in growing layers are the factors causing the decrease in the dimensions of crystallites. Further development of process leads to improving the morphology of surface. After 45 min the contour height decreases to ~15 nm, and after 60 min the surface becomes practically smooth (contour height ~10 nm,). Dynamics of alteration of surface morphology at 530°C is analogous, and after 60 min of oxidation the surface becomes sufficiently smooth.

For the V_2O_5/InP structures formed by magnetronic spraying before thermooxidation smooth surface of applied layer of chemostimulator is characteristic with the contour height no more than 5–10 nm. In some cases the structure of surface is inherited from the initial substrate having the shape of bands and microscratches remained after the mechanic polishing and the subsequent treating with polishing etching reagents of the semiconductor InP plate.

After 30 min the beginning of thermooxidation at 500°C lateral dimensions of crystallites reach 150–200 nm (height ~25 nm), and after 60 min it decreases to 25–30 nm (height ~10 nm). Dynamics of alteration for 530°C is analogous to the preceding case of thermooxidation of V_2O_5/InP structures at 500°C.

The change in the surface morphology at the highest temperature of oxidation 560°C must be considered specially. Smoothing of surface of the structures synthesized by the soft method proceeds in the course of 30 min, and at longer time of oxidation the degradation of the surface is observed. The pores appear and the structure of surface begins to resemble the orange peel [7]. Development of this process is determined by the intense evaporation of phosphorus, the most volatile component, also in the form of an oxide, especially at high temperatures [8]. For the structures synthesized by means of hard method 60 min after the beginning of the thermooxidation at 560°C analogous effect is observed. The degradation of surface analogous to the above-described case of soft method takes place. Hence, neither rigid nor soft method of application of chemostimulator favors the retention of volatile component at high oxidation parameters.

Analysis of bright field images (transmission electron microscopy) of all the samples under the study after thermooxidation showed higher regularity of films structure with chemostimulator applied by means of hard method as compared to the structure of films obtained by precipitation from gel. Dimensions of separate crystallites for the films formed by oxidation of structures with the magnetron applied chemostimulator is significantly smaller as compared with those obtained from gel. The average dimension is 30 nm in good agreement with the data of surface morphology studies. For the oxidized InP surface modified by means of soft method the dimensions of crystallites are significantly larger, 250–300 nm. Hence, only the films of nanometer thickness synthesized by oxidation of structures with the magnetronically applied chemostimulator are nanostructurated.

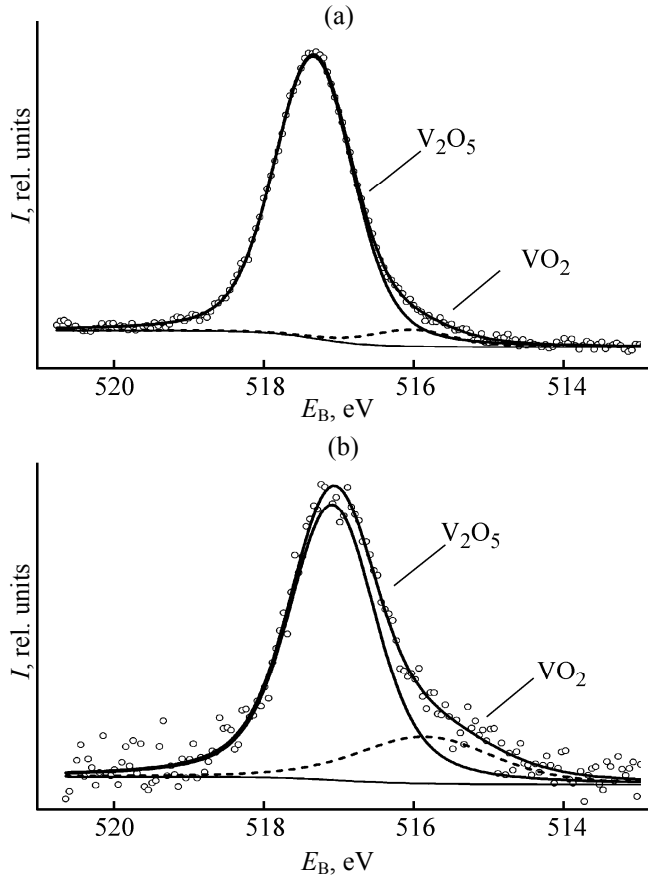
From the data of X-ray photoelectron spectroscopy of the samples obtained by both methods and exposed to thermooxidation during 60 min at 500°C it is seen that the location of main lines in photoelectron spectra (see Table 1) corresponds to bond energy of electrons of this level with the accuracy 0.1 eV, depth of analyzed surface layer in all the cases is ~2–3 nm. The location of the line In3$d_{5/2}$ corresponds to the charge state of indium in In_2O_3 [9], and the line P2$p_{3/2}$, to the P–O bond [10].

Asymmetric peaks O1*s* may be described by two components. O1*s*(I) with lower bond energy corresponds to the charge state of oxygen O^{2-} in In_2O_3. O1*s*(II) probably belongs to hydroxy groups on the

surface of In_2O_3 or the chemisorbed water molecules [9]. The presence of this component is characteristic of the structures which have been initially treated by chemostimulator both by hard and soft method. The peak of photoemission of electrons of V2$p_{3/2}$ level (see the figure) also contains two components. V2$p_{3/2}$(II) has bond energy characteristic of vanadium in V_2O_5, and V2$p_{3/2}$(I) may be attributed to the charge state of vanadium in VO_2 [11].

The difference in quantitative content of vanadium and the charge forms of oxygen (see Table 1) is caused by the method of application of chemostimulator on the surface of indium phosphide. From the presented data (Table 1, last column) it is seen that in the case of soft method of chemostimulator application the content of vanadium in the near to surface layer is lower than in the case of magnetronic spraying. It can be connected with its initial smaller amount as well as with the intense interaction in the course of oxidation and redistribution of components in the growing layer. Hard method to a greater degree favors retaining this chemostimulator in the course of oxidation than the soft method because the interaction with InP substrate of magnetronically applied layer of vanadium oxide begins before its oxidation [3]. The application of vanadium oxide layers by means of precipitation from gel took place in water solution, therefore the component O1*s*(II) prevails in the photoemission peak of oxygen of this sample. Note that according to the results of previous studies [3, 12] main components of films after thermooxidation are V_2O_5, VO_2, In_2O_3, and $InPO_4$ in agreement with the X-ray photoelectron spectroscopy data. Ratio of these components depends on the way of application of chemostimulator.

Hence, the dependence of morphology and the surface composition of thermal oxide films of nanometer thickness (laser ellipsopmetry data) on InP on the method of application of chemostimulator and thermooxidation regime is established. The surface of layers of chemostumulator applied by means of magnetronic spraying as well as by precipitation of vanadium(V) oxide gel is sufficiently smooth (scanning tunnel microscopy). The greatest heterogeneity of surface morphology of growing films is achieved after 30 min (at 500 and 530°C) and then smoothening of contour takes place. At maximum values of time and temperature of oxidation the degradation of films takes place (scanning tunnel and atomic force microscopy) due to evaporation of volatile component. The films formed by both methods



X-ray photoelectron spectra of the (a) V2$p_{3/2}$ region of the structures V_2O_5/InP (hard method) and (b) V_xO_y/InP (soft method) (b) oxidized at 500°C for 60 min.

are polycrystalline, but hard method of application provides more regular structure, and only in this case they are nanostructured (transmission electron microscopy, scanning tunnel microscopy). Average dimension of crystallites is 30 nm against 250–300 nm for soft method. Content of vanadium in the near to surface layer of oxidized structures depends on the way of application of chemostimulator. It is higher in the case of magnetronic spraying (X-ray photoelectronic spectroscopy). Hence, variation of method of chemostumulator application and the regime of subsequent thermooxidation permits to obtain complex oxide films of nanometer thickness with the given morphology of surface and composition on the InP substrate.

EXPERIMENTAL

Polished plates of indium phosphide [FIE-1A brand, orientation (100)] with the concentration of main charge carriers at 300 K no less than 5×10^{16} cm^{-3}, *n*-type conductivity, were used. They were treated with

Table 2. Thickness of films obtained after 60 min of thermooxidation of structures synthesized by soft and hard methods (laser ellipsometry data)

T, °C	Soft method	Rigin method
500	41	90
530	49	119
560	43	113

the polishing etching reagent of the composition: H_2SO_4 (chemically pure grade, GOST 4204-77, 92.8%):H_2O_2 (specially pure grade, TU 6-02-570-650, 56%):H_2O 2:1:1 in the course of 10 min and many times washed with bidistilled water.

Application of layers of vanadium oxide on InP surface was carried out by magnetronic spraying (hard method) and precipitation of vanadium pentoxide gel from aerosol phase with the subsequent annealing (soft method). Magnetronic spraying was carried out on a modernized UVN-2M installation in the oxygen-argon atmosphere using vanadium target (purity 99.20%, distance between the target and substrate 10 cm). The application of V_2O_5 gel on InP surface was carried out according to [6]. The precipitation was performed on a cooled substrate in the course of 3 min. Annealing of films formed by means of vanadium pentoxide gel was carried out in air in a flow quartz reactor of a horizontal furnace of the resistive heating (MTP-2M-50-500) with the temperature regulation accuracy ±1°C (OVEN TPM-19) during 60 min at 200°C. All the samples were oxidized in the same furnace in the temperature range 500–560°C with the step 30°C in an oxygen flow (30 l h^{-1}). The oxidation time was 15–60 min with the 15 min step.

Thickness control of the layers of applied chemostimulator and the films formed in the course of thermooxidation was carried out by the laser ellipsometry method (LEF-754, accuracy ±1 nm). Thickness of layers before thermooxidation in the case of magnetronic method of application was 30±1 nm, and at the use of the soft method, 5±1 nm. Values of thickness of films obtained after 60 min of thermooxidation at the temperatures used are listed in Table 2.

The morphology of surface of the samples obtained was evaluated by means of scanning tunnel microscopy (complex of nanotechnological apparatus "UMKA") and the atomic force microscopy (scanning sounding Solver P47 Pro microscope of NT-MDT corporation). Treating of scanning tunnel microscopy data and formation of 3D-images was carried out by means of SPIP (Scanning Probe Image Processor) complex of programs. The structure of films was established by transmission electron microscopy on a H-80 (Hitachi) high-resolution transmission electron microscope. The preparation of samples for investigation was carried out by thinning method. It consisted of three steps. At first 3 mm disks (dimension of holder of the transmission electron microscope) were cut from the plate fragments by means of the abrasive boring on a South bay Technology Inc Model 360 device. Abrasive solution was prepared on the basis of the boron carbide powder with the grain dimensions 14.5 μm. Then spherical craterlets were grinded from the side of substrate on the Gatan Dimple Grinder Model 656 installation with the thinning to 20–25 μm. Diamond paste 1–2 μm was used as the abrasive. After that the samples were sprayed from the side of substrate by bombarding with a beam of Ar^+ ions with the energy 5 keV and the flow density 600 A m^{-2} until the formation of perforation of the substrate. Ion bombarding regime was chosen that prevented the crystallization of the amorphous phase. The treatment was carried out on a ION-TECH installation. Results of electron microscopy studies were presented as the bright field images of structure.

Establishing of composition of samples surface after their thermooxidation was carried out by the X-ray photoelectron spectroscopy (Kratos Axis ultra DLD microscope, monochromated AlK_α radiation hn 1486.6 eV in a vacuum no less than 10^{-9} mm). In the course of measurement a neutralizer compensating the charge of sample was used. The correction of charge shift was performed by the peak of the ground state C1*s* with the bond energy 285 eV corresponding to hydrocarbon contaminations on the surface. Spectra in the Ind3, O1*s*, V2*p*, and C1*s* regions were recorded with the step 0.05 eV with the Pass Energy parameter 40 eV. Quantitative composition was calculated using the coefficients of elemental sensitivity by the calculated values of peak areas limited by the base line.

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