

## The XPS investigations of the surface composition of nanoscale films formed by thermal oxidation of $V_xO_y/InP$ heterostructures

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The dependence of oxide films surface layers' compositions on the method of depositing of  $V_2O_5$  on InP and regimes of thermal oxidation of the formed heterostructures was established by the XPS method. Lower indium content near the surface for all samples in comparison with the standard indicates a partial blocking of its diffusion into films during the chemostimulated thermal oxidation of the semiconductor. The presence of vanadium oxides in certain oxidation states and their ratio depends on the method of deposition for the chemostimulator, and on the regime of thermal oxidation. In the case of the electric arc synthesis method, at shorter reaction times, vanadium compounds in the +4 and +5 oxidation states were present in the near-surface layer, which gives evidence for the catalytic mechanism.

**Keywords:** indium phosphide, XPS, nanoscale films, vanadium pentoxide, thermooxidation.

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### 1. Introduction

Oxide films, grown by thermal oxidation of the  $A^{III}B^V$  semiconductor materials, have poor dielectric properties [1] unlike films, formed by oxidation of elemental semiconductors such as silicon. Inherent to the mechanism of phosphides oxidation formation of component A in the free form [1] with simultaneous evaporation of  $P_2O_5$  leads to a "metallizing" the film and degradation of its surface.

However, indium phosphide, in comparison with silicon, is a direct-gap semiconductor, and therefore it can be used in areas related to the conversion of electromagnetic radiation. Oxidation of InP (thermal, chemical, electrochemical, anodic and plasmic) makes it suitable for the creation of high-frequency field-effect transistors and long-wavelength lasers (based on MIS structures), solar cells (multilayer heterostructure (Indium tin oxide)/InP) etc. [2,3].

The poor quality of  $A^{III}B^V$  oxide films grown on clean substrates can be overcome by introducing a system of chemostimulators, altering the mechanism of oxidation, accelerating the growth of films on the surface of a semiconductor with simultaneous modification of their structures and properties.

The introduction of a chemostimulator in the oxidation system is possible in two ways: 1) through the gas phase in the thermal oxidation process; 2) directly on the semiconductor surface in the form of films or nanoscale islands before oxidation [4,5]. In the latter case, two groups of methods were used: hard (magnetron sputtering, electric explosion), acting on the surface prior to the thermal oxidation; soft (sol-gel processes, low-temperature metallo-organic chemical vapor deposition (MOCVD), etc.), which made little change to the surface during the process of chemostimulator deposition. The unique properties of the  $V_2O_5$  chemostimulator allow the use of both the approaches and the two groups of methods (in one approach) deposition on the surface of InP. A distinctive feature of the vanadium oxides, in particular its pentoxide, is transition mobility  $V^{+5} \leftrightarrow V^{+4}$ , allowing both the catalytic and transit mechanisms of InP thermal oxidation [4]. In previous studies, the phase composition of the films was constantly monitored by X-ray diffraction, but a detailed examination of the surface layer requires establishing the peculiarities of the effect of the heterostructure synthesis method on the mechanism of their thermal oxidation. The use of X-ray photoelectron spectroscopy (XPS) allows investigating this urgent issue and it was used for the first time for these studies. The goal of this study was establishing the dependence of the composition of the surface of films formed by thermal oxidation of  $V_xO_y/InP$  heterostructures upon the method of chemostimulator application and the thermal oxidation regime by the XPS method.

## 2. Experimental

In this experiment, the polished substrates of monocrystalline indium phosphide FIE-1A (100), with a concentration of majority carriers no lower than  $5 \cdot 10^{16} / \text{cm}^{-3}$  at 300 K, n-type conductivity (doped by Sn), wafers of 0.5 mm thickness were used.

Before the synthesis of heterostructures, the surfaces of the semiconductors were treated with  $\text{H}_2\text{SO}_4$  (reagent grade, Russian State Standard GOST 4204-77, 92.80 %) :  $\text{H}_2\text{O}_2$  (analytical grade, Russian State Standard GOST 177-88, 56 %) :  $\text{H}_2\text{O} = 2 : 1 : 1$  etchant [6] for 10 min and then rinsed repeatedly in doubly-distilled water and air-dried to remove a natural oxide film surface and various contaminants.

The chemostimulator (vanadium pentoxide) was deposited on the surface of the semiconductor by the method of electric explosion of conductor (EEC, hard method) and by method of deposition of  $\text{V}_2\text{O}_5$  gel via aerosol phase (soft method).

Synthesis by method of electric explosion conductor was performed in a modified vacuum universal post Shimadzu at a chamber pressure of 1.333 Pa. The residual oxygen in the system was sufficient to oxidize the metallic vanadium to vanadium pentoxide. A vanadium wire with the diameter of 0.5 mm and the length (L) of 30 mm (main substance content of 99.99 %) served as the explodable conductor. The voltage was 110 V. The distance (H) between the source and the substrate was 25 mm. Under these conditions, islands of  $\text{V}_2\text{O}_5$  were deposited on the surface of the InP with an admixture of metallic V, which under thermal oxidation conditions, also transformed into vanadium pentoxide (XRD data [7]). Thus islands of nanoheterostructures ( $\text{V}_2\text{O}_5$ )/InP were formed. According to scanning electron (SEM) and scanning tunneling (STM) microscopy [5, 7] the lateral dimensions of islands ranged from 80–150 nm, their surface concentration –  $15\text{--}20 \text{ mkm}^{-2}$ . The choice of such a regime is justified by numerous experiments [5, 7] and is due to optimization to maximize the rate of thermal oxidation for the nanoisland heterostructures compared with that of pure InP, which has been adopted as the standard.

The second method consisted of using a vanadium pentoxide gel and precipitation of it from the aerosol phase using a compressor disperser, using a detailed previously-described synthetic procedure is described in the study [8]. The freshly prepared  $\text{V}_2\text{O}_5$  gel was precipitated for 3 min onto a cooled InP substrate. For the removal of the chemically bound water and crystallization of the resulting amorphous layers, the samples were thermally annealed in the flowing quartz reactor of a horizontal resistance heating furnace (MTP-2M-50-500) with temperature accuracy of  $\pm 1 \text{ }^\circ\text{C}$  (OWEN TRM-10) at  $200 \text{ }^\circ\text{C}$  during 60 min. At the same time, layers of nanometer thickness range (20–25 nm) were formed on the semiconductor surface. The specific use of vanadium pentoxide gel leads to a complication in the composition of the layers deposited, vanadium oxides of varying oxidation states are present in them even before the start of the thermal oxidation process (X-ray phase analysis data [XRD] [9]). The composition is also affected by the annealing parameters; therefore, the corresponding thin-film heterostructures were subsequently labeled as  $\text{V}_x\text{O}_y/\text{InP}$ .

The samples of heterostructures synthesized by these methods and InP standards without a chemostimulator were thermally oxidized in the same apparatus at temperatures of 500 and  $530 \text{ }^\circ\text{C}$  in a flow of oxygen at a flow rate of 30 l/h (linear velocity 10 cm/min). A method with full oxidation was used. This method includes the termination of the process at certain intervals to control the thickness, followed by thermal oxidation, until the total process time reached a maximum value of 60 min.

The thickness of the growing films was determined by the express ellipsometric method using a single-wavelength laser ellipsometer LEF-754 with a HeNe laser (radiation wavelength was 632.8 nm, the accuracy was  $\pm 1 \text{ nm}$ ) at three surface points with an averaging of the obtained data.

The composition of the films near the outer interface was investigated by X-ray photoelectron spectroscopy (XPS) using the SIA 100 CAMECA-Riber spectrometer (studies were carried out at the University of Burgundy, Carnot Institute, Dijon, France). Despite the fact that the thickness of the investigated films does not exceed 80 nm, this method, due to its nature, gives a representation of the composition of the near-surface layer (2 nm). The processing of the spectra was done using CasaXPS software: smoothing spectra, subtracting the background using a linear function, approximation of the photoelectronic lines was carried out using the Gaussian function. The comparison and identification of compounds was based on data from literature sources and databases [10].

## 3. Results and discussion

Table 1 shows the characteristics of the samples studied by the XPS method, after thermal oxidation in an oxygen atmosphere.

TABLE 1. Characteristics of studied samples

Sample no.	Method for the production of heterostructures	Thermal oxidation mode	Film thickness, nm
1	InP (reference)	530 °C, 60 min	54
2	(V <sub>2</sub> O <sub>5</sub> )/InP: electric explosion, wire length 30 mm, distance 25 mm		28
3	(V <sub>2</sub> O <sub>5</sub> )/InP: electric explosion, wire length 30 mm, distance 25 mm	530 °C, 60 min	80
4	(V <sub>2</sub> O <sub>5</sub> )/InP: electric explosion, wire length 30 mm, distance 25 mm	500 °C, 60 min	48
5	V <sub>x</sub> O <sub>y</sub> /InP: precipitation of the gel from the aerosol, annealing at 200 °C, 60 min	500 °C, 60 min	55

It is known that the XPS method is mainly a method of elemental analysis, but based on the magnitude of the chemical shift the binding energy can be related to the corresponding compound [11]. First, let us consider the general patterns obtained from the analysis of X-ray spectroscopy data.

TABLE 2. The quantitative content of elements in the samples (according to XPS data)

Sample no.	Content of elements, %			
	O	P	In	V
1	41.3	3.0	22.1	0.0
2	39.0	1.9	17.2	2.9
3	43.2	3.7	16.7	2.5
4	42.5	2.7	18.1	3.8
5	44.1	0.3	0.4	14.2

*O 1s level.* In all samples, peaks, which can be decomposed into several components corresponding to different binding energies, were found. Peaks with a binding energy of 528.9–530.8 eV were characteristic for oxygen in indium and vanadium oxides [12]. In addition, sample no. 3 revealed an additional peak corresponding to a higher binding energy of 531.6 eV, corresponding to the O–P bond in oxides or phosphates [13].

*P 2p level.* In all samples, a peak corresponding to the binding energy of 132.7 eV (132.6 and 132.8 eV) which is attributed to the P–O bond in the phosphates  $\text{HPO}_4^{2-}$  was detected [14]. The P–O bond, characteristic for phosphorus oxides  $\text{P}_2\text{O}_5$  was higher based on energy (135.6 eV [15]). Consequently, during oxidation, indium phosphate compounds and not phosphorus oxides were formed, but their number in all cases was very insignificant. This fact is associated with intensive evaporation of the volatile component – phosphorus in the form of its volatile oxide from the samples, which is especially manifested in nano-island structures with the given oxidation parameters.

*In 3d level.* In the indium spectra, doublet peaks characteristic for unoxidized indium (443.5 and 451.1 eV) and its oxygen-containing compound  $\text{In}_2\text{O}_3$  (444.2 and 452.1 eV) were observed [1].

*V 2p level.* In samples no. 2–5, the doublet peaks  $\text{V}2p_{1/2}$  (522–523.9 eV) and  $\text{V}2p_{3/2}$  (515.4–517.2 eV), characteristic for the V–O bond in vanadium oxides of different oxidation states:  $\text{V}_2\text{O}_3$ ,  $\text{VO}_2$ ,  $\text{V}_2\text{O}_5$  [16,17], which correlates, to a certain extent with the XRD data obtained for these samples in earlier studies were detected [5].

For samples 2 and 3, which were nano-island ( $\text{V}_2\text{O}_5$ )/InP heterostructures formed by the EEC method, and were oxidized at the same temperature (530°C) with different durations – 10 minutes. (no. 2) and 60 min (no. 3), the peaks corresponding to the oxygen-element bonds in the oxides were somewhat different in shape (Figs. 1(a,b)); with increasing thermal oxidation time, the peak becomes asymmetric. This was explained by the increased indium oxide content in films, which is one of the main reaction products. Along with the phosphate phases [1] indium oxides were predominant, at the final stages of the process. The peaks that correspond to phosphorus in the two compared samples correspond to the P–O bonds in the phosphates ( $\text{HPO}_4^{2-}$  group).

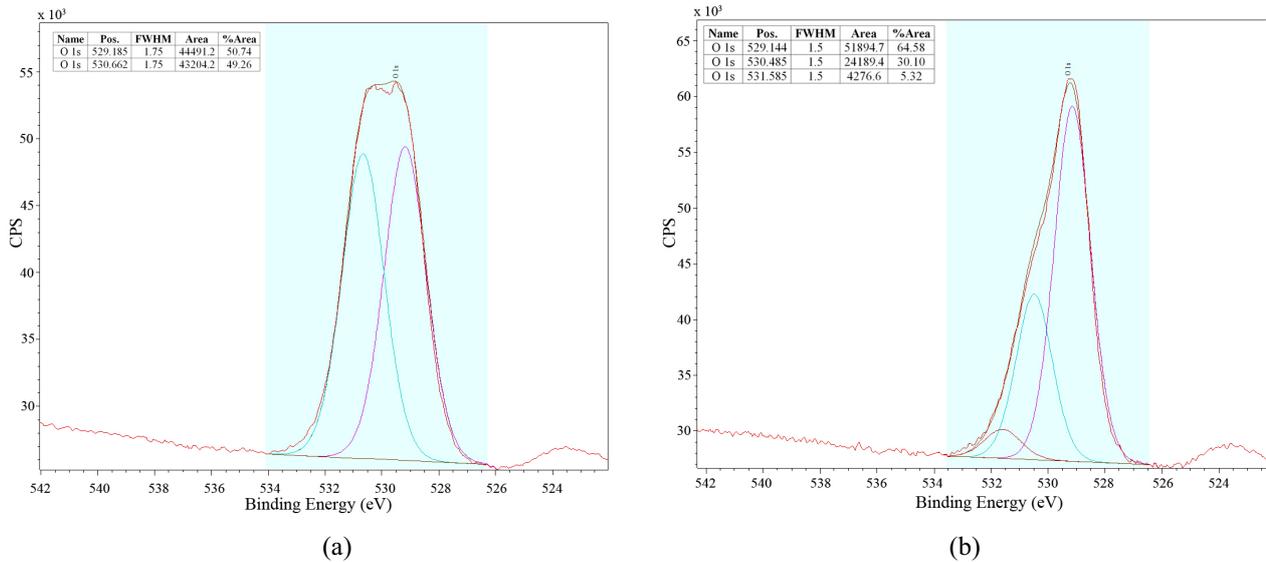


FIG. 1. XPS for the O1s- region for nano-island ( $V_2O_5$ )/InP heterostructures, formed by the EEC method and thermooxidized in oxygen under the following conditions: 530 °C, 10 min (a) and 530 °C, 60 min (b)

Indium in samples no. 2 and 3 was present both in the form of  $In_2O_3$  and in the form of unoxidized In. Thus, correlation with spectral ellipsometry data [18] was detected, indicating absorption near 500 nm, caused by the presence of unoxidized indium in films. For nano-island heterostructures, at short oxidation times, the presence of peaks corresponding to the semiconductor substrate was noted and it was associated with the specificity of these samples themselves - an incomplete initial coating by the surface chemostimulator. At low oxidation times, the surface undergoes extensive overgrowth in the lateral direction, thus nanoscale islands act as active catalytic centers.

The total content of vanadium in samples no. 2 and 3 was different, being somewhat higher in sample no. 2 (Figs. 2(a,b), Table 2). Vanadium was mainly present in the form of oxides (peaks corresponding to V–O bonds),  $VO_2$ ,  $V_2O_5$  were predominant, and after 60 min of oxidation (sample no. 3), peaks corresponding to  $V_2O_5$  were mainly observed. The presence of vanadium compounds in oxidation states of +4 and +5 at the initial stage of oxidation (the first 10 min) confirms the catalytic mechanism of the process due to the easy transition  $V^{+5} \leftrightarrow V^{+4}$  [19]. During the advanced stage of oxidation, the effect of  $V_2O_5$  islands was practically absent; the process is actually the proper oxidation of indium phosphide [5], which was due to the peculiarities of the  $V_2O_5$  presence in a small amount on the surface (islands).

The comparison of the XPS results for the two samples (no. 2 and 3) and the reference (sample no. 1) demonstrated that the intensity of the phosphorus peaks was approximately the same for samples no. 1 (reference) and no. 2 (oxidation for 10 min at 530 °C) and slightly less for sample no. 3 (oxidation for 60 min at 530 °C). In the reference sample, as well as in samples no. 2 and 3, indium is also present in the form of  $In_2O_3$  and In, however, based on the intensity of the corresponding peaks, the content of In in free form is higher for the reference, which demonstrates partial blockage of the diffusion of indium into the growing film by chemostimulator, even in the case when it present in the form of islands on the surface of the semiconductor (Figs. 3(a–c)).

Comparison of samples of the same type (the same optimal EEC parameters, see Table 1), oxidized for the same time, but at different temperatures (530 °C (no. 3) and 500 °C (no. 4)), allowed detecting the dependence of the surface composition of the films upon the temperature of the oxidation process.

The peaks for oxygen were generally similar in intensity and shape (the difference in temperature was not too significant – 30 degrees, which explains this similarity) and corresponded to oxides, in particular, vanadium pentoxide and indium oxide (Fig. 1(b), Fig. 4(a,b)).

The phosphorus peaks had a similar shape and corresponded to the P–O bonds in phosphates. In both samples, indium predominates in the form of its oxide, but free indium was also present, indicating incomplete blocking of its diffusion into the film during the studied process. Vanadium in both samples was mainly present in the form of  $V_2O_5$  and  $VO_2$ , but at a lower temperature, after 60 min of oxidation, vanadium oxide (III) was also found.

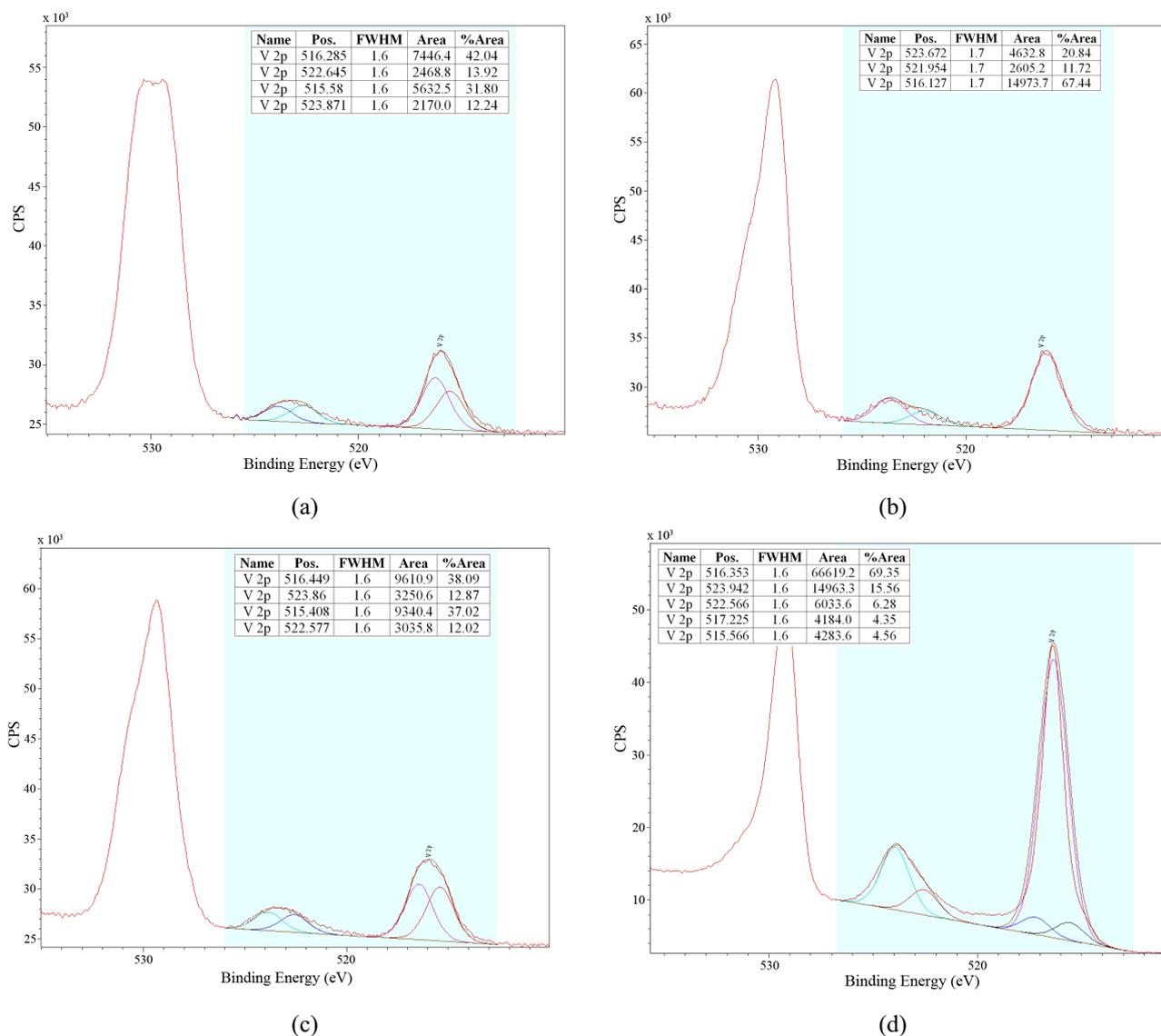


FIG. 2. XPS spectra for the V2p-region for nano-island heterostructures (V<sub>2</sub>O<sub>5</sub>)/InP, formed by the EEC method and thermooxidized in oxygen under the following conditions: 530 °C, 10 min (a) 530 °C, 60 min (b), 500 °C, 60 min (c), and a thin film heterostructure V<sub>x</sub>O<sub>y</sub>/InP (no. 5) formed by precipitating the gel with annealing at 200 °C, 60 min, and thermooxidized with oxygen at 500 °C, 60 min (d)

A more correct comparison of samples no. 4 and 5 (see Table 1 and Table 2), synthesized by hard and soft methods, respectively, but oxidized under the same conditions – 500 °C, 60 min. The content of vanadium in them significantly differed: it was much higher in sample no. 5 and it was represented by compounds with lower oxidation states (Figs. 2(c,d), Table 2). The synthesis of the vanadium pentoxide gel, its further precipitation from the aerosol and annealing in air lead to the presence of vanadium in the form of a number of oxides, e. g. films had a complex composition already before oxidation [8], depending on the type of annealing (fast high-energy pulsed photon annealing or long term thermal). The quantitative and qualitative ratio of vanadium oxides was also determined by the duration of annealing in an oxidizing or reducing atmosphere [9]. The low phosphorus content in the surface layer of samples no. 4 and no. 5 was due to the fact that the film formed as a result of thermal oxidation does not prevent the evaporation of volatile component. In this case, a correlation with the Auger electron spectroscopy (AES) data [8] was observed, which indicate a very low amount of phosphorus on the surface of the film and in the volume.

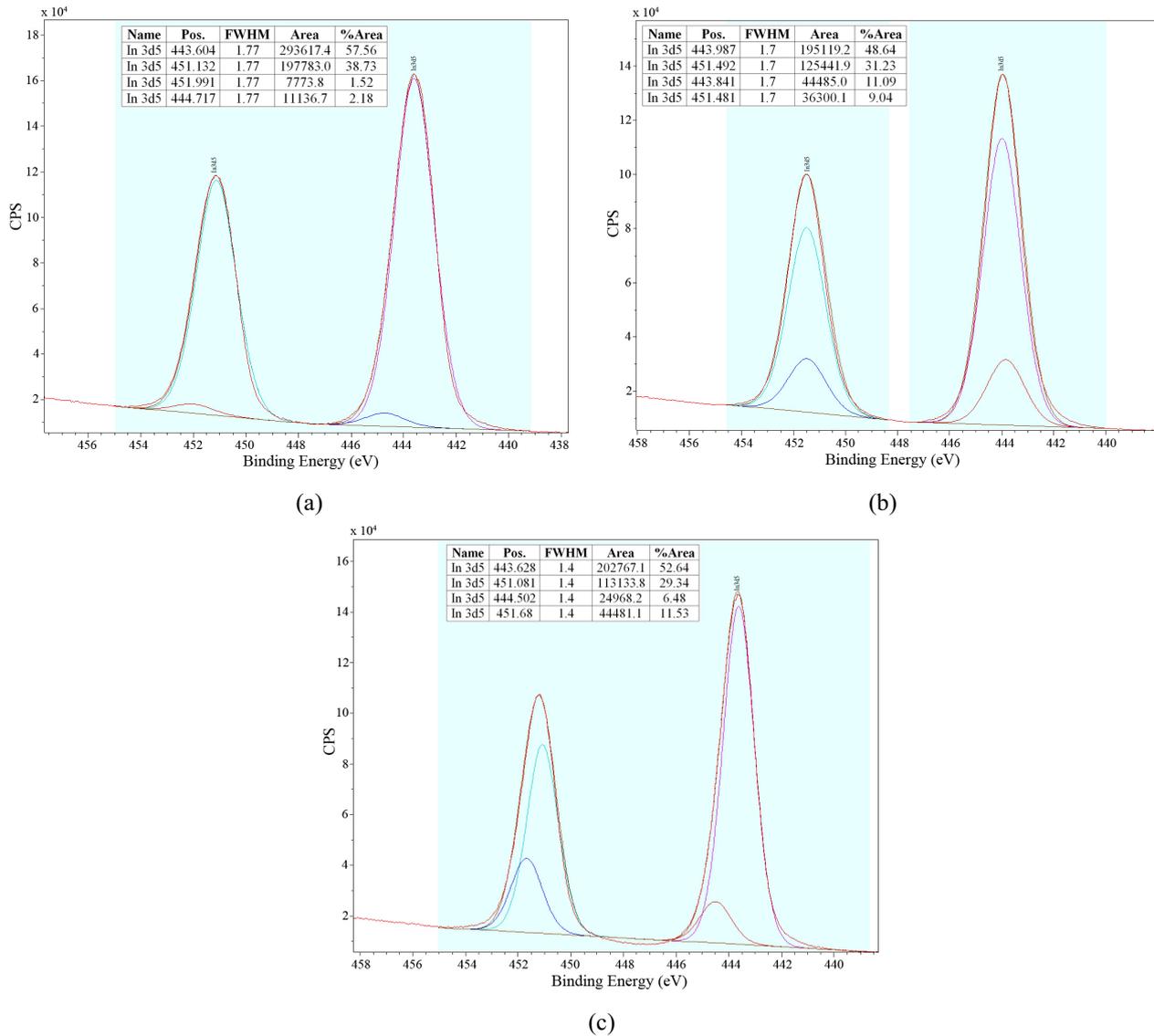


FIG. 3. XPS spectra for the In3d-region in a reference sample, oxidized in the 530 °C regime, 60 min (a), and nano-island heterostructures ( $V_2O_5$ )/InP, formed by EEC method and thermooxidized in oxygen under the following conditions: 530 °C, 10 min (b) and 530 °C, 60 min (c)

In samples formed by EEC (for example, no. 3), the shapes of the peaks for oxygen differ from those for samples synthesized by gel dispersion (Figs. 4(a,c), Table 2). In the case when the gel was used, the intensity of the peaks was lower, corresponding to the oxygen bonds in the oxides, however, in the sample no. 3, P–O bonds characteristic for phosphates were also present. The peak corresponding to phosphorus in sample no. 5 was much smaller in comparison with the sample no. 3.

A common feature of the studied processes of oxidation of both nano-islands and thin-film heterostructures is the depletion of the film by the volatile component-phosphorus, which was shown by its minute content both in the near-surface layer and in the volume. At the same time, in the composition of films, it was mainly present in the form of phosphates. Thus, both methods do not fully contribute to the retention of the volatile component and its binding, in contrast, for example, to the hard magnetron method of depositing of vanadium pentoxide films [4].

Another feature is the fact that the XPS method did not reveal peaks, which could be interpreted as corresponding to the bonds in the  $InVO_4$  compound, on the surface of the films. The presence of such peaks was established by X-ray diffraction analysis for thin-film heterostructures formed by the soft method [9]. The presence of this compound indicates the binding of vanadium, which causes the absence of its regeneration and the violation of the cyclicity of the process. The formation of  $InVO_4$  predominantly at the internal interface confirms the earlier

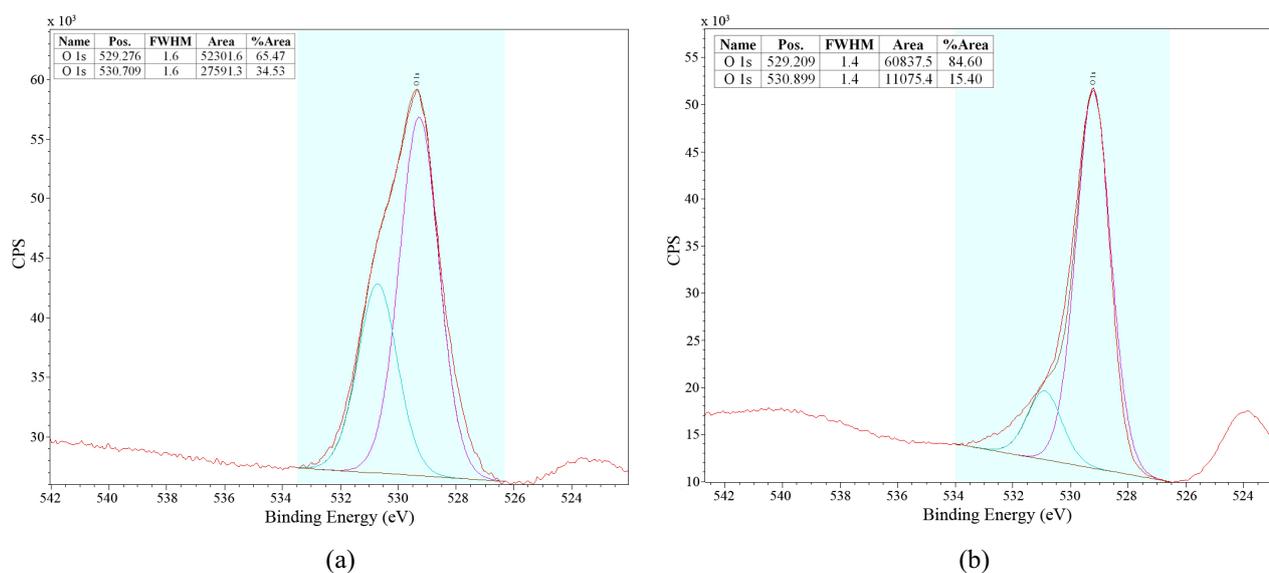


FIG. 4. XPS spectra for the region O1s- for nano-island ( $V_2O_5$ )/InP heterostructures, formed by EEC method and thermooxidized in oxygen at 500 °C, 60 min (a), and  $V_xO_y$ /InP thin-film heterostructure (no. 5) formed by precipitation of the gel with annealing at 200 °C, 60 min and thermooxidized by oxygen at 500 °C, 60 min (b)

conclusions [19] about the effect of the chemostimulator application method on the mechanism of the oxidation process.

#### 4. Conclusions

The dependence of the composition of oxide films' surface layers on the deposition method of  $V_2O_5$  on InP and the regimes of thermal oxidation for the formed heterostructures was established by the XPS method. The lower indium content near the surface for all samples in comparison with the standard indicates a partial blocking of its diffusion into films during the chemostimulated thermal oxidation of the semiconductor. Phosphorus in the near-surface layers was predominantly in the form of phosphate compounds, but its content in all studied samples was very small, which is associated with the intensive evaporation of volatile phosphorus oxide during thermal oxidation. The presence of vanadium oxides in certain oxidation states and their ratio depends on the method of chemostimulator application, and on the temperature and duration of thermal oxidation. The application of a chemostimulator by a soft method leads to a higher variety of vanadium oxides with differing oxidation states. In the case of the electric arc synthesis method, for short reaction times, vanadium compounds in the +4 and +5 oxidation states were present in the near-surface layer, which provides evidence for the catalytic mechanism.

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#### References

- [1] Wager J.F., Wilmsen C.W. Thermal oxidation of InP. *J. Appl. Phys.*, 1980, **51**(1), P. 812–814.
- [2] Oktyabrsky S., Ye P.D. *Fundamentals of III-V Semiconductor MOSFETs*. Springer, New York, 2010, 445 pp.
- [3] Pakes A., Skeldon P., et al. Composition and growth of anodic and thermal oxides on InP and GaAs. *Surface and Interface Analysis*, 2002, **34**, P. 481–484.
- [4] Mittova I.Ya., Tomina E.V., et al. Thermal oxidation of A<sup>III</sup>B<sup>V</sup> semiconductors with  $V_2O_5$  nanolayers on the surface. *Glass Physics and Chemistry*, 2011, **37**(2), P. 230–234.
- [5] Mittova I.Ya., Sladkoptsev B.V., et al. Effect of  $V_2O_5$  nanoislands on the surface composition and structure of InP during thermal oxidation. *Inorganic Materials*, 2011, **47**(8), P. 811–815.
- [6] Sangwal K. *Etching of Crystals: Theory, Experiment, and Application*. North-Holland Physics Publishing, Amsterdam, 1987, 497 pp.
- [7] Mittova I.Ya., Tomina E.V., et al. Synthesis and catalytic performance of  $V_2O_5$  nanoislands produced on the surface of InP crystals by electroexplosion. *Inorganic Materials*, 2010, **46**(4), P. 383–388.
- [8] Sladkoptsev B.V., Mittova I.Ya., et al. Growth of vanadium oxide films on InP under mild conditions and thermal oxidation of the resultant structures. *Inorganic Materials*, 2012, **48**(2), P. 161–168.

- [9] Mittova I.Ya., Tomina E.V., et al. Effect of different types of annealing on the thermal oxidation of  $V_xO_y/InP$  structures formed by the deposition of vanadium(V) oxide gel on the phase composition and morphology of films. *Journal of surface investigation X-Ray, synchrotron and neutron techniques*, 2014, **9**, P. 91–100.
- [10] XPS, AES, UPS and ESCA database (<http://www.lasurface.com/accueil/index.php>)
- [11] Seah M.P., Briggs D. *Practical surface analysis. Auger and X-ray photoelectron spectroscopy*. Wiley & Sons, Chichester, 1996, 674 pp.
- [12] Pho Nguyen, Sreeram Vaddiraju, et al. Indium and tin oxide nanowires by vapor-liquid-solid growth technique. *Journal of electronic materials*, 2006, **35**(2), P. 200–206.
- [13] Shih P.Y., Yung S.W., et al. Thermal and corrosion behavior of  $P_2O_5-Na_2O-CuO$  glasses. *Journal of non-crystalline solids*, 1998, **224**, P. 143–152.
- [14] Wagner C.D., Moulder J.F., et al. *Handbook of X-ray Photoelectron Spectroscopy*. Perkin-Elmer, Minnesota, 1979, 190 pp.
- [15] Yarn K.-F. High sensitive hydrogen sensor by Pd/oxide/InGaP MOS structure. *Modern physics letters B*, 2006, **20**(28), P. 1781–1787.
- [16] Suchorski L., Rihko-Struckmann L., et al. Evolution of oxidation states in vanadium-based catalysts under conventional XPS conditions. *Applied Surface Science*, 2005, **249**, P. 231–237.
- [17] Benayad A., Martinez H., et al. XPS investigations achieved on the first cycle of  $V_2O_5$  thin films used in lithium microbatteries. *Journal of Electron Spectroscopy and Related Phenomena*, 2006, **150**, P. 1–10.
- [18] Mittova I.Ya., Tomina E.V., et al. High-speed determination of the thickness and spectral ellipsometry investigation of films produced by the thermal oxidation of InP and  $V_xO_y/InP$  structures. *Inorganic Materials*, 2013, **49**(2), P. 179–184.
- [19] Krylov O.V. *Geterogenyyi kataliz (Heterogeneous Catalysis)*. Akademkniga, Moscow, 2004, 679 pp.