

EFFECT OF THE MILD METHOD OF FORMATION V_xO_y /InP STRUCTURES USING V_2O_5 GEL ON THE PROCESS OF THEIR OXIDATION AND COMPOSITION OF NANOSIZED OXIDE FILMS

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A V_xO_y /InP structure was formed by the deposition of a V_2O_5 gel aerosol on an InP surface, followed by thermal annealing. This approach avoids chemostimulator interactions with the substrate prior to thermal oxidation, which is characteristic of ‘hard’ methods of chemostimulator deposition. The oxidation process of such structures occurs in the transit mechanism with a slight increase growth rate of films by 20–40 % in comparison with the oxidation of InP. The transit action of chemostimulator has been associated with the chemical bonding of V_2O_5 into $InVO_4$ (XRD), which predominates over mutual transformations of vanadium oxide, which forms in different oxidation states.

Keywords: indium phosphide, chemical stimulated oxidation, V_2O_5 gel.

1. Introduction

Advantages of the $A^{III}B^V$ semiconductor materials compared with silicon is largely shown by the low dielectric properties of thin films grown on surfaces by thermal oxidation. This is due to a lack of quality and technologically compatible dielectric, which in silicon electronics is silicon dioxide. Based on InP, it is possible to create heterostructures for high-frequency field transistors, long-wavelength lasers, multi-layered structures (ITO)/InP for use in solar cells [1–4], etc. One approach is the formation of insulating films on a semiconductor surface (as in the case of silicon), which can serve methods based on various kinds of oxidation processes for $A^{III}B^V$ semiconductors. There are various methods for indium phosphide oxidation, such as thermal, chemical, electrochemical, anodic and plasmic [5–10].

Released unoxidized indium promotes the growth of metallization layers on the indium phosphide surface, dramatically affecting their electrical properties and making them unsuitable for use as insulators or semiconductors in semiconductor electronics (due to ohmic conduction). Furthermore, the evaporation of the volatile component (phosphorus) degrades the surface and does not provide regular film growth with satisfactory dielectric characteristics.

In order to increase the efficiency of thermal oxidation of $A^{III}B^V$ semiconductors, substance-chemostimulators are used. At present, there are a large number of papers related to the study of chemical stimulating processes for indium phosphide oxidation [11]. The nature of these processes is the introduction into the system of substances, which, depending on the conditions, change the mechanism of the process, accelerate growth of films on semiconductor surface, modify composition and improve its characteristics, primarily electrical. Oxides, sulfides, chlorides, oxochloride and some other compounds may act as chemostimulators.

V_2O_5 is the most interesting of the d-metal oxides, which are efficient chemostimulators for the thermal oxidation of $A^{III}B^V$ -semiconductors [12]. This oxide is capable of providing

a stimulating effect on the oxidation process of a semiconductor on both transit and catalytic mechanisms [13, 14].

The composition of films formed by chemostimulating the thermal oxidation InP and hence the properties of the synthesized structures and the quality of the interface are determined by the physico-chemical nature and method of chemostimulator introduction - through the gas phase or directly on the surface of the semiconductor. In the latter case, two groups of methods are used - hard (magnetron sputtering, electric explosion) and soft (sol-gel processes, low temperature MOCVD, etc.).

The widely used magnetron sputtering of chemostimulators is a high-energy method, which intensively acts on the substrate surface, stimulating interaction between the chemostimulator and the components of the semiconductor prior to thermal oxidation. So the question of finding less harsh methods for modifying the semiconductor's surface by vanadium oxide, which occurs at low temperature, is relevant. The ability of V_2O_5 to form sols and gels can be used in a V_2O_5 gel aerosol deposited on indium phosphide, is one such mild method. This does not significantly affect the surface of the semiconductor substrate prior to its oxidation.

The purpose of this research is to establish the features for an oxidation process of V_xO_y /InP structures, formed by mild methods, in comparison with the hard magnetron sputtering of V_2O_5 , as well as determining the composition and morphology of the formed oxide films.

2. Experimental

The synthesis of vanadium oxide gel was carried out by the sol-gel method using the procedure proposed in [15]. A dispersed V_2O_5 gel was deposited via aerosol phase on the surface of InP FIE-1A [100], which was treated prior to the thermal oxidation with a H_2SO_4 (reagent grade, Russian State Standard GOST 4204-77, 92.80 %) : H_2O_2 (analytical grade, Russian State Standard GOST 177-88, 56 %) : $H_2O = 2 : 1 : 1$ etchant for 10 minutes and then rinsed repeatedly with doubly-distilled water.

The aerosol, with 4–5 micron droplets, was obtained using a dispersant compressor that allows the use of viscous solutions. Deposition was carried out for 3 minutes on a substrate cooled by a Peltier element.

Annealing of the V_2O_5 gel layer, deposited on the surface of InP, was carried out in a horizontal quartz reactor of resistive heating furnace (MTP-2M-50-500) with a temperature control accuracy of ± 1 °C (OWEN TPM-10) at various time-temperature conditions. Oxidation of the V_xO_y /InP structures was carried out at 480–580 °C for 60 minutes, while control of the layer thickness growth was carried out every 10 minutes. The thicknesses of the deposited and growing films were determined by laser ellipsometry (LE, LEF-754, $\lambda = 632.8$ nm, absolute accuracy ± 1 nm).

Surface morphology of the samples was measured by scanning tunneling microscopy (STM) by a complex of nanotechnological equipment 'UMKA'. The data were processed using the microscope's software. The software of microscope and SPIP editor were used for processing the results (construction profiles, 3D-visualization). The phase composition of the formed films was studied by X-ray phase analysis (XRD) by diffractometer ARL X'TRA on copper radiation ($\lambda = 1.5406$ Å). The elemental composition of the oxide films on InP and distribution of the components thickness was investigated by Auger electron spectroscopy (AES, ESP-3 analyzer DESA-100, an accuracy of ± 10 %) with layer etching by argon ions.

3. Results and discussion

The structure of the $V_2O_5 \cdot nH_2O$ gel, is that the layers are connected by the edges of the VO_5 tetragonal pyramids, in which the space between the water molecules are introduced [16,

17]. Heating first leads to the removal of adsorbed water at about 100 °C followed by removal of part of the polymer chain-associated water, and at temperatures of about 370–400 °C the crystallization of vanadium oxide is completed [18, 19]. Thermal annealing of V_2O_5 gel layer on the surface of indium phosphide is necessary for removal of water from the interlayer space and the crystallization of the amorphous phase. This leads to the formation of polycrystalline films with a sufficiently ordered structure with an average crystallite size of 250–300 nm [15].

According to the results of XRD [15], the deposit on the indium phosphide layer after thermal annealing is composed of the vanadium oxides V_2O_5 and VO_2 . Components of a semiconductor substrate have not been detected. The presence of V^{+4} cation is a necessary factor for the process of gelation [18]. The cation ratio of V^{+4} to V^{+5} was determined by the temperature and residence time of the melt [20]. V^{+4} content increases with increasing temperature, so the optimal mode of melting vanadium pentoxide was chosen to increase the content of V^{+5} in the deposited layer. Furthermore, the vanadium pentoxide may be decomposed to vanadium dioxide during thermal annealing. In the limiting case, non-stoichiometric vanadium dioxide, similar in composition to V_6O_{13} , can be formed when $V_2O_5 \cdot nH_2O$ films are heated in vacuo [20, 21]. Since in our work, the deposition on InP gel layers are heat treated aerobically to complete the transition, V_2O_5 vanadium oxides with low oxidation states do not occur.

Thus, the XRD data shows that the formation of chemostimulator layers on the surface of InP by the mild method (using of vanadium oxide (V) gel) interactions between chemostimulator and components of the semiconductor do not occur prior to the process of thermal oxidation. Deposition of the activator by hard electric explosion of wire leads to the oxidation of InP with the formation of indium phosphate prior to thermal oxidation of the substrate [22].

Kinetic curves of oxidation of the structures V_xO_y/InP from 480–580 °C are shown in Fig. 1, while the parameters of the equation $d = k^n t^n$ [11] of the process are displayed in Table 1. The effective activation energy of the process (EAE) is determined from the Arrhenius dependence of the rate constant averaged $\ln k_{av} = f(10^3/RT)$, shown in Fig. 2. For its calculation, they are averaged over n in a single mechanism of the process, and then, we find the value of $\ln k_{av}$. The values of n , ranging from 0.23 to 0.35, are typical for the diffusion-limited processes in the solid phase [11]. In this case, there is a similarity with thermal oxidation processes of V_2O_5/InP structures formed by magnetron sputtering with deposited layers of chemostimulator of varying thickness [23]. However, the value of EAE for the oxidation process of mildly-formed structures (Table 1) in the same order, although somewhat reduced in comparison to the EAE of indium phosphide oxidation (270 kJ/mol [11]). This fact points to the transitory nature of interaction between the deposited activator and the components of the semiconductor in thermal oxidation process. For structures formed by the hard magnetron sputtering method, the EAE value is much lower (30 kJ/mol) as compared with its own oxidation, regardless of the thickness of V_2O_5 layer deposited on InP surface [23]. This result and the lack of influence of the amount of deposited activator (change in amount of V_2O_5 by more than 20 fold) on the rate of oxidation and significant quantities of accelerating the rate of the film growth (from 70 % to 115 %) are proof of the catalytic mechanism of the oxidation [23].

Low values of relative increase of the rate process (20–30 %) were observed for the oxidation of V_2O_5 gel-formed structures in comparison to the direct oxidation of InP (see Fig. 3). Calculation of these values for the deposited layers (by magnetron sputtering, using the V_2O_5 gel) is carried out as follows:

$$b = \frac{\Delta d_{V_2O_5/InP} - \Delta d_{InP}}{\Delta d_{InP}} \cdot 100 \%$$

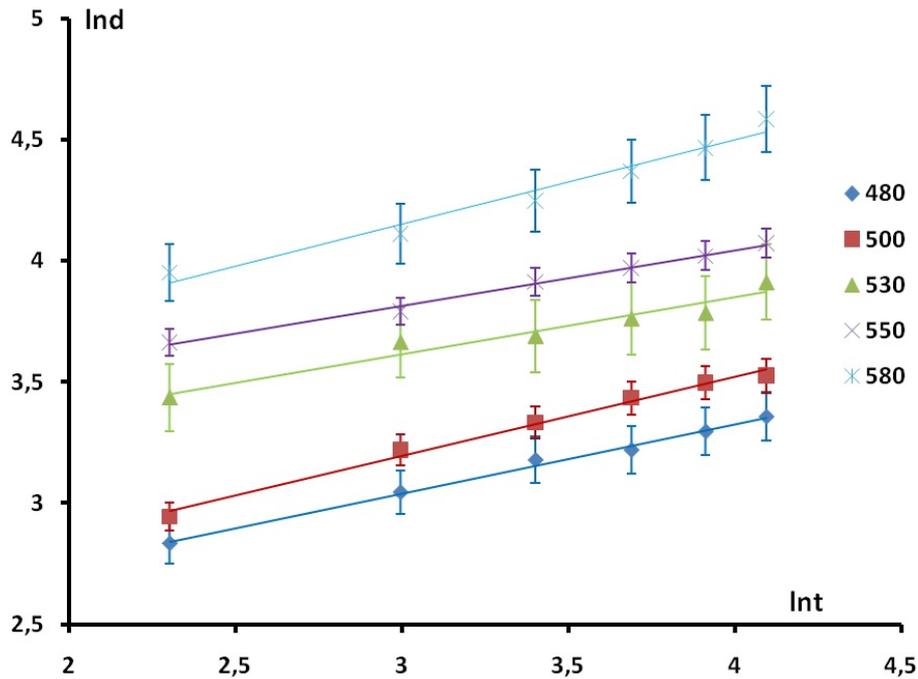


FIG. 1. Isotherms of V_xO_y/InP structures oxidation at 480, 500, 530, 550 and 580 °C under oxygen (in double logarithmic coordinates)

TABLE 1. Kinetic parameters of oxidation of V_xO_y/InP structures, formed using the gel of vanadium oxide (V)

T, °C	480	500	530	550	580
$\ln k_{av}$	7.65	7.75	10.20	10.95	10.90
$n \pm \Delta n,$ $nm^{1/n} \min^{-1}$	0.29 ± 0.006	0.33 ± 0.009	0.23 ± 0.055	0.23 ± 0.006	0.35 ± 0.031
n_{av}	0.29				
EAE, kJ/mol	210				

The maximum rate of the process, when compared with the standard was achieved by 10 minutes of oxidation (Fig. 3, curve 1), when the diffusion restrictions have little effect, and the concentration of the reactants at the inner interface is maximized. During the developed stage, the values of acceleration fall, reaching a plateau, which is typical for chemical stimulated oxidation processes occurring on a transit mechanism. This is due to the absence of chemostimulator consumption and regeneration of the active form of vanadium in the +5 oxidation state during oxidation. With oxidation of magnetron-formed V_2O_5/InP structures (see curve 2 in fig. 3), the value of the acceleration changes little over time, and increases slightly at the maximum time of oxidation. This characteristic of the curve is proof for the regeneration of the chemostimulator V_2O_5 during the oxidation and, accordingly, its catalytic mechanism of action.

After thermal oxidation, the V_xO_y/InP structures formed by the proposed mild method, in oxide films are present VO_2 and $InVO_4$ (XRD), the latter is a product of the of secondary interaction between V_2O_5 and In_2O_3 (Fig. 4). The $InVO_4$ formation determines the transit mechanism of thermal oxidation due to chemical bonding of vanadium pentoxide, prevailing over the mutual transformations of various forms of vanadium oxide. VO_2 , unlike V_2O_5 , can

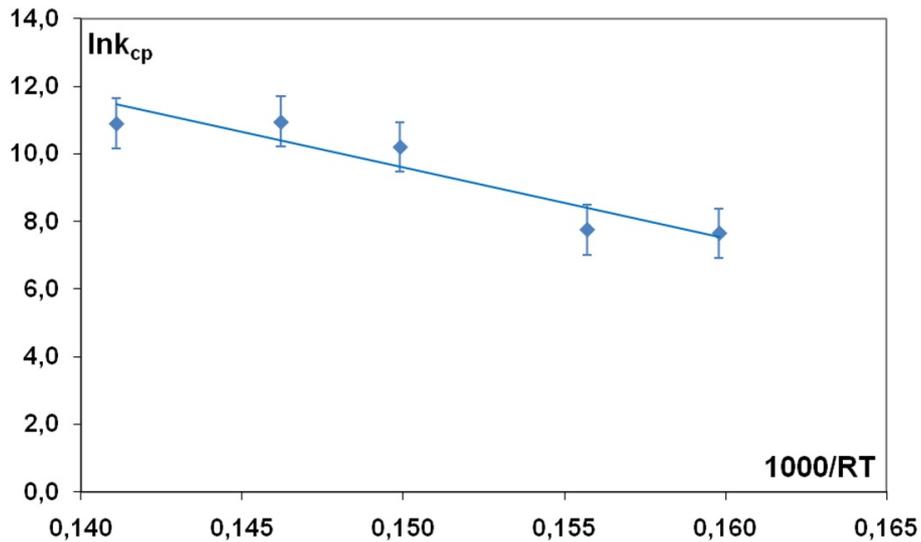


FIG. 2. Arrhenius plot of the average of the rate constant $\ln k_{av} = f(10^3/RT)$

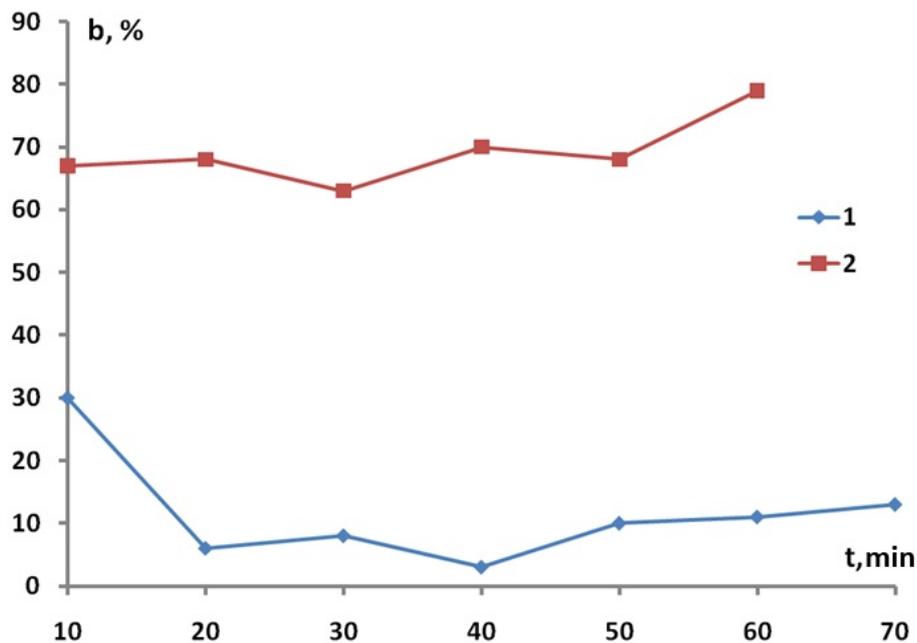


FIG. 3. Dependences of relative acceleration of oxidation process at 500 °C structure V_xO_y/InP formed by using the gel of vanadium pentoxide (1) and formed by magnetron structure V_2O_5/InP (2) compared with oxidation of InP

transmit oxygen only the semiconductor components due to transit interactions with its ability to transit much less pronounced than that of vanadium (V) oxide [23].

The results of Auger electron spectroscopy prove transit mechanism of chemostimulating action of deposited V_2O_5 gel in the oxidation of these structures. For the oxide film synthesized at 500 °C for 60 min (Fig. 5) there is an uneven vertical distribution of vanadium. In the region corresponding to the InP substrate, the vanadium content is about 5–6 at.%, which suggests a noticeable diffusion of the active chemostimulator element into the substrate (see fig. 5, the concentration profile of vanadium). The diffusion of the element-activator through the internal interface of the structure, leading to its partial regeneration, is inherent in the transit mechanism

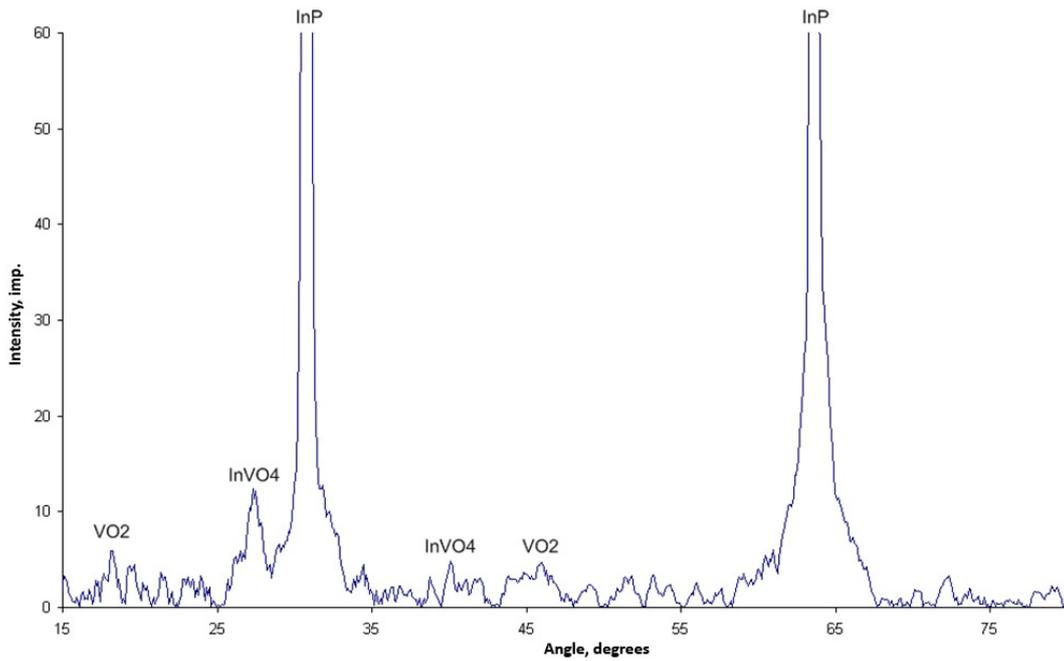


FIG. 4. The XRD pattern of the V_xO_y/InP structure after oxidation at 530 °C during 60 min.

of oxidation and proved by numerous experiments [11]. A characteristic feature of the films is a strong depletion of subsurface region by phosphorus. The curve corresponding to the profile of the distribution of phosphorus, appears closer to the interface ‘substrate-film’ (see Fig. 5, the profile of phosphorus concentration), which is a result of the evaporation of the volatile component of the semiconductor during the thermal oxidation.

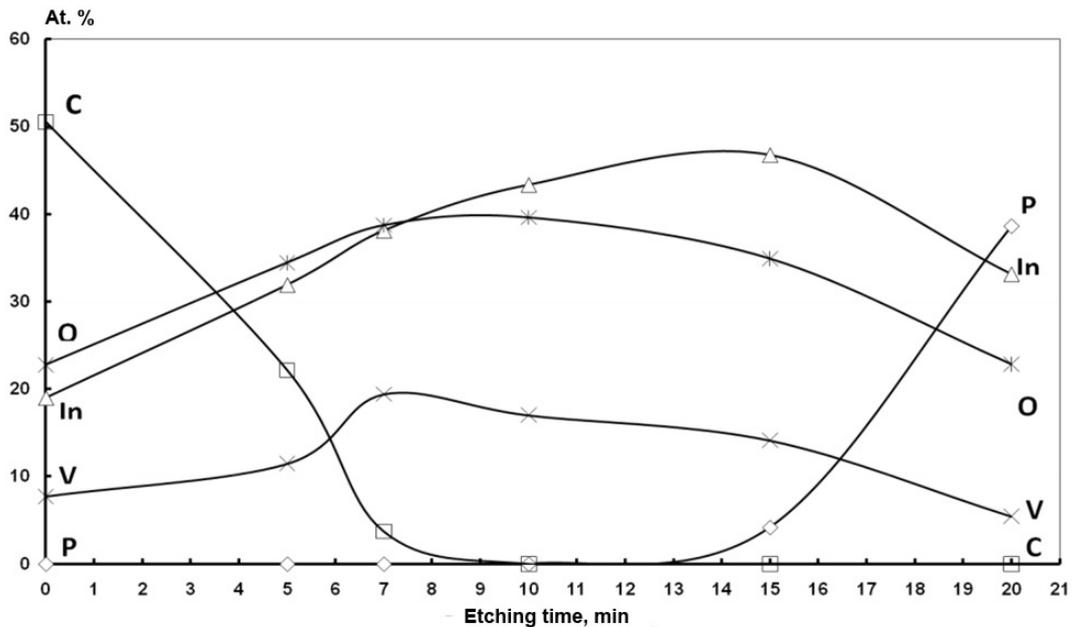


FIG. 5. Concentration profiles of elements (AES) in the sample V_xO_y/InP , synthesized using the vanadium oxide gel (annealing 200 °C, 120 min.) after 60 min. oxidation at 500 °C

Sufficiently smooth films are formed as a result of InP oxidation with deposited V_2O_5 layers, formed with both hard and mild methods (Fig. 6). The size of the structural elements of the films averaged 300–400 nm, depending on the oxidation temperature in the case of modification of InP by mild method, elevation topography ~ 30 –40 nm. When applying the magnetron, the size of V_2O_5 structural elements of the oxide films are 30–40 nm, with a relief height of 10–20 nm [24].

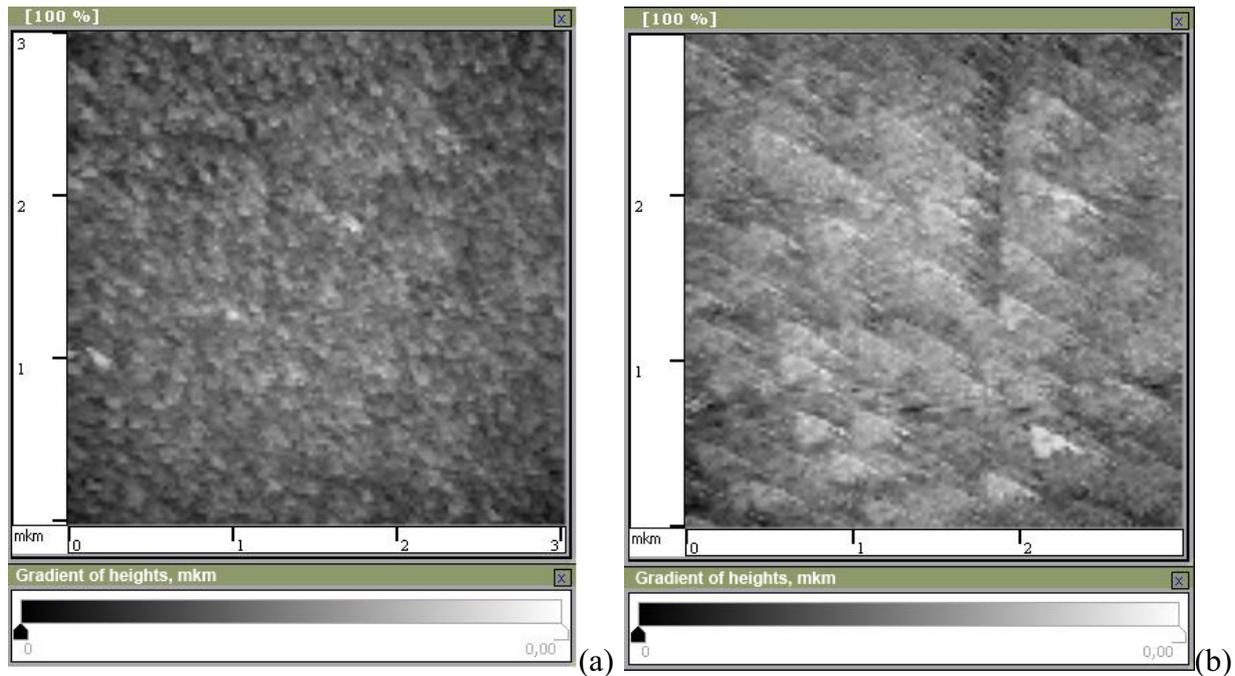


FIG. 6. STM image of surface of V_xO_y/InP structures (mild method) oxidized at 500 °C, (a) and 530 °C, (b). Scan size 3×3 mkm

4. Conclusions

Layers with an average crystallite size of 250–300 nm (STM) were formed on the surface of InP by mild deposition method of vanadium oxide gel via aerosol phase followed by thermal annealing. This method is characterized by the lack of interaction chemostimulator-substrate before thermal oxidation of V_xO_y/InP structures (XRD). Modified of InP by V_2O_5 gel leads to oxidation of semiconductor via a transit mechanism with low acceleration values for the process compared with oxidation of InP (about 20–40 %) in contrast to the oxidation process of V_2O_5/InP structures, formed by magnetron sputtering. The implementation of the activator action on transit mechanism is due to preferential binding of V_2O_5 in $InVO_4$, prevailing over the mutual transformations of various forms of vanadium oxide.

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