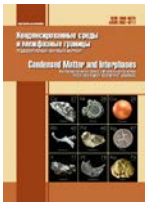

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Activation of film growth on indium phosphide by pulsed photon treatment

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Abstract

Photon activation of various physicochemical processes by the radiation of powerful pulsed xenon lamps (radiation range of 0.2-1.2 μm) is one of the promising areas of material science. The aim of this study was to determine the effect of pre-oxidative pulsed photon treatment on the process of thermal oxidation of indium phosphide with a nanosized layer of V_2O_5 on the surface, as well as its effect on the composition and morphology of the formed films.

We determined the optimal mode of pre-oxidative pulsed photon treatment of magnetron-formed V_2O_5/InP heterostructures with a radiation density of 15 J/cm^2. By laser and spectral ellipsometry methods, photon activation of V_2O_5/InP before thermal oxidation was found to increase the thickness of the formed films practically twofold. X-ray diffraction analysis confirms the intensification of the phosphate formation process. The morphological characteristics of the films were determined by atomic force microscopy.

Pre-oxidative pulsed photon treatment with an optimal radiation density of 15 J/cm^2 activates the thermal oxidation of V_2O_5/InP heterostructures. It is associated with the formation of new active centres and accelerated rearrangement of chemical bonds in the intermediate complexes of the V_2O_5 catalyst with semiconductor components.

Keywords: Indium phosphide, Vanadium (V) oxide, Thermal oxidation, Thermal oxidation, Pulsed photon treatment

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1. Introduction

Oxidation of $A^{III}B^{V}$ binary semiconductors is of great importance in various technological areas, such as designing optoelectronic devices, solar cells, and anti-reflective coatings, etc. [1–5]. Thermal oxidation of InP can be widely used in the development of cheap and highly efficient photoconverters of natural and linearly polarised radiation [6], it provides new approaches to the formation of MOS structures based on this semiconductor [7].

d-metal oxides are effective chemostimulators for the thermal oxidation of $A^{III}B^{V}$ semiconductors [8, 9]. Among them, vanadium (V) oxide has the highest potential. Deposited on the semiconductor surface even in a small amount, in the form of nanosized islands, it provides a catalytic mechanism for the thermal oxidation of indium phosphide [10].

The activation of physicochemical processes by irradiation with electrons, ions, and light is widely used to modify the subsurface layers of materials. One of the promising areas is pulsed photon treatment (PPT) by the radiation of powerful pulsed xenon lamps (radiation range of 0.2–1.2 μm) [11].

The aim of this study was to determine the effect of pre-oxidative PPT on the process of thermal oxidation of indium phosphide with a nanosized layer of V_2O_5 on the surface, as well as its effect on the composition and morphology of the formed films.

2. Experimental

For this study, we used monocrystalline indium phosphide plates (100), FIE-1A grade (indium phosphide, electronic conductivity), doped with tin, with the concentration of the main charge carriers no less than $5 \cdot 10^{16}$ cm^{-3}. The substrates were pre-treated in H_2SO_4 (92.80 %) : H_2O_2 (56 %) : H_2O = 2 : 1 : 1 for 10 min, then washed with distilled water. Nanosized layers of the chemostimulator, V_2O_5 oxide (~30 nm) were applied on the InP surface by magnetron sputtering (Covap II vacuum ion sputtering unit). The heterostructures were formed in a chamber vacuumised to a pressure of $2 \cdot 10^{-5}$ mm Hg. Metallic vanadium with a purity of 99.99 % was used as the initial target material, and O_2+Ar gases with a purity of 99.99 % were used as an ion source.

The process of thermal oxidation (TO) of the InP-based heterostructures was carried out in an MTP-2M-50-500 resistance heating furnace at a temperature of 530 °C for 1–60 minutes. Temperature was controlled by the TPM-10 unit with a precision of ± 1 °C. Oxidation was carried out in an oxygen flow (the volume flow rate was 30 l/h and the linear flow rate was 10 cm/min). Indium phosphide, oxidised in the same way without a chemostimulator, was used as a reference standard.

Pulsed photon treatment of the samples was carried out using a modernized UOLP-1M unit, designed for pulsed photon annealing of semiconductor materials. Heating was provided by the radiation of three INP 16/250 gas-discharge xenon lamps. The radiation dose for one treatment cycle was determined by the annealing time. It was regulated within the range of 0.02–20 s, which corresponds to 2–2000 unit pulses. The radiation dose varied from 15 to 120 J/cm^2.

To determine the thickness of the films of the formed heterostructures and films after TO (PPT), we used the methods of laser ellipsometry (LE, LEF-754) and spectral ellipsometry (SE, Ellips-1891).

To characterise the heterostructures and thin films formed on the semiconductor surface, a set of instrumental methods was used: X-ray diffraction analysis (XRD, ARL X'TRA diffractometer, Cu$K_{\alpha 1}$ with λ = 1.540562 Å); infrared spectroscopy (IRS, Vertex 70 IR Fourier spectrometer); atomic force microscopy (AFM, Solver P47 Pro (NT-MDT) scanning microscope with the HA_NC Etalon cantilever); scanning tunnelling microscopy (STM, Umka laboratory nanotechnology complex, based on the improved Umka-02-U scanning tunnelling microscope).

3. Results and discussion

A number of studies [12–15] revealed that the activating effect of PPT is expressed in the acceleration of diffusion processes, synthesis of thin films of the compounds, and recrystallisation. It is also associated with the decrease of temperature thresholds of phase formation, increase in the dispersity of synthesised structures, the formation of metastable phases, as well as nanocrystallisation of amorphous metal alloys. Nanocrystallisation leads to the increase in microhardness, while plasticity is preserved.

In order to select an optimal PPT mode for V_2O_5/InP heterostructures, a batch of samples were prepared. They underwent pulsed photon treatment at various radiation density values of 15, 30, 50, 60, and 90 J/cm^2. While optimising the PPT effect, we determined that the use of modes with a radiation dose of more than 50 J/cm^2 leaded to degradation of the surface of the heterostructure up to its complete destruction. We found out that a radiation density of 15 J/cm^2 can be considered optimal for the purposes of this study. Under these conditions the film grows most intensively with no degradation of the heterostructure.

Fig. 1 and Table 1 show the thickness values of the films formed by thermal oxidation of indium phosphide (intrinsic oxidation, reference standard), by the thermal oxidation of the V_2O_5/InP heterostructure without PPT, and upon pre-oxidative pulsed photon treatment carried out in the optimal mode.

The use of the Cauchy model for the interpretation of spectral ellipsometry data is confirmed by the good correlation (especially in the wavelength range above 500 nm) between the calculated and experimental spectra of the ellipsometric parameters Ψ and Δ (Fig. 2).

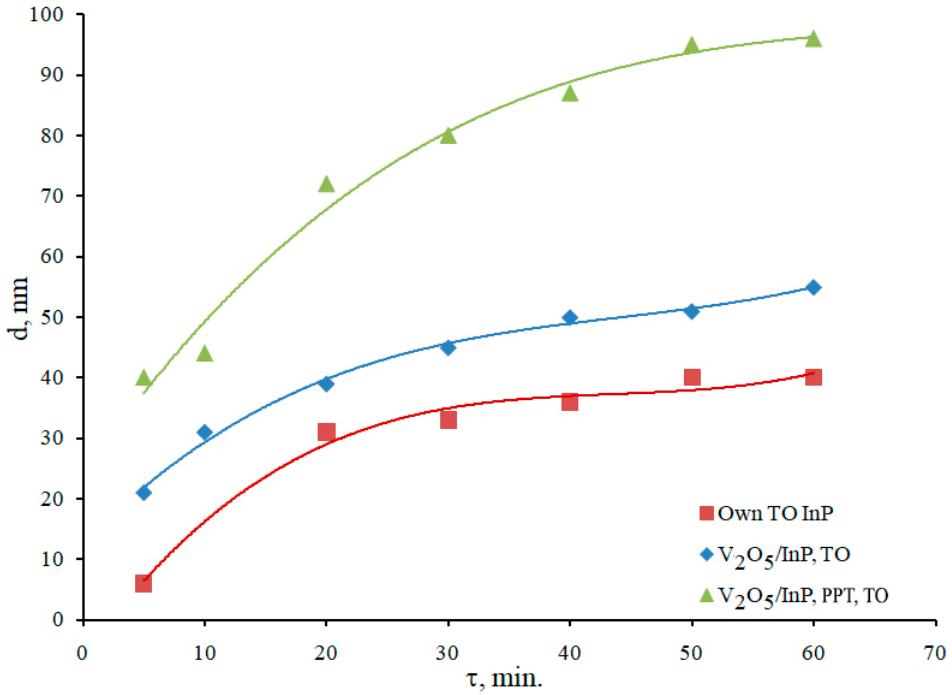

Fig. 1. Kinetic curves of the InP intrinsic thermal oxidation and the V_2O_5/InP heterostructures thermal oxidation, without PPT and upon PPT for 0.2 s. Oxidation temperature: 530 °C

Table 1. The thickness of the films formed by thermal oxidation of InP (reference) and V_2O_5/InP heterostructures without and with pre-oxidative PPT. Oxidation temperature: 530 °C

Oxidation time, min	Film thickness *d*, nm		
	InP intrinsic oxidation	V_2O_5/InP, thermal oxidation at 530 °C, without PPT	V_2O_5/InP, PPT 15 J/cm^2 and thermal oxidation at 530 °C
5	6	20	39
10	25	32	44
20	31	39	72
30	33	44	80
40	36	49	86
50	39	50	94
60	39	52	96

We had previously determined [8, 16] that thermal oxidation of InP with a magnetron-deposited nanoscale layer of V_2O_5 (25 nm) was carried out by the catalytic mechanism due to cyclic regeneration of V_2O_5 (the transition of vanadium from the oxidation state +5 (V_2O_5) to +4 (VO_2) and vice versa). We suggested the following "phase" evolution of the magnetron-formed V_2O_5/InP heterostructures during their thermal oxidation (Fig. 3).

At the initial stage of oxidation, due to the chemostimulating effect of V_2O_5 of the catalytic type, there is a sharp increase in the concentrations of oxides In_2O_3 and P_2O_5. In contrast to transition oxides (for example, NiO), which are consumed during the oxidation process, V_2O_5 is cyclically regenerated throughout the entire process. According to [17], this transition occurs quickly and with low energy consumption through the intermediate vanadium oxides V_3O_7

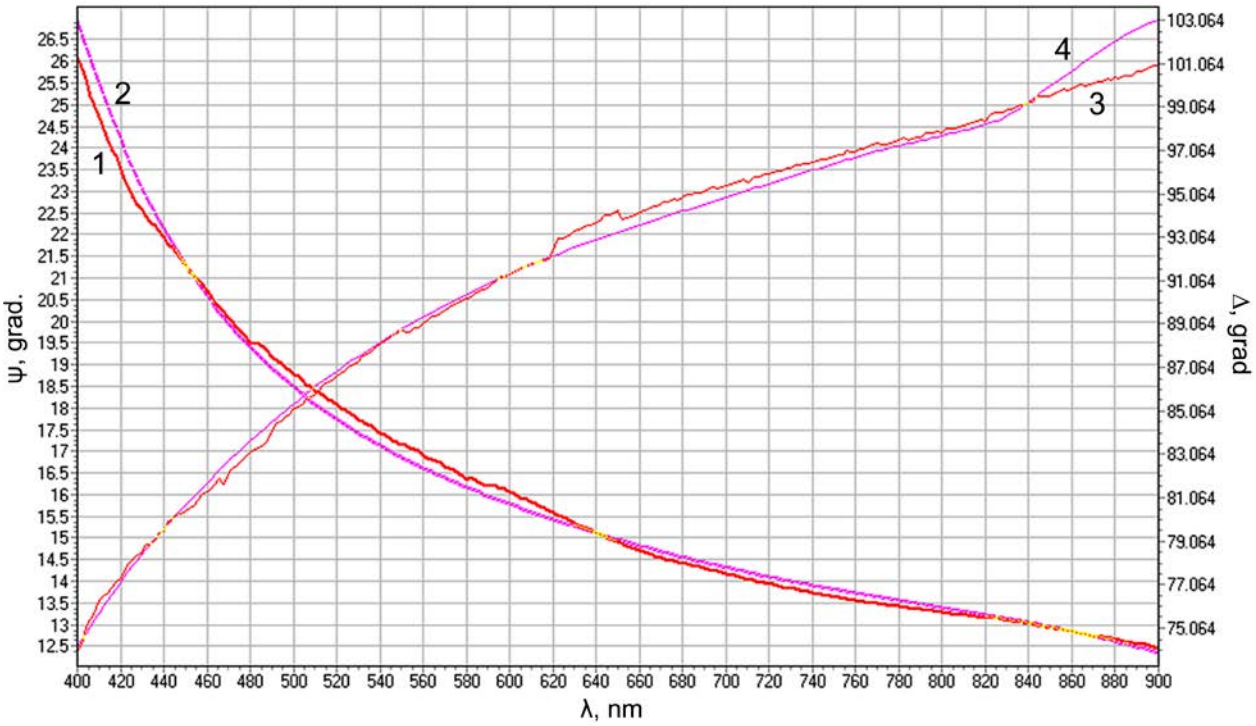

Fig. 2. Spectra of the ellipsometric parameters ψ (*1*,*2*) and Δ (*3*,*4*) of the V_2O_5/InP sample, which underwent preliminary PPT at 15 J/cm² and TO at 530 °C for 60 min (*1*,*3* – measured, *2*,*4* – calculated by the Cauchy model)

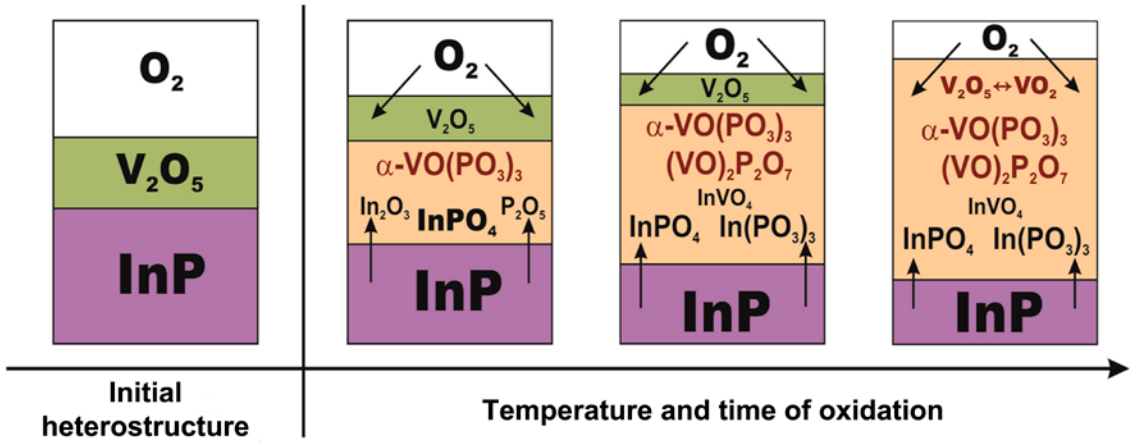

Fig. 3. Diagram of the evolution of V_2O_5/InP heterostructures during thermal oxidation

and V_4O_9, which were detected in the formed films by the XRD method. Thus, the chemostimulating effect of vanadium pentoxide, which involves the intensive oxidation of semiconductor components by the catalytic mechanism, persists throughout the entire thermal oxidation process. A rapid increase in the concentration of A^{III} and B^{V} oxides leads to the intensive development of secondary interactions in the system. They are accompanied with the formation of indium phosphate and are prominent due to the large acid-base difference between the A_2O_3 and B_2O_5 oxides. Due to the chemical nature of the vanadium (V) oxide, taking into account the isostructurality of vanadate ions with phosphate ions, vanadium in the form of vanadate is included in the forming phosphate framework of the films (in the form of $InVO_4$). Due to the electronic configuration V and the covalent type of chemical bonds between vanadium and oxygen, the metal is present in the films on the surface of indium phosphide in the form of vanadyl phosphates $VO(PO_3)_3$ and $(VO)_2P_2O_7$. It can be explained by the pronounced acidity of phosphorus oxide.

According to [17–19] the stepwise redox mechanism of catalytic oxidation at high temperatures is typical for most reactions where transition metal oxides act as catalysts, as the reduction and re-oxidation rates of the catalyst are rather high. Under other conditions of catalysis, for example, with a change in temperature, a transition from the stepwise mechanism to the associative mechanism is possible, when oxygen and the oxidised reagent interact simultaneously [17, 19]. The simultaneous presence of vanadium oxides exhibiting oxidation states +5 and +4 in the V_2O_5/InP heterostructures formed during the oxidation process, established by XRD and IRS methods, is an argument in favour of the stepwise oxidation mechanism. However, according to classical concepts [20], catalytic reactions, in the course of which the formation of an activated complex is preceded by the breaking of bonds in the initial reagent (dissociative mechanism), have high activation energy values, although lower as compared to the non-catalytic reaction. Low activation energy values are characteristic of catalytic reactions proceeding through an activated complex, which involves the particles of both reactants and the active centre of the catalyst at the same time (synchronous mechanism). For V_2O_5/InP heterostructures, the hard method of deposition (magnetron sputtering, exploding wire method) "imposes" the formation of interface intermediate complexes of the catalyst V_2O_5 with semiconductor components already in the synthesis process. That is, the weakening of the In-P bond and the beginning of the formation of the In-O and P-O bonds are simultaneous. Taking into account the low EAE values of the V_2O_5/InP thermal oxidation process, non-classical objects of study (solid reagent and catalyst, nanoscale state of the catalyst), it can be said these intermediate complexes are transformed by the mechanism of associative substitution by reactive oxygen species.

The pre-oxidative PPT of V_2O_5/InP heterostructures almost doubles the thickness of the films formed during thermal oxidation. According to [21], various physicochemical processes are activated by the PPT mainly due to the excess of a certain critical heating rate and athermal processes initiated by the interaction of the light flux with the substance. The effect of pulsed photon activation of the thermal oxidation process can be caused by an increase in the number of active centres. Interface intermediate complexes of the V_2O_5 catalyst with semiconductor components are formed on them, possibly, of a different chemical nature. In addition, a significant energetic effect on the heterostructure significantly facilitates the rearrangement of chemical bonds in intermediate complexes during oxidation and accelerates the formation of indium and phosphorus oxides, and, consequently, various phosphates. The XRD data for the film formed by thermal oxidation of the V_2O_5/InP heterostructure upon preliminary PPT (15 J/cm^2) indicate the formation of a pronounced phosphate and vanadate framework during oxidation (Fig. 4).

The pre-oxidative PPT of V_2O_5/InP heterostructures affects the morphological characteristics of the films formed by thermal oxidation. Thus, the surface of the film synthesised by oxidation of V_2O_5/InP at 530 °C for 60 min with preliminary PPT (E = 15 J/cm^2) is smooth, with no pronounced grain structure (Fig.5a). The difference in the relief height does not exceed 7 nm, the arithmetic mean roughness S_a is 0.4

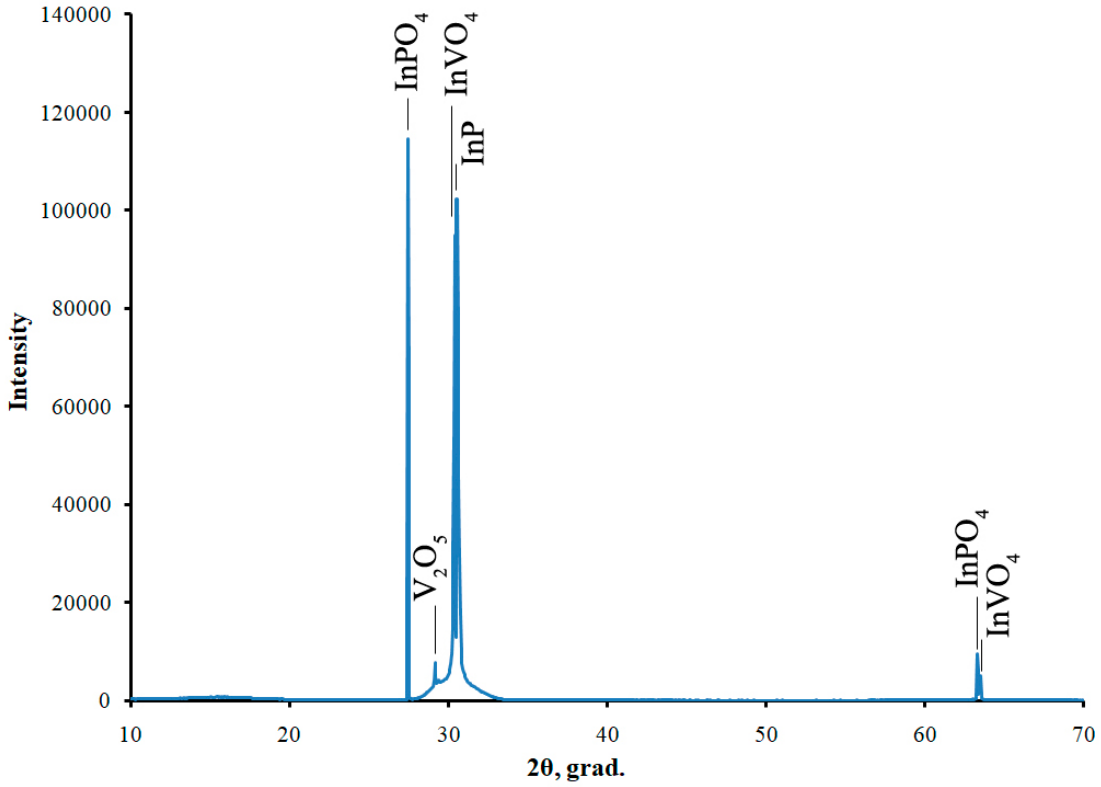

Fig. 4. Diffraction pattern of the V_2O_5/InP sample after preliminary PPT at 15 J/cm^2, followed by TO at 530 °C for 60 min

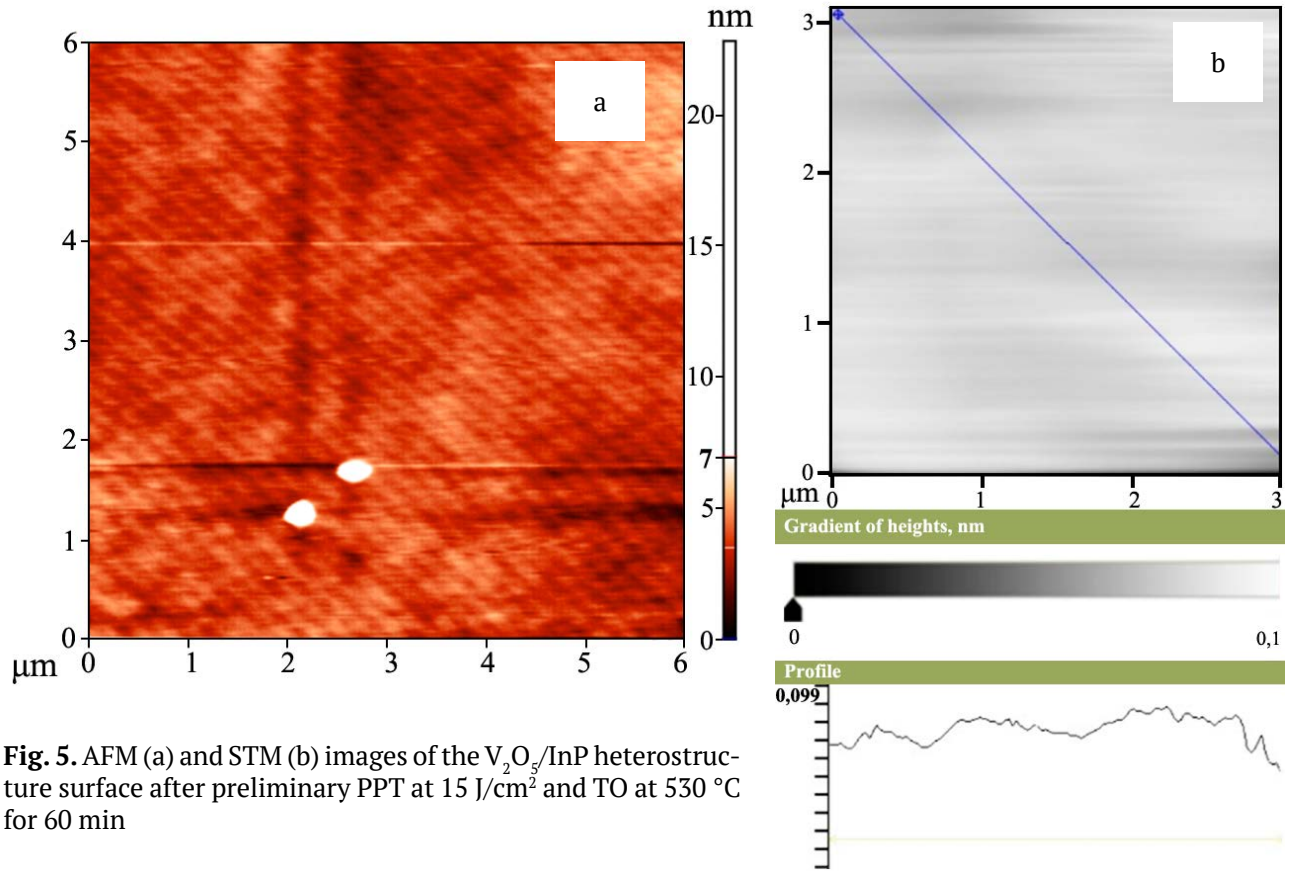

Fig. 5. AFM (a) and STM (b) images of the V_2O_5/InP heterostructure surface after preliminary PPT at 15 J/cm^2 and TO at 530 °C for 60 min

nm, the mean square roughness S_q is 0.6 nm. The STM data also confirm the high smoothness of these films (Fig. 5b). The height gradient does not exceed 10 nm.

4. Conclusions

Pre-oxidative PPT with an optimal radiation density of 15 J/cm^2 activates the thermal oxidation of the V_2O_5/InP heterostructures, resulting in an almost twofold increase in the thickness of the formed films. The PPT effect is associated with the formation of new active centres, where intermediate complexes of the catalyst V_2O_5 with semiconductor components are formed. The transformation of chemical bonds in these complexes also accelerates, resulting in the formation of indium and phosphorus oxides. Preliminary PPT stimulates the growth of films with a smooth surface, which arithmetic mean roughness S_a is 0.4 nm.

Author contributions

All authors made an equivalent contribution to the preparation of the publication.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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