

Studying the Modes of Nanodimensional Surface Profiling of Gallium Arsenide Epitaxial Structures by Local Anodic Oxidation

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Abstract—In this work we present the results of studying the influence of the local anodic oxidation (LAO) technological modes on the process of formation of oxide nanodimensional structures (ONSs) at the surface of Gallium Arsenide epitaxial structures (ESs). We have studied the influence of the amplitude and duration of pulses of voltage applied to the system probe–substrate and amplitude of cantilever vibrations on the geometric parameters of GaAs ONS. The influence of LAO modes on the geometric parameters of profiled nanodimensional structures (PNSs) obtained at the surface of GaAs ES after etching the ONS formed by LAO has been studied. It is established that an increase in the amplitude and duration of pulses of the applied voltage by LAO results in an increase in the height, depth, and diameter of oxide and profiled nanodimensional structures at the surface of GaAs ES. It is shown that an increase in the amplitude of the cantilever vibrations from 3 to 26 nm results in a decrease in the PNS from 9.1 ± 1.6 to 3.4 ± 0.3 nm and diameter of PNS from 274 ± 34 to 167 ± 29 nm. The results may be used for developing the technological processes for preparing an element base for nanoelectronics based on Gallium Arsenide.

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INTRODUCTION

The basic trends in the evolution of modern technology are associated with the development of new devices and elements of micro- and nanoelectronics and micro- and nanosystem engineering based on arrays of self-organizing semiconductor nanostructures (SSNs) (quantum dots and whiskers), which refer to a promising class of nanomaterials [1]. An analysis of employing SSNs based on gallium arsenide for the creation of the elements of nanoelectronics shows the necessity of the precision control of the geometric parameters, density, and local position of the structures to be formed. There are several methods of positioning and localization of growth of self-organizing semiconductor nanostructures of gallium arsenide which can be partitioned into several groups: the formation of SSNs using the orientation effects of the substrate surface; mesastructures and masks; and arrays of profiled nanodimensional structures (PNSs) formed at the surface of the substrate by optical lithography, focused ion beams, or probe nanolithography [1]. Among a wide spectrum of methods of nanodimensional profiling of the surface [2–7] based on probe nanolithography, one of the most promising for positioning and localization of SSN growth is the local anodic oxidation (LAO), the use of which provides a high spatial resolution, the possibility of profiling the surface of the substrate without any additional opera-

tions associated with the deposition of a photoresist, and high reproducibility at minimum disturbances in the structural perfection of the epitaxial layer [6–13]. However, despite the numerous scientific publications on this problem, the influence of the modes of local anodic oxidation on the geometric parameters of the profiled nanodimensional structures at the surface of gallium arsenide remains unstudied.

This work is aimed at studying the influence of the modes of local anodic oxidation (the amplitude and duration of pulses of the voltage applied to the system probe–substrate and the intensity of interaction of the AFM probe with the sample surface) on the geometric parameters of oxide and profiled nanodimensional structures at the GaAs surface.

EXPERIMENTAL

By carrying out experimental studies, epitaxial structures of GaAs were used as samples obtained by module-molecular-beam epitaxy (MBE) STE35 (NTE, Russia) of multifunctional nanotechnological complex NANOFAB NTK-9 (NT-MDT, Russia). The growth of the structures was carried out on semi-insulating plates of GaAs (001) “epi-ready.” After the standard procedure of removing the protective oxide at 580°C and the subsequent exposure of the surface in a flux of As₄ at a pressure of 3.5×10^5 Pa for 10 min, the

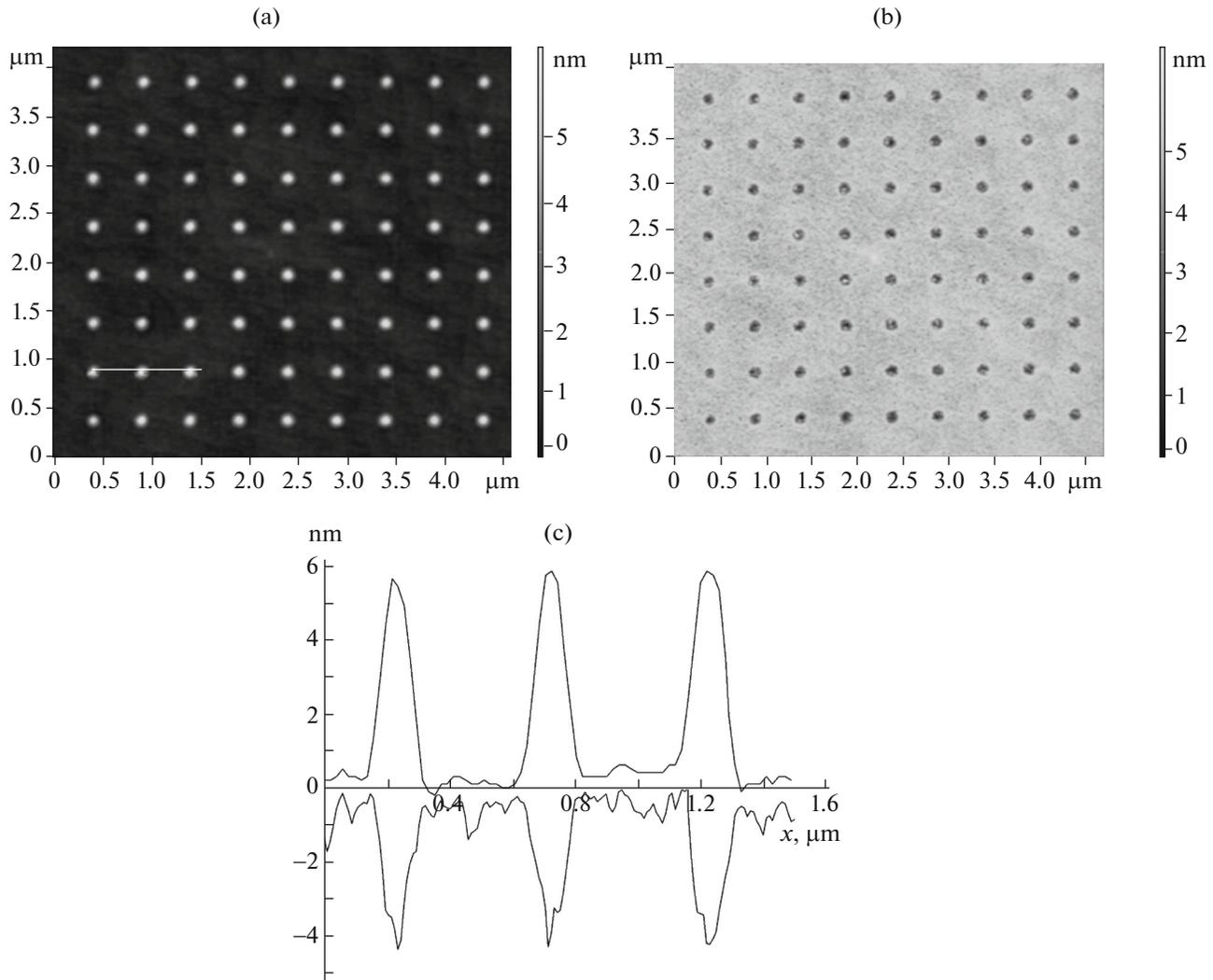


Fig. 1. AFM images of the ES of gallium arsenide: (a) after the formation of ONS using LAO, (b) after the formation of PNS, and (c) the profilogram along the lines on (a) and (b).

growth of a buffer was performed by depositing 800 nm of nondoped GaAs. Then, a GaAs layer with a thickness of 2 μm and impurity concentration of $3 \times 10^{18} \text{ cm}^{-3}$ doped with silicon was deposited.

The formation of GaAs ONSs was carried out with the use of the probe nanolaboratory Ntegra (NT-MDT, Russia) in a semicontact mode of AFM. As probes for LAO process, we used cantilevers of the DSP 20 brand with a conducting carbon coating. The amplitude of voltage pulses in the probe–substrate system (U) was varied from 8 to 15 V, duration of pulses (t) was from 100 to 800 ms, and the value of the current of feedback circuit (SetPoint) was from 0.5 to 2 nA. As a result, an array of ONSs was formed at the surface of the substrate whose AFM image and profilograms are presented in Figs. 1a and 1c.

It was shown earlier in [12, 13] that an increase in the humidity inside the technological chamber

increases the geometric sizes of GaAs ONSs and decreases the value of the threshold voltage, which is caused by an increase in the number of active particles providing the reaction of oxidation. Therefore, the value of the humidity level of working atmosphere inside the technological chamber of the scanning probe microscope was constant and amounted to $90 \pm 1\%$. The control of humidity was carried out on an Oregon Scientific ETHG913R digital humidity measurer.

According to the technique described, by using LAO we have formed 18 arrays, each of which is composed of 72 isletlike GaAs ONSs at the surface of a GaAs:Si epitaxial layer (Figs. 1a, 1b). After this, the samples to be studied were placed into the MLE module, where the oxide was removed from the surface of the GaAs substrate.

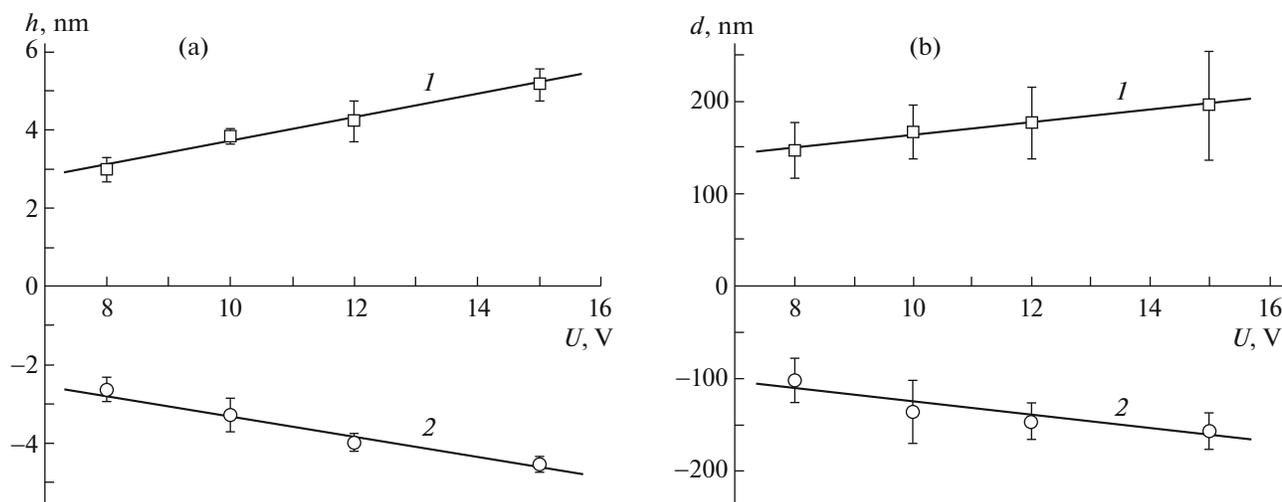


Fig. 2. Dependences of the geometric parameters of nanostructures on the voltage amplitude by LAO of the ES surface of gallium arsenide: (a) height of ONS (1) and depth of PNS (2); (b) diameter of ONS (1) and PNS (2).

The surface of GaAs under usual conditions is covered with a film of the native oxide, the thickness of which amounts to 2–3 nm and is not practically changed with time [14, 15] (in contrast to roughness, which increases from 4 to 15 nm with time [15]). The oxide has an amorphous structure and is composed of Ga_2O_3 , As_2O_3 , As_2O_5 , and elementary As, which is accumulated at the boundary with the crystalline substrate and between grains [16–19]. The elementary As is released as a result of both a reaction in a cationic sublattice and a solid-phase reaction at the oxide/substrate interface [17].

In the process of MLE, the oxide, as a rule, is removed thermally, also at the expense of the interaction with the crystalline substrate material [20]. In this case, the morphology of the surface deteriorates substantially. As was shown in [21], the main reason for this is the etching of the surface with oxides of As. In order to reduce the influence of the processes of the native GaAs oxide interaction with the profiled surface, it was proposed in [22, 23] to use a preliminary deposition of Ga over the oxide at low (400–500°C) temperatures with the subsequent high-temperature ($\geq 550^\circ\text{C}$) annealing in the As atmosphere, which makes it possible to reduce mean-square roughness of GaAs surface. The effect is achieved at the expense of the formation of a volatile oxide Ga_2O according to a more beneficial (from the point of view of thermodynamics) reaction:



instead of the reaction Ga_2O_3 with the substrate material [24]:



Therefore, in this work, in order to minimize the influence of the processes of the GaAs native oxide

interaction with the surface of samples on the geometric parameters of PNS to be formed, the removal of the oxide was carried out with the help of a preliminary deposition of Ga from a vapor phase in a growth chamber of MLE. The process was carried out at a sample temperature of 500°C (below the point of reaction (1.2) activation) by the deposition of 5 Ga monolayers with a rate of 1 monolayer/s and a period of 1 min. As was shown in [22, 23], the temperature of activation of the metallic Ga interaction with the components of GaAs oxide is substantially lower than the temperature of the start of the oxide reaction with the substrate surface, while the rate of reaction is higher. The optimal values of the effective thickness of Ga deposition on the surface were determined experimentally and were chosen so that the whole deposited material would be expended for the interaction with the oxide. The control of oxide removal was performed by observing the diffraction pictures of reflected fast electrons from the surface.

After this, the samples were transferred to the module of a NANOFAB NTK-9 SPM complex, where the scanning of the GaAs surface was carried out; the AFM images and profilograms are presented in Figs. 1b and 1c.

RESULTS AND DISCUSSION

Statistical processing of the AFM images was carried out with the use of the Image Analysis 3.5 software packet according to the technique of taking measurements approved in accordance with GOST R8.563-96 [25]. Using the obtained statistical data, we have built the dependences of the values of the geometric parameters for GaAs ONS (height and diameter) and GaAs PNS (depth and diameter) on the amplitude, the duration of the pulse of the applied

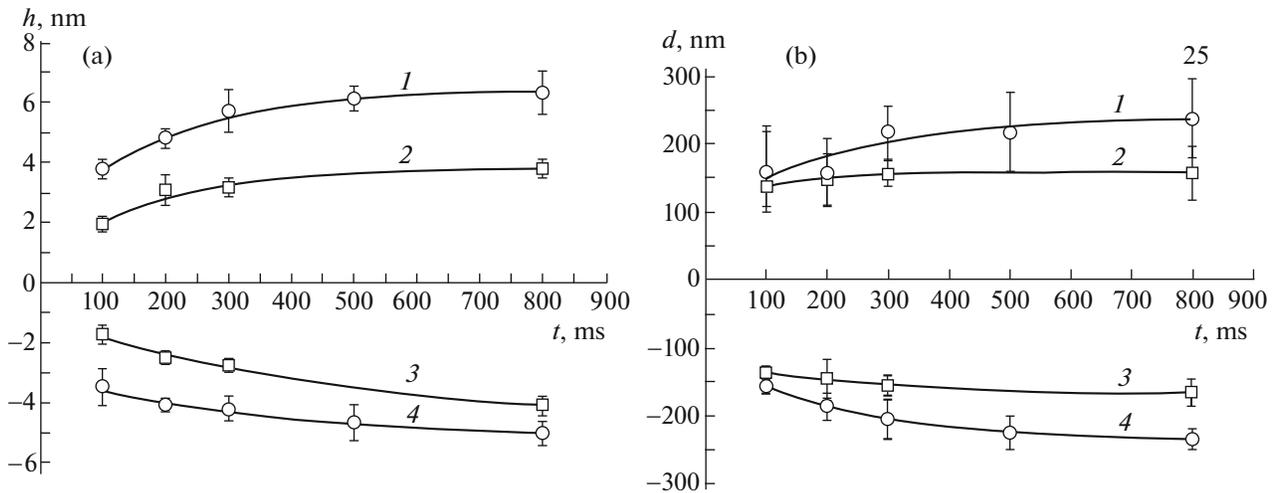


Fig. 3. Dependences of the geometric parameters of nanostructures on the duration of the voltage pulse by LAO of the ES surface of gallium arsenide: (a) height of ONS (1 at $U = 15$ V, 2 at $U = 10$ V) and depth of PNS (3 at $U = 10$ V, 4 at $U = 15$ V); (b) diameter of ONS (1 at $U = 15$ V, 2 at $U = 10$ V) and PNS (3 at $U = 10$ V, 4 at $U = 15$ V).

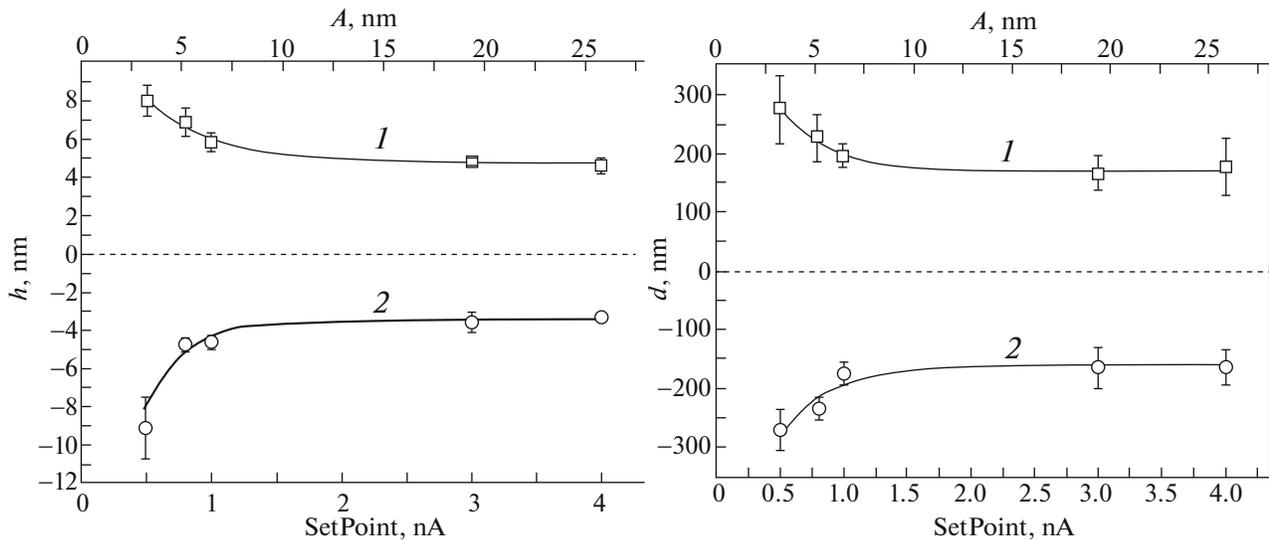


Fig. 4. Dependences of the geometric parameters of nanostructures on the amplitude of the cantilever vibrations and the parameter SetPoint by LAO of the surface of ES of gallium arsenide: (a) height of ONS (1) and depth of PNS (2); (b) diameter of ONS (1) and PNS (2).

voltage, and the parameter SetPoint at a fixed at a level of $90 \pm 1\%$ value of relative humidity presented in Figs. 2–4.

An analysis of Fig. 2 has shown that, at SetPoint = 2 nA, $t = 500$ ms, an increase in the amplitude of voltage pulse from 8 to 15 V results in a linear increase in the GaAs ONS height and depth of GaAs PNS from 2.9 ± 0.3 to 5.1 ± 0.4 nm and from 2.6 ± 0.3 to 4.5 ± 0.2 nm, respectively. The diameter of GaAs ONS and PNS at the GaAs surface in this case also linearly increased from 147 ± 28 to 195 ± 21 nm and from 103 ± 24 to 157 ± 19 nm, respectively. The ONS

dependences $h(U)$ and $d(U)$ obtained for GaAs correlate well with the data of [12, 13].

Figure 3 presents the experimental dependences of the height of ONS and depth of PNS, as well as of the diameter of ONS and PNS on the duration of a voltage pulse, which were obtained at various values of voltage of 10 and 15 V, and SetPoint = 2 nA.

It can be seen from Fig. 3 that, at 10 V and a change in the pulse duration from 100 to 800 ms, the height of ONS and the depth of PNS increase from 1.9 ± 0.2 to 3.8 ± 0.3 nm and from 1.7 ± 0.3 to 4.1 ± 0.3 nm, respectively. In this case, the diameter increased from 137 ± 29 to 156 ± 39 nm and from 137 ± 10 to $167 \pm$

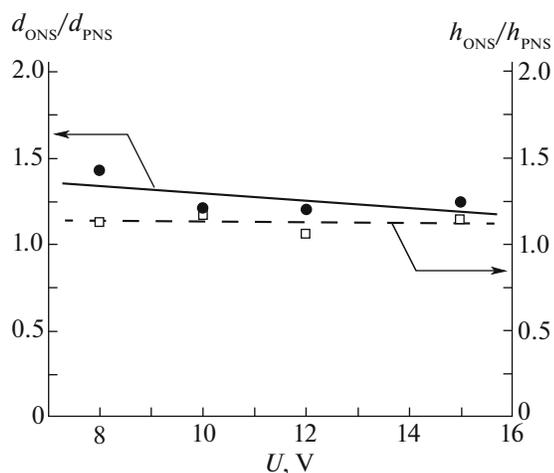


Fig. 5. Dependence of the ratio of the height (diameter) of ONS and depth (diameter) of PNS on the voltage amplitude by LAO of the surface of ES of gallium arsenide.

20 nm for ONS and PNS, respectively. An increase in the pulse amplitude to 15 V, as follows from the dependences shown in Fig. 3, results in an increase in the height of ONS and Depth of PNS from 3.8 ± 0.3 to 6.3 ± 0.7 nm and from 3.4 ± 0.6 to 4.9 ± 0.4 nm, while the diameter changed from 157 ± 59 to 235 ± 59 nm and from 157 ± 10 to 235 ± 15 nm in the same range of changes in the pulse duration.

When the voltage amplitude by LAO increases, the beginnings of the regions of saturation of characteristics are shifted from 300 ms at $U = 10$ V to 600 ms at $U = 15$ V. This correlates well with the experimental data and explanation of this effect presented in [12, 13].

The dependences of the geometric parameters of the profiled nanodimensional structures formed by LAO at the surface of GaAs on the parameter SetPoint obtained at $t = 500$ ms and $U = 15$ V are presented in Fig. 4. The value of the parameter SetPoint in this case varied in a range of (0.5–4) nA. An analysis of the dependences presented in Fig. 4 has shown that, by an increase in SetPoint from 0.5 to 4 nA, the values of the height of ONS and depth of PNS of GaAs decrease from 8.0 ± 0.8 to 4.6 ± 0.4 nm and from 9.1 ± 1.6 to 3.4 ± 0.3 nm, and those of the diameter decrease from 274 ± 59 to 176 ± 49 nm and from 274 ± 34 to 167 ± 29 nm, respectively.

A decrease in the geometric parameters of the structures formed can be accounted for by the fact that an increase in the parameter SetPoint in a semicontact mode of AFM is equivalent to an increase in the amplitude of the cantilever vibrations, which, in turn, results in a decrease in the time of interaction with the sample, a decrease in the rate of the formation of ONS, and a decrease in the geometric sizes of the profiled nanodimensional structures of gallium arsenide [12].

Figure 5 shows the dependence of the ratio of the height of ONS to the depth of PNS on the voltage

amplitude by carrying out LAO of the surface of gallium arsenide, from an analysis of which follows that $h_{\text{ONS}}/h_{\text{PNS}}$ amounts to about 1.2 ± 0.1 and by a variation in the applied voltage amplitude it is changed inessentially. In this case, an estimation of the ONS material density through the ratio of the volumes of the obtained oxide and of a crystalline GaAs expended for its formation gives a value close to the density of Ga_2O_3 , which correlates well with the results of [26] and makes it possible to come to a conclusion in an indirect way about the predominant phase of the formed oxide.

CONCLUSIONS

As a result of the studies carried out, we have obtained dependences of the geometric parameters for the oxide and profiled nanodimensional structures at the surface of epitaxial structures of gallium arsenide on the amplitude and duration of the pulses of voltage applied to the system probe–substrate and the amplitude of the cantilever vibrations by carrying out local anodic oxidation in a semicontact mode of AFM. It is established that an increase in the amplitude and duration of the applied voltage pulses by LAO results in an increase in the height and diameter of ONS and to an increase in the height and diameter of PNS at the surface of ES of gallium arsenide. It is shown that the amplitude of the cantilever vibrations is also a control parameter of the LAO process; upon its increase, decreases in height, depth, and diameter take place for the oxide and profiled nanodimensional structures.

Thus, it is shown that local anodic oxidation is a promising method of nanolithography, the use of which allows us to profile the substrate surface with a nanometer resolution. The results may be used in developing technological processes for fabricating the element base of nanoelectronics.

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REFERENCES

1. P. Atkinson, et al., "Formation and ordering of epitaxial quantum dots," *C.R. Phys.* **9**, 788–803 (2008).
2. C. Taylor, et al., "Directed self-assembly of quantum structures by nanomechanical stamping using probe tips," *Nanotechnology* **19**, 1–10 (2008).

3. S. Kohmoto, et al., "Site-controlled self-organization of InAs quantum dots," *Mater. Sci. Eng. B* **88**, 292–297 (2002).
4. H. Nakamura, et al., "Novel nano-scale site-controlled InAs quantum dot assisted by scanning tunneling microscope probe," *Phys. E* **7**, 331–336 (2000).
5. J. Kapsa, et al., "STM and FIB nano-structuration of surfaces to localize InAs/InP(001) quantum dots," *Appl. Surf. Sci.* **226**, 31–35 (2004).
6. H. Z. Song, et al., "Growth process of quantum dots precisely controlled by an AFM-assisted technique," *Phys. E* **21**, 625–630 (2004).
7. J. Martin-Sanchez, et al., "Ordered InAs quantum dots on pre-patterned GaAs(001) by local oxidation nanolithography," *J. Cryst. Growth* **284**, 313–318 (2005).
8. O. A. Ageev, B. G. Konoplev, V. A. Smirnov, et al., "Photoactivation of nanostructures formation processes by means of titanium film local anode oxidation," *Izv. Vyssh. Uchebn. Zaved. Elektron.*, No. 2(82), 23–31 (2010).
9. O. A. Ageev, B. G. Konoplev, V. A. Smirnov, et al., "The way to research photonically stimulated probe nanolithography by means of titanium film local anode oxidation," *Nano- Mikrosistemn. Tekhn.*, No. 1(90), 14–16 (2008).
10. O. A. Ageev, B. G. Konoplev, V. A. Smirnov, et al., "Probe photonically stimulated nanolithography for structures based on titanium film," *Mikroelektronika* **36** (6), 403–408 (2007).
11. V. I. Avilov, O. A. Ageev, V. A. Smirnov, et al., "Memristor matrixes based on titanium oxide: formation and research by means of probe nanotechnology," *Izv. Vyssh. Uchebn. Zaved. Elektron.*, No. 2 (106), 50–57 (2014).
12. O. A. Ageev, M. S. Solodovnik, V. A. Smirnov, et al., "Gallium arsenide oxide nanosized structures: formation by means of local anode oxidation," *Izv. Vyssh. Uchebn. Zaved. Elektron.*, No. 2(94), 43–50 (2012).
13. O. A. Ageev, M. S. Solodovnik, V. A. Smirnov, et al., "Gallium arsenide oxide nanosized structures: formation by means of local anode oxidation," *Izv. Yuzhn. Federal. Univ. Tekhnich. Nauki*, No. 4(117), 8–13 (2011).
14. D. A. Allwood, et al., "Characterization of oxide layers on GaAs substrates," *Thin Solid Films* **364**, 333–339 (2000).
15. B. K. Tanner, et al., "Kinetics of native oxide film growth on epitaxial GaAs," *Mater. Sci. Eng. B* **80**, 99–103 (2001).
16. M. R. Vilar, et al., "Characterization of wet-etched GaAs (100) surfaces," *Surf. Interface Anal.* **37**, 673–682 (2005).
17. N. N. Bezryadin, et al., "Effect of gallium arsenide surface preparation onto electronic state spectrum of N-GaAs(100)," *Fiz. Tekhn. Poluprovodn.*, No. 6, 756–760 (2012).
18. D. P. Valyukhov, et al., "Interaction between oxygen and A3B5 surface," *Vestn. Severo-Kavk. Gos.-Tekhnol. Univ.*, No. 2, 1–6 (2010).
19. J. F. Bauters, et al., "Oxygen-enhanced wet thermal oxidation of GaAs," *Appl. Phys. Lett.* **99**, 142111 (2011).
20. N. Isomura, et al., "Investigation on GaAs(001) surface treated by As-free high temperature surface cleaning method," *J. Cryst. Growth* **301-302**, 26–29 (2007).
21. A. Guillen-Cervantes, et al., "GaAs surface oxide desorption by annealing in ultra-high vacuum," *Thin Solid Films* **373**, 159–163 (2000).
22. P. Atkinson and O. G. Schmidt, "Gallium-assisted deoxidation of patterned substrates for site-controlled growth of InAs quantum dots," *J. Cryst. Growth* **311**, 1815–1818 (2009).
23. Y. Asaoka, "Desorption process of GaAs surface native oxide controlled by direct Ga-beam irradiation," *J. Cryst. Growth* **251**, 40–45 (2003).
24. A. F. Pun, et al., "Reduction of thermal oxide desorption etching on gallium arsenide," *Thin Solid Films* **515**, 4419–4422 (2007).
25. O. A. Ageev and V. A. Smirnov, *The Way to Measure Geometrical Parameters of Oxide Nanosized Structures Clusters by Means of Atomic-Force Microscopy no. MVI 14* (2009).
26. M. Lazzarino, et al., "Chemical composition of GaAs oxides grown by local anodic oxidation: a spatially resolved Auger study," *Chem. Phys. Lett.* **402**, 155–159 (2006).

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