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NANOTECHNOLOGY

Photoactivation of the Processes of Formation of Nanostructures by Local Anodic Oxidation of a Titanium Film

O. A. Ageev, N. I. Alyab'eva, B. G. Konoplev^, V. V. Polyakov, and V. A. Smirnov

Taganrog Institute of Technology, Southern Federal University, Taganrog, 347928 Russia

^e-mail: kbg@tsure.ru

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Abstract—Experimental results on the conditions of activation of probe nanolithography of a thin titanium film by means of local anodic oxidation are reported. It is established that ultraviolet stimulation reduces the geometric dimensions of nanometric oxide structures. The stimulation is accompanied by an increase in the amplitude and duration of the threshold voltage pulse, correspondingly, from 6 to 7 V and from 50 to 100 ms at the relative humidity 50%. The experimental data on the effect of the cantilever coating material and substrate temperature on the geometric dimensions of nanometric oxide structures are reported.

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1. INTRODUCTION

The formation of the elemental base of nanoelectronics is connected with the development and study of the methods of modification of substrate surfaces with a nanometric resolution. One of the promising techniques of formation of the elemental base of nanoelectronics is nanolithography by local anodic oxidation (LAO) with the use of a scanning probe microscope (SPM) [1, 2]. The main advantage of LAO is the feasibility of real-time control of the electrical and topographical characteristics of nanostructures. In addition, the probe nanolithography technique provides a means for forming insulator barriers, resistive masks for selective etching, and gauges that can be used to form nanoelectronic elements (quantum dots, nanowires, single-electron transistors, etc.) [1–4].

During LAO, the surface is treated by applying voltage pulses to the (conducting probe)–substrate system. In this case, a liquid meniscus composed of water molecules adsorbed at the substrate surface is formed under the probe tip. Under the voltage fed to the system, an electrochemical reaction proceeds in the meniscus, which is accompanied by the processes of charge carrier and mass transport of ionized atoms of the oxidizer and substrate with the formation of oxides and hydrogen [2, 4, 5].

It is established that the kinetic of the LAO process is influenced by the adsorbate film thickness and chemical composition dependent on the relative humidity of the environment in the process chamber, as well as by the duration of the voltage pulse applied to the probe and by the electric field strength dependent on the voltage pulse amplitude and probe–substrate spacing [1–5].

At the present date, the basic mechanisms of probe LAO lithography have been rather well understood, which allows the use of this technique for development of manufacturing processes for the production of elements of nanoelectronics and nanotechnology [1–3]. At the same time, it is a topical problem to study additional external effects (induced by radiation, variations in temperature, electric field, etc.) on the kinetics of the LAO process in order to control the parameters of oxide nanostructures (ONSs) formed in the process and modify their properties. Specifically, previous studies showed that photonic stimulation had an additional activation effect on the LAO process. This effect can be used to improve the reproducibility and the degree of uniformity of the geometric parameters of elements of metal-based nanoelectronics [6, 7].

In addition, such studies will make it possible to refine the mechanisms of formation of nanostructures by the LAO technique.

The purpose of this study is to explore the conditions of activated probe LAO lithography and analyze the effects of UV and infrared IR radiation, variations in the substrate temperature, and cantilever conducting coating materials on the features of formation of oxide nanostructures in a titanium film.

2. EXPERIMENTAL

The conditions of activated processes of formation of ONSs in a titanium film by means of the LAO technique were studied with the use of the SOLVER P47 Pro SPM (Nanotechnologies–MDT Ltd., Zelenograd). In the studies, we used the tool kit and software delivered with the SPM.

A thin Ti film was deposited onto a Si substrate covered by a grown SiO_2 layer. The deposition was accomplished with the Univex setup (Oerlikon, Germany) for magnetron-assisted sputtering. The metal film

Effect of the cantilever material on ONS geometric parameters in titanium

Cantilever parameters [8]				ONS geometric parameters			
				Without photon stimulation		With UV stimulation	
trademark	conducting coating material	tip radius, nm	tip cone angle, deg	height, nm	diameter, nm	height, nm	diameter, nm
NSG 11	W_2C	~10	≤22	2.8 ± 0.12	31.3 ± 6.41	1.9 ± 0.18	21.9 ± 3.13
NSG 20	Pt	~10	≤22	2.5 ± 0.41	45.7 ± 3.63	1.8 ± 0.27	35.7 ± 1.29
NSG 10	TiN	~10	≤22	2.3 ± 0.31	70.5 ± 7.81	1.8 ± 0.37	66.7 ± 5.45
NSG 10	Polysilicon	~10	≤22	1.6 ± 0.86	39.2 ± 3.84	0.8 ± 0.23	21.5 ± 3.57
DSP 20	Diamond (Di)	~50–70	≤22	4.7 ± 0.43	119.3 ± 4.22	4.5 ± 0.37	107.2 ± 2.11

thickness was determined from the step measured with the use of a Teylor Hobson probe microscope (England) in the contact mode of scanning with a diamond needle, as well as with the use of a CrossBeam 1540XB scanning electron–ion microscope (SEM) (Carl Zeiss) via the formation of a cross section of the structure by focused ion beams. Analysis of the images obtained with an atomic force microscope (AFM) and SEM showed that the film structure was amorphous and the film thickness was about 6 nm.

The humidity in the process chamber was monitored with an Oregon Scientific ETHG913R digital humidity meter. Nanolithography was accomplished in semicontact AFM conditions with the use of the Nova RC1 (1.0.26.1238) applied program package.

The effect of photon stimulation on the formation of ONSs by the LAO technique was studied at the relative humidity of air inside the process chamber 50, 70, and 90 ± 1%. In the semicontact AFM mode of nanolithography, the strength of the probe–(substrate surface) interaction is inversely proportional to the current in the feedback circuit of the SPM control system (this current corresponds to the SetPoint parameter in the Nova RC1 program). The studies were conducted at three values of the SetPoint parameter, 0.1, 0.3, and 0.5 nA. We used Si NSG10 cantilevers with a conducting W_2C coating; the parameters of the cantilevers are given in the table [8]. Upon application of voltage pulses with an amplitude from 5 to 10 B and the duration 100 ms, matrixes consisting of 49 oxide island nanostructures (OINSs) were formed on the surface of the thin titanium film (Fig. 1). Such arrays of OINSs formed in one manufacturing cycle represent objects the number of which suffices for statistical processing of experimental data with confidence.

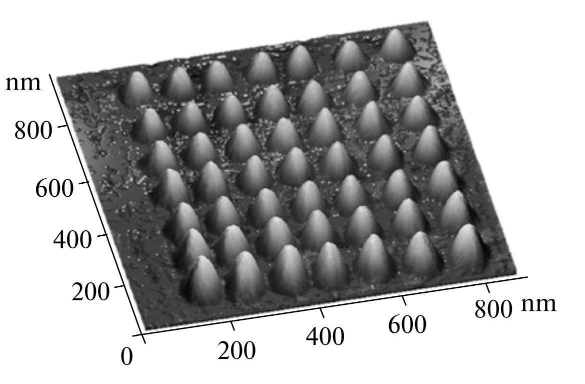

Fig. 1. The AFM image of ONSs formed on the titanium film surface by the LAO process.

To study the effect of UV and IR stimulation on the kinetics of LAO, we exposed the region to be subjected to LAO to radiation of a UV-light-emitting diode (LED) (CREE, USA) and an IR LED (AL-103A). The maximum intensities of these UV and IR LEDs corresponded to the wavelengths 395 and 900 nm, respectively.

The influence of the voltage pulse duration on the geometric parameters of ONSs formed by LAO was studied in the semicontact AFM mode of operation on application of voltage pulses with the amplitude 10 V and the duration ranging from 10 to 1000 ms at three values of the relative humidity (50, 70, and 90%). The experiments were conducted with and without UV and IR stimulation. The current in the feedback circuit of the SPM control system (the SetPoint parameter) was 0.5 nA.

In the studies of the conditions of thermal activation, the substrate was heated in the temperature range from 25 to 110°C with the use of an SU003 temperature plate (Nanotechnologies–MDT Ltd., Zelenograd). The LAO procedure was accomplished by means of the semicontact method in the vector mode of nanolithography with the use of Si cantilevers with a conducting W_2C coating upon application of voltage pulses (with duration 100 ms, amplitude 10 V, SetPoint = 0.1 nA, and scanning rate 0.5 μm s^{-1}). In this case, the arrays of nanostructures in the form of oxide strips were formed in the titanium film (Fig. 2).

In the studies of the influence of the cantilever conducting coating material on the ONS geometric parameters, probe LAO nanolithography was carried out for titanium film on application of voltage pulses to the probe–substrate system (at pulse amplitude 10 V, pulse duration 300 ms, and SetPoint = 0.3 nA). At constant relative humidity (70 ± 1)%, ONSs were

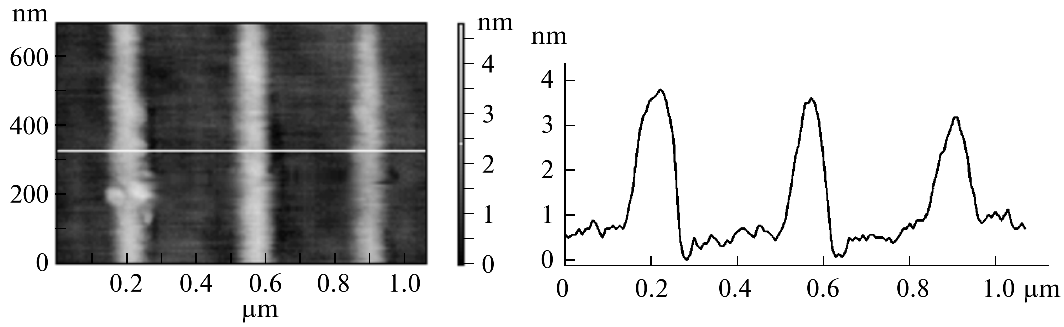

Fig. 2. (a) The AFM image and (b) surface profile of the titanium film treated by LAO at the substrate temperature 110°C.

formed with the use of Si cantilevers with different conducting coatings (W_2C, Pt, TiN, polysilicon, and diamond). The parameters of the coatings are listed in the table [8].

The results were used to study the conditions of forming nanometric channels in the titanium film by means of the LAO technique. In this case, nanolithography was conducted in the scanning mode of operation, with the use of a special gauge—specifically, a graphic *.bmp file. By means of the Nova RC1 SPM control program, this file was arranged in the 1 × 1 μm scan field so that the spacing between neighboring strips was about 10 nm. Then, in the semicontact mode of operation, on application of voltage pulses with the amplitude 10 V, we carried out LAO, which occurred in accordance with a specified pattern. This was done at the scanning rate 1 $\mu m\ s^{-1}$, the relative humidity (70 ± 1)%, and SetPoint = 0.5 nA.

Statistical processing of the AFM images and determination of the ONS geometric parameters (the heights and diameters of local oxide regions rising above the unoxidized part of the titanium film) were carried out with the use of the Image Analysis 2.0 program package (Nanotechnologies–MDT Ltd., Zelenograd) using the specially developed procedure certified in accordance with State Standard R8.563-96 [9].

3. RESULTS AND DISCUSSION

From the resulting statistical data, we established the dependences of the ONS average height and diameter on the amplitude of the voltage pulse applied to the probe–substrate system at different values of the humidity and different currents in the feedback circuit of the SPM control system. Some of the dependences (at humidity 50% and Setpoint = 0.3 nA) are exemplified in Figs. 3–5. Other dependences obtained at the humidity 70 and 90% and SetPoint = 0.1 and 0.5 nA are not shown because of the limited size of this paper.

Nevertheless, the analysis of the dependences shows that, as the current in the feedback circuit of the SPM control system is increased, the ONS geometric dimensions decrease. A possible cause of this effect is the decrease in the lateral dimensions of the water

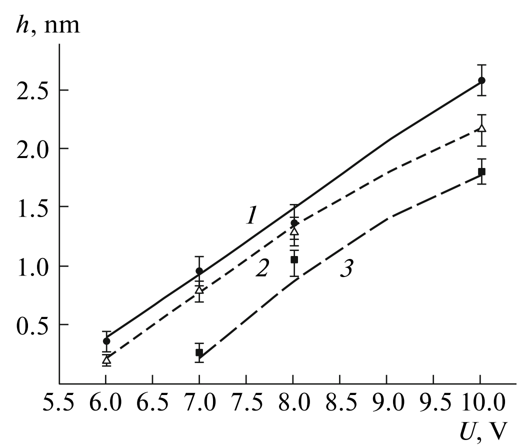

Fig. 3. Dependences of the height of titanium ONSs on the amplitude of the applied voltage pulse at the relative humidity 50% and SetPoint = 0.3 nA, as obtained (*1*) with no photon stimulation and (*2*, *3*) with (*2*) IR and (*3*) UV stimulation.

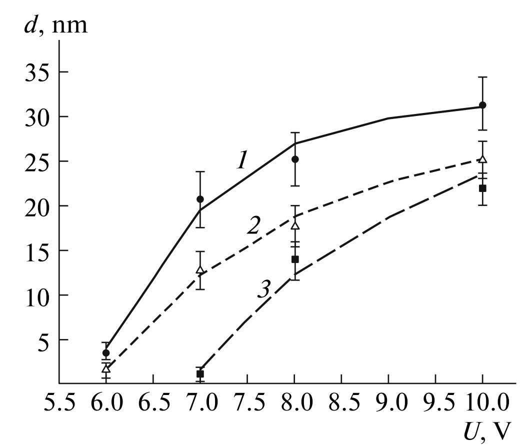

Fig. 4. Dependences of the diameter of titanium ONSs on the amplitude of the applied voltage pulse at the relative humidity 50% and SetPoint = 0.3 nA, as obtained (*1*) with no photon stimulation and (*2*, *3*) with (*2*) IR and (*3*) UV stimulation.

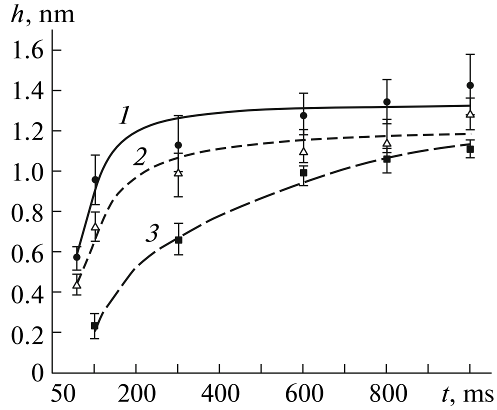

Fig. 5. Dependences of the height of titanium ONSs on the duration of the applied voltage pulse at the relative humidity 50% and SetPoint = 0.5 nA, as obtained (*1*) with no photon stimulation and (*2*, *3*) with (*2*) IR and (*3*) UV stimulation.

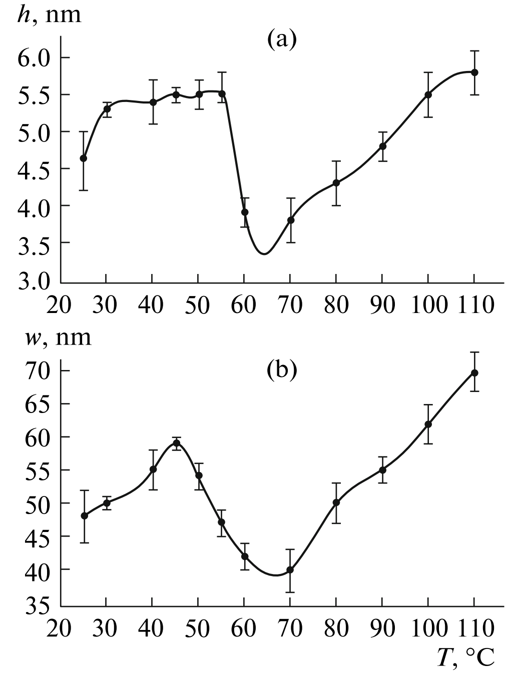

Fig. 6. The influence of the substrate temperature during the LAO process on the (a) height and (b) width of resulting ONSs.

meniscus between the probe and the substrate surface because of the increase in the probe–substrate spacing. Such a trend of the change in the ONS geometric dimensions was also demonstrated elsewhere [5].

It is established that the stimulation with UV and IR radiation suppresses the LAO process in the film. As a result, the ONS height and diameter are reduced. In addition, from the experimental data, it follows that the UV stimulation of the LAO process in the titanium film induces an increase in the threshold voltage corresponding to the onset of active oxidation from 6 to 7 V at the relative humidity 50% (see Figs. 3, 4). At lower voltages, the ONS height is practically zero.

By statistical processing of the AFM images, we obtained the dependences of the ONS height on the applied voltage pulse duration (see Fig. 5). From the results, it follows that the height of ONSs formed with UV and IR stimulation is smaller than that in the case of LAO without stimulation. This supports the above inferences (see Figs. 3, 4).

From the data presented here, it also follows that, at the relative humidity 50%, the UV stimulation increases the voltage pulse duration, at which oxidation starts to proceed actively, from 50 to 100 μs. The less-pronounced effect of the UV stimulation on the threshold pulse duration was observed at the relative humidity 70 and 90% as well.

The mechanism of the effect of photon stimulation on the ONS geometric dimensions and the threshold voltage pulse amplitude and duration may be associated with a change in the volume charge density in the probe–substrate gap. Such a change yields a change in the distribution of the surface potential and a decrease in the characteristic diameter of the region where the basic charge and mass transport processes occur.

Figure 2 shows the AFM image of ONSs fabricated at the substrate temperature 110°C. From the statistical data (the sampling volume $N = 25$), we established the dependences of the ONS geometric parameters (height and width) on the substrate temperature (Fig. 6). Analysis of the dependence shows that, as the substrate temperature is increased from 25 to 55 2C, the ONS height increases from (4.6 ± 0.4) to (5.6 ± 0.2) nm.

As the substrate temperature is increased further to 70°C, the ONS height and diameter decrease to 3.8 ± 0.3 and 40 ± 3, respectively. The dependence of the ONS geometric dimensions on the substrate temperature in the range from 70 to 100°C is practically linear, and, in this case, the ONS height increases to (5.8 ± 0.3) nm at 110°C and the ONS diameter to (70 ± 3) nm.

Analysis of the dependences shown in Fig. 6 allows us to distinguish three characteristic portions.

(i) In the initial stage of heating (the substrate temperature is below 55°C), the ONSs grow due to the electrochemical reaction in the liquid meniscus formed under the probe tip on the basis of water adsorbed at the substrate surface.

(ii) At the substrate temperatures above 70°C, the LAO mechanism is apparently associated with the electrothermal activation of the gas–vapor mixture of saturated water vapor with gaseous oxygen in the region located near the probe–substrate gap. In this case, the water vapor dissociates and the OH^- and O^{2-} ions are generated that are to be involved in the formation of the oxide [10]; as the substrate temperature is increased, the concentration of the ions increases.

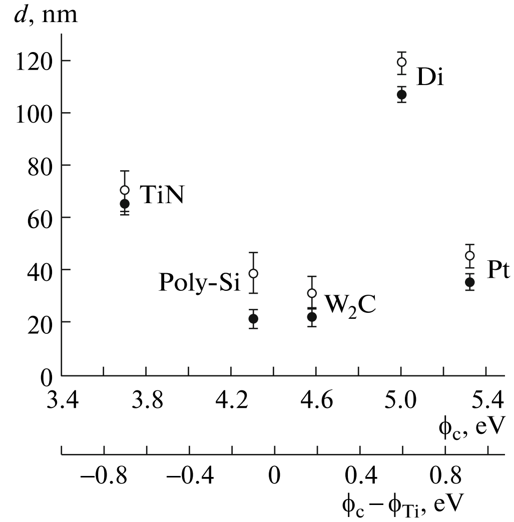

Fig. 7. The dependence of the diameter of titanium ONSs formed with the LAO technique (open circles) with no photon stimulation and (solid circles) with UV stimulation on the work function of the cantilever conducting coating f_c and the difference between the work functions of the cantilever coating and titanium film $f_c - f_{Ti}$.

(iii) The range of substrate temperatures between 50 and 70°C is transitional; in this range, the adsorbate film vaporizes, and the concentration of ions increases.

Replicates of the experiment on thermal activation of the LAO process give similar results, which supports their reproducibility. Gaining more specific data on the possible mechanisms of thermal activation of the LAO processes requires additional experiments.

Statistical data (see table) are used to establish the dependence of the ONS diameter on the work function of the cantilever coating material (Fig. 7). Analysis of the dependence shows that ONSs fabricated with cantilevers with a smaller work function of the conducting coating (TiN) are larger in diameter ($d \sim 70$ nm) than are ONSs obtained with cantilevers with poly-Si and W_2C coatings ($d \sim 40$ and 32 nm, respectively). At the same time, no pronounced dependence of the ONS height on the cantilever coating material is observed. The larger geometric parameters of the ONSs formed with cantilevers with diamond (Di) coating (Fig. 7) can be attributed to the larger diameter of the probe (see table). As in the above-described experiments, in this experiment, it is found that the UV stimulation of the LAO processes yields a decrease in the ONS geometric parameters. These experimental results correlate with the data of [11] on the influence of the cantilever coating material on the LAO process. It should be noted that the experiments described in [11] were conducted in other conditions, but the cantilevers used in that study were of the same type as those used here.

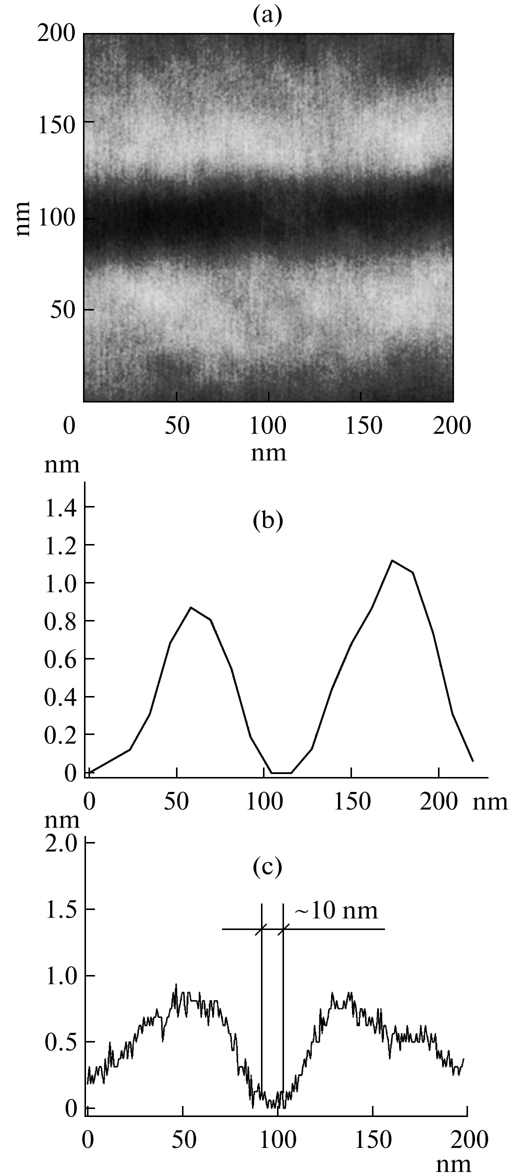

Fig. 8. Example of (a) the AFM image and (b, c) surface profiles of different nanochannels after LAO treatment of the titanium film.

Using the results obtained in this study for the conditions of activated processes of formation of ONSs by means of the LAO technique, we fabricated nanometric channels (Fig. 8) with lateral dimensions of about 20 and 10 nm. Such channels can serve as a basis for designing various elements of nanoelectronics [1–5]. Analysis of the AFM images of nanochannels fabricated in different conditions shows that, with UV stimulation, we have obtained the ~10-nm-wide channel most homogeneous in the longitudinal direction (Fig. 8c). If the LAO process is conducted in the same conditions with IR stimulation or no photon stimulation, the nanochannels formed in this case are highly inhomogeneous in the longitudinal direction.

In addition, in this case, there are some regions where the channel is shut because of splicing of two oxide lines.

The nanochannels were formed with cantilevers with a tip radius smaller than the dimensions of the objects under study and a cone angle smaller than 22° (see table) [8]. This allowed us to minimize the convolution effect.

4. CONCLUSIONS

By means of studies of the conditions of photon-stimulated LAO of a titanium film, the dependences of the ONS geometric dimensions on the amplitude and duration of voltage pulses applied to the probe–substrate system are obtained. It is established that UV stimulation yields a decrease in the ONS geometric dimensions in combination with an increase in the threshold voltage. The results show that the effect of UV stimulation on the increase in the duration of the threshold voltage pulse applied to the probe–substrate system becomes more profound at reduced values of relative humidity.

From the experiments conducted here, it is established that the geometric dimensions of ONSs formed in the titanium film by the LAO technique depend on the substrate temperature. The data on the formation of ONSs at the substrate temperature 100°C and higher show that the water film adsorbed at the substrate surface is not the only limiting factor of the LAO process.

No distinctly pronounced dependence of the ONS geometric parameters on the cantilever conducting coating material is observed. However, from practical experience, it is known that, for a positive result, the material chosen for the cantilever coating is the decisive factor. Therefore, studying the role of the cantilever coating material requires additional investigations concerned with the extended nomenclature of cantilever coating materials.

Activation of the processes of probe lithography is a powerful tool and an additional factor that provides a means for controlling the lithographic process and modifying the parameters of nanostructures formed in the process in a wide region. The results of this study can be used in the development of manufacturing processes of formation of the elemental base of nanoelectronics.

The problem of optimization of manufacturing conditions invites further investigations of the experimentally observed effects with the use of radiation sources operating with different powers in a wide spectral region.

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