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NANOTECHNOLOGY

Formation of a Memristor Matrix Based on Titanium Oxide and Investigation by Probe-Nanotechnology Methods

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Abstract—The results of investigation of a memristor-matrix model on the basis of titanium-oxide nanoscale structures (ONSs) fabricated by methods of focused ion beams and atomic-force microscopy (AFM) are presented. The effect of the intensity of interaction between the AFM probe and the sample surface on the memristor effect in the titanium ONS is shown. The memristor effect in the titanium ONS is investigated by an AFM in the mode of spreading-resistance map. The possibility of the recording and erasure of information in the submicron cells is shown on the basis of using the memristor effect in the titanium ONS, which is most promising for developing the technological processes of the formation of resistive operation memory cells.

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1. INTRODUCTION

The development of electronic-device technology is related to the application of nanotechnology methods, which make it possible to decrease sizes, to increase the density of structures of active cells of integrated chips on a crystal and to decrease the power consumed [1–4]. Nanotechnologies make it possible to fabricate a memristor, the operating principle of which is based on switching between the high-resistance state (HRS) and low-resistance state (LRS) upon the application of an electric field [1, 5]. The prospective application of memristors is in the fabrication of cells of resistive random-access memory (RRAM) [1–5]. The basic advantages of such memory are energy independence, high speed, small sizes of the information-recording cell, and low consumed power [1–4].

There is a large number of metal oxides, which possess the memristor effect and can be used to fabricate structures of RRAM cells [1]. Titanium oxide (TiO_2) is one of the most promising and investigated oxides [6].

The fabrication of memristor structures for RRAM cells is related to developing and investigating the processes of substrate-surface modification with nanometer resolution. The analysis of existing lithographic methods of profiling a substrate surface such as an electron-beam, X-ray, and ion lithographies showed that their use is limited because of the complexity and high cost of the equipment [7].

The real solution to this problem lies in the development of new processes of nanoscale treatment on the basis of probe-nanolithography methods: focused ion beams (FIBs) and local anodic oxidation (LAO) [7–13]. Use of these methods makes it possible to form nanoscale structures on the surface of various conducting and semiconductor materials, which can be used in developing the elemental base of nanoelectronics, microsystem and nanosystem equipment [7–13]. The advantages of the FIB and LAO methods are: high spatial resolution, the possibility of the in situ diagnostics of the results of forming nanoscale structures, the absence of additional technological operations upon deposition, exposure, and photoresist removal, and the relatively low cost of the technological equipment [10–13].

The purpose of this study is the development and investigation of the formation processes and regularities in the manifestation of the memristor effect in titanium-oxide nanoscale structures by probe-nanotechnology methods.

2. EXPERIMENTAL

To carry out experimental investigations of the characteristics and estimate the correctness of the accepted solutions, we fabricated a memristor-matrix model in the form of 16 titanium oxide nanoscale structures (ONSs) (Fig. 1). As the initial substrate, we used a titanium film 20 nm thick deposited onto the SiO_2/Si-structure surface by magnetron sputtering using an Auto 500 (BOC Edwards, the Great Britain) multipurpose installation. Then the titanium film was etched on a NANOFAB NTK-9 (JSC "NT-MDT" Zelenograd) ultrahigh-vacuum cluster nanotechnological complex by the method of focused ion beams. As a result, four-lower contact structures with sizes of 0.30×1.89 μm were obtained. Further, a titanium ONS

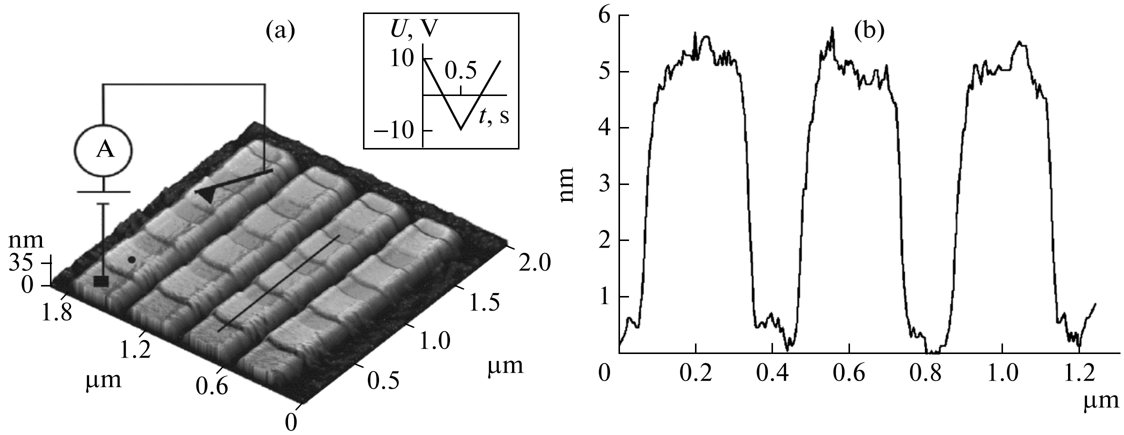

Fig. 1. Representation of memristor-matrix structures on the basis titanium ONS formed by the LAO method: (a) AFM image (in the inset, the time variation in the voltage is shown upon measurement of the *I*–*V* characteristics); (b) the profilogram along the line.

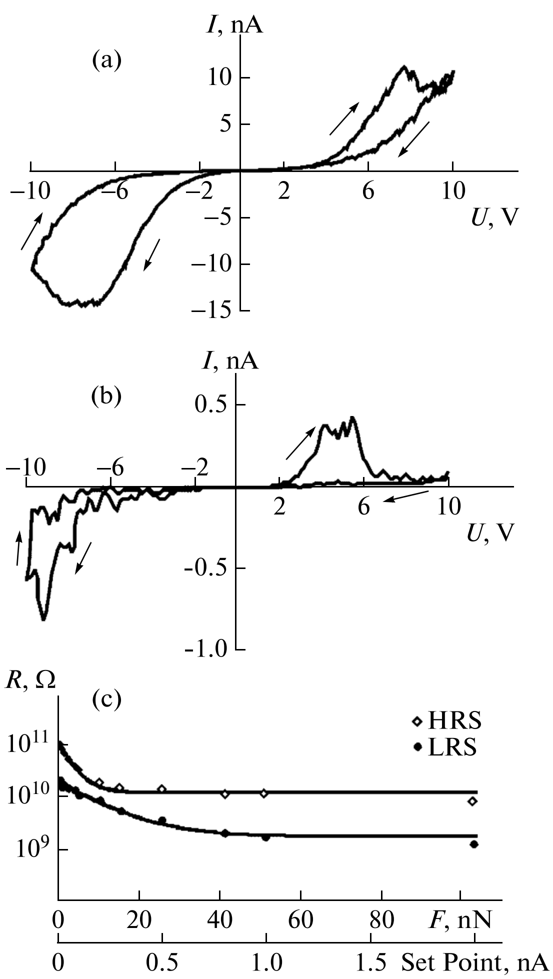

Fig. 2. Influence of the intensity of interaction of the AFM probe with the titanium-ONS surface on the memristor effect: the *I*–*V* characteristics of the titanium ONS obtained at a Set Point of (a) 2 nA and (b) 0.01 nA (the arrows show the direction of signal variation); (c) the dependence of the titanium-ONS resistance on the Set Point.

about 6 nm in height and with lateral sizes of 300 × 300 nm (see Fig. 1) was formed by the LAO method in the AFM semi-contact mode using a probe nanolaboratory (PNL) Ntegra (JSC "NT-MDT" Zelenograd) and NSG11 silicon cantilevers with a conducting platinum coating. Local anodic oxidation of the structures was carried out through a raster pattern upon the application of pulses of negative voltage of 10 V in amplitude to the probe–substrate system and a probe-scanning speed of 4 μm/s. The humidity was controlled using an Oregon Scientific ETHG913R digital humidity sensor and amounted to 40 ± 1%.

The memristor effect on the formed titanium ONSs was investigated in air by AFM spectroscopy in the contact mode with the help of the PNL Ntegra according to the schematic shown in Fig. 1a. In this case, one electrode was connected to the lower contact (titanium film), and, as the second electrode, a NSG11 cantilever with a conducting platinum coating was used. The bipolar *I*–*V* characteristics of the $Pt/TiO_x/Ti$ structure were measured by varying the voltage in time (see the inset in Fig. 1a).

In the beginning, we investigated the dependence of the memristor effect on the intensity of interaction of the AFM probe with the titanium ONS surface, which is determined by the feedback-circuit current of the PNL-Ntegra control system (the parameter Set Point in the Nova control program). Investigation was carried out in the AFM-spectroscopy contact mode at values of the Set Point parameter in the range from 0.01 to 2 nA, which corresponds to a pressing force of the AFM probe on the sample surface from 0.5 nN to 0.1 μN. In Figs. 2a and 2b, we show a portion of the bipolar *I*–*V* characteristics of the structures from which the values of the structure resistance were determined in the HRS and LRS states (Fig. 2c).

For studying the memristor-effect stability, we carried out 50 measurements of the *I*–*V* characteristics

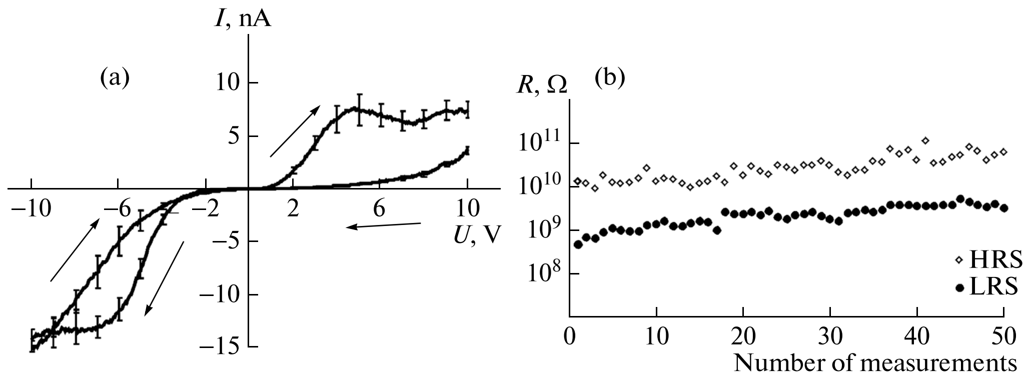

Fig. 3. Investigation of the memristor-effect stability of the titanium ONS at point 1 (see Fig. 1a): (a) average *I*–*V* characteristic of the Pt/TiO_x/Ti structures (the arrows show the direction of signal variation); (b) dependence of the titanium-ONS resistance on the number of measurement cycles.

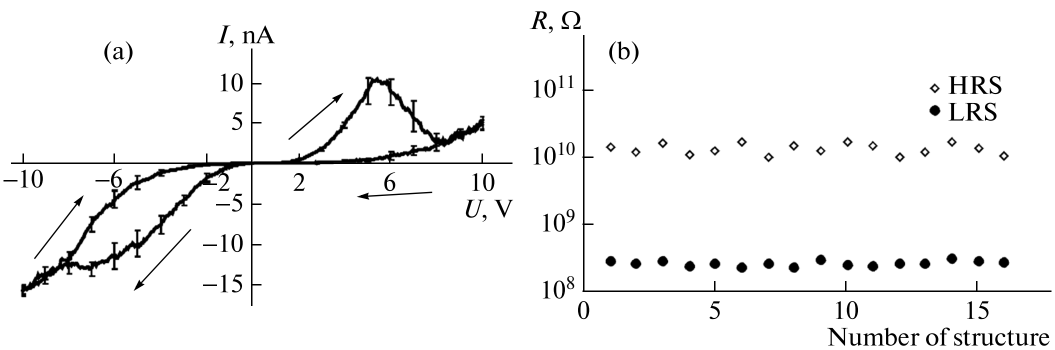

Fig. 4. Investigation of the memristor-effect uniformity for the titanium ONS: (a) average *I*–*V* characteristic of the Pt/TiO_x/Ti structure from measurements on 16 titanium ONSs (the arrows show the direction of signal variation); (b) resistances of 16 titanium ONSs.

for the Pt/TiO_x/Ti structures at point 1 (see Fig. 1). In Fig. 3a, we show the average bipolar *I*–*V* characteristic of the Ti/TiO_x/Pt structures from which the resistances in the HRS and LRS states (Fig. 3b) were determined at a voltage of 5 V corresponding to the largest difference in resistance values.

To investigate the uniformity of the memristor effect, the bipolar *I*–*V* characteristics for 16 titanium ONSs (see Fig. 1a) were measured. In Fig. 4a, we show the average *I*–*V* characteristics of the Pt/TiO_x/Ti structure. The resistances in the HRS and LRS states (Fig. 4b) were determined at a voltage of 5 V, which corresponds to the largest difference in the resistance values.

The possibilities of recording and erasing the information in the submicronic cells based on application of the memristor effect in the ONSs formed by the local anodic oxidation of titanium film were studied by the AFM method. In Fig. 5, we show the schematic representation of the technique of the experiment during which the surface of the test oxide structure containing areas in the high- and low-resistance states were scanned in the mode of spreading-resistance map. The test structure was formed by the LAO method under conditions of feeding pulses of negative voltage with an amplitude of 10 V, scanning with an AFM-probe speed of 2.4 μm/s, and with a relative humidity of 40 ± 1%. As a result, we obtained a titanium ONS 4.5 nm in height with lateral sizes of 4 × 4 μm on the surface. The AFM images of the topology and current contrast of the ONS are shown in Fig. 6. Further, we measured the bipolar *I*–*V* characteristic of the formed test titanium ONS by the described technique at Set Point value of 1 nm. Analysis of the obtained *I*–*V* characteristic showed that the switching process between the HRS and LRS states in the structure begins at voltages of ±4 V. To fabricate LRS areas 500 × 500 nm in size inside the HRS area, the ONS surface was scanned in the AFM contact mode upon application of a positive voltage of 4 V to the raster pattern. To switch the low-resistance areas to the high-resistance state in 30 min, the ONS surface was scanned upon the application of a negative voltage of 4 V. In Fig. 7, we show the obtained AFM images of the spreading-current distribution over the titanium ONS surface.

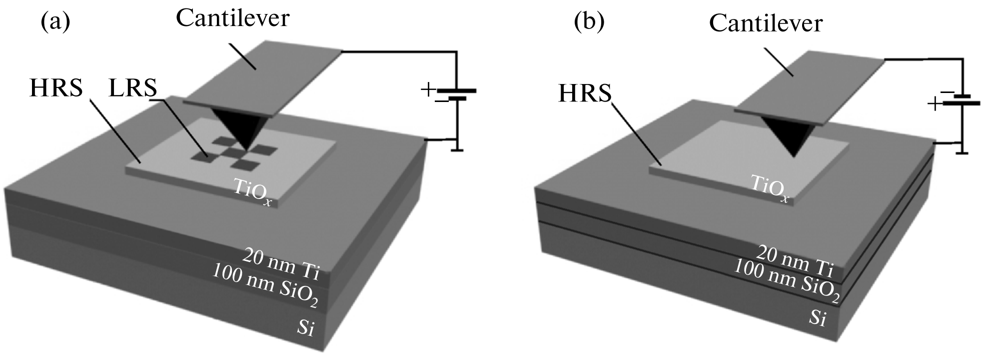

Fig. 5. Schematic representation of the process of the formation of areas of low-resistance and high-resistance states on the titanium-ONS surface at (a) positive and (b) negative voltage across the probe.

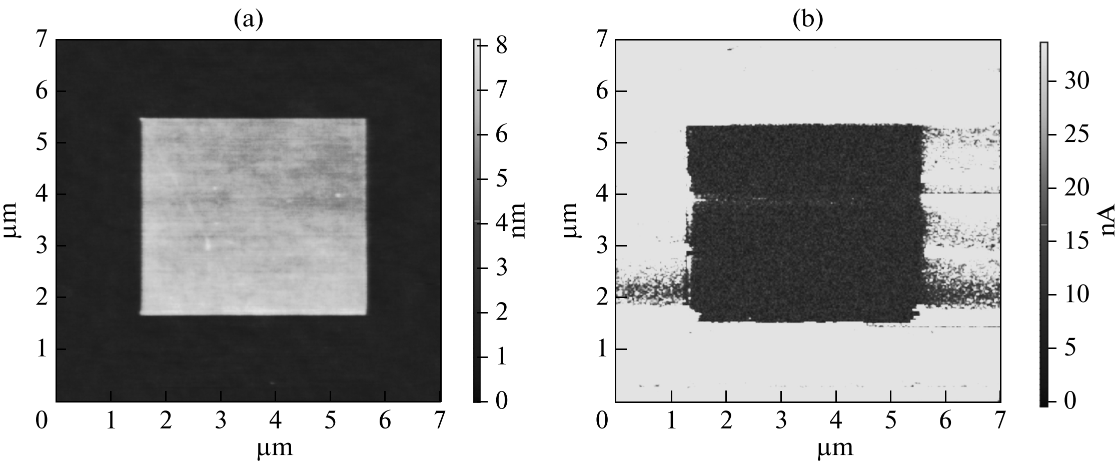

Fig. 6. AFM images of the test titanium ONS formed by the LAO method for investigating the memristor effect: (a) topology; (b) current contrast of the ONS in the initial state (HRS).

3. RESULTS AND DISCUSSION

Analysis of the *I–V* characteristics of the experimental memristor-matrix sample presented in Figs. 2–4 shows that the titanium ONS formed by the LAO method possess the memristor effect uniform within the matrix.

The experimental results of investigation of the effect of the interaction intensity of the AFM probe with the titanium ONS surface on their resistance testify to the fact that the resistance of the titanium ONS in the high-resistance state decreases from 112.1 ± 12.0 GΩ to 9.6 ± 1.1 GΩ and in the low-resistance state from 22.8 ± 2.1 GΩ to 1.2 ± 0.1 GΩ (see Fig. 2) with increasing force of the AFM-probe pressure on the ONS surface from 0.5 nN to 0.1 μN. A variation in the titanium-ONS resistance with increasing the pressure force can be related to an increase in the radius of the probe–substrate contact, the redistribution of oxygen vacancies, and a decrease in the potential-barrier height. Analysis of the dependences presented in Fig. 2b showed that steady-state contact of the AFM-probe–oxide-nanoscale structure is formed at a pressure of 50–100 nN. The obtained results well correlate with published data [14].

Analysis of the *I–V* characteristics averaged over 50 measurements at point 1 (see Figs. 1 and 3) showed the stability of the manifestation of the memristor effect in the structure. An increase in the resistance for the high-resistance state from 11.5 ± 1.4 GΩ to 52.2 ± 6.9 GΩ and from 0.6 ± 0.1 GΩ to 3.7 ± 0.3 GΩ for the low-resistance state (see Fig. 3b)is, probably, related to the process of additional oxidation of the ONS and the titanium film in air under the action of applied voltage. The obtained results well correlate with the results of experimental investigations reported in [15].

The results of analysis of an averaged *I–V* characteristic measured on 16 titanium ONSs (see Fig. 4) testify that the obtained structures possess a uniform memristor effect. The titanium ONS is switched from the high resistance state with 11.2 ± 3.1 GΩ to the low-resistance state with 0.7 ± 0.1 GΩ; in this case, $R_{\mathrm{HRS}}/R_{\mathrm{LRS}} \approx 16$.

The shape of the obtained *I–V* characteristics (see Figs. 2–4) well correlates with the results [15], where

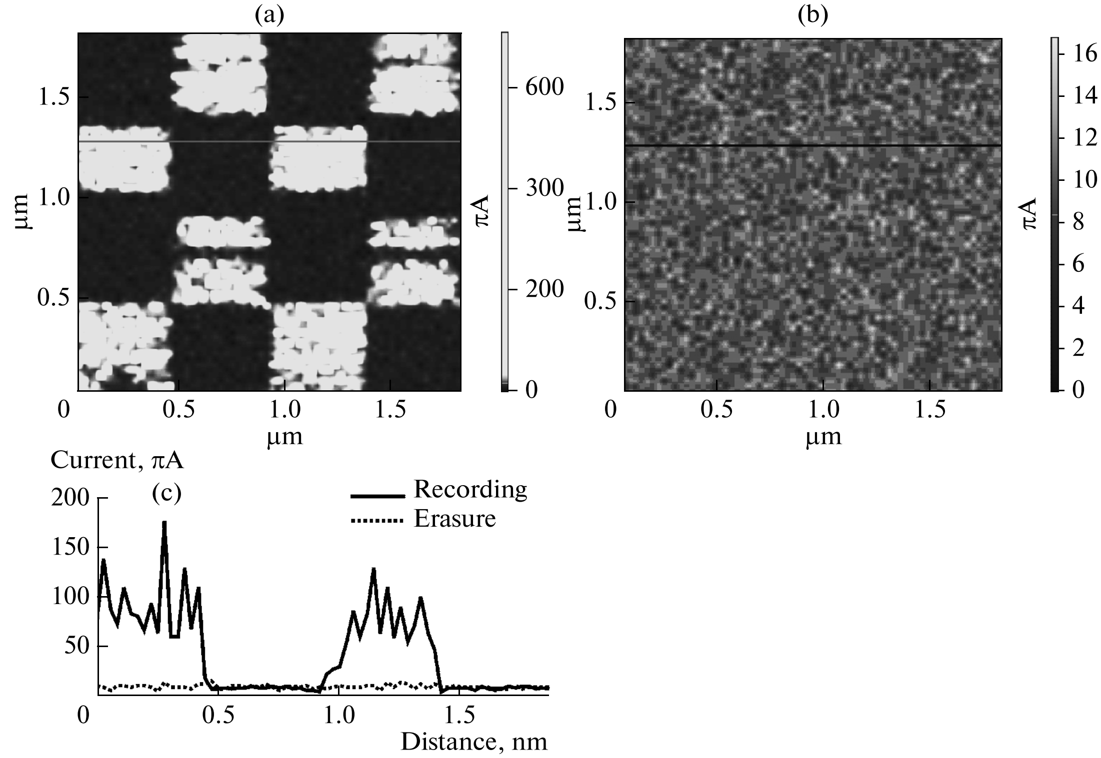

Fig. 7. AFM images of the current contrast of the titanium-ONS surface after (a) recording and (b) erasing information, and (c) the profilogram of current along lines in Figs. 7a and 7b.

the memristor effect on the structures obtained by the LAO method is attributed to the electrical migration of oxygen vacancies into the ONS under the action of an external electric field. Results with a similar shape of the *I*–*V* characteristics were obtained also for other structures [16–18]. The difference in the observed character of the current-variation direction with increasing voltage from that discussed in [19] is explained in [15, 16] by the effect of Schottky barriers on the metal–oxide contacts. The mechanism of formation of *N*-shaped *I*–*V* characteristics was attributed in [17] to the capture of electrons on defects formed as a result of the electrical migration of oxygen vacancies in the ONS bulk.

The analysis of existing methods of the formation of memristor structures for promising RRAM cells [1–5] confirms the fact that, to provide the memristor properties to titanium oxide and also to decrease the values of working voltages, it is necessary to carry out an additional electrical-formation operation [20]. Analysis of the presented results of experimental investigations showed that the electrical formation occurs during local anodic oxidation of the titanium film (10 V), and the memristor effect manifests itself in the titanium ONS right after their formation. In [7, 10–13], the possibility of carrying out LAO processes is shown at even lower voltages.

Experimental investigations of the memristor effect by the AFM method in the mode of the spreading-resistance map for the test titanium ONS formed by the LAO method (Figs. 6–7) showed that, as a result of scanning its surface upon the application of a positive voltage of 1.5 V across the probe–substrate system, a current of 31.5 nA and 9.8 πA flows through the film and the titanium ONS, respectively, (see Fig. 6b). In Fig. 7a, we show an AFM image of the current contrast of an area of 1.85 × 1.85 μm of the titanium-ONS surface containing regular submicron low-resistance cells 500 × 500 nm in size formed by the raster pattern, the current through which amounts to about 135 πA. In Fig. 7b, we show an AFM image of the current contrast of the area of the titanium-ONS surface after switching the low-resistance cells to the high-resistance state. In this case, the current through the ONS decreases practically to the initial value of 9.1 πA. In Fig. 7c, we show the profilograms of the current over the titanium-ONS surface after recording and erasing information. The obtained results well correlate with the *I*–*V* characteristics shown in Figs. 2–4. Additional experimental investigations are necessary for estimating the time of reading and recording the information, and also the limiting time of preservation of the low-resistance state (the information-storage time) by the titanium-oxide nanoscale structure.

Thus, we formed a model of a memristor matrix based on titanium oxide by the methods of focused ion beams and atomic-force microscopy. Titanium ONS about 6 nm in height obtained by the method of local anodic oxidation possess the uniform memristor effect. An increase in the pressure force of the probe on the titanium-ONS surface results in a decrease in the resistance in the high-resistance and low-resistance states. Therefore, to obtain authentic and reproducible results in investigation of the memristor effect, the formation of stable elastic contact between the probe and substrate is necessary. The optimum interaction of the probe with the titanium-oxide surface is achieved for a pressure force of the cantilever on the sample surface of 50–100 nN.

As a result of carrying out 50 measurements of the bipolar I–V characteristics of the $Pt/TiO_x/Ti$ structure at point 1 (see Fig. 1) on the titanium-ONS surface, it was clarified that the obtained ONSs possess the stable memristor effect. In this case, the resistances for the HRS and LRS states amounts to 11.5 ± 1.4 GΩ and 0.6 ± 0.1 GΩ, respectively, which well correlates with the results of the experiments presented in publications.

Investigation of the memristor-effect uniformity upon measuring the bipolar I–V characteristics on 16 titanium ONSs showed that the obtained structures possess the uniform memristor effect ($R_{HRS}/R_{LRS} \approx 16$).

The possibility of recording and erasing information in the form of low-resistance areas about 500 nm in size on the titanium-ONS surface is experimentally confirmed, and their visualization was carried out using the method of spreading-resistance map.

Analysis of the published data [7, 10–13] shows that the LAO methods make it possible to form ONSs with sizes of several nanometers, which, according to the presented results, manifest the memristor effect.

The LAO method is promising in development of the design and technological processes of manufacturing matrices of interrelated resistive-memory cells based on titanium-oxide nanoscale structures with the use of high-efficiency multiprobe systems and methods of nanoprint lithography. In this case, the formation of contact metallization can be carried out by methods conventional for microelectronics technology.

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