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Local anodic oxidation of silicon for create crossbar architecture

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Paper present possibility of creation a neuromatrix in the form crossbar architecture on a silicon substrate is shown. Crossbar architecture in the form of a set of nanosized conductors, between which there is a layer of titanium oxide, capable of changing its conductivity under the action of the applied voltage, it is proposed to form using the method of local anodic oxidation. The results is present of the study technological parameters of the method of local anodic oxidation silicon and titanium for the implementation of the elements of this neuromatrix in the form of a memristor structures.

Keywords: Silicon, titanium, local anodic oxidation, neuromatrix, crossbar.

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Introduction

The modern organization of computer architecture, based on the von Neumann principles, includes the joint storage of commands and data in computer memory. Such a structure of computer memory has a number of limitations, one of which is the limit of the bandwidth of the cache interface -memory. Moreover, the technological barrier of manufacturing integrated circuits has been reached. Overcoming these barriers makes it necessary to create a new generation of computers based on the use of other materials, elements, principles of organization and technologies. Also, these problems lead to slowing down the speed and limiting the memory of modern computers. Modern security programs, such as the Internet of Things, work on the basis of artificial neural networks, for the implementation of which it is necessary to create new integrated circuits, as well as technologies for their creation, which will help overcome a number of technological barriers. To solve this problem, it is proposed to use the architecture of computer systems based on the work of the human brain, which is a set of parallel connected low-power computing elements (neurons) connected to each other using special channels (synapses) [1]. Creating an energy efficient and ultrafast neuromorphic system also faces challenges. The implementation of high-performance vector matrix multiplication requires a compact implementation of synaptic weights (the strength or amplitude of the connection between two junctions of a neural network, which is similar to human intellectual activity) and effective integration. Therefore, such schemes are usually implemented using CMOS- technology. Synapses formed on the basis of CMOS technology can somewhat facilitate the integration process. However, the implementation of synapses using CMOS technology is insufficient to meet the size requirements, since they are still excessively bulky [1–3]. The solution to this problem may be the use of resistive („memristive“) memory. At the same time, some authors propose the implementation of neural networks, structurally combining memristors with CMOS elements. The technological process, materials, approaches to solving various tasks for the implementation of such neuromatrices can help in the creation of quantum computers that will resemble the human brain according to the principle of operation. To implement such neuromatrices based on crossbar architecture, it is planned to use the methods of probe technologies, while the method of local anodic oxidation (LAO) using a probe microscope can serve as the main method of forming a crossbar architecture. The mechanism of the LAO method consists in the application of a potential difference between the probe and the substrate. Under the action of an electric field, water molecules from the layer adsorbed on the surface decompose, the oxygen ions formed in this way are transferred to the substrate, where an electrochemical oxidation reaction occurs. The LAO method allows you to create objects with high spatial resolution, and also has high reproducibility. In addition, the LAO method has a number of advantages, which include the possibility of carrying out the LAO process without additional molding operations, as well as the absence of the need to create expensive photomasks, as in the photolithography method [4]. To form the crossbar architecture, it is planned to use the LAO method using atomic-force microscopy (AFM) and liquid chemical etching, which makes it possible to obtain oxide nanoscale structures (ONS) on the surface of various materials with different geometric parameters. The ONS structures formed by the LAO method can form the basis for the development and creation of micro- and nanoelectronics elements, elements of memristor structures of resistive memory, lithographic masks, as well as catalytic centers for growing filamentous nanostructures [5–8]. In addition, the combination of the LAO method and liquid etching makes it possible to profile the surface of substrates to form microfluidics structures, which are used to create laboratories on a [9] crystal.

However, despite a fairly large number of scientific publications on this problem [10–12], the regularities of the influence of technological modes of local anodic oxidation and liquid etching on the geometric parameters of profiled nanoscale structures on the silicon surface remain insufficiently studied.

1. Experiment

In this paper, a crossbar architecture was chosen for the implementation of the neuromatrix, in which memristors are used as synaptic connections. Fig. 1 shows a diagram of such an architecture [1]. Since today all existing processors are implemented using silicon technology, we have chosen silicon substrates on which synapses and neurons will be formed to perform the neuromatrix. To implement the CMOS-technology structure, the silicon substrate must be oxidized, for which the LAO method was used. The LAO method has a number of advantages associated with the ability to create structures on a nanometer scale with minimal costs, as well as the ability to control the process by monitoring the parameters in real time.

To implement the crossbar architecture, a technological route for its manufacture was developed, shown in Fig. 2.

At the first stage, an insulating layer of silicon oxide is formed on the silicon substrate by the LAO method. At the second stage, the lower contacts are formed by magnetron sputtering of the titanium film. Then, at the third stage, the LAO method forms a working memristive region by oxidation of titanium by the LAO method. Further, at the fourth stage, the upper contacts are formed.

According to the developed route, the modes of operation of local anodic oxidation of silicon for the implementation of an insulating layer, as well as the operation of forming a working memristive layer using local anodic oxidation of the formed titanium film were experimentally investigated.

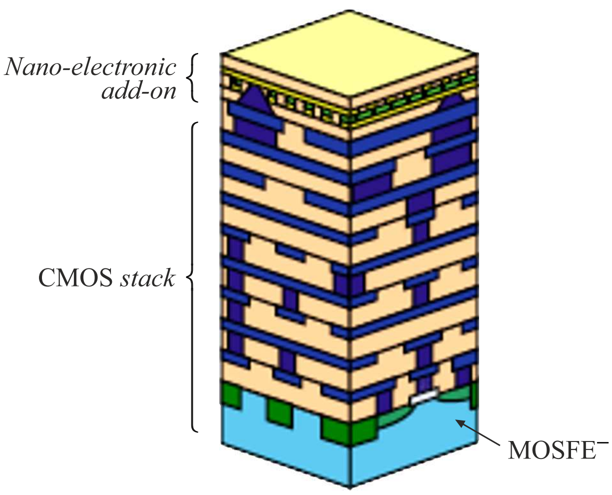

Figure 1. The principle of constructing a hybrid CMOS/memristor integrated circuit [1].

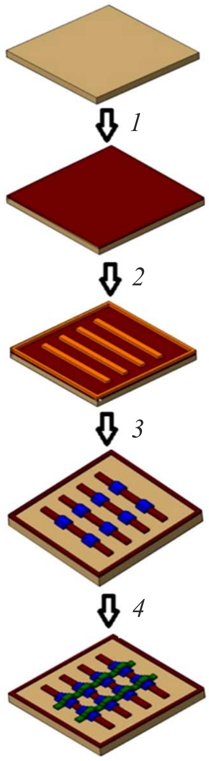

Figure 2. Technological route of formation of the crossbar architecture of memristor structures.

Also, in the course of experimental studies, in order to implement such a neuromatrix, it was necessary to study the modes of formation of nanoscale silicon structures. For this purpose, the modes of silicon profiling by LAO and liquid etching were investigated.

In the experiment, silicon substrates of the KEF 0.1 brand were used, which underwent a preliminary purification procedure from natural oxide [13]. Then, using the Ntegra Vita probe nanolab (CJSC „NT-MT“, Russia), nanolithography of the silicon surface by the LAO method in the contact AFM mode using NSG 10 cantilevers with a conductive Pt coating was carried out. The contact AFM was carried out with the following parameters: the amplitude of the voltage pulses varied from 5 to 20 V, the duration of the voltage pulses was 100 ms, the oscillation frequency of the probe was 0.3 Hz, the feedback circuit current (in the PNL control program, the Set Point parameter) was 0.3 nA. The LAO time of structures according to the developed template in vector mode was determined automatically by the Ntegra Vita AFM, and for the oxidation of 49 ONS (Fig. 3, *a*) was 4.9 s, and for the oxidation by the LAO method 5 lines (Fig. 3, *b*) was 125 s. Relative humidity in LAO was controlled by the Oregon Scientific ETHG913R moisture meter and ranged from 30 ± 1 to $90 \pm 1\%$ (which corresponds to 0.005 to 0.016 kg/m^3 for absolute humidity). The temperature inside the process chamber was 20°C. As a

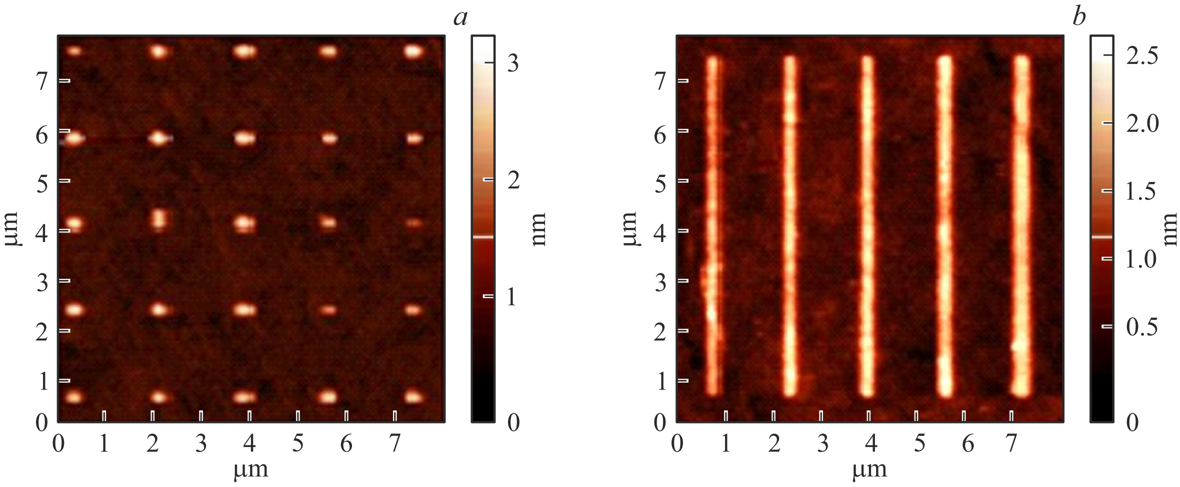

Figure 3. AFM images of the silicon surface: *a* — after the formation of a matrix of 49 silicon ONS by LAO; *b* — after the formation of linear structures by LAO.

result of the processes carried out, matrices of 49 ONS were formed on the surface of the silicon substrate (Fig. 3, *a*), as well as linear structures (Fig. 3, *b*).

Since the obtained ONS structures in the LAO process grow not only above the surface of the substrate, but also into the depth, we conducted studies of the etching process of the obtained silicon oxide in HF solution. To do this, at the first stage, ONS matrices were formed on the surface of the silicon substrate, then, at the second stage, these structures underwent the etching procedure in a 30%-HF solution at a temperature of 70°C, after which matrices were formed on the surface of the silicon substrate from 49 profiled nanoscale structures (PNS) (Fig. 4, *a*), linear structures were also subjected to this procedure (Fig. 4, *b*).

The conducted experimental studies allowed us to construct the dependences of the geometric parameters of the ONS (height and diameter) and the PNS (depth and diameter) of silicon at different relative humidity LAO.

Fig. 5 shows the dependences of the height and diameter of nanoscale oxide structures obtained at a voltage of 15 V on air humidity. Analysis of these graphs shows that an increase in the level of relative humidity leads to an increase in the geometric dimensions of silicon ONS, which is explained by an increase in the concentration of the oxidizer.

In addition, for the formation of the crossbar architecture, a technique was developed for profiling silicon ONS using the LAO method and liquid etching in KOH+IPA (isopropyl alcohol) solution, thanks to which the obtained ONS can be used as a mask [14]. For etching silicon, a solution of 60% KOH was used with the addition of IPA in a ratio of 5 : 1, the etching temperature was 70°C. AFM-an image of the surface of linear silicon structures obtained after LAO and etching in KOH+IPA is shown in Fig. 6, *a*. The etching time of 9 linear silicon structures shown in Fig. 6, *a* was 40 s, while their height above the substrate surface was 240−10 nm.

Along with this, the effect of etching time in KOH+IPA on the height of the resulting nanoscale structures was experimentally investigated, the results are presented in Fig. 6, *b*. The graph shows that as the etching time increased, the height of the resulting structures grew from 100 to 350 nm, then the structures collapsed. We associate these processes with etching under the formed mask layer.

Experimental studies of the modes of LAO of titanium after its sputtering on the formed ONS of silicon were also carried out. The deposition of the titanium film was carried out on the magnetron sputtering unit VSE-PVD-DESK-PRO (AkademVak, Russia). The deposition time of the titanium film was 30 ± 1 s, the thickness of the resulting titanium film was 20 ± 5 nm.

After sputtering of the titanium film with the LAO method, memristor structures of titanium oxide were formed using the Ntegra Vita scanning probe microscope. LAO was conducted in contact mode, with probes with platinum coating of the NSG11 brand. AFM was carried out with the following parameters: the amplitude of the voltage pulses varied from 5 to 9 V, the duration of the voltage pulses was 100 ms, the oscillation frequency of the probe was 0.3 Hz, the feedback circuit current was 0.3 nA. The LAO time of structures according to the developed template in vector mode was determined automatically by the Ntegra Vita AFM and for oxidation by the LAO method of 5 lines (Fig. 7) was 125 s. Relative humidity in LAO was controlled by the Oregon Scientific ETHG913R moisture meter and ranged from 30 ± 1 to 90 ± 1% (which corresponds to 0.005 to 0.016 kg/m^3 for absolute humidity). The temperature inside the process chamber was 20°C.

AFM image of linear structures of titanium oxide obtained at various pulses of applied voltage 4, 5, 6, 7, 8 V from left to right, respectively, at a relative humidity of 70% (0.012 kg/m^3 for absolute humidity), shown in Fig. 7. This data made it possible to select a number of technological

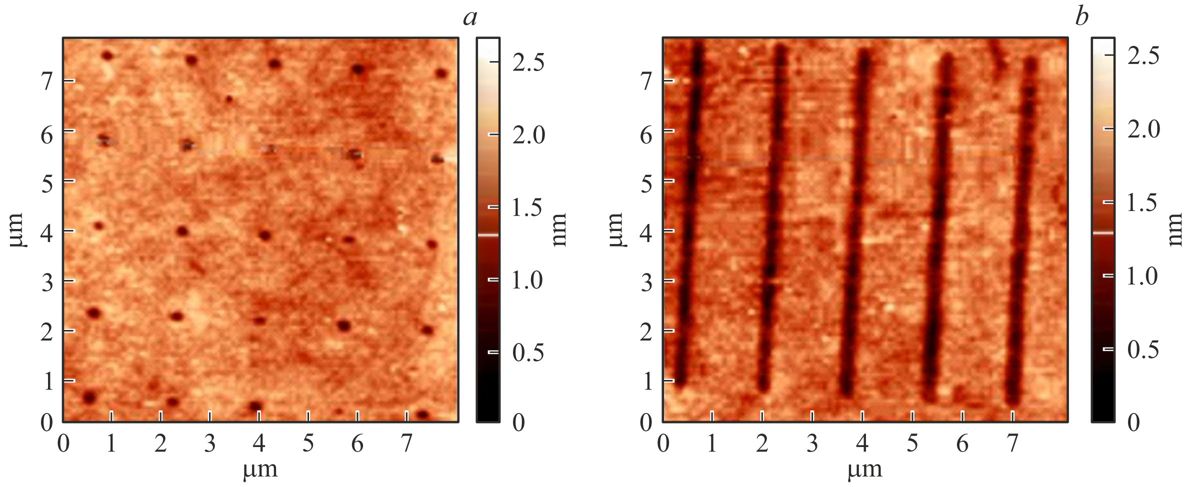

Figure 4. AFM images of PNS: *a* — after the formation of a matrix of 49 silicon ONS by the LAO method and liquid etching in HF; *b* — after the formation of linear structures by the LAO method and liquid etching in HF.

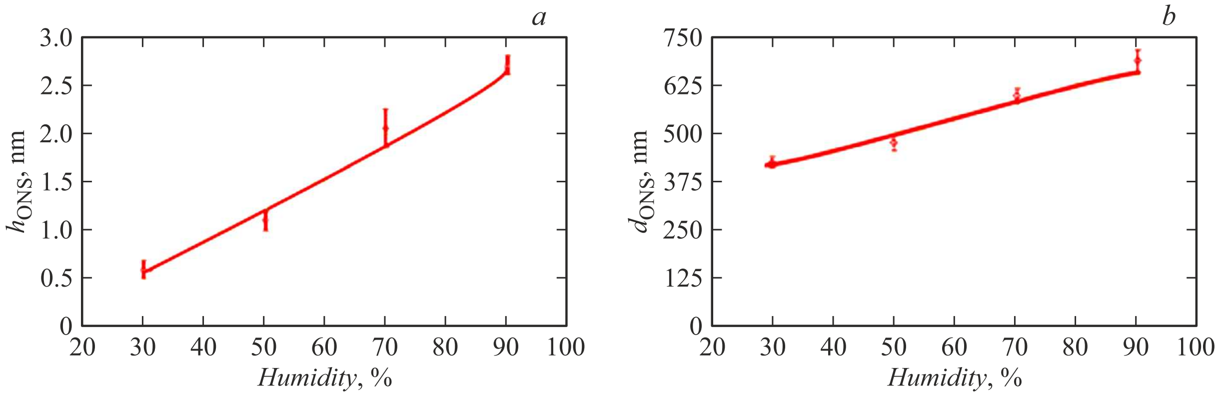

Figure 5. Dependences of geometric ONS parameters (*a* — height; *b* — diameter) when applying voltage 15 V.

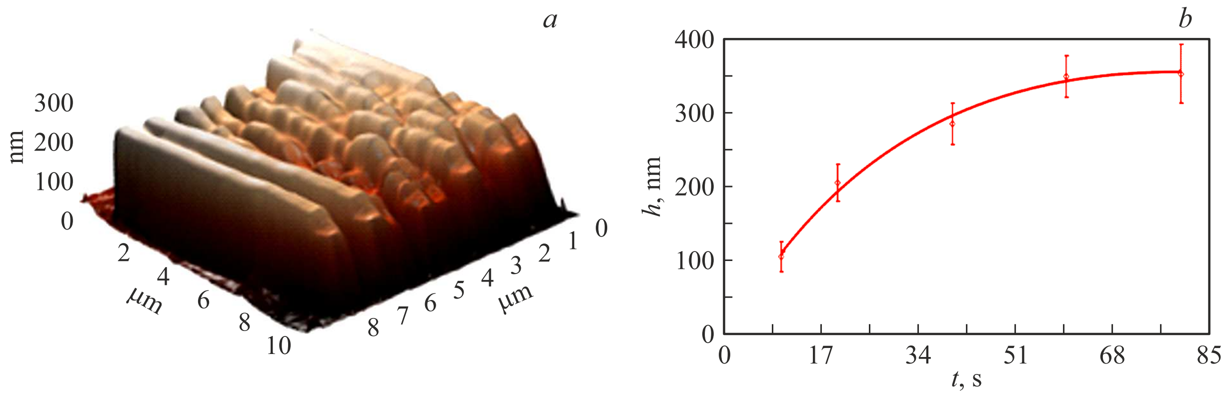

Figure 6. *a* — AFM image of the surface of linear silicon structures after etching in KOH+I; *b* — dependence of the height of silicon structures on the etching time in KOH+IPA.

parameters at which the best test samples of the ONS titanium were formed.

The analysis of the obtained results of LAO titanium showed that an increase in the amplitude of the applied voltage pulses from 5 to 8 V at a relative humidity of 70% (0.012 kg/m^3 for absolute humidity) leads to an increase in the height of the obtained ONS from 2.6 ± 0.2 to 8.2 ± 0.3 nm, and also to increase the diameter from 230 ± 20 to 425 ± 30 nm. At the same time, the resulting titanium ONS had a memristor effect. The Ntegra Vita

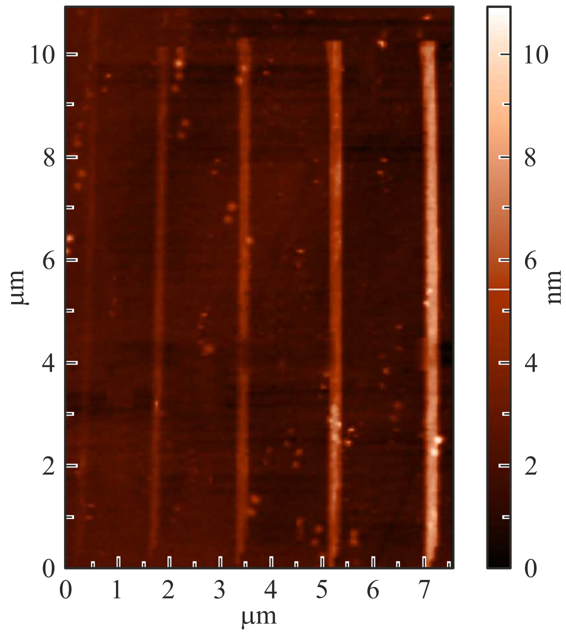

Figure 7. AFM image of linear titanium oxide structures obtained at different voltages.

probe laboratory was used to study the memristor properties of titanium ONS in contact mode using NSG11 platinum-coated probes. A Ti film on the substrate surface was used as the lower contact, and an AFM probe with a platinum coating was used as the upper contact. The layout of the structure is shown in Fig. 8, *a*. When applying a voltage in the probe system–substrate from −1 to 1 V, volt-ampere characteristics (VAC) ONS of titanium were obtained (Fig. 8, *b*).

2. Results and discussion

Thus, for the formation of the crossbar architecture, a technique for the formation of silicon ONS by the AFM method was developed, with the help of which experimental studies of silicon LAO were carried out at the first stage. The dependences of the height and diameter of nanoscale oxide structures obtained at a voltage of 15 V on air humidity shown in Fig. 5 show that an increase in the level of relative humidity leads to an increase in the geometric dimensions of silicon ONS, which is explained by an increase in the concentration of the oxidant. Also, a technique was developed for profiling silicon ONS using the LAO method and subsequent liquid etching in KOH+IPA (isopropyl alcohol) solution, thanks to which the obtained ONS can be used as a mask [14]. For etching silicon, a solution of 60% KOH was used with the addition of IPA in a ratio of 5:1, the etching temperature was 70°C. AFM image of the surface of linear silicon structures after LAO and subsequent liquid etching in KOH+IPA solution is shown in Fig. 6, *a*. Along with this, the effect of etching time in KOH+IPA on the height of the resulting nanoscale structures was experimentally investigated, the results are presented in Fig. 6, *b*. From this graph it can be seen that as the etching time increases, the height of the resulting structures increases from 100 to 350 nm, then the structures were destroyed. We associate these processes with etching under the formed mask layer. In addition, experimental studies of the modes of LAO of titanium after its deposition on the formed silicon ONS were carried out. The analysis of the obtained results of LAO titanium showed that an increase in the amplitude of the applied voltage pulses from 5 to 8 V at a relative humidity of 70% (0.012 kg/m^3 for absolute humidity) leads to an increase in the height of the obtained ONS from 2.6 ± 0.2 to 8.2 ± 0.3 nm, as well as

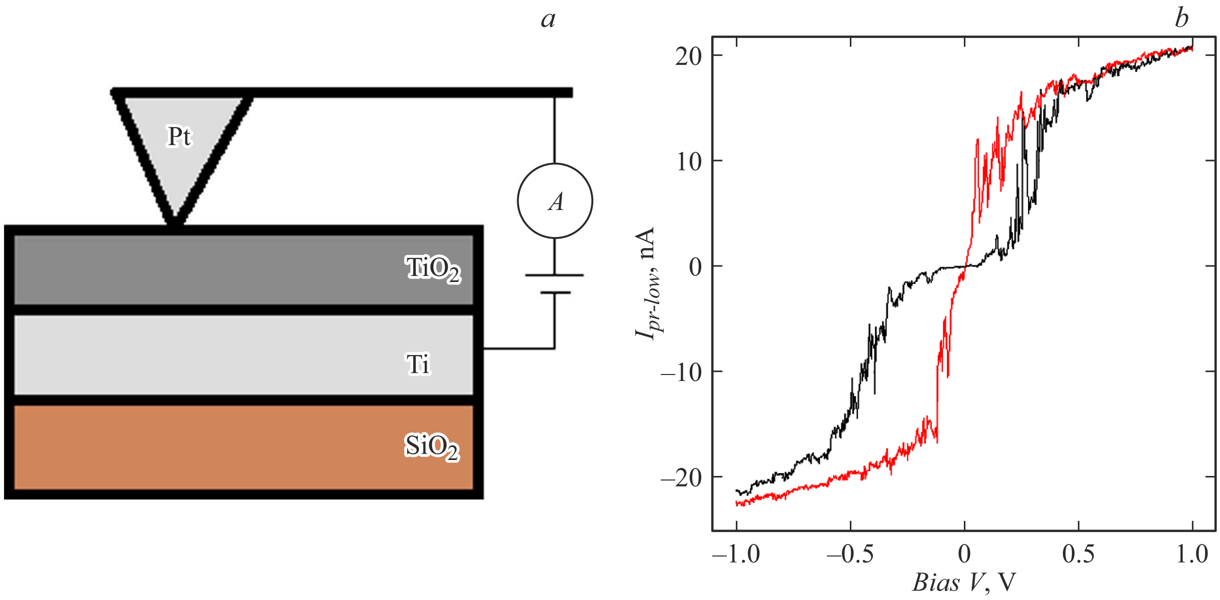

Figure 8. *a* — VAC measurement scheme; *b* — VAC ONS of titanium.

to increase the diameter from 230 ± 20 to 425 ± 30 nm. At the same time, it should be noted that the obtained titanium ONS had a memristor effect, which is confirmed by the obtained titanium ONS VAC, presented in Fig. 8, *b*.

Conclusion

As a result of the experimental studies of the LAO modes of the silicon substrate surface, it was found that an increase in the amplitude of the applied voltage pulses at LAO from 10 to 20 V leads to an increase in the height and diameter of the ONS. So, at a fixed relative humidity of 50% (0.009 kg/m^3 for absolute humidity), the height of the ONS increased from 0.61 ± 0.1 to 1.8 ± 0.1 nm, and the diameter increased from 375 ± 15 to 530 ± 18 nm. In the course of experimental studies, it has also been established that one of the control parameters of the LAO process is relative humidity, its increase leads to the proliferation of ONS. With an increase in relative humidity from 30 to 90 ± 1% (which corresponds to 0.005 to 0.016 kg/m^3 for absolute humidity) and a fixed value of the voltage of the applied pulses 15 V, the height of the received ONS increases from 0.5 ± 0.1 to 2.7 ± 0.2 nm, and the diameter of the received ONS increases from 380 ± 10 to 630 ± 18 nm. In addition, it was found that an increase in the amplitude of the applied voltage pulses at LAO from 10 to 20 V leads to an increase in the height and diameter of the PNS after etching in HF, and at a fixed relative humidity of 50% (0.009 kg/m^3 for absolute humidity) PNS height increases from 0.7 ± 0.1 to 1.3 ± 0.3 nm, and their diameter increases from 375 ± 15 to 530 ± 18 nm.

The experiment showed that the silicon ONS obtained by the LAO method can be used as a mask for etching in KOH+IPA solution. After etching the ONS in KOH solution(60%)+IPA(5 : 1) according to the developed technique, the height of the obtained structures lies in the range from 1.1 ± 0.1 to 330 ± 30 nm, while the etching time was 60 s. It was found that at an etching time of more than 80 s, the resulting structures are destroyed, which is associated with etching under the formed mask layer.

The analysis of the obtained results of LAO titanium showed that an increase in the amplitude of the applied voltage pulses from 5 to 8 V at a fixed relative humidity of 70% (0.012 kg/m^3 for absolute humidity) leads to an increase in the height of the obtained ONS from 2.6 ± 0.2 to 8.2 ± 0.3 nm, as well as an increase in diameter from 230 ± 20 to 425 ± 30 nm. The formed titanium ONS have a memristor effect.

Thus, a technology has been developed and experimental data has been obtained that can form the basis for the creation of elements of neuromorphic artificial intelligence systems, modern computers and elements of synaptic electronics.

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Conflict of interest

The authors declare that they have no conflict of interest.

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