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Fabrication of tunnel superconducting structures by selective chemical etching of aluminum

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A technological route for manufacturing tunnel superconductor structures using liquid selective etching of aluminum to break the electrical contact along the lower layer of a three-layer tunnel structure and form a bridge suspended above the substrate surface is proposed and tested. It is demonstrated that, according to the proposed technological route, the formation of a three-layer structure can be performed by all methods of film deposition, including magnetron sputtering, and not only by thermal sputtering, as was done previously. Samples with Al/AlO$_x$/Nb tunnel junctions were manufactured to test the technology. The manufactured structures were measured at temperatures down to 2.8 K, the ratio of the differential resistance in the zero voltage region to the normal resistance reaches 12. The tunnel structures superconductor–insulator–normal metal–insulator–superconductor are studied, where palladium is used as a normal metal. The problem of the negative effect of palladium on aluminum-based tunnel barriers is studied and methods for solving this problem are proposed.

Keywords: Superconducting tunnel structures, tunnel barrier, SINIS, CEB, NISIN, wet etching, magnetron sputtering.

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Introduction

The creation of modern highly sensitive receivers based on superconductor-insulator-normal metal-insulator-superconductor (SINIS) structures [2] is an urgent task for subterahertz radio astronomy [1]. This type of receiver is based on the bolometric (thermal) method of radiation detection [3,4]. As is known, the tunneling current in the superconductor-insulator-normal metal (NIS) junction exponentially depends on the temperature [5], which makes them highly sensitive thermometers that register small temperature changes in the metal absorber due to heating by external radiation. Cold electron bolometers (CEB) is another name for this type of detector [6,7], since the temperature of the electronic subsystem of the absorber can decrease below the physical (phonon) temperature in this type of structure [8,9]. One of the directions of development of such receiving systems is to increase the sensitivity of these devices by creating an absorber (absorber) made of normal metal suspended above the surface of the substrate, which will eliminate or reduce losses associated with heat loss into the substrate. The potential of this approach has been demonstrated: a quantum efficiency of 15 electrons per quantum of radiation at a frequency of 350 GHz was experimentally achieved [10] . However, the technology of creating such devices requires further development: increasing the reliability and reproducibility of the result, which is the main task of these studies.

Previously, the technology of production of receiving structures with a suspended absorber using liquid etching of aluminum was tested in the manufacture of SINIS structures using the technological platform of Chalmers University of Technology, Sweden (Fig. 1). Within the framework of this technology, first of all, wiring on a chip and contact pads are formed from a three-layer Ti/Au/Pd structure. Then, a three-layer Al/AlO$_x$/normal metal structure is applied and

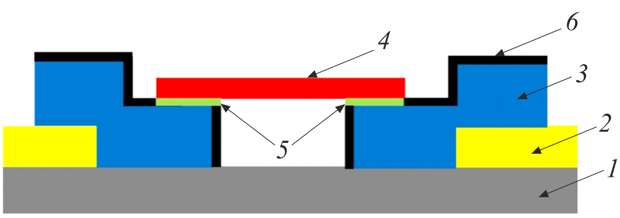

Figure 1. Schematic representation (not to scale) of the previously studied [10] SINIS structure design: *1* — silicon substrate, *2* — wiring and antennas (Ti/Au/Pd), *3* — superconductor (aluminum), *4* — absorber made of normal metal (copper, palladium, or hafnium), *5* — tunnel barrier, *6* — oxidized on the surface.

formed in a single sputtering cycle (without breaking the vacuum). At the end, an aluminum layer is selectively etched off under the absorber in the area defined by the window in the resistor. The aluminum under the normal metal bridge is completely removed by liquid etching in a weak base (Microposit MF CD 26 developer). Etching of aluminum in acids is less reproducible [11], and dry etching in plasma has small lateral etchings of the material under the bridge. There was a problem of sagging of bridges due to the reduction of the thickness of the absorber made of normal metal to 20 nm and below and the contact of bridges with the substrate during drying of samples after liquid etching because of capillary forces. Drying at a critical point in liquid CO_2 was used to avoid this. But the main disadvantage of the original version is the suppression of superconductivity by a normal metal of interconnects at the boundaries of the SIN junctions. A modification of the technology was proposed to resolve this problem: additional etching of the upper layer of normal metal was added, but it was feasible only for a certain set of materials of the upper electrode.

1. Description of the developed technology

Based on the initial technology (without additional etching), a variant of the task card for manufacturing SINIS structures with a suspended absorber using magnetron sputtering was proposed, adapted to the features and capabilities of the existing technological base at the Kotelnikov Institute of Radioengineering and Electronics of the Russian Academy of Sciences. The samples are made on silicon substrates with orientation $< 100 >$, KDB 10 (silicon with hole conduction) with size 24×24 mm. To prevent leakage through the substrate during measurements at room temperatures, the substrate was coated with 100 nm thick amorphous layer of Al_2O_3 using magnetron sputtering (Fig. 2). The layer of antennas and interconnects was made of aluminum with a thickness of 50 nm, the aluminum surface was protected from oxidation by a thin layer (3–5 nm) of palladium. This made it possible to solve the problem of suppressing superconductivity in NIS superconducting aluminum electrodes with transitions from a nearby normal metal of interconnects, which existed in an early version. In some variants, Nb interconnects were used ($T_c = 9.2$ K), the advantage of choosing Nb is the ability to form this layer not only by lift-off lithography, but also by plasma-enhanced chemical etching according to existing and well proved task cards.

The three-layer rectangular structure of $Al/AlO_x/Pd$ was formed by lift-off phtolithography and magnetron sputtering, which is a significant difference from the thermal electron beam sputtering used in the prototype. A three-layer $Al/AlO_x/Pd$ film with a thickness of 70/1/15 nm was sputtered in one cycle without vacuum break. The parameters of deposition parameters of a three-layer structure in a

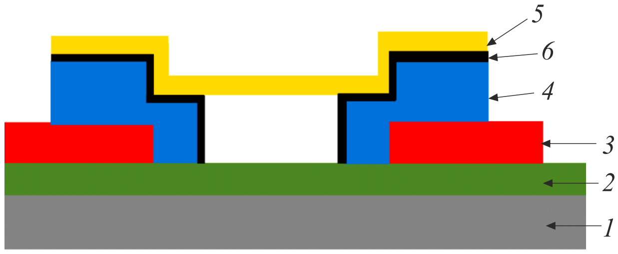

Figure 2. Schematic representation (not to scale) of the proposed bolometer design: *1* — silicon substrate, *2* — aluminum oxide protective layer, *3* — interconnects and antenna, *4* — superconducting aluminum, *5* — normal Pd absorber, *6* — tunnel barrier AlO_x and oxide on the surface.

single vacuum cycle for the Leybold Heraus L-560 UV installation are shown in the table. AlO_x barrier can be formed in the static or dynamic oxidation mode. The choice of oxidation modes is determined by the target value R_nS — the normal resistance of the tunnel junction (resistance with voltages above the gap voltage) per unit area. To use SINIS structures as single receiving elements, sufficiently high normal resistances of structures, on the order of 1 kΩ, are required for optimal matching with measuring circuits and minimizing noise on such structures. The target value $R)nS = 1000\,\Omega \cdot \mu\text{m}^2$ was selected for the studied samples, the barrier was formed in static mode at a pressure of 16 mbar for 30 min.

The smoothness of the deposited aluminum films strongly depends on the thickness of the film and the type of substrate, the temperature of the substrate during film deposition, and other factors. According to the authors' experience, all other things being equal, films of the studied thicknesses (about 70 nm) deposited by magnetron sputtering turn out to be smoother (having a finer crystalline structure) than films deposited by thermal methods (boat sputtering or electron beam spraying), i.e. magnetron sputtering allows creating high-quality smooth thin aluminum films and, accordingly, homogeneous tunnel barriers on it. But there is a risk of micro-closures of the three-layer structure in case of sputtering into a small window in the resist and the subsequent process of lift-off lithography. Due to the isotropy of magnetron sputtering, metal is deposited on the vertical walls of the resist, and short circuits are possible during lift-off photolithography. A resistor with a strong reverse profile AZ 5214 [12] was used to avoid problems when forming a three-layer structure, and it is also possible to use two-layer resistors, for example, LOR 3A + S1813.

The next stage is the formation of windows in the resistor for selective liquid etching of aluminum to create a suspended absorber made of normal metal and at the same time an electrical rupture along the lower layer of aluminum (formation of SINIS structure). The etching of aluminum is conducted in a weak alkali solution (KOH at a concentration of 1 %). Since the resists used also manifest themselves in

Deposition of a three-layer structure in a single vacuum cycle

Operation	Type	Pressure, mbar	P, W	I, A U, V	Sputtering time	Thickness, nm (speed, Å/s)
Deposition of Al	DC	$2.5 \cdot 10^{-3}$	604	1.6 A 383 V	39 s	70 (17.9)
Oxidation		$1.6 \cdot 10^{2}$			30 min	$R_nS \sim 1000\,\Omega \cdot \mathrm{m}^2$
Deposition of Al	DC	$2.5 \cdot 10^{-3}$	102	0.3 A 370 V	50 s	≈ 70 (1.4)
Deposition of Pd	RF	$2.1 \cdot 10^{-3}$	265	RF DC bias 108 V	26 s	≈ 150 (5.8)

alkali, it was decided to combine the stage of developing the resist and etching aluminum, and the final selected optimal etching time includes the time of developing the resist (the development time is about 30 seconds). The pre-development time can be calibrated by etching the aluminum film, however, it should be noted that the etching rates of the exposed surface and under the bridge differ significantly. Etching was stopped by transferring the sample to distilled water, drying was carried out by a stream of dry nitrogen. Thick gold (200 nm) was also sputtered in the area of the contact pads to ensure reliable electrical contacts. But the primary test measurements were conducted by direct contact to niobium or aluminum pads (cleaned with a thin layer of palladium).

The developed technological process has several key parameters. One of them is the thickness of the aluminum layer in the three-layer structure: the greater the thickness of the aluminum layer, the better the liquid will penetrate into the areas under the bridge, and the faster is the aluminum etching process. The ratio of bridge width and aluminum thickness is an important parameter. However, it must be borne in mind that thick aluminum films have a pronounced granular structure [13,14] and are not suitable for the formation of high-quality tunnel barriers. The thickness of the normal metal layer is also important: reducing this thickness reduces the volume of the normal metal, which improves the bolometric properties of such a structure, but, on the other hand, thin bridges are less reliable, prone to sagging and touching the substrate, as well as to tears. The reliability of the formation of suspended bridges strongly depends on the selected normal metal in a three-layer structure: for example, hafnium bridges are more reproducible, and copper bridges are more flexible and prone to deformations and sagging [10]. The choice of more rigid materials makes it possible to create suspended absorbers of longer length, which is important from the point of view of matching the impedance of planar antennas, where the structures developed by SINIS are embedded. Palladium, a noble metal of the platinum group, which is not a superconductor, was chosen for the production of the test series. First of all, the choice is determined by the fact that working with this metal fits into the existing technological cycle.

2. Sample production and research

A chip design with a size of 7×7 mm with 16 contact pads around the perimeter was developed to refine the manufacturing technology and study the properties of SINIS structures with a suspended absorber. In total, three types of the test chips were developed with different width of the bridge: 1, 1.5 and 2 μm. Each chip had 4 structures for measurements: 4 μm long bridge in a double slot antenna, 3, 4 and 6 μm long bridges. Accordingly, the dimensions of the absorber (bridge) varied both in length and width, while the dimensions of the NIS junctions also changed, since the length of the three-layer structure always remained constant and equal to 20 μm. The developed topology included relatively large transition areas from 7 to 25.5 $\mu\mathrm{m}^2$ without taking into account size deviations. The size of the NIS junctions is not critical for the test samples, and they were made large to increase reliability and test the technology. Each structure had the possibility of measurements using a four-probe connection scheme to exclude the influence of contact resistances and resistances of the supply wires. Additionally, two test structures are placed on each chip (Fig. 3) for testing etching and optical control modes, containing a set of bridges with a width of 1, 1.5, 2 μm and lengths of 2, 3, 4, 6, 8 μm. These structures are located at the bottom of the chip and are rotated 90° relative to each other.

The developed technology is critical to the accuracy of layer alignment. The sizes of the NIS junctions and the uniformity of their sizes in the NIS structure strongly depend on the position of the area of the aluminum etching. The etching area has a shape of an hourglass (Fig. 4), which, in our experience, improves the flow of liquid into the etching area. In a later version, aluminum etching was added from the edges of the three-layer structure, which made it possible to reduce the areas of NIS-junctions and mitigate the positioning requirements for lithography of the three-layer structure.

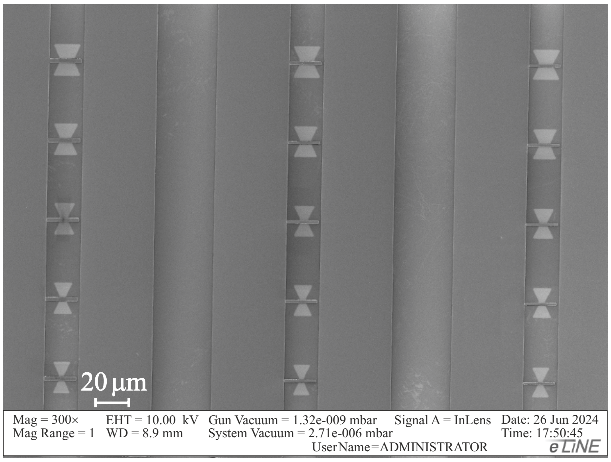

Figure 3. Type of test structure with a set of bridges of various lengths and widths.

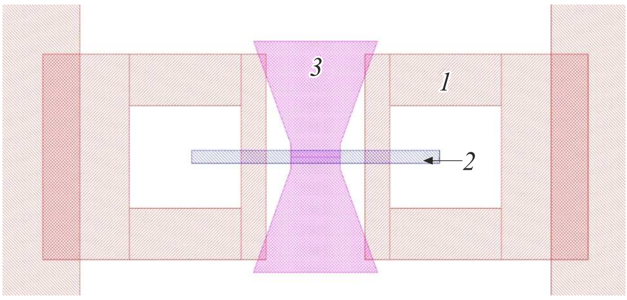

Figure 4. View of the area of the developed design of the SINIS structure: *1* — Al/Pd interconnects, *2* — three-layer structure of $Al/AlO_x/Pd$, *3* — area of liquid etching of Al.

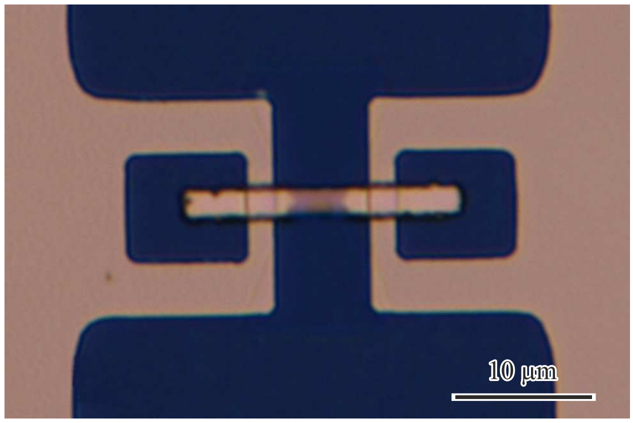

Figure 5. View of the area of the produced SINIS structure. The area with etched aluminum has darker color.

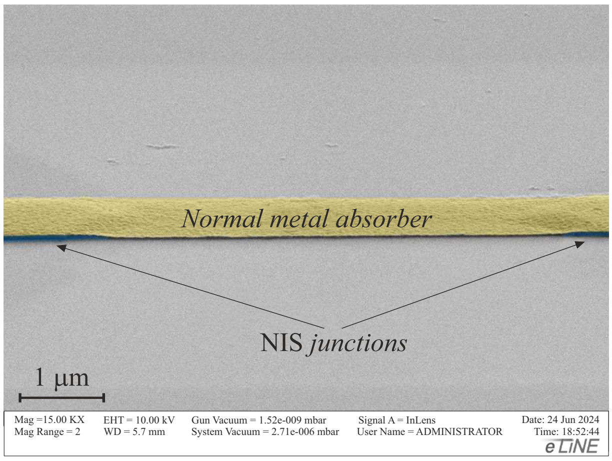

Figure 6. View of the bridge with NIS junctions along the edges in an electron microscope obtained with tilted sample.

Each technological stage was monitored in an optical microscope. After selective etching of aluminum, when viewed under an optical microscope in reflection mode, the metal in the etched region appears darker (more transparent), allowing the endpoint of the etching process to be monitored (Fig. 5). An optical microscope also shows a characteristic etching profile and small lateral etchings (up to $0.5\,\mu$m) on the sides of the junctions. When the optimal etching time is exceeded, the blemishes become significant, up to the complete etching of aluminum in the area of the NIS junctions, with insufficient etching time, a thin aluminum bridge remains, which is visible when monitored in an optical microscope. It is recommended that the etching time is greater than the minimum required time for increasing the reliability and complete removal of aluminum under the bridge. The selected optimal etching time, including the stage of development of the resist for bridges with a width of $1-1.5\,\mu$m, was $100-110$ s.

It is not possible to examine the profile of the structure and assess whether the bridge touches the substrate or not when using only an optical microscope for examination. A scanning electron microscope was used for this purpose and for precise size control. To obtain profile images of the structure, the sample was tilted at an 85° angle to the stage surface. The boundary where the aluminum is etched and where it is not can be distinguished in the images obtained in an electron microscope. But even such studies do not give „a glimpse“ under the suspended bridge, but rather give an idea of its profile. The research data also confirm that suspended thick Nb absorbers retain their shape, and thin Pd bridges sag and touch the substrate after liquid etching (Fig. 6), i.e., Pd bridges also tend to sag, like the previously studied copper bridges, unlike bridges made of more rigid metals. for example, hafnium.

3. Measurement results

A series of samples with a three-layer structure Al,$(100\,\text{nm}) - AlO_x$ $(R_nS \sim 1\,\text{k}\Omega) - \text{Nb}\,(80\,\text{nm})$ was produced to test the stages of lithography, film deposition and liquid etching of aluminum. To test the technology, the thin Pd layer was replaced with a sufficiently thick layer of rigid metal Nb, which made it possible to quickly measure such structures in liquid helium at a temperature of 4.2 K.

This structure is a normal metal-insulator-superconductor-insulator-normal metal (NISIN) at 4.2 K is measured in the same way as the SINIS structure — as two consecutive NIS-junctions. The interconnects on the chip was made of aluminum to avoid the proximity effect (induced superconductivity) in the aluminum electrodes of the NIS junctions.

The direct current-voltage curve (CVC) of the manufactured NISIN structures were studied at a temperature of 4.2 K in a probe insert in a Dewar transport helium vessel and in a closed-cycle cryostat at temperatures up to 2.8 K. The resistances of each of the four test structures on the chip were measured with a four-probe connection scheme and a two-probe connection circuit. In the second case, the resistance of the supply wires, interconnects on the chip, and the contact resistances (which could vary in different measurement cycles) are added to the resistance of the actual structure. Spring-loaded contacts (pogo pins) were used for electrical contact with the sample pads in the holder.

The measurements were carried out in the current setting mode, the choice of the current setting range was regulated by ballast resistances. A circuit with low-noise operational amplifiers was used to amplify the signal. The entire circuit, including ballast resistances from 2 kΩ to 1 GΩ, current and voltage channel amplifiers, as well as a switchboard for selecting measuring channels, were assembled in a shielded enclosure and kept at room temperature. The scanning voltage setting the current was supplied from a specialized DAC/ADC board manufactured by National Instruments from a control computer. These boards were operated under the control of specialized software IRTECON [15]. The warm amplifier unit was connected to the DAC/ADC switching board using standard shielded coaxial cables.

Figure 7 shows the measured CVC and the calculated dependences of the differential resistance of one of the test structures at temperatures of 4.2 and 2.8 K. The quality parameter for SINIS structures at a certain temperature is the ratio of the differential resistance without bias to the asymptotic resistance above the energy gap voltage (R_d/R_n).

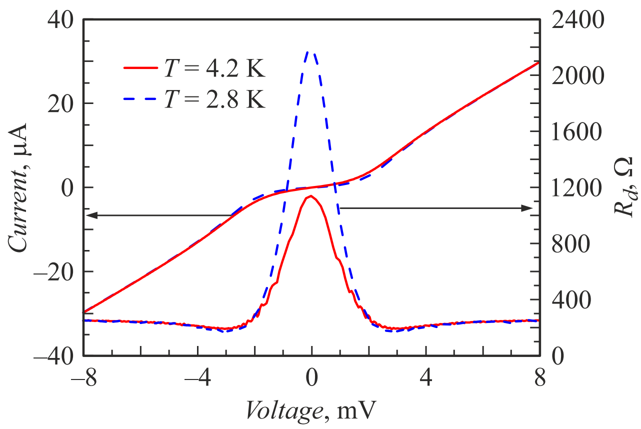

Figure 7. The measured CVC and differential resistance curves of the NISIN structure at temperatures of 2.8 and 4.2 K.

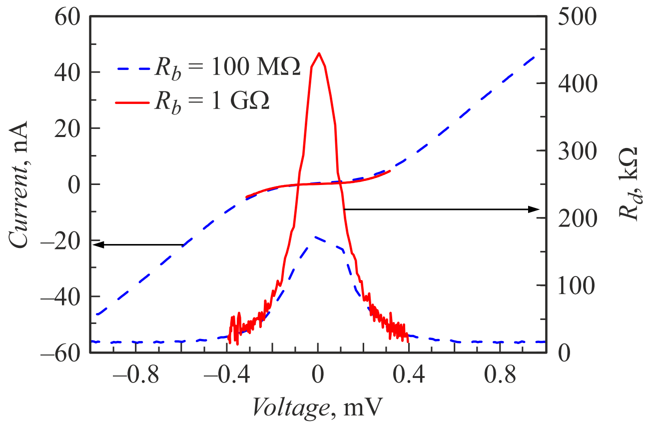

Figure 8. The measured CVC and differential resistance curve of the SINIS structure with junctions Al/AlO_x/Si-Pd at a temperature of 100 mK at different current setting ranges.

The measured resistance ratio R_d/R_n at a temperature of 4.2 K was 4.5, and at a temperature of 2.8 K it reached 9. The slit voltage corresponds to the double slit Nb and is 2.8 mV. The resistance of the interconnects before switching to a four-point connection scheme is about 75 Ω for this series of samples. If we take into account these successive resistances, the resistance ratio reaches 12 at a temperature of 2.8 K. The measured resistance ratio turned out to be noticeably less than the limit value calculated using the formulas for the NIS transition [16]. First of all, we attribute this to overheating of unprotected structures by external electrical noise. In general, the measurements carried out demonstrate that it is possible to create high-quality structures with tunnel crossings along the proposed technological route.

According to the results of the first electrical measurements of SINIS structures with Al/AlO_x/Pd junctions at a temperature of 300 mK in a helium-3 sorption cryostat HELIOX-AC-V, the obtained CVC differed greatly from the theoretically expected ones. This behavior has been attributed to the chemical activity of palladium and its effect on aluminum tunnel barriers. It was proposed to use a thin (3–5 nm) buffer layer of aluminum before palladium deposition, but this did not significantly improve the quality of NIS junctions. However, the use of a thin buffer layer of copper significantly improves the characteristics of NIS junctions. Fig. 8 shows the CVC of such a SINIS structure in a log-periodic antenna, measured in different ranges of current setting. The measurements were carried out in a ^{3}He/^{4}He dilution cryostat at temperatures up to 100 mK. The resistance ratio R_d/R_n reaches 30, which is also far from the limit values, but already allows such structures to be used as bolometric receivers. The resistance ratio in the simple test structures was more than 100, which is higher than for the structures in the antenna. This indicates a suboptimal optical scheme in the cryostat and the presence

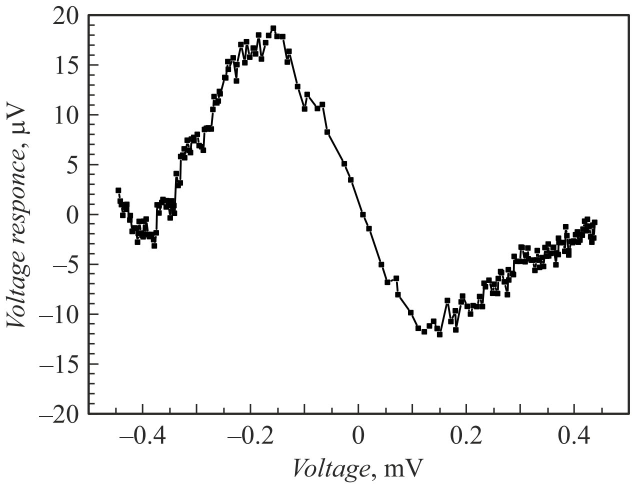

Figure 9. Measured voltage response of the SINIS structure in a log-periodic antenna with Al/AlO$_x$/Si-0Pd junctions for the study of a black body with a power of about 4 pW at a temperature of 100 mK.

of overheating of the antenna structures by radiation from warmer stages of the cryostat.

The voltage response (Fig. 9) of such a structure was measured at a temperature of 100 mK, integrated into a broadband log-periodic antenna mounted on a lens, to blackbody radiation with a temperature of about 9 K (the power of the radiation incident on the antenna is approximately 4 pW.). The experimental methodology and scheme are similar to those used in previous studies [10]. The volt-watt sensitivity was $4 \cdot 10^6$ V/W, without taking into account the optical path and the mismatch of the log-periodic antenna used and the SINIS structure.

Conclusion

A technology for manufacturing structures with tunnel junctions using selective liquid etching of aluminum has been developed and tested. The proposed technology can be used to manufacture structures of the SINIS type, as well as NISIN and superconductor-insulator-superconductor-insulator-superconductor (SIS'IS), depending on the materials used, operating temperatures and tasks set. Using the proposed technology, NISIN structures with Al/AlO$_x$/Nb junctions were manufactured and measured, the resistance ratio (R_d/R_n) reaches 12 at a temperature of 2.8 K. These measurements confirm that the proposed technology has succeeded in forming an unshunted NISIN structure with tunnel barriers. Studies of structures with Al/AlO$_x$/Pd junctions have revealed the problem of the negative effect of Pd on the tunnel barrier with aluminum. A thin buffer sublayer of copper makes it possible to solve this problem and obtain a SINIS structure of acceptable quality (R_d/R_n more than 30 at 100 mK) for bolometric applications.

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Conflict of interest

The authors declare that they have no conflict of interest.

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