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Influence of ion irradiation on the properties of thin superconducting NbN films

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It is shown that composite ion irradiation of a thin NbN film to a fluence of $8.5 \cdot 10^{16}\,\mathrm{cm}^{-2}$, smaller than the optimal one ($10 \cdot 10^{16}\,\mathrm{cm}^{-2}$), can be used to create cryogenic integrated resistors if the values of the operating currents of the device are greater than all the characteristic transition currents for irradiated and stabilized by annealing films. At the same time, smaller resistance values per square are realized, which allows one to create smaller values of integrated resistance. It is demonstrated that annealing of the irradiated film at a temperature of 600°C leads to a partial return of superconducting properties and is accompanied by the appearance of two superconducting transitions at critical current densities of $0.45 \cdot 10^6\,\mathrm{A/cm}^2$ and $1 \cdot 10^6\,\mathrm{A/cm}^2$, which must be taken into account when it is necessary to use stabilizing annealing at elevated temperature.

Keywords: NbN thin superconducting films, radiation methods for changing the atomic composition of thin-film superconductors, ion irradiation, cryogenic electronic devices.

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1. Introduction

Research Center „Kurchatov Institute“ has been recently working on creation of the main logical elements for designed classic cryogenic computers [1]. Logical elements are based on nanowires from NbN with integrated areas of normal metal, which are formed under the exposure to ion radiation of the corresponding segments in nanoconductors through windows in a mask developed by electronic lithography methods. Irradiation modes (ion energy, radiation fluence, beam composition) to develop integrated resistances are selected experimentally so that after irradiation and stabilizing annealing the current-voltage curve of the film at operating temperature of the device had linear appearance and was stable in time [2]. Previously we demonstrated that under exposure to radiation in certain doses a new crystalline phase of NbNO is formed due to partial replacement of nitrogen atoms for oxygen atoms in NbN in process of irradiation [3].

Since the issue of time stability of characteristics created under the irradiation of resistances integrated in superconducting nanowires is critical and determines stability of characteristics in developed devices, research was done on the dependence between formed nominals and time of delay at room temperature. This research demonstrated that resistance increases in total approximately by 20% with time; maximum growth speed is observed immediately after their manufacturing, then resistance growth speed reduces and falls down to zero, i.e. the developed resistance reaches saturation. Since stabilization of resistance nominals by their delay at room temperature seems inconvenient from practical point of view, stabilizing annealing is used to accelerate the process of the nominal advancement to saturation. Annealing temperature (200°C) is selected so that it does not exceed temperatures used in the process cycle, and annealing duration provides for the required achievement of properties stabilization. When multilayer devices are created, the stabilizing annealing is used once for all integrated resistances in different layers.

For cryogenic circuits working at high frequencies it is often required to create a low nominal resistor, for example $50\,\Omega$, to match signal transmission lines with the measurement equipment. For this purpose it is desirable for the material after irradiation to have as lower resistance value as possible per square to minimize geometric dimensions of low nominal resistors. From the point of view of using conversion of superconducting film properties into metal under exposure to ion irradiation, such requirement means that it is necessary to use minimum possible doses of irradiation, since resistance of irradiated films per square increases as the dose rises [2].

It is also necessary to take into account the fact that when standard parameters are used to create integrated resistances under exposure to irradiation in open areas of superconducting nanowire, between them and the superconducting wire there is always a transition area, provided for by availability of the profile in the protective mask from resist, therefore, in the transition area the superconductor receives an intermediate dose, which is lower than the maximum one in the open areas of the superconductor.

It is commonly known that the course of the process of selective nitrogen atom replacement for oxygen atoms under mixed ion irradiation requires certain thermal activation of both release of knocked-on nitrogen atoms to drains with subsequent removal into vacuum and oxygen atoms movement deep into the film to replace the knocked-on nitrogen atoms [4]. Despite the increased value of resistance per square after annealing, current-voltage curve linearity persists after annealing, and integrated resistance developed in such manner is stable and does not vary in time. Therefore, use of irradiation to a certain dose in a combination with stabilizing annealing at moderate temperature (200°C) produces good result when making integrated resistances in process of development of multi-layer cryogenic logical devices [1].

The purpose of this paper was to demonstrate the possibility of using irradiation doses that are lower than usually used in creation of integrated resistances, in process of conversion of superconducting NbN into metal phase at operating temperature in process of implementing the radiation method of selective atom replacement developed in Research Center „Kurchatov Institute“ [4,5]. In connection with the potential need to use higher temperatures of stabilizing annealing when developing multilayer devices, this paper studies impact of annealing at higher temperatures at properties of films irradiated to develop integrated resistances.

2. Experiment procedure

The research item was NbN films with thickness of 5.5 nm by method of cathode sputtering at room temperature of the substrate with dimensions of active elements $20 \times 20\,\mu\text{m}^2$ on a substrate from single-crystal sapphire [6,7]. Irradiation was carried out by a mixed ion beam from protons and ions of oxygen [4]. Ion energy was 1 keV, ion current density — 0.849 A/m^2. This paper investigates properties of NbN films after irradiation to maximum fluence $8.5 \cdot 10^{16}\,\text{cm}^{-2}$, which is slightly lower than usually used to develop integrated resistances ($10 \cdot 10^{16}\,\text{cm}^{-2}$) [2], therefore their current-voltage curve is not straight and has a small fold in the area of low currents. Integrated resistances based on such irradiated films may be used, if current-voltage curve of integrated resistors is linear at operating currents of nanoconductors in devices, despite a blurred transition at lower currents. Recalculation of currents produced by measurement of film characteristics at their width $20\,\mu$m, to operating currents of nanowires made of such films, is carried out proportionately to the width of nanowires used in the device. The possibility of using lower fluences makes it possible to form a film under the exposure to irradiation with lower resistance per square as the base to form an integrated resistor.

Electrophysical characteristics were measured using a measurement complex „Keithley-4200“.

Samples of transverse cuts — thin lamellae — for research of microstructure by methids of transmission electron microscopy were made by a plant with a focused ion beam „Helios NanoLab-650“ [8]. Microstructure was researched using a transmission electron microscope „Titan 80-300ST“ with accelerating voltage of 200 kV, equipped with a spectrometer of energy losses of electrons „GIF-2003“.

3. Results and discussion

The developed method of directed change of atomic composition of materials under the exposure to mixed ion irradiation with the purpose to regulate their physical properties in this case is used to convert the superconducting phase of cubic niobium nitride NbN into metal phase, where some nitrogen atoms are replaced with oxygen atoms. It is obvious that such conversion will not happen simultaneously in the entire film thickness, since it requires both displacement of nitrogen atoms from their equilibrium states and further removal of nitrogen atoms to the surface (process of selective atom removal), and also delivery of oxygen atoms inside the film to replace the removed nitrogen atoms (process of selective replacement of nitrogen atoms). To detect the mechanisms of processes occurring in the film when exposed to mixed irradiation, this paper investigated impact of annealing at various temperatures at electrophysical properties and parameters of microstructure of the irradiated thin films of niobium nitride.

Fig. 1 shows impact of ion irradiation at dependence of film resistance on temperature for several fluences, while transition temperature exceeds 4.2 K. All curves $R(T)$ in Fig. 1 are given in the condition after irradiation and stabilizing annealing at 200°C. Also Fig. 1 (see curve *6*) shows $R(T)$ after irradiation to fluence $8.5 \cdot 10^{16}\,\text{cm}^{-2}$ (and annealing 200°C) that is lower than the base fluence ($10 \cdot 10^{16}\,\text{cm}^{-2}$), usually used to create integrated resistances. For fluence $8.5 \cdot 10^{16}\,\text{cm}^{-2}$ the curve $R(T)$ is also given after high-temperature annealing at 600°C, where partial return of superconducting properties is seen (Fig. 1 curve *7*). In Fig. 1 for the initial film two transitions are seen: first transition at ~ 9 K — it is the transition of the film itself (main resistance drop). After the main transition the film is in superconducting state, but sample resistance does not become equal to zero, but makes $\sim 50\,\Omega$. This is due to the fact that in a (serial) circuit the metering contacts lie directly on NbN film. Due to proximity effect NbN transition under the contacts moves to the area of temperatures ~ 7 K, and the corresponding step is seen in all $R(T)$. Since contacts have substantial thickness (Ni + Pt) ~ 70 nm, irradiation will not impact NbN under the contacts. From curves in Fig. 1 you can see that this additional transition under the contacts always happens at the same temperature. In Fig. 2 current-voltage curves are shown for initial and irradiated samples (after stabilizing annealing at 200°C), corresponding to $R(T)$ in Fig. 1. From Fig. 2 it is seen that as a result of exposure to irradiation the current-voltage curve moves to the area of lower currents, and hysteresis by current of transition from superconducting state to normal one and back disappears.

Fig. 3 separately shows current-voltage curves of the sample after irradiation to fluence $8.5 \cdot 10^{16}\,\mathrm{cm}^{-2}$ and annealing at various temperatures. After irradiation and standard stabilizing annealing at 200°C Fig. 3 shows weakly noticeable fold.

Increased annealing temperature causes the following effects. First of all, annealing at high temperature initiates

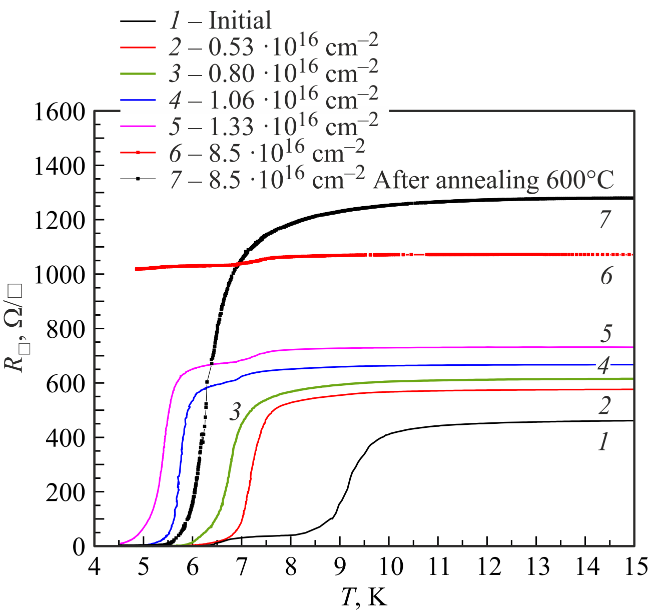

Figure 1. Dependence of resistance per square on temperature for initial NbN film and after irradiation and stabilizing annealing at 200°C.

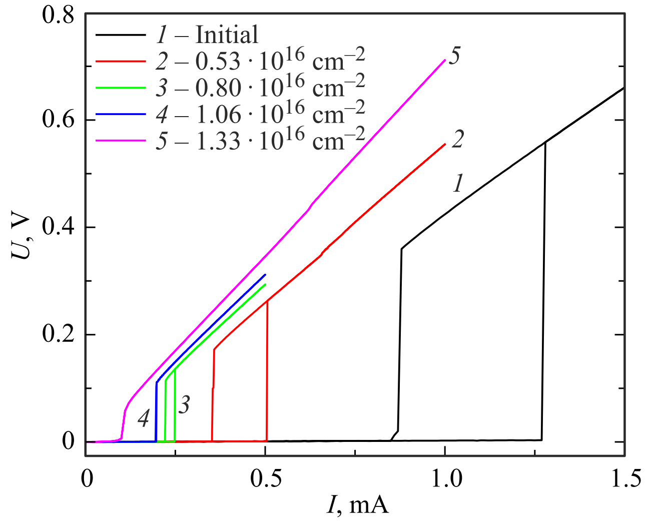

Figure 2. Current-voltage curves of the initial NbN film and after irradiation to some fluences and stabilizing annealing at 200°C.

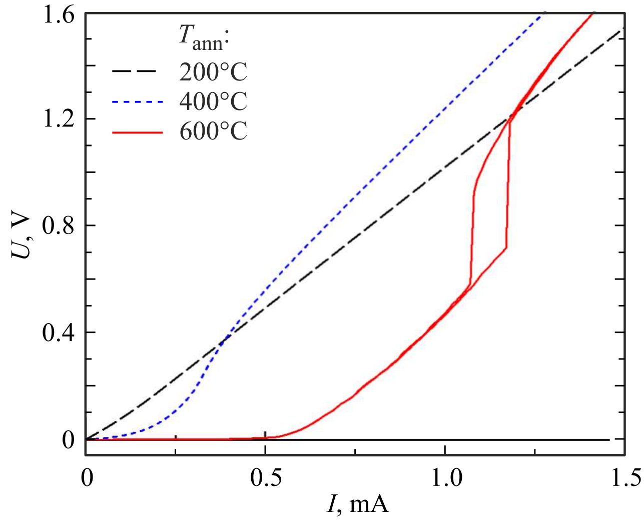

Figure 3. Current-voltage curves after irradiation to fluence $8.5 \cdot 10^{16}\,\mathrm{cm}^{-2}$ and annealing at different temperatures.

partial restoration of superconducting properties, which is expressed in appearance of low (zero) values of resistances, there is a blurred transition of certain area of the material to normal state, and then — sharp transition into normal state with the specific hysteresis loop.

Secondly, in Fig. 3 one can see growth of the resistance value per square of film in normal state after annealing, which increases with increased annealing temperature.

From the current-voltage curve produced after annealing at high temperature it is seen that the internal structure of the film after irradiation and annealing is a serial connection of two phases: superconducting phase with highly blurred transition in the area of low currents and superconducting phase, characterized by sharp transition to superconducting state and hysteresis loop of forward and backward transition.

According to our ideas, the first (main) phase is a underradiated niobium oxynitride, where not the entire half of nitrogen atoms is replaced with oxygen atoms yet, and the second phase is close to the initial one by composition, where radiation defects produced in process of irradiation are annealed at high temperature. The produced nature of current-voltage curve shows that the second superconducting phase is in the film in the form of separate isolated pellets (grains), while the first phase occupies the entire remaining film (pudding model). Isolated nature of the second phase localization and continuity of the first phase is confirmed by the fact that before current value, when the second phase is a superconductor and has zero resistance, a delayed transition of the first phase in the normal state manifests itself in the curve. Total resistance of the entire film after transition increases with growth of annealing temperature, which is due to progress of the process activated by annealing for additional oxidation of areas damaged under radiation, where implanted oxygen atoms are present.

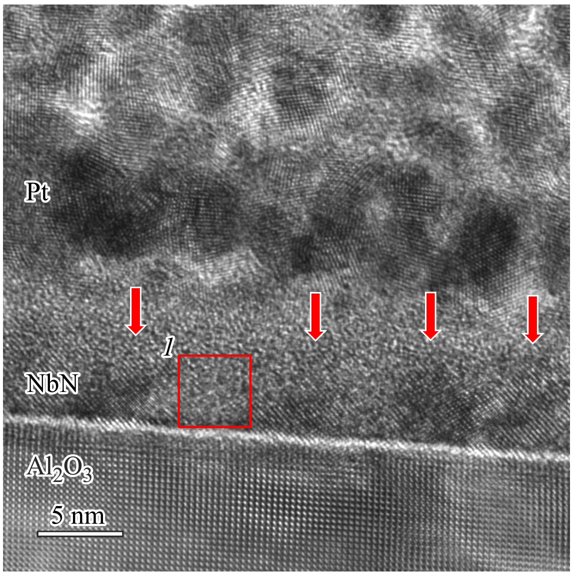

Figure 4. Electron-microscopic image of atom structure in the transverse cut of NbN film on a substrate of single-crystal sapphire after irradiation to fluence $8.5 \cdot 10^{16}\,\mathrm{cm}^{-2}$ and annealing at temperature of 600°C: *1* — area between grains with loss of crystallinity (indicated with a square)

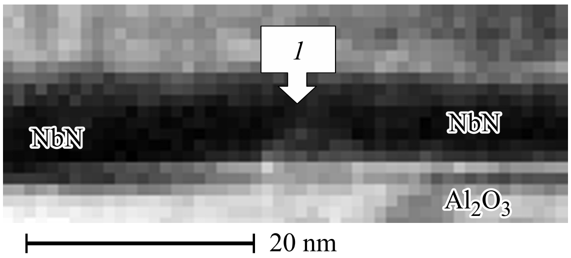

Figure 5. Chart of oxygen distribution in transverse cut of the NbN film after irradiation to fluence $8.5 \cdot 10^{16}\,\mathrm{cm}^{-2}$ and annealing at temperature 600°C, produced by characteristic electron energy losses spectroscopy (EELS) method in the following mode: *1* — area between grains with higher oxygen content.

Such model of phase distribution is confirmed by data of direct microstructure studies made on samples of transverse cuts of irradiated films after annealing at high temperature. Fig. 4 shows TEM images of film microstructure after annealing to fluence $8.5 \cdot 10^{16}\,\mathrm{cm}^{-2}$ and annealing at 600°C. Below you can see a substrate of single-crystal sapphire, then grains of polycrystalline NbN film coated with platinum on top deposited to protect the surface in process of thin lamella cutting for TEM research. As shown in Fig. 4, between individual crystalline grains (indicated with vertical red arrows) there are areas, with lost crystallinity (indicated with a red square), which is due to the fact that in such areas at high oxygen content the long-range order is destroyed in the location of atoms, which is specific for grains of stoichiometric superconducting phase in grains.

This is also confirmed by data of oxygen distribution (see Fig. 5), obtained by mapping using characteristic electron energy losses spectroscopy (EELS) method in the mode of transmission scanning electron microscopy (STEM). In the lower part of Fig. 5 you can see a substrate by intense signal from oxygen atoms in sapphire. Despite prevalence of oxygen in the upper part of the film, between individual grains in the lower part of the film there is effect of increased oxygen concentration seen (see area *1* in Fig. 5).

4. Conclusion

Therefore it is shown that annealing at 600°C for films irradiated to fluence $8.5 \cdot 10^{16}\,\mathrm{cm}^{-2}$ initiates the following processes. First of all, partial return of superconducting properties in the grain body occurs due to annealing of radiation defects, as a result of which zero resistance arises in the initial section of the current-voltage curve, as well as critical current and hysteresis when the film changes by current to normal state and back. Secondly, annealing initiates additional oxidation of those microstructure areas, where this process did not happen fully in process of irradiation by a mixed ion beam, in particular, at the boundaries of individual grains, therefore, an amorphous superconducting phase is produced between the grains that differs from the initial one (with high oxygen content), characterized by lower value of the critical current, and also by blurred (smooth) transition by current from the superconducting to normal state.

If a device is designed on the basis of results produced in this paper that is based on nanowires with width of 100 nm, the specific currents of superconducting phase transition formed after irradiation to fluence $8.5 \cdot 10^{16}\,\mathrm{cm}^{-2}$ and annealong at 600°C, to normal state, according to data of Fig. 3, will make $2.5\,\mu$A. Therefore, for proper operation of such device it is necessary that the operating current through a nanowire is more than $2.5\,\mu$A, then integrated resistance will function as a resistor.

Therefore, when selecting a dose of irradiation to create an integrated resistance, it is necessary to take into account the stabilizing annealing and to properly select its temperature, providing for the required level of properties at the operating parameters of the device.

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Conflict of interest

The authors declare that they have no conflict of interest.

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