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Creation of functional nanostructures under ion irradiation

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The paper describes a method developed in National Research Centre „Kurchatov Institute“ for creating different functional nanostructures using ion beam irradiation. As an example, the formation of an integrated resistive elements in a low-temperature NbN superconductor nanowire is demonstrated. The possibility of producing an insulating layer of aluminum oxide with a thickness of 15 nm on the aluminum surface at room temperature under 0.2 keV oxygen ions irradiation was shown.

Keywords: Ion irradiation, NbN thin superconducting films, integrated cryogenic resistors, creation of dielectric layers under irradiation.

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Introduction

Methods, developed in the National Research Centre „Kurchatov Institute“ of directional modification of properties of thin-film materials under ion beam irradiation, allowing to change an atomic composition and properties of materials for giving the required functional characteristics, are used in this study. The following is used as parameters: energy and type of the particles in use, fluence, ion beam composition, substrate temperature during irradiation.

Among the developed experimental methods the following can be highlighted: method of conversion of dielectrics to metals [1], metals and semiconductors to dielectrics [2], non-magnetic materials to magnetic materials [3], change of optical index of refraction, conversion of superconductors to metals [4] and dielectrics [5], etc. under ion beam irradiation.

Protective mask should be formed to select the areas for irradiation for making the required topology of nanostructures. The mask is created by probe methods using focused electron beam or focused ion beam.

After protective mask formation the properties change during nanostructure forming is performed by wide ion beam of various composition at any ion source (plasma generator, accelerator, etc.), that can be used for a large number of applications.

The created various functional nanosized devices and functional elements were demonstrated: metal nanowires in dielectric matrix [6], high-density patterned magnetic media [3], nanosized logical elements based on low-temperature superconductors [7].

1. Experimental procedure

Functional thin films, of which the nanostructures are made, are applied to substrate using sputtering methods (cathode, magnetron, laser sputtering, etc.). In this study the thin films of low-temperature superconducting niobium nitride were made using cathode sputtering method at substrate temperature of 800°C [8]. Metallic aluminum films with thickness of ~ 50 nm were made at room temperature using cathode sputtering method [9] on substrates of single-crystal silicon.

Mask of positive electron resist PMMA, in which the windows were made using electron lithography method for ion beam irradiation, was formed on the film surface. Nanowires forming of solid NbN film was also performed using electron lithography and the following reactive etching.

Conversion of the thin-film niobium nitride was performed under the composite ion beam irradiation using wide beam of protons and ions of (OH^+) composition $c = 1.2 \cdot 10^{-3}$ [2]. In this study the thin-film niobium nitride conversion to phase [10], exhibiting the metallic properties at temperature of 4.2 K, was performed under the composite ion beam irradiation to nitrogen dose of ~ 1 dpa [4]. Radiation-induced oxidation of aluminum was performed at sample room temperature under irradiation with oxygen ions with energy of 0.2 keV.

Cross-section samples for microstructure studies were prepared using focused ion beam (FIB) method at „Helios Nanolab 650“ (FEI) unit with Ga ions energy at pre-cutting stage of 30 keV, at final smoothing stage — 2 keV.

Determination of distribution of chemical elements atomic concentrations was performed using relative concentrations method by means of analysis of electron energy losses

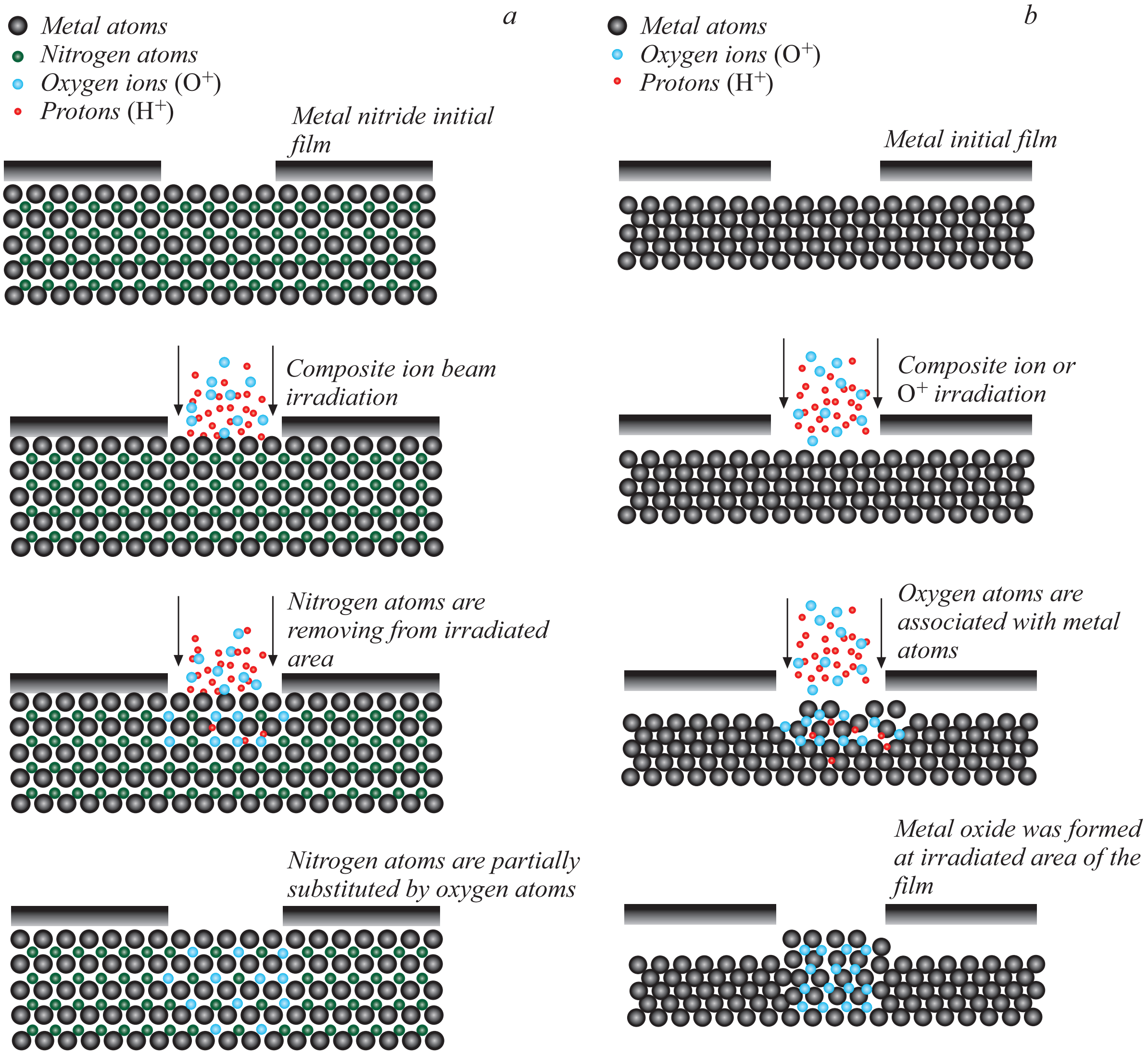

Figure 1. Scheme of processes of the selective change of atomic composition: *a* — nitrogen atoms displacement with oxygen atoms at thin-film niobium nitride irradiation through the mask with the composite beam, consisting of protons and oxygen ions; *b* — atomic compounds during target material irradiation with the composite ion beam or oxygen ions.

spectrum (EELS) [11] by means of scanning transmission electron microscopy (STEM) using transmission electron microscope „Titan 80-300 ST“ (FEI), equipped with spectrometer „GIF-2001“ (Gatan) with electrons energy of 200 keV.

2. Results and discussion

In this study the process of formation of the integrated low-nominal resistance ($\sim 50\,\Omega$) in nanowires of superconducting NbN is observed as an example of application of methods of directional modification of thin-film materials atomic composition under ion beam irradiation for nanostructures making. Integrated resistances are used at building the schemes for cryogenic logical elements.

The scheme of the atoms selective displacement process [2] under composite ion beam irradiation of niobium nitride is presented in Fig. 1, *a*. Thin-film niobium nitride is irradiated through the mask with the composite ion beam, resulting in removal of nitrogen atoms at certain irradiation doses from a target material, substituting with oxygen atoms. As it was shown earlier, after niobium nitride film irradiation with the composite ion beam, consisting of protons and ions of oxygen (or OH^+ ions), to nitrogen doses of $(1-2)$ dpa the partial displacement of nitrogen atoms with oxygen atoms is performed, thus initiating the formation of niobium oxynitride crystalline phase [10], exhibiting the metallic properties at temperature of 4.2 K [4]. Change of the composition and properties of the superconducting niobium nitride was performed by means of irradiation through the mask, formed of electron resist, using electron lithography method. In this study the electron positive resist PMMA was used as mask material.

Fig. 2, *b* shows the superconducting nanowire, formed of niobium nitride film using electron lithography method and the following reactive ion etching, with width of 350 nm. In the middle part the width varies, reaching the value of 6400 nm, which is performed for integrated resistance with low nominal. Large width of nanowire in the place of resistance with low nominal is required to form small number of squares in the area of irradiation, where the normal metal is formed from superconductor.

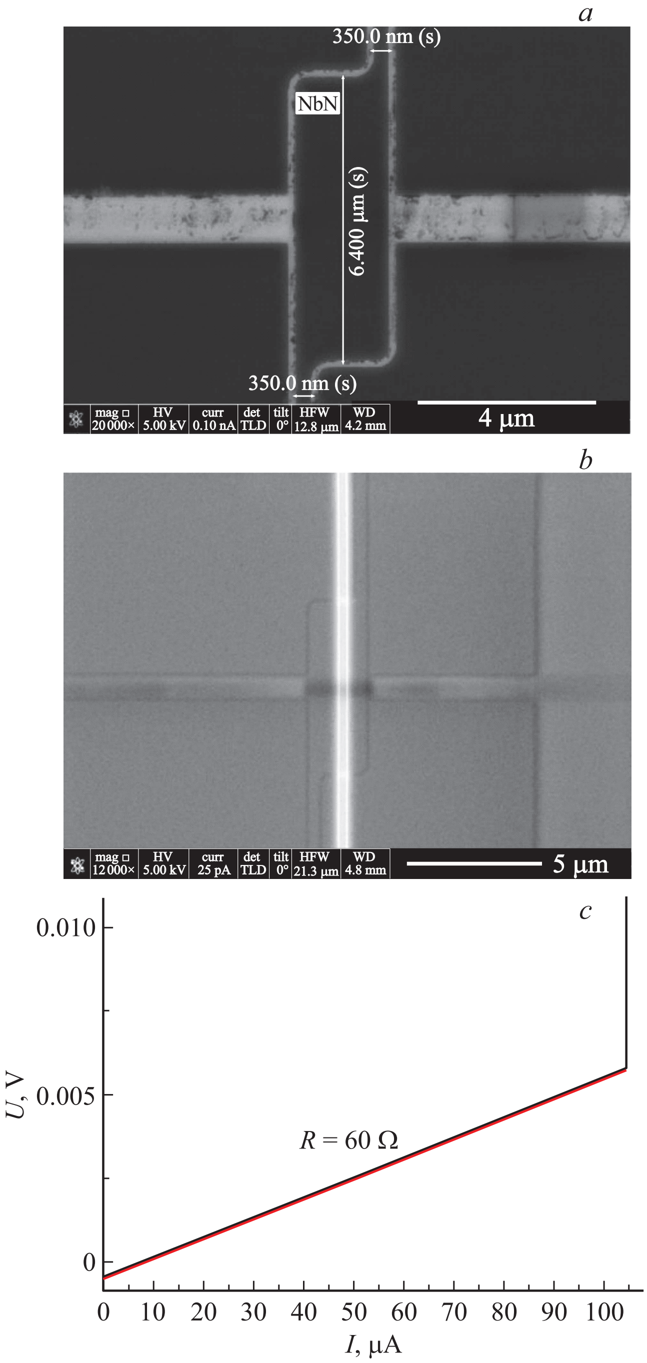

Figure 2. *a* — superconducting nanowire, made of solid NbN film using reactive ion etching through the mask of PMMA, structured by electron lithography method; *b* — mask of PMMA with the formed slot for irradiation at resistance creation; *c* — dependence of electric voltage at nanowire on current, flowing through it.

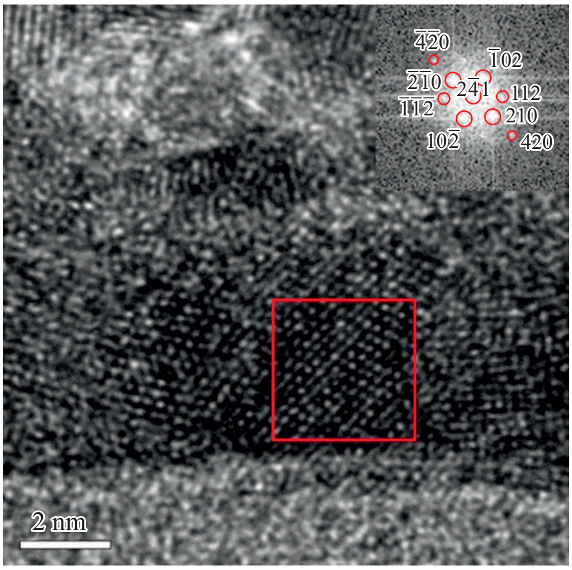

Figure 3. TEM image of resistance material atomic structure after modification under irradiation (NbNO). Insert — Fourier transformation image.

Fig. 2, *b* shows the slot mask for ion beam irradiation. Such combination of small width of a slot in the mask and high width of nanowire in the place of resistance forming allows to create small integrated resistance nominal of 60 Ω (see the volt-ampere characteristic in Fig. 2, *c*).

Fig. 3 shows high resolution TEM image of the film material after irradiation with composite ion beam to nitrogen fluence of ∼ 1 dpa, observed on cross-section sample of nanowire open area after irradiation, prepared using focused ion beam (FIB) method. According to interpretation of atomic grain structure in Fig. 3, after the process of the selective displacement of atoms under irradiation part of atoms was substituted with oxygen atoms, resulting in formation of niobium oxynitride, exhibiting the metallic properties at temperature of 4.2 K.

Another application of the methods of directional modification of materials thin layers under ion beam irradiation is the use of the selective association of atoms (SAA) technology, scheme of which is presented in Fig. 1, *b*: thin metal film is irradiated through the mask with the composite ion beam, after which the oxygen atoms penetrate the target material to a depth of projective range of the light constituent of ion beam (protons), creating a metal oxide. Thus, the thin surface layer of the target is oxidized at irradiation of material with ion beams of mixed composition (protons and ions of oxygen) or monocomposition (oxygen ions). Radiation defects, appeared in material during ion beam irradiation, provide free volume for formation of oxide, that occupies larger specific volume compared to initial metal, and oxygen atoms are directly implanted into material with incident beam energy (irradiation with oxygen ions) or diffuse from implantation area by defects, created by lighter component of ion beam (in case of composite ion beam use — protons). Differences in case of irradiation with mono-ion or composite ion beams are in oxidation rate and in oxidation area depth. As it was shown earlier through example of the radiation-induced oxidation of silicon [2], oxidation depth is defined by value of the whole projective range of oxygen ions in target material (in case of oxygen beam) or value of the whole projective range of protons (in case of composite irradiation).

In this study the radiation-induced oxidation of metallic aluminum under irradiation with oxygen ions with energy of 0.2 keV to dose of $1.3 \cdot 10^{18}\,\mathrm{cm}^{-2}$ was performed. Irradiation of oxygen ions with energy of 0.2 keV allows, on one hand, to prevent from significant effect of sputtering the surface atoms during oxidation, and, on another hand, to perform oxidation to significant depth to provide electrical insulation by means of high quality dielectric forming.

For studying the properties of dielectric, formed under metallic aluminum irradiation with oxygen ions with energy of 0.2 keV, in this study we performed microstructure studies of irradiated samples cross-sections by electrons energy loss spectroscopy using scanning transmission electron microscopy (STEM) Cross-section samples were prepared using focused ion beam (FIB) method. Fig. 4 shows the distribution of atomic concentrations of aluminum and oxygen in terms of irradiated sample depth. As it can be observed in Fig. 4, oxidation depth at this irradiation dose is ~ 15 nm, while ratio of atomic concentrations of the elements corresponds with the limiting aluminum oxide Al_2O_3.

Beside studying the distribution of elements in target depth, the measurements of electrical properties of the formed aluminum oxide film were performed in this study. For that purpose the measurements of volt-ampere characteristics in vertical geometry were performed (Fig. 5, *a*). Since thickness of the film of the radiation-induced oxide *3* is less than thickness of initial aluminum layer, the remaining unoxidized aluminum layer was used as bottom contact *2* during current measurement in vertical geometry. Layer

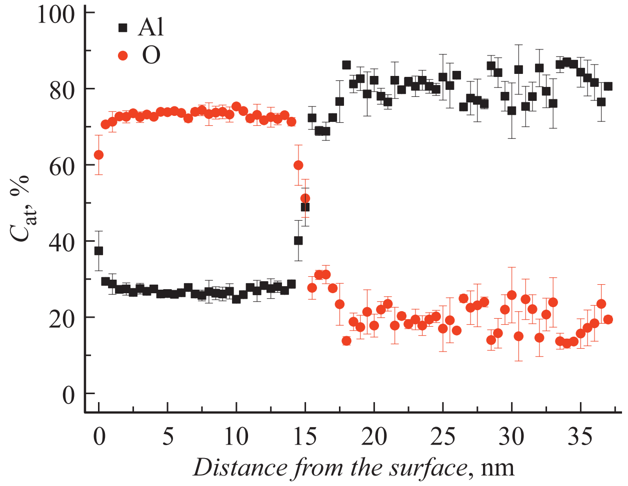

Figure 4. Profiles of distribution of elements (Al, O) in aluminum film depth, irradiated with oxygen ions with energy of 0.2 keV to dose of $1.3 \cdot 10^{18}\,\mathrm{cm}^{-2}$.

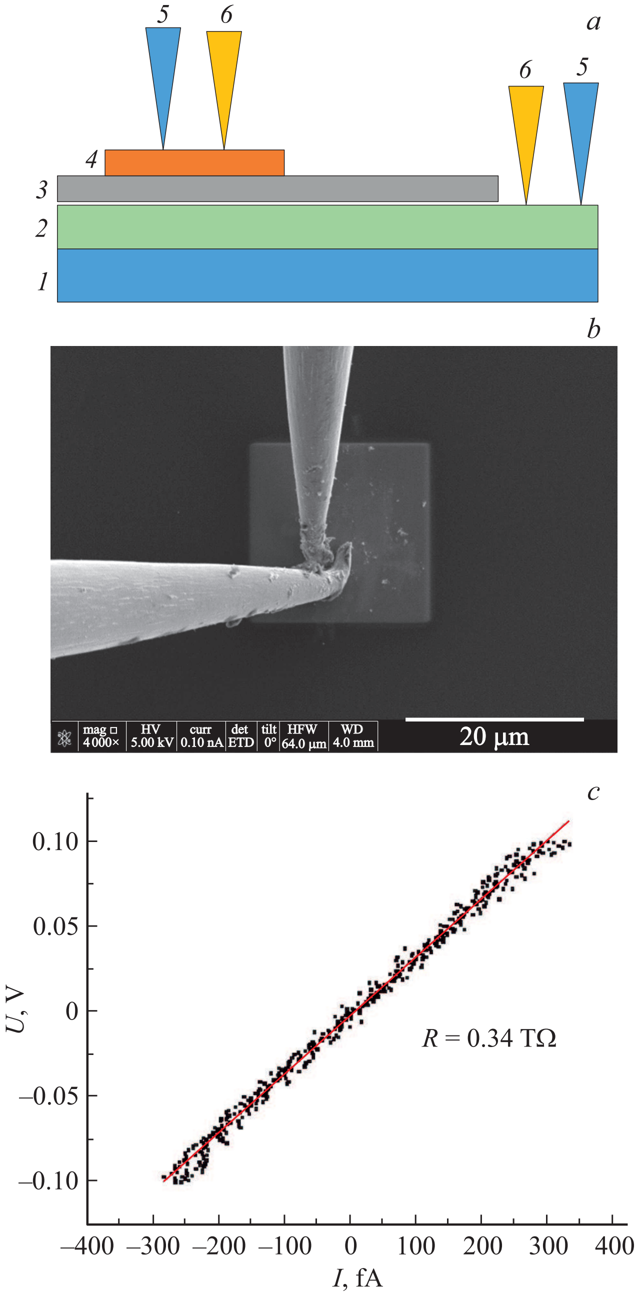

Figure 5. *a* — scheme of measurements of electrical properties of the formed oxide: *1* — substrate, *2* — sputtered aluminum, *3* — aluminum oxide formed under irradiation, *4* — top contact of platinum, sputtered using FIB, *5* — current probes, *6* — voltage probes for four-point measurements performing; *b* — TSM image of the top contact area with measurement probes; *c* — volt-ampere characteristic of the created aluminum oxide, measured in vertical geometry using four-probe method.

of FIB-sputtered area of platinum with dimensions of $20 \times 20\,\mu\mathrm{m}^2$ *4* was used as the top measurement area (also Fig. 5, *b*).

Electrical measurements were performed using four-probe method for reliable signal registration at low measuring currents and for prevention of contact resistances influence. During these measurements the large values of electrical resistance impose restrictions on possible measuring currents, since potential difference, appearing on vertical structure, should not exceed value of dielectric breakdown voltage. According to volt-ampere characteristic in Fig. 5, *c*, at maximum measuring current of 300 fA the voltage on structure reaches 100 mV, i.e. the electric field voltage of 66 kV/cm is slightly below breakdown intensity (250 kV/cm). According to curve slope in Fig. 5, *c* the value of electrical resistance of structure in vertical geometry was defined ($0.34\,\mathrm{T}\Omega$), that corresponds with the specific electrical resistance of $\sim 10^{10}\,\Omega\cdot\mathrm{m}$, exceeding the value of specific resistance of aluminum oxide films, made by conventional methods of anodizing in alkali ($\sim 10^{8}\,\Omega\cdot\mathrm{mm}$) and acid ($10^{7}-10^{13}\,\Omega\cdot\mathrm{mm}$) solutions [12].

Conclusions

Method of selective atomic displacement is demonstrated in the study through the example of low nominal integrated resistance forming from superconducting niobium nitride, irradiated with the composite ion beam through the mask. Mask window geometry provides the correct value of resistance nominal. Application of the method of the selective atomic connection was also demonstrated through the example of dielectric layer creation on conductor surface by means of metallic aluminum irradiation with oxygen ions at room temperature. Measurements of electrical characteristics of the created aluminum oxide were performed and high dielectric properties were observed ($\rho \sim 10^{10}\,\Omega\cdot\mathrm{m}$). Method of materials irradiation through the mask of a certain geometry allows to form the various functional elements (metallic, magnetic, optical, etc.), including of nanometric sizes.

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Conflict of interest

The authors declare that they have no conflict of interest.

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