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Radiation nanotechnology for selective modifications of atomic composition and properties of thin film materials

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Abstract. We have demonstrated using of ion beam irradiation to control the atomic composition and properties of thin film materials by three different ways. Selective removal of atoms (SRA) technique allows us to transform Co_3O_4 to Co. By EELS on cross-section samples in STEM mode it was shown that target depth recovery profile has no monotonic character that proved the radiation nature of SRA process. Selective displacement of Atoms (SDA) technique under oxygen ion irradiation was used to control the critical current of ultrathin superconductive NbN film that can have an implementation during new cryogenic logic device design.

1. Introduction

In National Research Centre "Kurchatov Institute" over the past ten years, we were actively developing radiation nanotechnology to create functional elements of nanometer scale. Due to the impact of low-energy ion beams of different composition (protons, oxygen ions, nitrogen, etc.) at different doses, there is a controlled modification of the atomic composition and physical properties of the selected areas of thin-film materials (insulators, conductors, superconductors). This technology includes three methods of selective changes in the atomic composition of thin films: the method of selective removal of atoms (SRA), the method of selective association of atoms (SAA), and method of selective displacement of atoms (SDA) [1]. The main advantages of these methods are as follows. It is possible to create elements of specified shapes and sizes (minimum size from 3 – 10 nm). It is also possible of parallel transformation of the local composition and properties in different layers of multilayer thin-film structures.

In this paper we consider all three of the above mentioned methods of selective modification of the atomic composition and properties of thin-film materials. Radiation technology of selective removal of atoms (SRA) is presented by the example of removal of oxygen atoms from cobalt oxide Co_3O_4 [2], selective association of atoms by the example of alumina oxidation under oxygen ion irradiation [3], and selective displacement of atoms by the example of NbN thin superconductive film oxygen irradiation [4].

The reduction of cobalt oxide by radiation methods can be used to create a high-density patterned magnetic media (PMM). The formation of a media with a high recording density requires the creation of a special carrier consisting of separate magnetic granules (single-domain bits) with a size of 15 to 30 nanometers of the same size, shape and orientation (pattern magnetic media) [5]. In addition, when creating such structures, it is important to ensure the stability of the magnetization of individual bits



when the external magnetic field is switched off, which can be achieved by creating an antiferromagnetic layer, for example, from CoO along the ferromagnetic Co – bit boundary.

The application of the method of selective association of atoms (SAA) [1] is demonstrated to create a layer of aluminum oxide on the surface of a thin film of metal aluminum [3]. For the realization of radiation-induced oxidation of aluminum the irradiation with oxygen ions of low energy was used. Irradiation-induced high quality oxide can be used as of interlayer dielectric in the formation of the metallization and, on the other hand, to prevent unwanted sputtering of aluminum in the process of ion irradiation. The results obtained in this paper can be used in the creation of electrical insulation of metal conductors as an alternative to the methods of deposition of dielectric layers in traditional microelectronics and nanotechnology. The advantages of this method include precision oxidation of aluminum in depth, high dielectric properties of the resulting aluminum oxide and the ability to reduce the number of technological operations in the process of creating devices.

2. Instruments and experimental techniques

In this work, thin films of Co₃O₄, Al, NbN were irradiated with ion beams of various compositions extracted from a high-frequency (HF) plasma discharge (13.56 MHz). All experiments on irradiation in this work were carried out on a special installation "Copra Cube", the main part of which is the HF plasma source. The subsequent extraction of ions onto the sample was carried out by applying a pulsed HV bias to the table with the fixed sample. The ion beam consisted of protons with an energy of 1 keV and irradiation was carried out in the dose range (0.94-3.75)·10¹⁸ ions/cm² in the SRA process; in the process of SAA samples were irradiated with oxygen ions with energy 0.2 and 0.5 keV in the dose range (0.1-0.4)·10¹⁷ ions/cm² at room temperature; SDA was carried out under irradiation with oxygen ions with energy (0.1–1) keV in the dose range (0.62-6.25)·10¹⁵ ions/cm².

To analyze the degree of modification of films by depth after irradiation, the analytical transmission electron microscopy TEM and STEM techniques were used, the main advantage of the latter is the possibility of local analysis of the chemical composition of cross-section samples. The microstructure, phase composition of the initial and irradiated samples were studied using high-resolution TEM (HRTEM) bright-field images. The chemical composition of the samples was evaluated by electron energy loss spectroscopy (EELS) using GIF-2001 installed at "Titan 80–300ST" transmission electron microscope at an accelerating voltage of 200 kV. The phase composition of individual grains and irradiated samples was determined by diffraction patterns obtained by Fourier transform in the Digital Micrograph from the corresponding high-resolution images. The application of this technique is due to the fact that the analysis of SAD electron micro diffraction patterns obtained directly is difficult due to the blurring of the reciprocal lattice sites for nano-size grains.

The chemical composition of the experimental samples was determined by analyzing the profile spectra of electron energy losses by the method of relative concentrations:

$$\frac{N_A}{N_B} = \frac{I_A(\beta, \Delta)}{I_B(\beta, \Delta)} \cdot \frac{\sigma_B(\beta, \Delta)}{\sigma_A(\beta, \Delta)} \quad (1),$$

where I_A , I_B — the integrated intensity of the peaks under the curve of energy loss after subtraction of the background, and σ_A and σ_B is the cross section of inelastic scattering of atoms A and B for a given collection angle of the spectrometer β [6].

For thin films cross section sample preparation we used the focused ion beam technique on the "Helios Nanolab 650" FIB facility with an accelerating voltage of the Ga ion gun of 30 keV and a current of 2.5 nA and a final thinning of the sample was held at a voltage of 2-5 keV and a current of 0.12 nA.

3. Results and discussion

3.1. Selective removal of atoms

After the proton irradiation of thin films of Co₃O₄ at different fluencies and temperatures the depth profiles of chemical composition of the film were measured out by EELS technique.

To find out the effect of the temperature during irradiation, figure 1 shows the distribution profiles of the elements in depth of the films irradiated to doses of 3.75·10¹⁸ ions/cm² at substrate temperatures

of 20°C and 100°C. It is shown that at a temperature of 100°C film of cobalt oxide at a given dose is reduced to pure cobalt at a depth of 17 nm, in contrast to irradiation at 20°C. This is due to the faster release of displaced oxygen atoms from the sample during the selective removal of atoms from Co_3O_4 under proton irradiation. In addition, it was found that at both irradiation temperatures the target depth recovery profile is no monotonic, due to the no monotonic distribution of the damaging dose during irradiation. The direct correspondence of the cobalt reduction profile to the dose distribution profile at the target depth proves the radiation nature of the process of selective removal of atoms.

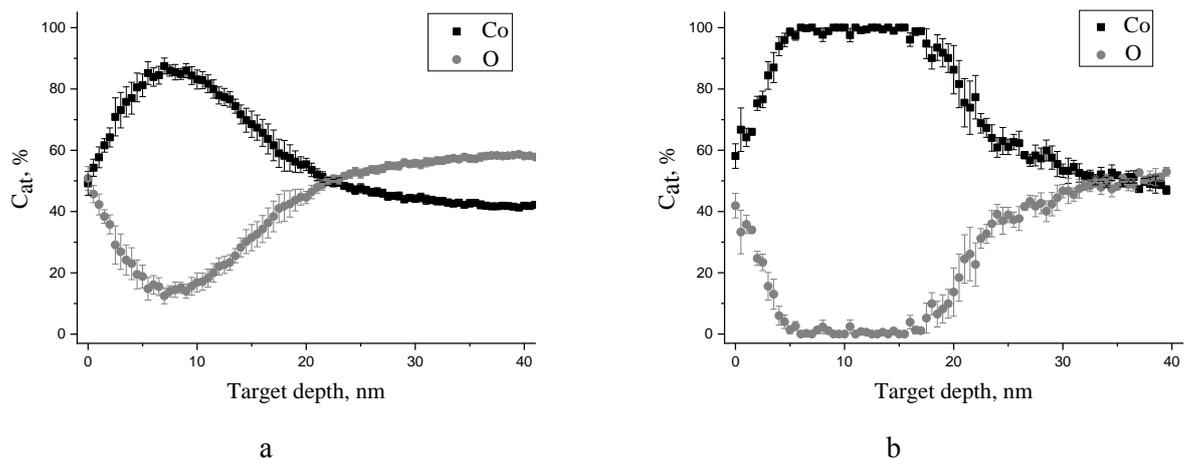


Figure 1. Depth distribution profile of elements in the Co_3O_4 film after irradiation with 1 keV protons (calculated from EELS data) for dose of $3.75 \cdot 10^{18}$ ions/cm² at different temperatures: (a)— 20°C; (b)— 100°C

The analysis of the diffraction patterns constructed by Fourier transform from the corresponding grains on high-resolution images is in full agreement with the EELS data. Figure 2 shows that the grains of the Co_3O_4 film irradiated at a dose of $3.75 \cdot 10^{18}$ ions/cm² at a temperature of 100°C correspond to the phase of pure Co hexagonal symmetry (P63/mmc) with the lattice parameter $a=b=0.2514$ nm, $c=0.4105$ nm.

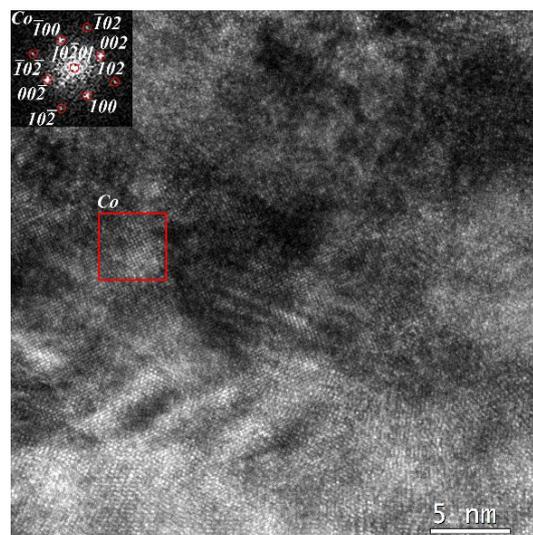


Figure 2. HRTEM image of the Co_3O_4 film cross section sample irradiated with 1 keV protons to dose of $3.75 \cdot 10^{18}$ ions/cm² at a temperature of 100°C, FFT diffraction (inset)

3.2. Selective association of atoms

Figure 3 shows the depth distribution profiles of elements of the aluminum film irradiated with oxygen ions with energy 0.2 keV to a dose of $2.6 \cdot 10^{18}$ ions/cm². As can be seen from figure 3, aluminum oxide is formed to a depth of ~20 nm, and a layer of metal aluminum remains below it. This result confirms the possibility of using the radiation method of aluminum oxidation to create an insulator layer on the metal surface. This is an example of ion beam irradiation implementation for forming an insulator layer at mask open areas on the surface of the sample.

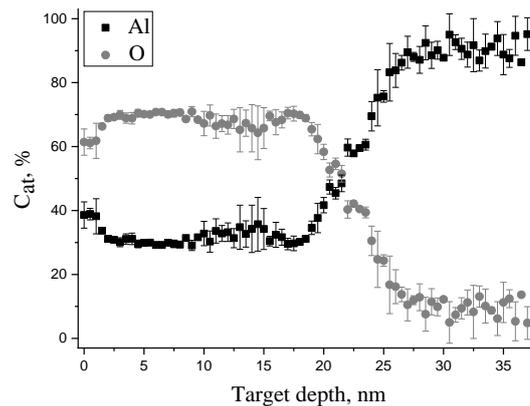


Figure 3. Depth-distribution profile of elements of aluminum film irradiated with oxygen ions with energy 0.2 keV to a dose of $2.6 \cdot 10^{18}$ ions/cm²[3].

3.3. Selective displacement of atoms

From the point of view of the development of a new element base to build low heat and high speed supercomputers, one of the most promising is the use of thin-film superconductors. In this regard, one of the examples of application of the method of selective displacement of atoms (SDA) is the development of a method of controlled reduction of the thickness of the superconducting ultra-thin (5 nm) film of niobium nitride under the low-energy oxygen ions irradiation, based on the replacement of nitrogen atoms with oxygen atoms in the irradiation zone [7]. The depth of radiation-induced replacement of nitrogen atoms with oxygen atoms is determined by the value of the total projective length of oxygen ions in the target material and reaches (2-3) nm at the particle energy (100-300) eV [7].

Figure 4 shows a controlled decrease in the thickness of the thin film of the superconducting NbN as a result of the process of selective displacement of atoms under the low-energy oxygen ions irradiation [7]. Reducing the thickness of the film allows you to change the superconducting properties and opens the possibility of manufacturing functional devices based on these changes.

The most important physical characteristic is the magnitude of the critical current of the superconductor, since the control of the critical current in the required places of the superconductor allows as to create different logic devices.

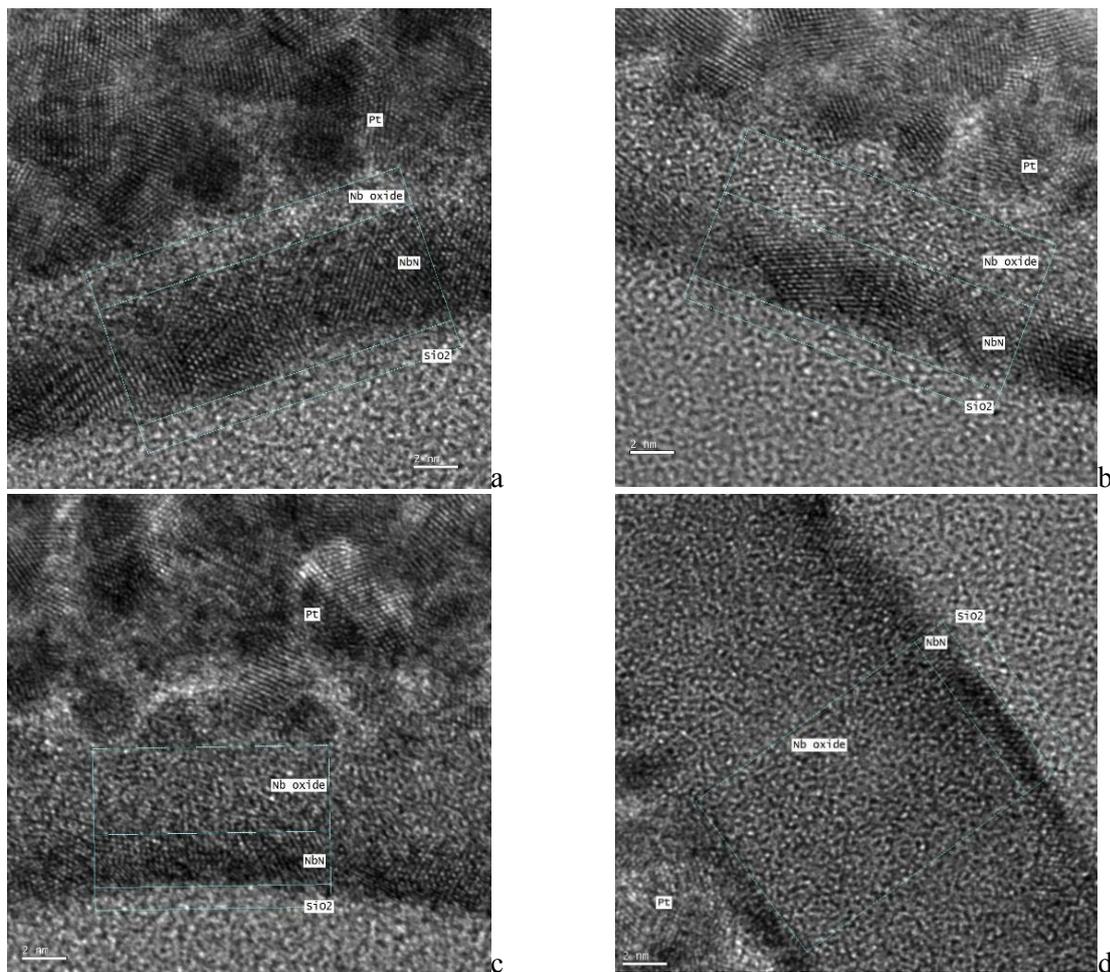


Figure 4. HRTEM images of ultra-thin NbN film irradiated with oxygen ions with low energy at different radiation doses [7].

With an SRA technique, it is possible to make a controlled local change in the critical parameters of NbN thin films: the critical current I_c and the superconducting transition temperature T_c , and to reduce the section of superconducting channel.

In this paper, the creation of areas with suppressed critical parameters (I_c and T_c) was made due to a controlled change in the composition and properties of the original NbN films under the irradiation with oxygen ions with an energy (0.02-0.1) keV in the dose range 0.7-1.8 d.p.a. (for nitrogen) at room temperature.

Forming of structures for electric measurements was carried out by the electron lithography and plasm-chemical etching, in a manner similar to that described in [8]. As samples for research of controlled changing of I_c , the microbridges the sizes of 20x20 μm (see figure 5,a) made using a photolithography method with metal contacts were used.

Cooling was carried out by placing the measuring model, with the sample fixed on the measuring table, in the vessel with liquid helium “STG-40”. The sample was mounted on the measuring table using clamping contacts. Figure 5,b shows the current-voltage characteristics of samples exposed to oxygen irradiation with various doses (for nitrogen).

From the figure 5,b it can be seen that with increasing dose the critical current of transition to the superconducting state drops. Thus, it was shown that oxygen irradiation can be used to control the change in the critical current value of thin-film niobium nitride.

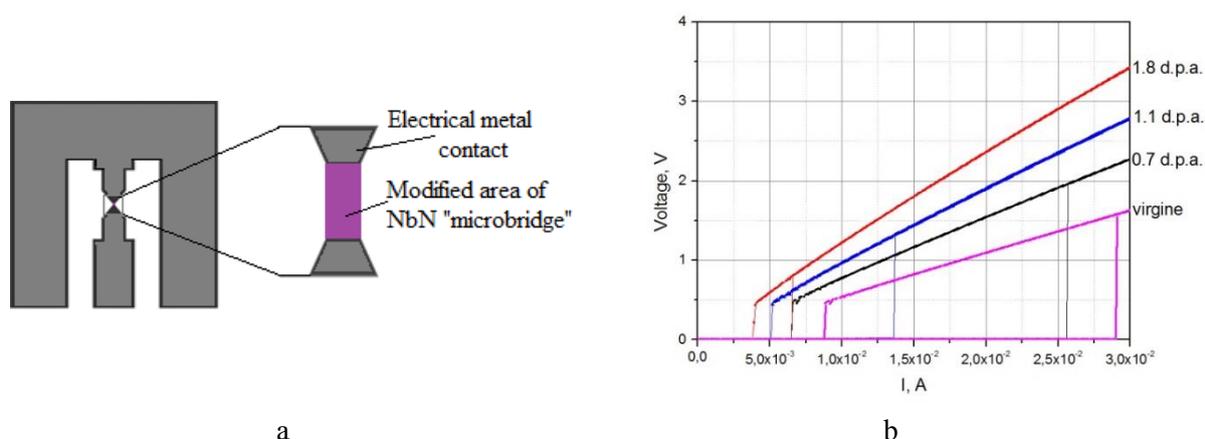


Figure 5. Sample for electrical measurements (top view) (a) and Current-voltage characteristics of samples exposed to oxygen irradiation with various doses (for nitrogen) (b).

4. Conclusion

In this work we have shown the implementation of Selective Removal of Atoms, Selective Association of Atoms and Selective Displacement of Atoms techniques in thin film materials under ion beams irradiation to create different functional nano structures for various applications.

The most important results are as follows. We have shown that the transformation of cobalt oxide to metal cobalt under proton irradiation (SRA) characterized by no monotonic depth recovery character. This is the direct evidence that SRA process has radiation nature and begins at the depth with highest damage density production by ion beam.

Another important result is that we have found the possibility to control the critical current value of the ultrathin superconductive NbN film. This can be used during new generation of cryo- electronic device production.

Acknowledgments

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