IOP Conf. Series: Materials Science and Engineering **130** (2016) 012046 doi:10.1088/1757-899X/130/1/012046

Study of phase transitions in NbN ultrathin films under composite ion beam irradiation

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Abstract. This work demonstrates implementation of Selective Displacement of Atoms (SDA) technique to change the crystal structure and atomic composition of thin superconductive film of NbN under low dose composite ion beam irradiation. All structure investigations were performed using High Resolution Transmission Electron Microscopy (HRTEM) technique by the analysis of Fourier transformation of bright field HRTEM images. It was found that composite ion beam irradiation induces the formation of niobium oxynitrides phases.

1. Introduction

Last years in the area of radio electronics superconducting microelectronics comes to the forefront. The phenomenon of superconductivity is widely used for creation of electronic devices large capacity memory, high-speed digital switches, the highly sensitive radio receiving equipment.

The advantages of the phenomenon of superconductivity in comparison with the most common semiconductor should include lower energy dissipation caused by disappearance of resistance at cryogenic temperatures, as well as faster performance digital devices. This allows the use of superconducting elements as the basic units of electric circuits with a frequency range up to hundreds of GHz.

In accordance with active progress in the physics of thin films, which began after the creation of the microscopic theory of superconductivity Bardeen-Cooper-Schrieffer and development of technological approaches that can generate low-temperature materials, has opened up new prospects for the development of integrated Cryoelectronics.

Niobium nitride (NbN) is one of the most promising materials in the field of low-temperature superconducting electronics to build electronic devices such as bolometers (THz HEB), single-photon counters superconductor (Superconducting Single-Photon Detector, SSPD), quantum devices [1]. This advantage over other materials caused by high strength characteristics, resistance to thermal cycling. Of all the refractory metals NbN has the highest critical temperature of the superconducting transition ~ 14 K.

Today there is the problem of creating technological approaches for the production of nanoscale cryoelectronics elements and improve their quality of basic parameters. In our institute developing many methods of radiation-induced modification of atomic structure, electrical, optical and magnetic properties of materials under irradiation with accelerated particles. The basis of these methods are the mechanisms of selective removal of atoms (SRA), a selective association of atoms (SAA) and

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selective displacement of atoms (SDA) [2, 3]. These approaches allows to create a composite structure with a locally changing the chemical composition and properties of thin film materials by a controlled way.

2. Experiment

Ultrathin films of niobium nitride (NbN) were grown on a mono-crystalline silicon substrate covered with a 0.15 μm amorphous oxide SiO_2 layer by cathode sputtering method using a niobium target controlled gaseous mixture of nitrogen and krypton at an operating vacuum of ~ 10^{-5} Torr. A necessary condition for the growth of film is heated substrate up to temperatures of ~ 800°C [4]. The thickness of the starting film was 5 nm. The critical temperature of the superconducting transition ~12 K [4,5].

Samples were irradiated by composite ion beams extracted from the high-frequency plasma discharge and consisting of oxygen ions and protons [3] with energies (0.1-4) keV in a dose range (1-2) d.p.a. for nitrogen. The ratio of oxygen to hydrogen ion composition in the composite ion beam was monitored by measuring the partial pressures of the residual H_2O component and hydrogen supplied [6]. In our case the beam composition was c = $1.2 \cdot 10^{-3}$. The dose rate of nitrogen atoms displacement was performed using SRIM code [7] and in our case was $2.25 \cdot 10^{-2}$ d.p.a./s.

To studies the microstructure and phase composition of the initial and the irradiated samples were performed using High Resolution Transmission Electron Microscopy (HRTEM) technique at Titan 80-300 electron microscope at an accelerating voltage of 200 kV. Cross section samples $NbN/SiO_2/Si$ were manufactured at the facility FIB Helios Nanolab 650.

The phase composition of individual grains for initial and irradiated films was determined by analyzing the corresponding diffraction patterns. However, because that films were characterized by an ultra-small grain size (~ 5 nm), the analysis of the pictures of conventional electron selected area micro-diffraction pattern was ineffective due to a strong blurring of the reciprocal lattice points.

In this paper for obtaining diffraction patterns were used bright-field high-resolution images of a cross section of films, obtained at magnifications more than x500000. For phase identification the region of interest in the HRTEM image was selected and construction performed by the Fourier transform of the art, for example, in Digital Micrograph program.

Computer calculated Fourier transform of HRTEM image is a complete analogue of the physical picture of micro-diffraction pattern, because the intensity of reflections on an experimental micro-diffraction pattern is proportional to the square of the Fourier transform of the electron density of the study phase.

The procedure for phase identification by pair reflex technique includes the following. In the diffraction pattern defines a set of non-parallel reciprocal lattice vectors $H_{h1,k1,l1}$, $H_{h2,k2,l2}$,…,etc., with indexes (h_1,k_1,l_1), (h_2,k_2,l_2), ..., etc., by measuring the distance from the center of the diffraction pattern to the corresponding reflexes. Interplanar distances for the reflex data d_1, d_2, d_3, ..., etc. calculated as the inverse of the length of the reciprocal lattice vectors: $d_{hkl} = 1/H_{hkl}$. We also defined a set of angles between different reciprocal lattice vectors α_1,, α_2,… α_i.

For phase identification was carried out comparing the experimental values of the interplanar distances and angles between the vectors of the reciprocal lattice with published data for a large number of chemical compounds containing niobium, nitrogen and oxygen in various combinations. In this paper, the identification phase was carried out using X-ray spectra database ICSD PDF-4.

For the phase analysis the correspondence between measured and database interplanar distances were compared. Then we calculated all the possible angles between the crystallographic planes ($h_1k_1l_1$) with interplanar distance d_1 and ($h_2k_2l_2$) with interplanar distance d_2. During angles calculations we took into account the symmetry elements in each family set for a given syngony. If there was a match between both the lattice parameters and all angles for the experimental and calculated diffraction pattern from the database, then concluded the successful identification of this phase was found.

Such an approach allows us to determine the phase composition of the films with nano-sized grains in the initial state and also after composite ion beam irradiation to the different doses.

3. Results and discussion

The objective of research was an experimental study of the evolution of structural-phase state of thin superconducting films NbN, irradiated by composite ion beams by using a high-resolution bright field TEM images. It is well known [4], the irradiation of thin films of superconducting niobium nitride by composite ion beams causes a reduction in the superconducting transition temperature and increasing resistance of the film in a wide temperature range from 4.2 K to 300 K.

Typical HRTEM image of a cross section of the starting niobium nitride film on a substrate of amorphous silicon oxide is shown in Figure 1. As seen in Figure 1, after the deposition the niobium nitride film has a polycrystalline structure with a grain size of (4-5) nm. If different grains of polycrystalline films are differently oriented to the electron beam, a contrast with the image of the atomic planes for them is significantly different. The most successful and sophisticated are the images of the grains, the orientation of which corresponds to a slight deviation angles between crystallographic zone axis of the grain and incident electron beam direction. According to the pair reflexes technique we must have as big numbers of pairs of different reflections as possible. To get these conditions we selected grains oriented with crystal zones along the electron beam for analysis. An example of such grain is shown by isolated square in Figure 1.

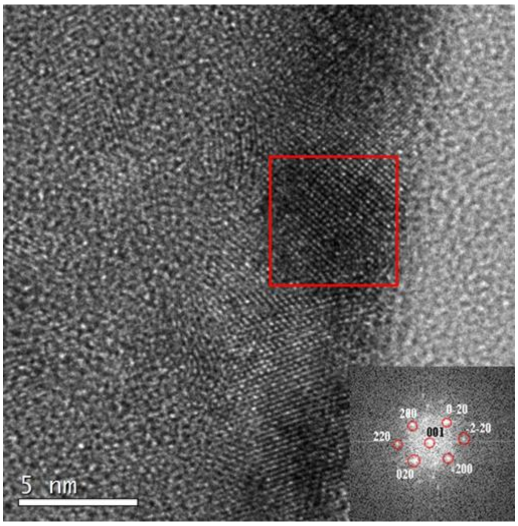

Figure 1. Bright-field HRTEM image of the cross section of the film NbN, synthesized on a substrate of SiO_2, diffraction (inset).

An analysis of the diffraction pattern in Figure 1 shows that grain starting material corresponds to the phase NbN cubic system (Fm-3m) with the lattice parameter a = 0.4394 nm.

By increasing the dose to ~1 d.p.a. for nitrogen observed change in the phase composition of the grains, as shown in Figure 2. The analysis of pictures of high resolution to grains in Figure 2 showed the formation of the monoclinic phase NbNO (P21/c(14)) with unit cell parameters a=0.4977 nm, b=0.50217 nm, c=0.52053 nm, $\alpha = \gamma = 90$ °, $\beta = 100$ °.

A further increase of the radiation dose up to ~(1.5-2) d.p.a. for nitrogen showed the formation of individual grains of $NbN_{0,64}O_{1,36}$ phase monoclinic (P21 / c (14)) with unit cell parameters a=0.49808 nm, b=0.50250 nm, c=0.52097 nm, $\alpha = \gamma = 90$ °, $\beta = 100°$. Together with grains of $NbN_{0,64}O_{1,36}$ phase under dose of ~(1.5-2) d.p.a. we also observed above mentioned NbNO phase grains (Figure 3).

It should be noted that closeness of the unit cell parameters of niobium oxynitride phases NbNO and $NbN_{0,64}O_{1,36}$, allowing to talk about their semi-identical atomic structure. At the same time the ratio of oxygen atom numbers to the nitrogen atom numbers in the latter phase is higher than the first. The increase in the proportion of oxygen atoms with increasing radiation dose reflects the general tendency of flow selective displacement of atoms (SDA) process.

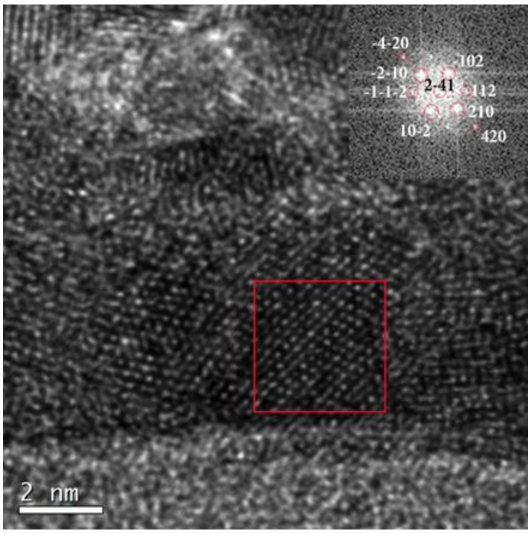

Figure 2. Bright-field HRTEM image of a cross section of the irradiated NbN film at a dose of ~1 d.p.a. for nitrogen, diffraction pattern (inset).

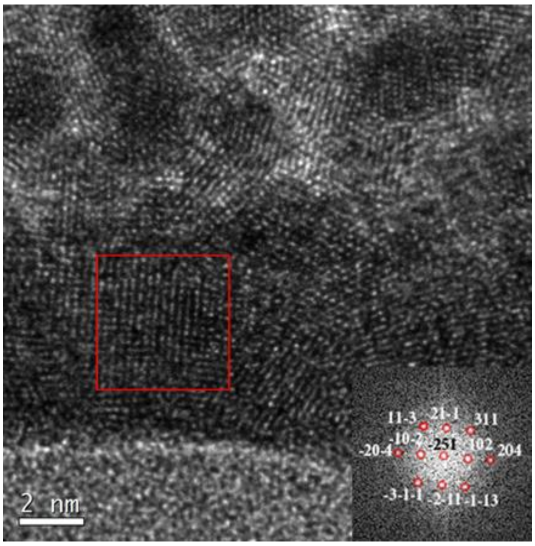

Figure 3. Bright-field HRTEM image of a cross section of the irradiated NbN film after composite irradiation to a dose of ~(1.5-2) d.p.a. for nitrogen, diffraction pattern (inset).

It should also be noted that delivery of oxygen atoms from the composite beam during irradiation remains approximately constant, while in terms of phase transformations of initial NbN to niobium oxynitrides it is not possible to implement the "continuous" phase transformation of the structure since there are only a fixed number of niobium oxynitride phases “available”.

For this reason, it is expected that in the region of existence a certain phase of a niobium oxynitride, for example NbNO, within a certain range of irradiation doses the concentration of oxygen in it will grow, and besides part of the oxygen atoms will be in the lattice interstitial positions. The formation of the next phase will take place only when there is a phase for it with the respective intermediate atomic composition, for example, $NbN_{0,64}O_{1,36}$ in this case. If the crystalline phase with a suitable atomic structure does not exist, it should be expected to increase the distortion of the crystal lattice with increasing radiation dose due to the increase of the concentration of interstitial oxygen atoms, up to a total loss of crystallinity, and form an amorphous film.

4. Acknowledgments

The authors thank Stolyarov V.L. and Olshansky E.D. for the production of the original films of niobium nitride, Komarov D.A. for carrying out experiments on ion irradiation, and Kutuzov L.V. for making the cross-sectional samples. The work was supported by the Ministry of Education and

Science of the Russian Federation - Agreement on Subsidies № 14.607.21.0005 (project code RFMEFI60714X0005) under the Federal Program "Research and development on priority directions of scientific-technological complex for 2014-2020."

5. Conclusions

By methods of high resolution transmission electron microscopy were studied changes in the phase composition of ultra-thin films of superconducting niobium nitride as a result of the process of selective displacement of atoms under the influence of composite ion beam irradiation. It was shown that the composite ion beam irradiation of initial NbN film to doses (1-2) d.p.a. for nitrogen initiated the formation of niobium oxynitride phases NbNO and $NbN_{0,64}O_{1,36}$ of monoclinic crystal system while maintaining the polycrystalline structure of the film.

Acknowledgements

This work was performed within the framework of the Center of Nuclear Systems and Materials supported by MEPhI Academic Excellence Project (contract № 02.a03.21.0005, 27.08.2013).

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