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Investigation of radiation-induced transformations in thin NbN films by analytical electron microscopy

K Prikhodko[1, 2], B Gurovich[1], M Dement'eva[1], L Kutuzov[1] and D Komarov[1]

[1]National Research Centre "Kurchatov Institute", Kurchatov sq.1, Moscow, 123182, Russia
[2]National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Kashirskoe highway, 31, Moscow, 115409, Russia

E-mail*:* prihodko_ke@nrcki.ru

Abstract. This work demonstrates implementation of low energy electron energy loss technique (EELS) in scanning transmission electron microscopy (STEM) to investigate the changes of free electron density at room temperature in ultra-thin NbN films under composite ion beam irradiation up to the deses of ~3 d.p.a. for nitrogen atoms. It was found the constant value of the free electron density ~$1.6\cdot10^{29}$ m^{-3} in this dose range while the irradiated material was characterized by metal type of electrical conductivity.

1. Introduction

Last years in the area of cryo-electronics based on superconducting materials comes to the forefront. Nowadays the superconductivity is widely used for radio-frequency electronic devices, high-speed digital switches, the highly sensitive radio receiving equipment. One of the main advantages of the superconductivity are low power consumption and high frequencies of operation.

Niobium nitride has been widely studied because of the high transition temperature and critical current values [1-3]. The main aim of the well-known experiments of irradiation influence on NbN was to understand the nature of high resistance to radiation damage of this material under neutron irradiation [4]; and to study the effects of ion irradiation on its superconducting properties [5]. It have been shown that fast neutron irradiation of NbN films up to the fluence of $1.5*10^{20}$n/cm^2 decreased the transition temperature by ~6% only [4]. This high resistance to radiation damage was attributed to the highly defective nature of the NbN films [4]. At the same time high energy ion irradiation of NbN films by 200 keV Ar^+ [5] and 350 keV Ne^+ [6] ions showed the larger transition temperature reduction due to the damage production. It was found [6] that the radiation-induced resistivity changes saturate at increases after damage value more than 1 d.p.a. per target atom.

Nowadays niobium nitride is one of the most promising materials in the field of low-temperature superconducting electronics to build electronic devices such as bolometers (HEB), superconducting single-photon detectors (SSPD), quantum devices [7].

We are developing the radiation-induced transformation of the thin film niobium nitride to change the electrical properties under low energy ion beam irradiation [8]. We performed the composite ion beam irradiation [9, 10] to get metal type of electrical conductivity of ultra-thin (5nm) NbN films at 4.2 K[11].

Ultra thin NbN superconductive films structure being modified under low energy ion beam irradiation needs to be characterized by the local technique that can provide high spatial resolution together with analytical signal to find out radiation-induced changes in the atomic content of the film. For this purpose, we used analytical STEM techniques on the cross-section samples of the films.

The main task of the present work was to apply low energy loss electron spectroscopy to investigate the free electron density at room temperature changes under composite ion beam irradiation up to the doses of ~3 d.p.a. for nitrogen atoms.

2. Experiment

Ultrathin niobium nitride films with thickness of ~5 nm were deposited by sputtering niobium target by nitrogen ions on the oxidized (~0.15 m amorphous SiO_2) monocrystalline silicon substrate heated to a temperature of about ~800^{o}C [8]. Thus created NbN film characterized by a high superconducting transition temperature of about 12 K and a critical current density of ~$5{\cdot}10^6$ A/cm^2 at 4.2 K.

Samples were irradiated by composite ion beams extracted from the high-frequency plasma discharge and consisting of OH ions and protons [9,10] with energies (0.1-1) keV in a dose range (1.6-3) d.p.a. for nitrogen. The ratio of OH ions to hydrogen ones in the composite ion beam was monitored by measuring the partial pressures of the residual H_2O component and hydrogen supplied [9,10]. In our case the beam composition was c = $1.2\cdot10^{-3}$. The dose rate of nitrogen atoms displacement was performed using SRIM code [12] and in our case was ~0.02 d.p.a./s.

Analytical Transmission Electron Microscopy investigations were performed in STEM mode to get highest spatial resolution together with the detecting of inelastic electron energy loss signal at “Titan 80-300ST” electron microscope at an accelerating voltage of 200 kV. Cross section of the virgin and irradiated samples were made at the Focusing Ion Beam facility “Helios Nanolab 650”.

STEM mode was very attractive to perform the chemical elements depth-distribution analysis at cross-section samples, because of the small size of electron probe (~0.14 nm) that the elements distribution profiling of the irradiated ultra-thin film was available.

Electron Energy Loss Spectroscopy (EELS) was used to get analytical information from the thin sample area under electron probe focus. Together with the standard elements relative distribution technique [13] we used low energy loss plasmon peak analysis [14]. The energy of plasmon peak $E_p$was defined [14]:

$$E_p = \frac{h}{2\pi}\omega_p = \frac{h}{2\pi}\sqrt{\frac{ne^2}{\varepsilon_0 m}}, \tag{1}$$

where h – Plank’s constant; ε_0 – permittivity of free space; ω_p – plasmon frequency; n– free electron density; e and m – electron charge and mass. Because of the strong influence of the ion irradiation on the electrical properties of the thin NbN film [11], it was important to find out the dependence of free electron density on the dose of composite ion beam irradiation.

3. Results and discussion

Figure 1 shows the plasmon peak energy loss spectra for NbN virgin samples and for samples irradiated by composite ion beam up to doses 1.6 and 3 d.p.a. The intensities of spectra on Figure 1 was normalized by the intensity of the last plasmon peak at ~45 eV. One can use the highest peak on Figure 1 (at ~24 eV, indicated by arrow) to calculate the materials free electron density.

From the shape of the curve on Figure 1 it was obvious the presence of the small first peak at energies ~15 eV, that was lower than the energy of the main plasmon peak. This first peak fitting results indicated on Figure 1 by dotted line. Because the free electron excitations were attributed to the smallest value of electron energy loss, to our opinion, this first peak must be used to calculate the free electron density using equation (1).

Calculations of the value of the free electron density using the first peak at ~15 eV yielded a value of $1.6\cdot10^{29}$ m^{-3}, while using a main plasmon peak at ~24 eV yielded a value of $4\cdot10^{29}$ m^{-3}. The comparing of these densities with the literature data for NbN showed that the first value is closer to the literature one $n_e \cong 2\cdot10^{29}$ m^{-3} [15]. Arguments: 1) that the plasmon excitations correspond to minimum electron energy loss and 2) that the experimental free electron density, calculated from the first peak position, was close to the literature data were the basis for selecting this first peak as the main one in this work.

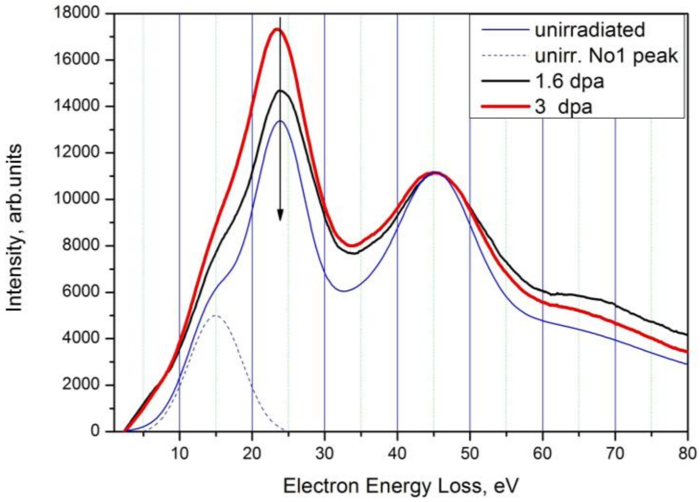

Figure 1. Low energy electron loss spectra for virgin sample and after irradiation up to 1.6 and 3 d.p.a. Dotted line indicates the position of the first peak for virgin sample with lowest energy. Arrow shows the position of the maxima of the curve for virgin sample.

Table 1 shows the experimental results of energy position of the first peak dose dependence. We can see the that up to doses of ~3 d.p.a. the energy position of the first peak did not change significantly and the error was attributed to the energy dispersion of the EELS spectrometer and accuracy of zero-loss peak position determination. The stable value of free electron density suited with the metal type of electrical conductivity for low dose (1.8-9 d.p.a.) irradiated samples [11].

During study of elements concentration evolution under composite ion beam irradiation was shown [16] that the functional conductive part of the film was transformed to the NbNO oxynitride at the range of doses ~(1-4) d.p.a., while the layer close to the irradiated surface of the sample became more oxidized due to the higher degree of nitrogen atoms substitution by oxygen atoms. In spite of this more oxidized upper layer did not take part in electrical transport of the film, we put to Table 1 the value of the first peak position to demonstrate its shift towards zero. This shift was corresponded to the decrease of free electron density on the way of superconductor-metal-insulator transformation under composite ion beam irradiation.

Table 1. Experimental energy position if the first energy loss peak and corresponded free electron density for different doses.

Dose, d.p.a.	E_1 (eV)	n_e, $\cdot10^{29}$ (m^{-3})
0	15.0±0.1	1.62±0.05
1.6	15.1±0.1	1.64±0.05
3	15.2±0.1	1.67±0.05
Top oxidized layer	14.5±0.1	1.51±0.05

In the future investigations we are going to use this low energy electron loss spectra analysis up to high doses of composite ion beam irradiation to characterize the transformation of niobium nitride to niobium oxide from the point of EELS technique in comparing with the electrical properties measurements.

4. Conclusions

By methods of low electron energy loss (EELS) in scanning transmission electron microscopy (STEM) were studied changes of the free electron concentration on the ultra-thin NbN films under composite ion beam irradiation to different doses. It was found the first peak in EELS spectra at the energy ~15 eV and corresponded free electron density $\sim 1.6 \cdot 10^{29}$ m^{-3} at room temperature. It was shown that composite ion beam irradiation up to dose of ~3 d.p.a. did not significantly change the free electron density of the functional layer.

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