Creation of ultrathin niobium nitride films at temperatures less than 100 °C

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Abstract. Thin NbN films were synthesized by a method of magnetron sputtering of solid Nb targets by nitrogen ions at temperatures less than 100 °C on substrates of the sapphire. The dependences of electrical resistance of films on the temperature in range 4.2 K–300 K were measured. Volt-ampere characteristics and critical current density vs film thickness of films were made at a temperature of 4.2 K. The microstructure and film-depth chemical composition of thin films were investigated by analytical methods of the transmission electronic microscopy (HRTEM, EELS) on a cross-section samples made by the FIB technique. HRTEM and EELS study showed the Nb0.84N phase and poly-crystal structure of niobium nitride films. It was found that the critical current density falls down by an order of magnitude when the film thickness was less than 4 nanometers.

1. Introduction

Ultrathin superconducting NbN films synthesis at low temperatures is relevant for the tasks that are associated with the manufacturing of multilayer structures containing a large number of nanoscale functional elements.

High temperatures (800–1000 °C) of the substrate during deposition are common for producing ultrathin NbN films, with superconducting properties at cryogenic temperature [1,2]. Thus creating a large number of functional nanoscale elements in every layer faces with the problem of maintaining properties. Deposition of each layer anneals all of the underlying. In this work we present the methods of manufacturing NbN films, produced at temperatures that are close to room temperature, with properties comparable to films, produced at temperatures of 800 °C and higher.

2. Materials and Experimental Methods

Thin films of NbN (thickness 3.75 – 7 nm) were produced using cathode and magnetron sputtering techniques at a substrate temperature of~100°C. Monocrystalline sapphire substrates were used.

The “microbridges” with the sizes of 20x20 μm, and nanowires of different geometry were used as samples for electrical measurement. Structures for electrical measurements were fabricated by photolithography and plasma-chemical etching in a manner similar to that described in [3]. Figure 1
shows the SEM image of the experimental samples used for electrical measurements. The metal Ni(50nm)/Pt(20nm) measuring contacts were made by cathode sputtering technique (Figure 1b).

![SEM image of nanowire and NbN microbridge with Ni/Pt contacts.](image)

**Figure 1.** (a) SEM image of nanowire and (b) NbN microbridge with Ni/Pt contacts.

Samples were cooled by placing them in a liquid helium. Measurements of temperature dependences of resistance were performed in a temperature interval from 4.2 K to 300 K at direct measuring current 100°CµA. “4-wire” measure method was used. I(V) characteristic were measured at temperature 4.2 K using a Keithley-4200SCS parameter analyzer. Critical current densities were calculated using equation:

\[ j_c = \frac{I_c}{S} \]  

where \( I_c \) — direct critical current, \( S \) — sample cross-sectional area.

In this work we used transmission electron microscopy HRTEM for phase analysis and STEM coupled with electron energy loss spectroscopy (EELS) technique to characterize the elements depth distribution. Transmission electron microscope “Titan 80-300ST” operated at 200KV, equipped with a GIF-2001 energy loss spectrometer was used. The EELS profiles were collected with an energy dispersion of 0.5eV/ch and 2 s dwell time, convergence angle \( \alpha \) was 10°mrad and collection angle \( \beta \) was 14.85°mrad. A cross-section samples NbN/Al₂O₃ were prepared by Focusing Ion Beam (FIB “Helios Nanolab 650”) technique. Determination of phase composition in the initial samples was performed by the Fourier transform diffraction pattern obtained from the corresponding high-resolution transmission electron microscopy (HRTEM) image similar to the method used in the work [4].

3. Results and Discussion

It was shown by HRTEM investigations that the structural state of initial ultrathin NbN films were polycrystalline. Phase analysing data is demonstrated on figure 2(a). It was established that phase composition of individual grains corresponds to the R-3m rhombohedral Nb₀.₈₄N phase with cell parameters: \( a=b=2.985 \) Å, \( c=23.843 \) Å.

Quantitative analysing data were completely consistent with results of phase composition studies. Figure 2,b shows depth profile distribution of Nb, N, O atomic concentrations, calculated according to the EELS data. Increased nitrogen content in superconducting thin films were observed during magnetron sputtering at low temperatures. Phase analysis demonstrated that atomic concentration of nitrogen atoms in Nb₀.₈₄N phase corresponded to 55 at.%. According to the EELS analysis results this...
the average nitrogen content was (64 ± 3) at.% (see fig.2,b). Increasing of oxygen concentration at the film surface was owing to oxidation film after sputtering. Thus the total film thickness was ~4 nm, and the effective superconductive Nb$_{0.84}$N film thickness was ~ (3 – 3.5) nm.

Figure 3 shows sheet resistance $R_{sq}(T)$ dependence for NbN films of different thickness. Value of superconducting transition temperature gets to a presumable interval (6 – 11) K.

The dependence of critical $T_c$ temperature for the various thicknesses of NbN films on the film thickness is presented in Figure 4.a. It was shown that at thickness lower than 3.75 nm there were no superconductivity at 4.2 K liquid helium temperature. Current density vs film thickness is presented on
figure 4,b and it is comparable with NbN films produces at high temperatures. When the film thickness is less than 4 nanometers, the critical current density falls by an order of magnitude.

![Figure 4](image)

(a) Dependence of $T_c$ vs film thickness b) Critical current density calculated from $V(I)$s for different film thicknesses.

4. Conclusion
Thin NbN films were synthesized by the method of magnetron sputtering of solid Nb targets with nitrogen ions at room temperature on mono-crystal sapphire substrates. HRTEM and EELS investigations showed that niobium nitride film obtained at room substrate temperature was $\text{Nb}_{0.84}\text{N}$ phase and characterized by poly-crystal structure.

The measured dependences of electrical resistance of films on the temperature in the range 4.2K – 300K showed a typical trend for thin superconducting films. The received volt-ampere characteristics at a temperature of 4.2K allowed to calculate the values of critical current density for the films and also its dependence on the total thickness of NbN. The high density of critical current at a total thickness $\sim$7 nanometers indicates wide range of application for NbN films produced at room temperature in the field of cryogenic nanotechnologies, and multilayer applications.

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References
[1] Gurovich B A, Tarkhov M A, Prikhod’ko K E et al. 2014 Controlled modification of superconducting properties of NbN ultrathin films under composite ion beam irradiation Nanotechnologies Russ. 9 386–390.
[2] Gurovich B A, Prikhodko K E, Tarkhov M A et al. 2015 Investigation of the Mechanism of Conductivity of NbN Thin Films, Modified Under Composite Ion Beam Irradiation Micro Nanosyst. 7 (3) 172–9
[3] Gurovich B A, Prikhod’ko K E, Dement’eva M M et al. 2015 The use of ion irradiation for converting superconducting thin-film NbN into niobium oxide $\text{Nb}_2\text{O}_5$ Nanotechnologies Russ. 10 (7–8) 530–6
[4] Prikhodko K E, Gurovich B A, Dement’eva M M 2016 Study of phase transitions in NbN ultrathin films under composite ion beam irradiation IOP Conf. Ser. Mater. Sci. Eng. 130 1–5