Creation of thin superconducting MoCN thin film by cathode sputtering technique as a basic material for functional cryogenic nanoelements

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Abstract. Thin MoCN films were synthesized by a method of cathode sputtering of mosaic Mo-C targets by nitrogen ions at temperature of 800°C on substrates of the oxidized silicon. The temperature dependences of electrical resistance of the films in the range of 4.2–300 K were measured. Volt-ampere characteristics of the films and critical current density vs film thickness were obtained at a temperature of 4.2 K. The microstructure and film-depth chemical composition profiles of thin films were investigated by analytical techniques of the transmission electron microscopy (HRTEM, EELS) on a cross-section samples made by the focused ion beam (FIB). It was established that MoCN thin film at a thickness of 8 nm contained MoC and Mo₅N₆ layers. The high density of critical current in these films indicated prospects of their application in the field of cryogenic nanotechnologies.

1. Introduction

At present, studies of thin superconducting films as a basis for nanoscale electronic devices such as superconducting single-photon detectors (SSPD), hot electron bolometers (HEB), and other nanodevices are of great interest in connection with high values of critical current densities (3-6 MA/cm²) and relatively high superconducting transition temperatures (12-14 K). Nowadays, different types of thin film superconductive materials, for instance NbN, are used to build up SSPD and HEB devices. However, with the rapid development of cryoelectronics, one needs to search for new materials.

The literature contains data on a possibility of MoCN thin films deposition by a cathode sputtering technique, in which X-ray diffraction peaks from phases of molybdenum carbide and molybdenum nitride were found [1]. In this regard, thin films of MoCN were found to be a prospective material for the formation of functional cryogenic nanodevices, because carbides and nitrides of molybdenum were showing superconducting properties with a critical temperature of superconducting transition of about 10-14 K [2].

2. Experimental

Samples of molybdenum carbon and nitrogen (MoCN) thin films were prepared by cathode sputtering of mosaic Mo and C target on oxidized (~0.15 µ amorphous SiO₂) monocrystalline silicon substrate. The temperature of a substrate was 800°C. The thickness of the initial films was in the range of 4-12 nm.
Figure 1. Scheme of the sample for electrical measurements with 20x20 $\mu$m$^2$ MoCN microbridge.

The phase and chemical composition of the thin MoCN film were studied using the “Titan 80-300 ST” transmission electron microscope, operated at 200°kV, equipped with a GIF-2001 electron energy loss spectrometer (EELS). The EEL spectra were obtained with an energy dispersion of 0.5°eV/ch, convergence angle $\alpha$ was 10°mrad and collection angle $\beta$ was 14.85°mrad. A cross-section samples MoCN/SiO$_2$/Si were prepared by Focusing Ion Beam (FIB “Helios Nanolab 650”) technique.

Quantitative EELS analysis of relative atomic concentrations of A and B elements was carried out using equation:

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

where $I_A$, $I_B$ – integrated intensities of the EELS peaks after background subtracting, and $\sigma_A$ and $\sigma_B$ – ionization cross sections [3]. Determination of the phase composition in the initial samples was performed by the Fourier transform diffraction pattern obtained from the corresponding HRTEM image similar to the method used in Ref. [4].

Formation of structures for electrical measurements was performed by photolithography and plasma-chemical etching, in a manner similar to that described in Ref. [5].

For electrical measurement, the microbridges with the sizes of 20x20 $\mu$m$^2$ were used (Fig. 1).

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

$$j_c = I_c / S,$$

where $j_c$ – critical current density, $I_c$ – direct critical current, $S$ – sample cross-sectional area.

Figure 2. (a) Elements depth distribution profiles of the MoCN thin film in initial state, calculated according to the EELS data, (b) HAADF STEM image.
3. Results and discussion

Structural studies showed that MoCN film was multilayer. Figure 1a shows depth profile distribution of Mo, C, and N atomic concentrations, calculated according to the EELS data. The total film thickness was 8 nm. In this case, MoCN films were bilayer and consisted of a layer of nitrogen atoms (region 1 in Fig. 2a) and a layer of Mo and N atoms only (region 2 in Fig. 2b). In obedience to the EELS studies results, the thickness of the upper layer (layer 1) was 3.5 nm and that of the lower one (layer 2) being close to the SiO$_2$/Si substrate was 4.5 nm. The corresponding contrast was observed on STEM dark-field image of the Pt/MoCN/SiO$_2$/Si cross-section structure. The MoCN thin film layers are labelled 1 and 2, similarly to Figure 2a.

Quantitative analysis data were completely consistent with the results of phase composition studies. Phase analysing data are shown in Figure 3. It was established that phase composition of individual grains corresponded to the P63/mmc hexagonal MoC phase with cell parameters: $a=b=2.932 \text{ Å}$, $c=10.97 \text{ Å}$ and the P63/m hexagonal Mo$_5$N$_6$ phase with cell parameters $a=b=4.8924 \text{ Å}$, $c=11.0643 \text{ Å}$.

Figure 4 shows $R(T)$ dependence for MoCN film, and it is typical for a superconducting thin film. The value of superconducting transition temperature $T_c$ gets to a presumable interval $7-11 \text{°K}$. One can see a small additional down step of $R$ at a temperature of approximately $2 \text{°K}$ below $T_c$ for all layers.
characteristic curves (Fig. 4). It was apparently due to the superconducting transition of a MoCN film under the measuring contacts (MoCN-Ni/Pt) as a result of proximity effect of superconducting suppression by the normal metal at the interface.

The dependence of critical temperature $T_c$ for the various thicknesses of MoCN films on the film thickness is presented in Figure 5. The value of $T_c$ for film thickness 4 nm in Figure 5 was evaluated by the trend of $R(T)$ to fall down just above the transition temperature, because the full superconducting transformation did not appear at this thickness due to the 4.2 K liquid helium temperature limitation.

It is clear that at total MoCN film thickness of 4 nm and lower there is no superconductivity at the temperature of liquid helium.

Figure 6a shows the V(I) characteristic for MoCN film thickness of 12 nm (microbridge 20x20 $\mu$m$^2$). Figure 6b shows the dependence of critical current density on the total MoCN film thickness which is comparable with corresponding value for NbN films [6].

4. Conclusion

Thin MoCN films were synthesized by the cathode sputtering method of mosaic Mo-C targets nitrogen ions at a temperature 800°C on substrates of the oxidized silicon. TEM studies showed the two-layer structure of MoCN film at a total thickness of 8 nm. The inside layer close to a substrate (~4.5 nm) consists of molybdenum nitride (Mo$_5$N$_6$) grains, while the external layer (~3.5 nm) contains grains mainly of molybdenum carbide (MoC).
The measured dependences of electrical resistance of films on the temperature in the range 4.2–300°C showed a typical trend for thin superconducting films. The received volt-ampere characteristics at a temperature of 4.2°C allowed calculating the values of critical current density for the films and also its dependence on the total thickness of MoCN. The high density of critical current at a total thickness ~8 nm indicates wide range of application for a thin MoCN films in the field of cryogenic nanotechnologies.

It was shown that MoCN thin films characterized by a high superconducting transition temperature in range of about 8-11°C (for different thickness) and high values of critical current density in range of ~1.4-5x10⁶ A/cm².

Acknowledgements
The work was supported by the NRC “Kurchatov Institute” (№1359).

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