Superconducting Properties of NbN–SiO$_2$ Sol–Gel Derived Thin Films

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This work presents results of superconducting properties studies of xNbN–(100–x)SiO$_2$ (where $x = 80$ mol%) films of the thickness from 450 to 1950 nm. The films were prepared by thermal nitridation of sol–gel derived xNb$_2$O$_5$–(100–x)SiO$_2$ coatings. The nitridation process of Nb$_2$O$_5$–SiO$_2$ coatings leads to the formation of weakly disordered structures, with NbN metallic grains dispersed in the matrix of insulating SiO$_2$. All the samples in the normal state exhibit negative temperature coefficient of resistivity. Superconducting transition was not observed for the sample 450 nm thick. To examine the influence of magnetic field on superconducting properties of the films, the resistance versus temperature of 1350 and 1650 nm thick samples was measured in high magnetic fields. Resistive superconducting transitions are broadened due to the magnetic flux creep. The perpendicular upper critical magnetic fields for 1350 and 1650 thick samples are about 4.4 T. The critical temperatures of the superconducting transitions are about 4.5 K. Specific features of the magnetic field induced superconductor–insulator transition are found.

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1. Introduction

The electrical properties of strongly disordered and granular materials have been the subject of intensive investigations for decades. Such systems are very interesting from the point of view of the mechanisms of electrical conductivity, relationships between normal and superconducting state and the interplay between local and global superconductivity, especially, superconductor–insulator (S–I) transition and unusual negative magnetoresistance. In these materials, the superconducting transition occurs in two steps. Firstly, the isolated metal grains transit into the superconducting state. Secondly, the Josephson junctions between grains are formed and the global superconducting state sets up. A very interesting system from the point of view of above mentioned properties is NbN doped with SiO$_2$. Moreover, NbN is one of the leading materials in superconducting applications. It may be successfully used in several superconducting microelectronic applications such as SQUID, filters, antennae [1, 2] or superconducting cavities for particle accelerators [3]. Recently it

has been reported that Si or SiO$_2$ addition may improve some physical properties of NbN [4, 5].

NbN films are usually prepared by magnetron sputtering method and physical or chemical vapour deposition. Another very promising method of the nitride and oxynitride films preparation is a thermal nitridation of sol–gel derived films. This method allows to cover any size and shape surfaces. The coatings obtained by sol–gel methods are especially suitable for the ammonolysis because of their porosity. The microporous structure allows both a significant incorporation of nitrogen and its distribution through the film. The ammonolysis of sol–gel derived Nb$_2$O$_5$–SiO$_2$ films allows one obtaining NbN grains dispersed in SiO$_2$ matrix.

This work is devoted to the superconducting properties of xNbN–(100–x)SiO$_2$ (where $x = 80$ mol%) films of the thickness from 450 to 1950 nm, prepared by thermal nitridation of sol–gel derived xNb$_2$O$_5$–(100–x)SiO$_2$ coatings.

2. Experimental

To obtain xNb$_2$O$_5$−(100 − x)SiO$_2$ (where $x =$ 80 mol%) films a starting solution was prepared by mixing tetraethoxysilane (TEOS, 98%) from Fluka and nio-

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bium(V) chloride (99.9%) from Aldrich with ethanol and acetyloacetone as the complexing agent. The films were deposited on a silica glass substrate by a spin coating technique at a rate of 100 rps, then aged for 24 h in room temperature and heated at 250 °C for 1 h. Repeating the above procedure three times gave approximately 450 nm thick films. To examine the superconducting properties of the films, samples with the different thickness were also prepared. In this case the preparation procedure was repeated more times. To obtain xNbN$-(100-x)$SiO$_2$ coatings, the resulting layers were subsequently nitrided by ammonia treatment at the temperature 1200 °C. The nitridation was carried out in a silica glass tube under NH$_3$ gas flow (4 l/h) at a heating rate of 1 °C/min up to 1200 °C and held isothermally at this temperature for 1 h. The samples were cooled under NH$_3$ gas flux. The structure investigations of the NbN–SiO$_2$ prepared by above method were described in [6].

Measurements of resisitivity as a function of temperature were performed in the temperature range of 5–280 K, with a DC technique in the standard four-terminal configuration.

Transport measurements in magnetic field were performed with the standard four-probe technique in the superconducting magnet system (Oxford Instruments) with the maximum magnetic field 14 T and a variable temperature insert providing a temperature range 1.4–300 K.

3. Results and discussion

The results of sheet resistivity versus temperature for samples with thickness $d = 450$, 750, 1050, 1350, 1650 and 1950 nm are shown in Fig. 1. All the samples before transition exhibit negative temperature coefficient of resistivity. The $T_{C\,onset}$ of the superconducting transition in zero magnetic field increases with the sample thickness increase, from 8.2 K to 10.8 K, respectively, for the samples 750 and 1950 nm thick. These temperatures are lower from those usually observed for NbN (up to 16 K). As it was shown by Roberts et al. [7], even small deviation from stoichiometry or the presence of Nb–O bonds in the system can decrease the superconducting transition temperature. Another reason for this behaviour may be lattice disorder caused by not uniform nitrogen distribution during ammonolysis process. For the sample 450 nm thick, superconducting transition has not been observed. Figure 2 presents the results of resistance versus temperature of the sample 1350 nm thick at the different values of magnetic field H perpendicular to the film. The superconducting transitions are very broad that may be explained by the giant magnetic flux creep. In this case the temperature dependence of resistance is thermally activation type, $R = R_0 \exp(-U/kT)$, where U is the activation energy [8]. The $R(T^{-1})$ dependences are shown in Fig. 3.

Magnetoresistance of samples with $d = 1350$ and 1650 nm measured at different temperatures are presented in Figs. 4 and 5, respectively. Magnetic field was
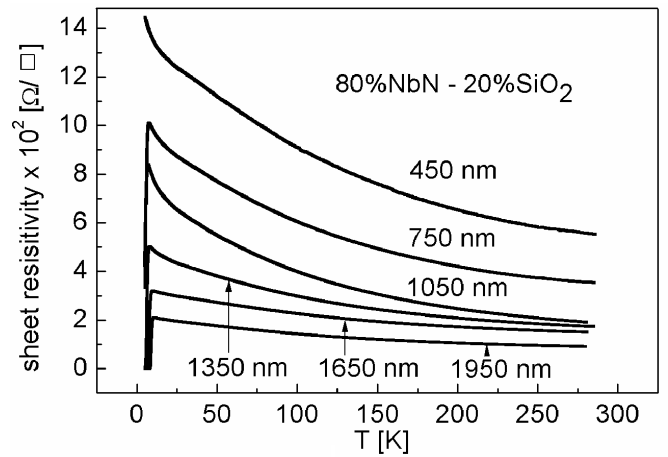

Fig. 1. The evolution of the temperature dependence of sheet resistivity of 80%NbN–20%SiO$_2$ films with increasing thickness.
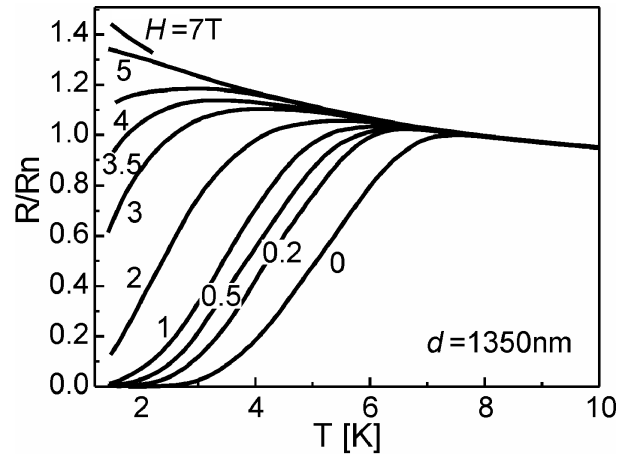

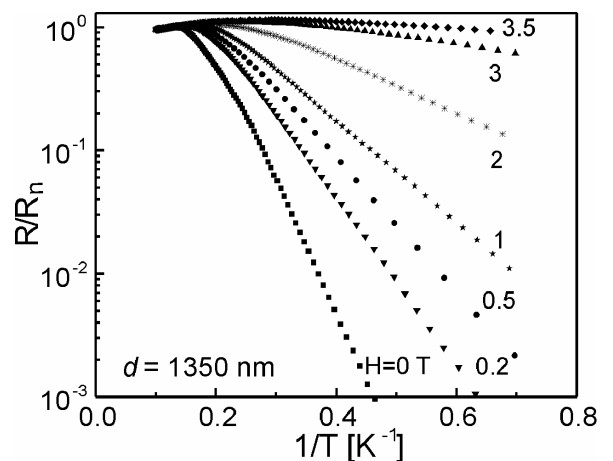Fig. 2. R/R_n versus temperature of the 1350 nm thick sample in the different values of magnetic field.

Fig. 3. R/R_n of the 1350 nm thick sample as a function of T^{-1}, for magnetic fields 0, 0.2, 0.5, 1, 2, 3 and 3.5 T.

perpendicular to the films. The perpendicular critical magnetic field is about 4.4 T for both samples. The critical temperatures of the superconducting transitions are about 4.5 K.
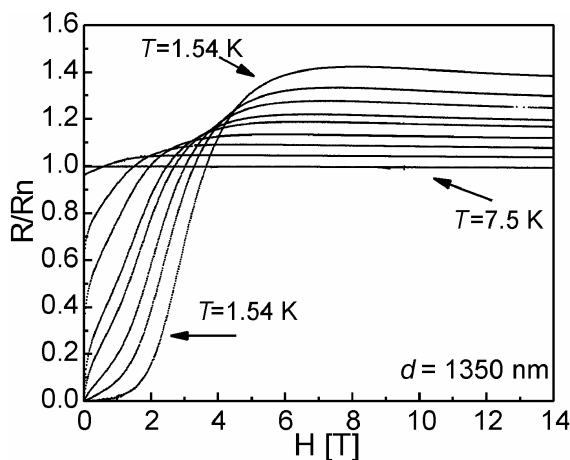

Fig. 4. Magnetoresistance of the 1350 nm thick sample, measured at different temperatures. The curves from right to left correspond to the temperatures: 1.45, 1.54, 2.11, 2.53, 3.09, 3.46, 3.56, 4.19, 5, 6 and 7.5 K.
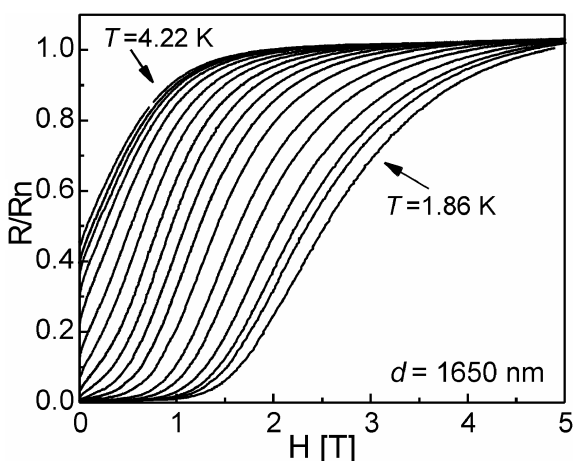

Fig. 5. Magnetoresistance of the 1650 nm thick sample, measured at different temperatures. The curves from right to left correspond to the temperatures: 1.86, 2.01, 2.11, 2.26, 2.48, 2.67, 2.91, 3.11, 3.27, 3.43, 3.56, 3.73, 3.86, 3.99, 4.00, 4.14, 4.18 and 4.27 K.

Specific features of the magnetic field induced superconductor–insulator transition are found on the sample with $d = 1350$ nm. First is the fan-like set of $R(T)$ curves (see Fig. 2): they go down with the tem-

perature decrease at the fields $H < 3$ T, and go up at fields $H > 4$ T. The second is the crossing of $R(H)$ curves (see Fig. 4) and the third is the appearance of negative magnetoresistance with the temperature decrease. This behaviour can be described using the model of superconductor grains coupled via Josephson junctions [9]. It will be discussed in the further publication.

4. Conclusions

For the sample 450 nm thick, superconducting transition was not observed. Resistive superconducting transitions are broadened due to magnetic flux creep. The perpendicular upper critical magnetic fields for 1350 and 1650 thick samples are about 4.4 T. The critical temperatures of the superconducting transitions are about 4.5 K. Specific features of the magnetic field induced superconductor–insulator transition are found.

The ammonolysis of $x\mathrm{Nb_2O_5}-(100-x)\mathrm{SiO_2}$ sol–gel derived films seems to be a promising method of superconducting NbN–SiO₂ films preparation.

Acknowledgments

References

[1] J.J. Bantista, *IEEE Trans. Magn.* **21**, 640 (1985).

[2] J.B. Walker, *IEEE Trans. Appl.* **25**, 885 (1977).

[3] P. Bosland, S. Cantacuzene, in: *P. Bosland, S. Cantacuzene, J. Gobin, M. Juillard, J. Martignac in Proc. VI Workshop of RF Superconductivity*, CEBAF, Newport News (USA) 1993, p. 1028.

[4] J. Wang, Z. Song, K. Xu, *Surf. Coat. Technol.* **201**, 4931 (2007).

[5] B. Kościelska, W. Jurga, *J. Non-Cryst. Solids* **354**, 4345 (2008).

[6] B. Kościelska, A. Winiarski, *J. Non-Cryst. Solids* **354**, 4349 (2008).

[7] B.W. Roberts, *J. Phys. Chem. Ref. Data* **5**, 581 (1976).

[8] A.P. Malozemoff, Y. Yeshurun, L. Krusin-Elbaum, T.K. Worthington, D.C. Cronemeyer, T. Dinger, T.R. Foltzberg, T.R. McGuire, P.H. Kes, *High Temperature Superconductivity*, Vol. 9, World Sci., Singapore 1988, p. 112.

[9] I.S. Beloborodov, A.V. Lopatin, V.M. Vinokur, K.B. Efetov, *Rev. Mod. Phys.* **79**, 469 (2007).