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Point-Contact Spectroscopy of Thin Superconducting NbN Films

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Superconducting niobium nitride films are ideal candidates for electronics applications among low-T_c materials due to comparatively high critical temperature, large critical magnetic fields and relative ease of fabrication. The superconducting properties of NbN are known to be strongly dependent on the formation of a correct crystallographic phase. The tunneling spectroscopy data for NbN films are in good agreement with existing theoretical concepts, while contact methods provide significantly lower values of the superconducting order parameter. In this paper, we present corresponding results for a representative NbN film with T_c about 14 *K*, obtained using a point contact made by bringing a sharp metallic tip of silver in touch with the sample surface. We have observed fundamental difference between the gap values extracted from the differential conductance measurements and those following from the standard BCS theory. Despite the almost perfect contact of the normal tip with the film surface, the energy gap was nearly two times smaller than theoretically expected. At the same time, the gap values did not vanish at appreciably lower temperatures compared to the bulk of the NbN film, but rather continued to decrease slowly up to the bulk critical temperature. This finding is explained by significant deformation of the near-surface layer leading to the local suppression of superconducting parameters. Such behavior is a typical example of the superconducting proximity effect when the temperature dependence of the smaller gap strongly deviates from the BCS prediction but remains however finite up to the critical temperature of the larger gap, which is the same for two contacting spaces with superconducting parameters that differ significantly from each other. This conclusion is important for practical applications, in particular, for creating integration circuits based on superconducting NbN thin layers.

Keywords: NbN films, Point-Contact Spectroscopy, Superconducting Energy Gap, Proximity Effect.

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1. INTRODUCTION

Transition-metal nitrides show exceptional combination of physical characteristics as hardness, high mechanical strength, excellent thermal stability, resistance to corrosion and oxidation, high melting point, nontrivial band topology, etc. [1-3] Besides it, they are good metallic conductors and sometimes demonstrate superconductivity [4-6]. Among the large number of transition-metal nitrides, the binary niobium nitride systems occupy a special place since they can realize a variety of crystal structures with outstanding mechanical, electronic and superconducting properties. The superior (comparing to Nb-based carbides or oxides) mechanical characteristics are arising due to strong covalent bonds between niobium and nitrogen atoms [7]. Electronic structure of the NbN conducting bands critically depend on nearest-neighbor niobium-nitrogen interactions [8] and, in particular, one can anticipate significant changes of the density-of-states curves in the presence of vacancies in Nb or N sublattices [8].

Superconductivity (S) in niobium-nitrogen compounds deserves special attention since "NbN remains as the material of choice in developing future generation quantum devices" [9]. The superconducting parameters depend on both the Nb/N ratio and the crystal structure [10]. Due to relatively high transition temperatures and high hardness, δ and γ phases of niobium nitride are widely applied in radio frequency circuits, Josephson junction qubits [11], and especially in superconducting nanowire single-photon detectors [9]. Even more, NbN films may belong to materials that exhibit both superconductivity and nontrivial band topology and hence are excellent candidates to study

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the fascinating phenomena such as topological superconductivity and Majorana fermions [6, 12]. Recently, significant progress has been made in the use of NbN layers in superconducting electronics, which gives hope for the possibility of achieving an integration scale of 10^8 Josephson junctions per chip [13]. To meet the specific electronics applications in superconductor digital and neuromorphic circuits, we need NbN layers carefully designed and processed to achieve the desired device performance.

Further progress in this direction requires precise knowledge of the superconducting parameters and primarily the magnitude of the order parameter Δ in the given material for optimizing the performance of NbN-based devices. First careful study of the surface topography and the tunneling current-voltage (*I-V*) characteristics of NbN thin films were performed in the work [14] using a low-temperature scanning tunneling microscope. Histograms of best-fit gap values demonstrated a peak centered around 2.6 meV with a width of about 1 meV. In addition, there was a significant "tail" to lower gap energies [14]. Strongly reduced gaps were attributed to inhomogeneities in the sample since the features in the gap image were often correlated with anomalies in surface topographic images. To address this issue, tunneling experiments have been proposed.

The problem was discussed also in the work [15] using measurements of the optical transmission spectra and current-voltage (*I-V*) curves for NbN/AlN/NbN trilayers. The authors [15] found that with increasing temperature, the optical conductivity significantly differed from the theoretical Bardeen-Cooper-Schrieffer (BCS) model with the Drude scattering time value obtained from low-temperature data fitting. They argued that the superconducting energy gap is complex $\Delta = \Delta_1 + i\Delta_2$ with the superconducting gap broadening parameter Δ_2 independent from Δ_1. The values of Δ_2 well agreed in both measurements and increased with growing temperature up to the critical temperature T_c about 14 K. In particular, tunneling experiments revealed $\Delta_2 = 0.032$ meV at 4.8 K. The values of Δ_2 obtained in both measurements well agreed. Concerning the real part of the order parameter, the gap frequency was found to be about 1.2 THz ($2\Delta_1 \approx 5.0$ meV) from the optical experiments while the *I-V* curves of the tunnel junctions showed the current rise at the gap voltage of 5.6 mV corresponding to 1.4 THz.

The authors of the paper [16] used another powerful method for detecting the superconducting gap – point-contact spectroscopy. Since to create a stable and clean point contact by conventional techniques is a difficult task, they fabricated multiple point contacts by depositing Au nanoparticle arrays on the surface of the NbN superconducting film with $T_c = 16$ K. The normalized differential conductance spectra exhibited superconducting coherence peaks below 13-14 K. It means that the authors were in fact dealing with a tunnel-like characteristic. The peak positions made it possible to estimate the gap value $\Delta_1 \approx 2.88$ meV at zero temperature in agreement with former reports.

The aim of our work was to create a point contact with a very small potential barrier between the needle and the superconductor under study using the traditional approach and investigate the near-surface gap sizes in NbN superconducting films. Below we discuss their fabrication and measurements of the conductance spectra carried out under various temperatures and analyzed within the Blonder-Tinkham-Klapwijk (BTK) theory [17]. Our results indicate the presence of a near-surface layer with suppressed superconductivity. Its presence was the reason for the significant decrease in local gap values in the work [14].

2. EXPERIMENT

The main details of the samples fabrication are as follows. The pulsed laser deposition (PLD, Omicron system with Coherent Compex Pro 201 F laser) of NbN films was carried out in an ultrahigh vacuum chamber using an excimer KrF laser with 248 nm wavelength, the pulse duration of 35 ns, and the laser fluency of 4.94 J·cm^{-2}. The NbN thin films were deposited on the *c*-cut Al_2O_3 substrates, ultrasonically cleaned in acetone, isopropanol and deionized water, from a 2-inch Nb target (99.9 %) in the N_2 + 1% H_2 reactive atmosphere at the gas flow of 80 sccm and the pressure of 9.3 Pa. The substrate temperature was kept constant at 600 °C. After deposition, the chemical and structural properties of NbN thin films were carefully characterized by several analytical techniques. Related experimental details can be found in Ref. 18.

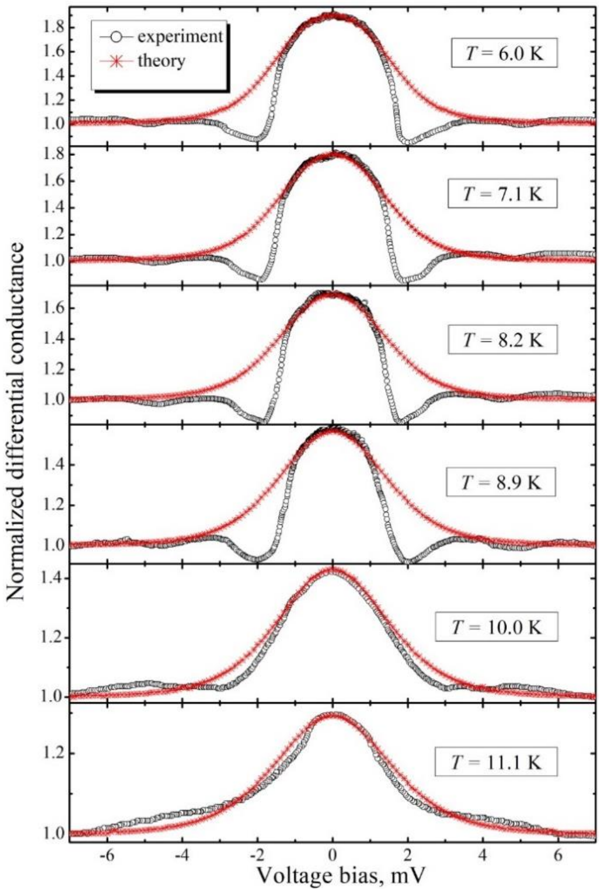

Fig. 1 – Temperature effect on the normalized differential conductance d*I*(*V*)/d*V* of a representative point contact formed by a silver tip and a superconducting NbN film. Experimental data and results of the calculations with the energy gap as a fitting parameter shown by circles and stars

Point contacts on the NbN films were made by bringing a sharp metallic tip of silver in touch with the sample surface. The superconducting transition temperatures T_c between 13 and 14 K were found resistively with the conventional four-terminal approach. In Fig. 1 we demonstrate the temperature effect on the differential conductance $G_S(V) = dI(V)/dV$ of a representative point contact that is normalized to the corresponding value G_N at voltages $V >> \Delta/e$ (Δ is the expected gap value) where the contact conductance coincides with that in the normal (N) state.

We note the presence of a pronounced dip in the differential conductance at the voltage bias of 2 mV that cannot be adequately modeled using conventional BTK theory [17] describing the behavior of the $G_S(V)/G_N$ curve in the gap region. The origin of such anomaly was explained in our publication [19] by inhomogeneous superconducting state in the studied layer, conditionally divided into two parts with different gap values and a semitransparent potential barrier between them. According to Ref. 19, the initial device is a double-barrier structure in which the space between the two barriers transfers into a new state due to the escape time of recombination phonons from the interlayer acting as a bottleneck in the quasiparticle relaxation process [20]. The estimates [19] showed that at low voltage biases the carriers in the interlayer are mostly scattered elastically keeping its quantum phase, which has a definite relationship to the incident phase.

Hence, we can identify $G_S(V)$ at high voltages with the normal-state value G_N and ignore the presence of the dip in measured conductance spectra comparing them with theoretical expectations for an N/S point-contact junction:

$$G_S(V) = \left(G_N / e\right)\frac{d}{dV}\int_{-\infty}^{\infty}[1 - R_S^{ee}(\varepsilon) + R_S^{eh}(\varepsilon)][f(\varepsilon - eV) - f(\varepsilon)]d\varepsilon,$$

where $R_S^{ee}(\varepsilon)$ and $R_S^{eh}(\varepsilon)$ are the probabilities for an incoming electron with the energy ε to be elastically scattered into an electron (e) or a hole (h), respectively, $f(\varepsilon)$ is the Fermi-Dirac distribution function [21].

In the BTK approach [17], scattering at the N/S interface is characterized by a dimensionless parameter Z that determines the reflection probability $R_N^{ee} = Z^2/\left(1+Z^2\right)$ in the normal state as well as the normal-state conductance value G_N that is proportional to $1 - R_N^{ee} = 1/\left(1+Z^2\right)$. The effect of inelastic collisions in a superconductor is often taken into account by introducing a constant imaginary part in the electronic energy $\varepsilon \to \varepsilon + i\Gamma$, where Γ is the so-called Dynes parameter. To our surprise, it turned out that good agreement between theory and experiment was achieved for values $Z \approx 0$ and $\Gamma \approx 0$. Hence, we had the only fitting parameter – the energy gap Δ varied with temperature T.

This finding means that we were dealing with an almost ideal N/S contact, the probability of passing through which was close to unity, and a superconductor that is well described by the standard Bardeen-Cooper-Schrieffer (BCS) theory. If so, then $R_S^{ee}(\varepsilon) = 0$ and $R_S^{eh}(\varepsilon)$ is determined solely by the probability of the Andreev electron-into-hole retroreflection equal to unity at $V < \Delta/e$ below the energy gap and rapidly decreasing to zero at $V > \Delta/e$. We followed such procedure in the calculations, which resulted in the curves in Fig. 1. However, despite this, the extracted gaps $\Delta(T)$ were roughly two times less than those in the BCS theory if we set T_c equal to the measured magnitude $T_c = 13.7$ *K*, see Fig. 2.

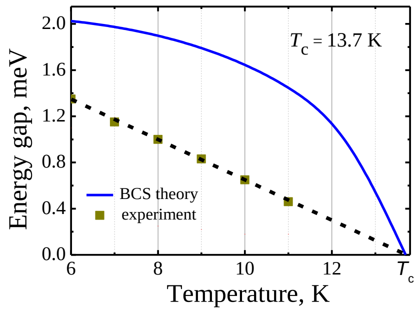

Fig. 2 – Temperature dependences of the expected BCS energy gap (solid line) and extracted Δ values from the data shown in Fig. 1 (squares). The straight dashed line is a guide for the eye

3. DISCUSSION

We have observed fundamental difference between the Δ values extracted from contact measurements and those expected from the BCS theory as well as found in experiments with tunneling-like probes [15, 16]. From the experimental point of view, their main distinction from our measurements consists in the absence of the near-surface degradation of the films under the strong pressure that results in the suppression of the local superconducting gap value as follows from Fig. 2. Although the ratio $2\Delta\,(T = 0)/k_BT_c$ is much smaller than the universal value of 3.528 in the BCS theory, the extracted gaps Δ do not vanish at appreciably lower temperatures compared to the bulk of the NbN film, but continue to decrease slowly up to the bulk T_c.

Such behavior is a typical example of the superconducting proximity effect when the temperature dependence of the smaller gap strongly deviates from the BCS $\Delta(T)$ prediction but remains however finite up to the critical temperature T_c, which is the same for two contacting spaces with superconducting parameters that differ significantly from each other [22, 23]. The ultra-thin sheath formed by surface deformation is one of the contacting sections of the NbN film, while the second is the superconducting bulk with T_c about 2.5 K. The regions with suppressed superconductivity observed in the work [14] are probably of the same origin.

The conclusion may be of practical importance. Superconductivity and geometrical effects in low-dimensional samples with length scales comparable or smaller than the coherence length and magnetic field penetration depth are currently the focus of numerous theoretical and experimental studies. It is stimulated by the fundamental importance of the problem as well as by the variety of applications of thin-film superconductors including NbN layers [13]. Our work demonstrates possibility of a significant decrease of the order parameter near the superconducting surfaces. In ultra-thin layers, due to proximity effect it can lead to the reduction of T_c as well. Protecting the superconducting film with appropriate buffers and protection layers can lead to a critical-temperature T_c increase.

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Точково-контактна спектроскопія тонких надпровідних NbN плівок

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Для застосування в електроніці надпровідні плівки нітриду ніобію є ідеальними кандидатами серед матеріалів з низькими T_c через порівняно високу критичну температуру, великі критичні магнітні поля та відносну легкість виготовлення. Відомо, що надпровідні властивості NbN сильно залежать від утворення потрібної кристалографічної фази. Дані тунельної спектроскопії плівок NbN добре узгоджуються з існуючими теоретичними уявленнями, тоді як контактні методи дають значно нижчі значення параметра надпровідного порядку. У цій роботі ми представляємо відповідні результати для репрезентативної плівки NbN з T_c біля 14 *K*, отримані за допомогою точкового контакту, створеного шляхом приведення гострого металевого вістря зі срібла до контакту з поверхнею зразка. Ми спостерігали фундаментальну різницю між значеннями щілини, отриманими з вимірювань диференціальної провідності, і тими, що випливають із стандартної теорії БКЩ. Незважаючи на майже ідеальний контакт нормального вістря з поверхнею плівки, енергетична щілина була майже вдвічі меншою, ніж теоретично очікувалося. У той же час вона не зникали при помітно нижчих температурах порівняно з об'ємною щілиною плівки NbN, а продовжувала повільно зменшуватися до критичної температури об'єму. Це пояснюється значною деформацією приповерхневого шару, що призводить до локального пригнічення надпровідних параметрів. Така поведінка є типовим прикладом надпровідного ефекту близькості, коли температурна залежність меншої щілини суттєво відрізняється від передбачення БКШ, але залишається кінцевою до критичної температури для більшої щілини, яка є однаковою для двох контактуючих масивів з параметрами надпровідності, які суттєво відрізняються один від одного. Цей висновок є важливим для практичних застосувань, зокрема для створення інтеграційних схем на основі надпровідних тонких шарів NbN.

Ключові слова: Плівки NbN, Точково-контактна спектроскопія, Надпровідна енергетична щілина, Ефект близькості.