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Ultrathin Niobium in the Si/Nb/Si Trilayers

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We study magnetotransport properties of the Si/Nb/Si trilayers, in which the thickness of niobium, d, changes from 1.1 nm to 50 nm, while the thickness of Si is fixed at 10 nm. The niobium films are amorphous for $d < 4$ nm, while in thicker films the alligned polycrystalline grains are formed. We observe that the Hall coefficient changes sign into negative in the films with $d < 1.6$ nm. We also find that in the ultrathin films the magnetic field induces a transition from the superconducting into a metallic phase with the resistance smaller than the normal-state resistance.

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1. Introduction

The studies of the properties of ultrathin superconducting films are important for the applications in various nanosize devices, and for general understanding of superconductivity at reduced length scales. The decrease of the film thickness, d, may introduce many changes to the film properties, both in the superconducting and in the normal state, because of close proximity of the film interfaces. Some of such effects include the increase of the film resistivity resulting from the boundary scattering [1], the suppression of superconducting transition temperature, T_c, leading eventually to the superconductor–insulator transition (SIT) [2], or modifications of the structural properties due to strain or interdiffusion, leading to changes in the electronic structure.

In this work we focus on the properties of ultrathin films of niobium, one of the best known, and widely applied superconductors. Since Nb is easily oxidized, it is usually necessary to cover the film with protecting layer, such as, for example, Si or Ge. There have been numerous studies of thin films of niobium, which may be roughly divided into two groups. One group studies single crystalline films, usually grown on sapphire substrates and at elevated temperatures. While these films routinely display exceptional superconducting quality, they frequently suffer from interdiffusion when d becomes small [3]. The second group includes films grown by magnetron sputtering at room temperature, thus largely avoiding interdiffusion, so that smaller d may be reached. Such films are usually dirtier, but useable for some applications, such as, for example, single-photon detectors [4].

In the present work we use the second method to produce amorphous ultrathin Nb films, with d as small as 1.1 nm, sandwiched between Si layers. In addition to structural study, we measure resistivity and the Hall coefficient (R_H). The surprising result, never described before, is a change of sign of R_H into negative in the thinnest films, which we attribute to the influence of the boundary scattering on the carriers lifetime. We also discuss briefly the properties of the SIT measured in these ultrathin films.

2. Experimental details

The samples are grown on glass substrates by magnetron sputtering in the high-vacuum chamber at room temperature. To prevent the diffusion of oxygen into niobium two silicon layers are grown, both below and above Nb layer. The thickness of Nb, d, is varied from 50 nm down to 1.1 nm with a fixed Si thickness of 10 nm. The structural properties of the films are characterized by the X-ray diffraction and by the high-resolution transmission electron microscopy (HRTEM). The HRTEM images are used to determine d with good accuracy.

The resistance per square, R_{sq}, is measured on a lithographically patterned resistance bridge in perpendicular magnetic field B, using a standard four-probe method, by dc measurements at high temperatures ($T > 2$ K), and by ac measurements in the mK temperature range. The Hall effect is measured on the Hall bar structure at temperatures between 2 and 300 K, using Physical Property Measurement System (PPMS, Quantum Design).

3. Results and discussion

Figure 1a,b shows the HRTEM images for samples with d equal to 11.3 nm and 3.3 nm. The Nb layer (dark) is sandwiched between two amorphous Si layers (light). The boundary between Nb and Si layers is sharp, which suggests that the diffusion of Si into Nb is not significant. In the thick sample, 11.3 nm, the aligned polycrystalline grains are visible inside the dark Nb layer. However, at the top boundary between Si and Nb we observe a layer of amorphous niobium, about 2.5 nm thick. This suggests that during the initial stage of deposition niobium forms amorphous layer. Only after sufficiently thick film is deposited, polycrystalline grains begin to form. This is confirmed by the fact that polycrystalline grains are absent in the thinner sample.

This conclusion is further confirmed by the X-ray diffraction spectra of Si/Nb/Si trilayers, which are shown in Fig. 1c. The spectrum for the Si layer (without Nb) contains a broad maximum at low angle, characteristic

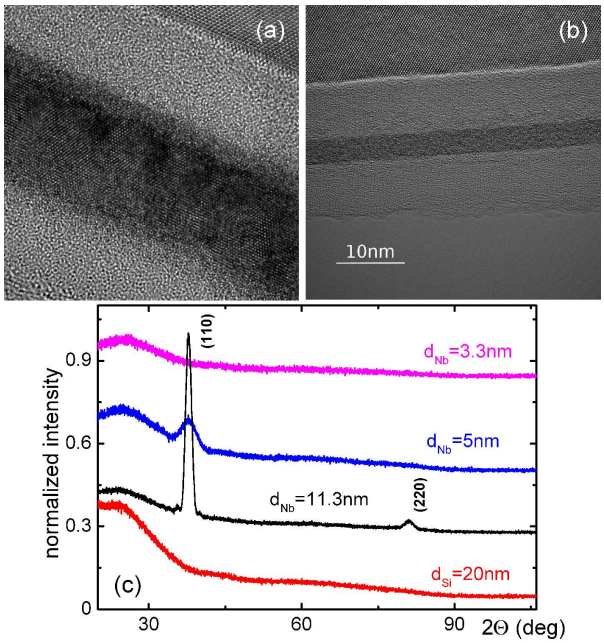

Fig. 1. HRTEM images for Si/Nb/Si trilayers with the thickness of niobium, d (in nm), equal to 11.3 (a) and 3.3 (b). On each image from top there are Si-substrate, layer of amorphous Si, layer of Nb and layer of amorphous Si with glue. (c) X-ray diffraction spectra for trilayers with different thickness of Nb and for Si-film without Nb.

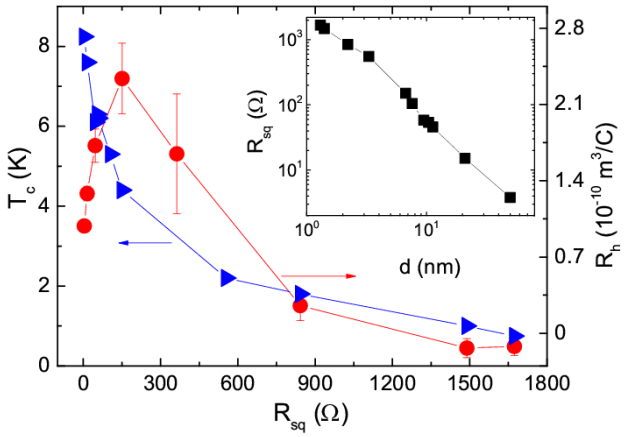

Fig. 2. Inset: the sheet resistance $R_{\rm sq}$ (extracted at $T = 200$ K) as a function of d. Main figure: T_c vs. $R_{\rm sq}$ (triangles, left axis) and $R_{\rm H}$ vs. $R_{\rm sq}$ (circles, right axis) for a series of trilayers. The data for $R_{\rm H}$ are measured at $T = 60$ K.

for amorphous material. On the other hand, two peaks may be identified in the spectrum of the trilayer with $d = 11.3$ nm, indicating that the polycrystalline Nb films have the bcc crystal structure and space group $Im\bar{3}m$, and the polycrystalline grains are aligned. The lattice parameter of polycrystalline Nb-layer is less than the value for bulk Nb. In the spectra of the trilayer with $d = 5$ nm only one peak is visible, and it is substantially broadened. This suggests that this film still contains some polycrystalline grains, but a substantial portion of the film is amorphous. Finally, no polycrystalline phase is present in trilayer with $d = 3.3$ nm. Thus, we conclude that a transition from the amorphous to polycrystalline film occurs for d between 4 and 5 nm, but the thicker films contain thin amorphous layer close to the Nb/Si boundary.

The effect of the decrease of d on the superconducting and normal-state properties is presented in Fig. 2. The $R_{\rm sq}$, measured for a series of trilayers at $T = 200$ K, is shown versus d in the inset. The dependence is very close to $R_{\rm sq} \sim d^{-2}$. Such behavior is predicted for the size effect resulting from the boundary scattering in thin films [1, 5], and it has been observed before in single-crystalline Nb films with $d > 2$ nm, grown on sapphire [6]. We note that $R_{\rm sq}$ reported in that study has been lower than in the present amorphous or polycrystalline films, nevertheless the $R_{\rm sq}(d)$ dependence is similar. This suggests that in our films the boundary scattering is an important scattering mechanism.

The main Fig. 2 shows the dependence of the superconducting transition temperature, $T_{\rm c}$ (left scale) and the Hall coefficient $R_{\rm H}$ (right scale) versus $R_{\rm sq}$. Here the $T_{\rm c}$ is defined as the midpoint of the transition, and $R_{\rm H}$ is measured at $T = 60$ K. The $T_{\rm c}$ is seen to decrease to zero for samples with $R_{\rm sq} > 1800$ Ω, i.e. when d decreases below 1.3 nm. The $T_{\rm c}(R_{\rm sq})$ dependence is similar to the one reported for Nb films electron-beam evaporated on sapphire substrates (textured polycrystalline films) [7] and for dc sputtered films on Si substrates [8]. In this last study no detailed structural data has been reported, but deposition procedure similar to the one used in the present study probably results in similar films.

The dependence of $R_{\rm H}$ on $R_{\rm sq}$ has never been reported for thin Nb films, and it is the central result of the present study. We observe that with increasing $R_{\rm sq}$ the Hall coefficient initially increases above the value observed for the thick films (which is close to the bulk value, equal to 0.9×10^{-10} m^3/C [9]). According to theories, the boundary scattering should result in the increase of the Hall coefficient [5]. However, when $R_{\rm sq}$ exceeds about 150 Ω (i.e. when d decreases below 6 nm), the $R_{\rm H}$ starts to decrease. Eventually, it changes sign into negative for very thin films, when $R_{\rm sq}$ exceeds about 1300 Ω (i.e. when d decreases below 1.6 nm).

This change of sign in the thinnest samples is further enhanced when temperature is decreased. To emphasize this we show in Fig. 3 the B-dependence of the Hall resistance, R_{xy}, measured at several temperatures for samples with different d. The slope of the $R_{xy}(B)$ dependence changes dramatically, from positive in the thick, polycrystalline sample ($d = 11.3$ nm) to negative in the thin, amorphous sample ($d = 1.4$ nm). Note that in this last case the $R_{xy}(B)$ dependence becomes slightly nonlinear at the lowest temperatures. The intermediate sample ($d = 2.2$ nm) shows linear $R_{xy}(B)$ with positive

slope at high T, followed by a gradual development of nonlinearity as T is lowered, until at $T = 2$ K a negative slope appears at small B. This behavior indicates that in thick polycrystalline samples the hole carriers dominate the transport, similar to bulk niobium. However, as d is decreased, two types of carriers, holes and electrons, contribute to the conduction. The electron contribution becomes increasingly dominating as d decreases. It is also more pronounced at low temperatures and at small magnetic fields.

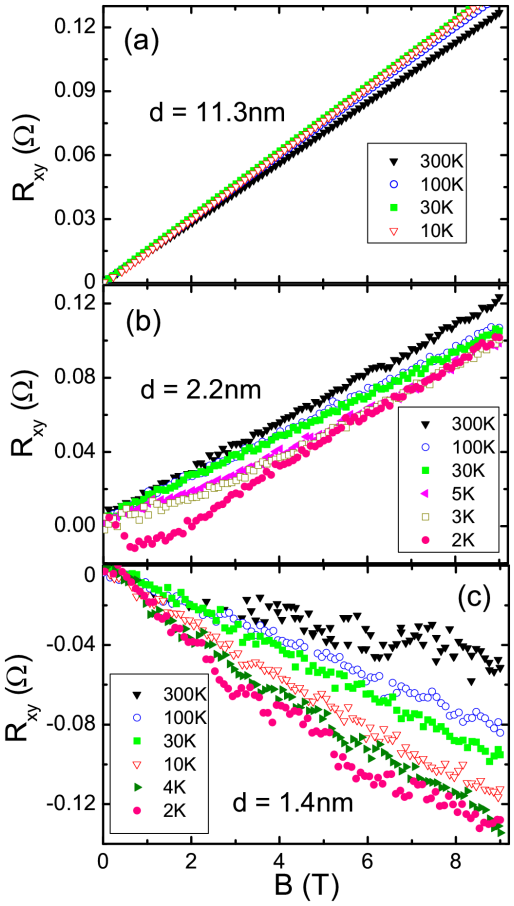

Fig. 3. Hall resistance R_{xy} versus B at different temperatures for samples with $d = 11.3$ nm (a), $d = 2.2$ nm (b), and $d = 1.4$ nm (c).

The appearance of the electron contribution to the conduction in the thin-film limit may have several origins. One possibility is that in the thin amorphous films the niobium band structure is modified so strongly that the character of the dominating carriers changes. However, the films become purely amorphous for $d = 3.3$ nm, while $R_{\rm H}$ is still positive, so there is no strict correlation between these two effects. Another possible origin is the formation of silicide niobium layer at the Nb/Si interface, with may have negative $R_{\rm H}$ [10]. While neither X-ray diffraction nor TEM shows a sign of sizeable layer of such compound, it is conceivable that such a layer is very thin, or forms separate islands immersed in niobium, and therefore it is undetectable by these methods. If such a layer exists, than the conduction may proceed via two parallel conduction channels with carriers of different signs.

Still another possibility is the effect similar to the one reported for polycrystalline films of indium, in which a change of sign of $R_{\rm H}$, from positive in thick films to a negative in the low-field limit in thin films, has been reported [11, 12]. The effect has been explained by the influence of boundary scattering on the relaxation times of the two types of carriers which exist in In, that is, the heavy holes in the second Brillouin zone, and light electrons in the third zone [9]. In the bulk the $R_{\rm H}$ is positive, indicating that the relaxation time for holes is larger than for electrons, presumably because electrons are more strongly scattered by impurities. When the boundary scattering is added in thin films, it affects similarly both types of carriers, so that it tends to equalize the relaxation rates and the electron contribution to $R_{\rm H}$ becomes detectable. As a result of the difference in the effective masses of electrons and holes, the negative electron contribution is dominating at low magnetic fields, while in the limit of large fields positive hole contribution to $R_{\rm H}$ prevails. Trying to access if such mechanism may exist in Nb, we note that the Fermi surface in bcc niobium consists of closed-hole surface in the second zone, while in the third zone there are distorted hole ellipsoids and an open multiply connected surface known as "jungle gym", which may support both hole and electron orbits [13, 14]. While in the amorphous films this structure will be modified (the energy bands will be broadened), it is quite plausible that the essential feature, that is the possible existence of electron orbits in the third zone, survives. In the bulk they do not affect $R_{\rm H}$, but in ultrathin films the boundary scattering uncovers the electron contribution to the $R_{\rm H}$. It is important to stress that in our experiment the negative $R_{\rm H}$ is most pronounced in the low-field limit, just as it is expected in this mechanism.

Finally, we note that the presence of two types of carriers in the thinnest films does not seem to modify the properties of the SIT in comparison with the typical observations in case of weakly disordered materials [2]. To illustrate this, in Fig. 4 we show dependences of the $R_{\rm sq}$ on B and on T, measured for the film with $d = 1.3$ nm in a magnetic field applied perpendicular to the sample plane. In part (a) a set of isotherms crosses at one point, marked $B_{\rm c}$, so that for $B < B_{\rm c}$ we observe $\mathrm{d}R_{\rm sq}/\mathrm{d}T > 0$ while for $B > B_{\rm c}$ we have $\mathrm{d}R_{\rm sq}/\mathrm{d}T < 0$. The magnitude of $R_{\rm sq}$ at $B_{\rm c}$ is about 1800 Ω, so our films belong to a class of weakly disordered, homogeneous systems, which also includes many other amorphous materials, such as $\mathrm{Mo}_x\mathrm{Ge}_{1-x}$, $\mathrm{Nb}_{0.15}\mathrm{Si}_{0.85}$, $\mathrm{Mo}_x\mathrm{Si}_{1-x}$, Be, or α-Bi. In these materials the magnetic field seem to induce a transition to a dirty metal, rather than to an insulating phase. This is opposed to another group, of strongly disordered systems, such as TiN or InO_x, in which $R_{\rm sq}$ at $B_{\rm c}$ reaches much higher values, indicative of an insulating phase [2].

Until recently, it has been customary to identify a

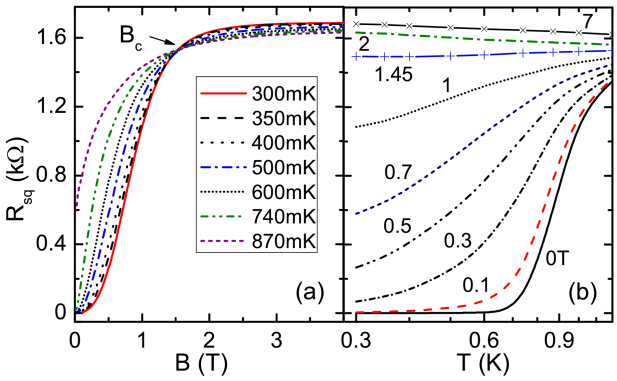

Fig. 4. $R_{\rm sq}$ for the film with $d = 1.3$ nm as a function of B for fixed temperatures (a), and as a function of T for fixed magnetic fields (b). $B_{\rm c}$ is the field at which $R_{\rm sq}$ is T-independent.

crossing point at $B_{\rm c}$ as a signature of the quantum critical point (QCP), at which the long-range superconducting phase coherence is suppressed by the magnetic field. Some theories predict that the QCP is the point at which a SIT in a two-dimensional system occurs, i.e. the Cooper pairs lose global phase coherence, but they survive locally on the insulating side of the SIT [15], and some experiments on strongly disordered systems confirm these predictions [2]. In this picture the metallic state should exist only at QCP (i.e., at $B_{\rm c}$).

However, in our films these predictions do not seem to be followed. Figure 4b shows that, in a finite magnetic fields, from about 0.3 T up to $B_{\rm c}$, the $R_{\rm sq}$ decreases, but it is unlikely to reach a zero-resistance state in a zero temperature limit. Rather, $R_{\rm sq}$ tends to saturate at a finite value, lower that the normal-state resistance, suggesting the existence of the metallic nonsuperconducting phase in a broad field range. This is similar to behavior reported for many amorphous, homogeneously disordered materials [16–24]. In a recent microwave study of the SIT in weakly disordered InO_x films the frequency-dependent superconducting fluctuations in the metallic phase have been found, while they become undetectable in the fields above $B_{\rm c}$ [24]. It has been proposed that the true QCP in weakly disordered systems lays below $B_{\rm c}$, and the metallic phase between QCP and $B_{\rm c}$ may consist of superconducting islands immersed in the normal metal. Our experiment suggests that such a picture may be valid for the ultrathin Nb films.

In conclusion, we have studied the properties of ultrathin Nb films in the Si/Nb/Si trilayers. We show that Nb films are amorphous for $d < 4$ nm. In thinnest amorphous films we observe a change of the sign of the Hall coefficient into negative, most likely as a result of the influence of boundary scattering on the relaxation rate of carriers. We have also studied the B-induced SIT in this system, and found that magnetic field induces a transition from superconducting to a metallic, nonsuperconducting state, which displays the resistance smaller than that of the normal state.

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