Superconducting Tunneling in Ultrathin Nb Films

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Good-quality tunnel junctions have been fabricated on ultrathin films of Nb whose thicknesses ranged from 9 to 900 Å. As the film thickness is reduced below 50 Å, T_c decreases, $2\Delta/kT_c$ increases, and mode softening is observed through d^2V/dI^2 measurements. These results imply that as the thickness decreases below 50 Å the electron-phonon constant, λ, becomes larger than expected from the drop in T_c.

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Even though many experiments have been done on the superconducting properties of ultrathin films (< 20 atoms thick), it has not been possible to relate the behavior to the microscopic parameters except in a few cases.[1,2] Research until now has depended upon transport measurements which are possible as soon as one has an electrically continuous film regardless of homogeneity.

In this Letter, we report tunneling results on Nb films which show a mode softening in the phonon spectrum as the film thickness is reduced. This is the first direct observation of phonon softening (i.e., an increase in the weight of low-energy modes) in an ultrathin transition-metal film or for any other kind of ultrathin metal film. This softening, together with an unusually large value of $2\Delta/kT_c$ to be discussed below, implies a substantial increase in the electron-phonon coupling constant λ. As of now, there is no localization or interaction theory which predicts the behavior of λ as the film becomes more disordered. On the other hand, the Coulomb pseudopotential μ^* is expected to increase as the sample gets more disordered, as a result of the change in electron screening.[3] Using McMillan's equation[4]

$$T_c = \frac{\theta_D}{1.45} \exp\left[\frac{-1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}\right], \qquad (1)$$

we see, assuming that the preexponential factor, the Debye temperature θ_D, is not changing too drastically, that μ^* has to increase at a faster rate than λ is increasing in order to account for the observed depression in T_c.

The Nb samples are electron-beam evaporated onto $(1\bar{1}02)$ orientation single-crystal sapphire substrates at 100 °C. The substrates undergo an Ar^+-ion beam cleaning at a beam voltage of 500 eV for 1 min just prior to the Nb deposition.[5] The Nb film is covered with a thin layer (~ 25 Å) of Si to prevent Nb from oxidizing and to be used as an artificial barrier for the tunnel junctions. The Si-covered samples are oxidized in air for 3 d after which 2000-Å-thick Pb counterelectrodes are thermally evaporated to complete the tunnel junctions. On one $6\times6\text{-mm}^2$ sapphire, four identical tunnel junctions ($200\times200\ \mu\text{m}^2$) are fabricated.

The films were studied through x-ray photoemission spectroscopy, reflection high-energy electron diffraction, LEED, transmission electron microscopy, and x-ray diffraction techniques to ensure their homogeneity and uniformity. Detailed results will be published elsewhere. In summary, the Nb films are highly textured along the (100) direction, are absent of any voids, and have not reacted chemically either with the Si layer or the substrate. It is crucial for the ion-beam cleaning to be included in the preparation procedure to obtain high-quality films and good tunnel junctions.

In addition, both T_c and $R_\square$ behave in a smooth and consistent manner as shown in Figs. 1 and 2. If at any thickness the film started to be composed of linked chains or connected islands instead of a homogeneous film of relatively uniform thickness, $R_\square$ and T_c would not behave as smoothly as observed. Moreover, 90% of the time all four junctions patterned on a given sap-

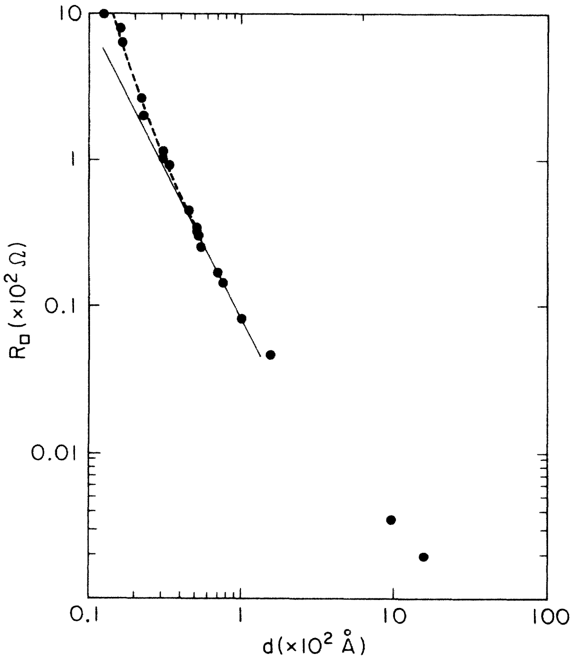

FIG. 1. Sheet resistance as a function of film thickness. The solid line has an inverse power of 2 as predicted by the Fuchs theory.

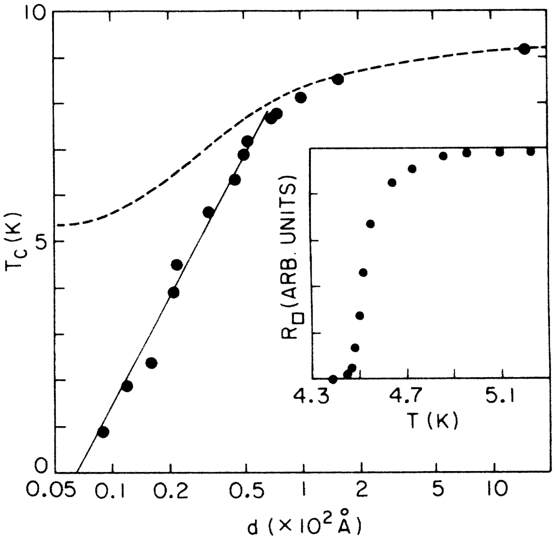

FIG. 2. T_c as a function of film thickness. The dashed line is the T_c of bulk Nb with the same resistivity as the film whose thickness is given on the x axis (with the exception of limiting value $d=0$ which is estimated as described in the text). Inset: A typical resistive transition for a 22-Å film.

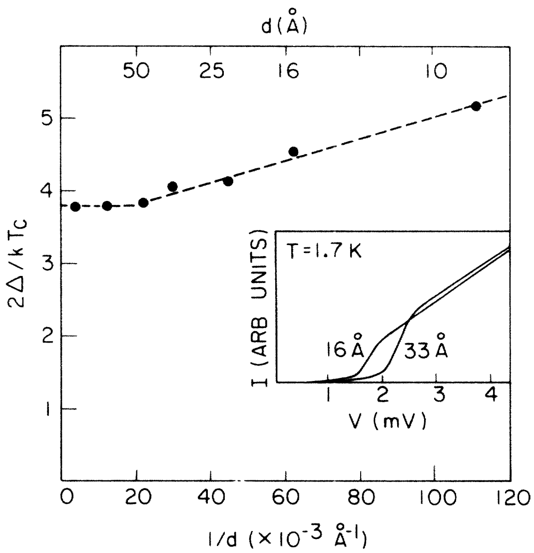

FIG. 3. $2\Delta/kT_c$ as a function of inverse film thickness. Inset: The I vs V data for 33- and 16-Å films at $T=1.7$ K.

phire are good even down to the Nb thickness of 9 Å. These facts, coupled with a low $R_\square$ for a given thickness, suggest that Nb grows layer by layer on the sapphire substrate.

Most size-effect theories, including the Fuchs boundary-scattering theory, predict $\rho \propto 1/d$ (or $R_\square \propto 1/d^2$) when the film thickness d gets smaller than the mean free path l. With the value of $\rho l = 3.72 \times 10^{-6}$ $\mu\Omega$ cm^2 for Nb,[6] the mean free path of our thick films at low temperature equals ~ 120 Å. In Fig. 1, we see that indeed starting from around 110 Å, our data fit the solid line which has the inverse power of 2 down to the thickness of 50 Å. The gradual deviation of the data points for the samples thinner than 50 Å is assumed to originate from any or all of the following: dead layers at the surfaces, the imperfect nature of the real surface,[7] and/or weak localization.

Figure 2 shows T_c as a function of thickness, where T_c's are measured both resistively and by our noting when the sheet resistance of the Nb film modifies the high-bias tunneling conductance. For the 9-Å sample, T_c was measured only by the latter method. Both methods yield mid-transition points that are in good agreement (within 50 mK) with each other. The inset shows a typical resistive transition curve for a 22-Å-thick sample.

Lifetime broadening of momentum states can account for most of the T_c depression in our Nb films > 50 Å as discussed previously.[5] The limit of the reduction in T_c through this mechanism should be given by bulk amorphous Nb. Amorphous Nb has a T_c of 5.2 K and a $2\Delta/kT_c$ of 3.7.[8] The dashed line in Fig. 2 is an estimate of the effect of lifetime broadening in our films. We see that T_c starts to deviate sharply from that dashed line starting at about 50 Å.

In Fig. 3, we plot $2\Delta/kT_c$ vs $1/d$ and see that it also starts to deviate from the bulk value at about 50 Å and has risen to about 5.2 by 9 Å. The quality of the junctions is quite good as indicated by the typical values of the ratio of the conductances above (at 5 mV) and below (at 1 mV) the sum gap $\Delta_{\rm Nb}+\Delta_{\rm Pb}$ which are 30–60 even down to the Nb thickness of 9 Å for temperatures such that $T/T_c^{\rm Nb} < 0.3$. The inset in Fig. 3 shows typical I vs V curves for 16- ($T_c = 2.2$) and 33-Å ($T_c = 5.7$) films at $T = 1.7$ K. In order to arrive at a reasonable and consistent estimate of $\Delta(0)$ for Nb, we subtract $\Delta_{\rm Pb} = 1.35$ mV from the sum gap determined from the inflection point in the superconductor-insulator-superconductor I vs V (and/or from the maximum in the superconductor-insulator-superconductor dI/dV vs V) curves. For measurements above the gap to study the Nb phonon structures, a parallel field of 1.35 kG is applied.

$2\Delta/kT_c$ of 5.2 is exceptionally large, larger than observed in any other tunneling experiments to our knowledge.[9] The large magnitude indicates an enhanced electron-phonon coupling at low energy. Bulk Nb has two peaks in $\alpha^2F(\omega)$ at energies 16 and 24 mV (as evidenced by minima in the second derivatives) and an additional shoulder for energies between 9 and 12 mV.[10] $F(\omega)$ is the phonon density of states and $\alpha^2(\omega)$ is an effective electron-phonon coupling function. As shown in Fig. 4, the low-energy mode gains weight relative to the bulk Nb peaks as the film thickness gets smaller. From 900 to 80 Å, there is not much change from the bulk "$\alpha^2F(\omega)$" inferred from the second derivative. By 45 Å, there is a more defi-

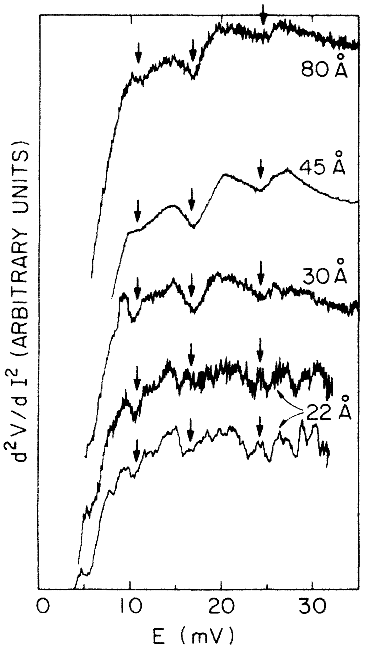

FIG. 4. d^2V/dI^2 for several films. The y scale for each trace is arbitrary and does not indicate their relative strengths.

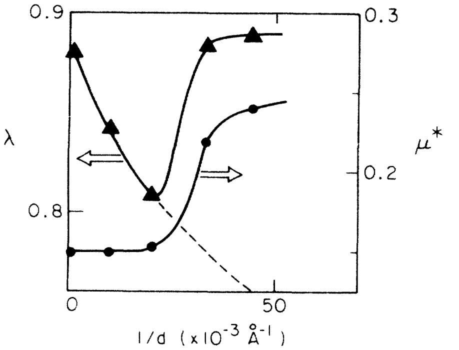

FIG. 5. λ estimated as in the text and the resulting μ^* as a fitting parameter in Eq. (1) as a function of inverse thickness. The dashed line is from Ref. 14.

nite peak developing in the low-energy part, and the peak is fully developed at 30 and 22 Å. This is consistent with the data of $2\Delta/kT_c$ vs thickness; $2\Delta/kT_c$ starts to increase above the bulk value below 45 Å.

For films thinner than 22 Å, the second-derivative measurements are dominated by structures that we believe are due to the quantum size effect since the structures are periodic and are still observed in the normal state. That will be addressed in a separate paper.

In addition to the second derivative we have also measured the tunneling conductances of Nb in its superconducting and normal states, and a full inversion of the Eliashberg equations is in progress.[11] It is apparent in the data that down to 30 Å there is no major change in the appearance and the magnitude of the deviation from the Bardeen-Cooper-Schrieffer conductance curve with the exception of the low-energy mode gaining weight. We also observe phonon structure out to ~ 30 mW in all thicknesses indicating that θ_D is not changing significantly.[12]

We interpret our data as follows. Down to about 50 Å the depression of T_c shown in Fig. 2 is mostly accounted for by the broadened density of states (DOS). The little difference in this thickness range was shown to be in the order of correction predicted by the weak-localization theory in our previous paper.[5] We also noted that for films thinner than 40 Å ($R_\square > 50\ \Omega$), weak-localization theory overestimates the reduction in T_c. According to the Varma-Dynes theory[13] λ should gradually decrease, reflecting the change in DOS down to about 50 Å. The situation is very similar to the disordered bulk Nb case.[14] In Fig. 5, we plot the values of λ obtained by our assuming that all T_c depression is due to the reduction in λ through the reduced DOS down to about 50 Å. The dashed line is the λ value for disordered bulk Nb films calculated from the experimental values of θ_D and T_c.[14] We see that they are in good agreement. For the same thickness range, μ^* should be rather constant since weak-localization contribution to T_c reduction is so small. The expected behavior of μ^* is shown in Fig. 5 as well.

Below 50 Å, the mode softening and the rise in $2\Delta/kT_c$ signal the increase in λ relative to what would be expected from the drop in T_c.[15] To estimate the change in λ due to the softening, we assumed a simple "$\alpha^2F(\omega)$" guided from our analog and digital second derivative measurements. The digital one is obtained by our taking a numerical derivative of the ratio of the conductances in superconducting and normal states, and gives not only the location but the magnitude of the second derivative minima. An increase in λ by approximately 10%–15% over the value suggested by the reduced DOS is estimated, which happens to bring λ back to near its bulk value for the 30-Å film. By using the value of T_c and the enhanced λ, we obtain μ^* simply as the fitting parameter assuming Eq. (1) is valid. The results are shown in Fig. 5.

Since the low-energy peak in the spectrum becomes more dominant as the film becomes very thin, it likely derives from surface modes. It is observed at about the same range of thickness where the normal-state resistivity becomes affected by surface roughness, i.e., where the effective surface area becomes appreciably larger than the film area.

The increase in μ^* is expected theoretically in both weak- and strong-localization regimes.[3,16] Our films clean ($k_Fl >> 1$) so that the strong-localization theory is not applicable. On the other hand, the existing weak localization seems to break down for ultrathin films (below 40 Å in our case and in the Graybeal-Beasley study[1] of MoGe). The large increase may have to do with a dimensional crossover in the screening property.[17]

In the simplest 2D limit the Coulomb potential is screened with an inverse-cube dependence on distance, much slower than the exponential decay obtained in the 3D case. Since the Coulomb pseudopotential is sensitive to screening, we may be observing the changes brought about by the dimensional change in the screening properties in addition to the changes in the screening properties caused by the disorder.

In conclusion, we have prepared a nearly ideal set of homogenous ultrathin Nb films. Tunnel junctions have been successfully fabricated down to a thickness of 9 Å. We can account for most of the T_c depression for films down to 50 Å by invoking momentum-broadened DOS brought about by smaller grain size. In this thickness range λ slowly decreases, with μ^* remaining relatively constant. In thinner samples, we observe a sharp decrease in T_c as a function of thickness. Detailed tunneling measurements show a phonon-mode softening accompanied by a rise in $2\Delta/kT_c$ which together implies an increase in λ. A large increase in μ^* is inferred in order to account for the observed decrease in T_c.

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[15] A rise in $2\Delta/kT_c$ alone would not warrant a rise in λ since a temperature-dependent pair-breaking mechanism could lead to such a rise. If the origin of the T_c reduction is due to pair breaking, then for the 16-Å film where $T_c/T_c^{\text{bulk}} \sim 0.35$, the density of states should be gapless with no noticeable maximum. This is not at all consistent with the data.

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[17] If we consider the picture of a particle in a box to describe the energy quantization in the direction normal to the film, the energy spacing is about 88 K for a 50-Å film when we assume that the effective mass is $m^* = 2m$. For a real film with imperfect surface, the effective spacing will be smaller. When the effective spacing becomes $>> kT$, the screening will become two dimensional.