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Disorder effects in ion-implanted niobium thin films

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New data on the depression of T_c related to disorder effects for N^+ ion-implanted niobium films are presented, extending up to a resistivity $\rho_0 \cong 150\ \mu\Omega$ cm. The results are discussed in the framework of the existing theories. Tunneling measurements on the same ion-implanted films show a fall of the measured value of $2\Delta(0)/kT_c$ below the BCS value for very disordered films.

INTRODUCTION

Disorder effects in superconducting transition metals and alloys have recently received great attention, especially for the striking "universal" character of the T_c versus resistivity curves.[1] In the past a progressive smearing of the peak in the single-particle density of states at the Fermi level with increasing disorder, related to electron lifetime effects, was considered to be responsible for the observed drop of the critical temperature T_c with the residual resistivity ρ_0.[2]

More recently, a completely different approach, based on Anderson localization theory, has been proposed to explain the observed universal behavior of the T_c vs ρ_0 curves in $A15$ compounds.[3]

In a recent paper[4] Gurvitch carefully analyzed the state of the art of experiments and theories on disorder effects in transition-metal elements and alloys, pointing out how the existing theories contradict the experimental evidence in many cases.

The aim of the present paper is to report new T_c versus resistivity results obtained by nitrogen ion-implantation on niobium sputtered thin films. The measurements extend up to $\rho_0 = 150\ \mu\Omega$ cm. The rate of T_c depression versus ρ_0 is in excellent agreement with previous works.[5] The experimental data are analyzed in the framework of the various existing theories.

Preliminary results on tunneling in the same ion-implanted films are also reported. As already observed in some $A15$ compounds and in other systems, the measured value of $2\Delta(0)/kT_c$ falls below the Bardeen-Cooper-Schrieffer (BCS) value for very disordered films.

EXPERIMENT

The Nb films were realized by sputtering in Ar atmosphere (4×10^{-3} torr) using conventional rf diode-type equipment. The vacuum system was based on a 3000 l/s diffusion pump equipped with a (LN_2) cooled baffle. Typical pressures before deposition were in the 10^{-7}-torr range.

The films were deposited at room temperature on Corning 7059 glass substrates. The peak-to-peak voltage was 2.1 kV for all the reported deposition (500-W rf power) corresponding to a rate of 250 Å/min. Film thickness was 4000 Å for most "pure niobium" samples and 2000 Å for films to be used for ion implantation. The thickness was inferred from the sputtering time after an accurate calibration of the rate. The Nb samples show a polycrystalline structure with preferential orientation along the (110) direction. The lattice constant for the best films was $a = 3.326 \pm 0.003$ Å. Typical T_c values for the nonimplanted films ranged between 8.9 and 9.1 K, depending on the specific preparation conditions.

Implantation of nitrogen ions was performed at room temperature with a nominal dose ranging from 5×10^{15} to 5×10^{16} N^+/cm^2, corresponding to an amount of nitrogen in the film varying from ~0.5% to ~5% of niobium atoms. The ion energy (100 keV) was selected in order to ensure a good uniformity for the N^+ profile in the film. No significant thickness reduction by sputtering effects due to implantation was observed. As discussed below, both the structure and the electronic properties of the films were significantly affected by implantation.

The transition temperature for all the films was measured by a germanium resistance thermometer. A standard direct uv photolithography was employed in order to obtain a suitable pattern to perform precise resistivity measurements.

RESULTS AND DISCUSSION

The implanted nitrogen ions occupy interstitial sites in the niobium lattice. Indeed, x-ray measurements reveal that the bcc structure is preseved in the implanted samples with a significant increase of the lattice parameter a. For instance, we have observed an increase of a from the value 3.326 ± 0.003 to 3.364 ± 0.003 Å ($\Delta a/a = 1.1\%$) in a sample implanted with a dose of 5×10^{16} N^+/cm^2. Displacements also take place yielding an enhancement of the resistivity as a function of the amount of implanted ions. As previously reported[6-9] the superconducting critical temperature T_c in niobium is affected by the nitrogen ion-implantation processes, decreasing from the bulk value of 9.2 K to a few degrees.

Since diffused nitrogen in niobium, at least for the quantities considered, has a small effect on the superconductive properties,[10] it is possible to assume that the origin of the behavior of implanted samples is not directly connected to the kind of ions employed, but is related to the modification of the lattice produced by the ion bombardment. Indeed, similar effects can be produced by implantation of noble gases, by irradiation processes, and by the inclusion in the lattice of residual gas. Moreover, T_c in Nb is also affected by the deposition parameters.[11,12] The relation between T_c and the resistivity ratio ρ_{273}/ρ_{10}, independently of the specific method used among those mentioned above, and in spite of the large number of competing factors which have a role in determining both T_c and ρ_0, seem to show a universal behavior for niobium. In Fig. 1, in fact, T_c vs ρ_{273}/ρ_{10} is reported for our implanted samples, together with data from Face and co-workers[5] in which Xe and Kr ions are diffused in the niobium films and with data from Ref. 12. Excellent agreement is also found with recent data from Linker[8] on implanted niobium. The curve displayed resembles very closely the "universal curve" already reported for disordered $A15$ compounds. This universal relation is no longer valid whenever the T_c depression is produced by "other" factors as chemical effects or presence of ferromagnetic impurities.[13,14]

The T_c dependence versus the residual resistivity ρ_0 for our films is reported in Fig. 2. For $\rho_0 \leq 50\ \mu\Omega$ cm the data are in close agreement with the results reported by Face and co-workers[5] ($dT_c/d\rho_0 \simeq 0.10$ K/$\mu\Omega$ cm) whereas some inconsistency is found with data from Ref. 8 ($dT_c/d\rho_0 \simeq 0.15$ K/$\mu\Omega$ cm). In the high disorder region ($\rho_0 \geq 100\ \mu\Omega$ cm) a saturation value of T_c ($T_c = 2.5$ K) is observed, as in Refs. 7 and 8.

From a theoretical point of view the effects of disorder on the physical properties of bcc transition metals and $A15$ materials has been quantitatively considered by Testardi and Mattheiss.[2] To fit our data we have used a simplified version of the Testardi-Mattheiss calculation. We have modeled the peak at the Fermi energy E_F in the normal-state density of states by a Lorentzian curve with energy half-width equal to E_0. The "broadening" function used is also a Lorentzian curve.[2,15]

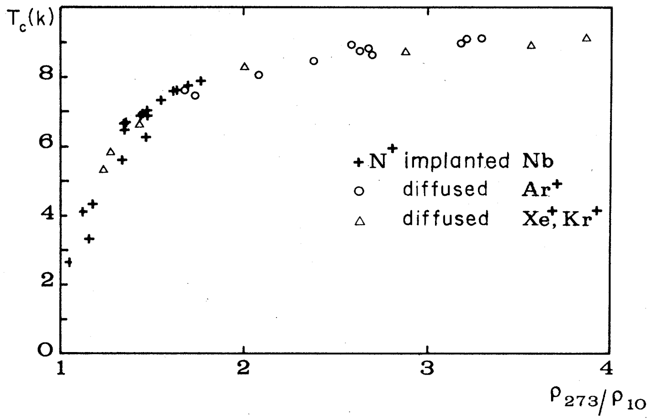

FIG. 1. Superconducting transition temperature of Nb vs resistivity ratio ρ_{273}/ρ_{10}. N^+ implanted film data (+) are reported with the data on Nb taken from the works of Costabile *et al.* (Ref. 12) (O) and of Face and co-workers (Ref. 5) (Δ).

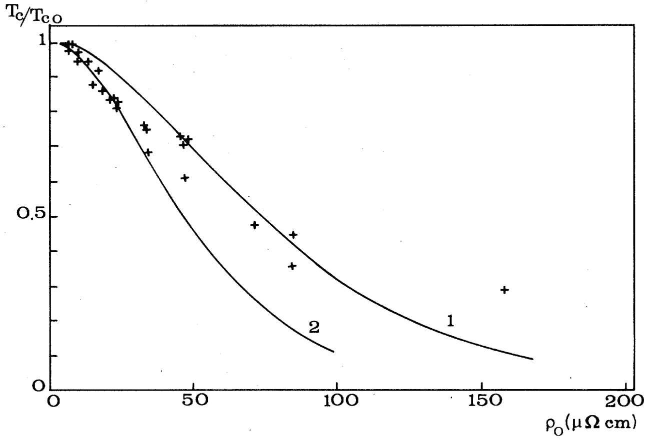

FIG. 2. Normalized superconducting transition temperature vs the residual resistivity of N^+ implanted films. The solid curves are obtained by Testardi-Mattheiss model (see text), choosing a value $\hbar\langle\Omega_p^2\rangle^{1/2}=6$ eV for the curve (1) and $\hbar\langle\Omega_p^2\rangle^{1/2}=7.5$ eV for the curve (2).

Assuming a constant averaged Drude plasma frequency[16] ($\langle\Omega_p^2\rangle^{1/2}$), we get the following result:

$$\langle N(E_F)\rangle = N_0(E_F)\left[\frac{(4/\pi)\xi\tan^{-1}(\xi)-1}{\xi^2-1}\right],$$

where

$$\xi=\frac{\hbar\langle\Omega_p^2\rangle\rho_0}{4\pi E_0}.$$

The dependence of T_c normalized to the value T_{c0} of the pure metal, as a function of ρ_0, has been calculated by using the McMillan formula[17] and a direct proportionality between the electron-phonon interaction parameter λ and $\langle N(E_F)\rangle$. The solid curves in Fig. 2 are obtained taking for the Coulomb pseudopotential the standard value for niobium $\mu^*=0.1$, for the pure niobium λ a value $\lambda_0=0.95$, for the energy E_0 a value of 250 meV,[18] and a value for $\hbar\langle\Omega_p^2\rangle^{1/2}$ of 6 (curve 1) and 7.5 eV (curve 2), respectively.[16]

A reasonable agreement is found with the experimental data up to $\rho_0=80\ \mu\Omega$ cm. In the region of low resistivity curve 2 seems the most appropriate, whereas curve 1 gives a better fit in the higher resistivity region. This could be due to a slight decrease of $\hbar\langle\Omega_p^2\rangle^{1/2}$ for increasing resistivity.[2] Assuming $\hbar\langle\Omega_p^2\rangle^{1/2}=9$ and $\mu^*=0.15$ and keeping constant all the other parameters, our simplified model reproduces fairly well the theoretical curve reported by Testardi and Mattheiss[2] to fit the data of Ref. 13. With these values of the parameters a good fit of the data from Ref. 8 is also obtained.

A different approach to the problem has been pointed out more recently by Anderson, Muttalib, and Ramakrishnan[3] on the basis of localization theory. Their model gives a possible explanation of the T_c depression for $A15$ compounds but it does not seem to be appropriate for our data on niobium. In fact, if we assume that the localization effects in niobium become important when the mean free path of electrons is comparable with the lattice parameter, we can estimate the dependence of μ^* on ρ_0 by using relation (4) of Ref. 3 and, by means of McMillan's relation, the T_c vs ρ_0 dependence.

Using a value of 95 $\mu\Omega$ cm for the parameter ρ_c, that is, the critical value of resistivity above which the Anderson model holds, a curve that reasonably reproduces the trend of the data in the high resistivity region can be drawn, whereas no suitable choice of ρ_c can reproduce the low ρ_0 region.

Finally, we mention that the use of the formula derived by Laughlin[19] for the depression of the density of states in the framework of the exchange theory does not give a reasonable fitting of our data using "realistic" values for the saturation resistivity ρ_{sat}.

TUNNELING

High-quality tunnel junctions have been prepared on the described ion-implanted Nb films. The desired geometry of the base layer was defined also in this case by direct photolithography. A sputter etching procedure removing approximately 600 Å of oxide and niobium was performed in the rf sputtering system described above.

The tunneling barrier was obtained by rf plasma oxidation in O_2/Ar (5%) atmosphere (peak to peak voltage =40 V for 20 min). A proper lead counterelectrode was deposited by thermal evaporation.

In Fig. 3, $2\Delta(0)/kT_c$ values are reported as a function of T_c for various ion-implanted samples. The $\Delta(0)$ values have been determined by measuring the voltage corresponding to the peak in the dV/dI curve of the junctions at $\Delta_{Nb}+\Delta_{Pb}$ at low tempeature and assuming $\Delta(0)_{Pb}=1.32$ meV. The data were taken at 1.5 K and were consistent with data taken at 4.2 K. T_c was measured resistively on the junction electrode. T_c data obtained by gap opening measurements gave identical results within the experimental uncertainty. The fall of the measured value of $2\Delta(0)/kT_c$ below the BCS value (3.53) for the highly disordered films is inconsistent with the results of the strong-coupling theory.[20] A similar behavior already has been observed in disordered *A*15 compounds[21,22] and might be related to the presence of a damaged layer at the Nb interface causing proximity effects or, possibly, to a breakdown of the theory for highly disordered systems. Detailed tunneling studies, aimed to obtain precise values for the parameters λ and μ^* are in progress.

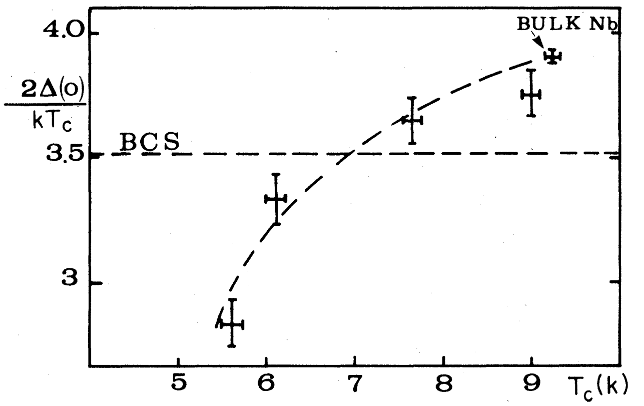

FIG. 3. Experimental $2\Delta(0)/kT_c$ values vs superconducting transition temperature T_c, for tunnel junctions with a N^+ implanted Nb electrode.

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