Localization and proximity effect in ultrathin superconducting films

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The effects of metal coatings (Ag, Au, Mg) and superconducting coatings (Zn) on the properties of ultrathin (<50-Å), homogeneous films of a morphous Bi have been studied. Thin metal coatings raise the superconducting transition temperature. The results confirm that the superconductivity of films with a homogeneous disorder is governed by electron localization. © *1994 American Institute of Physics.*

A pronounced nonmagnetic disorder disrupts superconductivity. [1,2] The superconducting transition temperature T_c of thin films decreases systematically with decreasing film thickness d (Ref. 3). It is generally believed that this effect in homogeneous amorphous films stems from an interference of the Coulomb interaction of electrons with a scattering by impurities. [1,4,5] However, there has been no direct experimental verification of the role played by the long-range Coulomb interaction in $2D$ systems. [6] Also warranting attention are the conventional approaches, in which the lowering of T_c of thin films with decreasing film thicknesses is attributed to a surface effect, a proximity effect, charging effects, etc. [3,7,8]

In the present experiments we altered the conditions at the surface of a thin film of an amorphous superconductor by depositing a normal metal or a low-T_c superconductor on the film. If processes associated with the disorder are important, then the factor which primarily determines T_c in the 2D case is the surface resistivity $R_\square$. A decrease in the resistance of an N/S sandwich due to deposition of metal should lead to a decrease in effects which stem from a localization of electrons. At small thicknesses of the metal film, with a competition between localization and a proximity effect, we would expect that the T_c of the two-layer system would be higher than the original value.

In studies of ultrathin two-layer systems, attention must be paid to the homogeneity of the films and the possible formation of compounds with higher T_c's. In our experiments, homogeneity was achieved by condensing the films at liquid-helium temperature on a substrate coated beforehand *in situ* by a monolayer of germanium. [3] The only way to draw conclusions about the formation of compounds is to look at the experimental data.

As the superconductor in our N/S sandwiches we used films of cold-deposited, amorphous bismuth ($T_{c0}^{\mathrm{Bi}} \simeq 6.1$ K; Ref. 9). Preliminary results regarding the deposition of silver on an island bismuth film were published in Ref. 10.[2)]

The films were deposited, and their properties studied, in an apparatus immersed

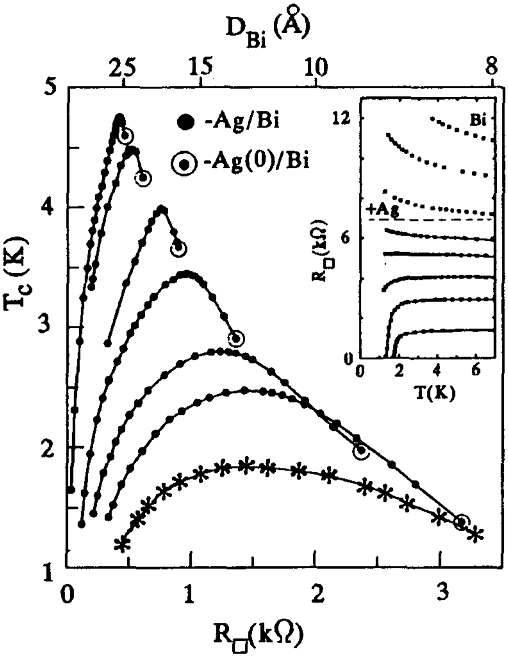

FIG. 1. Plot of T_c of Ag/Bi sandwiches (●,*) versus the surface resistivity $R_\square$. ⊙—T_c of the original Bi films. The inset shows $R(T)$ of a Bi film (the dots) as the thickness of this film is progressively increased. Silver is deposited on this film beginning at $d_{\mathrm{Bi}}=6.5$ Å (the points are connected by lines). In the main part of the figure, the $T_c(R_\square)$ of the sandwich is shown by the asterisks.

completely in a ^{4}He bath. The films were condensed at $T \simeq 8$ K on glass coated just beforehand with a layer of germanium or antimony 6–8 Å thick. The resulting films began to conduct at a thickness $\simeq 4$ Å. They were continuous and homogeneous at monolayer thicknesses.[12,13] The substrate temperature did not exceed 15 K. The resistance was measured by the four-contact method. A system of gates made it possible to deposit up to six sandwiches simultaneously, with various thicknesses of the S and N layers, with good reproducibility at thicknesses above 5 Å. The film thickness was determined within 0.02 Å (for Bi and Ag) from the frequency shift of a quartz resonator. In determining the thicknesses we used the densities of the bulk materials. We first deposited several bismuth films on one substrate and verified that their properties were the same. We then deposited the second metal in small sequential amounts on these bismuth films, measured their surface resistivity $R_\square$, and recorded the temperature dependence of their resistance. We determined T_c at the midpoint of the superconducting transition. This procedure was repeated several times, and the sandwich was produced as the result of repeated depositions of metal on the same bismuth film.

The symbols ⊙ in the figures show the T_c's of the original bismuth films. The lines in the figures connect the points for a given N/Bi sandwich as the thickness of the coating, d_{N} (N = Ag, Au, Zn, Mg), is varied. All the ⊙points conform well to the $T_c(R_\square)$ curve for one Bi film. Figure 1 shows data on sandwiches in which the coating is a normal metal (Ag, Au), while Fig. 2 shows corresponding data for a superconductor (Zn). The results are qualitatively the same. Also shown in Fig. 1 is a scale of the thicknesses of the Bi films, which gives an idea of the scale of the changes in T_c with the thickness. The properties of the Bi films produced in the present experiments agree well

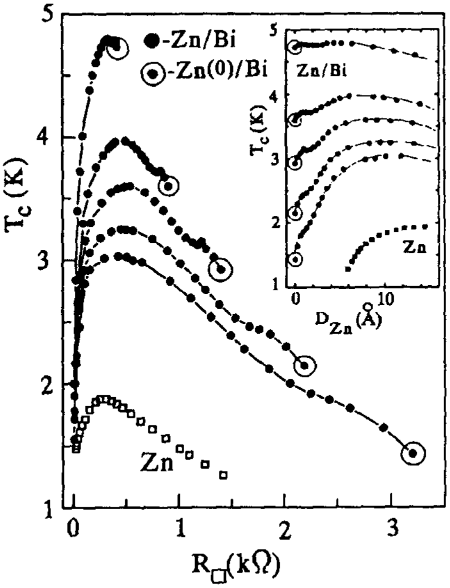

FIG. 2. T_c of Zn/Bi sandwiches (●) versus the surface resistivity $R_\square$. ⊙—T_c of the original Bi films. The inset shows T_c of Zn/Bi sandwiches (○) versus the thickness of the zinc layer.

with data in the literature.[12] Beginning at thicknesses of only $\geqslant 6$ Å and at resistances $\leqslant 10^4$ Ω, the conductivity of the bismuth films has a logarithmic temperature dependence $R_\square^{-1} \sim A \cdot (e^2/\pi h)\ln T$. In a perpendicular magnetic field of 36 kOe, the coefficient A is approximately one ($A \simeq 1.1$), in accordance with the theory of weak localization for homogeneous films.[14] As the film thickness is raised from 10 Å ($T_c \simeq 2$ K) to 100 Å ($T_c \simeq 5.9$ K), the slope of the upper critical field H_{c2} at $T = T_c$ changes only from $\simeq 25$ kOe/K to the value 11 kOe/K, which is characteristic of thick bismuth films.[15] Working from the slope of H_{c2} at $T = T_c$, we can estimate the electron diffusion coefficient: $D \simeq 1$ cm^2/s.

Figure 1 shows data on seven Ag/Bi sandwiches. A good agreement is found for the Ag/Bi and Au/Bi films, although silver does not form superconducting compounds with bismuth, and the compound Au_2Bi, with $T_c \approx 1.8$ K, occurs in the gold–bismuth system.[16]

At a small silver thickness, the $T_c(R_\square)$ of the Ag/Bi sandwiches increases with increasing deposition of bismuth in nearly the same way as that of the original film (Fig. 1). The most interesting point is the increase in T_c when silver is deposited on a film 6.5 Å thick, with $R_\square(14\text{ K}) = 6.7$ kΩ (the lower curve in Fig. 1). Using the data of Ref. 12, where the T_c's of bismuth films deposited under similar conditions were measured down to 0.4 K, or extrapolating the T_c of bismuth according to our data and the data of Ref. 12 to zero (since we have $T_c \sim -1/d$), we conclude that a bismuth film 6.5 Å thick should still be nonsuperconducting. The deposition of silver on its surface gives rise to a superconductivity with increasing amount of the nonsuperconductor in the system. The maximum T_c of the Ag/Bi (6.5 Å) film was 1.8 K. At a silver thickness of 20 Å we still observed a decrease in the resistance with decreasing temperature. In cold-deposited Ag_xBi_{1-x} mixtures, T_c vanishes at $x \simeq 0.5$ (Ref. 17). The inset in Fig. 1 shows experi-

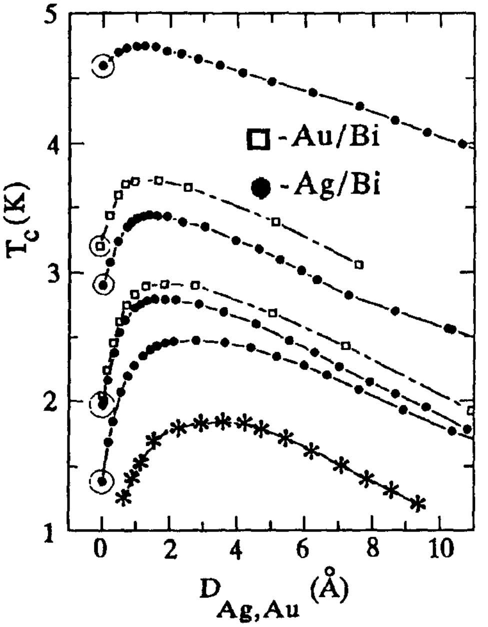

FIG. 3. T_c of the Ag/Bi sandwiches (●,*) (Au/Bi—□) versus the thickness of the silver (gold) layer. ⊙—T_c of the original Bi films; ●,*—points from Fig. 1.

mental data on $R(T)$ of the original bismuth film (the dots) and of the Ag/Bi (6.5 Å) sandwich (the curves) after the deposition of silver on this film. This is a typical picture of the insulator–superconductor transition in homogeneous systems. [12]

Figure 3 shows T_c versus the coating thickness for several films from Fig. 1. Also shown here are two curves for Au/Bi films. An increase in T_c is observed at small coating thicknesses; at large thicknesses, the T_c of the sandwiches acquires a behavior $T_c \sim \exp(-d_{Ag}/d_{Bi})$, which is characteristic of a proximity effect in thin films. [18] With increasing thickness of the original bismuth films, the maximum T_c of the sandwiches shifts toward a smaller metal thickness. We believe that this behavior indicates that the increase in T_c is not due to surface effects. If it were, all the changes would have occurred at the same thickness of the metal coating. For the Bi film 23 Å thick, the maximum T_c corresponds to a silver thickness of only 1 Å . At this thickness it is meaningless to speak in terms of individual properties of the silver film or, especially, a screening of the metal film by a Coulomb interaction in the superconductor.

The increase in T_c is at its greatest for the thinnest original Bi film; it decreases for the thick films. Probably the only reason why we can see an increase in T_c of the relatively thick bismuth films is the circumstance that the resistivity of silver ($\rho_{Ag} \simeq 20$ $\mu\Omega \cdot$cm) is smaller than that of bismuth ($\rho_{Bi} \simeq 100\,\mu\Omega \cdot$cm).

The suppression of superconductivity in the sandwiches due to the proximity effect should be weaker if the second metal is a superconductor with a T_{c0} lower than that of bismuth. As this superconductor we selected zinc. The thin, cold-deposited Zn films in our experiments apparently had T_{c0} higher than 2 K (Fig. 2), possibly because of the formation of an amorphous Zn phase in the thin films (a control deposition of zinc was

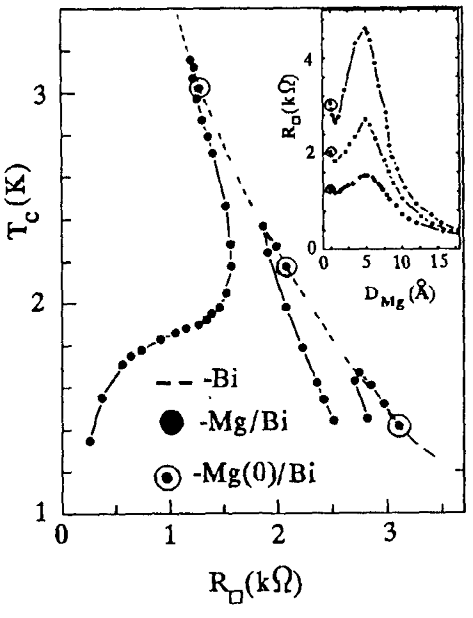

FIG. 4. T_c of the Mg/Bi sandwiches (●) versus the surface resistivity $R_\square$. ⊙—T_c with the original Bi films. The inset shows the resistance of the Mg/Bi sandwiches versus the thickness of the magnesium layer.

carried out on glass covered with a monolayer of germanium). As in the case of the metal coatings, we observe an increase in the transition temperature at small zinc thicknesses in the Zn/Bi system (see Fig. 2 and the inset there). On all the $T_c(d_{\mathrm{Zn}})$ and $T_c(R_\square)$ curves there is a structural feature at a zinc thickness $\simeq 1$ Å . We believe that this feature corresponds to the thickness at which a film of superconducting zinc proper begins to form. Up to this thickness, the properties of the zinc were not determined, and the behavior $T_c(R_\square)$ of the Zn/Bi films was nearly the same as in the Ag/Bi system. A nonmonotonic dependence of the transition temperature at a zinc thickness $\simeq 1$ Å like that in Fig. 2, can be observed even on a bismuth film 39 Å thick with $T_c = 5.3$ K $(\simeq 0.9 T_{c0})$.

If the two-layer systems are studied *in situ*, as in our experiments, we can work from the structural features on the plot of the sandwich resistance versus the coating thickness (d_{N}) to determine the points at which compounds form on the surface. When we attempted to use magnesium as the normal metal, we found that magnesium in Mg/Bi films is a metal up to a thickness $d_{\mathrm{Mg}} \simeq 1$ Å ; beyond this point, a nonmetallic compound similar to amorphous Mg_3Bi_2 apparently forms. [19] Since the compound forms because of the surface bismuth layer, the resistance increases, and T_c decreases (Fig. 4). Because of the formation of the MgBi compound, $R_\square$ and T_c of the sandwich are nonmonotonic functions of the magnesium thickness, but all the structural features are observed at the same thickness of the magnesium coating for the bismuth films of the various thicknesses.

These results can be analyzed on the basis of the following qualitative considerations.

For a thin film of a uniformly disordered superconductor of thickness

$d \ll \sqrt{\hbar D/kT}$, the film resistance $R_\square = 2\pi^2/e^2 \times [2\pi\varepsilon_F\tau(2k_F d/3\pi)]^{-1}$ is a measure of the disorder; here ε_F and k_F are the Fermi energy and Fermi momentum, and τ is the time scale of elastic collisions of electrons.[1] The lowering of T_c with decreasing thickness and with increasing $R_\square$ can be described in general by [1,4,5]

$$T_c = T_c(R_\square, T_{c0}, \tau). \tag{1}$$

At small values of $R_\square$ we have $(T_{c0} - T_c)/T_{c0} \simeq (1/3) g_1 (e^2/2\pi^2\hbar) R_\square [\ln(\hbar/kT_{c0}\tau)]^3$, where $g_1 \simeq 1$ is a constant which describes the screened Coulomb interaction.[1] Expressions like (1) describe the lowering of T_c due exclusively to an intensification of the Coulomb interaction in scattering by impurities. The effect of disorder on the electron–phonon interaction with increasing $R_\square$ is ignored.[1,4,5] It is usually assumed that T_{c0} already incorporates all the corrections to the electron–phonon interaction for the disorder and the finite τ (Refs. 1, 4, and 5). In other words, it is assumed that T_{c0} is the bulk T_c of the film material.

The N/S sandwiches studied in the present experiments satisfy the condition $d_{\mathrm{N,S}} \ll \sqrt{\hbar D/kT}$. From the standpoint of electron transport and localization, a two-layer film of this sort is a single system. The T_c of this system, with disorder ignored, is governed by the electron–phonon interaction "averaged" over the thickness, $\bar{\lambda}$ (Ref. 18):

$$T_{c0} \sim \exp(-1/\bar{\lambda}), \tag{2}$$

$$\bar{\lambda} = \frac{\lambda_{\mathrm{N}}[N_{\mathrm{N}} d_{\mathrm{N}}] + \lambda_{\mathrm{S}}[N_{\mathrm{S}} d_{\mathrm{S}}]}{N_{\mathrm{N}} d_{\mathrm{N}} + N_{\mathrm{S}} d_{\mathrm{S}}}. \tag{3}$$

Here $N_{\mathrm{N,S}}$ and $\lambda_{\mathrm{N,S}}$ are the densities of states and the constant of the electron–phonon interaction in N and S, respectively. For a two-layer system, the T_c found from expressions (2) and (3) should be regarded as a new T_{c0}, and the conductivities should add (at small values of $R_\square$). Using the specific expressions of Refs. 1, 4, and 5, along with expressions (2) and (3) of the present paper, we can see that the initial change in T_c of the system is an increase when a normal metal ($\lambda_{\mathrm{N}} \simeq 0$) with a small resistivity ($\rho_{\mathrm{N}} \leq \rho_{\mathrm{S}}$) is deposited on a thin superconducting film. At large thicknesses d_{N}, this increase gives way to a decrease. This increase in T_c in an N/S system contradicts the standard interpretation of the proximity effect,[18] but it is a natural result when we take into account the localization of electrons: In this case the behavior is governed to a greater extent by the resistance $R_\square$. We wish to stress that in this analysis the value of T_c is governed not by the screening of the Coulomb interaction in the superconductor by the metal film but by a competition between the proximity effect (a decrease in the electron–phonon interaction) and localization as $R_\square$ of the entire system decreases. It is apparently not possible to offer a more rigorous analysis of the experimental results at this point.

This study of bismuth films unambiguously proves that the superconductivity of thin, homogeneous films of amorphous superconductors is governed by a localization of electrons, not by surface effects.

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[2] There was a misprint in the original paper. The $R_\square$ scale in Fig. 3 of that paper, which is a plot of $T_c(R_\square)$, should be larger by a factor of 10 (Ref. 20). The Bi films were deposited on glass and had $T_c \simeq 3$ K (at the transition midpoint) with $R_\square \simeq 15$ kΩ. Such Bi films are island films not far from the percolation threshold ($\simeq 10-15$ Å under our conditions) (see, for example, Ref. 11). The increase in the "T_c" of an island Bi film as silver is deposited on it is a trivial effect.

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