Superconductivity in amorphous Ta/Ge multilayers

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This paper reports measurements of the superconducting transition temperature (T_c) of Ta/Ge multilayers for a range of individual layer thicknesses. Thick amorphous Ta layers which are isolated by thick insulating (Ge) layers have a transition at 0.9 K, and it is noted that for thinner isolated layers T_c approaches zero as the resistance per square approaches the quantum resistance $h/(2e)^2$. However, the transition temperature is enhanced in samples with thin Ge layers, and in films with Ta layers thinner than 1.5 nm T_c rises to near 3 K. The enhancement is consistent with a proximity effect involving layers of a Ta-Ge alloy at the layer boundary. [S0163-1829(96)02621-5]

I. INTRODUCTION

The study of superconducting properties of superconducting-insulating and superconducting–normal-metal layered structures has recently seen an enhanced level of activity, prompted in part by the insight such studies might give into the properties of the cuprate superconductors. The layered nature of these materials clearly plays a major role in their superconductivity, and an understanding of the behavior of layered conventional superconductors is essential to establish which properties of the cuprates might follow simply from their geometry.

Most of the multilayers studied to date have superconducting layers which are amorphous in the thin limit, but microcrystalline when the individual layer thicknesses exceed about 2 nm (see, for example, Refs. 1 and 2). The exceptions (e.g., MoGe/Ge) (Ref. 3) are formed of alternating alloys with pure insulating layers. The Ta/Ge system appears initially as a particularly simple system in which to work, for it consists of elemental layers which retain their amorphous structure[4,5] up to temperatures of several hundred degrees C in samples with layer thicknesses up to at least 20 nm (Ta) and 1 μm (Ge). Very high-purity multilayers can readily be formed by vapor deposition in a vacuum.

Against this background there exist a number of predictions in the literature[6] that layered superconductor-insulator materials might show superconductivity at a temperature above that in the homogeneous bulk superconductor itself. In particular Chakravarty *et al.*[7] have suggested an enhancement of T_c due to tunneling of Cooper pairs between CuO_2 planes in the cuprate superconductors. It was thus clearly important to follow up an observation that superlattices of amorphous Ta/Ge showed a more than twofold increase in T_c when the insulating Ge layers were thinned to permit tunneling between the superconducting Ta layers. In this work we report on a careful study of the transition temperature and its dependence on the Ta- and Ge-layer thicknesses. Although it now seems unlikely that the layering directly enhances the transition temperature, the system nonetheless represents an interesting complex layered superconductor.

We have already reported[5] the normal-state conducting characteristics of Ta/Ge multilayers, which can be understood on the basis of parallel conduction along amorphous-structured sheets of metallic charge density, showing increasingly two-dimensional behavior as the Ta layer thickness is reduced.

II. EXPERIMENTAL DETAILS

Films of amorphous Ta layers separated by amorphous Ge were prepared on glass substrates by vapor deposition in a vacuum chamber with a base pressure of 10^{-9} torr, using a rotating substrate assembly described previously.[8] The layering was inspected with transmission electron microscopy and electron and x-ray diffraction. As we have made clear in our previous work,[4,5] there is no evidence for crystallinity in any of the diffraction results, and the magnitude and temperature dependence of the resistance of the films establish that the conducting Ta layers are noncrystalline with electron mean free paths approaching the interatomic distance.[5] Annealing studies show the effects of significant diffusion and crystallization only above 500 °C.[4] Furthermore we have found no indication of a change of resistance at the bulk crystalline Ta transition temperature (4.5 K) in any of our films, to an accuracy of better than one part in 10^5.

The number of periods in a given film was determined from the deposition conditions, and the layer thicknesses were then measured using Rutherford backscattering spectroscopy (RBS). Note that RBS measures the two-dimensional (2D) atomic density, but below we quote layer thicknesses derived by assuming 3D atomic densities of 4.55×10^{22} cm^{-3} and 4.35×10^{22} cm^{-3}, respectively, for Ta and Ge.

The in-plane resistivities were measured on rectangles of approximately 2×6 nm scratched onto the films. We quote the results as the product of the number of Ta layers (N_{Ta}) and the resistance per square of the entire film (R_{sq}), which represents the resistance per square of one Ta layer in the

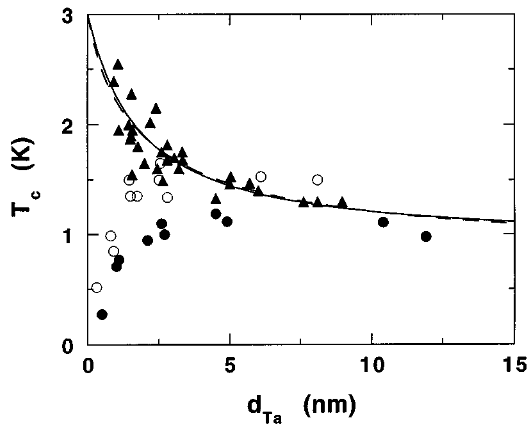

FIG. 1. Transition temperatures plotted vs the thickness of the Ta layers. The different symbols indicate the Ge film thickness: $d_{Ge}<2.2$ nm (full triangles), $2.2<d_{Ge}<5$ nm (empty circles) and $d_{Ge}>5$ nm (full circles). The almost identical lines show the expected behavior due to the proximity effect between films of two different superconductors, fitted to the T_c values for the multilayers with thin Ge films; the full line is for the Cooper–de Gennes model, and the dashed line for the McMillan model, as discussed in the text.

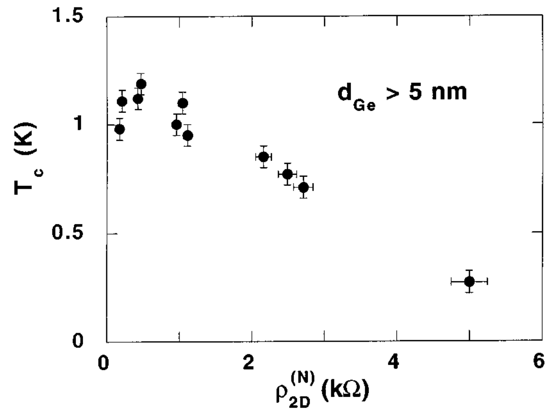

FIG. 2. Transition temperatures for films with thick (>5 nm) Ge layers vs the normal-state sheet resistance of a single Ta layer.

approximation that those layers provide parallel conducting paths. For convenience we label this product as ρ_{2D}. The conductivity of amorphous Ge in this temperature range is many orders of magnitude smaller than that of amorphous Ta, and it can be safely ignored.[5]

III. RESULTS

This work concentrates on the transition temperatures defined by the temperature at which the resistance becomes immeasurably small, typically 5 orders of magnitude below the normal-state resistance. In Fig. 1 the transition temperature is shown plotted vs the Ta-layer thickness (d_{Ta}) to illustrate the expected reduction in T_c with increasing 2D resistivity in the normal state ($\rho_{2D}^{(N)}$). Contrary to that expectation it can be seen that the transition temperatures simply spread out to cover a much wider range of values than in the thicker (''bulk'') Ta layers. The underlying pattern is that the films with thick Ge layers all lie in the low-temperature limit of the fan, while those with thinner Ge layers show a substantial enhancement of the transition temperature as the Ta layers are prepared thinner.

In Fig. 2 we display T_c plotted vs $\rho_{2D}^{(N)}$ for films with Ge layers thicker than 5 nm, sufficient to prevent tunnelling effects in the normal state.[4,5] In line with expectation,[9] the transition temperatures for this selection of our films fall approximately linearly with $\rho_{2D}^{(N)}$, finally reaching 0 K near the quantum resistance $h/(2e)^2$ (6.45 kΩ). Note that the transition temperature in the thickest Ta layers (smallest $\rho_{2D}^{(N)}$) falls below the extrapolation of the rest of the data, against the trend normally observed.[9,10] We return to this point below.

The systematics of the observed T_c enhancement are further illustrated by plotting T_c as a function of d_{Ge}, as in Fig. 3. Again there results a fan at low d_{Ge} unless the data are restricted to limited ranges of d_{Ta}. Notice that within the ranges shown there is approximately a 30% variation in T_c even for isolated layers, which leads to the scatter in the plots of Fig. 3. We call attention to the following trends: (a) T_c rises as d_{Ge} falls below 5 nm, reaches a maximum for Ge layers in the range of 1–2 nm, and thereafter T_c falls with diminishing d_{Ge}; (b) the enhancement is greatest for the samples with the thinnest Ta layers, and is by a factor of

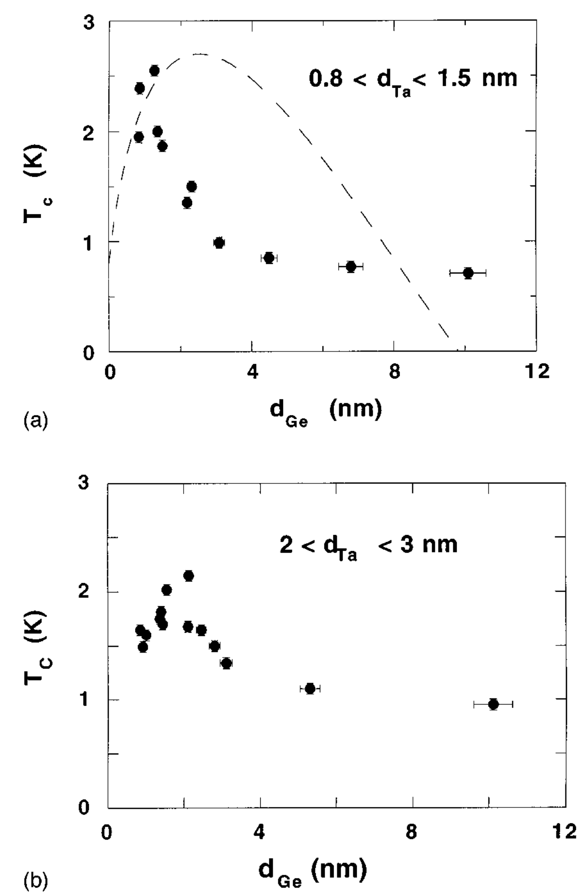

FIG. 3. Transition temperatures plotted against the Ge-layer thickness for Ta-layer thicknesses between (a) 0.8 and 1.5 nm and (b) 2 and 3 nm. The dashed line in (a) shows the transition temperatures of the alloy with the same average composition as the multilayer.

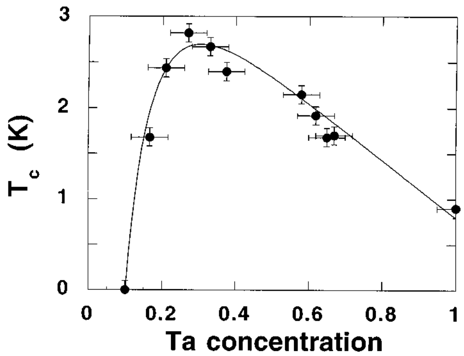

FIG. 4. Transition temperatures of amorphous Ta-Ge alloys vs the Ta concentration. The line is intended as a guide to the eye and is used to display the alloy expectation (dashed line) in Fig. 3(a).

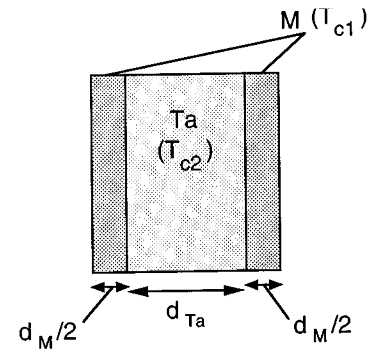

FIG. 5. Model for the superconducting proximity effect between a Ta film and films of a Ta-Ge mixture (M) with higher intrinsic T_c.

more than 3 (0.7–2.4 K) for d_{Ta} less than 1.5 nm.

A natural explanation for the observed enhancement in these amorphous multilayers, particularly those with thin layers and thus a high density of interfaces, can be found by noting that Ta-Ge alloys form superconductors with transition temperatures above 2 K.[11] Since earlier work on these alloys was performed on materials which showed conductivities typical of crystalline metals (resistivities below 50–100 $\mu\Omega$ cm with positive temperature coefficients), we have repeated the measurements on amorphous alloys prepared by coevaporation. In Fig. 4 we show our results on these alloys plotted as T_c vs the atomic concentration of Ta, and it can be seen that there is a broad range of compositions with T_c between 2 and 3 K. We thus propose that the enhancement we observe in the layered films is related to an alloy phase which forms at the interface between the Ta and Ge layers.

An upper limit to the range over which mixing occurs in our multilayers can be estimated from the data of Fig. 3. We note that if the period of the multilayer is smaller than twice the mixing range, then the films would be completely mixed into an alloy and would show alloy characteristics. Furthermore when the Ge layers are vanishingly thin the data must approach the value (0.9 K) corresponding to thick Ge-free amorphous Ta films. Thus as an aid to estimate the range of mixing we have shown as a dashed line in Fig. 3(a) the transition temperatures which would be observed if the multilayer films were mixed throughout their depth. That dashed line is generated by the line fitted to pure alloy data (see Fig. 4), and noting that the average Ta concentrations in the multilayer films are determined by the ratios of the Ta- and Ge-layer thicknesses. As expected the data are in reasonable agreement with the alloy predictions in the thin-layer limit, but they differ for $d_{\mathrm{Ge}}>1.5$ nm, setting an upper limit of about 0.7 nm of Ge being lost to the mixed layer at each interface. The upper limit for the thickness of the mixed layer is then about 1.5 nm, which can be compared with the value of less than 1 nm commonly found in amorphous semiconductor-semiconductor multilayers.[8]

The enhancement of Figs. 1–3 is understood by modeling our multilayers as shown in Fig. 5, with each Ta layer sheathed by mixed Ta-Ge layers (M), and the entire M/Ta/M structure separated from its neighbors by insulating layers of Ge. Since the layer thicknesses are smaller than the coherence lengths in these low-T_c superconductors, we do not expect large variations in the superconducting parameters across a single film. The increase of T_c for samples with thin Ge layers in Fig. 1 is ascribed to the proximity effect between the superconducting M and Ta layers, with the T_c of the combination being intermediate between the intrinsic values $T_{c1}\sim3$ K for M and $T_{c2}\sim0.9$ K for Ta. As the thickness d_{Ta} of the Ta layers is reduced, the superconducting carriers spend a smaller fraction of their time in the Ta layers and more in the M layers, which leads to an increasing T_c as the larger pairing interaction in the M layers dominates. When the Ge layer is thicker, the enhancement of T_c as d_{Ta} is decreased is terminated for $d_{\mathrm{Ta}}<5$ nm by the impending localization transition as the resistivity of the M/Ta/M structure rises towards $h/(2e)^2$, as indicated in Figs. 1 and 2. This suggests that the coupling between adjacent M/Ta/M structures when the Ge layers are thin is required to avoid this localization transition and allow the full T_c enhancement for $d_{\mathrm{Ta}}<5$ nm.

The data of Fig. 3 are then understood qualitatively as follows: as the Ge thickness falls below 1.5 nm there is insufficient Ge to form an alloy with a high transition temperature, and T_c then falls towards 0.9 K. When d_{Ge} rises substantially above 1.5 nm the superconducting transition temperature falls toward that of isolated Ta layers, 0.9 K, or lower if the Ta layers are thin (see Fig. 2).

As shown by the lines in Fig. 1, the shape of the increase in T_c as d_{Ta} decreases (for thin Ge layers) is that typically expected for the superconducting proximity effect. The calculations are made for two different models for the proximity effect between very thin films. The first is the Cooper–de Gennes model[12] which takes the effective pairing interaction as the weighted average of that in the two films:

$$\lambda_{\mathrm{eff}}=\frac{N_1d_1\lambda_1+N_2d_2\lambda_2}{N_1d_1+N_2d_2} \tag{1}$$

where N_i, d_i, and λ_i are the density of states at the Fermi level, the film thickness and the pairing parameter, respectively, in the two films. This model represents the limit of the more general model of Takahashi and Tachiki[13] for the case where the thicknesses of the films are smaller than their superconducting coherence lengths.[14] In our case, film 2 is the amorphous Ta, and film 1 is the Ta/Ge mixture (M), taken as including the M layers on *both* sides of the Ta to give the correct averaged pairing parameter. The transfer of carriers between neighboring M/Ta/M structures is a further complication, but should not alter the calculation significantly since the value of T_c is governed by the fraction of time spent by the carriers in the M and Ta layers, which is the same for all the M/Ta/M structures. The values of λ_i are estimated from the intrinsic T_c values for the films, and the value of T_c for the proximity sandwich is then calculated, using the usual BCS-type formula.

As shown by the full line in Fig. 1, this model gives a good fit to the data for thin Ge films. The fitted value of the parameter N_1d_1/N_2 is 2.55 nm, which taking[10] the ratio N_1/N_2 as the same as λ_1/λ_2 (approximately 1.27) gives $d_1=2.0$ nm for the thickness of the Ta/Ge alloy layer. This corresponds to a Ta-Ge alloy layer of thickness about 1 nm on either side of the Ta layer. Although this procedure is of course very approximate, the resulting value for the thickness of the Ta-Ge layers is similar to the maximum value deduced from our data above, and so the model seems reasonable. We obtain better agreement with the Cooper–de Gennes model than was found for Nb/Ge multilayers,[10] possibly because our layers are thinner.

Golubov[15] has emphasized the need to take account of finite transparency of boundaries between different layers in calculations of the superconducting proximity effect, and showed that the appropriate way to do this in our case of very thin films is to use the McMillan tunneling model.[16] Provided the layer thicknesses are small, the formalism of the model was found[15] to be valid for arbitrary transparency of the boundary, rather than only for the case of small transparency for which the model was initially derived.

To illustrate that our ascription of the increase in T_c to the proximity effect does not depend on neglecting finite boundary transparency, we also show in Fig. 1 a fit of the data for thin Ge films to the McMillan model.[16] In this model, the link between the films is by single-particle tunneling. The superconducting transition temperature T_c of a pair of superconducting films with transition temperatures T_{c1} and T_{c2} is given by[17]

$$\left[\frac{\Gamma_1}{\ln(T_{c1}/T_c)}+\frac{\Gamma_2}{\ln(T_{c2}/T_c)}\right]\left[\psi\left(\frac{1}{2}+\frac{\Gamma_1+\Gamma_2}{2\pi kT_c}\right)-\psi\left(\frac{1}{2}\right)\right]=\Gamma_1+\Gamma_2, \tag{2}$$

where $\psi(x)$ is the Euler psi function,[18] k is Boltzmann's constant, and $\Gamma_i=\hbar/(2\tau_i)=c_i/d_i$ is the transfer parameter from film i to the other film. Here τ_1 and τ_2 are the mean times that carriers spend in films 1 and 2, respectively, before transferring to the other film, which are taken as proportional to the respective film thicknesses, i.e., c_i is constant for a particular film. Equation (2) has been solved iteratively and the result is fitted to the data taking $c_1=c_2$ and $\Gamma_1=0.26$ meV. It is difficult to make our comparison with the data more quantitative in the McMillan model, but the close agreement with the Cooper–de Gennes model shows the generality of the shape of the increase of T_c caused by the proximity effect as a function of film thickness.

The dependence of T_c on Ge-layer thickness can thus be qualitatively understood: the rise with diminishing d_{Ge}, evident for Ge layers thicker than 2 nm, is associated with the 2D-3D transition as tunneling through the Ge layers increases. The fall for thinner layers arises from the depletion of Ge, so that the Ge-rich alloy required for $T_c>2$ K is no longer found in the mixed layer. The maximum of T_c, reached for Ge thicknesses of near 2 nm and represented by the upper data points in Fig. 1, then corresponds to the *bulk* value (ignoring the localization transition) for a proximity-enhanced Ta layer sheathed by two mixed layers.

IV. CONCLUSIONS

We find that the likely cause of an enhancement is T_c that we observe in Ta/Ge multilayers is the formation at the interfaces of the Ta and Ge films of a Ta-Ge mixture with higher T_c than amorphous Ta. As illustrated in Fig. 1, the variation of T_c with the thickness of the Ta layers (when the Ge layers are thin) agrees with that calculated using the Cooper–de Gennes and McMillan models for the proximity effect between neighboring superconductor films of Ta and the Ta-Ge mixture (M). The role of coupling between the M/Ta/M composite superconductors through the interleaving Ge layers appears to be to suppress localization in the M/Ta/M layers when the Ge layers are very thin, thus allowing the superconductivity to persist. When the Ge layers are made thicker the coupling through them is reduced and the value of T_c for thin M/Ta/M layers is reduced due to the impending localization transition.

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