SUPERCONDUCTING TRANSITION TEMPERATURE OF THIN FILMS*

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Results have previously been reported[1] which show that the major part of the increase in T_c in thin regions of Al films cannot be accounted for by stresses, and also that these regions have critical fields near the Clogston-Chandrasekhar limit. The results were interpreted as possible evidence for Ginzburg surface superconductivity[2] in the thin regions of the film edges.

Further experiments on the transition temperatures of thin Al and other metal films with their edges trimmed are reported here.

In Fig. 1 thickness versus critical temperature data are given. The films with the edges removed have sharp transitions, while the film with edges shows a broad transition, probably due to the distribution of film thicknesses in the edge region. After the edges were removed, this film showed a sharp transition. In Fig. 1 results are also presented for a film deposited on a Teflon substrate.[3] From these data it is estimated that the effect of stress on the 100Å films on glass is about 0.2°K relative to the bulk transition.

The data shown in Fig. 1 indicate that (in films without edges) T_c increases as the film thickness decreases. These effects are consistent with a unique surface region, which we call the Ginzburg surface layer, being in contact with the normal film under it. Therefore, in practice, the Ginzburg surface layer and the normal regions below it might be treated as superimposed or layered films, as in Fig. 2. In this model a high effective T_c in the surface would be reduced as the thickness of the normal material is increased, in accord with the observations on Al. In order to make the model more quantitative, use is made of de Gennes's[4]

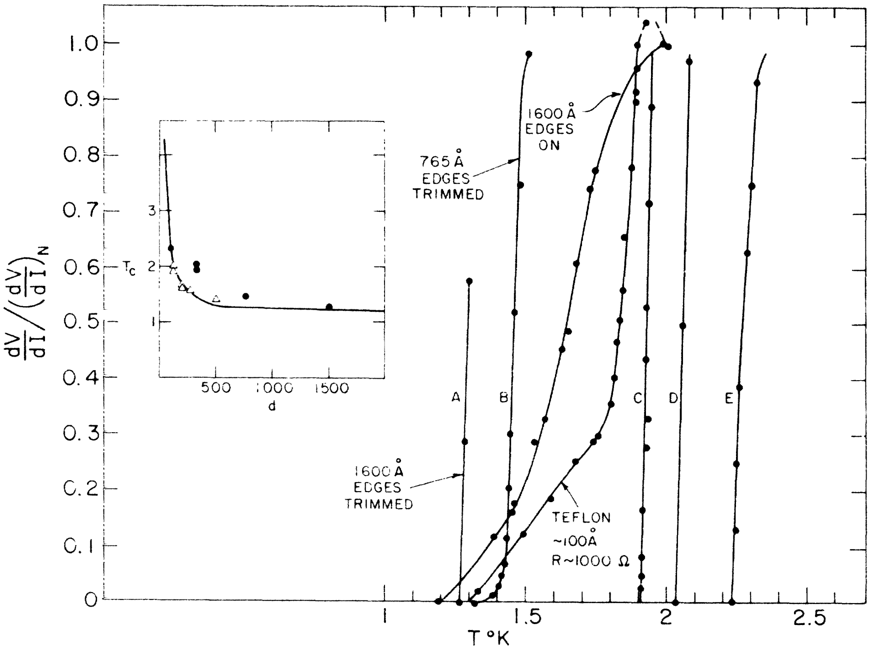

FIG. 1. dV/dI transitions of thin Al strips. 10-μA ac currents were used. For the very high-resistance strips the ac current was 1 μA. The transitions were sensitive to either ac or dc currents. The films were about 2.5 cm long and about 0.4 cm wide with the following properties: (A) $R_{300°\mathrm{K}} = 1\Omega$, $R_{\mathrm{N}_2} = 0.5\Omega$, $R_{\mathrm{He}^4} = 0.35\Omega$, edges removed; (B) $R_{300°\mathrm{K}} = 21\Omega$, $R_{\mathrm{N}_2} = 14\Omega$, film thickness = 765 Å, edges removed; (C) $R_{300°\mathrm{K}} = 110\Omega$, $R_{\mathrm{N}_2} = 100\Omega$, film thickness = 300 Å, edges removed; (D) $R_{300°\mathrm{K}} = 190\Omega$, $R_{\mathrm{N}_2} = 175\Omega$, film thickness = 300 Å, edges removed; (E) $R_{300°\mathrm{K}} = 1000\Omega$, film thickness = 100 Å, edges removed. Using the parameters given in the text the layered model theoretical T_c-vs-d curve is compared with the data. The open triangles are additional data and have similar transitions to the ones shown.

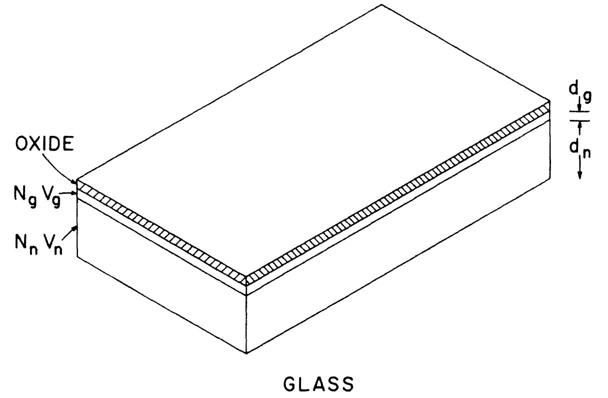

FIG. 2. Diagram indicating layered film model.

layered-film analysis. The general analysis depends on the relative values of the coherence lengths (ξ), mean free paths (l), and thicknesses (d). For simplicity we are using the case of $d_G < \xi_G$, $d_n < \xi_n$, and $l < \xi$.

The Ginzburg surface interaction is taken to extend over a region d_G superimposed on a normal region d_n. The Debye temperature Θ and the density of states N are taken as equal in the surface- and normal-film regions.[5] Characterizing the surface and normal interactions as V_G and V_n, respectively, from de Gennes,[4] we obtain $kT_c = 1.14\langle\hbar\omega\rangle \exp(-1/\rho)$, where

$$\rho = \frac{N_n^2 V_n d_n + N_G^2 V_G d_G}{N_n d_n + N_G d_G} \cong N_n V_n \left[\frac{d_n + (V_G/V_n) d_G}{d_t}\right].$$

In Fig. 1 we compare experiment and the theoretical variation of T_c with the total film thickness d_t. In making the comparison the parameters used[6] were $N_n V_n = 0.19$, $\langle\hbar\omega\rangle = k\Theta/2$, $\Theta = 380°\text{K}$, and $N_G V_G = 0.35$. The value of $N_G V_G$ lies within the range of values estimated by Ginzburg for surface superconductivity. In the calculation, the range of the surface interaction was arbitrarily taken as the order of the oxide thickness, about 20 Å. If the value of d_G is reduced, an increased V_G would be required to obtain the observed agreement. In comparing theory with experiment, strain was not added as a separate correction. This follows from a generalization of the layer model to include any localized layer which may be characterized by $N_x V_x d_x \cong N_n V_x d_x$. Therefore, the strained layer near the glass-metal interface may be included in terms of an effective $\langle V_x d_x\rangle$ which is an average of the strained $V_x d_x$ near the surface. Assuming that $d_t > d_x$, it is apparent that in the Cooper limit,[4] $\langle V_x d_x\rangle$ may be included in the empirical $V_G d_G$ term, with an appropriate renormalization of d's. Thus the empirical value $V_G d_G$ used in obtaining the agreement shown in Fig. 1 implicitly includes the small strain correction. It might be noted that the layered model can itself explicitly handle strain and yields essentially the same quantitative behavior as those previously found by Toxen.[7]

Other mechanisms also exist which could raise T_c, such as mean free path,[8] changes in Θ, and disorder effects. For instance, resistivity and perpendicular critical-field measurements have indicated that K increases, and hence the mean free path decreases, for decreasing film thickness. In bulk materials short mean free paths are found to raise T_c, whereas in some thin films, T_c is found to decrease as the thickness is made smaller.[10,11] This would be reasonable on the layer model, as T_c decreases in thinner films if $N_G V_G < N_n V_n$. In the cases of Pb and Ta where T_c goes down,[10] the bulk $N_n V_n$ is large, and hence it is plausible that $N_G V_G < N_n V_n$. The small mean free path also indicates disorder. Estimates indicate that the effect of disorder on NV is small. Disorder and light impurities (oxygen) may change the vibrational modes and cause a higher Θ. However, the factor of two in Θ, necessary to explain the rise in T_c, makes this explanation unlikely.

We have also found superconductivity in Ti films up to about 1.3°K, and in W films up to about 3°K.[12] In Sn films all rises in T_c could be attributed to stresses in the films. For Sn the bulk NV is about 0.3, and if $N_G V_G$ were comparable to the Al case, only small changes in T_c would be observed.

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[1] M. Strongin, A. Paskin, O. F. Kammerer, and M. Garber, Phys. Rev. Letters 14, 362 (1965).

[2] V. L. Ginzburg, Phys. Letters 13, 101 (1964).

[3] Since the Teflon contracts more than Al, stresses should lower the T_c of Al films relative to the unstrained case. It is indeed found that the Teflon-based films have a lower T_c than a comparable film on glass, and the difference between the Teflon substrate and the glass substrate, whose differential contraction with the film raises T_c, allows one to estimate the effect of stresses. It is immediately evident from the data that the T_c of the Al films on Teflon is raised, and

hence cannot be accounted for by stresses.

[4] P. G. de Gennes, Rev. Mod. Phys. 36, 225 (1964).

[5] This assumption may neglect a real effect due to a different phonon energy on the surface, as discussed by Ginzburg. However, the analysis of de Gennes for superimposed films can easily be generalized to include this effect.

[6] The value of N_nV_n for Al and the approximation that $\langle\hbar\omega\rangle = \Theta k/2$ are taken from D. Pines, Phys. Rev. 109, 280 (1958).

[7] A. M. Toxen, Phys. Rev. 123, 442 (1961). For small changes in T_c and $d_t \gg d_x$, Eq. (1) goes to $\Delta T_c \propto d_t^{-1}$ in accord with the data of Toxen and is of the same form as that found by Toxen using a stress analysis approach.

[8] D. M. Ginsberg [Phys. Rev. 136, A1167 (1964)] suggests that the mean free path will influence the T_c of alloys in the region of small mean free paths.

[9] R. Hilsch [Non-Crystalline Solids, edited by V. D. Frechette (John Wiley & Sons, Inc., New York, 1958), p. 348] suggests that disorder can increase T_c.

[10] J. J. Hauser and H. C. Theuerer, Rev. Mod. Phys. 36, 80 (1964).

[11] R. Glover, in Thin Films (American Society for Metals, Metals Park, Ohio, 1964), p. 174, mentions that the T_c of thin films of lead decreases as the films are made thinner.

[12] The preliminary work on the W films has also indicated perpendicular critical fields higher than 34 000 Oe. The effect of trace impurities on T_c has not been completely investigated and may affect these preliminary results.

SURFACE SUPERCONDUCTIVITY AND MEAN FREE PATH*

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Ginzburg has recently suggested that superconductivity in very thin films may be enhanced by contact with a dielectric, e.g. oxide layer, which can be polarized to give an attractive electron-electron interaction at the surface.[1] Two consequences of this effect are anticipated; a surface enhancement due to the fact that the average of the interaction over the entire volume is increased, and a two-dimensional "surface superconductivity" of the electrons in surface levels.[2] Strongin, Kammerer, and Paskin have suggested that this be treated as a superposed film problem, where the bulk interaction is augmented by a surface interaction V_G in a surface layer of thickness d_G.[3]

The energy gap function at the critical temperature obeys the integral equation

$$\Delta(r) = \int V(r)K(r, r')\Delta(r')dr',$$

where $V(r)$ is the electron-electron interaction and $K(r, r')$ is the impurity-averaged square of the normal Green's function.[4] The kernel may be treated as the sum of a diffusion kernel, $K^{\rm diff}$, and a rapidly oscillating correction term, $K^{\rm corr}$, which has a strong $(|r-r'|^{-2})$ singularity.[5] The range of this second term is roughly l, the electronic mean free path, and because of its oscillating nature it can be neglected if the energy gap function is slowly changing over the distance l.

Therefore, as long as the thickness of the surface layer is larger than the mean free path, $\Delta(r)$ is governed by the diffusion equation. If the film thickness is small compared to the coherence length $\xi \sim (\hbar v_f l/6\pi kT)^{1/2}$, the de Gennes formula for the critical temperature in the thin-film limit[6] is applicable.[3]

If, on the other hand, the thickness of the surface layer is less than l, the oscillations in $K^{\rm corr}$ do not average out the contribution of this singular term, and $\Delta(r)$ can become large at the boundary. It is possible in this case to obtain highly localized correlations in the boundary layer, because the falloff of $\Delta(r)$ is characterized by the short range l of $K^{\rm corr}$ rather than the diffusion length ξ. If we take the limit $d_G \to 0$, keeping $V_G d_G = \text{const.}$, the energy gap function diverges logarithmically at the surface, and the critical temperature, which is a sensitive function of d_G, can be arbitrarily large.

The two phenomena described above are easily distinguished. Because "surface enhancement" is actually a volume effect, it depends strongly on the thickness of the film. True surface superconductivity, on the other hand, should be relatively independent of film thickness. In many cases, of course, a mixture of the two effects may be expected.

The thickness dependence of the data of Strongin, Kammerer, and Paskin indicates that they are observing primarily surface enhancement.[3] Assuming that the thickness of the surface layer is about five atomic spacings,[7] which is 20