Oscillations of the critical temperature in thin film superconductor-dielectric structures

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Several extrema have been observed in the dependence of the critical temperature T_c of molybdenum films doped with carbon and of technetium films on the dielectric coating thickness d_c at $0 < d_c < 20$ Å. Artificial diamond films were used as the coatings. The critical temperature of the technetium films also depends on the thickness d_0 of the diamond sublayer in nonmonotonic fashion. The positions of the extrema of the function $T_c = f(d_c)$ depend only weakly on the material of the superconducting film and do not depend on its thickness. The positions of the extrema on the $T_c = f(d_0)$ curve are determined by the thickness of the outer dielectric coating.

In 1967, Naugle[1] found a maximum in the dependence of the superconducting transition temperature of thallium films on the thickness of the germanium covering at a covering thickness of 10 Å. The reason for this anomaly has remained unexplained. Studies undertaken by us on films of molybdenum doped with carbon$^{1)}$, which have a protective diamond covering, have shown[2] that the function $T_c(d_c)$, where T_c is the critical temperature and d_c the thickness of the covering, can possess several extrema at small d_c.

In the present work, we have carried out more detailed studies of the dependence of T_c of thin Mo—C and technetium films on the thickness of the protective diamond covering and the diamond sublayer.$^{2)}$

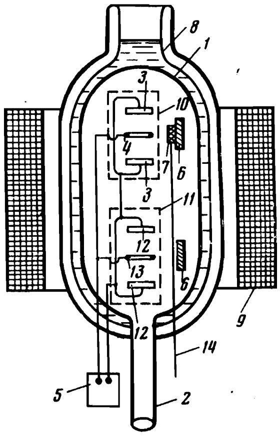

FIG. 1. Diagram of discharge chamber of the ion deposition apparatus: 1—air volume, 2—connecting pipe, 3—graphite cathode, 4—copper anode, 5—source of constant voltage, 6—holder, 7—substrate, 8—dewar, 9—solenoid, 10—upper ion deposition section, 11—lower ion deposition section, 12—cathode of deposited metal, 13—copper anode, 14—manipulator.

PREPARATION OF THE SAMPLES AND METHOD OF MEASUREMENT

To obtain the samples, we used a ultrahigh vacuum apparatus for ion deposition, the scheme of which is shown in Fig. 1. The discharge chamber consists of two independent sections for ion deposition, 10 and 11. Two plane cathodes and a ring anode are placed in each section. The lower section 11 was used to obtain metal films, and its cathodes were made of the deposited metal. The upper section 10 was used to obtain films of artificial diamond, [3] and its cathodes were made of graphite. The backing 7 was so located that material from both the upper and the lower cathodes fell on it during the deposition process. The backing could be moved rapidly from one section to the other by means of the manipulator 14.

Before the beginning of the experiment, the apparatus was heated for ten hours at 250° C with continuous pumping by a magnetic discharge pump. The composition of the gases during the entire experiment was controlled by the omegatron IPDO-1. After the preliminary conditioning, the partial pressure of hydrogen was $\lesssim 10^{-9}$ Torr, and the total partial pressure of the other residual gases was $< 10^{-10}$ Torr. In the deposition process, all parts of the apparatus had a temperature close to nitrogen temperature, which was achieved by filling the liquid nitrogen dewar 8 and circulating the liquid nitrogen along a coil through sections 10 and 11 (not shown in the drawing). The temperature in the various parts of the chamber was controlled by copper-copel thermocouples.

The deposition was carried out in spectrally pure krypton, the working pressure of which amounted to 5×10^{-6} Torr. A discharge appeared between the cathodes and the ring anode in the presence of a magnetic field. The discharge current amounted to 1 mA at a voltage 4 kV and a magnetic field ~0.7 kOe. The magnetic field was obtained from the solenoid 9 located outside the vacuum volume. During the time that the gas discharge reached the prescribed regime and during the time of cleaning the electrodes by the discharge, the backing was screened by a metallic baffle (not shown in the drawing), which was then removed by remote control for the time necessary to obtain a film of the prescribed thickness.

The construction of the apparatus allowed us to obtain eight pairs of samples with different layer thicknesses during the course of a single experiment. The samples forming a pair were prepared simultaneously and the difference in their properties was due only to accidental causes.

The thickness of the films was determined from the rate and time of the deposition. Numerous experiments, carried out on the apparatus, showed that at constant discharge parameters the rate of growth of the films was constant. The rate of deposition of each material was determined by means of control samples, the thickness of which amounted to ~1000 Å. The determination of the thickness of these samples was made by an interference method. The error in the determination of the thickness of the working films consisted chiefly of the error in the determination of the thickness of the control samples and the error connected with the instability of the discharge parameters. The total error did not exceed 5% over the entire range of thicknesses. The growth rates of the films amounted to 13 Å/min for technetium, 12 Å/min for Mo—C and 2 Å/min for artificial diamond.

The determination of the growth rate was repeated after several experiments.

The samples represented films of rectangular shape, 5 x 9 mm, deposited on a polished glass substrate with platinum wire leads soldered in. In order to eliminate edge effects, the edges of the films were cut by a diamond microsaw. The films were made of materials whose purity was no worse than 99.94%. The carbon concentration in the Mo—C films, studied in this paper, amounted to above 20 at.%.

As the results of the investigation of the physical, mechanical, and chemical properties and structural investigations have shown, the films obtained in the precipitation of carbon by the method described above represent a finely-disperse, microcrystalline diamond body of the "carbonado" type.[4] Electron-microscopic transmission investigations of free films of artificial diamond have shown that these films become continuous when their thickness amounts to two atomic layers of carbon (about 3 Å).[5]

The measurement of the critical temperature was made by a resistance method in the cryostat, to which the samples were transferred after warming of the deposition apparatus to room temperature and unsealing. The temperature was measured by a germanium thermometer made by the firm "Scientific Instruments," the resistance of the samples was measured by a null-method. The width of the junctions, determined from the levels $R = 0.1\,R_n$ and $R = 0.9R_n$, where R_n is the residual resistance, amounted to 30, 60 and 120 Å. For films of technetium with thicknesses d = 50, 100 and 300 Å, the width of the junction amounted to 0.3; 0.1 and 0.05°K.

Figure 2 gives the curves $R/R_n = f(T)$ for a number of samples of technetium (d = 50 A) with different thicknesses of the diamond covering. It is seen that the slope of the curve does not change, and consequently the difference in the critical temperatures of these samples does not depend on the choice of the point on the curve R(T), along which the determination of T_c is carried out. We defined the transition temperature to be the temperature for which $R = 0.5\,R_n$. The residual resistance was measured to within 0.1%. For calculation of the resistivity, the geometrical dimensions of the samples were determined by means of an optical comparator. The final error in the determination of ρ was no more than 7%.

RESULTS

Figures 3 and 4 give the dependences of the critical temperature of Mo—C and technetium films of different thicknesses on the amount of diamond covering. Attention is called to the oscillatory character of the curves and their similarity with one another. All the curves have two extrema: a maximum T_c at $d_c \approx 7$ Å for technetium films and at $d_c \approx 5$ Å for Mo—C films, and a minimum at $d_c \approx 10$ Å for both materials. In all probability, the oscillatory character is preserved up to a thickness of covering of 50—100 Å. The amplitude of the oscillations of the critical temperature increase with decrease in the thickness of the metallic film. The initial portion of the graph of $T_c(d_c)$ $(0 < d_c < 5$ Å) changes with decreasing film thickness more rapidly than the remaining curve, and this difference is more sharply expressed for films of technetium than for Mo—C.

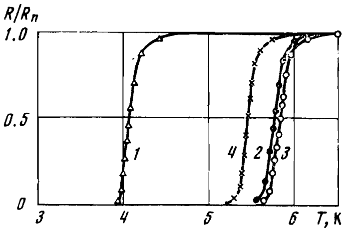

FIG. 2

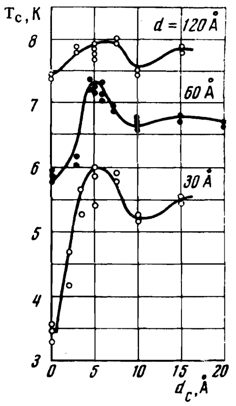

FIG. 3

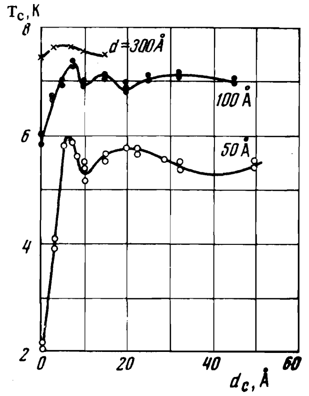

FIG. 4

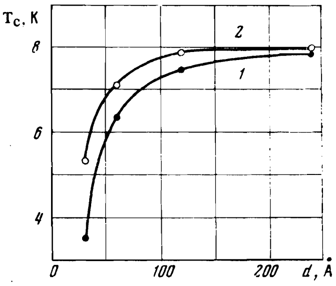

FIG. 5

FIG. 2. Curves of transition to the superconducting state of films of technetium (thickness d = 50 Å) with diamond covering of varying thickness d_c: 1) $d_c = 3$ Å, 2) $d_c = 5$ Å, 3) $D_c = 7$ Å, 4) $d_c = 10$ Å.

FIG. 3. Critical temperature of molydenum films doped with carbon, as a function of the thickness of the diamond covering for three thicknesses of the superconducting film.

FIG. 4. Critical temperature of the technetium films as a function of the thickness of the diamond covering for three thicknesses of the superconducting layer.

FIG. 5. Critical temperature of films of molybdenum doped with carbon as a function of the thickness of the superconducting film: 1—samples without covering, 2—samples with diamond covering; $d_c = 5$ Å.

The temperature of transition of Mo—C films to the superconducting state is shown in Fig. 5 as a function of the characteristic thickness of these films d. Curve 1 corresponds to samples without a cover, and curve 3 to films with a covering of thickness 5 Å, which corresponds to maximum critical temperature on the $T_c(d_c)$ graph. It is seen from the drawing that the effect of covering begins to be important only for those thicknesses of the superconducting film for which the critical temperature differs significantly from the T_c of the "bulk" material, and the increase of T_c under the action of cover does not compensate for the decrease in the critical temperature due to the size effect. A similar result is observed also for the technetium films.

The samples of technetium with different thickness of the diamond covering were studied by electron-microscopic and electron diffraction methods.

For this purpose, we deposited a pair of samples on a substrate of NaCl crystal. It was found that the covering affected neither the structure of the film nor the size of the grain and, consequently, the non-monotonic character of the behavior of $T_c(d_c)$ is not connected with structure changes of the samples.

Measurements of the specific resistance have shown that there is evidently a correlation between T_c and ρ of films with different thicknesses of covering, and these quantities change in contrary fashion: the maximum T_c corresponds to minimum ρ. However, the insufficient reproducibility of the resistivity makes this correlation not very well defined.

The possibility of oxidation of metallic films without a covering and with thin ($d_c < 5$ Å) covering during the transfer from the vacuum chamber to the cryostat is a shortcoming of the method used by us. In order to establish whether the oxidation affects the character of the $T_c(d_c)$ dependence, we carried out the following experiment: two sets of samples were prepared with variable thickness of the diamond sublayer d_0 for a specified thickness of the technetium film (d = 50 Å). The samples of the first series were covered by a carbon layer of thickness 40 Å, and those of the second series, by a layer of 10 Å. The $T_c(d_0)$ dependences of these samples are represented in Fig. 6. The presence of a maximum in the $T_c(d_0)$ curve (Fig. 6a) at $d_0 \approx 7$ Å shows that oxidation is not the reason for the oscillatory character of the function $T_c(d_c)$. Attention is called to the fact that the maximum values of the critical temperature on the curves $T_c(d_c)$ (Fig. 4, lower curve) and $T_c(d_0)$ (Fig. 6a) hardly differ. As a consequence the $T_c(d_0)$ curve has no section with a sharp increase in T_c at $0 < d_0 < 7$ Å, since the transition temperature of the samples, which corresponds to the initial point $d_0 = 0$ of the $T_c(d_0)$ curve, is already increased by the applied covering. The absence of a section with a sharp rise in T_c can be explained by two reasons. First, the sample without the covering can have a lower transition temperature because of the partial oxidation; second, some similarity between the properties of the glass substrate and the diamond layer can come into play.

Figure 6b gives the dependence of $T_c(d_0)$ for a number of samples with a covering d_c = 10 Å. The nonmonotonic character of the curve is preserved but the maximum is shifted and occurs at $d_0 \approx 3$ Å. Figure 6b also shows the minimum for $d_0 \approx 7$ Å. The existence of a mutual influence of the dielectric layers located on the opposite sides of the substrate seems important to us for understanding the nature of the observed phenomenon.

DISCUSSION OF THE RESULTS

The mechanisms proposed to date for the effect of a dielectric layer on a superconducting film (for example, the "charge-exchange effect,"[6] the exciton mechanism of superconductivity,[7] the effect of surface phonons[8]) result in a monotonic dependence of $T_c(d_c)$ with saturation at larger covering thicknesses. To explain the nonmonotonic dependence of the critical temperature, it is necessary to assume either a superposition of several known mechanisms, which make contributions of opposite sign, or the existence of some unknown mechanism which leads to the oscillatory $T_c(d_c)$ dependence. The second assumption, in our opinion, is the more probable. If such a mechanism exists, then the other characteristics of the sample should vary in nonmonotonic fashion along with T_c in all probability. In this connection, attention is called to the work of Chopra and Randlett[9] and Schaffs.[10]

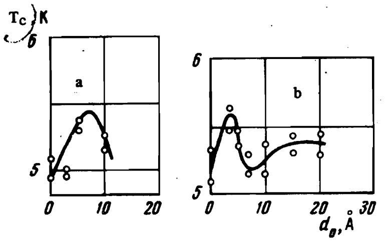

FIG. 6. Critical temperature of technetium films (d = 50 Å) as a function of the thickness of the sublayer of artificial diamond for samples with different thickness of the diamond covering: a) d_c = 40 Å, b) d_c = 10 Å.

Chopra and Randlett observed the nonmonotonic dependence of the resistance of a copper film on the thickness of the germanium covering at a maximum covering thickness 5 Å. Schaffs studied the contact potential difference for copper and gold as a function of the thickness of the copper oxide layer. He discovered sharp oscillations with a period of 20 Å, which were observed up to an oxide thickness of several hundred angstroms. Such a behavior of the resistance and of the contact potential difference can be a consequence of the effect of the dielectric layer on the density of the electron states near the surface of the metal. The oscillations of T_c of our films can also be connected with the change in the density of states; in this case a correlation should be observed between the critical temperature and the resistivity.

The most probable reason for the oscillatory change in the properties of the superconducting film under the action of the dielectric covering seems to us to be the interferences experienced by the quasiparticles that exist in the superconductor-dielectric system. The similarity of the dependences of $T_c(d_c)$ for different materials and different thicknesses of the superconducting film for a given covering material indicates that the important dimension for the interference is the thickness of the dielectric layer, and the material of the superconducting film and its thickness have an effect only on the amplitude of the oscillations. A direct consequence of such an interference can be the appearance, at certain thicknesses of the covering and sublayer, of additional surface phonon modes or, for example, surface electron states, which in turn can lead to a change in the critical temperature.

Still another mechanism is possible, which also leads to oscillations of the critical temperature.3) The basis of this mechanism is the assumption of the quantization of the transverse components of the momenta of the electrons and phonons. The critical temperature should increase for those thicknesses of the dielectric for which satisfaction of the law of conservation of transverse momentum is possible for the electron-phonon interaction.

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1)In the following, we shall denote this material by the symbol Mo– C.

2)We call the sublayer the dielectric layer applied to the backing (substrate) before the deposition of the superconducting film.

3)This idea belongs to R. O. Zaĭtsev.

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[1] D. G. Naugle, Phys. Lett. **25A**, 688 (1967).

[2] M. N. Mikheeva, M. B. Tsetlin, A. A. Teplov, V. M. Golyanov, A. P. Demidov, ZhETF Pis. Red. **15**, 303 (1972) [JETP Lett. **15**, 213 (1972)].

[3] V. M. Golyanov, L. A. Elesin and M. I. Mikheeva, ZhETF Pis. Red. **18**, 569 (1973) [JETP Lett. **18**, 335 (1973)].

[4] V. S. Veselovskiĭ, Uglerod, almazy, grafity i ugli i metodologiya ikh issledovaniya (Carbon, Diamonds, Graphites and Coal in the Methodology of Their Study) Moscow-Leningrad, 1936, p. 41.

[5] V. M. Golyanov and V. N. Grigor'ev, Dokl. Akad. Nauk SSSR seriya biol. **215**, 1485 (1974).

[6] P. Hilsch and D. G. Naugle, Z. Physik **201**, 1 (1967).

[7] V. L. Ginzburg and D. A. Kirzhnits, Zh. Eksp. Teor. Fiz. **47**, 2318 (1964) [Sov. Phys.-JETP **20**, 1549 (1965)].

[8] D. G. Naugle, J. W. Baker and R. E. Allen, Phys. Rev. **B7**, 3028 (1973).

[9] K. L. Chopra and M. R. Randlett, J. Appl. Phys. **38**, 3144 (1967).

[10] W. Schaffs, Z. Angew. Phys. **11**, 2220 (1959).

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