CRITICAL TEMPERATURE OF SUPERCONDUCTING TRANSITION OF THIN TIN FILMS

K. K. MAN'KOVSKIĬ, V. V. PILIPENKO, Yu. F. KOMNIK, and I. M. DMITRENKO

Physico-technical Institute of Low Temperatures, Ukrainian Academy of Sciences

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The critical temperature of the superconducting transition of thin films is altered by many factors, particularly by variation of the thickness, the degree of equilibrium of the film, the type of substrate, the degree of development of the surface, the texture, etc. An investigation was carried out of the influence of different factors on T_c of thin tin films with the aid of a "comparison" method, i.e., on a number of samples obtained under conditions when all the parameters influencing the structural properties of the films and T_c were maintained constant, with the exception of a single parameter, say the condensation temperature or the film thickness. In addition, an investigation was made of the structure characteristics of thin tin films. It is shown that tin films obtained at low temperatures have a less perfect structure, even after heating, than films obtained at room temperature; this is the reason for the increase of T_c with decreasing condensation temperature below 250 °K. In addition, an increase of the condensation temperature above 250 °K also leads to a growth of T_c, in spite of the improvement of such characteristics as the resistivity of the films and the growth of the ratio $\delta = R_{293}/R_{4.2}$. For tin films obtained at ~300 °K, a growth of T_c is observed with increasing thickness in the region adjacent to the critical thickness L_c. The possible causes of the variation of T_c of thin tin films are discussed in connection with the existing theories.

1. INTRODUCTION. FORMULATION OF PROBLEM. PROCEDURE

It is known that the critical temperature T_c of the superconducting transition T_c of thin films differs as a rule from the critical temperature of bulky pure samples. It was observed, for example, that films obtained at low temperatures and having a non-equilibrium structure have increased values of T_c.[1-5] For many metals, a dependence of T_c on the film thickness L was observed. The greatest increase of T_c with decreasing L is observed for aluminum,[5-9] but it has been noted also for films of tin,[10, 11] indium,[12, 13] and others. In small-thickness films deposited at low temperatures, a different dependence is observed, namely a decrease of T_c with decreasing L.[2, 14-17] In a number of investigations,[18-21] an attempt was made to establish a correlation between the variation of T_c and the dimensions of the crystallites in the films. It was shown experimentally[22, 23] that the stresses arising in the film when it is cooled can cause a change of T_c, and that the degree of this influence depends on the orientation of the crystallites in the film.[10] The large number of recent investigations in this field has been stimulated both by the appearance of a number of theoretical models predicting the change of the critical temperature in thin films, and by the practical interest in the search for ways of increasing the critical temperature of superconductors.

Thus, the change of T_c in thin films occurs under the influence of many very different factors, frequently acting jointly (film thickness, substructure characteristics, stresses), and the contribution of each of them can be determined only by a "comparison method." We have attempted to find variants of experiments with thin tin films in which all the parameters describing the conditions for condensation and influencing the structure properties of thin films (temperature and physicochemical properties of the substrate, rate of condensation, composition of the residual gases in the vacuum chamber, etc.) are kept constant for a given series of samples except for one, say the condensation temperature or the film thickness. To this end we prepared, in a single experiment (in a vacuum of 10^{-6} mm Hg), a series of samples of strictly equal thickness on a single substrate—a plate on which a temperature gradient was produced (by cooling or heating one end of the plate). When glass or thin (~0.5 mm) quartz plates were used (24 × 45 mm), it was possible to obtain a temperature drop up to 150°. The temperature distribution was determined with the aid of glued-on copper-constantan thermocouples. In other experiments, the substrate temperature was constant throughout, and the samples were of different thickness. After the samples were produced, they were heated to room temperature and transferred to a cryostat. The average heating time was one hour. Thus, the heating rate depended on the initial condensation temperature. For films produced, say, at 100 °K it amounted to 3 deg/min, and for films obtained at higher temperatures it was somewhat lower.

2. EXPERIMENTAL RESULTS

1. Using electron microscopy and electron diffraction, we investigated the structure characteristics of films obtained at different temperatures and then heated to room temperature. Thus, electron diffraction was used to determine the average dimension of crystallites (regions of electron coherent scattering) in the substrate plane for several series of films 300–400 Å

thick, obtained in the interval 170–270°K; the dimensions were obtained from the spreading of the maxima of the diffraction from the plane (011). The instrumental line width was assumed to be the width of the maximum on the electron diffraction pattern of a film obtained near room temperature and producing a nearly point-like ring structure (crystallite dimension > 100 Å). With increasing condensation temperature, the average dimension of the crystallites increases, as is clearly seen from the table, which gives the data for a series of films 500 Å thick. In the case of prolonged annealing at room temperature, the average crystallite dimension turns out to be somewhat larger than after heating (the increase reaches 50%) thus evidencing that the recrystallization processes are not completed during the period of film heating, and continue with ever decreasing rate when the films are kept at room temperature.

2. The electron-diffraction study has shown that as a rule the films obtained in practically the entire investigated condensation-temperature interval reveal a texture, namely, the crystallographic axis [100] is normal to the plane. The degree of perfection of the texture, characterized by the average deviation of the [100] axis from normal, has a tendency to increase with increasing condensation temperature (see the table). In different series of samples, the average angle of deflection of the texture axis from the normal fluctuates in the range 5–30°; the degree of perfection of the texture depends also on the condensation rate, the disorientation of the texture axis increasing somewhat with increasing condensation rate.

3. The change of the dimension of the crystallites with condensation temperature corresponds to the temperature dependence of the critical thickness L_c, corresponding to the appearance of the conductivity of the film.[24] The data for L_c of tin films were obtained by us by continuously recording the conductivity during the course of condensation, and are listed in the table for different substrates. The film thickness (and accordingly the rate of condensation) were determined from the thickness dependence of the optical density, plotted by the method described in [9]. The growth of the critical thickness with increasing condensation temperature is due to the decrease of the surface concentration of the nucleation centers, and this determines the increase of the average dimension of the crystallites in the film at a thickness close to critical. It is probable that this is the cause of the change of the critical thickness with changing type of substrate. We note that the average dimension of the crystallites was determined with the aid of electron diffraction for films prepared on acetate lacquer. The dimensions of the crystallites in films prepared on other substrates can be qualitatively estimated by taking into consideration the ratio of the critical thicknesses on these substrates to those on acetate lacquer.

Thus, for films obtained at different temperatures, the structural differences both before heating to room temperature and after prolonged annealing remain the same, in spite of the partial recrystallization processes occurring during the heating and during the annealing. The hindering of the recrystallization processes is attributed by many authors to the influence of the oxygen dissolved in the film.[25, 26] We note that the rate of occurrence of the recrystallization processes depends also on the degree of the initial non-equilibrium state of the film, and recrystallization should be deeper for films obtained at large condensation rate (see, for example, [10, 11]). The following results of electrical measurements pertain mainly to films not subjected to prolonged annealing.

4. The improvement of the perfection of the film structure with increasing temperature of condensation was confirmed by measurements of the film conductivity (Fig. 1). The quantity $\delta = R_{293}/R_{4.2}$ increases with increasing T, but this growth is not very noticeable for films obtained in the temperature interval 80–220°K (a plateau is frequently observed in the 150–220°K region), and is more considerable for films obtained at temperatures above 220° K. The highest values of δ (up to 100) were obtained for large-thickness films ($\gtrsim 3000$ Å) deposited at ~ 330°K. Further increase of

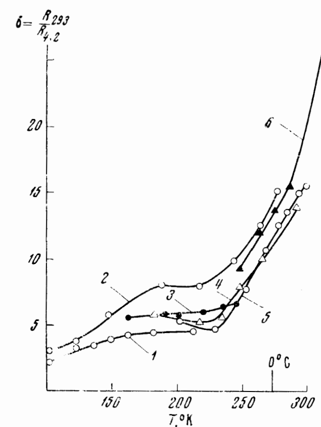

FIG. 1. The ratio $\delta = R_{293}/R_{4.2}$ of thin films vs. the condensation temperature. The series of samples 1 and 2 were obtained on quartz, the remainder on glass. Sample thickness in the series: 1–150, 2–3000, 3–1150, 4–300, 5–360, 6–1600 Å.

	Condensation temperature, °K						
	170	200	225	250	260	275	300
Average dimension of crystallites in films of thickness 500 Å on acetate lacquer, A	200	400	500	750	900	($\gtrsim$1000)	--
L_c for films on a glass substrate, Å	40	50	80	100	120	140	180
L_c for films on acetate lacquer, Å	100	170	270	380	430	500	800
L_c for films on acetate lacquer, Å	--	230	340	460	500	—	1000
Average value of disorientation angle of the texture axis in a film of thickness 400 Å at a condensation rate 10 Å/sec, deg	--	~ 30	~ 15	~ 10	—	~8	—
l in films 500 Å thick at 4.2°K, (from $\rho l = 1.1 \times 10^{-11}$ ohn/cm²), Å	440	550	710	880	990	1200	1500

the temperature of the substrate leads to a sharp change in the structural characteristics of the films, this being connected with changes in the condensation mechanism at $T_l \approx 0.66T_S$ (T_S—melting temperature, and for tin $T_l \approx 340°K$).[27] Values of the film resistance and of δ deviating from the monotonic dependence were observed by us not only for films obtained at a substrate temperature $T > T_l$, but in some cases also at $T < T_m$, where $T_m \approx 0.34T_S$ (for $T_m \approx 170°K$ for tin). A number of papers[28, 29] report observations indicating that the structural characteristics and the structure-sensitive properties of films change with changing condensation temperature near T_m. All that can be deduced from our observations is that in some cases, for films obtained at $T < T_m$, the texture turned out to be much more perfect than for films obtained at higher temperatures. This agrees with observations by others.[30] We shall therefore discuss subsequently the possible correlations between the critical temperature of tin films and their structural characteristics mainly on the basis of data for films produced in the interval $T_m < T < T_l$.

It should be noted that δ is only a qualitative characteristic of the degree of perfection of the film, and is suitable only when films of equal thickness are compared. That it is incorrect to use it for a comparison of the properties of films of different thicknesses will be demonstrated later.

Using electrical measurements, we estimated the electron mean free path at 4.2°K in films obtained at different temperatures using for this purpose the known value of the quantity $\rho l = 1.1 \times 10^{-11}$ ohm-cm².[31] The table lists the values of $\bar{l}$ in tin films 500 Å thick. The mean free path exceeds in many cases the thickness of the film, and in all cases exceeds the average dimension of the crystallites. Naturally, the estimate of $\bar{l}$ from ρl cannot claim to be highly accurate.

5. The critical temperature T_c was determined by us from the R(T) plot using the restoration of 1/10 of the normal resistance.[1)] For tin films, the temperature range of the transitions was on the average 0.02 (±0.01)° K. It decreases somewhat with increasing condensation temperature and film thickness, and after moving the edge away. The smallest transition interval (~0.005°K) was observed by us for thick films with remote edge, obtained at 250–340°K.

The use of the procedure of obtaining a series of samples of identical thickness under equal conditions and at different substrate temperatures has made it possible to observe a regularity in the dependence of T_c on the condensation temperature; this regularity might have gone unobserved had the many-sample procedure been employed. Namely, a minimum of T_c (Fig. 2) is obtained for films of small thickness at a substrate temperature 220–270°K. The critical temperature for films obtained in the temperature interval

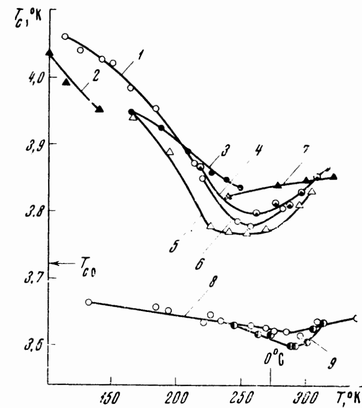

FIG. 2. Dependence of T_2 of thin tin films on the condensation temperature. Series of samples 1 and 2 were obtained on quartz, 3, 4, 5, and 7 on glass, 6 on acetate lacquer, and 8 and 9 on methylmethacrylate. Sample thickness in the series: 1–150, 2–3000, 3–750, 4–330, 5–400, 6–1000, 7–2400, 8–3000, 9–1600 Å.

80–220°K decreases monotonically from ~4.1 to ~ 3.8°K. In the region of the minimum and at higher condensation temperatures, a scatter exceeding 0.1°K is observed in the values of T_c for different series of samples. For the samples in each series, however, a monotonic growth of the critical temperature is observed for films obtained at condensation temperatures above 270° K. For films of small thickness ($L \approx 200$–400 Å), this growth is appreciable, namely, an increase of the condensation temperature by 10° increases T_c by 0.01–0.02°K. For large-thickness films ($L > 2000$ Å) obtained in the interval 200–350°K, the growth of T_c is either insignificant or practically nonexistent.

Figure 2 shows also the data for the change of the critical temperature with changing condensation temperature of tin films deposited on methylmethacrylate. Unlike quartz or glass, methylmethacrylate has a much larger temperature coefficient of linear expansion than metal, and consequently is compressed more strongly than tin by cooling.[33] As a result, the film is not under tension, as on glass or quartz, but under compression. Figure 2 illustrates the influences of planar stresses on the critical temperature of thin films. The critical temperatures for tin films on methylmethacrylate are lower than T_c of bulk tin; however, the general character of the dependence of T_c on the condensation conditions is the same as for films deposited on quartz and glass. We note that as a result of the higher values of the critical thickness on methylmethacrylate and on glass, thicker films were correspondingly used for the measurements of T_c.

6. We have determined, with the aid of the tunnel procedure, the superconducting gap for several series of films obtained at different substrate temperatures. To this end, several Sn–I–Sn tunnel junctions were produced with samples condensed on a plate with a temperature gradient. The criterion for the value of the gap was the inflection point on the current-voltage characteristic, which was determined by plotting the derivative $dV/dI = f(V)$ with the aid of a modulation procedure.[34] The position of the minimum on the derivative was determined with accuracy not worse than 10 μV.

[1)] We note that the determination of T_c of films with a diffuse edge from the R(T) plot at the point corresponding to $R_n/2$, can result in too high a value of T_c, since the removal of the edge makes the transition as a rule more abrupt, and what vanishes in the main is the "tail" near the normal resistance, and not near the zero resistance; [32] this leads to a shift of the central point towards lower temperatures. We have verified that at the chosen criterion $R_n/10$, the shift of T_e following the removal of the edge is not significant.

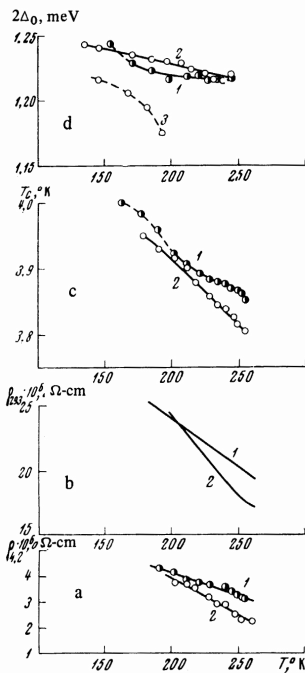

FIG. 3. Dependence of the resistivity at 4.2°K (a) and at 293°K (b), of the critical temperature (c), and of the energy gap (d) on the condensation temperature of thin tin films for two series of samples. In series 1, the sample thickness is 1150 Å and the substrate is glass; in series 2 the sample thickness is 1700 Å and the substrate is acetate lacquer. T_c for series 3 are given in Fig. 2, curve 3.

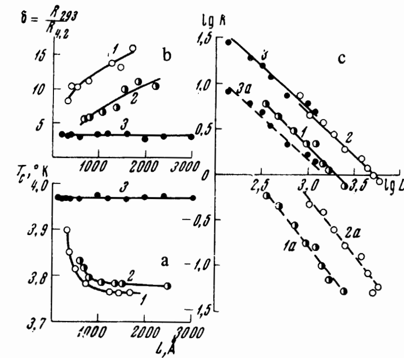

FIG. 4. Dependences of the critical temperature (a), of the ratio $\delta = R_{293}/R_{4.2}$ (b) and of the resistance (c) on the thickness of thin tin films. The series of samples 1 and 2 were obtained with the substrate at room temperature, and series 3 at 80°K. The straight lines 1, 2, and 3 on the right correspond to film resistances measured at room temperature, while lines 1a, 2a, and 3a were obtained at 4.2°K.

Figure 3d shows the data for the plot of the gap $2\Delta_0$ against the condensation temperature for three series of thin films, and also the corresponding critical temperatures, determined for the same samples (curves 1 and 2 on Fig. 3c and curve 3 on Fig. 2). Unfortunately, we were unable to produce high-grade tunnel junctions with thin films obtained at 300°K and above. Apparently, tunnel junctions are not feasible technically with such films, owing to the great friability of the structure (see below). This has not enabled us to trace the variation of the gap in the region where a growth of T_c with increasing condensation temperature is observed. On the other hand, a monotonic decrease of the gap similar to the decrease of T_c, is observed in the investigated interval of condensation temperatures. The ratio $2\Delta_0/kT_c$ remains, on the average, constant at 3.6, a value somewhat lower than that observed by others.[7, 35]

Figures 3a and 3b show plots of the resistivities at 4.2 and 300°K against the condensation temperature for the same two series of films as in Figs. 3c and 3d.

7. A study of the dependence of T_c on the thickness of thin films has shown that two cases are possible: 1) for films obtained at low temperatures there is no dependence of T_c or δ on the film thickness (curves 3 on Figs. 4a and 4b); 2) for films obtained at temperatures close to room temperature, a dependence of T_c and δ on the film thickness is observed, and with decreasing L the critical temperature increases while δ decreases (curves 1 and 2 on Figs. 4a and 4b). In many cases the $T_c(L)$ dependence can be approximated by the formula $\Delta T_c/T_{c_0} = \alpha + \beta/L^n$, where $T_{c_0} = 3.72$°K. The coefficient α gives the temperature shift, relative to T_{c_0}, which the $T_c(L)$ dependence approaches asymptotically with increasing L, and ranges from 0 to 0.02. The exponent n assumes a value in the range 0.4–1.2. Similar approximations are given in [10, 11], where a and n assume respectively the values 0.1 and 1,[10] and 0.04 and 2.3.[11] Such differences between the data given by different authors are due apparently to the differences in the technological methods used to obtain the films and also to structural features of small-thickness films close to the critical thickness; these features will be elucidated below.

3. DISCUSSION

We observed the growth of T_c of tin films with changing condensation temperature in two cases: films obtained at temperatures below 250°K, and thin films obtained in the interval 250–350°K (the left and right branches of Fig. 2, respectively); we have also observed the growth of T_c with decreasing thickness in films obtained at 300°K. It follows apparently from these data that there is no single universal mechanism causing the increase of T_c in all the indicated cases.

1. In a number of recent papers[36–39] they succeeded in determining the main causes of the variation of T_c in films with a nonequilibrium ("disordered") structure (for example in films deposited at low temperatures or in films of alloys). These causes are the change of the phonon spectrum and the change of the density of state of the electrons on the Fermi surface. Experimental investigations in which the character of the phonon spectrum in non-equilibrium films was determined with the aid of the tunnel technique[40–42] are in good qualitative agreement with the theories that take into account only changes in the density of state of the phonons.[38] A more general approach was developed by Maksimov,[39] who took into account, in general form, the change in the character of the electron-ion interaction (the increase in the contribution of the diffuse scattering of the electrons) with increasing disorder of the film structure.

The same causes apparently lead to an increase in the value of T_c, as observed by us for films deposited on cooled substrates. The final decision whether distinguishable changes are retained in the phonon spectrum in this case can be made only on the basis of direct determinations of the phonon spectrum. We have therefore noted only the correlations that follow directly from the data presented above.

According to [39], a connection between the changes of T_c and the changes of the resistance of the metal at

high temperatures should be observed in the case of disordered superconductors:

$$\frac{\Delta T_c}{T_{c0}} \sim \alpha \frac{\Delta\rho}{\rho} \ln \frac{\vartheta_D}{T_{c0}}. \quad (1)$$

Such a correlation is observed qualitatively in all series of samples obtained at temperatures much below room temperature. Figures 3b and 3c permit a comparison of the character of the variation of the resistivity of the films, at room temperature, ρ_{293}, and at the critical temperature T_c with changing condensation temperature, for two series of samples. In each series the films were strictly equal in thickness; small deviations of the value of $\rho_{4.2}$ from the average curve are due to deviations of the two other geometrical dimensions (mainly the distance between the potential contacts), which were allowed for in the calculation. To obtain the curves for ρ_{293}, the corrected value of $\rho_{4.2}$ were multiplied by $\delta = R_{293}/R_{4.2}$, a quantity independent of the geometry. The experimentally determined values of ρ_{293} are distributed with a small scatter (up to about 8%) about the curves shown in Figs. 3b. From a comparison of Figs. 3b and 3c it can be noted, for example, that the series of films with a smaller dependence of ρ_{293} on the condensation temperature corresponds to a smaller change of T_c. The coefficient α in (1) turned out to equal $\sim 10^{-2}$ (at $\rho_0 = 11.4 \times 10^{-6}$ ohm-cm, $T_{c0} = 3.72\,^\circ$K, and $\vartheta_D = 190\,^\circ$K).

We note that a similar comparison of the experimental data with relation (1) cannot be made in ordinary experiments with nonequilibrium films, namely condensation with the substrate at helium temperature and successive stage by stage annealing at different temperatures, since at high temperatures the resistivity of the film in the initial state and in the intermediate stages of the annealing remains unknown.

We shall attempt to show that any other approach to the explanation of the growth of T_c of tin films with decreasing condensation temperature is less realistic. For example, we can propose the following model, which takes into account the observed correlation between T_c and the dimension of the crystallites in the film (see Fig. 2 and the table): the crystallites have a perfect structure, and the growth of the resistivity of the films, obtained at temperatures below 250°K, and the decrease of δ are due to changes in the structure of the intercrystallite boundaries. If the structure of the boundaries is such that the electrons are reflected from them, then to explain the growth of T_c with decreasing crystallite dimension it is possible to take into account the investigations dealing with the possible changes of the electron-phonon interaction constant near the boundaries under the influence of the oxide layer,[43, 44, 21] or the boundary conditions of the propagation of the electron waves in small crystals[45] or of the size effect are taken into account.[46]

According to [46], a growth of T_c due to size quantization should be observed at a crystallite dimension smaller than the characteristic dimension $D_c = (\lambda_F^2 \xi_0)^{1/3}$ (λ_F is the wavelength of the Fermi electrons and ξ_0 is the coherence length). For tin, this dimension amounts to ~ 80 Å (at $\lambda_F = 15$ Å[47] and $\xi_0 = 2300$ Å[48]), thus exceeding the aforementioned mean dimensions of the crystallites in the investigated films. (In addition, according to [46], an increase of the ratio $2\Delta_0/kT_c$, which could not be traced by us, should have been observed with increasing T_c.)

Better agreement is obtained by comparison with Shapoval's theory,[45] according to which the relative increase of T_c at a crystallite dimension 200 Å should amount to 5×10^{-2}. There are no grounds in our case, however, for assuming that the crystallites are completely isolated. Calculation shows that if the entire additional resistance $\Delta\rho = \rho - \rho_0$ is attributed to the intercrystallite boundaries, assuming their thickness to be $\delta^* = 20$ Å, then the resistivity of these regions turns out to be approximately $\rho^* = (D/\delta^*)\Delta\rho = 10^{-4}$ ohm-cm, whereas the resistivity of tin oxide lies in the interval $(0.5-1) \times 10^4$ ohm-cm,[49] and the corresponding value for the most transparent Josephson tunnel junctions exceeds 10^2 ohm-cm. In connection with these estimates, there is no need for discussing other models that take into account the effect of the oxide layer on the intercrystallite boundaries. The intercrystallite boundaries should be regarded as disordered-structure regions, and one should assume that the effective reflection of the electrons occurs only on the outer surfaces of the film (we note that the aforementioned theory can be easily applied to the explanation of the dependence of T_c on the film thickness).

At the same time, the role of the crystallite dimension in the variation of T_c can become manifest in the following manner. It is easy to modify the Toxen model,[12] in which account is taken of the influence of stresses on T_c, by assuming that the dimension limiting the length of the dislocations and determining their mobility is not the film thickness but the crystallite dimension. Higher elastic stresses are then attained in a finely-dispersed film under deformation than in a large-crystal sample. However, if the proposed mechanism were the only cause of the growth of T_c in films deposited at decreased temperatures, then the plots of T_c vs. condensation temperature (Fig. 2) for tin films on methylmethacrylate and on glass would have mirror symmetry with respect to $T_{c0} = 3.72\,^\circ$K, whereas in the case of a mechanism that does not depend on the magnitude and sign of the stresses the configurations of the plots should be similar but shifted along the temperature axis. On the other hand, the plots obtained for T_c of films deposited on methylmethacrylate (Fig. 2) apparently represent an intermediate case, thus evidencing that whereas the proposed mechanism does make a certain contribution to the observed plot of T_c vs. the condensation temperature, it is still not decisive.

2. The Toxen model with allowance for the results of Blumberg and Seraphim[10] for textured films can apparently be used also to explain the growth of T_c with increasing condensation temperature in the region of the right-hand branch on Fig. 2. It is shown in [10] that the influence of the thermal stresses is stronger in the case when the tetragonal **c** axis lies in the plane of the film. This is due to the anisotropy of the elastic constants of the crystal lattice of the tin, causing the stresses σ_c produced upon deformation along the **c** axis to exceed the stresses σ_a, and in addition, $\partial T_c/\partial\sigma$, which characterizes the sensitivity of T_c to stresses, is larger for the **c** axis than for the **a** axis.[50] It was assumed in [10] that the texture orientations in the tin

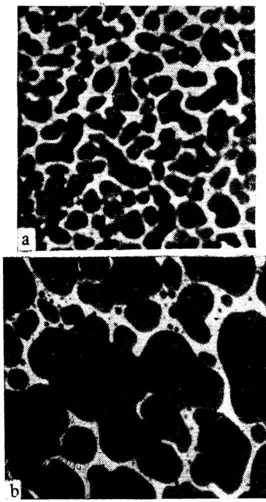

FIG. 5. Electron-microscope photographs of the structure of tin films obtained at room temperature on the substrate and having a thickness close to critical L_c: a—$L < L_c$, b—$L \gtrsim L_c$, ×25,000.

films are changed with changing condensation temperature. Our electron-diffraction data indicate that only one orientation is produced in the entire investigated condensation-temperature interval, but the degree of perfection of the texture increases somewhat with increasing condensation temperature, and this in principle might lead to a growth of T_c. However, experiments with films condensed on methylmethacrylate show that the improvement of the texture is not the decisive cause of the growth of T_c of films obtained above 250°K. Indeed, for films on methylmethacrylate, besides the shift of the characteristic values of T_c to the region of temperatures below 3.72°K, there should be observed a dependence opposite to that on glass and quartz, i.e., T_c should decrease with improvement of the texture. The experimental data, however, indicate that this does not take place (see Fig. 2).

The improvement of the film structure with increasing condensation temperature contribute also to a better manifestation of the quantum size effect,[51] which for very thin films might lead to a growth of T_c.[52] It has been shown in [47], however, that the monotonic part of the dependence of T_c on the thickness of the film is determined not so much by the quantum size effect as by the structural parameters of the film. This result gives grounds for disregarding in this case the influence of the quantum size effect.

3. At the same time, the causes leading to the growth of T_c of thin films with increasing condensation temperature above 250°K, and the causes leading to the growth of T_c with decreasing thickness of films condensed at 300°K should be related. Indeed, attention should be called to one circumstance that is common to both cases, namely: both in the case of the growth of the condensation temperature at constant thickness and in the case of a decreasing film thickness at constant condensation temperature, the samples prepared by us approach the critical thickness. The structures of the films obtained at room temperature and of films of nearly critical thickness have singularities connected with the kinetics of formation of the condensate. The condensate goes in succession through the following structural stages: individual particles (nuclei)—island structure—formation of aggregates—labyrinth structure—continuous film. The structure of the condensate during the third and fourth stages is illustrated by electron-microscope photographs (Fig. 5) of tin films of nearly critical thickness. During the state of the labyrinth structure, the film has a normal metallic conductivity, and it is interesting to note that the presence of narrow channels between the aggregates does not affect the conductivity noticeably. This can be attributed to the fact that the electron mean free path is smaller than the characteristic dimension of the aggregates, i.e., the film resistance is determined by the scattering of the electrons inside the aggregates, and not by scattering from their contact boundaries. With further increase of the thickness, the channels collapse (at $L \lesssim 2L_c$), and the surface of the film becomes smooth.

The existence of channels in films with a labyrinth structure leads to an increase of the per-unit surface of the film, and this can cause a growth of the critical temperature. The channels cause the change of the size of the surface per unit volume of the film with changing thickness to noticeably overtake the corresponding change for a smooth film: $S/W = 2/L$. If there are factors causing the growth of T_c under the influence of the contribution of the surface, such as the increased electron-phonon interaction constants in the surface layer[43, 44] etc.[2)], then their effect in "labyrinth" films turns out to be more significant.

Thus, in the case under consideration, the growth of T_c with decreasing film thickness is due to two simultaneous mechanisms—development of the labyrinth structure and the factor $1/L$. The observed growth of T_c for equal-thickness films obtained at different substrate temperatures (right-hand branch in Fig. 2) occurs under the influence of the change in the labyrinth structure only.

We note one more observation, which is in our opinion of independent interest. For films of small thickness, the growth of T_c with increasing condensation temperature is accompanied by the growth of the ratio $\delta = R_{293}/R_{4.2}$ (Figs. 1 and 2), i.e., it accompanies the improvement in the perfection of the film structure. Yet for films condensed at room temperature, a growth of T_c with decreasing thickness corresponds to a decrease of δ (Figs. 4a and 4b) This disparity has the following simple explanation. Figure 4c shows, in logarithmic coordinates, the dependence of the film resistance on the thickness at room and helium temperatures. The series of samples 1 and 2 were obtained with the substrate at room temperature, while series 3 was obtained at near-nitrogen temperature (the samples in the different series differed in their geometrical dimensions, particularly in the width of the film, but for this construction this circumstance is immaterial). At room temperature, all the plots are straight lines

[2)]Arguments favoring the probable increase of the electron-phonon interaction constant near the surface were advanced in a number of theoretical papers. Such causes may be surface superconductivity [43,44] or an additional mechanism of pairing of the electrons because of the polarization of the oxide or the adsorbed layer on the surface [43,53], the influence of the electric field of the oxide [54], or else the disordered structure of the near-surface layer. A direct experimental verification of these models is difficult, although they have been used to explain the experimental results in a number of papers [8,9,13,21].

with slope −1. Consequently, at room temperature the resistivity of tin films in the interval 350–5000 Å does not depend on the film thickness. In exactly the same manner, at 4.2°K the resistivity of films obtained at 80°K does not depend on the thickness (curve 3a on Fig. 4c) (i.e., the processes of electron scattering are determined mainly by the defects within the volume of the film. But for films obtained at room temperature the plots of log R against log L at 4.2°K have a larger slope (approximately −1.4), i.e., the resistivity increases with decreasing thickness, which apparently is a manifestation of the classical size effect.[55] This indeed is the reason for the ratio $\delta = \rho_{293}/\rho_{4.2}$ changes with changing film thickness. The use of the very arbitrary quantity $\delta = R_{293}/R_{4.2}$ to describe the degree of equilibrium and the impurity of thin films of different thicknesses is therefore obviously incorrect.

Thus, the causes of the variation of T_c of thin tin films in the three cases under consideration (lowering of the condensation temperature below 250°K, increase of the condensation temperature above 250°K, and decrease of thickness) are different and are connected to one degree or another with the structural characteristics of the films. Non-equilibrium films are characterized by small crystallite dimensions and large disorientation of the texture axis; films of thickness close to critical have a "labyrinth" structure, etc. The structure characteristics of the films depends strongly on the concrete conditions of their production, but knowledge of these characteristics is very desirable, since it is precisely these characteristics which determine, in the case of disordered structures, the changes in the electron and phonon spectra, and for the "labyrinth" structure also the ratio of the film surface to its volume, etc. Since an exact quantitative description of the structural characteristics of the films cannot always be obtained, a discussion of the observed changes of the superconducting properties of the films has frequently only a qualitative character. This, unfortunately, could likewise not be avoided in the present investigation.

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