Electric conductivity and superconducting properties of thin mercury films

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A procedure is developed for obtaining mercury films at condensation temperatures 2.3–4.2°K under maximally reproducible conditions. We investigated the electric-conductivity and superconductivity properties of cold-deposited mercury films (effective thickness d =0–1000 Å). It was observed that up to 20 atomic layers the resistance is $R_f=\rho/d \geqslant 10^{10}$ Ω; at a thickness of 20–23 atomic layers, the films are not superconducting, but at larger thicknesses they become superconducting. We measured the functions $R_f(d)$ and $T_c(d)$ and investigated in detail the nonsuperconducting films. The superconducting-transition films are compared with the theory of Aslamazov and Larkin. A value $g^{AL}_{expt}=(1.7\pm0.3)\times10^{-5}$ Ω^{-1} is obtained. The change of the electric-conductivity and superconductivity properties of the films upon recrystallization is investigated.

Thin films have been attracting the attention of researchers for several decades as research and technical-application objects. Much less attention, unfortunately, is paid to the conditions under which they are produced, for without understanding the peculiarities of these conditions the study of the properties of thin films cannot lead to reliable and unambiguous results. This circumstance is not significant for the extensive use of films for technical purposes, so long as the manufacturing process admits of an adquate technology. On the other hand, for investigation of the physics of specific processes in thin films of matter, it is of decisive significance to satisfy a number of conditions during the course of film production.

It goes without saying that single-crystal films would be the most interesting research objects, but barriers to their production are created by nature itself. In essence, we know of no way of obtaining in the general case objects in which the crystallites have macroscopic dimensions. Methods used to obtain thin layers, such as plasma evaporation of a substance followed by its "precipitation" or even thermal evaporation and condensation inevitably lead to highly dispersed samples in which the dimensions of the crystal blocks do not exceed their thickness in order of magnitude. The block structure is also typical of thin films obtained by epitaxial growth. An increase in the dimensions of the crystal blocks by directional recrystallization appears to be possible in principle, but has not been used by anyone in practice.

Another object, diametrically opposite in its properties to the single-crystal film, is the amorphous film, i.e., a film obtained under conditions under which no crystal lattice can be produced at all. The structure of such a film is similar to that of a liquid, and the characteristic dimension is in this case the interatomic or intermolecular distance. Such films can be obtained reliably only by condensing "cold" vapor on a substrate having extremely high thermal conductivity and furthermore cooled to extremely low temperatures. Unfortunately, these conditions have usually been neglected in the dozens of studies devoted to such "cold-deposited" films. In some studies, laser pulse in the free-generation regime has even been used for evaporation. Even if we disregard the temperature of the vapor produced (~10 000°), up to 80% (by weight) of macroscopic particles produced by the spattering of the molten material is deposited under these conditions on the substrate, which usually has low thermal conductivity. If, for example, complicated multicomponent systems are evaporated under these conditions, then there can be no talk, of course, of maintenance of stoichiometry. Any thought of seemingly observable phase transitions in conglomerates of this type is likewise meaningless.

Our main purpose was to satisfy as fully as possible most of the requirements that are obligatory for the production of "amorphous" films, choosing the only feasible object for detailed study, namely thin films of mercury. Mercury is the only metal that has, together with a low melting temperature, a vapor tension sufficiently high, so that the rate of condensation can be controlled in a wide range. Mercury can be rid of impurities and dissolved gases by multiple recondensation. Owing to the maximum value of the accommodation coefficient (α = 1) of the vapor relative to the liquid surface of the evaporator, the effective thicknesses of the obtained films can be determined with high reliability. The negligible power consumption in the film-production process makes it possible to decrease the dimensions of the apparatus and to lower the condensation temperature to 2.3°K.[1)]

To satisfy as far as possible the stringent requirements imposed above, we constructed the apparatus shown in Fig. 1. In this apparatus it was possible to prepare films with minimal overheating of the substrate (the maximum heat input due to radiation and the heat of condensation was ~20 μW, and the substrate overheating did not exceed 0.05°), while at the same time monitoring the film thickness. To repeat the experiment it was sufficient to heat the entire apparatus, cooling only the stub containing the mercury, and to recondense all the mercury that had condensed on the small vessel in the evaporator. Thus, a series of films with thicknesses chosen arbitrarily beforehand could be prepared in the same instrument at a constant geometry.

A molecular mercury beam limited to the cross section A – A was condensed on the optically polished surface of the bottom of a small vessel of chemical glass, into which four platinum wire electrodes of 0.3 mm diameter were sealed and polished flush. To improve the contact with the film and to protect against the corrosive action of the mercury, a molybdenum layer ~1000—2000 Å thick was first deposited on the surface of the platinum electrodes by plasma evaporation. The

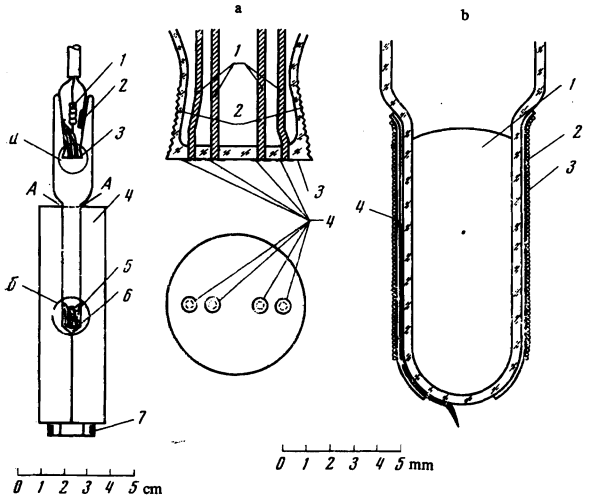

FIG. 1. Overall view of the apparatus: 1—thermocouple; 2—Allen-Bradley thermometer; 3—optically polished bottom of vessel; 4—foam-plastic jacket; 5—mercury; 6—heater; 7—heating coil for heating the helium bath; a—vessel: 1—platinum electrodes; 2—roughened surface of vessel; 3—optically-polished bottom of vessel; 4—molybdenum coating; b—evaporator: 1—mercury; 2—copper form of heating coil oven; 3—constantan heater; 4—thermocouple.

dimension of the current leads obtained in this manner[2)] was 0.5—0.6 mm. To eliminate the influence of the edges of the condensed film, the side wall of the vessel was roughened. Two projections of the overall view of the vessel are shown in Fig. 1a.

We had great difficulty with contact damage by amalgamation. Uncoated platinum contacts were spoiled after one or two experiments, those of nickel withstood 3—4 experiments, chromium 6—8, and tantalum 10—12. A molybdenum coating, on the other hand, withstood more than 30 cycles of deposition and removal of the mercury film without noticeable deterioration in the properties of the contacts.

The mercury was heated by an external heating coil wound on a copper form placed over the evaporator. The temperature was monitored with a thermocouple. Thermal protection from the helium bath was by a tight foam-plastic jacket fitted over the apparatus. In the evaporator heating and cooling operations, the melting and solidification points determined with the thermocouple differed from the tabulated melting temperature of mercury by no more than 1°. The evaporator temperature was maintained constant within ~0.1° by an automatic-control system. The power required to heat the mercury to +25°C did not exceed 1.5 W. An overall view of the evaporator is shown in Fig. 1b.

The film thickness was determined from the tables of the vapor tension of mercury, the distance from the substrates to the evaporator, and the condensation time (assuming that the accommodation coefficient of mercury on glass is $\alpha = 1$); the total thickness error did not exceed ~10%.

During the course of preparation, the apparatus was conditioned by evacuation with an oil diffusion pump at ~400°C for 4 hours. An ampule with mercury that had been outgassed beforehand was placed in a separate stub. After the preconditioning of the apparatus, the ampule was broken with a magnetic striker and the required amount of mercury was distilled over into the apparatus. The initial (residual) pressure in the sealed apparatus did not exceed $\sim 10^{-5}$ Torr and was maintained constant during the entire time of use of the apparatus.

The small dimensions made it possible to place the apparatus, mounted on a thin-wall stainless tube, through which the wires passed, in a metallic helium Dewar through a lock in the cap. A temperature in the interval 4.2—5.1°K was obtained by heating liquid helium in a closed cryostat and was determined from the equilibrium vapor pressure of the helium, and also with an Allen-Bradley carbon thermometer, the readings of which were registered with an x-y recorder. The error in the measurement of the helium-bath temperature did not exceed 0.002°K. The sample was heated to 100—150°K by raising the apparatus over the level of the liquid helium, and the film temperature was measured with a thermocouple of chromel and gold with 0.03% iron and was maintained constant within 1°.

The film resistances, were measured in the range from 10^6 to 10^9 Ω at a constant voltage (by determining the current) with an F18 microammeter, with accuracy ~3%, and from 0.1 to 5×10^6 Ω with an R309 potentiometer, with accuracy 0.01%. The measurement current was low enough not to exert a noticeable influence on the superconducting-transition curve. The possible temperature differential between the film and the bath did not exceed 0.001° in this case. The superconducting-transition curves were plotted with an x-y recorder while the temperature was decreased at a rate not exceeding 0.02 deg/min.

To determine the absolute values of the resistivity we measured, for each electrode configuration (in different instruments) the geometric factor γ corresponding to the effective ratio of film length to film width at rectangular geometry. To determine this factor, a thin layer of copper was vacuum deposited simultaneously on the bottom of the vessel of the apparatus and on the substrate in a separate experiment with rectangular-geometry electrodes. The accuracy with which γ was determined was not less than ~5%.

To measure the effect of a magnetic field on the film's properties, the apparatus was placed between the poles of an electromagnet that produced a homogeneous field up to 6000 Oe in a volume ~1000 cm^3. The film plane was made parallel to the magnetic field, accurate to 0.5°, by rotating the magnet. The field intensity was measured with an IMI-3 instrument with accuracy ~2%.

The films were condensed at rates 0.01—0.5 Å/sec at substrate temperatures 2.3—4.2°K. To measure the dependence of the resistance on the film thickness (up to 1000 Å thickness), we used rates of 0.1—0.5 Å/sec; for more detailed study of the dependence of the resistance on the thickness at high film-resistance values, we used condensation rates lower by one order of magnitude. The plots of film resistance against condensation time that were obtained in different experiments could be made congruent by changing the scale on the time axis in proportion to the ratio of the vapor tensions of the mercury in these experiments; in other words, the dependence of the film resistance $R_f = \rho/d$ on the effective film thickness d did not change with changing condensation rate. The results obtained at small and large thicknesses are shown in Figs. 2 and 3, respectively.

Our procedure did not make it possible to measure the electric properties of the films at resistances R_f

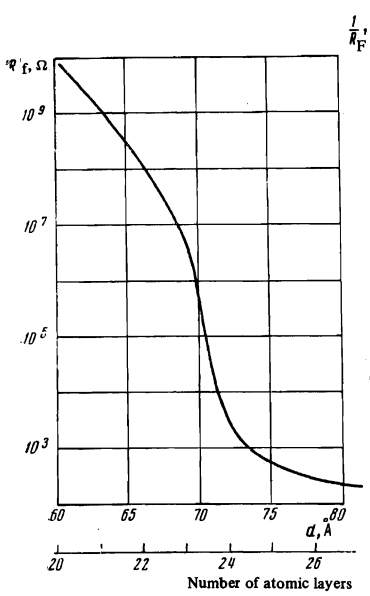

FIG. 2

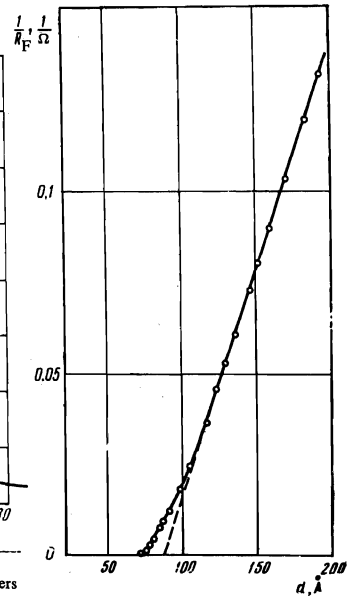

FIG. 3

FIG. 2. Film resistance $R_f = \rho/d$ vs. effective film thickness d at small thicknesses.

FIG. 3. Dependence of $1/R_f$ on d at large thicknesses.

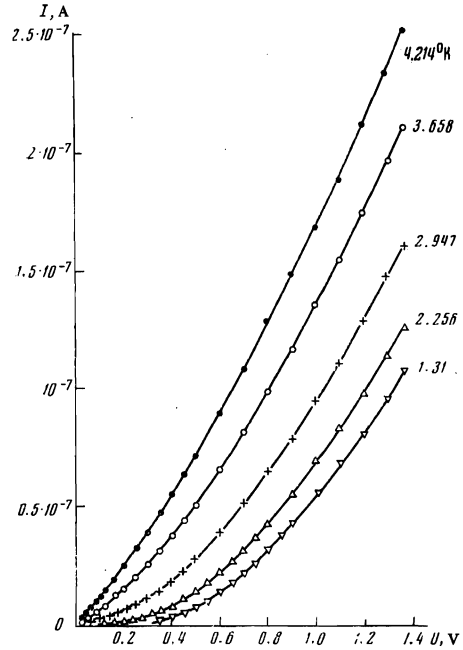

FIG. 4. Current-voltage characteristic of film ($R_f = 1.4 \times 10^7$ Ω, d = 68Å) at different temperatures.

$\gg 10^{10}$Ω (d ~ 60 Å), so that the initial period of the dependence of R_f on the condensation time is characterized by a certain "induction time," which depends on the condensation rate. (The "induction time" is the time interval from the time of establishment of the working evaporation regime to the appearance of conductivity ($R_f \sim 10^{10}$ Ω).) Subsequently, the film resistance decreased approximately logarithmically, and at thicknesses $d \geq 120$ Å the plot followed a linear dependence of $1/R_f$ on d up to d ~ 1000 Å. The plot of the resistance against the thickness can be subdivided into the following sections that differ in their electric-conductivity and superconductivity properties:

I. $R_f \gg 10^{10}$ Ω (d = 0–60 Å). Interval corresponding to the "induction time."

II. $R_f = 2 \times 10^6 - 10^{10}$ Ω (d = 60–70 Å). Films of this thickness remain nonsuperconducting down to ~1.3°K.

III. $R_f = 20 - 2 \times 10^6$ Ω (d = 70–120 Å). The films become superconducting, but have an anomalously high resistivity.

IV. $R_f \leq 20$ Ω (d ≥ 120 Å). The film resistivity changes little with increasing thickness and approaches the limiting value $\rho_\infty = (7 \pm 0.7) \times 10^{-6}$ Ω-cm.

To determine the possible influence of the surface properties of the glass substrate on the induction time, we used vessels with bottoms polished to different degrees, and also a vessel that was not worked mechanically at all. We observed no significant influence of the surface quality on the length of the induction time.

The properties of the films of type II differ significantly from the properties of thicker films. They do not become superconducting down to ~1.3°K and have a nonlinear current-voltage characteristic (Fig. 4). In a certain temperature interval, the resistance is given approximately by $R_f \propto e^{\Delta/T}$. The dependence of Δ on d and R_f is shown in Fig. 5. The values of R_f and Δ were determined for U ≈ 1 V. A magnetic field up to 6000 Oe can be parallel to the substrate plane, exerted no significant influence on the film properties.

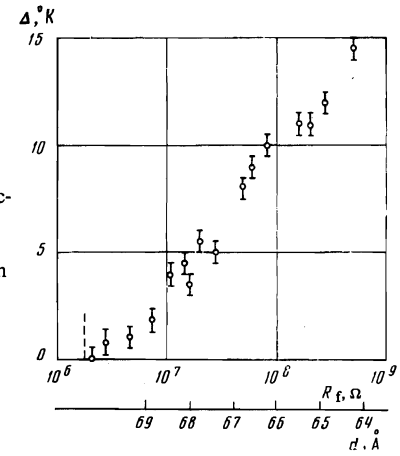

FIG. 5. Dependence of the parameter Δ on the effective thickness and resistance of the film. The dashed line shows the boundary between films of type II and III.

Typical superconducting-transition curves of cold-deposited films of types III and IV are shown in Fig. 6. The superconducting transition temperature T_c was taken to be the temperature at which the resistance had decreased by one-half. The dependence of T_c on d and R_f is shown in Fig. 7. Films of type III are characterized by an anomalously high resistivity (2.5×10^{-5} – ~1 Ω-cm). The critical temperature and the width of the superconducting transition were approximately constant at $T_c = 4.05–4.08$°K, $\Delta T = T(0.8R_{4.2}$°K) – $T(0{,}2R_{4.2}$°K) = 0.03–0.06°K. In this respect they differ from the films of type IV, the critical transition temperature of which decreases monotonically with increasing thickness, as does also the width of the transition (see Figs. 6c and 6d).

A magnetic field parallel to the film plane does not significantly change the form of the superconducting transition. The relation $H_c \propto \sqrt{T_{c0} - T_{cH}}$ for all superconducting films holds satisfactorily down to the smallest thicknesses. The reduction of the results by Abrikosov's formulas[8] yields for the depth of penetration a value $\delta_{00} = 1670 \pm 160$ Å.

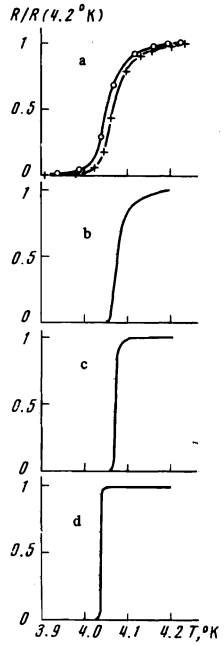

FIG. 6. Superconducting-transition curves of cold-deposited films. Case a: ○–$R_f = 1.4 \times 10^6\,\Omega$, d = 69.5Å; +–$R_f = 2.6 \times 10^4\,\Omega$, d = 70.8Å. Case b: $R_f = 187\,\Omega$, d = 81Å. Case c; $R_f = 40.0\,\Omega$, d = 110Å. Case d: $R_f = 650\,\Omega$, d = 215Å.

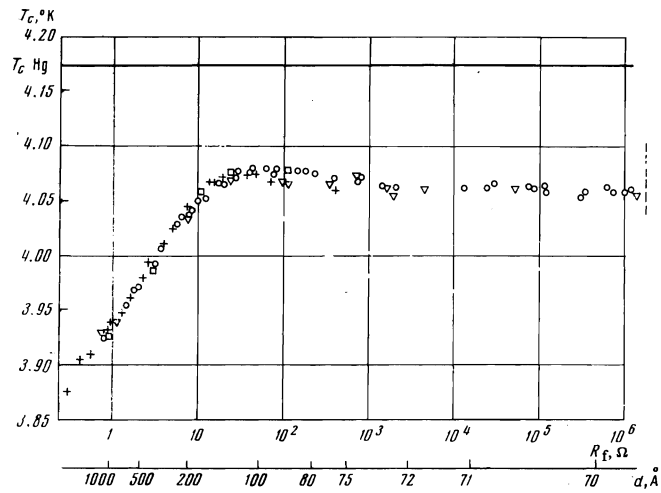

FIG. 7. Dependence of the superconducting transition temperature of cold-deposited films on the effective thickness and on the resistance: +, ○, ▽–for different instruments, condensation at 4.2°K; □–condensation at 2.3°K. Dashed–boundary between films of types II and III.

We compared the superconducting-transition curve of cold-deposited films with thickness $d \leq 300$ Å with the Aslamazov-Larkin theory. It is shown in[9] that fluctuation pairing of the electrons leads in the case of a thin film to a correction to the conductivity, $\sigma'_{fluct} = g^{AL}_{theor} T_c/d\,(T - T_c)$, if the two conditions $\sigma'_{fluct} \ll \sigma_0$ and $d \ll \xi(T)$ are satisfied. The parameter $g^{AL}_{theor} = 1.52 \times 10^{-5}\,\Omega^{-1}$ is a universal constant. We reduced that part of the superconducting-transition curve for which the criteria of[9] were satisfied. T_c was taken to be the temperature corresponding to the midpoint of the transition; by choosing T_c within the limits of the transition width, it was possible to vary g^{AL}_{exp} by no more than 10%. The dependence of g^{AL}_{exp} on d and R_f is shown in Fig 8. For films 90–200 Å thick, the mean value is $g^{AL}_{exp} = (1.7 \pm 0.3) \times 10^{-5}\,\Omega^{-1}$. The superconducting-transition curves of films of type III are similar, the parameter g^{AL}_{exp} is much smaller than the theoretical value, and the shape of the transition curve

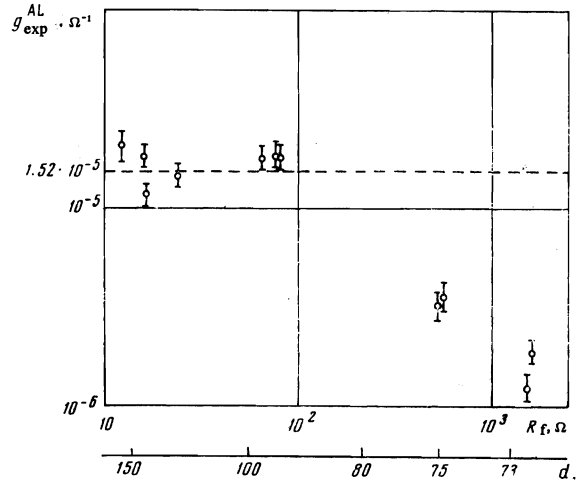

FIG. 8. Dependence of the constant g^{AL}_{exp} on the effective thickness and on the resistance of the film.

does not depend on the thickness and resistance of the film (see Fig. 6a).

We have investigated in detail the changes in the film properties after annealing. The films were recrystallized in accordance with the procedure indicated above, and the time necessary to establish the "annealing" temperature did not exceed ~3–10 min. The film was kept at the annealing temperature for ~15 min, after which it was again immersed in the liquid helium and the superconducting-transition curve was measured. A second annealing at the same temperature no longer exerted a significant influence on the film properties, provided that the film temperature did not reach ~50°K. At $T_{ann} \geq 50$°K, the second annealing revealed a certain decrease in the film resistance.

The crystallization of the films started already at a temperature ~8–10°K. Figure 9a shows the change of the resistance after annealing of films of type II and III, and Fig. 9b shows the same for films of type IV. Of particular interest is the annealing of films of type II and III. Their resistance decreased appreciably already at $T_{ann} \approx 10$–20°K, and the decrease at $T_{ann} \sim 80$°K amounted to 2–6 orders of magnitude, whereas the resistance of type-IV films annealed to ~80°K decreased by only a factor 10–20, the strongest influence of the annealing occurring at ~50°K. It is seen from Fig. 9b that the experimental points corresponding to films of type IV of different thickness can be fitted satisfactorily to a smooth curve.

The parameters Δ of films of type II decreased after recrystallization (Fig. 10). With further increase of the annealing temperature, the films already become superconducting (Fig. 11). The variation of the superconducting-transition temperatures of these films with increasing annealing temperature is shown in Fig. 12a.

The superconducting transition temperatures of films of type III increase after annealing (Fig. 12a), and the dependences of T_c on T_{ann} for films of different thicknesses were close to one another. The superconducting transition temperature of films of type IV after recrystallization varies in a nonmonotonic manner (Fig. 12b).

We have thus developed a procedure for obtaining amorphous (cold-deposited) mercury films in a wide range of thicknesses (up to 1000 Å), with the minimum

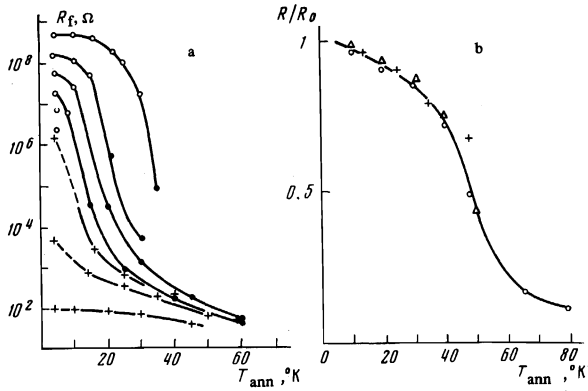

FIG. 9. Change in film resistance after annealing: a–type II and III (○–nonsuperconducting films, +, ●–superconducting films); b–type IV (○–R_f = 6.90 Ω, d = 205Å, △–R_f = 1.98 Ω, d = 490Å, +–R_f = 0.848 Ω, d = 1030Å; $R_0 \equiv R(4.2°K)$.

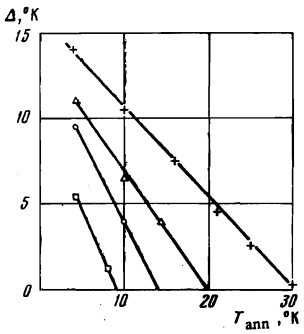

FIG. 10

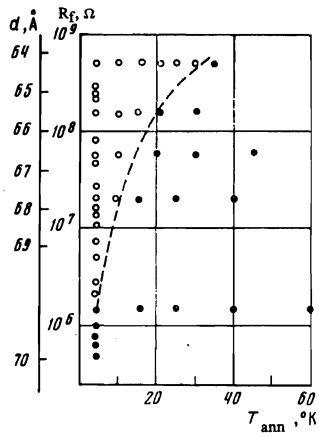

FIG. 11

FIG. 10. Dependence of the parameter △ on the annealing temperature: +–$R_f = 5 \times 10^8$ Ω, d = 64.5Å; ○–$R_f = 5.5 \times 10^7$ Ω, d = 66.5Å; △–$R_f = 1.58 \times 10^8$ Ω, d = 65.5Å; □–$R_f = 1.93 \times 10^7$ Ω, d = 67.5Å.

FIG. 11. Diagram of transition from the nonsuperconducting state to the superconducting state after recrystallization. ○–nonsuperconducting films, ●–superconducting films.

possible heat consumption during the condensation process. The film precipitation rate could range from 0.01 to 0.5 Å/sec. The procedure employed made it possible to produce film samples repeatedly in one and the same instrument without changing the vacuum conditions.

We have established that films up to ~23 atomic layers thick have no metallic properties and that their resistance increases with decreasing temperature. Films in the thickness interval ~23–40 atomic layers have an anomalously large resistivity (from ~2.5 $\times 10^{-5}$ Ω-cm to ~1 Ω-cm), but begin to reveal superconducting properties. With further increase of thickness, the resistivity of the films tends to its limiting value ($\rho_\infty = (7 \pm 0.7) \times 10^{-6}$ Ω-cm).

Recrystallization phenomena in amorphous films set in already at temperatures ~8–10°K, and after a brief annealing at ~80°K the resistivity drops to ~3×10^{-7} Ω-cm, which differs by only a factor ~10 from the resistivity of metallic mercury.

Unlike thin films of metals with higher boiling points, obtained by condensation at low temperatures and having metallic conductivity at the smallest thicknesses possible[10,11], the properties of the mercury films ob-

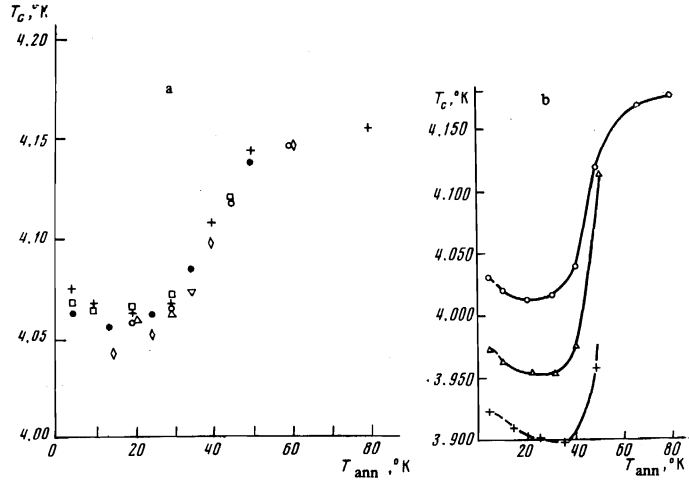

FIG. 12. Change of critical temperature of the superconducting transition on the annealing of films of different thickness. a–Films of type II: ▽–d = 64.5Å, △–65.5Å, ○–66.5Å, ◇–67.5Å; films of type III: ●–71.5Å, +–74Å, □–92Å; b–films of type IV; the symbols are the same as in Fig. 9b.

tained by us are quite anomalous. It is surprising that the transition from the nonmetallic to the metallic properties takes place when the effective thickness of the film is increased by only ~20% (on going from ~20 to ~25 atomic layers). We therefore found it necessary to perform special measurements of the accommodation coefficient of mercury on the surface of the glass, to be convinced that our data on the effective film thickness do not differ from the real thicknesses by more than ~10%. The observed phenomena still await explanation.

We are grateful to N. V. Zavaritskiĭ and Yu. V. Sharvin for interest in the work.

[1)]The first to investigate the resistivity and the superconducting properties of mercury films of thickness ≥300Å condensed on substrates at temperatures from 4.2 to 90°K were Appleyard and Bristow [1]. The depth of penetration of the magnetic field, the energy gap, and the tunneling characteristics were investigated in [2-7].

[2)]We are grateful to E. S. Antsiferov for help with depositing the contacts.

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