Concerning a method for the production and investigation of freshly deposited metal films

E. G. Astrakharchik and A. I. Shal'nikov

Institute of Physics Problems, USSR Academy of Sciences

(Submitted 15 November 1979)
Zh. Eksp. Teor. Fiz. **78**, 2033–2040 (May 1980)

The properties of cold-deposited bismuth films are investigated. The establishment of thermal equilibrium of the evaporator is studied. It is shown that the appreciable time of onset of superconductivity in films with critical temperature close to that of liquid helium, which was attributed by Lazarev *et al.* [Fiz. Met. Metalloved. **28**, 954 (1969)] to a phase transition, is due to overheating of the film.

PACS numbers: 81.15. – z, 74.70.Gj, 73.60.Ka, 68.55. + b

Lazarev, Semenenko, Tutov, and Sudovtsev[1,2] have reported that bismuth and gallium films freshly deposited on glass and kept at liquid-helium temperature go over spontaneously, with gradual decrease of resistance, into the superconducting state. By the same token, they postulate the existence of a noticeable mobility of the atoms of these metals near helium temperature. At the same time, the atoms of certain metals with much lower boiling temperature, such as mercury, cesium, and rubidium, have under the same condition practically no mobility and form a film that seems to be close to amorphous.[3,4] Since the overheating of the films was not measured in detail in Refs. 1 and 2, we have produced and investigated thin bismuth films under conditions that ensure practically no overheating.

The housing of the test unit (Fig. 1) was made of glass No. 29, whose expansion coefficient is close to that of cover glasses made in East Germany. Thus, in the apparatus used by us the condensing film was separated from the helium bath by an extremely thin wall 150 μm thick. The disks were glued to the cylindrical part of the instruments (after chamfering) with Stycast-1266 epoxy resin polymerized for about a day. The apparatus was subsequently conditioned by evacuation at 200°C for many hours.

A system of current and potential electrodes, in the form of molybdenum sectors ~1000 Å thick, was deposited beforehand on both planes and on the side surfaces of the disk by ion-plasma evaporation. Nickel masks were placed on the disk during the deposition of the electrodes.

When certain precautions were taken in the sealing process, one can count on a vacuum not worse than 10^{-5} Torr in instruments produced in small lots. The evaporation of a bismuth batch in an instrument fully immersed in a helium bath thus takes place at a helium pressure $<10^{-12}$ Torr.

The evaporator (tungsten wire of 100 μm diameter) was provided with current and potential leads (traverses) with which to measure its temperature and power consumption (not more than 0.5 W). The traverses to which the source was welded were made of ferrochrome 0.5 mm thick, annealed in hydrogen. To ensure good thermal contact with the bismuth batch, the tungsten wire was coated with zirconium (30 μg batch). The evaporator was preconditioned in a separate unit, with an appreciable fraction of the bismuth batch evaporated.

The instrument was mounted on a rod and could be moved inside a cylindrical dewar of 50 cm height. The film resistance and the voltage drop on the evaporator were registered with a Bryans two-pen x-y recorder. The substrate temperature was measured with an Allen-Bradley resistance thermometer.

It goes without saying that in our experiments we were unable to draw any quantitative conclusions concerning the absolute thicknesses of the films, nor was this included in our problem. We were able in producing only units that were more or less identical with respect to the relative geometry of the evaporator and the substrate.

The working current of the evaporator was chosen for the first unit of the lot after careful examination of the condensation process. Since several units were produced at the same time, we frequently reused evaporators whose working current was set with sufficient accuracy in the preceding experiments.

Figure 2 shows a typical time schedule of the production of a superconducting film. The upper curve is the evaporator voltage and is practically linear in temperature in this region. The current through the evaporator in this experiment was 986 mA. After turning off the heating current, a small measuring current

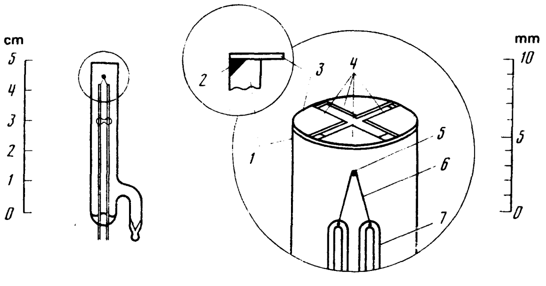

FIG. 1. Overall view of the unit and construction of substrate and evaporator: 1—housing, 2—adhesive (Stycast), 3—substrate (150 μm cover glass), 4—current and potential contacts of the film (Mo, ~1000 Å), 5—bismuth bead (~2 mg), 6—evaporator (W, 100 μm dia), 7—current and potential leads (ferrochrome, 0.5 mm dia).

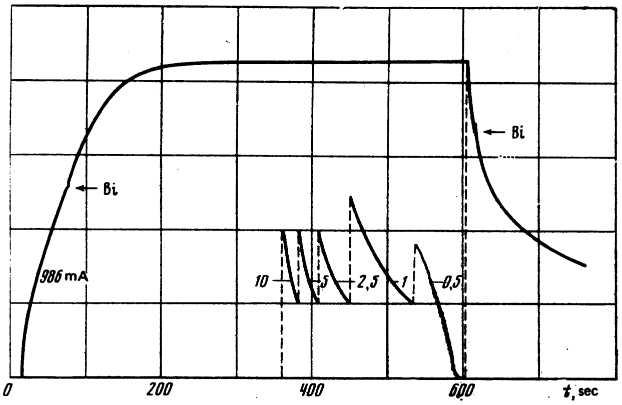

FIG. 2. Typical time plot of production of superconducting film. The reduced resistance $R_r = \rho/d$ [$k\Omega$] is marked on the lower curve.

was maintained in the cooling section (the heating and cooling sections are drawn to different vertical scales in the figure). The arrows indicate the melting and solidification points of bismuth (544 K). The lower curve is the time dependence of the film resistance. Conduction by the film occurred in this experiment after ~330 sec, the condensation process lasted ~260 sec, and the start of the superconducting state of the film became discernible after ~200 sec.

Figure 3 shows the records of production and investigation of the properties of several films condensed in succession in the same experiment. The first of the films obtained in this experiment was kept, as a control, at a temperature 4.2 K for two hours without any change in the resistance or in the $R_r(T)$ dependence. All the films, from the thinnest (nonsuperconducting) with $R_r > 10$ kΩ to the thickest with $R_r < 10$ Ω and $T_{cr} \sim 6$ K were similarly kept in the different units at helium temperature. No traces of a change of resistance or of other parameters were observed in any of the obtained films. Some increase in the resistance prior to the start of the second evaporation (Fig. 3) is due to the change of pressure in the helium loop. At the same time, as seen from Fig. 3, immediately after the end of the condensation there is observed a decrease in resistance, due to the gradual cooling of the film to the temperature of the helium bath. It was this phenomenon which was apparently taken in Refs. 1 and 2 to be a phase transition at liquid-helium temperature. Actually a film with $T_{cr} \sim 4.2$ K, having an abrupt superconducting transition (curve *I* of Fig. 4), behaves like a sensitive resistance thermometer heated by the radiation of the gradually cooling evaporator. This time dependence of the film resistance could be duplicated many times by turning on the evaporator current for a time too short for the evaporation to begin.

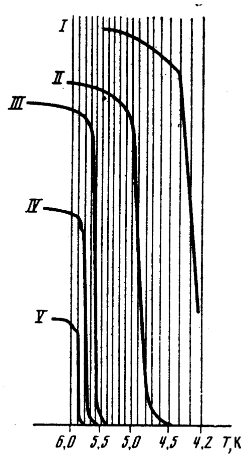

FIG. 4. Superconducting transition curves for films of various thicknesses and with resistances R_r equal to 965 (I), 573 (II), 215 (III), 144 (IV), and 69.1 (V) ohms. Different vertical scales are used for the resistances of the different films.

With further increase of thickness, the film became directly fully superconducting even in the course of condensation, and remained superconducting during the time of the succeeding depositions. Figure 4 shows plots of the resistance against temperature for five films produced in succession in this experiment.

We have performed a number of experiments on the recrystallization of films with initial resistance from 1 kΩ to 100 Ω. Maintaining the film at temperatures up to 15 K for half an hour led to no changes of the film properties whatever. The first signs of recrystallization were noted at 20 K: the film resistance decreased irreversibly by only 2%. With further rise in the annealing temperature the decrease in resistance become more and more noticeable and amounted already to 8% at 40 K. The superconducting-transition temperature changed in this case by not more than 0.02 K. This decrease of the resistance is apparently due not to a phase transition but to a gradual increase

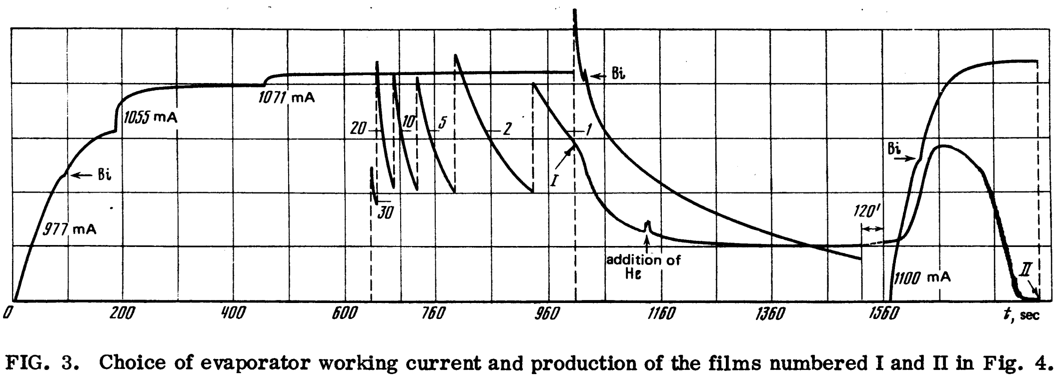

FIG. 3. Choice of evaporator working current and production of the films numbered I and II in Fig. 4. The increase of the film resistance in the cooling region is due to the increase in the loop when the helium is added. The numbers on the lower curve are the values of the resistance in $k\Omega$.

of film density with preservation of the amorphous phase of the bismuth. Finally, when heated above 50 K, an increase in the film resistance set in and was accompanied first by a change in the shape of the superconducting-transition curve, and at 70 K by a decrease of the critical temperature. Still greater heating caused the film to go over completely into the nonsuperconducting phase, and the resistance increased severalfold compared with the initial value. Thus, in bismuth films having approximately the same thickness as in Ref. 1 a phase transition sets in at a temperature not lower than 50 K.

The heat rise of the film during the condensation, relative to the helium bath, was 0.25–0.35 K in different units. The fact that this overheating is due to radiation from the evaporator is seen directly from the similarity of the curves in Fig. 5, in which the logarithmic scales of the evaporator temperatures and of the film overheating ΔT differ by a factor of four. Since the power Q that causes the overheat of the film is proportional to the fourth power of the evaporator temperature, the substrate cooling time constant should one-fourth the time constant of the evaporator cooling, and the dependence of the overheat on the time is given by

$$\Delta T=\frac{Qd}{\lambda_g}=\sigma T^4\frac{S}{4\pi r^2}\frac{d}{\lambda_g}=\frac{\sigma Sd}{4\pi\lambda_g r^2}(T_0e^{-t/\tau})^4=\frac{\sigma SdT_0^4}{4\pi\lambda_g r^2}e^{-4t/\tau},$$

where σ is the effective Stefan-Boltzmann constant of bismuth, S is the area of the evaporator, r is the distance from the evaporator to the substrate, d is the substrate thickness, λ_g is the thermal conductivity of the glass, is τ is the time required for the evaporator to cool down by a factor e. The measured values of ΔT and τ agree well with results of recalculations from the tabulated values of the heat capacity and of the thermal conductivity.[5]

In our experiments τ amounted to about 300 sec, which is much less than the characteristic times described in Refs. 1 and 2, where the time to establish superconductivity reached 1.5 hr. It must be noted, however, that quantities such as the film overheating and the evaporator cooling time are very difficult to decrease, but very easy to increase by several orders of magnitude. Our miniature evaporators have from this point of view near-optimal parameters. In fact, the main task in the construction of an evaporator is always the decrease of the power transferred from the evaporator to the liquid helium. After subtracting the radiation losses, which in our low-power evaporators amount to < 10%, this power amounts to

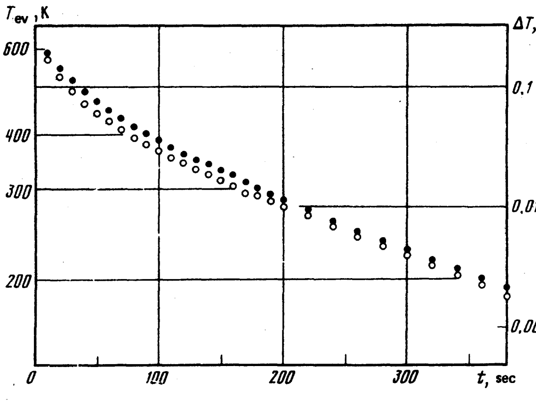

FIG. 5. Time dependence of the evaporator temperature (○) and of the film overheat (●) on the cooling system (Fig. 2).

$$W=T_0s\lambda_f/l,$$

where T_0 is the working temperature of the evaporator, s is the total cross-section area of the current leads, l is their length, and λ_f is the thermal conductivity of the ferrochrome. At a given evaporator temperature and current-lead cross-section area, chosen such that the leads are not overly heated by the current they carry, the power can be decreased only by increasing the evaporator posts. But this increases greatly the cooling time constant, whose value, as obtained from the solution of the heat-conduction equation, is

$$\tau=\frac{4c_f\rho_f}{\pi^2\lambda_f}l^2=\frac{4c_f\rho_f\lambda_f T^2s^2}{\pi^2}\frac{1}{W^2},$$

where c_f and ρ_f are the specific heat and the density of the ferrochrome. Thus, τ can be decreased only by shortening the current leads, and this increases the evaporator power. The cooling time, on the contrary, can be increased by many times even without changing the dimensions and the construction of the evaporator, by using, for example, a bulky batch of the evaporated material or large glass beads on the current leads.

The same statements can be made also with respect to the film overheating, which is governed by the thickness of the glass substrate. The use of polished glass substrates with fused-in platinum leads[3] results in at least a tenfold increase of the overheat. We have prepared a set of units with such substrates, without changing the construction and relative position of the evaporator. The overheat of the film in these units amounted to 2–3 K at a glass thickness 1–1.5 mm. The films in these experiments were nonsuperconducting in the course of condensation up to the largest thicknesses, and became superconducting, just as in Refs. 1 and 2, only a long time after the evaporator was turned off. The films that took longest to reach superconductivity were those whose superconducting transition was close to the helium-bath temperature.

We have thus observed no signs indicating that bismuth films undergo phase transitions at liquid-helium temperature. On the contrary, both their properties and their behavior are quite typical of those of cold-deposited amorphous films of other metals. Since it was not our task to measure the film thickness, we cannot make here any quantitative comparisons, but it is possible qualitatively to identify on the thickness-dependence curve the same sections as in mercury[3] or in cesium and rubidium.[4] These sections represent:

1) The "induction" period, in which the electric resistance of the film is practically infinite, corresponding to the time interval between the establishment of the chosen working evaporator temperature and the appearance of conductivity (Figs. 2 and 3).

2) The "semiconducting" section, in which the films

have nonlinear current-voltage characteristics and their resistance increases with decreasing temperature. None of the metal films are superconducting on this section.

3) "Metallic" films with linear current-voltage characteristic. Films of bismuth (whose amorphous state is superconducting) begin to superconduct in this region. The critical temperature of such films increases with increased thickness up to 6 K (Fig. 6), and the width of the superconducting transition decreases.

To explain the phenomena described in Ref. 1 it is important to note that the plot of the critical temperature of a bismuth film against thickness passes through the temperature of liquid helium. It is precisely films with transition temperatures close to that of the helium bath (4.2 K) which "feel" longest the heating by the evaporator. A similar form of $T_{cr}(R_r)$ is possessed also by gallium,[6] the other metal in which similar phenomena were observed. The difference between the resistances of the gallium and bismuth films is due to the fact that gallium, whose thick films have a higher critical temperature (8.4 K), forms at $T_{cr}=4.2$ K films with lower thickness and larger resistance. On the other hand, the reason why the superconductivity-onset times of the bismuth and gallium films described in Refs. 1 and 2 is the same is that the same evaporator and substrate construction was used.

In most studies of the properties of cold-deposited thin films, much too little attention was paid, in our opinion, to the conditions of condensation on the substrate surface. This can be justified when production problems are solved and it is necessary to ensure only reproducibility of some technical process. But it cannot be assumed that the use of liquid helium to cool the unit does in itself ensure that the produced film is at helium temperature, if the purpose of the investigation is to study the physics of film formation, and particularly such temperature-dependent properties as the mobility of the atoms or the presence of a phase transition. It is essential not only to monitor carefully the film temperature, but also to satisfy many conditions without which overheat cannot be eliminated. One cannot count, for example, on obtaining a homogeneous amorphous film by evaporating the investigated metal with a laser beam. Such an "evaporation" leads not only to strong overheating, but also to a spraying of the bulk of the metal in the form of macroscopic droplets.

Production of films under conditions when there is no overheating of any significance is possible in general only from a small number of low-boiling-point metals, with many precautions taken in the construction of the apparatus and the performance of the experiment. These requirements are met, for example, by the mercury evaporators used in Ref. 3, which were placed as far as ~100 mm from the substrate and were used at a working temperature up to −20°C, corresponding to a film growth rate 0.3 Å/min. This operating regime calls, of course not only for a thorough preliminary study of the evaporator characteristics, but also for an exact measurement of the temperature during time of the experiment. It is necessary also that the temperature be uniform over the entire surface of the evaporated metal. In an earlier study,[4] for example, the area of the evaporator was ~3 cm², and its temperature was measured and maintained constant during the experiment with the aid of an automatic control system with accuracy not worse than 0.01 K.

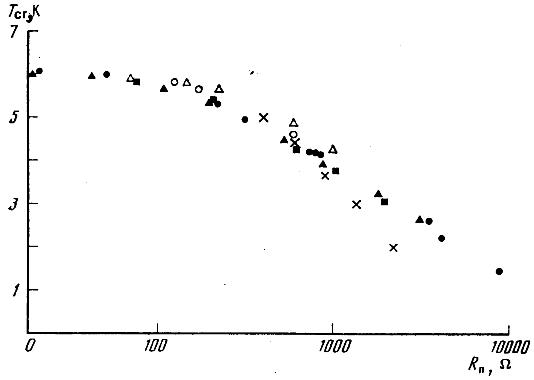

FIG. 6. Dependence of the critical temperature of bismuth films on the reduced resistance. The dark points correspond to units with substrate thickness 1.5 mm, and the light ones to 150 μm substrates. ×—data of Ref. 7.

Improvement of the operating conditions of the evaporator is an additional means of decreasing the overheat, principal among them being an increase of the thermal conductivity of the substrate. Since the use of substrates thinner than those used above is impossible, further increase of the thermal conductivity is possible only by changing the substrate material. Suitable materials are highly pure germanium and silicon single crystals, which have at liquid-helium temperature a thermal conductivity comparable with that of pure metals. Once some skill is acquired, it is possible to prepare from these single crystals substrates ~250 μm thick.[4] The overheating of a film on them is ~mK/W.

If the foregoing precautions are taken, it is possible to films of many metals at a temperature barely differing from that of liquid helium. It must be borne in mind, nevertheless, that this does not mean elimination of long-time thermal effects connected with the cooling of the evaporators, which will be particularly noticeable on films with $T\sim4.2$ K.

[1] B. G. Lazarev, E. E. Semenenko, and V. I. Tutov, Voprosy atomnoĭ nauki i tekhniki. Fundamental'naya i prikladnaya sverkhprovodimost' (Problems of Atomic Science and Technology. Basic and Applied Superconductivity), No. 1 (4), 3 (1976).
[2] B. G. Lazarev, E. E. Semenenko, and A. I. Sudovtsev, Fiz. Met. Metallov. 28, 954 (1969).
[3] V. L. Tsymbalenko and A. I. Shal'nikov, Zh. Eksp. Teor. Fiz. 65, 2086 (1973) [Sov. Phys. JETP 38, 1043 (1974)].
[4] E. G. Astrakharichik and A. I. Shal'nikov, Zh. Eksp. Teor. Fiz. 72, 1607 (1977) [Sov. Phys. JETP 45, 844 (1977)].
[5] M. L. Lyubimov, Spai metalla s steklom (Glass-Metal Seals), Energiya, 1968.
[6] D. G. Naugle and R. E. Glover, Phys. Lett. A18, 611 (1969).
[7] M. Strongin, R. S. Thompson. O. F. Kammerer, and J. E. Crow, Phys. Rev. B1, 1078 (1970).

Translated by J. G. Adashko