Electric properties of thin films of cesium and rubidium

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A procedure employed in an earlier study (V. L. Tsymbalenko and A. I. Shal'nikov [Sov. Phys. JETP **38**, 1043, (1974)] is used to investigate the electric properties of cold-deposited cesium and rubidium films (in the thickness interval up to 1000 Å). In contrast to mercury films, where the electric conductivity cannot be measured up to a thickness on the order of twenty atomic layers, the conductivity of cesium and rubidium films manifests itself already at a thickness ~0.7 atomic layer. The dependences of the film resistance R_f on the thickness d and temperature T are measured.

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A procedure for preparing freshly deposited thin films of mercury, in which reproducibility of the experimental conditions is ensured to a maximum degree, was described in[1] (henceforth cited as I). This procedure, which makes use of the relatively high vapor pressure of mercury, has made it possible to control fully the film condensation conditions, and consequently also the reproducibility of the experiments, a decisive factor when it comes to obtaining exact information, particularly on the properties of ultrathin films. We succeeded in applying this procedure in an investigation of cesium and rubidium films, and to satisfy the principal requirement, namely to decrease the power consumed by the evaporator to a minimum value, and making it possible at the same time to condense on the surface of the substrate up to six atomic layers per minute at helium temperatures.

The general form and the principal details of the apparatus used by us are shown in Fig. 1. In the course of production, the apparatus was preconditioned in a vacuum of $\sim 10^{-7}$ Torr for 12 hours at a temperature 400 C. At the end of the preconditioning period, several milligrams of alkali metal (with impurity $10^{-2}\%$) was distilled over into the apparatus from an auxilliary ampule. This metal was evaporated by high-frequency heating from the mixture (3% Al, 17% Zr, 80% $CsCrO_4$, or $RbCrO_4$). The evaporator was a platinum disk of 16 mm diameter and 0.2 mm thickness, sealed into the end face of a glass tube. A thermocouple was soldered to the outer side of the disk and made it possible, with the aid of an automatic control system, for a constantan heater to maintain the evaporator temperature within 0.02 °C.

All of the alkali metals separated in the auxiliary ampule was fully sublimated on the platinum disk, covering it with a dense homogeneous layer. The thermal shield against the helium bath was a foamed-plastic shell. The power required to heat the evaporator to 20 °C did not exceed 0.3 W. The residual pressure in the sealed apparatus did not exceed 10^{-5} Torr.

The films were condensed in different installations on glass, germanium, and silicon. The glass substrates (Fig. 1a) were similar to those used in I. To ascertain the possible influence of the character of the glass-substrate surface on the film properties, small vessels with differently polished bottoms were prepared, as well as vessels which were not mechanically finished at all. No noticeable influence of the surface quality on the film parameters was observed. The germanium and silicon substrates were single-crystal disks polished on all sides, on which molybdenum contacts ~1000 Å thick were deposited by the plasma sputtering method. To decrease the electric resistance between the molybdenum and the investigated film, a half-shadow was provided on the edges of the contacts, on which the thickness of the molybdenum coating was gradually decreased. The substrate disks were mounted on platinum current leads and were firmly clamped by molybdenum clips.

The film thickness was determined from the vapor-pressure tables of the evaporated metal,[2,3] from the geometrical dimensions of the installation, and from the time of condensation, under the assumption that the accommodation coefficient is $\alpha = 1$. The total thickness error did not exceed 10%.

The films were condensed at rates 0.005–0.5 Å/sec, and the accompanying variation in the vapor pressure was in the range 5×10^{-9}–5×10^{-7} Torr. The plots of the film resistance against the condensation time, obtained in different experiments, could be made congruent by changing the time scale in proportion to the ratio of the

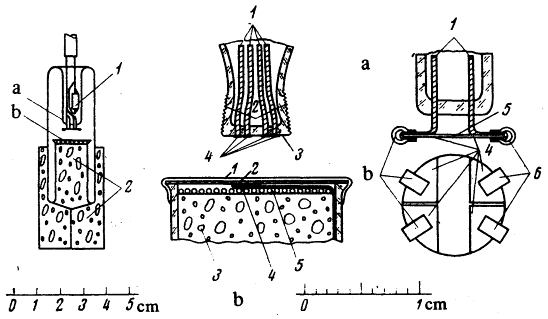

FIG. 1. Overall view of installation: 1—Allen-Bradley thermometer, 2—styrofoam, a—substrate: 1—platinum current leads, 2—matte surface, 3—polished bottom of vessel, 4—molybdenum coating, 5—germanium or silicon disk, 6—molybdenum clips; b—evaporator: 1—thin layer of alkali metal, 2—platinum disk, 3—styrofoam, 4—thermocouple, 5—constantan heater.

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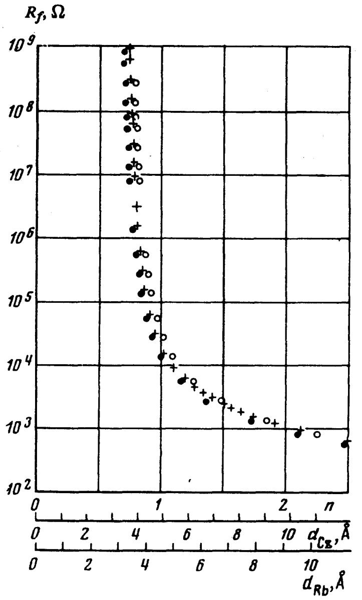

FIG. 2. Dependence of the reduced resistance R_f on the thickness: o, ●—cesium, +—rubidium.

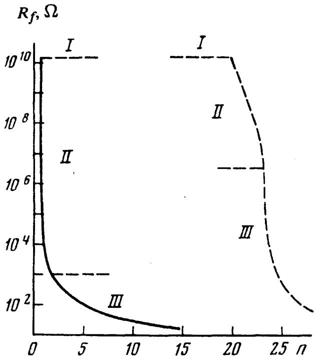

FIG. 4. Plot of $R_f(d)$: solid line—cesium and rubidium; dashed—mercury in accordance with data of *I*.

vapor tension of the evaporated metal in each experiment; in other words, the film resistance $R_f=\rho/d$ (ρ is the resistivity and d is the film thickness) is determined only by the film thickness and does not depend on the condensation time. The results obtained at small film thicknesses are shown in Fig. 2. Cesium exhibits the worst agreement out of a series of twenty experiments. Figure 3 shows a plot of R_f against the number of atomic layers and in the region of large thicknesses.

The film resistance, in the range from 5×10^5 to 10^{10} Ω, was measured at a constant voltage by determining the current with an F-18 microammeter accurate to ~ 3%, and from 0.1 to 2×10^6 Ω with an RZ09 potentiometer with accuracy 0.01%. This procedure did not make it possible to measure the electric properties of the films at resistances $R_f>10^{10}$ Ω, so that the initial period of the dependence of R_f on the condensation time is characterized by a certain "induction time"—a time interval from the instant when the operating evaporation regime is established to the appearance of conductivity ($R_f\sim10^{10}$ Ω). The film resistance drops subsequently approximately in accordance with a logarithmic law, and at $d>20$ Å the curve follows already a linear dependence of $1/R_f$ on d up to $d\sim1000$ Å. It is possible to separate on the plots of the resistance against the number of atomic layers (Fig. 4) the following sections, which differ in the electric-conductivity properties.

I. $R_f>10^{10}$ Ω—the section corresponding to the induction time. For cesium and rubidium films it occupies the region 0–3.7 Å, amounting to ~ 0.7 atomic layer, in contrast to the mercury films (see I), which reached $R_f\sim10^{10}$ Ω at a thickness ~ 20 atomic layers.

II. $R_f=10^3$–10^{10} Ω ($d=3.7$–10 Å)—"semiconducting" films, having an essentially nonlinear current voltage characteristic at an electric field intensity $E>1$ V/cm. In the temperature interval 4.2–2.5 K, the resistances of such films, measured in the ohmic region of the current-voltage characteristic ($E<0.1$ V/cm), follows approximately the law $R_f\sim e^{\Delta/T}$ (Fig. 5); the dependence of Δ on d and R_f is shown in Fig. 6. An analogous section for mercury films is located in the resistance region 2×10^6–10^{10} Ω and in the thickness region 60–70 Å.

III. $R_f<10^3$ ($d>10$ A)—"metallic" section, on which the film resistance was independent of temperature. The mercury films on this section become even superconducting. We observed no signs of superconductivity when the cesium and rubidium films were cooled to 1.2 K on all the employed substrates.

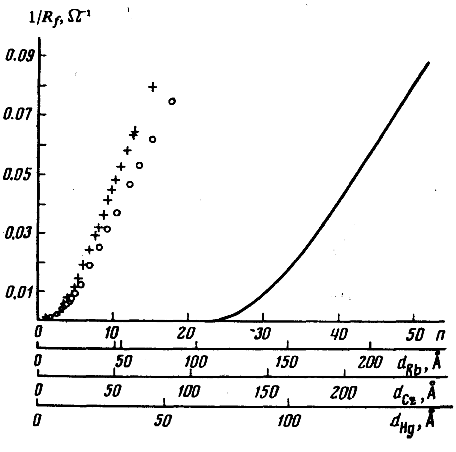

FIG. 3. Plot of $1/R_f(d)$: o—cesium, +—rubidium, solid line—mercury in accordance with the data of *I*.

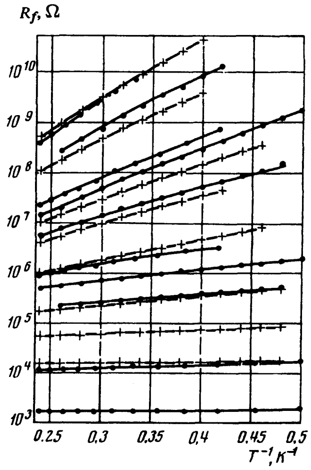

FIG. 5. Temperature dependence of R_f for films of various thicknesses: ●—cesium, +—rubidium.

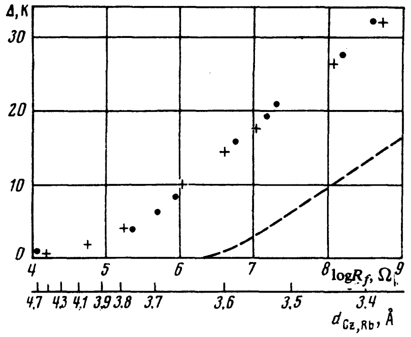

FIG. 6. Dependence of Δ on R_f at 4.2 K and on d: ●—cesium, +—rudibium, dashed line—mercury according to the data of *I*.

We investigated also recrystallized films. The freshly prepared film could be heated by raising the installation over the surface of liquid helium. The substrate temperature was measured in this case with an Allen-Bradley thermometer placed in a small vessel (see Fig. 1). The film resistance began to decrease irreversibly already when heated to 10 K and decreased by a factor of 5–10 when heated to 80 K. The recrystallized films of all thicknesses also revealed no superconductivity down to 1.2 K when heated to 200 K.[1)]

The electric properties of thin cold-deposited films of alkali metals and their behavior after annealing were investigated in[4,5]. It was also reported in[4] that cesium and lithium films are superconducting in the thickness range 100–2000 Å. Unfortunately, the methods of preparing the evaporators and the procedure of working with highly purified alkali metals were not described in these papers.

An important question in the theory of thin-film thickness is that of the minimum thickness at which a solid homogeneous film begins to conduct. In order for the investigated film to be as homogeneous as possible, the condensed atoms must be scattered over the surface in a perfectly random manner and in no way should they "climb" and gather into bridges or "drops." One can hope to obtain such a film in experiment by condensing as "cold" a metal vapor as possible on a surface that is in maximal thermal contact with the helium bath. Conditions close to these were attained in I. It was established that for an amorphous film of mercury, the induction thickness is ~ 20 atomic layers, whereas most metal films conduct already at a thickness ~ 1 atomic layer.[6,7] To ascertain what determines this result—the singularities of the procedure or the properties of the mercury itself—we have made a consecutive comparison of the electric properties of cesium, rubidium, and mercury films prepared under similar conditions on analogous substrates (Figs. 3, 4, 6). All the parameters of the cesium and rubidium films were close to one another and differed strongly from the properties of the mercury films, especially at small thicknesses.

An investigation of the accommodation coefficient of mercury atoms on glass at low temperatures[8] excludes an error in the calculation of the thickness of the mercury films. We think it impossible that such a difference between the properties of the films can be due to a difference in their structure, since the mobility of the metal atoms on the surface at helium temperature is negligibly small. In addition, the assumption that "drops" or other significant structural inhomogeneities are present in the mercury film cannot explain the behavior of the films when they are heated and leads to a contradiction when attempts are made to estimate the dimensions of such "drops" from the values of the parameter Δ and from the current-voltage characteristics. Films of both alkali metals and mercury, condensed under similar conditions, should have the same apparently fully amorphous structure. The reason for the difference between the properties must be sought in the difference between the valences of the mercury and of the elements of the first group. It is quite probable that the atoms of divalent mercury, which is a poor conductor, must form an essentially three-dimensional structure in order for the conductivity to set in, while a two-dimensional grid of the atoms of the monovalent alkali metals is sufficient for this purpose. It is also possible in principle that the start of the conductivity corresponds to a thickness phase transition from the amorphous phase (presumably nonconducting) to a conducting crystalline phase. Further experimental and theoretical investigations are needed to ascertain exactly what determines the anomalous value of the induction thickness in mercury films.

We are grateful to A. F. Andreev for a valuable discussion and to V. L. Tsymbalenko for help with the experiments.

[1)] Attempts were also made to observe the superconductivity of thin cold-deposited lithium films. Our procedures do not make it possible to prepare an installation in which to deposit many times lithium films with exact control of the thickness, and we have prepared a series of one-shot setups. The evaporator in these installations was a piece of "sandwich" made up of two layers of 20-micron tantalum foils and a layer of lithium 40 μm thick between them, mounted on a tungsten heating wire. We investigated both freshly deposited and crystallized films whose thicknesses we estimated at 20 to 3000 Å. Just as in the case of cesium and rubidium, the resistance of the thinnest films increased with decreasing temperature, and the resistance of the thicker films remained unchanged. No signs of superconductivity were observed down to 1.2 K.

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