Superconductivity of tribolayers formed on germanium by friction between germanium and lead

A. Dukhovskoĭ, S. S. Karapetyan, Yu. G. Morozov,
A. S. Onishchenko, V. I. Petinov, A. N. Ponomarev, A. A. Silin,
B. M. Stepanov, and V. L. Tal'roze

All-Union Research Institute for Optical–Physical Measurements
(Submitted 2 February 1978)
Pis'ma Zh. Eksp. Teor. Fiz. 27, No. 7, 409–412 (5 April 1978)

A superconducting state was observed for the first time in tribolayers of germanium produced by friction of germanium with lead at 42 K. The maximum value of T_c obtained in the experiment was 19 K, which is much higher than T_c of bulk lead itself or of lead films sputtered on germanium.

PACS numbers: 81.40.Pq, 81.40.Rs, 73.40.Jn, 74.70.Gj

When two solids rub against each other, tribolayers are produced on the rubbing surfaces; the structure of these layers can differ from the interior structure in the concentration of the defects or of the impurity ions, and even in the lattice symmetry. Obviously, the tribolayer state is in disequilibrium and can be stabilized by cooling the rubbing surfaces to sufficiently low temperatures.

We have noted previously[1] that when tribolayers are produced on the surfaces of rubbing materials in the superconducting state, the friction coefficient becomes quite low and remains such after subsequent heating of the samples to temperatures much higher than the transition temperature T_c. However, if the tribolayers are produced on the same metals at $T > T_c$, the friction coefficient remains quite high.

According to present-day concepts concerning the role that structure defects play in the increasing of T_c and H_c in thin films,[2] one can expect tribolayers of superconducting metals to have higher T_c and H_c than the initial metals. However, owing to the high conductivity of the substrate itself, it is difficult to measure the conductivity of tribolayers formed on a metal. It was therefore decided to investigate the electric conduction properties of tribolayers produced on the surface of a dielectric or a semiconductor at low temperatures by rubbing it against a superconducting metal.

It should be noted that, on the basis of general physical concepts concerning the transport mechanism, and when account is taken of the rather high activation energy of the mutual diffusion (not less than 1 eV[3]) of metals and semiconductors, the friction at very low temperatures might not have resulted in transport of one material to another. However, special investigations performed by us have shown that such a process does take place even at helium temperatures. Although the nature of this phenomenon has not yet been sufficiently well studied, the very fact of metal transport to a dielectric or a semiconductor indicates that energywise non: equilibrium or tunnel transport processes do take place in the region of the contact of the rubbing pairs.

To study the conductivity of the tribolayer we chose the pair "lead–germanium."

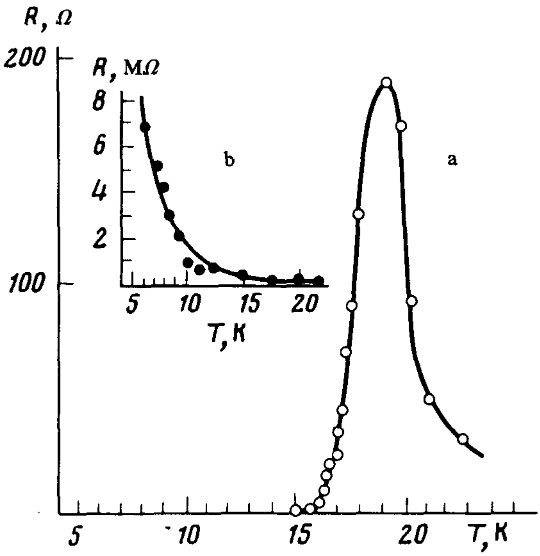

FIG. 1. Temperature dependence of the resistance of a Ge-Pb tribolayer formed at $T=4.2$ K (curve a) and of the initial germanium sample (curve b).

The friction was produced at a temperature $T=4.2$ K, which was subsequently raised. The resistance R of the tribolayer on the germanium surface was measured after the end of the coating, and the measurements were performed with a direct current of 1 μA in the direction along the friction track.

A typical plot of the resistance of the tribolayer against temperature is shown in Fig. 1. For comparison, the insert shows also a plot of $R(T)$ for the original germanium sample. As seen from the figure, which pertains to one of the experiments, when the temperature is lowered from 22 K the resistance of the tribolayer first increases noticably, reaches a maximum value at 19 K, and then drops abruptly to zero at $T_0=15$ K. Good reproducibility of the results of the measurements is observed in the course of heating and cooling the sample in the range 4.2–22 K. A similar experimental character of the $R(T)$ dependence was observed for all the investigated samples. On the other hand, the position of the maximum (T_{max}) in various experiments was somewhat different and ranged from 10.7 to 19 K. The temperature T_0 changed accordingly from 8.3 to 15 K.

The current-voltage charcteristics of the tribolayers corresponded to the superconducting state when plotted at temperatures below T_0 and to metallic conductivity at $T > 30$ K. The temperature dependence $R(T)$ of the tribolayers in the region 30–300 K was similar to the analogous dependence for strongly doped germanium.[4]

The annealing of the tribolayers at 300 K greatly decreased their conductivity and shifted the position of the maximum of the resistance towards lower temperatures. A similar but much weaker influence of the annealing appeared also when the samples were heated even to 30 K.

The most interesting of the results is the extremal character and the attained values of T_c. The cessation of the growth of the resistance of the tribolayer with decreasing temperature and its drop at $T < T_{max}$ are apparently due to the onset of superconducting formations in the layer. It should be noted that the passage through the maximum of the resistance in the superconducting state was observed earlier in granulated superconductors made up of small superconducting particles separated from one another by a dielectric barrier[5] and was attributed to the decrease of the single-particle layers following appearance of the gap and to the subsequent growth of the contribution of the two-particle currents with further decrease of temperature.

It is probable that the investigated tribolayers are also metallic island formations separated by superconducting layers. Such metallic formations can be islands of lead or of germanium sections strongly doped with lead. Taking into account the nonequilibrium state of the tribolayer, one can also assume that islands of metallic germanium phase, analogous to the high-pressure phase, are produced in this layer.[6] Such a model explains qualitatively the observed relations. At high temperatures, the conductivity of the tribolayers is determined by the conductivity of the semiconducting interlayers.

When the individual metallic islands go over into the superconducting state, Cooper pairs begin to permeate through these interlayers so that the total conductivity of the tribolayer begins to increase. With decreasing temperature, the total conductivity of the islands in the superconducting state increases until the resistance of the tribolayer becomes equal to zero. However, if barriers with low penetrability are present, then some residual resistance can remain in the tribolayer. In fact, in individual experiments, when the samples were cooled after the abrupt decrease of the resistance, a finite conductivity remained down to 4.2 K.

The experimentally observed smearing of the superconducting transition can be attributed also to the presence in the tribolayer of regions with different T_c. This is confirmed, in particular, by the aforementioned difference between T_{max} in different experiments in which the friction conditions differed somewhat. The smearing itself indicates that $T_c > T_{max}$ for some regions.

We have thus observed that in germanium tribolayers produced by friction with lead at 4.2 K a superconducting state is produced. The maximum value of T_c obtained in the experiments is larger than or at least equal to 19 K, which greatly exceeds the value of T_c of both bulky lead and of lead films sputtered on germanium.[7]

[1]E.A. Dukhovskoĭ, S.S. Karapetyan, Yu.G. Morozov, A.S. Onishchenko, V.I. Petinov, A.N. Ponomarev, A.A. Silin, B.M. Stepanov, and V.L. Tal'roze, Dokl. Akad. Nauk SSSR **235**, 331 (1977) [Sov. Phys. Doklady **22**, 407 (1977)].
[2]K.L. Chopra, Thin Film phenomena N.Y. McGraw Hill, 1969, Ch. 2.
[3]P.G. Shewmon, Diffusion in Solids, McGraw, 1963.
[4]K. Seeger, Semiconductor Physics, Springer, 1974.
[5]Yu. G. Morozov, I.G. Naumenko, and V.I. Petinov, Fiz. Nizk. Temp. **2**, 987 (1976) [Sov. J. Low Temp. Phys. **2**, 484 (1976)].
[6]Y. Witting, Zeitschrift fur Physik, **B195**, 5215 (1966).
[7]V.I. Zaporozhchenko and V.I. Rakhovskiĭ, Dokl. Akad. Nauk SSSR **217**, 544 (1974) [Sov. Phys. Dokl. **19**, 452 (1975)].