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Hyper-resistivity to global-superconductivity transition by annealing in quench-condensed Pb films

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The rapid rise in resistance occurring in barely conducting quench-condensed Pb films cooled through temperatures characteristic of the bulk superconducting transition is found to be strongly current dependent, the resistance increasing rapidly with decreasing current and temperature. Annealing the same film at temperatures below 40 K changes the behavior to that of a conventional superconductor with resistance that drops as the film current and temperature decrease. Experimental evidence suggests this results from a transition from quasiparticle-dominated to Josephson-dominated tunneling.

Several groups have recently reported measurements of the electrical sheet resistance $R_\square$ of films of superconducting metals deposited incrementally onto dielectric substrates cooled to reduce diffusion.[1-4] The thinnest conducting samples show behavior seemingly opposite to that of a superconductor. Below a temperature close to that of the bulk transition for the metal, T_C^B, the resistance rises rapidly with decreasing temperature. We call this "hyper-resistivity." As additional material is deposited on the film the behavior changes to that of a conventional superconductor with $R_\square(T)$ of the macroscopic sample dropping toward zero at a film critical temperature T_C^F. Following convention, this is referred to as "global superconductivity." An interesting feature is that the amount of additional material needed to cause this change corresponds typically to less than an atomic layer. We report strikingly similar behavior for films of Pb prepared in a one-shot evaporation and then incrementally annealed at cryogenic temperatures.

Lead was chosen because of the insensitivity of T_C^B to changes in lattice order. Vapor from a thermal source was condensed in ultrahigh vacuum onto liquid-helium-cooled crystalline quartz substrates. Films were 10.7 mm long and 3.3 or 1.8 mm wide. The mass of deposited Pb was measured with a quartz-crystal microbalance and converted to an equivalent "mass thickness" d_{mass}, assuming (unrealistically) a uniform parallelepiped geometry. In agreement with earlier work[5] we find that relatively large amounts of Pb must be deposited before appreciable electrical conduction occurs. For Pb deposited onto crystalline quartz at 11 K, a "critical (mass) thickness" $d_C = 90$ Å must be exceeded for $R_\square$ to drop below 20 MΩ.

Figure 1 shows $R_\square(T)$ measurements made using a four-probe technique. A 22-V mercury battery in series with a large resistor provided a current of about 2 μA. The arrow in a circle on the upper trace marks the deposition of the film. $R_\square = 145$ kΩ as the evaporation ended. The small break in the upper trace at $T_S = 11.3$ K indicates this as the highest temperature experienced during the deposition. Lowering T from this point resulted in reversible behavior on a time scale of hours (double headed arrows). The rapid increase in $R_\square(T)$ starting at about 6.9 K is presumably related to the onset of superconductivity.[6] Subsequent warming above 11.3 K caused irreversible annealing (single headed arrows). After warming from 11.3 to 13.2 K the sample was recooled to give the middle curve. The small dip just below 6.9 K is a characteristic feature of the present measurements.[7] In the next step the film was warmed from 13.2 to 20.5 K causing further irreversible annealing. Recooling gave the lowest trace showing a more or less usual superconducting transition. Further annealing (not shown) resulted in an increasingly abrupt approach to zero resistance.

Current I versus voltage V measurements were made for the film of Fig. 1 in all three states of anneal. Energy dissipated was limited to 10 μW. At $T > 6.9$ K all traces are approximately linear (Ohmic $R_\square$ independent of I). As T is lowered below 6.9 K, the traces become strongly nonlinear and are qualitatively different for a film showing hyper-resistive behavior versus the same film after annealing that leads to a conventional superconducting transition [compare Figs. 2(a) and 2(b) with 2(c)]. In the former case the I-V traces indicate increasing $R_\square$ with decreasing I. We are able to follow this increase to $R_\square(1.8\ \text{K}) > 200 \times 10^6\ \Omega$ at currents of 10^{-8} A.[8] A reasonable inference from the present measurements is that $R_\square$ for

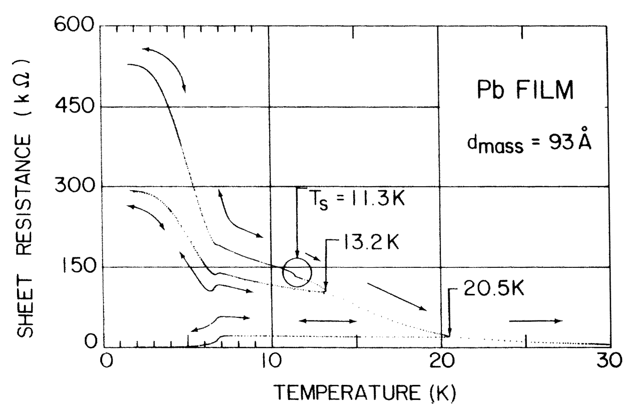

FIG. 1. Sheet resistance, $R_\square(T)$ for a Pb film deposited on a crystalline quartz substrate at $T_S = 11.3$ K. The film was subsequently annealed to 13.2 and 20.5 K. Double-headed arrows indicate reversible behavior.

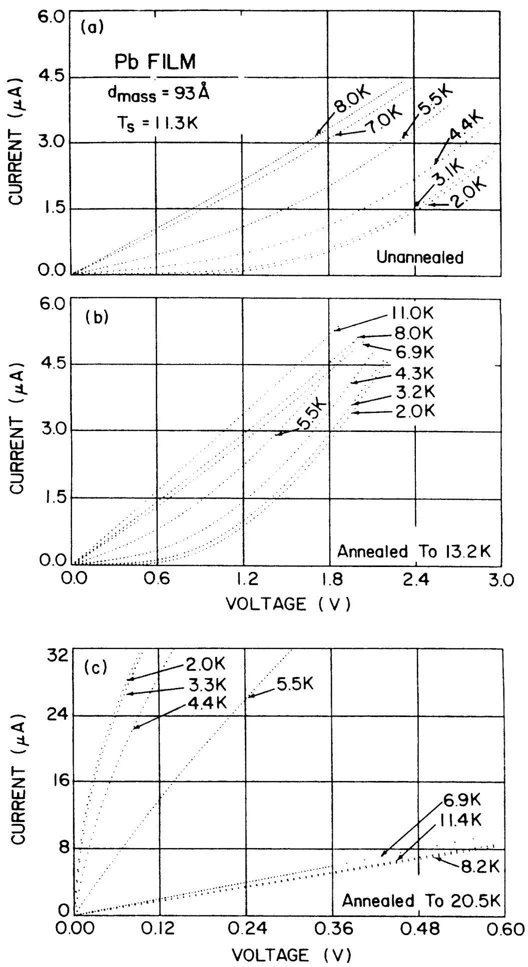

FIG. 2. I-V curves for the film in Fig. 1. (a) Results for the unannealed film; (b), (c) results for the film after warming to 13.2 and 20.5 K, respectively.

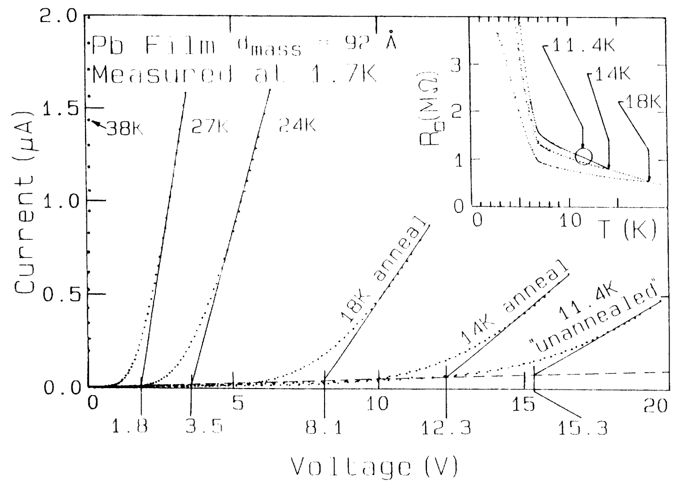

FIG. 3. I-V at 1.7 K for a Pb film with $d_{\text{mass}}=92$ Å in different states of anneal. The first three $R_\square(T)$ curves are shown in the inset. The end of the deposition is marked with a circle and arrow.

such films *increases* without limit as I and $T \Longrightarrow 0$. However, when the film is annealed sufficiently to show a conventional superconducting transition [Fig. 2(c) and the lowest curve in Fig. 1], $R_\square$ *decreases* with decreasing I as shown by the asymptotic approach to the ordinate of the lower T traces in Fig. 2(c).

The data presented so far were obtained from a single film. Figure 3 shows measurements for a sample with a slightly lower d_{mass} and a seven times higher $R_\square(10\text{ K})$. I-V curves are displayed for the film as deposited and after a series of anneals. $R_\square(T)$ for the initial stages is shown in the inset for $I \approx 2\ \mu$A. The measurements indicate rapidly rising resistance with decreasing I (or equivalently applied V) until a leakage resistance of 200 MΩ is reached, corresponding to the dashed line close to the abscissa. The I-V traces are reminiscent of superconducting quasiparticle tunneling, except that the rapid current increase occurs at large voltages. These voltages decrease with annealing as indicated by values across the bottom of the figure that result from a crude extrapolation of the rapidly rising part of the I-V curves. Qualitatively similar behavior was observed for the eight films for which suitable I-V measurements were made.

The usual model for the structure of high-resistance metal films is one of isolated islands. As far as we are aware, there are no direct observations for low-temperature quenched films grown in good vacuum. In the "normal state" above 6.9 K the unannealed or slightly annealed Pb films have very high $R_\square$, negative dR/dT values, and linear I-V characteristics. This behavior is also found for films in which electron microscope observation shows isolated metal particles imbedded in dielectric. It is expected behavior for thermally assisted tunneling.[9] The amount of material in the Pb films insures island heights well over 150 Å.

Accepting that electrical conduction in the unannealed and somewhat annealed films is controlled above 6.9 K by tunneling between normally conducting Pb islands, it is interesting to see how much of the behavior below 6.9 K can be understood in terms of the much studied properties of single superconducting tunnel junctions. Deposition of Pb in the present experiments was stopped as soon as appreciable conductivity was observed, presumably occurring along a quasi-one-dimensional percolation path or a few such paths with many tunnel junctions in series.[10] Figure 4 shows an imagined segment. The gap "j" is relatively narrow so that the normal-state tunnel resistance is small. Josephson tunneling of electron pairs would result in a zero-voltage drop so that the two superconducting islands would behave as one. The gap "g" is wider and, because of the exponential dependence, has a large normal-state resistance. Increased resistance will decrease the

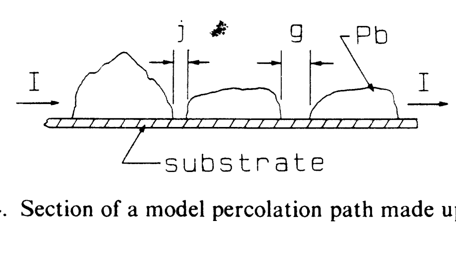

FIG. 4. Section of a model percolation path made up of Pb islands.

Josephson coupling energy relative to kT and tend to suppress Josephson tunneling,[11] in accord with experimental experience. In the absence of pair tunneling, quasiparticle tunneling becomes the controlling conduction mechanism. Very little current can flow until the applied voltage is increased to a value corresponding to the energy gap $2\Delta/e$, about 2.7 mV for Pb below 2 K. At this point there is a rapid turn-on followed by an approach to the value dictated by the normal-state tunnel resistance. On the order of 6000 such junctions in series[12] would support the 15.3 V indicated for the onset of rapidly increasing current[13] (decreasing resistance) in the unannealed film of Fig. 3. Such a chain of quasiparticle dominated tunnel junctions would show an increase of resistance with decreasing current qualitatively similar to that observed in the unannealed or slightly annealed films. Dividing the observed $R(7\text{ K})$ by 6000 gives a lower bound on the average normal-state junction resistance of 1500 Ω for the high-resistance junctions. The actual value is presumably higher because of parallel connections in the conduction path. The junction resistances, in any case, are large enough to effectively eliminate Josephson tunneling.[14] Assuming one conducting path going straight across the film, the average segment length between junctions controlled by quasiparticle tunneling would be 1.7 μm, an order of magnitude suggesting that we are dealing with tunneling between connected pieces of chain rather than between individual islands. As seen in Fig. 3, low-temperature annealing decreases the voltage at which the rapid increase in current sets in, corresponding in the proposed picture to a reduction in the number of high-resistance junctions that are dominated by quasiparticle tunneling.

The three-grain model of Fig. 4 offers an explanation for the dip in $R_\square(T)$ (middle trace of Fig. 1). As T falls the energy gap opens and $R_\square(T)$ drops as Josephson active junctions provide zero-resistance connections between some grains. As T is reduced further, quasiparticle junctions become increasingly effective in impeding current flow, and $R_\square$ rises. This suggests that reducing I should rise the temperature at which the minimum occurs, as is in fact observed.

Present experiments show that reductions in normal-state resistance larger than 3 orders of magnitude can be caused by annealing below 40 K. This implies movement of Pb atoms. In terms of the proposed model the change would be a decrease in the separation between islands which would increasingly favor Josephson over quasiparticle tunneling. Such a rearrangement at temperatures where appreciable diffusion is not expected could perhaps be surface tension driven. A narrowing of gaps between islands would certainly be expected in the incremental deposition experiments which show a similar change from hyper-resistivity to global superconductivity.[1-4]

It has been proposed on theoretical grounds that superconductivity with $R_\square \Rightarrow 0$ ("global superconductivity") should appear in films when the normal-state $R_\square$ falls below a value on the order of usually $h/4e^2 \cong 6.5\text{ k}\Omega$.[15] Experiments generally agree with this. A few report close agreement.[4] In the present investigation we have looked at three criteria for the transition from hyper-resistive to conventional superconducting behavior. Results are as follows:

(i) The change with $I \Rightarrow 0$, from increasing to decreasing $R_\square$ (measurements between 1.7 and 2 K; minimum current 0.02 μA) occurs for $R_\square(10\text{ K})$ between 20 and 30 kΩ. In these films $R_\square(T)$ approaches zero asymptotically if at all. (ii) $R_\square(T)$ extrapolates to zero for $T > 1.8$ K (measurement zero equals 0.05 Ω) when $R_\square(10\text{ K})$ is reduced by annealing to the 3–7-kΩ range. (iii) $\partial R/\partial T$ in the normal state becomes positive (metal-like) when $R_\square(10\text{ K})$ is reduced to the vicinity of 2.5 kΩ.

The relatively low normal-state resistance values suggest that a multiply connected two-dimensional array of tunnel junctions is a more appropriate model for the regime where the transition to global superconductivity occurs than the quasi-one-dimensional path considered in discussing hyper-resistivity at the onset of electrical conduction. It is certainly striking that all three of the above criteria give values on the order of magnitude of $h/4e^2$. This is perhaps the best agreement with a "universal criterion" that could be hoped for in light of the loose connection expected between the macroscopic sheet resistance $R_\square$ and the properties of an individual tunnel junction.

In summary, we report changes from hyper-resistive to global superconducting behavior brought on in barely conducting quench-condensed Pb films by annealing at temperatures below 40 K. We show in the former condition that decreasing the current greatly increases the indicated resistance. We argue that this and other evidence supports the position that the radical change in behavior results from a transition from quasiparticle-dominated to Josephson-dominated tunneling. In broad outline and in many details, the experimental results obtained here from single Pb films annealed in steps to higher and higher (but still low) temperatures agree with earlier reported work in which material is added to a film by sequential deposition. Comparison of the results, in addition to information about superconductivity, provides clues to the structure and the mechanism of low-temperature annealing in barely conducting metal layers.

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[6]For Pb films the T_C^F is approximately $T_C^B(1-A/d_{\text{geo}})$ where $T_C^B=7.23$ K, d_{geo} is the geometric thickness, and A is a constant on the order of a lattice spacing.

[7]A similar dip has been reported for incremental deposition experiments using clean insulating substrates. It seems to be absent when the substrates are preevaporated with a few monolayers of Ge, a procedure that considerably reduces the amount of metal that must be deposited to give appreciable electrical conductance (Ref. 4).

[8]The measured resistance (V/I) at 1.8 K increases more and more rapidly with decreasing current until a current independent value on the order of 10^8 Ω is reached. Unlike other measured quantities this background resistance does not change with annealing of the film. We believe it is the leakage resistance of the measuring circuit.

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[13]The turn-on of current with increasing voltage shown in Fig. 3 is certainly not discontinuous, as expected for tunneling between identical superconductors. A reasonable explanation is that the film contains a distribution of island sizes. This would cause a distribution of T_C's and energy gaps that could explain a more gradual turn-on of current.

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