Method for making low-resistivity contacts to high T_c superconductors

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(Received 29 October 1987; accepted for publication 30 November 1987)

A method for making low-resistivity contacts to high T_c superconductors has been developed, which has achieved contact surface resistivities less than $10\,\mu\Omega\,cm^2$ at 76 K and does not require sample heating above $\sim 150\,°C$. This is an upper limit for the contact resistivity obtained at high current densities up to 10^2–$10^3\,A/cm^2$ across the contact interface. At lower measuring current densities the contact resistivities were lower and the voltage-current curve was nonlinear, having a superconducting transition character. On cooling from 295 to 76 K, the contact resistivity decreased several times, in contrast to indium solder contacts where the resistivity increased on cooling. The contacts showed consistently low resistivity and little degradation when exposed to dry air over a four-month period and when repeatedly cycled between room temperature and 76 K. The contacts are formed by sputter depositing a layer of a noble metal—silver and gold were used—on a clean superconductor surface to protect the surface and serve as a contact pad. External connections to the contact pads have been made using both solder and wire-bonding techniques.

A largely unpublicized, though important, obstacle in the testing and application of high T_c superconductors is the high contact resistance that usually occurs where external leads are attached to the superconductor. Presently, contacts made with indium solder, silver paint or epoxy, direct wire bonds, and pressure contacts have contact surface resistivities typically in the range 10^{-2}–$10\,\Omega\,cm^2$, several orders of magnitude too high for many practical applications and critical current measurements. Superconducting magnet and circuit board applications require contact resistivities on the order of 10^{-4}–$10^{-5}\,\Omega\,cm^2$ or lower. Contact heating presently limits the measurement of critical current in bulk samples at low temperatures and low fields.[1] In thin-film superconductors, where critical current densities are much higher than in bulk samples,[2-4] it has been necessary to use pulsed-current methods[2] and sample necking techniques to make the measurements.[3]

In this letter, we report a method for making improved electrical contacts to high T_c superconductors, which reduces the contact surface resistivity three to four orders of magnitude below that obtained with conventional contacts. The contact method has achieved surface resistances of less than $10^{-5}\,\Omega\,cm^2$ at 76 K, at current densities exceeding 10^2–$10^3\,A/cm^2$ across the contact interface. The contact process is carried out at temperatures below $\sim 150\,°C$ and therefore affords good control and avoids possible degradation of the underlying superconductor from excessive diffusion of the contact material into the superconductor at high temperatures. Also, the low-temperature contact method allows post-reaction shaping and processing steps to be carried out on the superconductor before contacts are made.

Shortly after the discovery of superconductivity in the Y-Ba-Cu-O system,[5] we tried several different methods, including silver paint and indium solder, to make high current capacity contacts to this material in order to measure critical current characteristics. Silver paint contacts were found to burn out at relatively low currents (~ 0.1 A) and had poor mechanical properties. Indium solder contacts had relatively high resistivities covering a wide range; several examples of indium contacts are shown in Table I. (This table contains only a representative sampling of the more than 50 contacts tested in the course of this study.) Values of the contact resistivities (last column in Table I) are expressed here in terms of a surface resistivity $\rho_\square \equiv RA$, where R is the contact resistance and A is the contact area. These indium contacts were semiconducting in character; $\rho_\square$ increased about 3 to 7 times as the temperature was lowered from 295 to 76 K (see the second to the last column in Table I, samples 1–5). The contacts were also non-ohmic, with $\rho_\square$ decreasing as current was increased ($\rho_\square$ values are given in the low current limit).

A systematic investigation of these early indium contact samples indicated that rapid deterioration of the superconductor surface from air exposure and at the superconductor-indium interface was playing a significant role in degrading the contact resistivity. $\rho_\square$ was high (last column in Table I) and the voltage-current characteristic was non-ohmic (samples 1–4). Mechanical abrasion of the superconductor surface under the molten solder resulted in a decrease in $\rho_\square$ and more nearly ohmic behavior (sample 4). Polishing the superconductor surface in air only 5–10 s before applying the indium solder was not nearly as effective (e.g., samples 2 and 3). The best indium contacts were made by mechanically abrading the surface under the molten solder with either the tip of the soldering iron or with an ultrasonic soldering iron and using eutectic In-2% Ag solder (without soldering flux). The resistivity of the contact typically increased more than 50% several days after making the contact. These early contact results showed that, chemically, indium is not a good candidate material for making contacts where low contact resistivity is required.

In an attempt to make stable contacts with lower resistivities, a method was adopted consisting of (1) minimizing (and preferably eliminating) exposure of the superconductor surface to air before making the contacts, (2) sputter

 0003-6951/88/040331-03$01.00

TABLE I. Contact characteristics.

Sample	Contact pad material	Method	External lead connection method	Contact area A (mm^2)	Approx. air exposure time	$R(76\ K)$ ($m\Omega$)	Resistance ratio $R(76\ K)/R(295\ K)$	Contact resistivity $\rho_\square$, $R(76\ K) \times A$ ($\mu\Omega\ cm^2$)
1	In-2% Ag solder		In-2% Ag solder	1.7	38 d	3200	7.4	55 000
2	In-2% Ag solder	polished before soldering	In-2% Ag solder	11	14 d	220	2.9	26 000
3	In-2% Ag solder	polished before soldering	In-2% Ag solder	3.7	9 d	420	2.9	15 000
4	In-2% Ag solder	ultrasonically soldered	In solder	2.5	3 d	140	3.8	3 600
5	0.2 μm Cr/2μm Au	sputter etched & deposited	In-2% Ag solder	6.1	2 d	110	2.4	6 900
6	Cu	sputter deposited	In-2% Ag solder	30	1 d	19	···	5 700
7	5.9 μm Au	sputter etched & deposited	In-2% Ag solder	31	0.8 h	0.60	0.43	180
8	5.9 μm Au	sputter etched & deposited	Au ribbon bond	0.21	0.8 h	14	0.36	29
9	1.4 μm Ag	sputter etched & deposited	In-2% Ag solder	14	2 h	0.44	0.08	62
10	2.5 μm Ag	sputter etched & deposited	Au ribbon bond	0.07	0.8 h	19	0.22	13
11	2.5 μm Ag	sputter etched & deposited	Au ribbon bond	0.17	0.8 h	7.9	0.26	13
12	2.5 μm Ag	sputter etched & deposited	Au ribbon bond	0.06	0.8 h	15	0.32	9

etching the superconductor surface in order to remove the degraded surface layer immediately before deposition of contact pads, and (3) making the contact pads from inert (noble) metals. Silver and gold were used in these tests. Both are relatively inert chemically with strongly positive standard reduction potentials.[6] Silver has the added advantage that its oxides dissociate at a fairly low temperature, and its oxygen diffusion coefficient is fairly high, which allows oxygen permeability at moderate temperatures.[7,8]

All contacts tested using this new method were deposited on bulk-sintered samples of $Y_1Ba_2Cu_3O_{7-\delta}$ prepared in the same way as samples 1, 3, 4, and 5 above.[9] The average grain size of the samples was about 10 μm, the samples were about 75% dense, and the resistivity just above T_c ranged from about 350 to 600 $\mu\Omega$ cm. The critical current density J_c for these samples at zero applied magnetic field was measured to be about 200 A/cm^2.[10] The superconductor samples were removed from the oven after cooling in oxygen, cut into bars 0.6×3.2×12 mm and placed in a rf sputter vacuum chamber. Total exposure time of the $Y_1Ba_2Cu_3O_{7-\delta}$ material to air was 1–2 h. The sputter system was pumped down overnight to a base pressure of about 70 μPa. The superconductor surface was rf sputter etched to a depth of 200–500 Å in a 3-Pa pressure of argon at 1.25 kV rms. A 1–6 μm thick contact pad was then immediately sputtered onto the $Y_1Ba_2Cu_3O_{7-\delta}$ surface over a 15–30 min period, also in an argon atmosphere with 4.2 kV rms on the sputter target and no bias applied to the substrate. The $Y_1Ba_2Cu_3O_{7-\delta}$ sample was held at temperatures less than 100 °C by a water-cooled sample holder.

Figure 1 shows the four-terminal measurement technique that was adopted for these new contacts. Two wires were attached to the current pad, one to carry current, the other to detect voltage at the surface of the pad. The other voltage tap was soldered directly to the superconductor close to the contact pad using the indium-solder method described above. (This was acceptable because low contact $\rho_\square$ was not needed for the voltage detection leads.) The room-temperature value of the $\rho_\square$ was corrected for the short length of normal $Y_1Ba_2Cu_3O_{7-\delta}$ material between the contact pad and the voltage tap on the superconductor by measuring the resistivity per unit length of superconductor using another voltage tap attached to the superconductor. (At 76 K, where the $Y_1Ba_2Cu_3O_{7-\delta}$ was superconducting, no correction was needed.) Accuracy of the $\rho_\square$ measurement was about ± 10%.

Two different methods of attaching external leads to the sputtered contact pads were used, the first by soldering copper wires to the pads, and the second by thermosonically bonding fine gold leads. For the soldered connections, the contact pad was first coated with eutectic In-2% Ag solder, using minimal heating above the melting temperature (150°C), and then copper wires (which had been pretinned with indium solder using a zinc-chloride flux) were soldered to the contact pad. Areas of the contact pads for the solder connections ranged from about 10 to 35 mm^2.

For the contact samples with thermosonically bonded leads, fine gold ribbon (~8 μm × ~80 μm) was used. The temperature of the sputtered contact pad was elevated to about 100 °C. Higher temperatures of 150–200 °C would be desirable. Relatively small contact pads were used for the thermosonically bonded leads, about 0.05–0.3 mm^2 in area. Small area pads were needed to ensure that the thin contact pad was a nearly equipotential surface across its face and did not appreciably affect the resistivity determination of the contact. Measuring currents for the wire-bonded contacts ranged up to about 0.7 A, corresponding to current densities up to 10^3 A/cm^2 across the contact interface.

Table I shows results for some of the contacts made using the new method (samples 7–12). This is only a partial list and represents a sampling of each type of contact. Of 16 samples tested using this method, all showed consistently low contact resistivities. The lowest values of $\rho_\square$ were obtained with Ag contact pads and wire-bonded leads. The contact resistivities for these contacts (e.g., samples 10–12) were consistently and reproducibly on the order of 10 $\mu\Omega$ cm^2 or less, about three to four orders of magnitude low-

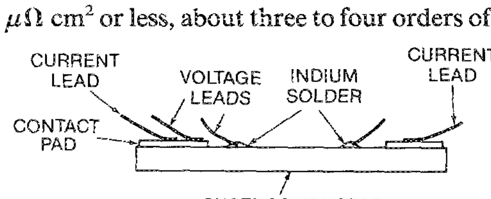

FIG. 1. Diagram of four-terminal method for measuring contact resistivity.

er than conventional contacts made from indium, silver paint, or pressure contacts. These values are an upper limit on $\rho_\square$ obtained at current densities up to 10^2–10^3 A/cm^2, which locally exceeds the J_c of the superconductor at the contact interface. At lower current densities, $\rho_\square$ was lower and the voltage-current characteristics were nonlinear, having a superconducting transition character.

When gold was used for the contact pad (samples 7 and 8), the values of $\rho_\square$ were somewhat higher than for silver. This may have resulted from better bonding of the silver with the $Y_1Ba_2Cu_3O_{7-\delta}$ surface. Contacts with soldered wire leads (samples 7 and 9, for example) had values of $\rho_\square$ that were several times larger than the contacts with wire-bonded leads, but still several orders of magnitude lower than the earlier contacts. Partial alloying of the solder with the noble metal pad may have degraded the contact interface.

The dependence of the current on temperature was much different from that of the earlier contacts. Whereas samples 1–6 were semiconducting in character, with $\rho_\square$ increasing as temperature was lowered, the new contacts were metallic in character, with $\rho_\square$ decreasing 3 to 12 times on cooling from 295 to 76 K (see samples 7–12 in Table I).

When silver contact pads were sputter deposited on old $Y_1Ba_2Cu_3O_{7-\delta}$ samples exposed to air for about nine weeks, $\rho_\square$ values were slightly higher (2 to 7 times) than for samples with less than 1 h air exposure. This was the case both for old samples not given any etch at all, or old samples with a 500-Å-deep etch. A very deep etch (2700 Å) produced values of $\rho_\square$ (8 $\mu\Omega$ cm^2) comparable to those of freshly prepared samples. Thus, low $\rho_\square$ contacts can be made even with samples exposed to air for a long time, and nearly as low $\rho_\square$ can be obtained without giving the samples any prior etch.

Modifications of the general method described here may also result in low contact resistivites. Glow-discharge cleaning and evaporative deposition of noble metals may yield low-resistivity contacts, although sputter deposition generally results in superior adhesion. Alternatively, instead of removing the degraded surface layer, it should be possible to keep it from forming in the first place. One example is to keep the superconductor in an oxygen atmosphere after firing. Another is to make the contact at the same time the superconductor is reacted. This involves forming the contact at high temperatures, however. After completion of this work, we learned of several examples of high-temperature contact methods, one involving a silver-filled epoxy applied to the sample before firing,[11] and others using leads embedded in, or wrapped around, pressed powder samples before firing. These processes use temperatures of 900 °C or more for contact formation and thus have several limitations. Post-reaction shaping and multistage processing steps, that might better take place before contacts are applied, are precluded. Degradation of the superconductor and lack of control may also result from excessive diffusion of the contact material or its carrier into the superconductor at such high temperatures.

In summary, stable contact resistivities less than 10 $\mu\Omega$ cm^2 at 76 K have been obtained by using a low-temperature (< 150 °C) technique. This is an upper limit for the contact resistivity at high current densities up to levels exceeding the J_c of the superconductor at the contact interface. At lower current densities, the contact resistivity was reduced and the voltage-current curve was nonlinear, having a superconducting transition character. The method has been shown to be effective even with samples exposed to dry air for several months. The contact resistivity decreased several times on cooling from 295 to 76 K. (This is in contrast to indium contacts which were semiconducting in character, with increasing resistivity on cooling.) We believe the low oxygen affinity of the noble metals plays an important role in passivating the contact interface. Microscopy studies are in progress to characterize the contact interface.

The method has been applied to bulk sintered samples of $Y_1Ba_2Cu_3O_{7-\delta}$, but there is no inherent limitation of the technique that would preclude its application to thin films, single crystals, and other high T_c superconductor of the general $Y_1Ba_2Cu_3O_{7-\delta}$ class. Further reduction in contact resistivity may result from complete elimination of air exposure, intermediate-temperature annealing in oxygen, use of other contact materials, and optimization of the sputter etch and deposition parameters.

We thank T. Larson, N. Bergren, and S. Bray for assistance with the acquisition and reduction of these data, and A. I. Braginski for help establishing this collaborative effort. Appreciation is also expressed to R. Radebaugh, G. Harman, R. Goldfarb, J. Moreland, R. Ono, J. Evetts, J. Callanan, L. Goodrich, and A. F. Clark for several helpful discussions and a critical reading of the manuscript. This work was supported at NBS in part by the U.S. Department of Energy and by a grant from the National Engineering Laboratory and the Director's Office of NBS. Work at Westinghouse was supported in part by Air Force Office of Scientific Research contract No. F49620-85-C-0043.

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