High T_c superconductor/noble-metal contacts with surface resistivities in the 10^{-10} Ω cm² range

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(Received 1 February 1988; accepted for publication 29 March 1988)

Contact surface resistivities (product of contact resistance and area) in the 10^{-10} Ω cm² range have been obtained for both silver and gold contacts to high T_c superconductors. This is a reduction by about eight orders of magnitude from the contact resistivity of indium solder connections. The contact resistivity is low enough to be considered for both on-chip and package interconnect applications. The contacts were formed by sputter depositing either silver or gold at low temperatures (< 100 °C) on a clean surface of $Y_1Ba_2Cu_3O_{7-\delta}$ (YBCO) and later annealing the contacts in oxygen. Annealing temperature characteristics show that for bulk-sintered YBCO samples there is a sharp decrease in contact resistivity after annealing silver/YBCO contacts in oxygen for 1 h at temperatures above ~500 °C and gold/YBCO contacts for 1 h above ~600 °C. Oxygen annealing for longer times (8 h) did not reduce the contact resistivity of silver contacts as much as annealing for 1 h. Auger microprobe analysis shows that indium/YBCO contacts contain a significant concentration of oxygen in the indium layer adjacent to the YBCO interface. Silver and gold contacts, on the other hand, contain almost no oxygen and have favorable interfacial chemistry with low oxygen affinity. Silver also acts as a "switchable" passivation buffer, allowing oxygen to penetrate to the YBCO interface at elevated temperatures, but protecting the YBCO surface at room temperature.

This letter reports a reduction of high T_c contact surface resistivities $\rho_\square$ to the 10^{-10} Ω cm² range ($\rho_\square = RA$, where R is the contact resistance and A is the contact area). The reduction was obtained in both gold and silver contacts, and represents a decrease in contact resistivity by over eight orders of magnitude from that obtained using indium solder connections. This is the first report of contact resistivites low enough to be considered for both on-chip and package interconnect applications.

The technique involves an optimized oxygen anneal of noble-metal contacts made using a method described earlier by Ekin, Panson, and Blankenship,[1,2] wherein silver or gold contact pads are sputter deposited on a clean surface of a high T_c oxide superconductor at low temperatures (< 100 °C). As deposited, the contacts have values of $\rho_\square$ in the 10^{-6}–10^{-5} Ω cm² range. When intermediate (500 °C) temperatures can be tolerated, we found that by annealing sputtered silver/$Y_1Ba_2Cu_3O_{7-\delta}$ (YBCO) contacts in oxygen at 500 °C for 1 h, $\rho_\square$ was reduced to the 10^{-8} Ω cm² range.[3] Similar results were also observed for silver/YBCO contacts by Tzeng *et al.*,[4] who used evaporative deposition and annealed at 500 °C for 5 h.

Here we report a reduction of $\rho_\square$ to the 10^{-10} Ω cm² range for gold as well as silver contacts. The reduction is obtained by optimizing the oxygen annealing process and by utilizing more sensitive measurement techniques. Different oxygen annealing conditions were found necessary for low-resistivity gold/YBCO and silver/YBCO contacts.

Auger microprobe depth profiles of the contacts are also presented which elucidate the role of these noble metals in achieving this extremely low contact resistivity. The explanation for the reduction in contact resistance has been the subject of speculation. Our earlier hypothesis[2] that the low oxygen affinity of the noble-metal contact pads is important for achieving low contact resistivity with oxide superconductors appears to be confirmed. The Auger results show negligible oxygen in the noble-metal pads and favorable interfacial chemistry. For indium contacts, on the other hand, significant oxygen is present in the indium adjacent to the YBCO interface, probably a semiconducting indium oxide layer.

The same starting material of bulk-sintered YBCO was used for all contacts.[5,6] Bulk-sintered samples of YBCO were used for convenience, but there is no inherent limitation of the contact method that would prevent its application to thin films, single crystals, or other high T_c oxide superconductors. The surface of the superconductor was sputter etched and silver or gold contact pads, 2–6 μm thick, were sputter deposited on the superconductor in argon at a rate of about 1 nm/s. Small contact areas (0.05–0.2 mm²) were scribed (to ensure an equipotential surface) and external leads were attached to the noble-metal pads using a thermosonic wire bond technique. Fabrication details, the technique for attaching external leads to the contact pads, and the four-terminal measurement method are described in Ref. 2. All measurements were carried out in liquid nitrogen at 76 K.

Figure 1 shows the *semiconducting* character of the voltage-current (V-I) curves for indium solder contacts (negative d^2V/dI^2) in contrast to the *superconducting* character (positive d^2V/dI^2) for the noble-metal contacts, as original-

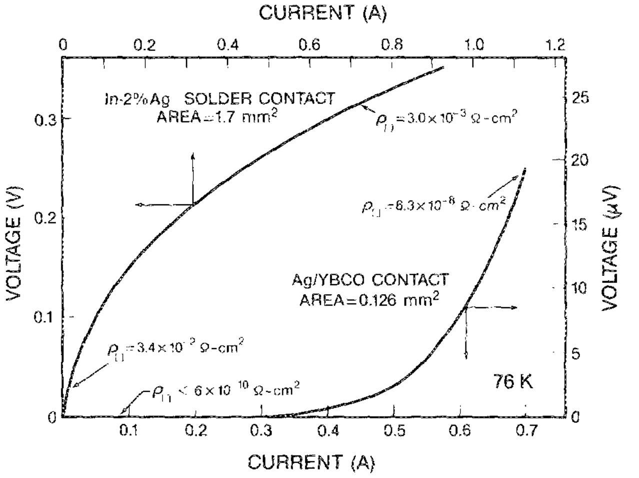

FIG. 1. Voltage-current (V-I) characteristics at 76 K for indium solder contacts contrasted with V-I characteristics of noble-metal contacts. The indium contacts are semiconducting in character, whereas the noble-metal contacts are superconducting in character with a J_c after annealing that is about equal to the J_c of the underlying superconductor material.

ly reported in Ref. 2. Values of $\rho_\square$ for the noble-metal contacts reported below correspond to the low current limit.

Figure 2 shows the effects of progressively annealing silver and gold contacts (with the underlying superconductor material) in oxygen. The anneal was carried out in flowing oxygen at atmospheric pressure for 1 h at each temperature. Annealing at times longer than 1 h did not improve $\rho_\square$. In fact $\rho_\square$ for Ag/YBCO was about twice as high after annealing 8 h compared with annealing only 1 h at a given temperature. The silver pads were about 3 μm thick (similar to sample 7 of Ref. 3); the gold pads were about 6 μm thick (similar to sample 8 of Ref. 2). Significant reduction in $\rho_\square$ of the gold contacts occurred about 100 °C higher than for silver contacts. At high enough annealing temperatures, the $\rho_\square$ of both silver and gold contacts reached the 10^{-10} Ω cm^2 range (or lower, since only an upper limit could be determined). We believe these to be the lowest values of contact resistivity reported for high T_c superconductors.

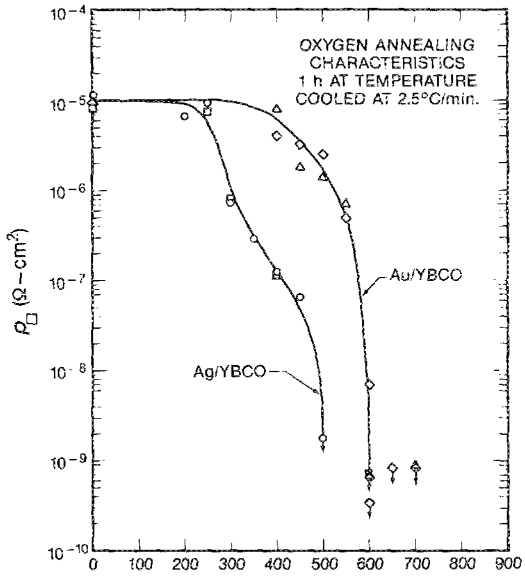

FIG. 2. Oxygen annealing characteristics for silver and gold contacts to bulk-sintered YBCO. Contact resistivities in the 10^{-10} Ω cm^2 range were obtained at 76 K for both silver and gold contacts when oxygen annealed for 1 h at temperatures above 500 °C for Ag and above 600 °C for Au. (○) and (□) Ag/YBCO samples; (△) and (◇) Au/YBCO samples. Arrows on the symbols indicate upper limits of the contact resistivity determined by the detection limit of our measurement system.

The 10^{-10} Ω cm^2 range is an upper bound on $\rho_\square$, limited by the voltage detection sensitivity of our equipment and the critical current density (J_c) of the superconductor. This value of $\rho_\square$ is not limited by the normal resistivity of the noble-metal contact pad. Taking the bulk normal resistivities of silver and gold at liquid-nitrogen temperature to be on the order of 2 or 3×10^{-7} Ω cm, and the thickness of the contact pads to be in the range of 2 to 6 μm, we find that the contribution of the noble metal to the contact surface resistivity is about 0.5 to 2×10^{-12} Ω cm^2. Thus, lower limits on $\rho_\square$ could be in the 10^{-12} Ω cm^2 range.

Silver contact pads were also sputter deposited on five-month old YBCO samples that had not been given any prior sputter etch. $\rho_\square$ was only several times higher than for sputter-etched samples. Silver is very mobile and apparently diffuses through the barium carbonate and hydroxides that form at the surface of YBCO after exposure to air.[7]

Auger electron spectroscopy (AES) depth profiling was performed using a scanning Auger microprobe (SAM) operating with an e-beam diameter of 0.2 μm. Sputter depth profiling was performed with a 3 kV Ar$^+$ ion beam and a system pressure of 13 μPa (1.0×10^{-7} Torr). Data were acquired in $N(E)$ mode (number of counts per energy interval) with a resolution of 0.6%.

The AES depth profile of an In contact on YBCO reveals a significant concentration of oxygen throughout the In layer, as well as In diffusion into the bulk YBCO, as seen in Fig. 3. Thermodynamically, the most favorable reaction for oxygen in indium forms In_2O_3, which is a semiconducting oxide with a band gap of 3.5 eV and a resistivity at liquid-nitrogen temperature that is much higher than for pure indium, silver, or gold.[8] These factors explain the poor contact $\rho_\square$ observed for In/YBCO as well as the semiconducting behavior of the V-I characteristic and the increase in $\rho_\square$ as the sample was cooled, described in Ref. 2.

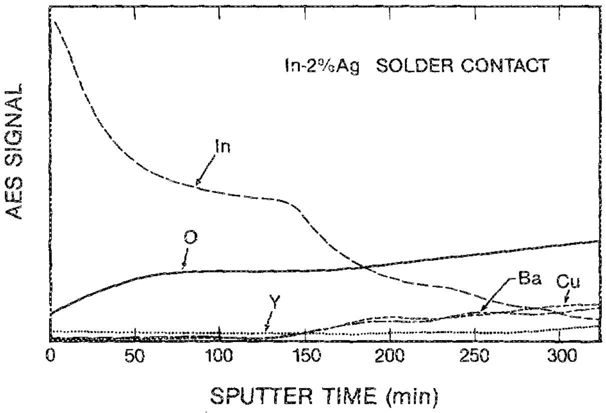

FIG. 3. Auger electron spectroscopy (AES) depth profile (Auger electron intensity, in arbitrary units, as a function of ion sputter time) for In-2% Ag solder contact to YBCO. There is a significant concentration of oxygen throughout the indium solder layer and indium diffusion into the YBCO.

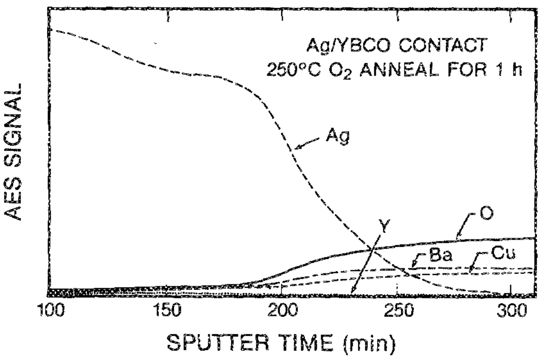

FIG. 4. AES depth profile for Ag/YBCO contact given only a low-temperature (250 °C) oxygen anneal. There is negligible oxygen in the silver contact pad compared with the indium contact shown in Fig. 3.

AES depth profile results for the Ag/YBCO sample that was given only a low-temperature (250 °C) oxygen anneal are shown in Fig. 4. The depth profile was carried out at a sputter etch rate of about 20 nm/min through the Ag layer. There was negligible oxygen in the Ag layer, with some interdiffusion between the Ag and YBCO. There appears to be an oxygen deficiency in the YBCO at the contact interface, as evidenced by the increasing oxygen signal into the bulk YBCO material in Fig. 4. The AES profile of the fully annealed (600 °C for 1 h) Ag contact on YBCO reveals significant differences (Fig. 5). First, considerable interdiffusion of Ag has occurred, as evidenced by the larger Ag signal in the bulk YBCO. Second, the YBCO material at the Ag/YBCO interface has a significantly higher oxygen signal relative to the Y-Ba-Cu content. Similar AES results were obtained for the gold/YBCO contacts (i.e., diffusion of Au into YBCO, no oxygen in the Au layer, and higher oxygen at the YBCO interface after oxygen annealing at 600 °C for 1 h).

The AES depth profile of a thin (2.5 μm) Ag contact, after external leads had been indium soldered to it several times, revealed no buffer of Ag remaining at the YBCO interface. Instead indium contacted the YBCO interface similar to the depth profile in Fig. 3.

We thus are able to draw the following conclusions.

(1) Oxygen annealing of silver/YBCO contacts at temperatures above ~500 °C for 1 h is effective in reducing the contact resistivity more than four orders of magnitude to the $10^{-10}\ \Omega\ \mathrm{cm}^2$ range. For gold/YBCO contacts, temperatures above about ~600 °C for 1 h are required for similar resistivity reduction.

(2) The Auger microprobe results indicate that the oxygen affinity of the contact material plays an important role. Indium has considerable oxygen throughout the indium contact layer and apparently forms a semiconducting layer at the contact interface. In contrast, there is negligible oxygen in the noble-metal contact pads.

(3) When indium solder is repeatedly used to attach external leads to thin silver pads, or when a high-temperature soldering iron is used, the indium can alloy through the Ag layer and degrade the YBCO surface. Depositing thicker noble-metal pads or, preferably, using a solder with a lower melting temperature appropriate for thin silver or gold films should help avoid such degradation.

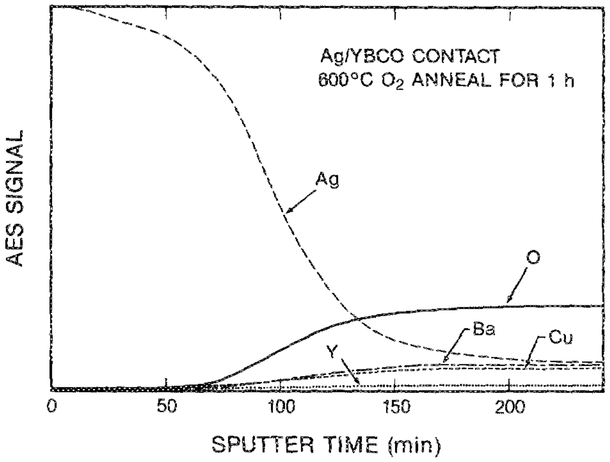

FIG. 5. AES depth profile for Ag/YBCO contact fully annealed at 600 °C for 1 h. There is still negligible oxygen in the silver layer, but significantly higher oxygen at the YBCO interface compared with Fig. 4. Significantly more interdiffusion of Ag into the YBCO surface has also occurred after high-temperature annealing.

(4) Silver contact pads act as a switchable passivation layer. Raising the temperature of the contact allows enough oxygen to diffuse through the thin silver pad in a matter of minutes to replenish the oxygen in the YBCO at the contact interface.[9] At room temperature, on the other hand, the diffusion rate of oxygen and air through the silver pad is reduced to a negligible level, protecting the YBCO under the contact pad.

(5) The AES profiles show that significant diffusion of silver into the surface of the YBCO occurs, even before annealing. We believe this interfacial chemistry for silver explains why relatively low contact resistivity can be obtained even when the superconductor is not given a sputter etch prior to contact deposition.[2]

We wish to thank D. L. Rule for help with data reduction; L. F. Goodrich and S. Bray for developing the low-noise current supply used in making these measurements; and R. H. Ono, J. J. Pellegrino, J. D. Verhoeven, C. A. Handwerker, J. M. Moreland, R. B. Goldfarb, and F. R. Fickett for helpful discussions and a critical reading of the manuscript.

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