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Non-volatile resistive switching in the dielectric superconductor $YBa_2Cu_3O_{7-\delta}$

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Abstract
We report on the reversible, non-volatile and polarity-dependent resistive switching between superconductor and insulator states at the interfaces of an Au/$YBa_2Cu_3O_{7-\delta}$ (YBCO)/Au system. We show that, upon application of electric pulses, the superconducting state of YBCO in regions near the electrodes can be reversibly removed and *restored*. In addition, four-wire measurements reveal that pulsing also induces significant non-volatile changes in the bulk resistance. We argue that our observations are compatible with a scenario where the switching effect is due to migration of oxygen ions along grain boundaries that control the inter-grain superconducting coupling.

(Some figures in this article are in colour only in the electronic version)

The improvement of the performance of silicon-based electronic memories is expected to begin reaching its limits within a decade or two. This is motivating a great deal of activity in the search for new materials that may enable alternative technologies. Among the most promising candidates one finds the resistive switching (RS) effect in capacitor-like metal/transition-metal oxide/metal structures [1]. It basically consists of the sudden change of the conductance of the system upon a strong electric voltage excitation applied on the electrodes. The key features are that the induced changes are non-volatile and *reversible*. The RS effect has already been reported in systems with a large variety of transition-metal oxides as the dielectric [2–11]. With the ultimate goal of achieving electronic device implementations, most of the work has focused on the behavior of thin films at room temperature. However, it has also been observed in bulk ceramic dielectrics [12, 13]. Many studies report on evidence which indicates that the effect occurs in regions of the dielectric near the electrode interfaces [7, 14]: nevertheless, there is still not a consensus on the physical origin of the switching mechanism [1].

In this paper we demonstrate the RS effect in a system where the dielectric is the cuprate perovskite $YBa_2Cu_3O_{7-\delta}$ (YBCO) which is a high critical temperature superconductor. We use a ceramic YBCO, with a distribution of grain sizes in the 5–20 μm range, which shows metallic resistivity and a superconducting transition at $T_c \simeq 90$ K. This is in contrast to all previous reports that used insulating or semiconducting dielectrics. Since our main focus is to unveil the physical mechanism of the switching, we consider a bulk dielectric where, by means of a multi-electrode configuration, one can study the switching of the interfaces and bulk behavior independently. After electric pulsing of a given polarity, we find that one interface becomes less resistive showing signatures of a superconducting transition at T_c. The other, in contrast, becomes more resistive and semiconductive without showing any anomaly at T_c. Interestingly, upon electric pulsing with the opposite polarity, the behavior of the resistance of the interfaces is interchanged. This switching effect is non-volatile and implies that superconductivity can be both suppressed and *restored* by electric pulsing. In addition, using a four-wire measurement, we find that the resistance of the bulk dielectric beneath the pulsed electrodes is affected by the amount of pulsing and that the effect is at least partially reversible. This indicates that the electric pulsing induces a change in the oxide which may extend over hundreds of microns out of the contact interfaces into the bulk. We shall argue that our observations suggest that strong electric pulsing may cause migration of

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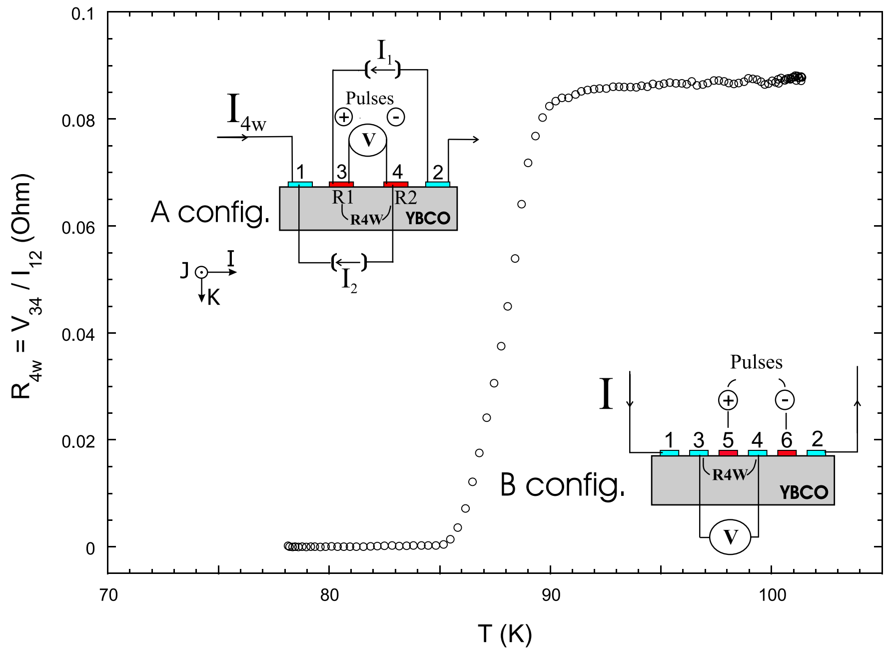

Figure 1. Temperature dependence of R_{4W} (V34/I12) of the YBCO sample before applying pulses ($T_c \simeq 90$ K). The inset shows the two contact configurations studied. Directions I, J, K are indicated to clarify the orientation of contacts in relation to sample dimensions. Current is applied sequentially in order to determine R_{4W} and the resistances that involve each of the pulsed contacts, R_1 (V_{34}/I_{32}) and R_2 (V_{34}/I_{14}).

oxygen ions along higher ion mobility regions, such as grain boundaries of YBCO.

To study the RS effect we fabricated two configurations of contact electrodes on a ceramic YBCO slab (of dimensions $8 \times 4 \times 0.5$ mm^3, labeled $I \times J \times K$; J_c (77 K) $\simeq 10^3$ A cm^{-2}). The configurations, denoted A and B, are schematically represented in figure 1. The samples were synthesized following a similar procedure to the one described elsewhere [15]. Contacts were made parallel to the J direction by sputtering rectangular gold pads onto one of the $I \times J$ faces of the slab and silver paint was used to fix the copper leads. The mean electrode's width was 1 mm while their separations ranged between 0.4 and 0.8 mm. The superconducting transition of the pristine sample is shown in figure 1. The applied pulsing consisted of trains of 20 000 square pulses of 10 V and 0.1 ms at 1 kHz. They were applied to electrodes 3–4 (5–6) of configuration A (B). The maximum applied power was about 0.25 W during a period of 20 s. Although after each pulsing treatment an increase <1 K was detected in a thermometer in close thermal contact with the sample, this small power applied to a well thermally anchored sample is not expected to produce significant overheating effects as to reach a local temperature (>300 °C), where the kinetics of the oxygen diffusion would increase, modifying irreversibly the oxygen contents of the sample in the timescale of the pulsing procedure. After the pulsing, resistance was measured using a standard DC technique with a small positive and negative test current (10–100 μA). To measure a particular electrode's resistance, current was forced to flow through that electrode and a third electrode, as depicted in figure 1 (configuration A). In this way, the measured quantity is the contact resistance plus a bulk YBCO contribution. The bulk resistance of the sample R_{4W} (proportional to the sample resistivity) was measured independently, using a standard four-wire technique (configuration A). The initial resistance of contacts were in the range of 20–1000 Ω, while the bulk YBCO resistance was about 0.1 Ω in its normal state (i.e. for T above T_c). Thus the bulk contribution in configuration A was always small or negligible.

Figure 2 shows the simultaneous time evolution at room temperature of the contact resistance of the two pulsed electrodes 3 and 4, with respective resistance $R_1 = V_{34}/I_{32}$ and $R_2 = V_{34}/I_{14}$. The polarity of the successive trains applied to electrode 3 is indicated in the figure. The observed resistance changes were non-volatile and may reach a ratio of up to 100 between the low and high resistance states. A remarkable feature of the observed resistive switching is that it always showed a complementary behavior, i.e. when one interface increased its resistance the other one decreased it. This type of behavior has also been observed in RS studies of systems using colossal magnetoresistive manganites as dielectrics [12, 14, 16]. Instabilities and relaxations are observed during the measurements, principally for the most resistive contact. As the relaxation is still noticed for periods over 30 min it may be related to a diffusive effect rather than to sample heating [17]. While in most instances the cathode was associated with a lower resistance state, exceptions were also eventually observed.

To further characterize the switching mechanism, we investigated the temperature dependence of the contact resistances. The results shown in figure 3 were obtained by first applying a train of pulses at room temperature that set one interface in the high resistance state (HRS) and the other in the low resistance state (LRS). The two contact resistances were measured simultaneously as the system was cooled down. Then, the sample is brought back to room temperature, a new

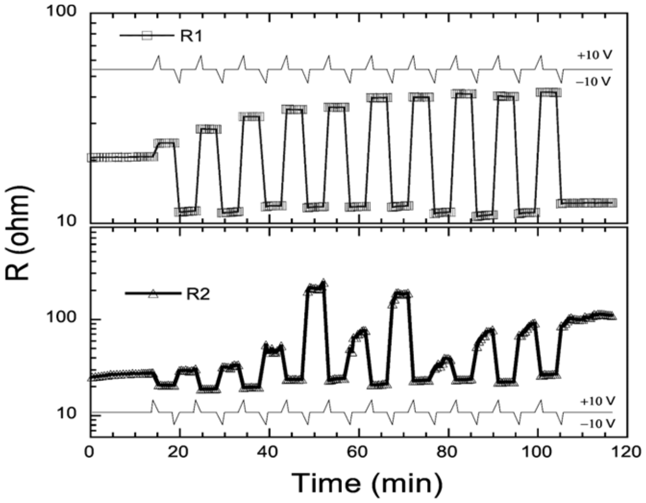

Figure 2. Room temperature time dependence of R_1 (V_{34}/I_{32}) and R_2 (V_{34}/I_{14}) while applying 2×10^4 ($+ = +3; -4$) and ($- = -3; +4$) electric field pulses using the A contact configuration.

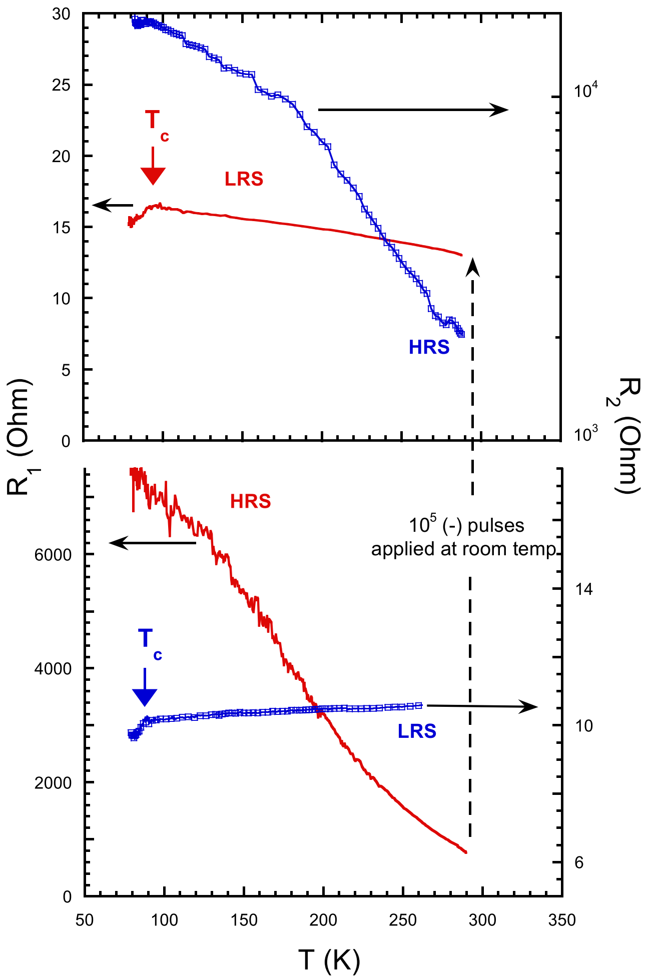

Figure 3. Temperature dependence of both pulsed electrodes, before and after applying over 10^5 negative ($-3; +4$) pulses, using the A contact configuration at room temperature. In the low resistance state (LRS), the contact resistance is small and tracks the R_{4W} resistance, particularly its superconducting transition. The arrows indicate the corresponding axis of each curve.

train of pulses of opposite polarity is applied that produced the inversion of the resistive state of the contacts and the resistance was measured under a new cooling process. We observed that, if pulses were applied at low temperatures ($\sim$100 K), they produced substantially smaller effects. The resistance in the HRS steeply increases with decreasing temperature, while in the LRS it has a relatively weak temperature dependence.

The most interesting feature revealed by the data of figure 3 is that the LRS showed a significant drop in the resistance at T_c, while the HRS did not show any similar anomaly. This demonstrates that pulsing can not only suppress but also *restore* the superconducting state of the YBCO material in the neighborhood of the pulsed electrodes. We should note that the magnitude of the observed drops in the contact resistances R_1 and R_2 in their respective LRS are about 1 Ω. Therefore, they cannot be ascribed to a bulk change since that contribution can be *at most* one order of magnitude smaller than the observed drops (figure 1).

A key insight on the resistive switching mechanism was obtained from the study of the bulk resistance $R_{4W} = V_{34}/I_{12}$ that involves a portion of the sample directly beneath pulsed electrode 5 in the contact configuration B. Initially, at room temperature, we observed that even the bulk resistance could be reversibly switched (inset of figure 4). The magnitude of the effect is, in any case, substantially smaller than that at the electrode contacts. Nevertheless, the significance of these data is that the physical effect of resistance change is not circumscribed to the contacts, but can reach deep into the bulk of the dielectric. Moreover, the fact that the effect can be reversed rules out overheating as a possible explanation of the observed behavior.

We were thus prompted to investigate further into the influence of electric pulsing on the full temperature dependence of the bulk superconducting transition. As the test current is kept low in order to avoid overheating and voltage measurements have a mean noise of $\pm$10 nV, our experimental resolution of resistance is of the order of 0.1 mΩ. This implies that the experimental points obtained from a measurement of a zero resistance associated with a superconducting state would indicate minimal values of about 0.1% of R_{4W} (92 K).

Our results are shown in figure 4 where we also include the data for the pristine sample for reference. At room temperature, we applied a long train of 10^7 (+) polarity pulses on electrodes (+) 5 and (−) 6. Only a slight increase of temperature (<1 K) was detected in the thermometer placed in good thermal contact with the sample. We then measured the superconducting transition and, within our experimental resolution, we observed that the onset of superconductivity T_c remained unchanged while both the temperature width of the transition and the residual resistance below T_c exhibited significant increase. The measurement was repeated on the stored sample one month later, showing negligible relaxation of the effect, and, in addition, confirming the stability and the thermal repeatability of our experimental set-up. Significantly, upon application of a reversed (−) polarity train of pulses at room temperature, the effect on the superconducting transition

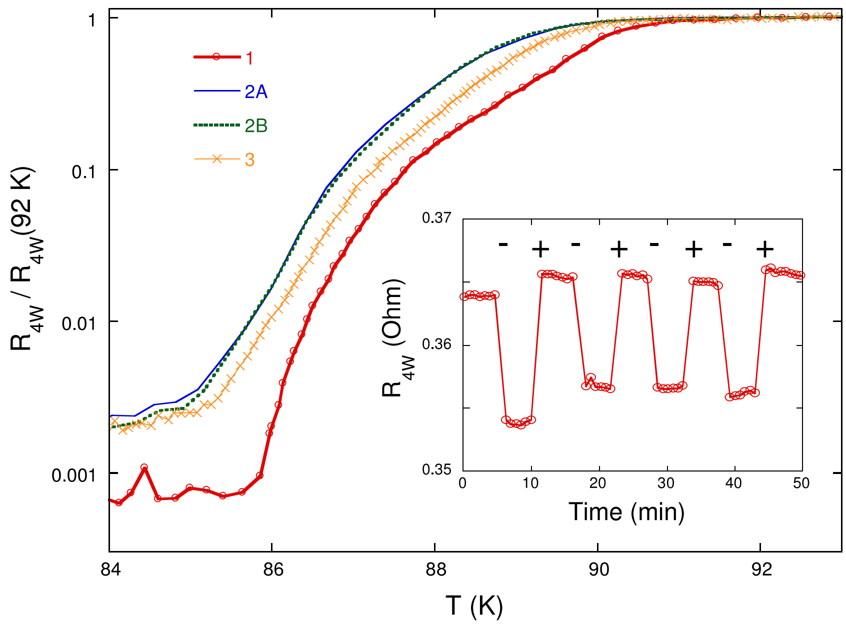

Figure 4. Superconducting transition sensitivity to pulses of opposite polarity, measured using the B configuration. All the pulses were applied at room temperature. The T_c onset remains unchanged. $R_{4W} = V_{34}/I_{12}$; (1) initial sample, (2A) 10^7 + cumulated pulses, width = 100 μs; 1 kHz, 10 V between electrodes 5 (+) and 6 (−). (2B) is sample 2A measured one month later to check stability and repeatability. (3) 10^8 − cumulated pulses. The inset shows the reversible behavior of R_{4W} upon applying trains of 2×10^4 pulses of opposite polarity at room temperature.

was reversed. However, the observed reversion was only partial, and even increasing to up to 2×10^8 (−) pulses we were not able to bring the sample back to the initial condition. In fact, we verified that this remained the case also upon producing successive changes of the polarity of the electric excitation. This long-pulsing study therefore produced a saturation of the RS effect of the bulk resistance. Significantly, the saturation was also verified for the RS at the contact interfaces as well.

The analysis of the experimental observations described above have several implications. The fact that we could achieve the suppression and restoration of superconductivity near the contacts, while there was no significant change observed in the temperature value for the onset of the superconducting transition T_c, implies that pulsing mainly affects the inter-grain Josephson junction coupling [18].

In fact, the hypothesis of controlled coupling between ceramic grains can also explain the observed increase in the residual bulk resistance at low temperatures, as a reduced grain coupling would lead to a reduction or even to null critical currents, suppressing superconductivity between measuring voltage electrodes.

Finally, the observed reversible control of the bulk resistance R_{4W} at room temperature and, more important, the fact that pulsing could remove all the superconducting percolating paths that short-cuts the sample on the macroscopically large region between voltage electrodes (which probes regions of YBCO that are relatively far from the pulsed electrodes (∼1 mm)) implies that pulsing produces significant effects up to hundreds of microns away from the pulsed contacts. This puzzling observation is nevertheless also consistent with the inter-grain coupling scenario, since the surfaces of the grains (i.e. grain boundaries) are strained regions which contain excess oxygen vacancies [19, 20] and thus provide channels that facilitate oxygen-ion migration [21]. From the extensive studies done on cuprate superconductors, it is well known that migration of either metal or oxygen ions at grain interfaces is one of the most effective parameters affecting the superconducting properties of polycrystalline samples [18, 22, 23]. Indeed, as shown by previous calculations [24], the oxygen vacancies at grain boundaries enhance their influence to larger areas as they produce space charge defects that reduce the hole contents of large portions of the bulk in the vicinity of boundaries, extending consequently the worsening of the superconducting coupling.

On the other hand, from a more general perspective, the inter-grain coupling control by oxygen-ion migration through grain boundaries is an expected common feature to all types of polycrystalline perovskites. In fact, perovskites are considered excellent oxygen-ion conductors as they possess a lot of vacancies in the oxygen sublattice and a small barrier for oxygen migration [25]. Therefore, in the light of our experimental observations, we may conclude that oxygen-ion migration at grain boundaries is at the origin of the RS effect in YBCO and can naturally account for its surprising universality in a wide variety of other transition-metal oxides [16, 17, 26].

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