Field-driven hysteretic and reversible resistive switch at the Ag–$Pr_{0.7}Ca_{0.3}MnO_3$ interface

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The hysteretic and reversible polarity-dependent resistive switch driven by electric pulses is studied in both $Ag/Pr_{0.7}Ca_{0.3}MnO_3/YBa_2Cu_3O_7$ sandwiches and single-layer $Pr_{0.7}Ca_{0.3}MnO_3$ strips. The data demonstrate that the switch takes place at the Ag–$Pr_{0.7}Ca_{0.3}MnO_3$ interface. A model, which describes the data well, is proposed. We further suggest that electrochemical migration is the cause for the switch. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1590741]

$Pr_{0.7}Ca_{0.3}MnO_3$ (PCMO) has attracted extensive interest recently. Below 150 K, its free energies corresponding to the paramagnetic, the charge-ordered, and the ferromagnetic states differ only slightly. Therefore, a slight external disturbance, e.g., magnetic field, light, isotope mass, pressure, or electric field, may lead to a large resistivity (ρ) change, but only at low temperatures.[1]

Therefore, it is interesting to note the report of Liu *et al.*[2] that the two-lead resistance, R, of a PCMO layer sandwiched between a Ag top-electrode and a $YBa_2Cu_3O_7$ (YBCO) or a Pt bottom electrode can be drastically and repeatably alternated at room temperature by applying electric pulses with different polarities.[3] This R switch may thus offer potential device applications, e.g., nonvolatile memory. Similar R changes in single-layer PCMO films with the four-lead configuration were also reported. The R switch has therefore been attributed to bulk properties of PCMO, in terms of the alignment of the presumed ferromagnetic clusters by the electric field.[2] The interpretation, if confirmed, presents a major challenge to the physics of manganites and, possibly, to the basic law of parity conservation. The reported R change of $\Delta R \geqslant 3000\ \Omega$ across a 600-nm-thick PCMO film represents a ρ-increase of $\Delta\rho \approx 10^5\ \Omega$ cm and suggests a state with a ρ (297 K) far greater than the $\ll 10^1\ \Omega$ cm previously reported in PCMO. According to the commonly accepted polaron model, ρ (297 K) of manganites is controlled by the polaron mobility and should be ultimately restricted by the hopping barrier (10^{-1} eV$\approx k_BT$ at 297 K) associated with the Jahn–Teller distortion, which is only a few electron volts.[4] The experimental ρ (297 K) is only 10^{-2} to $10^0\ \Omega$ cm in $(La_yPr_{1-y})_{1-x}Ca_xMnO_3$ for $0.2 \leqslant x \leqslant 0.5$ and $0 \leqslant y \leqslant 0.7$,[5] and $\leqslant 10^4\ \Omega$ cm even in extreme cases, such as $Nd_{0.7}Ba_{0.3}MnO_3$ and $LaMnO_3$.[6] A ρ (297 K) of $10^5\ \Omega$ cm or higher would suggest an insulating state never observed before and challenge the polaron model commonly accepted. In a more general sense, this polarity-dependent ρ in a uniform material reported, if proven, represents a violation of the law of parity conservation in the electromagnetic field. It may occur without parity violation only if the sample is asymmetric due to either an inhomogeneity in the thickness direction or poling by electric pulses (''training''); neither bears any obvious relation to the alignment model proposed.[2] The present study is motivated by our attempt to elucidate the mechanism responsible for, and the nature of, the R switch. Our data demonstrate that the switch occurs at the Ag–PCMO interface, possibly via an electrochemical process. The observation not only resolves the parity-violation puzzle but also provides insight into optimization for possible applications.

PCMO films were synthesized by ac sputtering at 760 °C under a 140 mTorr $Ar:O_2 = 2:3$ mixture atmosphere. YBCO films were synthesized by conventional pulsed laser deposition on $LaAlO_3$ substrates. The structure was determined by x-ray diffraction using a Rigaku DMAX–IIIB diffractometer. Both highly c-oriented and epitaxial PCMO films have been obtained and tested, with similar results. High voltage pulses were produced by a DEI PVX-4150 pulse generator. The resistivity was measured after applying the electric pulses by feeding a dc current from a Keithley 2400 current source and reading the corresponding voltages using a HP34401A multimeter through a Keithley 705 scanner. Both the ρ (297 K) $\approx 0.3\ \Omega$ cm and the H-induced metal–insulator transition around 120 K above 1 T observed before pulsing show that the PCMO films so prepared are typical of those previously examined.[7]

The Ag/(500 nm PCMO)/(500 nm YBCO) sandwich similar to that used by Liu *et al.*[2] was first examined. Ag pads of 0.8 mm diam were deposited on the tops of both PCMO and YBCO (inset, Fig. 1). It should be noted that the two-lead R varies greatly from pad to pad even before pulsing, in agreement with a previous report.[2] Additional three-lead measurements suggest that neither the YBCO layer nor the Ag–YBCO interface contributes significantly to R. Pulses of 30 V and 200 ns were applied between pads A and C (inset, Fig. 1). The pulse current density across both the interfaces and the PCMO layer was typically $\leqslant 30$ A/cm^2, a

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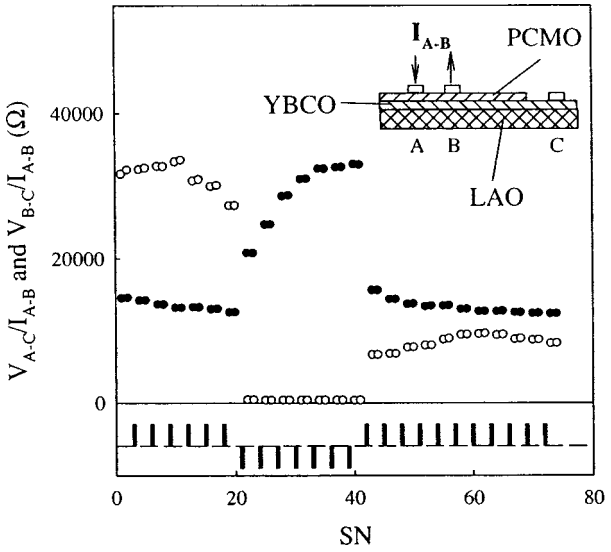

FIG. 1. R_{A-C} (●, ×1/30) and R_{B-C} (○). SN stands for the experimental sequence number. Individual ±30 V pulses are represented as bars at the bottom of the figure; two dc R measurements were carried out after each pulse.

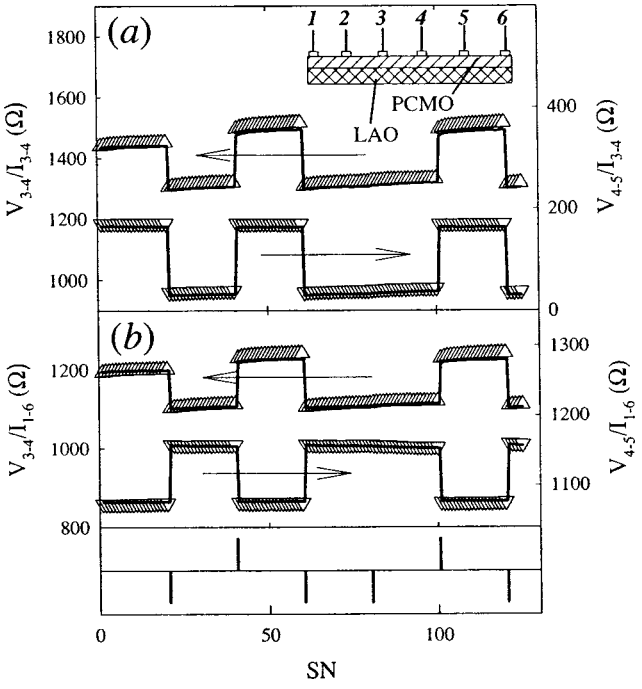

FIG. 2. (a) V_{3-4}/I_{3-4} (△) and V_{4-5}/I_{3-4} (▽). Solid lines: calculated. Inset: the electrode arrangement. (b) V_{3-4}/I_{1-6} (△). Solid lines: calculated. The ±150 V pulses across electrodes 3 and 4 are shown as bars at the bottom. Each bar represents 20 pulses of 150 V and 200 ns.

range adopted to cover the threshold estimated from previous data.[2,3] A measurement current was applied after each pulse to determine the two terminal R's. A possible thermoelectric effect on R was eliminated by switching the polarity of the measuring current. It should be pointed out that the $I-V$ characteristic associated is nonlinear but symmetrical against the polarity, similar to that reported for $Pb(Zr,Ti)O_3$ between ±1 V.[8] The data presented here are measured at a fixed current of 1 μA unless specified. The two-lead R observed exhibits the same polarity-dependent switch previously reported.[2]

To determine whether the apparent parity-violation is associated with the electric poling, we simultaneously determined the voltages V_{A-C} and V_{B-C} across electrodes $A-C$ and $B-C$, respectively, with both the pulses and the measuring dc current $I_{A-B}=1$ μA passing through $A-B$. This configuration represents two serially connected sandwiches since the PCMO resistance between A and B is 10^7 times higher than that perpendicular to the film. Both V_{A-C}/I_{A-B} and V_{B-C}/I_{A-B} are therefore expected to vary in the same fashion by pulsing if the pulse has generated a change in the bulk of the PCMO film, as the two sandwiches experience the same poling history. However, we found that R_{A-C} increases while R_{B-C} decreases (Fig. 1), depending only on the polarity of the electrode. The apparent parity violation and the associated switches, therefore, cannot be attributed to the poling.

To explore the issue further, a single-layer 3 mm wide and 500-nm-thick PCMO strip was measured in a multilead configuration with a 0.18 mm distance between the adjacent 0.32×3 mm^2 Ag pads [inset, Fig. 2(a)]. A train of 20 pulses of 150 V and 200 ns with a given polarity was applied between electrodes 3 and 4 at a specific time. The estimated current densities through the two pads and through the PCMO strip are 40 and 10^4 A/cm^2, respectively. Both are higher than the switching threshold$\approx$10–20 A/cm^2 estimated from both the data of Fig. 1 and the data of Ref. 2.[2,3] After the electric pulses were applied, the transport elements V_{l-k}/I_{m-n} were measured, where V_{l-k} is the voltage between electrodes (l,k); and $I_{m-n}=1$ μA is the measuring current through electrodes (m,n) with l, k, m, and $n=1-6$. Indeed, pulse-induced polarity-dependent switches were detected, as shown in Figs. 2(a)–2(b). The data demonstrate that the PCMO resistivity cannot be the dominant factor. First, the change of V_{3-4}/I_{3-4} (i.e., the two-lead resistance across the pulse path) with the pulses is only 10%, which limits the possible change of PCMO ρ (297 K) to below 0.1 Ω cm [Fig. 2(a)]. Such a change will only modify the V_{B-C}/I_{A-B} in Fig. 1 by 5×10^{-4} Ω, a million times lower than the 30 kΩ observed. Second, a similar switch was also observed in V_{4-5}/I_{3-4}, the contact resistance beneath pad 4 [Fig. 2(a), and its inset]. Therefore, contributions from the PCMO ρ (297 K), as the difference between the two-lead R and the contact resistance, should only be $(V_{3-4}-V_{4-5})/I_{3-4}<10$ Ω and within our experimental resolution.

However, a simple contact resistance model contradicts the observed switches in the conventional "four-lead resistance," i.e., V_{3-4}/I_{1-6}, in addition to the interface resistances of V_{2-3}/I_{1-6} and V_{4-5}/I_{1-6}. We attribute the contradiction to the nonzero size of the Ag pads: the large PCMO resistance may have forced the measuring current to detour through the Ag pads. A simplified resistive equivalent circuit for the Ag pads and the PCMO resistance underneath the pads is given in the inset of Fig. 3, where, for example, R_{2A} and R_{2B} are the effective interface resistances to PCMO on the left and right sides of pad 2, respectively; R_{2C} is the the resistance for the PCMO section between these two effective contact points; and R_{2D} is the PCMO resistance between pads 2 and 3. Changes of R_{2A}/R_{2B}, therefore, naturally lead to the change of V_{3-4}/I_{1-6}. A procedure was thus developed to simultaneously calculate all measured V_{l-k}/I_{m-n} by as-

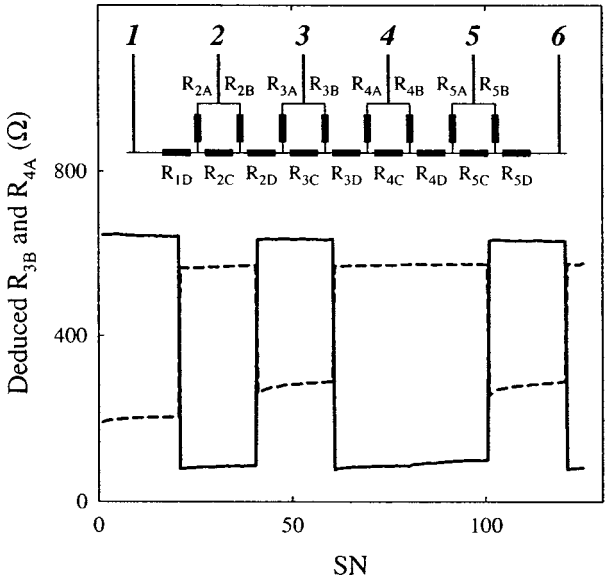

FIG. 3. The model-calculated R_{3B} (dashed line) and R_{4A} (solid line). Inset: the proposed equivalent circuit.

suming that only R_{3B} and R_{4A}, i.e., the contact resistances along the pulse path, are affected by the pulses, and that all other contact resistances, which are not crucial to the data-fit, are equal and independent of the experimental sequence number SN (inset, Fig. 3). The seven SN-independent parameters and the two SN-dependent parameters, therefore, can be uniquely deduced based on the 12 SN-dependent V_{l-k}/I_{m-n} observed. The deduced R_{3B} and R_{4A} are shown in Fig. 3. The calculated V_{3-4}/I_{3-4}, V_{4-5}/I_{3-4}, V_{3-4}/I_{1-6}, and V_{4-5}/I_{1-6}, as a few samples of the 12 V_{l-k}/I_{m-n}, are shown in Figs. 2(a)–2(b) as solid lines. The agreement is good with only two variables of R_{3B} and R_{4A}. Additional calculations further demonstrate that the additional contribution from PCMO ρ (297 K) should be less than a few percent of the resistance changes observed.

Very recently,[9] we examined the pulse-induced resistive switch in several PCMO ceramic/single-crystal samples with either Ag films or Ag epoxy contacts as electrodes. Similar switches were observed. Both the two-lead resistance and the contact resistance are typically switched from 10^2 to 10^3 Ω, similar to the data discussed earlier, although the measured four-lead resistance$\approx 1-10$ Ω is negligibly small and cannot account for the larger two-lead resistance switch observed. This is in perfect agreement with the proposition that the field-induced R switch does not occur in the bulk of PCMO but at the interface between the electrode and the PCMO. We have also observed similar switches in the interfaces between metals and other perovskite oxides (such as cuprates), suggesting that this is a rather general phenomenon.[9]

The electric field across the interface will be on the order of 10^7 V/cm based on the voltage drops in the sandwiches and an assumed interface thickness of 10 nm. The relatively slow dynamics (Fig. 1), which can be improved by applying higher voltages, suggests electrochemistry, e.g., oxygen vacancy creation/diffusion, as a route to the switch observed. Such oxygen–vacancy migration has been previously observed in perovskite oxides at lower electric fields ($\ll 10^4$ V/cm), although at even slower rates.[10] The extremely high field and defect density (as suggested by the unusually high room-temperature resistivity) in our case may be responsible for the relatively high mobility observed here.

In summary, the electric pulse-induced polarity-dependent hysteretic and reversible R switch is observed in both the Ag/PCMO/YBCO sandwich and the single-layer PCMO configurations. Detailed studies show that the large R change does not take place in the PCMO film but at the Ag/PCMO interface. A model based on interfaces is proposed to account successfully for the polarity-dependent R switch. We further propose that a field-induced electrochemical migration appears to be the driving mechanism for the switch.

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