Field-induced resistive switching in metal-oxide interfaces

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We investigate the polarity-dependent field-induced resistive switching phenomenon driven by electric pulses in perovskite oxides. Our data show that the switching is a common occurrence restricted to an interfacial layer between a deposited metal electrode and the oxide. We determine through impedance spectroscopy that the interfacial layer is no thicker than 10 nm and that the switch is accompanied by a small capacitance increase associated with charge accumulation. Based on interfacial I–V characterization and measurement of the temperature dependence of the resistance, we propose that a field-created crystalline defect mechanism, which is controllable for devices, drives the switch. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1768305]

Recent observation of room-temperature resistive switching driven by electric fields in various perovskite oxides has garnered attention due to the potential for nonvolatile memory applications. This field-induced resistive switch has been reported in several compounds.[1–6] The switching observed shares several features: a moderate switch speed; an altered resistance inconsistent with the well-accepted bulk resistivity; and a sensitivity to surface treatments. Various models have been put forth, but inconsistencies remain. For instance, bulk charge ordering in $Pr_{0.7}Ca_{0.3}MnO_3$ (PCMO) has been suggested, but this creates an apparent conflict with both the spatial symmetry and the reported bulk properties.[1] Although interface models have been proposed involving either lattice defects or carrier concentration,[2,5,7] the exact nature of this interface remains vague. We therefore investigate the interface properties associated with the resistive switch and have observed: (a) the switching is a common phenomenon to the metal-oxide interfacial layer; (b) the interfacial transport properties are rather different from that of the bulk; (c) the interfacial resistance is dominated by the carrier trapping with no indication of Schottky barriers; and (d) the capacitance of the interfacial layer, on the order of $1000 \ nF/cm^2$, changes with switching, which is indicative of a change in the space-charge. These observations can be self-consistently understood using a carrier-trapping model and suggest that the field-induced switch is not restricted to a small class of materials. Therefore, the potential for controlling this phenomenon for device applications is considerable.

Ceramic samples synthesized by standard solid-state reactions were determined to be single-phase based on x-ray powder diffraction patterns taken on a Rigaku DMAX-IIIB diffractometer. PCMO thin films were ac sputtered on $LaAlO_3$ substrates at $760 \ °C$ in an $Ar:O_2 = 2:3$ mixed atmosphere at 140 mTorr. The films were found to be highly epitaxial. Pt leads were attached to the ceramic samples using Ted Pella Leitsilber 200 Ag paint. The thin film samples received sputtered Ag electrodes to which Pt leads were also attached using Ag paint.

Ceramic $LaCoO_3$, $La_{0.7}Ca_{0.3}MnO_3$, $Pr_{0.7}Ca_{0.3}MnO_3$, $SrFeO_{2.7}$, $RuSr_2GdCu_2O_3$, and $YBa_2Cu_3O_7$ were tested. We adopted the multi-leads configuration developed by Baikalov *et al.*[2] to measure both the interfacial and bulk resistances of the samples (inset, Fig. 1). A DEI PVX-4150 pulse generator provided 150 V pulses of 200 ns width. A pair of electrodes (A and B in Fig. 1) at room temperature was exposed to
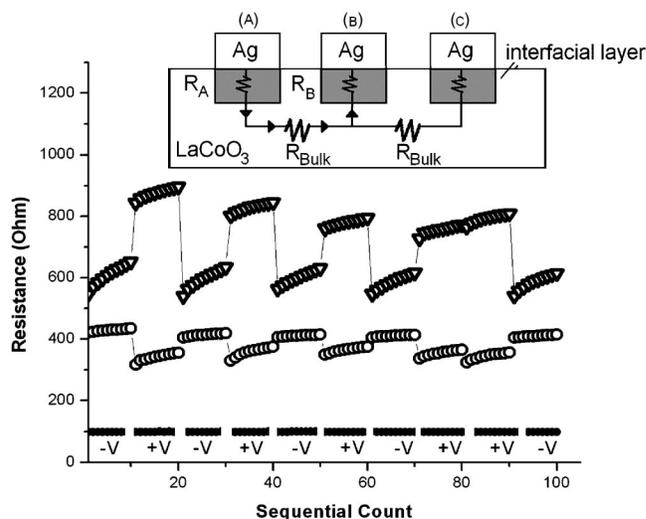

FIG. 1. Simultaneous switching of two electrodes on ceramic $LaCoO_3$ using twenty 150 V pulses of 200 ns width and 3 s apart. After pulsing, ten data points were measured. This was followed by another session of pulsing, after which another ten points were measured, as demarcated by the sequential count. The bold plot at the bottom shows the four-leads bulk resistance. The open triangle plot shows the three-leads interfacial resistance R_A, and the open circle plot shows R_B. The data are typical of the perovskite oxides we tested. Arrows indicate the current path for the three-leads measurement.

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twenty pulses spaced 3 s apart. As a typical example, data for $LaCoO_3$ (Fig. 1) revealed that the four-leads bulk resistance $R_{bulk} \sim 100\ \Omega$, which is consistent with previously published resistivity data,[8] remained unaffected by the pulses within an experimental resolution of 0.01 Ω. However, the three-leads interfacial resistances, R_A and R_B measured through the reference electrode C, showed hysteretic and polarity-dependent switching between a low (on)- and a high (off)-resistance state. The interfacial resistances at both states are much higher than that expected from the bulk value. All other tested compounds behaved similarly when exposed to pulsing. The data therefore suggest that the switching is a common phenomenon, but associated only with an insulating interfacial layer. In view of the different spin configurations, valences, and band structures of the tested compounds, the field-induced polarity-dependent resistive switch is unlikely to be associated with a particular phase transition or carrier doping.

In order to better characterize this interface, impedance spectroscopy was performed on PCMO thin films using a Schlumbergër SI 1260 impedance analyzer with a Solartron 12603 attachment. Measurements spanned a frequency range of 0.1 Hz to 20 MHz. The single layered PCMO strips received three parallel $0.2 \times 1.3\ mm^2$ Ag electrodes spaced 0.3 mm apart. The electrodes A and B experienced switching under the same 150 V, 200-ns-wide pulses. Electrode C served as a reference electrode. Both the two-leads impedances Z_{AB} and Z_{BC} were then measured. In general, the impedance can be modeled as three parallel RC circuits associated with the two interface regions and the bulk portion (inset, Fig. 2). Therefore, we expect the impedance spectrum to show three sections to account for our model, assuming that the corresponding time constants differ (Fig. 2).[9]

Indeed, Z_{AB} and Z_{BC} share a three-sectioned feature. The impedance spectra show two merged semicircles that begin on the Z' axis. Below 1 kHz, the spectra terminate on the Z' axis at values that correspond to the total two-leads dc resistance measured between the electrodes. Above 1 MHz, the spectrum again reaches the Z' axis at a left end point with a resistance in rough agreement with the bulk resistance measured in the four-leads configuration. Therefore, the Z' segment between the origin and the end point is attributed to the bulk portion of the sample based on the negligible C_{AB} and C_{BC} estimated. It should be noted that the positions of the left end points are unaffected by the switching, which is a further indication of the bulk contribution. At the intermediate frequencies, both spectra are dominated by a large semicircle. In the case of Z_{AB}, it represents a parallel RC circuit of 700 Ω/1.6 nF and 1500 Ω/2.2 nF for the on and off states, respectively. We assign this feature to electrode B based on the measured dc interfacial resistances. Similar results were obtained for Z_{BC} with some difference in the R_B and C_B deduced. We attribute the differences to inhomogeneity along the width of electrode B. An additional small segment appearing as a merged semicircle between these two major features is attributed to electrodes A and C, respectively. The interpretation is supported by the fact that the R_C and C_C deduced are not altered by switching, and the three-leads R_A changes only slightly with switching.

We expanded upon the spectroscopy data with a capacitance measurement across a multilayered Ag/PCMO/Pt sandwich similar to the configuration used by Liu *et al.*[1] In order to properly measure the capacitance of the interface,
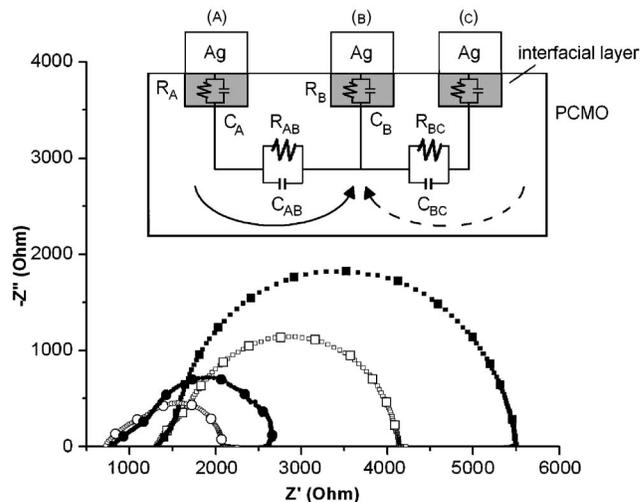

FIG. 2. Impedance spectra for a PCMO thin-film strip using two-leads measurements across either electrodes A/B or electrodes B/C. Squares represent measurements over Z_{BC} whereas circles represent Z_{AB}. Open and closed symbols represent the on and off states, respectively.

bypass current through the Pt bottom layer had to be prevented. This was achieved by making the Pt layer ultrathin with poor in-layer conductance, creating an overall resistance $\sim 10\ k\Omega$ between a switched electrode and a reference electrode. As a result, we were able to directly measure the interfacial 1.5 nF capacitance, a value consistent with the above spectrum analysis, using the three-leads configuration with a HP 4285A LCR meter.

Knowing the capacitance C, the thickness of the interfacial layer, $d = \epsilon_0 \epsilon S / C$, can be estimated, where ϵ_0, ϵ, and S are the vacuum permittivity, the dielectric constant, and the electrode area, respectively. With $\epsilon_0 = 8.85 \times 10^{-14}$ F/cm, $C \sim 2 \times 10^{-9}$ F, and $S = 0.02 \times 0.13\ cm^2$, a d is obtained to be 1 and 10 nm with $\epsilon = 1$ and 10, respectively.[10] Thus, the switching layer seems to involve no more than 30 unit cells in the thickness.

To further characterize the switching mechanism, we investigated the temperature dependence of the resistance and the $I-V$ characteristics of the interface. The temperature dependencies of the interfacial resistances of the PCMO ceramic at both on and off states were found to be identical (dashed lines, inset, Fig. 3), demonstrating that the hopping barrier, hence the mobility, is the same in both states. However, the temperature dependence of the bulk (solid line, inset, Fig. 3) differs visibly from that of the interfaces, suggesting that the interfacial layers are significantly altered.

Carrier transport in insulators and semiconductors has been extensively studied. The dominant factor will either be space-charge limited currents (SCLC), in which the carrier injection from the electrode is limited by the electric field of the accumulated space charges, or the carrier creation through thermionic emission limited conduction (TELC), electrothermal Poole–Frenkel emission, or Fowler–Nordheim quantum tunneling. These modes can be distinguished via the isothermal $I-V$ correlation: linear $I \propto V$ for TELC; exponential $\ln I \propto V$ for Poole–Frenkel or Fowler–Nordheim emission; and $I \propto V^2$ for SCLC.[11] Asymmetry in the $I-V$ polarities would suggest additional Schottky barriers.

The $I-V$ characteristics obtained for a Ag/ceramic PCMO interfacial layer (Fig. 3) show linear behavior up to approximately 0.1 V, suggesting that TELC is the dominant
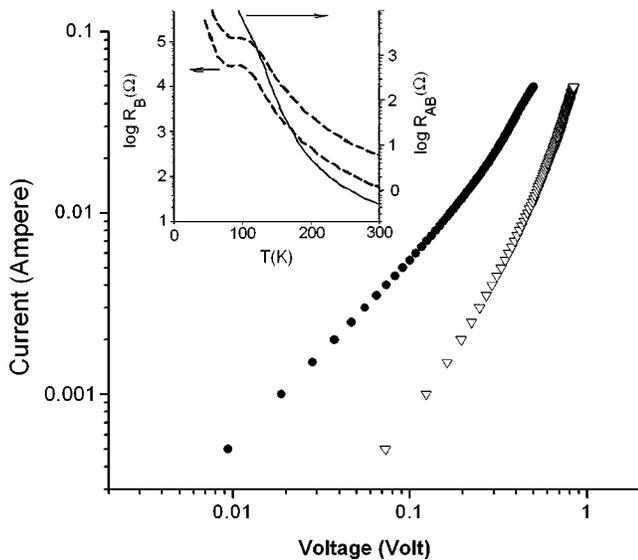
FIG. 3. $I-V$ data show TELC behavior in the lower voltage regime and SCLC behavior in the higher regime with $I \propto V^{2.3}$. The inset shows a visible difference in the temperature dependence between the interfacial and bulk resistances.

mechanism at the lower voltage regime where carrier injection plays a minor role. Beyond that, the behavior evolves into SCLC, as determined by the fit $I \propto V^{2.3}$ above 0.5 V. In this upper regime, carrier injection from the electrodes plays a dominant role. It is interesting to note that the resistance ratio in both regions is roughly voltage-independent. The data also show no appreciable asymmetry with the $I-V$ polarity within ± 1 V, so the role of Schottky barriers appears to be minor, if it exists at all.

Analysis of the SCLC regime can be carried out using widely accepted models. Rose[12] and Lampert[13] obtained

$$I = (\epsilon \mu_0 N_c e^{-E/kT}) V^2/(N_t t^3),\qquad(1)$$

where ϵ is the dielectric constant, μ_0 is the free carrier drift mobility, N_c is the effective density of states in the valence band, E is the effective trapping potential, N_t is the number of shallow traps, T is temperature, V is applied voltage, and t is the distance between electrodes. In particular, the doping level (or the carrier-creation rate) will not affect transport in SCLC, in which the dominant carriers are injected from the electrodes. The remaining factors will be the mobility and the fraction of free charge θ given by

$$\theta = (N_c/N_t)e^{-E/kT}.\qquad(2)$$

Both parameters will alter the resistance. However, significant changes in E or μ_0 contend with the identical temperature dependences of the on and off states (inset, Fig. 3). On the other hand, the pulse field of 10^7 V/cm is close to the decomposition threshold and can conceivably create dense crystalline defects through electromigration. We conse-

quently propose that a pulse-driven reversible change of the trap density, roughly a $5-100\times$ variation, is responsible for the switching. The variation of C_B with switching (Fig. 2) suggests a change in the space-charge distribution and supports the model. It should be noted that the same carrier trapping will increase the resistance in the TELC regime by the same factor, in agreement with our data.

In conclusion, we demonstrate that field-induced resistive switching is a common recurring phenomenon restricted to an interfacial layer between a metal and a perovskite oxide. We also characterize the interfacial layer responsible for the switching as an insulating region no thicker than 10 nm. Further characterization through $I-V$ measurements and the temperature dependence of resistance enables us to propose a conduction mechanism dominated by pulse-generated crystalline defects. The results obtained in the present study suggest that the switching is not compound-specific and can be optimized for device applications by modifying the interface.

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