Understanding electroforming in bipolar resistive switching oxides

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(Received 17 September 2010; accepted 19 December 2010; published online 25 January 2011)

We study electroforming on the resistive switching (RS) behavior of silver-manganite interfaces. Using the technique of hysteresis switching loops we define an electroforming procedure that enables us to study its influence on the RS behavior in a systematic manner. We show that two similar electroforming procedures may lead to either RS or no RS at all. We explain the observed behavior by associating the forming procedure and the memory switching operation to major and minor hysteresis loops, respectively. With the obtained insight we propose a simple and nearly optimal electroforming procedure. © 2011 American Institute of Physics. [doi:10.1063/1.3537957]

Nonvolatile memory concepts are presently based on resistance change rather than in charge storage.¹ Among several candidate technologies, electric-pulse induced resistance switching (RS) was shown to produce useful retention time capability for massive applications as resistive random access memory (RRAM).² Intense research is being devoted to the study of transition metal oxides (TMOs) contacted through metal electrodes³–⁷ due to demonstrated switching speed and scalability.

For actual RRAM devices, an initial “electroforming” (EF) procedure is usually invoked previous to the actually reported RS behavior. In highly insulating nonpolar binary-oxide based RRAM devices, EF consists of the application of strong voltage stress, driving the device close to the electric breakdown. Recent work on TiO₂ studied the dependence of the EF on a variety of external parameters.⁸–¹¹ Importantly, unless EF is performed on these insulating oxides, they would not show any RS effect. On the other hand, the RRAM devices based on conducting TMO with perovskite structure are “born switchers:” they may exhibit hysteresis effects even without an initial forming. Unfortunately, non-EF devices generally would not show reproducible I-V characteristics. Thus, also in these materials, an initial EF step is often invoked previous to a RS measurement. The details of the forming procedure are almost never described, rendering the EF a rather “mysterious,” if not “taboo,” subject in the field. A proper understanding on the EF is a key for reliable implementation of RRAM devices. The goal of this letter is to address this issue, namely, by studying the RS behavior that results from a systematic EF protocol.

We adopt for this study the hysteresis switching loop (HSL) methodology,⁶ a protocol that consists of a succession of electric pulses of varying amplitudes that follow the sequence −JMAX→+JMAX→−JMAX→+JMAX. The remnant resistance state right after each pulse is read out with a small bias current JBIAS to obtain the HSL curve. We thus define a procedure consisting of two HSLs: one associated to the EF process and the other to the resulting RS. The two HSLs differ in their maximal intensities, with JEF MAX>JR MAX. The definition of the EF loop in terms of a HSL allows us to systematize the EF procedure. The maximal intensity of the EF pulsing was chosen to be strong enough so as to “erase” all past pulsing history. We verified that the RS behavior obtained after the application of a given EF sequence always provided the same results, and that they were reproducible on the same sample. This fact validates the definition of the strong HSL as a systematic EF protocol, even if it is applied to a nonpristine sample. We tested over 20 samples always obtaining consistent results. The EF procedure is initiated by performing a set of three successive HSLs with a maximal current density JMAX. Then, the pulsing is stopped at a certain point through the loop. The stopping position defines the specific EF procedure implemented. With this methodology, the RS behavior only depends on the stopping position and not on any past sample history. Using this protocol, we shall show that two seemingly similar forming procedures may surprisingly lead to either RS or no RS at all on the same memory device.

Similarly to previous studies, millimeter sized silver electrodes were hand painted on top of a bulk polycrystalline sample of La₀.₃₂₅Pr₀.₃₀₅Ca₀.₃₇₅MnOi₂.¹²,¹³ The present results qualitatively do not depend on the contact separation (a few millimeters) since the interfacial resistance is much higher than the bulk one. Square pulses of 10 ms were injected at room temperature using a Keithley 2400 source-meter in current control mode (IPULSE). The remnant response, i.e., the nonvolatile behavior after each pulse, was obtained by applying a small bias current density (JBIAS) not affecting the resistance of the interface. Pulse and bias stimuli are injected through terminals A and D, while voltage is simultaneously measured at AB and CD contact pairs (Fig. 1). The current density JPULSE is injected during an electric pulse. We label the interface remnant voltages as VREM AB and VREM CD and their respective nonvolatile resistance as RREM AB=VREM AB/JBIAS and RREM CD=VREM CD/JBIAS.

A controlled EF procedure is defined as a set of three successive strong HSLs, pulsing between ±JMAX values. Starting with negative pulses of −JMAX=−55 A/cm², their strength was linearly increased in small steps up to +JMAX and then decreased back to −JMAX. The remnant resistance
data for contact D are shown with filled symbols in Fig. 1. Those were measured with a small current $\left(J_{\text{BIAS}} = 0.055 \, \text{A/cm}^2\right)$ applied 10 s after each $J^{\text{EF}}$ pulse. The remnant resistance for contact D exhibits a large hysteresis with concomitant low and high resistive states. This is fully consistent with previously reported data in manganite systems.\textsuperscript{6,13} We also note that the behavior during the three forming loops was essentially the same (for clarity data are shown for just a single loop). Contact A has qualitatively similar behavior, and its data—which were acquired simultaneously with those of contact D—are shown in Fig. 2.

To systematically investigate the effect of electroforming, we measured the resistive switching behavior of the system that results from stopping the EF at different points through the cycle. We study the RS by means of a HSL that results from stopping the EF at different points. We study the RS by means of a HSL that results from stopping the EF at different points through the cycle. We study the RS by means of a HSL that results from stopping the EF at different points through the cycle.

Our main observation is that, depending on the EF protocol, qualitatively different RS behavior may be obtained. Similarly to the familiar magnetic systems, major and minor loops can be obtained in the RS behavior and can be well described by a theoretical model that takes into account the motion of oxygen vacancies.\textsuperscript{14} In magnetic systems,\textsuperscript{15} the behavior of a minor hysteresis loop evidently depends on the place where it is performed within a major loop. Thus, we extend the analogy here to rationalize our results and think of the EF and RS as major and minor hysteresis switching loops, respectively. In fact, we observed in the results from the electroforming procedure EF1 [Fig. 1(b)] that, although the interface was strongly poled with solely negative $V$, there was no ensuing RS response. The interface was first poised to saturation with a negative current density up to $-J^{\text{MAX}}$, and then it was decreased with the same polarity. The data reveal that the absence of RS is due to the fact that the stress (i.e., $J^{\text{MAX}}=22 \, \text{A/cm}^2$) remains beneath the threshold value ($\sim 30 \, \text{A/cm}^2$) measured in the EF major loop. The RS of procedure EF3 [shown in Fig. 2(b)] is also consistent with the previous observation. After poling the system to saturation, a small RS nevertheless appears when the strength of the RS stimulus is now sufficient to drive the interface beyond the threshold value of $\sim 12 \, \text{A/cm}^2$.

The key difference between the results from procedures EF1 and EF3 is that in the former the EF brought the interface to saturation of its low resistance state $R_{\text{LO}}$, while in the latter EF brought it to its high resistance state $R_{\text{HI}}$. As previous results from model calculations of conducting bipolar memories showed,\textsuperscript{14,16} the $R_{\text{LO}}$ state corresponds to a few oxygen vacancies at the interface region, while plenty are present in the $R_{\text{HI}}$ state. Vacancies are microscopically associated to broken conductive chains of TM-O-TM producing a resistance increase. Therefore, for the same given current-density stress, the electric field that develops at the interface is larger in the $R_{\text{HI}}$ state with respect to the $R_{\text{LO}}$ one by a ratio of $J^*\text{R}_{\text{HI}}/J^*\text{R}_{\text{LO}}=R_{\text{HI}}/R_{\text{LO}}$. This explains why the RS threshold value is higher in the low-to-high resistance transition than the one in the high-to-low transition.

This discussion seems to imply that a preferable EF procedure would be to pole the interface with a negative potential, to induce there a large concentration of oxygen vacancies and set the system in the $R_{\text{HI}}$ state, and so to produce
larger electric fields. However, as our results demonstrate, this choice is not optimal. Interestingly, the results of the electroforming procedure EF2 show that the largest RS behavior is not obtained by saturating the interface with oxygen vacancies, but rather at an intermediate state. The initial state (EF2) for this RS loop was chosen within the fast transition from $R_{\text{HI}}$ to $R_{\text{LO}}$. The reason for the observed large RS response is that within the transition regime the vacancies are more prone to diffuse by the action of the applied electric field. In saturated states, in contrast, the vacancies have all found “deep” trapping sites, which are, in fact, the origin of the nonzero threshold values.\(^{16}\)

The behavior revealed by our study clearly identifies the optimal electroforming procedure. One should not simply pole the system to saturation. Instead, one should first pole it to saturation, then invert the polarity, and increase the electric stress until the fast change in the interface resistance is observed. More specifically, the following prescription for an optimal procedure may be defined: the interface is initially poled to saturation with a given polarity and the interface resistance is recorded, then the polarity is inverted and the system is again brought to saturation, and the new resistance state is recorded. Then, the polarity is again inverted and the stress is increased by successive steps until an intermediate value of the resistance, say the average $(R_{\text{HI}}+R_{\text{LO}})/2$, is attained. Note that in our current experimental setup there are two rather symmetric interfaces that were measured independently and allowed our systematic study. However, the simplest practical setup to adopt is a strongly asymmetric two-terminal one, with one highly resistive interface that dominates the total RS response.\(^{14}\) This may be obtained with electrodes of different metals, one Ohmic and the other more resistive, of Schottky type.

In conclusion, we implemented a procedure to study the effect of electroforming in TMO memory devices. We rationalized the behavior in terms of a major and a minor loop for the EF and the RS responses, respectively. This allowed us to understand the seemingly paradoxical result where strong same-polarity electroforming stress does not lead to optimal RS response, and may even lead to no response at all. Our systematic study identified the fast transitions between saturated states as the situations where optimal RS may be obtained. Our work is a contribution to the understanding of the seldom addressed and ill-understood issue of electroforming in conducting TMO. With our gained insight we proposed a simple practical procedure for nearly optimal electroforming of bipolar oxide memory devices.

We acknowledge A. Sawa, M. J. Sánchez, C. Acha, and R. Waser for insightful comments, and support from PIP-0047, CONICET-DuPont “MeMOSAT,” and the ANR projects “Nanomott” and “Oxitronics”. MJR and PL are members of Conicet.