Resistive switching and resonant tunneling in epitaxial perovskite tunnel barriers

Junwoo Son and Susanne Stemmer*
Materials Department, University of California, Santa Barbara, California 93106-5050, USA
(Received 21 May 2009; published 2 July 2009)

We report on the relationship between resonant tunneling, resistive switching, and memory phenomena in tunnel junctions with epitaxial $SrTiO_3$ barriers. Opening and closing of tunneling channels in these barriers are correlated with resonant tunneling from a specific defect that can be eliminated by oxygen annealing. Furthermore, strong coupling of the tunneling electrons with this specific localized state or vibrational mode is responsible for bistable switching, a memory effect, and negative differential resistance. The results impact the interpretation of a wide range of transport phenomena in high-permittivity thin films in metal/insulator/metal structures.

DOI: 10.1103/PhysRevB.80.035105 PACS number(s): 73.40.Gk, 73.40.Rw, 77.55.+f

I. INTRODUCTION

Nonvolatile, bistable resistive switching phenomena have been reported for material systems as diverse as molecular junctions[1] and metal/insulator/metal (MIM) structures with transition-metal oxides[2–6] and have generated considerable interest for memory devices. Many different mechanisms can be conceived that could give rise to bistable resistive switching, including ionic motion under an electric field,[2,6] charge trapping,[7] strong correlations,[8] polarons,[9] and ferroelectric switching.[10,11] Most experimental studies are, however, plagued by lack of evidence for a specific mechanism. In real systems, many different processes, such as emission over Schottky barriers, bulk-trap-induced currents, tunneling and strongly correlated phenomena, often occur in parallel, which makes it difficult to identify which of these play a role in resistive switching. Tunnel junctions can offer unique insights into electrical transport phenomena. In particular, deviations from the ideal tunneling behavior provide information about localized defect states, collective excitations, and even ferroelectricity,[11–14] all of which have been suggested as possible causes for resistive switching in metal-oxide films.

Complex oxides, in particular, the perovskites, are among the leading candidates for resistive switching memories.[2,3,10,15] In this paper, we fabricate tunnel junctions using a model perovskite oxide, $SrTiO_3$, as the barrier. We demonstrate that conductance switching in these barriers is directly correlated with resonant tunneling, closely resembling mechanisms that have to date only been reported for molecular junctions. Furthermore, we show that resonant tunneling gives rise to a memory effect and a metal-insulator transition, and is thus likely also the cause of the very similar phenomena that have been reported in thicker MIM structures with perovskite oxides.

II. EXPERIMENTAL

The experimental details to obtain high-quality, epitaxial tunnel $SrTiO_3$ barriers on epitaxial Pt electrodes on (001) $SrTiO_3$ substrates by rf magnetron sputtering have been reported previously.[16] The $SrTiO_3$ barriers in this study were 4–5 nm in thickness. For selected samples, an oxygen anneal was carried out at 700 °C for 10 min prior to tunnel device fabrication. Circular tunnel junctions with radii between 3 and 5 μm and Pt top electrodes were fabricated using a four-mask process.[16,17] Temperature-dependent current-voltage (*I*-*V*) characteristics down to liquid-helium temperature (5 K) were measured using a physical property measurement system (PPMS, Quantum design, San Diego, CA). The junctions were contacted using Au-wire bonding and the voltage across the tunnel barrier was measured as a function of temperature while the dc current was ramped up (or down). Additional room-temperature measurements were made with a voltage source using a semiconductor parameter analyzer (HP 4155B, Agilent Technologies, Santa Clara, California).

III. RESULTS AND DISCUSSION

Figure 1 shows the *I*-*V* characteristics of the tunnel barriers (no oxygen anneal) as a function of temperature for sweeps to three different current limits, $|I_{max}|$. For sweeps within low-current limits ($|I_{max}| \leq 2$ mA), the *I*-*V* characteristics were nonlinear, displayed no hysteresis and the barrier resistance decreased slightly with increasing temperature, characteristic for a tunnel barrier with good insulating properties [Fig. 1(a)]. For sweeps within intermediate-current limits, $|I_{max}| = 5$ mA [Fig. 1(b)], hysteretic *I*-*V* behavior was observed near liquid-helium temperatures. If $|I_{max}|$ was increased up to 15 mA [Fig. 1(c)], *I*-*V* hysteresis was observed at all temperatures, though the magnitude of the hysteresis was larger at low temperatures. A steplike (~60% at 5 K) increase in current around 0.4 V caused the change from a high-resistance state to a low-resistance state. Doubling the delay time from 2 to 4 ms did not affect the threshold voltage. In the decreasing sweeps, a large negative voltage (below −0.4 V) caused the slope of the *I*-*V* curve to decrease with further increase in voltage, returning the junction into the high-resistance state. Some devices even showed negative differential resistance (NDR), as shown in Fig. 2. The hysteresis was reproducible, reversible, and nonvolatile: Fig. 2 shows that the junction remains in a high-resistance state in sweeps after application of a large negative bias as long as the junction was not biased again to a large positive voltage.

The origin of the tunneling anomalies can be seen more readily in the calculated dynamic conductance (dI/dV vs V)

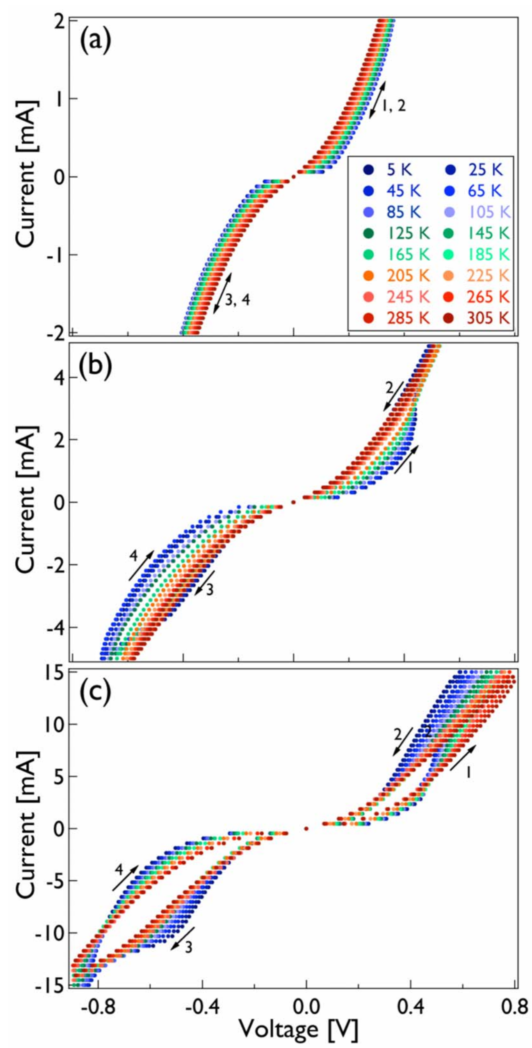

FIG. 1. (Color online) Current-voltage characteristics (double sweep) of $Pt/SrTiO_3/Pt$ tunnel junctions from 5 to 305 K for three different maximum current limits of (a) ± 2, (b) ± 5, and (c) ± 15 mA. The data points for the two-sweep directions overlap in (a). As indicated by arrows and numbers, the current source was swept from 0 to $+|I_{max}|$, followed by a sweep in the reverse direction to $-|I_{max}|$ and back to 0 (the hysteresis did not depend on the sweep direction or starting point). The tunnel junction radius was 5 μm.

plots shown in Figs. 3(a) and 3(b) as a function of temperature for the sweeps to ± 5 mA. At voltages greater than $\sim|0.2 \text{ V}|$ deviation from the parabolic shape reflected the onset of Fowler-Nordheim tunneling. Furthermore, a sharp peak was observed around the threshold voltage for resistive switching in the increasing sweep (0.43 V). The conductance showed a dip at high negative bias around -0.5 V below 145 K in the decreasing sweep [Fig. 3(b)]. The peak (dip) amplitude was larger at lower temperatures. While the peak position was almost independent of temperature, the peak decreased in height and broadened with increasing temperature. These characteristics are typical for resonant tunneling.[12,14,18,19] In particular, in contrast to hopping conduction, resonant tunneling is most pronounced at low

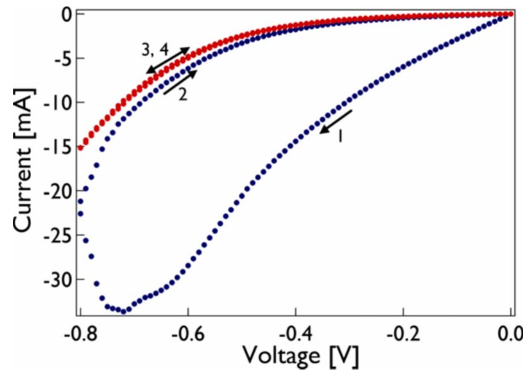

FIG. 2. (Color online) Room-temperature sweeps for a different device using a voltage source between 0 to -0.8 V showing a memory effect and NDR.

temperatures,[12,14] similar to what is observed here. Elastic resonant tunneling occurs when the Fermi level of the electrode coincides with the energy level of a localized state in the barrier, causing the tunneling current to become resonantly enhanced, which results in a peak in the conductance. In inelastic resonant tunneling the tunneling electrons resonantly excite phonon modes.

With respect to the specific defect level or vibrational mode giving rise to resonant tunneling in the $SrTiO_3$ junctions, Fig. 4 shows room-temperature *I-V* characteristics to ± 1 V for oxygen-annealed junctions. The tunneling current was reduced by several orders of magnitude and the junctions showed almost no *I-V* hysteresis. Thus, resonant tunneling in these junctions is associated with a defect or impu-

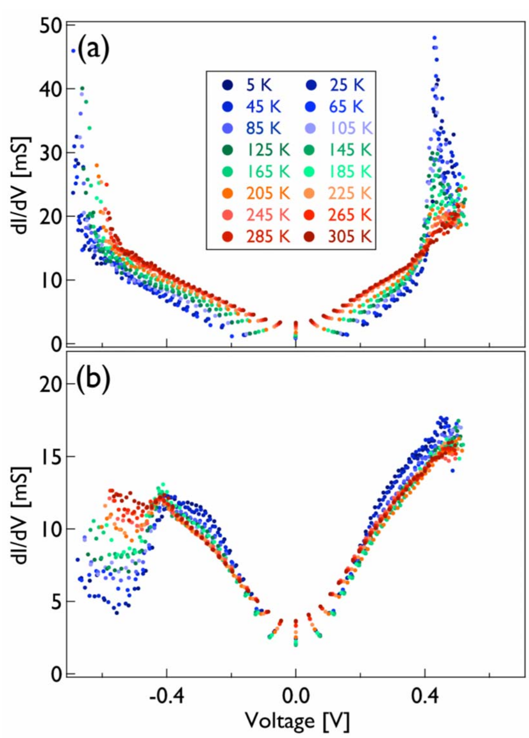

FIG. 3. (Color online) Dynamic conductance (dI/dV), calculated from Fig. 1(b) as a function of voltage and temperature for (a) the increasing sweep and (b) the decreasing sweep.

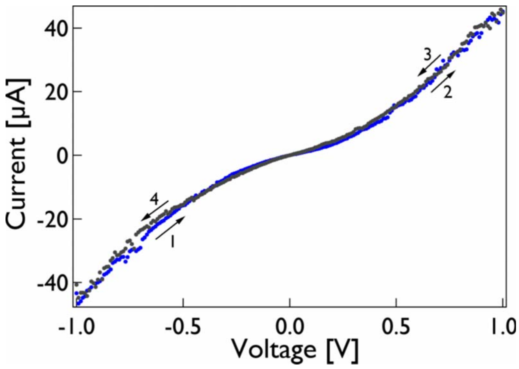

FIG. 4. (Color online) Current-voltage characteristics of an oxygen-annealed tunnel junction between ± 1 V (voltage sweep at room temperature). The sweep direction (arrows) and sequence (numbers) are indicated.

rity that is removed by oxygen anneals. Likely candidates are oxygen vacancies, a transition-metal impurity that changes its valence state upon oxygen annealing[20] or OH vibrational modes. Interestingly, the ~0.43 V threshold is similar to the energy of the OH stretching mode in $SrTiO_3$,[21] which can be removed by oxygen anneals.[20]

Before discussing the relationship between resonant tunneling and resistive switching, two features should be noted. First, the tunnel conductance has a single peak, in contrast to multiple peaks often observed in elastic resonant tunneling.[12,18,19] It is unlikely that the $SrTiO_3$ barriers only contain only a single trap level. Thus this behavior is indicative of either a very large Coulomb energy that needs to be supplied by the applied voltage before resonant tunneling can occur[14] or inelastic resonance tunneling. Second, the barrier resistance changes from insulating at low to intermediate currents to metalliclike at the highest currents, as shown in Fig. 5. The barrier resistance increases with temperature at high currents (or bias) opposite to what is expected for ideal tunnel junctions. Although field-induced metal-insulator transitions have recently been reported for $SrTiO_3$ channels in field-effect geometries,[22,23] it is likely that the origin of the observed transition in the tunnel junction resistance is connected to large resonant tunneling currents that start to dominate the current at low temperatures and large fields.[14]

Bipolar resistive switching has often been explained with migration of ions or oxygen vacancies under an electric field.[2,6,24] However, the results clearly show that this mechanism can be excluded as the origin of resistive switching because the *I-V* hysteresis increases at low temperatures, contrary to what would be expected for a thermally activated process. It is thus unlikely that electric-field-induced ion migration is the origin for resistive switching even in thicker films of related materials, given the large fields in this study. Rather, the results obtained here are evidence for a strong correlation between resonant tunneling and resistive switching; in particular, the critical voltage for resistive switching and the magnitude of the hysteresis are strongly correlated with the magnitude and position of the conductance peaks (dips). Resonant tunneling can give rise to resistive switching via a feedback mechanism. In molecular junctions, it has been proposed that hysteresis occurs via polaron formation

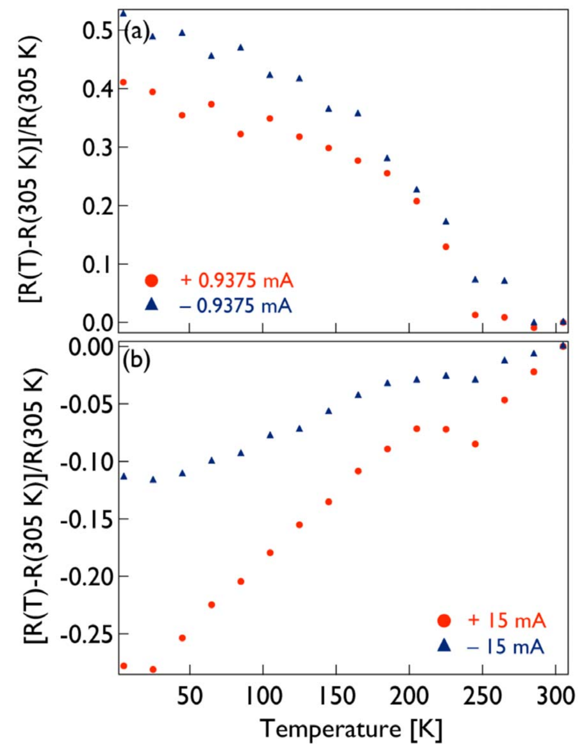

FIG. 5. (Color online) Resistance ratios, $R(T) - R(305\text{ K})/R(305\text{ K})$, where $R(305\text{ K})$ is the resistance at 305 K and $R(T)$ is the resistance at the temperature T, as a function of temperature at (a) low currents (± 0.9375 mA) and (b) at high current (± 15 mA), calculated from Fig. 1(c).

that shifts the resonant energy level.[9] Similarly, charging and decharging of trap levels can produce resistive switching by either shifting the energy of the defect level and/or the tunnel barrier height. The barrier height can change due to charge localization and image potential[25] and the resonant level can shift for a variety of reasons, including Coulomb interactions.[26] As reported previously, a change in barrier height was indeed observed after applications of a large bias.[16] In each case, long-lived electronic states and asymmetric interactions with the electrodes are a prerequisite for both the switching and the memory effect. Note that despite the symmetric device structure, the bottom and top electrodes were deposited differently and exposed to different conditions. Modeling of the resistive switching will likely require accounting for many-body effects, strong correlations, and electrostrictive effects.

IV. CONCLUSIONS

In summary, we have shown that even for temperatures as high as room temperature, resonant tunneling can control resistance switching and memory characteristics of perovskite tunnel barriers such as $SrTiO_3$. The results have important consequences also for thicker perovskite films in MIM structures. In particular, depending on field and defect densities, the electrical transport in MIM structures is often controlled by Fowler-Nordheim tunneling, so that essentially the same mechanisms that give rise to resistive switching and memory effects in the tunnel barriers will also be active in these structures. Furthermore, high leakage and dielectric loss have to date limited the application of perovskite oxides in many applications that could make use of their unique properties, such as ferroelectricity or field-tunable dielectric constants. Resonant tunneling will strongly enhance losses (essentially contributing to series resistance) (Ref. 27) and leakage, and thus will need to be taken into account in the interpretation of the conduction properties of high-permittivity thin films. It is likely that strong resonant tunneling phenomena will be discovered in other complex oxide thin films.

ACKNOWLEDGMENTS

The authors thank the DOE Office of Basic Energy Sciences (Grant No. DE-FG02-06ER45994) and NSF (Grants No. DMR-0602244 and No. CCF-0507227) for support of this research. We thank Hisashi Masui and Brent Melot for help with the wire-bonding and PPMS measurements, Joël Cagnon for TEM of selected samples, and Tae-Yeon Seong for valuable discussions. This work made use of the UCSB Nanofabrication Facility, a part of the NSF-funded NNIN network, and the MRL Central facilities supported by the MRSEC Program of the National Science Foundation under Award No. DMR 05-20415.

*stemmer@mrl.ucsb.edu

[1] C. Joachim and M. A. Ratner, Proc. Natl. Acad. Sci. U.S.A. **102**, 8801 (2005).
[2] R. Waser and M. Aono, Nature Mater. **6**, 833 (2007).
[3] A. Beck, J. G. Bednorz, C. Gerber, C. Rossel, and D. Widmer, Appl. Phys. Lett. **77**, 139 (2000).
[4] K. Szot, W. Speier, G. Bihlmayer, and R. Waser, Nature Mater. **5**, 312 (2006).
[5] M. J. Rozenberg, I. H. Inoue, and M. J. Sanchez, Phys. Rev. Lett. **92**, 178302 (2004).
[6] D. B. Strukov, G. S. Snider, D. R. Stewart, and R. S. Williams, Nature (London) **453**, 80 (2008).
[7] J. G. Simmons and R. R. Verderber, Proc. R. Soc. London, Ser.A **301**, 77 (1967).
[8] M. J. Rozenberg, I. H. Inoue, and M. J. Sanchez, Appl. Phys. Lett. **88**, 033510 (2006).
[9] M. Galperin, M. A. Ratner, and A. Nitzan, Nano Lett. **5**, 125 (2005).
[10] P. W. M. Blom, R. M. Wolf, J. F. M. Cillessen, and M. P. C. M. Krijn, Phys. Rev. Lett. **73**, 2107 (1994).
[11] E. Y. Tsymbal and H. Kohlstedt, Science **313**, 181 (2006).
[12] L. Esaki, P. J. Stiles, and L. L. Chang, Phys. Rev. Lett. **20**, 1108 (1968).
[13] J. Lambe and R. C. Jaklevic, Phys. Rev. **165**, 821 (1968).
[14] J. Halbritter, Surf. Sci. **122**, 80 (1982).
[15] Y. Watanabe, J. G. Bednorz, A. Bietsch, C. Gerber, D. Widmer, A. Beck, and S. J. Wind, Appl. Phys. Lett. **78**, 3738 (2001).
[16] J. Son, J. Cagnon, and S. Stemmer, Appl. Phys. Lett. **94**, 062903 (2009).
[17] J. Son, J. Cagnon, D. S. Boesch, and S. Stemmer, Appl. Phys. Express **1**, 061603 (2008).
[18] A. B. Fowler, G. L. Timp, J. J. Wainer, and R. A. Webb, Phys. Rev. Lett. **57**, 138 (1986).
[19] S. J. Bending and M. R. Beasley, Phys. Rev. Lett. **55**, 324 (1985).
[20] B. Jalan, R. Engel-Herbert, T. E. Mates, and S. Stemmer, Appl. Phys. Lett. **93**, 052907 (2008).
[21] D. Houde, Y. Lepine, C. Pepin, S. Jandl, and J. L. Brebner, Phys. Rev. B **35**, 4948 (1987).
[22] K. Shibuya, T. Ohnishi, T. Sato, and M. Lippmaa, J. Appl. Phys. **102**, 083713 (2007).
[23] K. Ueno, S. Nakamura, H. Shimotani, A. Ohtomo, N. Kimura, T. Nojima, H. Aoki, Y. Iwasa, and M. Kawasaki, Nature Mater. **7**, 855 (2008).
[24] A. Sawa, Mater. Today **11**, 28 (2008).
[25] J. Halbritter, J. Appl. Phys. **58**, 1320 (1985).
[26] A. B. Fowler, J. J. Wainer, and R. A. Webb, IBM J. Res. Dev. **32**, 372 (1988).
[27] J. Halbritter, IEEE Trans. Magn. **17**, 943 (1981).