Resistive switching and data reliability of epitaxial $(Ba,Sr)TiO_3$ thin films

R. Oligschlaeger[a] and R. Waser
Institut für Werkstoffe der Elektrotechnik, RWTH Aachen, 52074 Aachen, Germany

R. Meyer, S. Karthäuser, and R. Dittmann
CNI, FZ Juelich, 52425 Juelich, Germany

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We report on resistive switching of capacitor-like $SrRuO_3/Ba_{0.7}Sr_{0.3}TiO_3/Pt$ thin films epitaxially grown on $SrTiO_3$ substrates. We observe a weak but stable hysteresis in the current-voltage curve. By applying short voltage pulses, a high or low resistive state as well as intermediate states can be addressed even at room temperature. We demonstrate a multiple-branch hysteresis curve corresponding to multilevel switching modus revealing different subloops for different write voltages. Furthermore reliability issues such as cycling endurance and data retention are presented. Read-write operations over 10 000 cycles show a fatigue-like drift of both resistance states. No data loss is found upon continuous readout. © *2006 American Institute of Physics*.
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Many different material systems such as oxides,[1–4] organic materials,[5,6] semiconductors[7,8] show bistable switching of resistivity. This effect is of a great interest for future nonvolatile memories. For scalability reasons, resistive information storage concepts have the higher potential compared to charge based storage concepts.[9] Recently, dielectric perovskite type oxides (ABO_3) have attracted increasing attention as candidates for resistive information storage.[10–12] Multilevel storage was demonstrated for Cr-doped $SrZrO_3$ structures.[10] Here, different resistance levels could be addressed by a variation of length and amplitude of the programming voltage pulse. There is still some debate about the physical mechanisms of the resistance change and about the key experimental parameters. Mechanisms under discussion are (i) trapping/detrapping effects and charge transfer processes via donor and acceptor levels (Cr^{3+}/Cr^{4+}),[10,13] (ii) a Mott metal-insulator transition,[14] (iii) formation of local current domains,[12] (iv) redox processes of extended defects,[15] and (v) conductivity changes due to a reversal of a local spontaneous polarization.[16] Polarization changes might not be stringently of ferroelectric nature, but might also be due to defect dipoles, e.g., formed by acceptor/oxygen vacancy defect associates.[17]

In our present work, we investigate resistive switching of 0.2% chromium-doped $Ba_{0.7}Sr_{0.3}TiO_3$ (BST) capacitor-like thin films of around 40 nm thickness at RT. We investigate in detail multibranch type $I(V)$ curves, which have not been reported for perovskites dielectrics so far. We will present detailed measurements of the multilevel switching and focus on reliability issues such as cycling endurance and data retention.

$SrRuO_3$ (SRO) bottom electrodes of 100 nm thickness and BST layer of 40 nm thickness are grown *in situ* epitaxially on single crystalline (100) oriented $SrTiO_3$ (STO) substrates. The films are deposited by pulsed laser ablation while maintaining a substrate temperatur of 700 °C and an oxygen base pressure of 0.25 mbar. The epitaxial growth of the bilayers is confirmed by x-ray diffraction measurements [Philips PW 3020 (Cu $K\alpha$)]. Pt top electrodes are deposited by sputtering and patterned by optical lithography and a lift-off process to areas of 0.09 mm^2 down to 100 μm^2. The bottom electrode is contacted after removing the BST film from the sample edge by wet chemical etching. A postannealing step in oxygen is performed at 700 °C for 5 min. The current-voltage characteristics are measured with a Keithley 2410 source meter. To protect samples from damages due to high currents a current compliance is used. All samples reveal low initial resistances so that a high voltage treatment prior to quasistatic $I(V)$ characterization or pulse measurements to convert the sample from an insulating state into a low conductive state as described in Ref. 11 for $SrTiO_3$ single crystals ("forming process") is not required here. The stable switching behavior reported in this paper is found in approximately 40% of the pads. The other pads show fast resistance degradation and shorts after a few $I(V)$ loops or show no switching at all.

Figure 1(a) displays the quasistatic measurement of the hysteretic $I(V)$ characteristic between +6.0 and −6.0 V obtained at room temperature for ten subsequent cycles with a frequency of 25 mHz. The current compliance is set to 10 mA corresponding to an effective current density of 25 A/cm^2 for a pad size of 0.04 mm^2. The sample starts in the low resistance state when sweeping the voltage from zero to positive values (1). In the subsequent voltage sweep from positive to negative voltages [(2)–(3)], the sample shows an increased resistance. At negative voltage the sample resistance switches back from a high to a low resistive state (4). In the branch from zero to positive values (1) the virgin sample shows a slightly higher resistance than obtained in the subsequent cycles. The high and low current curves cross at zero voltage. The hysteresis at positive voltages is more pronounced than at negative voltages. The $I(V)$ characteristic shows a high asymmetry, which can be attributed to our asymmetric metal-insulator-metal structure. The maximum resistance change (R_{High}/R_{Low}) is about 5. In contrast to hysteretic $I(V)$ curves with abrupt resistance changes, reported in Ref. 10, a less distinctive resistance change is observed here.

On samples with stable $I(V)$ characteristic, switching in pulse mode is studied to demonstrate two level and multi-

[a]Electronic mail: oligschlaeger@iwe.rwth-aachen.de

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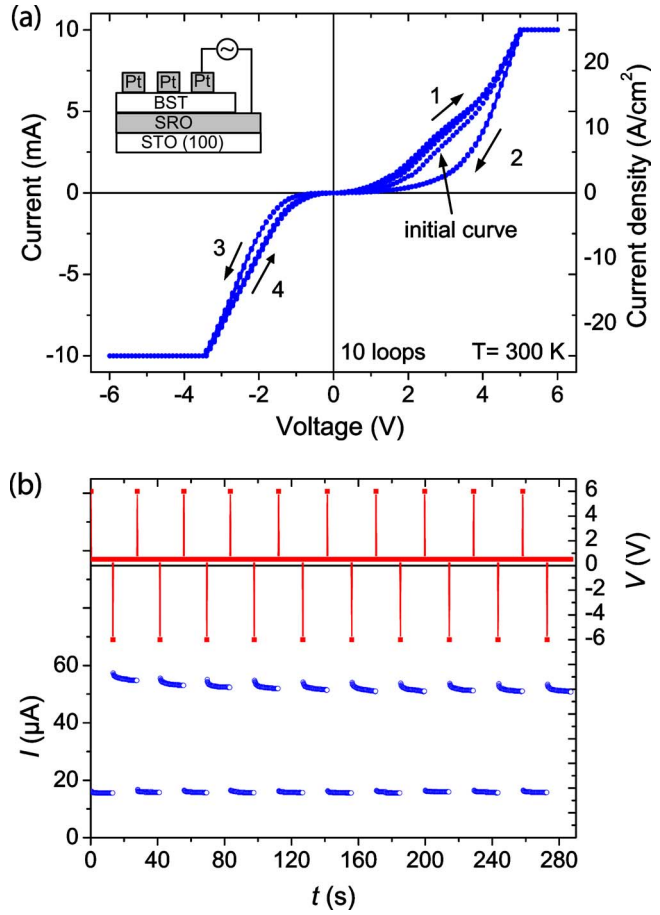

FIG. 1. (Color online) (a) $I(V)$ characteristics of a Pt/BST/SRO/STO (001) structure. Ten voltage sweeps with an amplitude of 6 V and 0.1 V/s at RT. Arrows show the sweep direction of the applied voltage. The current compliance is set to 10 mA. Electrode area is 0.04 mm^2. (b) Two state switching performance at RT. Applied voltage vs time (upper curve); readout current vs time (lower curve).

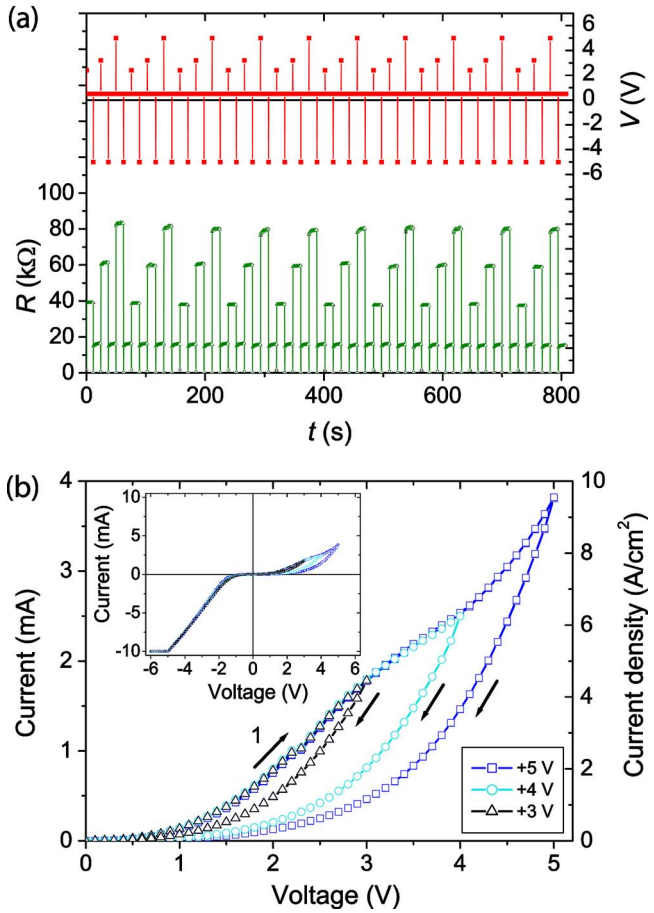

FIG. 2. (Color online) (a) Two-bit multistate resistive information storage of a Pt/BST/SRO/STO (001) structure at RT. Programming voltages for multi level switching: 2.4, 3.3, 5.0 V; erase voltage: −5.0 V. (b) $I(V)$ characteristics showing different subloops for different write voltages.

level data storage at room temperature. Results are illustrated in Fig. 1(b) (one bit) and Fig. 2(a) (two bit). Employing a positive voltage pulse of +6.0 V for 0.2 s switches the system into a high impedance state. After applying a negative pulse of −6.0 V for 0.2 s the low impedance state is recovered. Between these write and erase pulses the state is readout with 0.5 V continuously over 10 s. Employing write pulses of intermediate amplitudes allow to address different low impedance states. Different impedance states can only be set, if the programming voltage is in the window corresponding to the hysteresis in the $I(V)$ curve. Four stable equidistant impedance levels are obtained by applying 0.2 s long voltage write pulses of 2.4, 3.3, and 5.0 V and an erase pulse of −5.0 V, respectively. If the programming voltage is further increased (e.g., from 5.0 to 6.0 V), no additional resistance change is found. In Fig. 2(b) the $I(V)$ curves corresponding to multilevel switching modus are shown. Starting from negative erase voltages the voltage is raised to different write voltages resulting in different subloops. Even though for other materials different types of $I(V)$ curves have been reported,[4,10,18] in our case no threshold voltage V_{th} had to be reached to switch from R_{on} to a higher impedance state, this behavior has been shown recently for SRO, too.[19] To explain multilevel switching one has to take a nonuniform distribution of trapped charges into account, which can be altered by applying voltage in forward or reverse directions. One possible explanation of the observed switching mechanism is the formation of filaments which can undergo transitions between different resistive states by a certain voltage treatment.

Reliability of the stored resistance state is studied for once write-erase/continuous readout and for cyclic write/erase operation. Figure 3 displays the time dependence of the current corresponding to the high and the low resistive states, which show an exponential decrease especially after switching to the high resistance state. The relaxation time of several

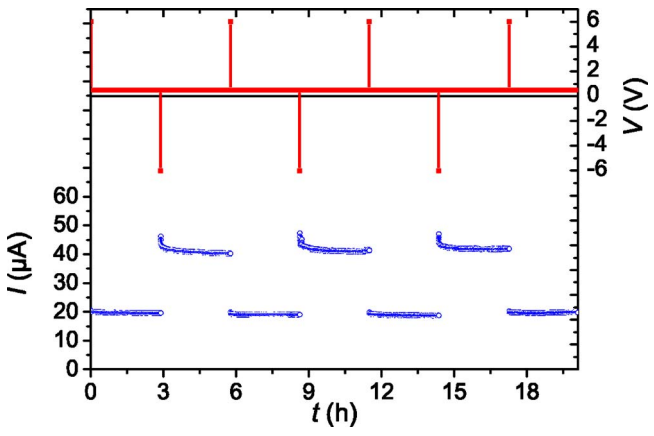

FIG. 3. (Color online) Demonstration of nonvolatile data readout in a write once/continuous read and an erase once/continuous read operation. Write/erase pulse time: 0.2 s. Readout time: 10^4 s.

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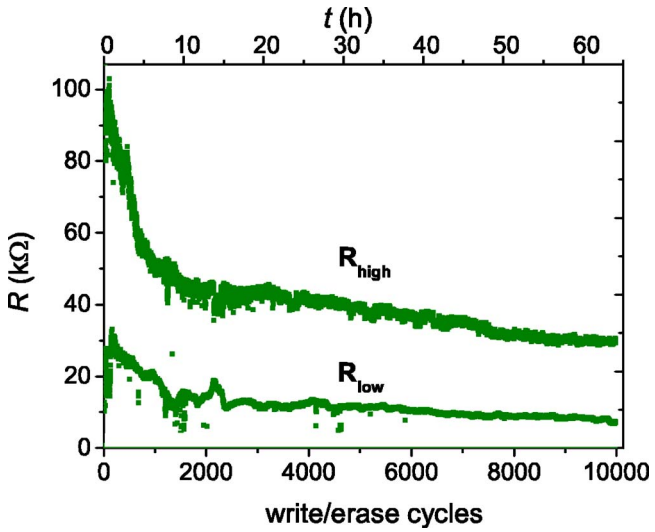

FIG. 4. (Color online) Switching reliability of a Pt/BST/SRO/STO (001) device for a "write-read-erase–read" sequence of 10000 cycles. Write/erase voltage: 6 V/−6 V.

hours, again suggests a participation of slow solid state electrochemical processes. Measurements show that both states are stable for at least 10^4 s at RT. Write/erase endurance measurements demonstrate switching over 10^4 cycles. Figure 4 shows a typical decrease of the resistance in both states. In order to determine the charge transport mechanism the temperature dependence of the current in both impedance states was measured. The current in both states (R_{on} and R_{off}) is found to be thermally activated with activation energies of 0.19 and 0.22 eV, respectively. These findings together with the nonlinear *I-V* curves indicate a thermally activated hopping between isolated states as the dominating mechanism for conduction in both states. No metallic behavior is seen analogous to Cr-doped $SrZrO_3$ reported in Ref. 10.

The question remains, whether one cause of resistive switching could be the existence of ferroelectricity in BST epitaxially grown on SRO/STO substrates. A tetragonal distortion of the unit cell even at room temperature originates from the lattice mismatch between substrate and film resulting in a compressive strain of the BST film.[20] To examine the influence of ferroelectricity on the resistive switching we investigated the temperature dependence of switching behavior up to 180 °C. Resistive switching is observed in BST thin layers (40 nm) below and above the ferroelectric-to-paraelectric transition assumed to be at 60 °C,[20] indicating a switching behavior independent from any ferroelectric lattice transition.

Measurements of the current densities as a function of the contact areas show a nonuniform current distribution, which can be attributed to a possible local mechanism. It is likely, that local current domains are built and attenuated resulting in the observable switching effect, when the voltage is varied.

In conclusion, we have demonstrated stable two-level and multilevel switching of epitaxially grown BST thin films at room temperature. Electrical measurements show a weak but stable hysteretic behavior in the current-voltage relation and no forming process was needed. Multiple-branch $I(V)$ curves corresponding to multilevel switching modus, revealing different subloops for different write voltages, are shown. Reliability studies for once write/continuous read operation and write/erase endurance are presented. It is shown that the stored resistance state is rather stable and can be well reproduced. Write/ erase operations over 10 000 cycles exhibit some decay in both the high and the low resistive state. Measurements by varying the temperature show for both impedance states no metallic behavior. Since switching is observed above the ferroelectric phase transition temperature, ferroelectricity can be ruled out as switching mechanism, while the building and dissolution of current domains (e.g., filaments) is a possible mechanism.

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