Reproducible switching effect in thin oxide films for memory applications

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(Received 13 March 2000; accepted for publication 15 May 2000)

Thin oxide films with perovskite or related structures and with transition metal doping show a reproducible switching in the leakage current with a memory effect. Positive or negative voltage pulses can switch the resistance of the oxide films between a low- and a high-impedance state in times shorter than 100 ns. The ratio between these two states is typically about 20 but can exceed six orders of magnitude. Once a low-impedance state has been achieved it persists without a power connection for months, demonstrating the feasibility of nonvolatile memory elements. Even multiple levels can be addressed to store two bits in such a simple capacitor-like structure. © *2000 American Institute of Physics.* [S0003-6951(00)04327-8]

Ever since the observation of switching processes in thin films of amorphous chalcogenide semiconductors,[1,2] amorphous Si, conducting polymers,[3] and of ZnSe–Ge heterostructures,[4] these materials have been proposed as potential candidates for nonvolatile memories. Bistable switching and voltage-controlled negative resistance phenomena were also reported for a variety of oxides such as Nb_2O_5,[5] Al_2O_3,[6] Ta_2O_5,[7] TiO_2,[8] and NiO,[9,10] but research on binary and ternary oxides for microelectronics devices has mainly focused on stress-induced leakage currents, breakdown, and dielectric dispersion effects. Due to their high dielectric constant ε, such oxides are investigated for their application in dynamic random access memories (DRAMs) or as gate insulators. Even in nominally pure films, significant leakage currents can occur in the presence of uncompensated charges due to intrinsic defects such as impurities or vacancies. Leakage can be reduced by compensation doping with transition metal (TM) elements such as Mn (Ref. 11) or Cr.[12] Whereas this compensation process has not yet been sufficiently investigated, the electronic character of TM impurities and of impurity-oxygen vacancy centers has been intensively studied by electron spin resonance (ESR).[13,14] Charge transfer and trapping processes have been identified in combination with optical absorption[15,16] and photocurrent experiments.[17] The latter, which describe memory effects in $SrTiO_3$ in the presence of Cr and Fe impurities, imply that similar charge transfer processes could be relevant for the switching and memory behavior in other compounds, at least in crystallized form. These bulk electronic mechanisms include such processes as field and impact ionization of traps,[4] whereas in chalcogenide semiconductors they involve amorphous-crystalline phase changes. Analogous memory effects in the leakage current of ferroelectric $BaTiO_3$ or $(Pb_{1-y}La_y)\times(Zr_{1-x}Ti_x)O_3$-based heterostructures were also reported and discussed in terms of band bending due to spontaneous polarization switching.[18,19]

We have investigated metal-insulator-metal (MIM) capacitor-like structures with areas of between 4×10^4 and $80\ \mu m^2$ and insulator thicknesses between 300 and 20 nm. Oxides prepared as insulator films are $(Ba,Sr)TiO_3$, $SrZrO_3$, $SrTiO_3$, $Ca_2Nb_2O_7$, and Ta_2O_5 doped with up to 0.2% Cr or V. In the following we restrict our discussion to $SrZrO_3$. The base electrode of the MIM structure is either an epitaxial $SrRuO_3$ film grown by pulsed laser deposition (PLD) on a $SrTiO_3$ (100) substrate or a Pt film grown by electron-beam evaporation. The insulating oxide was deposited *in situ* by PLD at two different temperatures, 700 and 300 °C, to grow an epitaxial or polycrystalline film, respectively. The top electrodes of Au or Pt with a Ti adhesion layer were sputtered and patterned by a lift-off process. Hard-baked photoresist was used as a protective top layer. The resistance of the MIM structures ranges typically between 100 kΩ and 100 MΩ. At equivalent thicknesses, polycrystalline oxide films had a greater resistance than epitaxial films due to the larger density of microstructural defects. The average surface roughness of the epitaxial oxide films ranges between 0.1 and 3 nm, as measured by atomic force microscopy over a $25\ \mu m^2$ area.

A typical current-voltage ($I-V$) characteristic of a 300-nm-thick $SrZrO_3$ film doped with 0.2% Cr and sandwiched between a $SrRuO_3$ bottom electrode and a Au top electrode is shown in Fig. 1 on a linear scale. The $I-V$ characteristic was recorded in the voltage control mode.

By sweeping the voltage V to negative values (with respect to the bottom electrode) at a rate of 0.2 V/min, the leakage current suddenly increases by one order of magnitude at -0.5 V and switches the oxide to a low-impedance state. Subsequently sweeping the voltage back to positive values leads to a sudden decrease of the leakage current and thereby restores the resistance of the oxide to its initial value. Hence switching behavior leads to a pronounced hysteretic $I-V$ characteristic with two different impedance states. This intrinsic memory effect is stable within ±0.5 V. The cutoff at large negative current in Fig. 1(a) is due to imposed compliance on the current source to prevent sample damage. The same $I-V$ characteristic is shown also as a semilogarithmic plot [Fig. 1(b)], and its positive branch as a log-log plot [Fig. 1(c)]. Interestingly, the ratio between the low- and high-impedance states appears almost constant. Both in the high- and low-impedance states the $I-V$ characteristic follows a linear ohmic behavior at low voltage with the addition of a quadratic term at higher voltage, $I(V)=aV+bV^2$. This volt-

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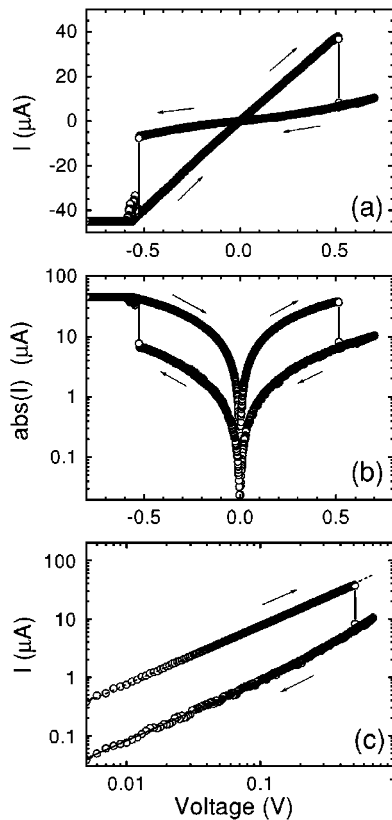

FIG. 1. Current-voltage characteristics of a 300-nm-thick epitaxial $SrZrO_3$ film doped with 0.2% Cr grown on a $SrRuO_3$ bottom electrode. The top Au electrode is $200\times200\ \mu m^2$. (a) Linear scale, (b) semilog scale, (c) log-log scale.

age dependence is typical of an insulator with shallow traps and space-charge-limited current injection.[20] The factor a in the low-impedance state is one order of magnitude greater than in the high-impedance state. In these two states the current measured at 0.2 V is found to be thermally activated with respective activation energies of 30 and 10 meV. This suggests that the carrier transport is of the same nature in both states, and that no metallic filaments are involved.

The switching operation of a Cr-doped $SrZrO_3$ device in the pulse mode is illustrated in Fig. 2. A negative voltage pulse of 2 ms switches the system into the low-impedance state. After applying a positive voltage pulse of 2 ms, the ''information'' written to the device is erased and the high-impedance state is recovered. Between each write and erase pulse the state is read every second for 1 min with 200 mV pulses of 2 ms duration. This switching behavior, which can be repeated reproducibly for longer periods, demonstrates the potential of such a simple capacitor-like structure to act as nonvolatile random access memory. In this example the write and erase voltages of ±1.1 V are fairly small compared to those currently used in ferroelectric and FLASH memories and within the range of operation required in the future generations of microelectronic circuits. Faster switching speeds, i.e., shorter write and erase pulses as used here, are also possible but require higher voltage amplitudes. So far the fastest reproducible switching could be achieved with 100 ns write/erase pulses at an amplitude of ±5 V. In our experiments the switching speed is limited mainly by the relatively large capacitance of our not yet miniaturized test structures but not by the switching effect itself. The speed of the memory state readout, done at low voltages, is independent of the switching process and thus limited only by the measurement setup.

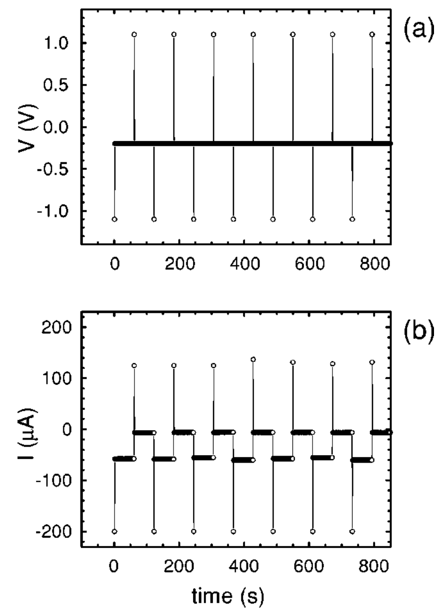

FIG. 2. Switching performance of a capacitor-like structure based on Cr-doped $SrZrO_3$. (a) Applied voltage vs time and (b) readout current vs time.

A relevant property of the memory cell is its ability to keep its information for longer times. We have performed a long-time retention test on the Cr-doped $SrZrO_3$ device and found little change over 10 months. After a sequence of switching with pulses of ±5 V, the device was electrically disconnected in the low-impedance state and then periodically reconnected in order to probe the leakage current with identical voltage parameters. The decay of the readout current after 10 months was found to be less than 1%, confirming the nonvolatile nature of the memory effect. Moreover, the readout of the device is nondestructive, and no electrical power is needed to maintain the memory cell in its given impedance state.

Another striking property is the observed multilevel switching. In the pulse operation mode, the actual value of the low-impedance (or high-current) state depends on the length and amplitude of the individual write pulses. Hence by changing these parameters, different low-impedance levels can be addressed, each corresponding to a specific state of the memory. This is illustrated in Fig. 3 with the example of a Cr-doped $SrZrO_3$-based MIM cell operated at 77 K.

By applying 1 ms voltage pulses of 6.5, 5.3, and 4.8 V, respectively, the memory can be set to three different high-current levels, denoted 1–3. After each write pulse, the reset to level 0 is done by a series of 30 erase pulses (1 ms, -6.5 V). Although more stable at low temperatures, the multilevel switching in our thin oxide layers is not restricted to low temperatures as was also frequently observed at 300 K. In order to generate the four equidistant impedance or current levels 0–3, the write pulses were tuned appropriately but, as seen in Fig. 3, their voltage levels are not necessarily equidistant. Noteworthy is that each low-impedance level can be moved individually by adjusting the amplitude of the corresponding write pulse. In our example, the existence of four distinct levels demonstrates that two bits of information

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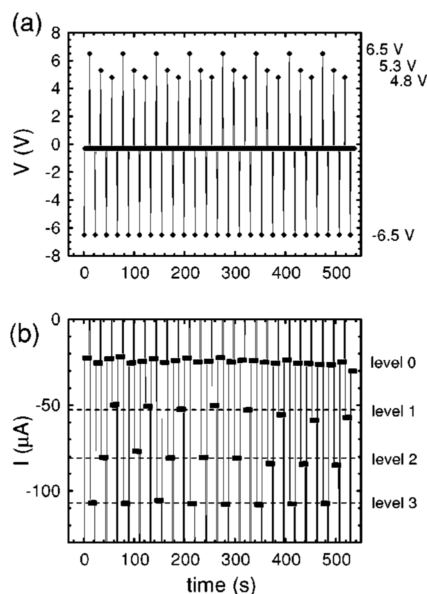

FIG. 3. Multilevel switching in a Cr-doped $SrZrO_3$-based MIM cell operated at 77 K.

can be stored in such a simple device. Nevertheless the operation of such a memory cell is not restricted to four levels; in principle more levels could be addressed.

We have demonstrated that the switching effect in epitaxially grown perovskites can be controlled to an adequate level required for memory applications. We rule out that a crystalline–amorphous phase transition is responsible for the switching from the low- to the high-impedance state. The reason is that in such oxide thin films the high-impedance state is fully crystalline. Moreover, as ferroelectricity is absent in the investigated compounds, its possible influence can be ruled out. From the roughness of the films, the presence of local defects, and the variation in their composition, one can expect an inhomogeneous flow of the current but metallic filaments will not occur in the low-impedance state. The switching observed also in a variety of nominally pure compounds seems to be a generic property of oxides in the presence of intrinsic defects. These defects consist partly of impurities having different oxidation states and vacancies (or combinations thereof), and can form a series of states at various levels within the energy gap. Charge-transfer processes via donor and acceptor levels (Cr^{3+} and Cr^{4+}) as studied by photocurrent and luminescence[17] measurements appear to be a plausible mechanism for carrier creation and transport within the insulator. At impurity concentrations of $10^{16}/cm^3$, memory effects were observed in these experiments as well. For the resistive memory effect, which has been stabilized in our case by high doping levels (typically $10^{19}/cm^3$), the combination of resistive, photocurrent and luminescence measurements is expected to provide further insight into the mechanism involved.

The authors acknowledge discussions with R. Laibowitz, who introduced them to the topic of leakage current in thin oxide films, and thank especially K. A. Müller, R. Macfarlane, and R. Allenspach for valuable suggestions. The experimental help of A. Bietsch and technical assistance of R. Stutz and M. Tschudy are also acknowledged as well as the continuous support of the project by P. F. Seidler.

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