Resistive switching at manganite/manganite interfaces

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We report bipolar resistive switching between the interfaces of manganite nanocolumns. La0.7Sr0.3MnO3 films were prepared on Al2O3 substrates, where the films grow in nanocolumns from the substrate to the surface. Conductive atomic force microscopy directly detects that the resistive switching is located at the boundaries of the grains. Furthermore, mesoscopic transport measurements reveal a tunnel magnetoresistance. In combination with the resistive switching, this leads to a total of four different resistive states. © 2011 American Institute of Physics. [doi:10.1063/1.3643425]

Resistive switching, the variation of resistivity by application of an electric field, holds the hope for nonvolatile resistive memory devices. The effect can be classified into unipolar and bipolar characteristics. In the bipolar or antisymmetric case, high and low resistive states are accessed by applying electric fields of opposite polarities. In typical bipolar switching setups, an insulating or semi-conducting material is sandwiched between metal electrodes. Although the switching behavior is observed in a vast variety of material systems, the underlying physical mechanism remains obscure. Different explanations proposed include the variation of the Schottky barrier width/height,1,2 a field-induced crystalline entropy explanations proposed include the variation of the is sandwiched between metal electrodes. Although the switch-

Up to today, only a few C-AFM studies on manganites have been reported; Chen et al.11 investigated polycrystalline manganite films and induced the resistive switching by applying a high voltage (3 V) to the cantilever. One finding of this early paper was that the switched regions show a granular distribution. C-AFM was employed on SrTiO3 (crystals and thin films); it was observed that the switching occurs at dislocations.9,10,12 However, no systematic investigation of the correlation between defects and the resistive switching induced and probed by C-AFM has been reported for manganites.

La0.7Sr0.3MnO3 (LSMO) films with thicknesses of 40–80 nm were grown on Al2O3(0001) substrates by means of a metalorganic aerosol deposition technique.13,14 According to x-ray diffraction, the films were predominantly (111)-orientated (95%) with a pseudocubic lattice parameter of 3.86 Å. In Fig. 1(a), a typical scanning electron microscopy image (SEM) showing triangular and hexagonal grains is presented; these grains correspond to the (111)-orientated LSMO. A plan-view transmission electron microscopy (TEM) image of grain boundaries between neighboring grains is given in Fig. 1(b). Selected area electron diffraction reveals that neighboring (111)-oriented grains are separated by 30° and 60° grain boundaries. The films grow in nanocolumns from the substrate to the film surface as determined from TEM cross sections (see supplementary information18).

The samples were structured by electron beam lithography using a Leo Supra 35 (Zeiss) microscope with a Raith lithography unit. During the first lithography step, a bone-like constriction was cut into the film via dry etching, see Fig. 1(c). In a second lithography step, the electrodes (5 nm chromium for adhesion and 50 nm gold) were deposited by thermal evaporation. The width of the manganite bridges is 1–5 μm, the distance between the electrodes is 10–20 μm.

The samples reveal a bipolar resistive switching as shown in Fig. 2(a). Initially the samples are in the high resistive state (HRS). By increasing the current, a switching from the HRS into the low resistive state (LRS) is achieved, the corresponding switching voltages are 2–10 V. Applying a field of opposite polarity switches the LRS back to HRS. The resistive switching is

FIG. 1. (Color online) Growth of LSMO/Al2O3: (a) SEM; (b) plan-view HRTEM; (c) SEM overview of structures.

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highly local in nature; hence, we assume that local structural differences lead to these variations.

The $R(I)$ characteristics presented in Fig. 2(a) were obtained at temperatures $T = 5–10 \, K$, at which a low field tunnel magnetoresistance (TMR) was also observed. The TMR ratio was $\Delta_{TMR} = (R_{\text{high}} - R_{\text{low}}) / R_{\text{low}} = 5\%–34\%$, where $R_{\text{high,low}}$ are the resistances at the coercive field. The different ratios correspond to different structures and samples. The inset of Fig. 2(b) shows a bipolar switching curve. The measurement of this characteristic was paused in the HRS and LRS at the points marked with the black square and the red triangle. Here $R(H)$, the dependency of the resistance on the in-plane magnetic field, was measured. Two TMR-like curves in the HRS and LRS have been found, see Fig. 2(b). The combination of resistive switching with TMR leads to four different resistive states; this has also been found for MgO-based magnetic tunnel junctions.\textsuperscript{15}

To determine the local nature of the resistive switching, C-AFM was employed. The measurements were carried out in an ultra high vacuum system at room temperature in contact mode; the cantilever was coated by conducting Pt/Ti. Since the films were grown on insulating $\text{Al}_2\text{O}_3$ substrates, the grounding was achieved by large silver paste contacts at the sample edges leading to an asymmetric setup. The initial resistive state is highly insulating (as in the previous “mesoscopic” measurements). Application of a positive voltage at the tip can switch the sample resistance remanently to LRS.

Fig. 3(a) shows the topography and corresponding current map of a switched area, recorded with a measurement voltage of $U_{\text{meas}} = +0.3 \, V$. Previous to these scans, a relatively high voltage of $+5 \, V$ was applied to the tip while scanning the central lines in the image. The voltage switched the resistance locally to LRS. While recording the displayed frames, a grid of $I(V)$ characteristics was measured. The $I(V)$ curves were classified into HRS and LRS regions as denoted by the colors given in the right image of Fig. 3(b). The corresponding averaged $I(V)$ characteristics are shown in the left plot of Fig. 3(b). The averaged LRS curves show kinks (see arrows), because the individual $I(V)$ characteristics are cut off due to a current saturation ($50 \, nA$) of the preamplifier. By averaging multiple curves, the kinks result from those LRS curves, in which the current saturates at low voltages.

In Figs. 3(c) and 3(e), the topography and current map of a larger scan area ($1 \times 1 \, \mu\text{m}$) are presented. Previously the area was completely in the HRS ($U_{\text{meas}} = +0.5 \, V$). The presented image frame was scanned from bottom to top; hence, the area below the dashed blue line was measured first, then, while the cantilever was scanning the lines marked by the dashed blue line, $+5 \, V$ were applied to the tip. This switched some areas from HRS to LRS, as can be observed in the upper part of the image frame. A subsequent scan (see supplementary information\textsuperscript{15}) showed that regions below the $+5 \, V$ line were also switched; no correlation between the position of the macroscopic silver paste contact and the direction, in which areas were switched from HRS to LRS, was found. Furthermore, no current path in the form of a single filament was observed.

Comparison of HRTEM with the AFM images shows that the islands seen in the topography correspond to individual grains. To highlight the boundaries of the grains in the topography in Fig. 3(c), the gradient of the height ($|\text{grad}(z)|$) is plotted in Fig. 3(d). Almost all grain boundaries seen in the gradient image can be found in the current map. Triangles and hexagons (red and green arrows) can be observed, showing that the interfaces of (111)-oriented LSMO grains have switched to LRS.

The difference in the topography image in Fig. 3(c) shows that the tip has changed after application of the high voltage. This change is attributed to a high current flow after the resistive switching. It can be excluded that the change of the cantilever is responsible for the effect since the switching was found with a number of cantilevers on different samples. Furthermore, by applying a negative voltage to the tip, the HRS can be restored (see supplementary information\textsuperscript{15}), which completes the bipolar characteristics.

C-AFM can directly image and induce the change of resistance on a local scale; we reveal switching at the boundaries of the manganite nanocolumns. In contrast to our setup, C-AFM measurements by other groups were mostly done in a top-to-bottom setup geometry.\textsuperscript{9,11,12} Thin films were grown on conducting substrates or bottom layers; hence, the current flows from the tip through the film to the bottom electrode. In this
case, when the resistive switching is induced by application of high voltage, the current path cannot be visualized by C-AFM.

In our setup, the current flows from the tip through the film to the silver contacts at the edge of the sample. In this setup, two different scenarios for the current flow geometry seem to be possible: in the first case, the current flows along the interfaces around the grains. The second possibility is that the current flows through the grains and passes across the grain boundaries. The first scenario is supported by the fact that the local resistance, probed by C-AFM, in the middle of the grains is much higher than the resistance at the boundaries in the low resistive state. However, the high resistance in the middle of the grains might be attributed to an insulating surface layer, as has been reported for manganite films. 

The second scenario is supported by the fact that the TMR and resistive switching are complementary. The TMR behavior might stem from the spin polarization in the undisturbed center of the individual manganite columns. C-AFM shows that the resistive switching takes place at the interfaces of the grains. In this case, the smallest conceivable device showing four different resistive states consists of two manganite nanocolumns. The interfaces of the grains are switched by application of electric field, the magnetization of the grains by a magnetic field.

Remarkably, the C-AFM images show grains, in which the interfaces have entirely switched. In our setup geometry, the direction of the electric field should be different at the three sides of, for example, a triangular grain. In the proposed structural phase transition scenario, the switching of the complete interface of a grain can be explained by an elastic distortion after the electric field has induced the transition. Resistive switching occurring preferentially in defect rich regions was also observed on SrTiO₃ films, for example, in top-to-bottom geometry, were explained in terms of the complete interface of a grain can be explained by an elastic distortion after the electric field has induced the transition. Resistive switching occurring preferentially in defect rich regions, which does not seem applicable in our case.

In summary, we have shown that the resistive switching takes place at the surface of the film as well as at the interfaces separating the individual nanocolumns, i.e., we observed resistive switching at the manganite/manganite interfaces. Furthermore, we have combined the resistive switching with the TMR, which gives a total of four different resistive states. These states can be addressed by a combination of magnetic and electric fields which could be the basis of multifunctional memory devices.

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18. See supplementary material at http://dx.doi.org/10.1063/1.3643425 for Fig. I: TEM cross sections; Fig. II: C-AFM current map, showing a subsequent scan of Fig. 3 e); Fig. III: C-AFM images, showing resistive switching from LRS to HRS.