Direct observation of oxygen vacancy-driven structural and resistive phase transitions in $La_{2/3}Sr_{1/3}MnO_3$

Yao, L.[1], Inkinen, S.[1] and van Dijken, S.[1]

[1] NanoSpin, Department of Applied Physics, Aalto University School of Science, P.O. Box 15100, FI-00076 Aalto, Finland

Oxygen defects can have a profound effect on the physical properties of transition metal oxides. Electric-eld driven migration of oxygen vacancies provides a viable mechanism for the formation, rupture and reconstruction of conducting laments in insulating oxides, an effect that is used in nanoscale resistive switching devices [1,2]. In complex oxides where magnetic, ferroelectric and superconducting phases emerge from strong correlations between localized transition metal valence electrons, oxygen vacancies can radically alter a plurality of intrinsic properties via valance changes and structural phase transitions [3]. The ability to reversibly control the concentration and prole of oxygen vacancies in oxide nanostructures would thus open up comprehensive prospects for new functional ionic devices. Advancements in this direction require experimental techniques that allow for simultaneous measurements of oxygen vacancy dynamics, atomic-scale structural effects and macroscopic physical properties. In this presentation, we report on deterministic voltage control of three structural phases with distinctive resistance states in $La_{2/3}Sr_{1/3}MnO_3$ (LSMO) epitaxial lms by in-situ transmission electron microscopy (TEM) [4].

In our experiments, we used aberration-corrected TEM and a double-tilt probing holder with a piezo-controlled metal tip. The samples, consisting of a 20 nm thick LSMO film on a conducting Nb-doped $SrTiO_3$ (STO) substrate, were grown by pulsed laser deposition and prepared into cross-sectional TEM wedges by mechanical polishing and Ar ion milling. Electrical contacts to the STO side of the sample were made by placing one of the wedges on a half Cu grid. After mounting the TEM sample into the microscope, we brought the electrically grounded tip into contact with the LSMO film. This produced an effective contact area with a diameter of about 30 nm. We continuously monitored the electrical resistance and simultaneously recorded scanning TEM (STEM) images with high-angle annular dark field (HAADF) contrast after the application of short triangular voltage pulses to the STO side of the specimen.

Our in-situ TEM measurements (Fig. 1) demonstrate reversible switching between low- and high-resistance states. The resistive switching events directly correlate with uniform structural transition between perovskite and brownmillerite phases in the LSMO film. Detailed STEM analyses of domain growth during switching, electron energy loss spectroscopy on the LSMO/STO contact area, and electro-thermal simulations indicate that horizontal and reversible migration of oxygen vacancies in LSMO, driven by combined effects of Joule heating and bias voltage, predominantly causes the transitions. A transition to an oxygen-deficient perovskite phase with intermediate resistance occurs at even larger voltage pulses (not shown in Fig. 1, see ref. [4]). Our findings open new prospects for ionotronic devices based on dynamic control of physical properties in complex oxide nanostructures.

References

[1] R. Waser and M. Aono, Nature Materials 6, 833 (2007).

[2] J.J. Yang, D.B. Strukov, and D.R. Stewart, Nature Nanotechnology 8, 13 (2013).

[3] S. Kalinin and N.A. Spaldin, Science 341, 858 (2013).

[4] L. Yao, S. Inkinen, and S. van Dijken, Nature Communications 8, 14544 (2017)

Acknowledgements:

This work was supported by the Academy of Finland (Grant No. 293929) and by the European Research Council (ERC-2012-StG 307502). TEM analysis was conducted at the Aalto University OtaNano-Nanomicroscopy Center (Aalto-NMC).

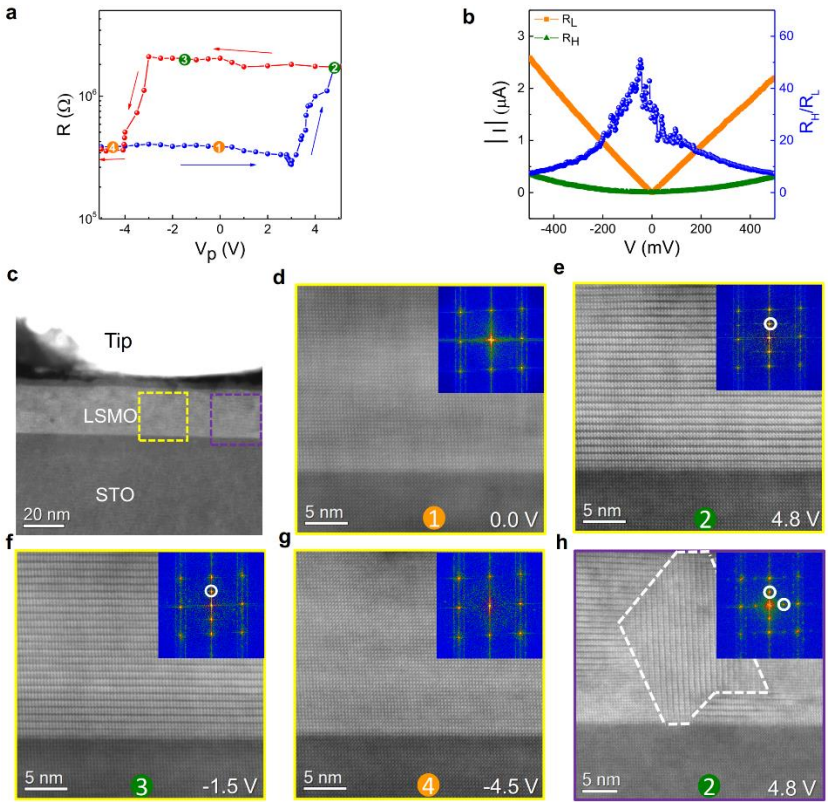

Figure1: (a) In-situ TEM resistive switching curve for a LSMO lm on top of a conducting STO substrate. The resistance is measured at V_m= 0.5 V after the applications of triangular voltage pulses with maximum voltage V_p and a duration of 100 ms. (b) I - V curves for the same lm, measured after switching to the low (orange squares) and high (green triangles) resistance states. The blue data points indicate the resistance ratio as a function of bias voltage. (c) Cross-sectional STEM image of the contact between the metal tip and the LSMO lm. (d)-(h) STEM-HAADF images and corresponding fast Fourier transform (FFT) patterns of the sample within the contact area, as indicated by the dashed boxes in c, at several stages of the resistive switching process. The images in (d)-(h) and data in (a) were collected simultaneously (colored dots indicate matching measurements). In some areas (see (h)), the horizontal brownmillerite phase coexists with a vertical brownmillerite structure.