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Report:

“Microscale XAFS studies of functional materials for terabit resistive memories”

Doped ABO_3 -perovskites are suitable functional materials for storage devices (resistive random access memory RRAM) with a density in the terabit range since extended defects such as dislocations or defect clusters with nanoscale dimensions are considered to be the single resistive switching units [1,2]. Acceptor-doping of $SrTiO_3$ films has been found to improve the stability of the resistive switching process.

Within the MNT ERA-Net framework (7FW) program MATERA, the participants (Prof. Waser, Dr. Dittmann, Prof. Szot, Prof. Purans, Prof. Kotomin, Prof. Szade) use a combinatorial approach to investigate the role of doping atoms in resistive switching $SrTiO_3$ thin films and to develop the basic science and technology for new functional ternary oxides for the use as future terabit memories.

For the presented experiments, homoepitaxial thin films of $SrTi_{0.95}Fe_{0.05}O_{3-\delta}$ deposited by Pulsed Laser Deposition (PLD) were fabricated into MIM devices to investigate resistive switching in a structure resembling the architecture of a storage device. The non-volatile nature of the resistance change allowed the devices to be set into specific resistance states before the experiment. Overall, three types of sample were measured and compared: a single crystalline sample that had been set into a well known chemical state by electrocoloration, homoepitaxial thin films (thickness 200 nm) in the virgin state and electrically

modified thin films. The single crystalline sample was characterized beforehand (experiment number MA-923) using complementary spectroscopic methods, and a detailed analysis of the defect structure will be given in a forthcoming paper[3]. Since the detailed analysis of the spectra presented here is currently under way, we will restrict the evaluation in this report to a comparative methodology, with full details to be published later.

The X-ray absorption near edge structure (XANES) recorded on the as-grown epitaxial thin films is depicted in fig.1, along with the XANES of the anodic and cathodic region of the electroformed single crystal. The region around the cathode of the single crystal (red line) contains primarily Fe^{3+} centers in octahedral coordination, with a heavy admixture of $\text{Fe}^{3+}-\text{V}_\text{O}^{**}$ complexes, while the anodic region (black line) contains a mixture of predominantly Fe^{4+} and traces of Fe^{3+} , both in octahedral coordination.

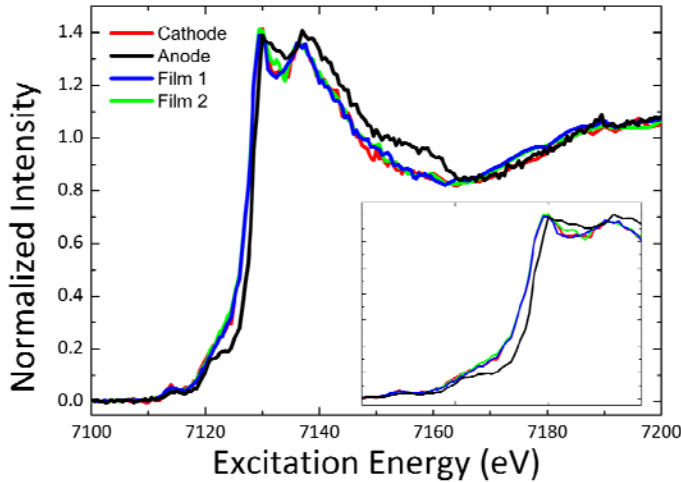


Figure 1: XANES of the cathodic (red) and anodic (black) regions of the electrocolored single crystal, and of two thin film samples fabricated under identical conditions. The near edge structure of the cathode and the thin films is close to identical, which demonstrates that the chemical state and local environment of Fe is similar in both cases. In contrast, the anodic region exhibits Fe centers in a different chemical state and shows a clear shift of the white line to higher binding energies, as well as pronounced differences in the pre-edge region. Inset: Magnification of the pre-edge region.

Comparing the XANES of the two thin film samples with that of the single crystal, their similarity to the cathodic region is readily apparent. From the shift of the white line with respect to the anode (Fe^{4+}) and the increased intensity in the pre-edge region, we can conclude that the as-grown thin film is in a reduced chemical state and contains a mixture of Fe^{3+} and $\text{Fe}^{3+}-\text{V}_\text{O}^{**}$, with no indication of Fe^{4+} .

To take full advantage of the micro-focused x-ray beam at ID03, metal-insulator-metal (MIM) capacitor structures of various sizes were fabricated onto the thin films by photolithography and set into defined resistance states. The details of sample fabrication and electrical treatment shall be provided in a forthcoming publication. Since the resistance change after electroforming is strongly localized [4], the first challenge in the spectroscopic characterization of the switched MIM-capacitors is to provide a fingerprint of the breakdown to provide a means of localizing the switched region. To achieve this, a $30 \times 30 \mu\text{m}^2$ capacitor was subjected to harsh electrical stress, after which the resistance over the whole stack was $R_{\text{MIM}} \sim 200 \Omega$. Fig.2 shows the XANES measured on different positions on this capacitor and on the adjacent film. The measurement positions are marked on the SEM micrograph in the inset, as estimated from the optical microscope on the beamline.

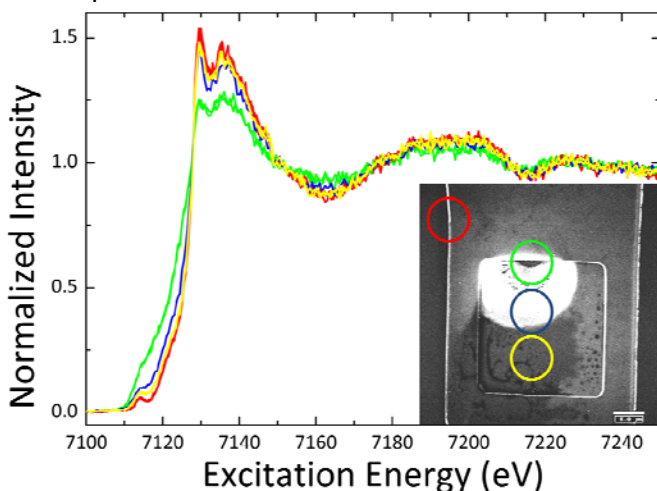


Figure 2: XANES taken at several positions on the MIM-capacitor after electrical breakdown. Inset: The SEM micrograph shows nicely the location where the breakdown occurred, as the top electrode layer was destroyed. The colored-coded circles mark the position of the x-ray beam during the measurement, which could be estimated during the measurement with an optical microscope.

A comparison of the XANES hints at an increased concentration of oxygen vacancies at the positions marked in yellow and blue, with an increase toward the destroyed part of the electrode. A large increase in pre-edge intensity is observable at the location of the breakdown (bright green), along with a decrease of the white line intensity. While it is impossible to be sure without a careful and detailed analysis, the shape of the XANES hints at either the presence of Fe in lower valence states than Fe^{3+} or at strongly increased local disorder.

The strong increase in pre-edge intensity at the site of the breakdown can be conveniently used as a fingerprint of localized changes introduced by the electric treatment. Fig.3 shows a x-y mapping of a $100 \times 100 \mu\text{m}^2$ capacitor that was switched into the “Set”-state, recorded at 7122 eV excitation energy chosen for a maximum contrast in the pre-edge region.

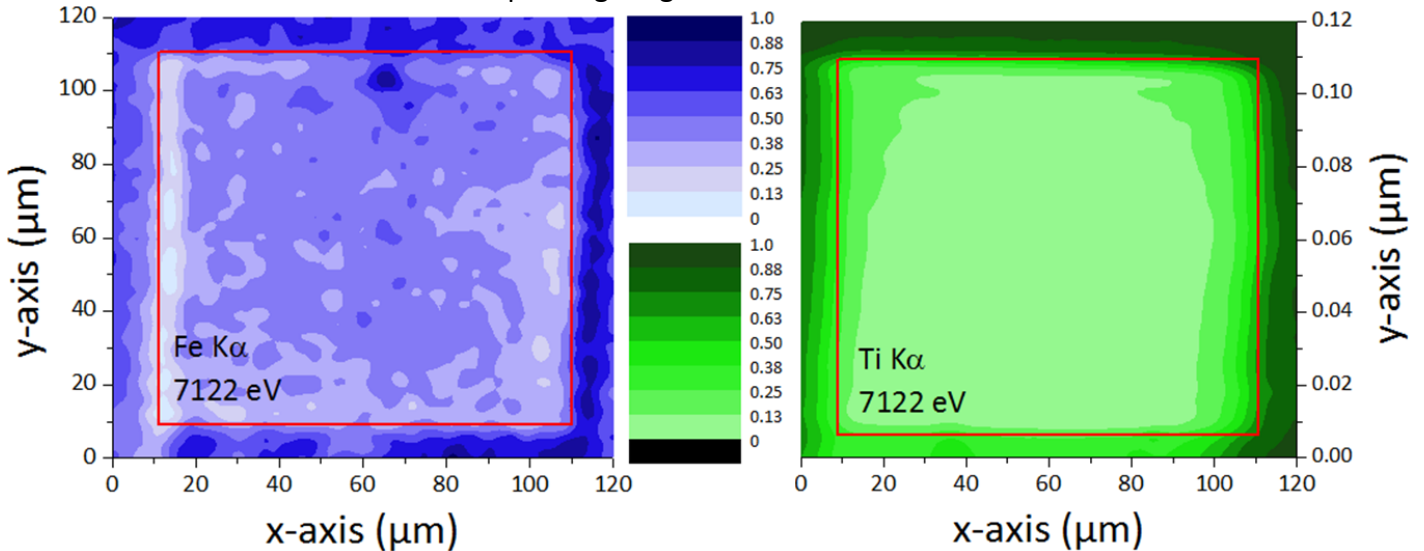


Figure 3: x-y maps of Fe $K\alpha$ and Ti $K\alpha$ recorded on a $100 \times 100 \mu\text{m}^2$ MIM capacitor at 7122 eV excitation energy.

The intensity scale of the Fe $K\alpha$ corresponds to the pre-edge intensity as seen in figs 1 and 2, showing an area of $\sim 5 \mu\text{m}$ diameter where the intensity is significantly increased. The Ti $K\alpha$ map shows a homogeneous intensity over the whole electrode area, demonstrating that there is no pin-hole or other artifact. The pad area is well defined by the area where the fluorescence radiation is attenuated by the Pt/Al/Pt electrode structure.

Performing absorption spectroscopy precisely on the area with increased pre-edge intensity seen in fig. 4 (region 1) and several μm away from it (region 2) reveals a very similar shape of the XANES as seen for the hard dielectric breakdown (see fig. 2). The comparison to the as-deposited film (reference) reveals an increase of oxygen vacancies in the first coordination shell of Fe close to the switched area, and indeed over most of the electrode pad, as can be inferred from the map in fig. 3 (and proven by XANES at several other points, data not shown).

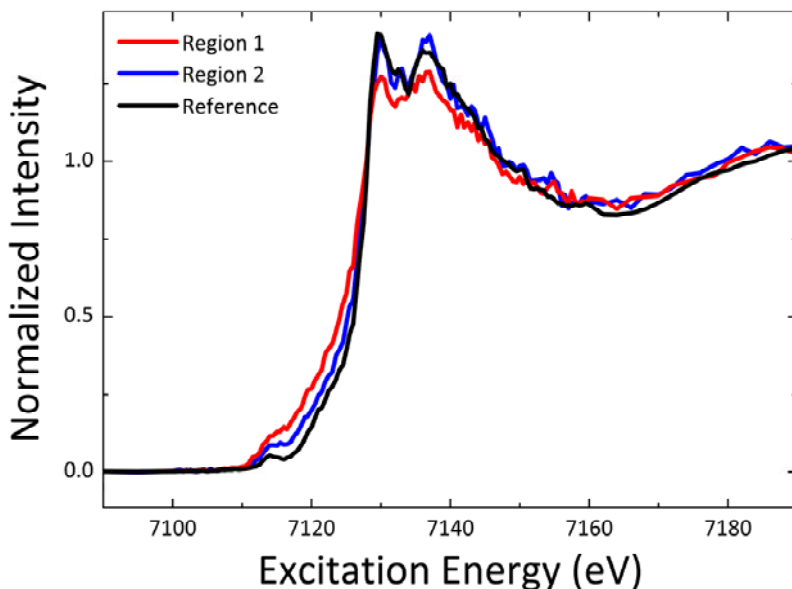


Figure 4: XANES at several points of the $100 \times 100 \mu\text{m}^2$ electrode pad. “Region 1” (red) corresponds to the switched area that shows the most prominent increase in pre-edge intensity visible in the Fe $K\alpha$ map in fig. 3, while “Region 2” (blue) is about $5 \mu\text{m}$ to the side. The “reference” (black) represents spectra taken on as-deposited thin films.

References

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