Technical Digest of

Frontiers in Electronic Materials

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Binary and ternary metal oxides as emergent materials for non-volatile memory applications are receiving an increasing amount of scientific attention due to the promising scalability, retention and switching characteristics of this material class [1]. The key role of oxygen non-stoichiometry and oxygen-deficient oxide-phases as the underlying mechanism of the resistance change has been recognized for many different oxide systems (e.g. TiO$_2$, Ta$_2$O$_5$, SrTiO$_3$). It is becoming widely accepted that the resistance switching process in SrTiO$_3$ is related to the movement and creation of oxygen vacancies and the associated electron doping. However, direct experimental reports of the redox-reaction induced by an electric field are rare [2].

In this contribution, the distribution of oxygen vacancies in a switched memristor fabricated from epitaxial Fe-doped SrTiO$_3$ will be investigated by spatially resolved x-ray absorption near-edge structure (XANES). SrTi$_{0.95}$Fe$_{0.05}$O$_3$ was grown epitaxially by pulsed laser deposition (PLD) on a conducting Nb: SrTiO$_3$ substrate, and Pt top electrodes were sputter-deposited and structured via optical lithography. XANES measurements at the Fe K-edge with a 7 µm beam spot on the sample were done at beamline ID03 (ESRF, France). Figure 1 compares the Fe K-edge XANES of the virgin thin film to that recorded in the anodic and cathodic regions of an electrocolored single crystal. The cathode was found to contain only Fe$^{3+}$ ions and Fe$^{3+}$-VO complexes in the ratio ~ 70/30, and notably no Fe$^{4+}$ [3]. The almost perfect coincidence of the thin film XANES with that of the reduced cathode implies that the thin film is already oxygen deficient after growth, and that the Fe$^{3+}$/Fe$^{4+}$ redox pair does not serve as an indicator for local resistance changes. The shoulder at 7122 eV excitation energy that marks Fe$^{3+}$-VO complexes is indicated by “S” in figure 1.

![Figure 1: Fe K-edge XANES recorded on the virgin thin film (dots), the cathode region (solid) and the anode region (dash) of an electrocolored Fe-doped SrTiO$_3$ single crystal. The intensity of the shoulder at 7122 eV excitation energy (marked S by the arrow) is a fingerprint of the presence of an oxygen vacancy in the first coordination shell of Fe$^3$. The chemical state of the virgin film – according to the XANES – is similar to that of the cathode, and the Fe centers in the film are primarily cubic Fe$^{3+}$ centers, with a significant percentage of axial Fe$^{3+}$-VO centers.](image-url)
After an electroforming step with a +7V DC voltage applied to the top electrode, the formed memristor can be switched between different resistance states with a bipolar voltage sweep. The current-voltage hysteresis is shown in figure 2(a), the “Set”-state is reached with a negative voltage sweep polarity. A low voltage readout (figure 2(b)) reveals the “Set”-state to show ohmic behavior, while the “Reset”-state shows distinctly non-linear behavior.

A Fe-K edge fluorescence map recorded at 7122 eV excitation energy to maximize the sensitivity to Fe$^{3+}$-VO reveals one location on the electrode pad with increased intensity, corresponding to the filament. Moreover, the Fe$^{3+}$-VO concentration as measured by the intensity of the shoulder S is increased under the whole electrode area as compared to the virgin film. The important consequence is that before breakdown is achieved during the electroforming, a homogeneous front of vacancy enrichment propagates into the material. Furthermore, the Fe K-edge XANES at the filament location is interpreted via full multiple-scattering calculations and indicates oxygen vacancy clustering in the first shell of Fe [4].