

# **X-Ray Spectromicroscopy Investigation of Soft and Hard Breakdown in RRAM Devices**

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## **Supplementary data**

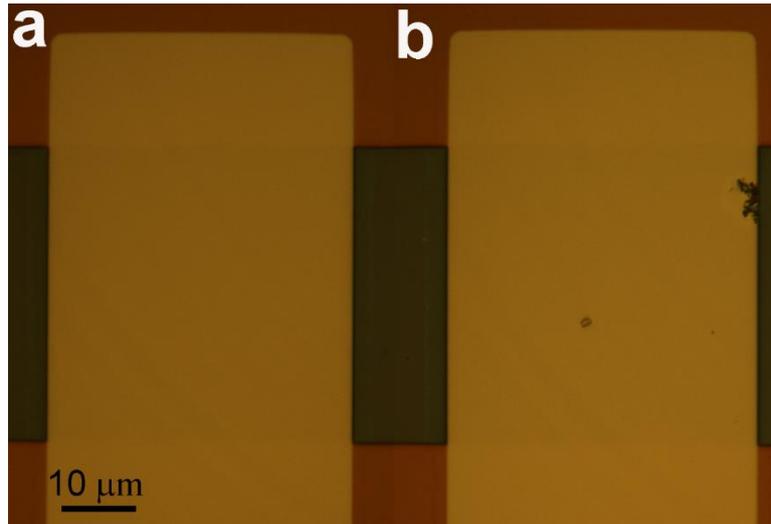
### **TXM-NEXAFS**

The Ti  $2p$  spectra consist of four main peaks (two doublets). The first doublet ( $2p_{3/2}$ ) (457-462 eV) originates from transitions to ( $2p_{3/2}$ ,  $3d-t_{2g}$ ) and ( $2p_{3/2}$ ,  $3d-e_g$ ) states while the second doublet ( $2p_{1/2}$ ) (462-468 eV) originates from transitions to the corresponding  $2p_{1/2}$  states. The  $2p_{3/2} - 2p_{1/2}$  splitting is due to spin-orbit coupling while the  $t_{2g}-e_g$  separation is the crystal-field splitting due to the surrounding O atoms. [1] In all spectra, the ( $2p_{3/2}$ ,  $e_g$ ) peak is broader than the ( $2p_{3/2}$ ,  $t_{2g}$ ) due to the large degree of hybridization of  $e_g$  orbitals with O ligand orbitals. [2]

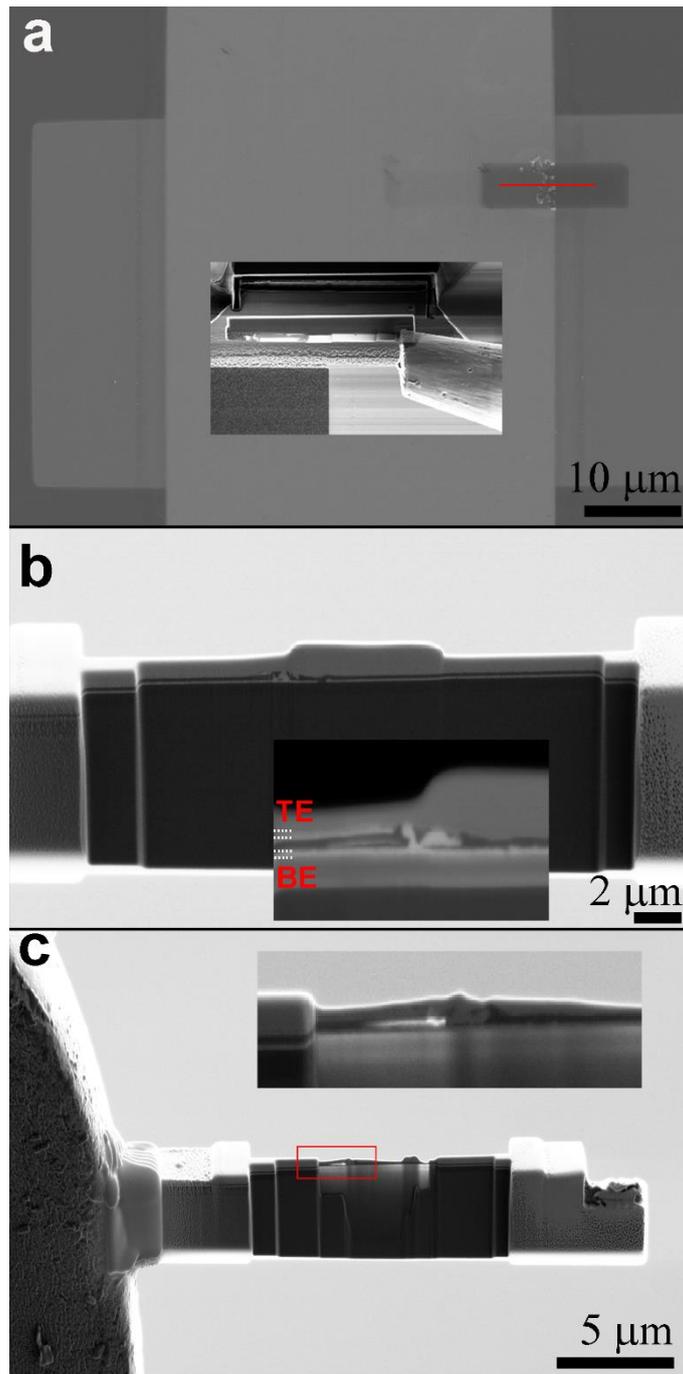
The O 1s spectra can be divided in two regions. The doublet between 528 and 536 eV can be attributed to O 1s excitation to hybrid excited states in which the final level is a mixture of O 2p and Ti 3d orbitals. The spectral features at 531 and 533 eV are assigned to the t<sub>2g</sub> and e<sub>g</sub> orbitals, respectively. [3] This region is very sensitive to local symmetry and coordination. Peaks in the region between 536 eV and 555 eV correspond to O 1s excited states in which the final level is a hybridization of O 2p and Ti 4sp orbitals. This region is more sensitive to long-range order. [3]

## References

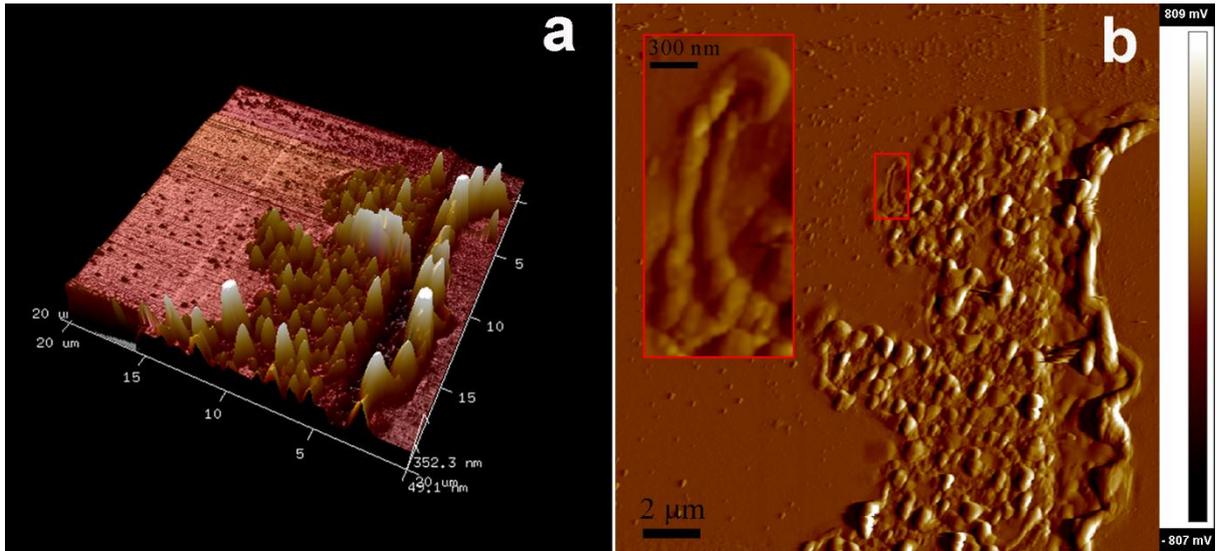
- [1] Stoyanov E, Langenhorst F, Steinle-Neumann G 2007 The Effect of Valence State and Site Geometry on Ti L<sub>3,2</sub> and O K Electron Energy-Loss Spectra of Ti<sub>x</sub>O<sub>y</sub> Phases. *Am. Mineral.* **92** 577–586.
- [2] Kucheyev S, van Buuren T, Baumann T, Satcher J, Willey T, Meulenberg R, Felter T, Poco J, Gammon S, Terminello L 2004 Electronic Structure of Titania Aerogels from Soft X-Ray Absorption Spectroscopy. *Phys. Rev. B* **69** 245102.
- [3] Lusvardi V S, Barteau M A, Chen J G, Eng J, Frühberger B, Teplyakov A 1998 An NEXAFS Investigation of the Reduction and Reoxidation of TiO<sub>2</sub>(001). *Surf. Sci.* **397** 237–250.



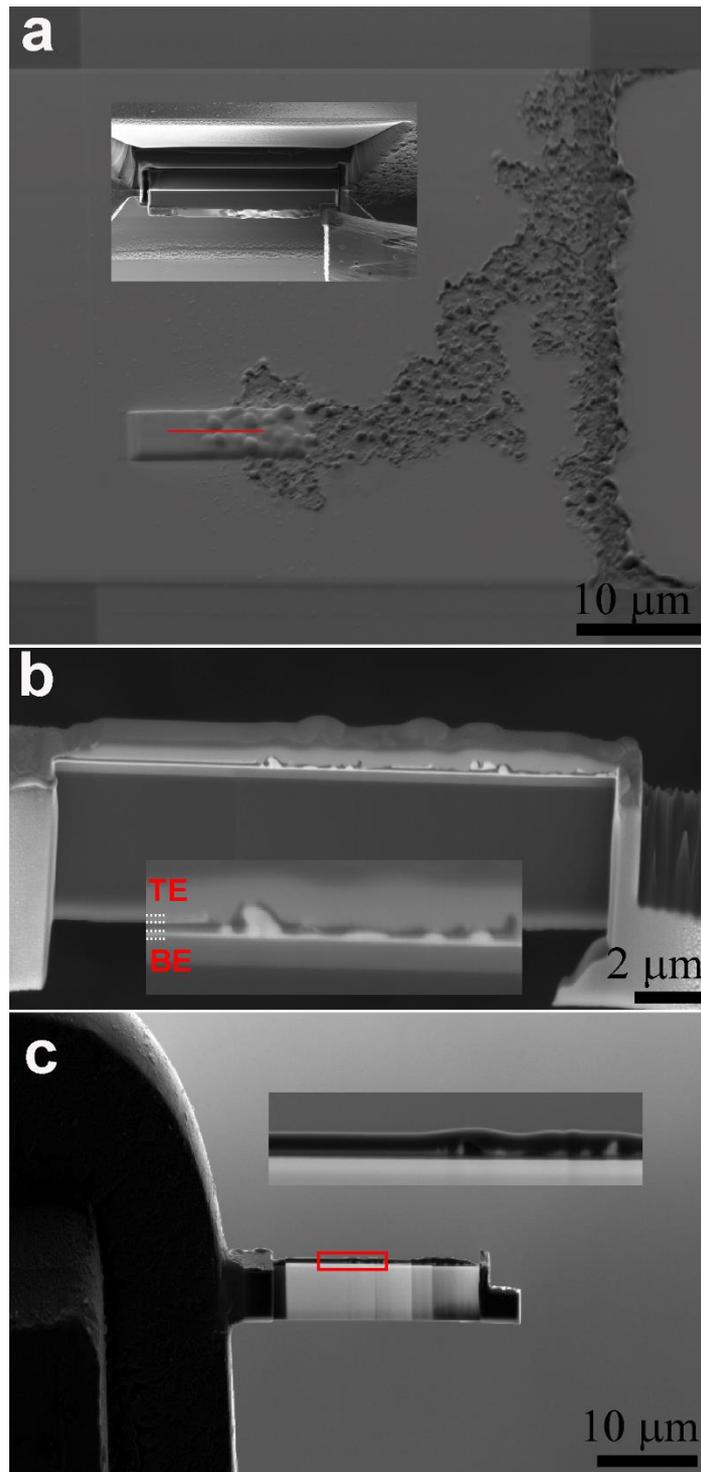
**Figure S.I.1.** Optical images of Dev\_SB viewed from the TE (a) before and (b) after switching



**Figure S.I.2.** SEM images of Dev\_SB: (a) device viewed from the top electrode with location of lamella cut (red line) and detail of lamella extraction (inset); (b) lateral view of lamella with details of the damaged region cross-section; (c) electron transparent thin lamella mounted on W pillar



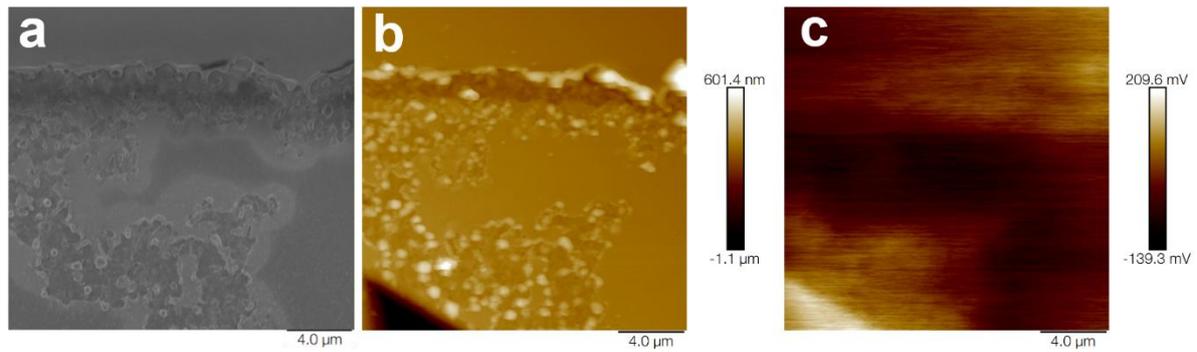
**Figure S.I.3.** Dev\_HB: (a) 3D AFM image of selected defect area; (b) deflection error image with detailed zoom on a “linear” crater



**Figure S.I.4.** SEM images of Dev\_HB. (a) device viewed from the top electrode with location of lamella cut (red line) and detail of lamella extraction (inset); (b) lateral view of lamella with details of the damaged region cross-section; (c) electron transparent thin lamella mounted on W pillar

## Kelvin Probe Force Microscopy (KPFM)

Kelvin Probe Force Microscopy (KPFM) measurements were carried out using a Bruker Icon microscope with a NanoScope V Controller. We used highly doped silicon cantilever (*Bruker Otespa R3*). Nanoscope analysis v1.5 [1] was used to process the imaging data.



**Figure S.I.5.** Selected area of Dev\_HB: (a) SEM image, (b) AFM topography, (c) KPFM potential map.

[1] <http://nanoscaleworld.bruker-axs.com/nanoscaleworld>