ESRF	**Experiment title:** Determination of the mechanism of X-ray nanopattering in TiO2	**Experiment number**: MA-4643
Beamline: ID16B-NA	**Date of experiment**: from: 03/02/2021 to: 09/02/2021	**Date of report**: 21/09/2022
Shifts: 15	**Local contact(s)**: Valentina Bonino	*Received at ESRF:*

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Report:

The possibility of locally changing the electrical properties of materials by means of X-ray nanobeams has been already demontrated in superconducting Bi-2212 oxide, where a decrease in the interstitial oxygen content, together with an increase in crystal mosaicity were reported [1, 2, 3].
This X-ray nanopatterning technique has been shown to be able to locally modify the oxygen content even in materials with more tightly bound oxygen atoms such as rutile TiO2, opening the possibility to increase the material conductivity and apply X-ray nanopatterning to the fabrication of memristive devices. In this regard, a previous experiment was performed at ESRF (MA-4361), where the formation of a conducting channel was detected [4].
Experiment MA-4643 is intended to further investigate the effect of X-ray irradiation on TiO_2 and get new hints on the possible microscopic mechanism underlying oxygen depletion in oxide materials.
For this purpose, samples were prepared depositing metal electrodes (Pt and Pt/Ta) on top of a rutile single crystal, separated by a ≈2µm gap.
Alignment XRF maps were collected to precisely localize the gap between the electrodes, and then lines were drawn by scanning the gap with the nanobeam at different photon fluxes and with different exposure times per point.
The experimental setup allowed for a multi technique analysis involving simultaneous XRF and XEOL mapping, together with on line two probe electrical measurement.
The results show a progressive increase in the sample conductivity upon increasing the X-ray dose on the sample, suggesting the introduction of oxygen vacancies which act as n-dopants in TiO_2.
Upon increasing the applied voltage during the collection of IV curves, a sudden increase in the current flowing in the device was observed, corresponding to the electroforming of a memristive device [5].

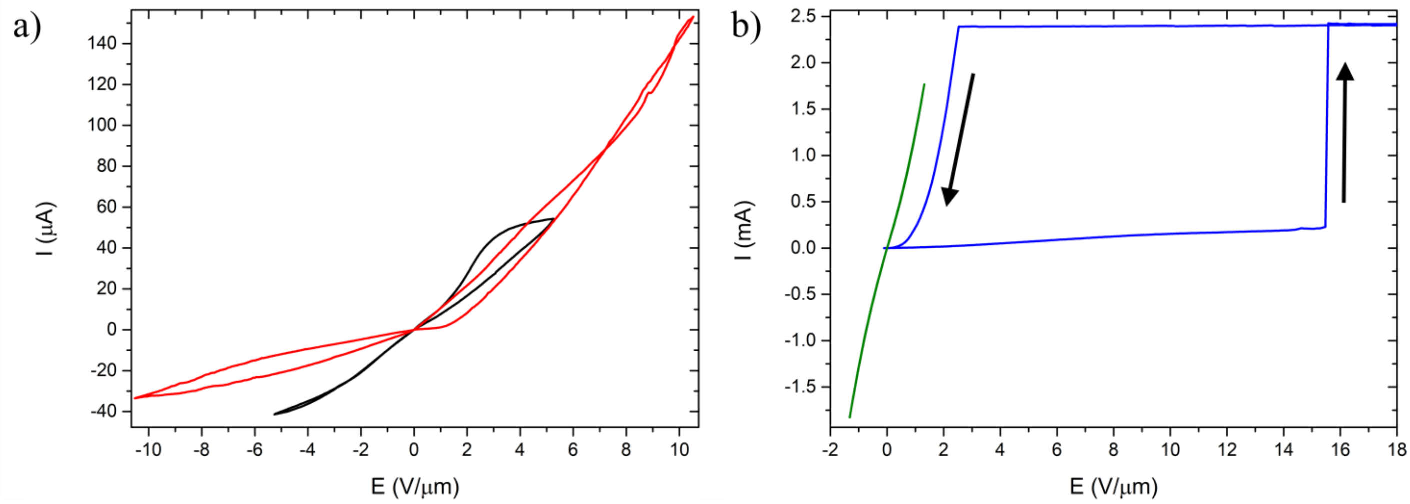

Figure 1 a) I vs E curves measured after irradiation, at increasing maximum voltages. b) I vs E curve showing the electroforming process (blue) and subsequent I vs E curve in the so-called "on" state (green) [5].

This electroforming process was not reversible possibly because of the large amount of current flowing in the device.
However, by performing XRF and XEOL mapping, together with C-AFM measurements, it was possible to confirm that: i) this electroforming process took place in correspondance of the conducting channel created by X-ray irradiation; ii) no ionic migration from the electrodes is implieid in the process; iii) X-ray nanopatterning can be suitable for pinning and guiding this fabrication step, but a better control of the process is needed.

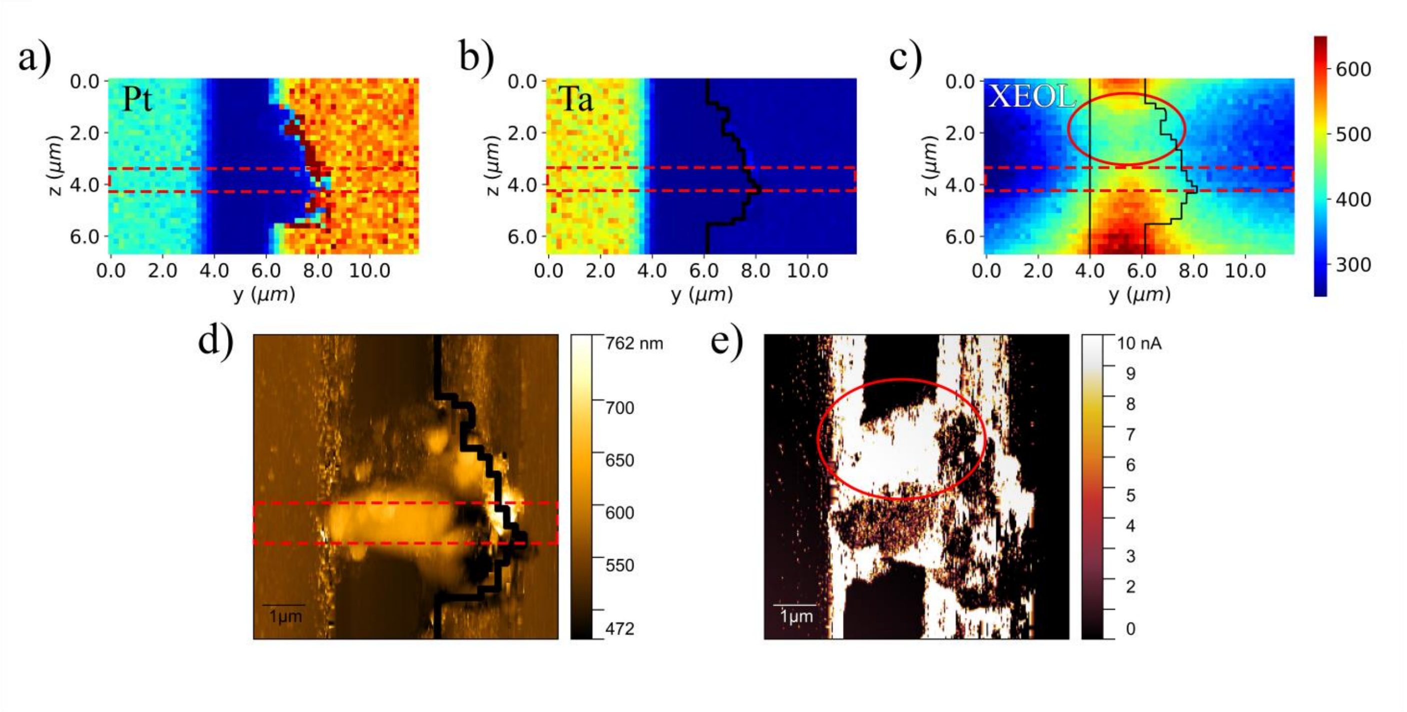

Figure 2 a,b) Typical XRF maps collected after irradiation and electroforming, corresponding to Pt–L (a) and Ta–L (b) lines. Corresponding XEOL (c), topographic (d), and C-AFM (e) images after irradiation and electroforming. The dashed red boxes highlight the irradiated region, and the solid red circles indicate the minimum in the XEOL (c) and the maximum in the C-AFM(e) signals, correspondingly [5].

References

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[5] A. Alessio *et al*. Phys. Status Solidi RRL, **15**, 2100409 (2021)