ESRF	**Experiment title:** Direct X-ray writing of conductive filaments for memristive devices	**Experiment number**: MA-4361
Beamline: ID16B-NA	**Date of experiment**: from: 24/11/2018 to: 30/11/2018	**Date of report**:
Shifts: 15	**Local contact(s)**: Jaime Alberto Segura Ruiz	*Received at ESRF:*

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Report:

It is well known that intense synchrotron beams can alter the state of materials, but this effect is generally considered undesired radiation damage. However, intriguing phenomena, which enable to modify materials in a controlled way, have been recently reported [1, 2, 3]. During experiment MA-4361 we have investigated the effect of irradiating selected areas of TiO_2 rutile single crystals, between metal contacts for electrical characterization, by the ~ 60 × 60 nm^2 synchrotron X-ray nanobeam at 17 keV available at the ID16B-NA beamline (see Figure 1A).

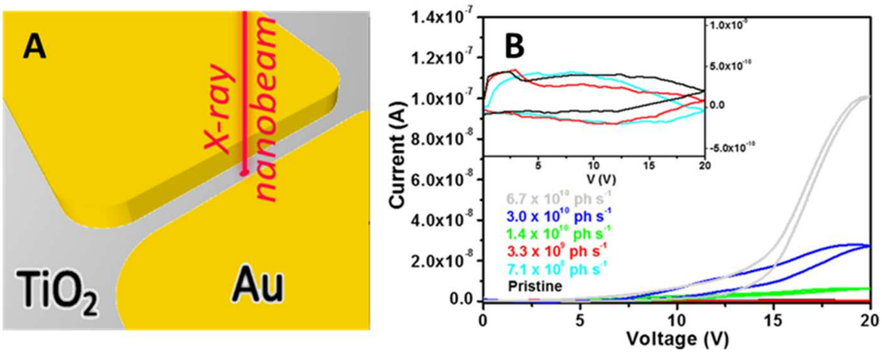

Figure 1. A. Scheme of the metal contacts deposited on the TiO_2 single crystal for electrical characterization during X-ray irradiation. **B.** I-V curves of the TiO_2 single crystal acquired after each irradiation line between two Au electrodes at increasing X-ray photon fluxes. In the inset a magnification of the I-V curves for the irradiation at low photon fluxes is reported.

Besides a transient increase of conductivity due to a photovoltaic-like process, we have measured a non-volatile localized change of resistance by about 4 orders of magnitude after X-ray exposure when an irradiation line is

realized with a photon flux in the order of 10^{10} photons per second (see Figure 1B). The non-volatile increase of conductivity can be modulated by varying the beam intensity and the exposure time. This effect can be ascribed to the local generation of oxygen vacancies by the X-ray nanoprobe, which are subsequently ordered by the electric field applied during the acquisition of the I-V curves. Conductive AFM measurements show that the conductive channels induced by the X-rays are sub-superficial.
Our results demonstrate that intense synchrotron beams can create oxygen vacancies in materials with tightly bound oxygen atoms, highlighting that X-ray nano-probes could become an effective tool for nano-fabrication of oxides, able to locally increase or decrease the material resistivity [4, 5, 6]. For instance, since the localized presence and migration of oxygen vacancies is an essential requisite for redox-based memristive devices, the possibility to locally induce oxygen vacancies in a prototype oxide like TiO_2 could represent a novel tool for the rational design and production of oxide-based memristive devices, replacing the problematic electroforming step. In this respect, we performed some preliminary trials to produce such kind of device. As reported in Figure 2A, after two subsequent irradiation lines connecting the metal contacts at the maximum available photon flux (ca. 10^{11} ph/s) we were able to induce resistive switching in our samples. The procedure led to the formation of a conductive filament resulting in a local crystal expansion as visible in the SEM image of the sample after X-ray irradiation (Figure 2B).

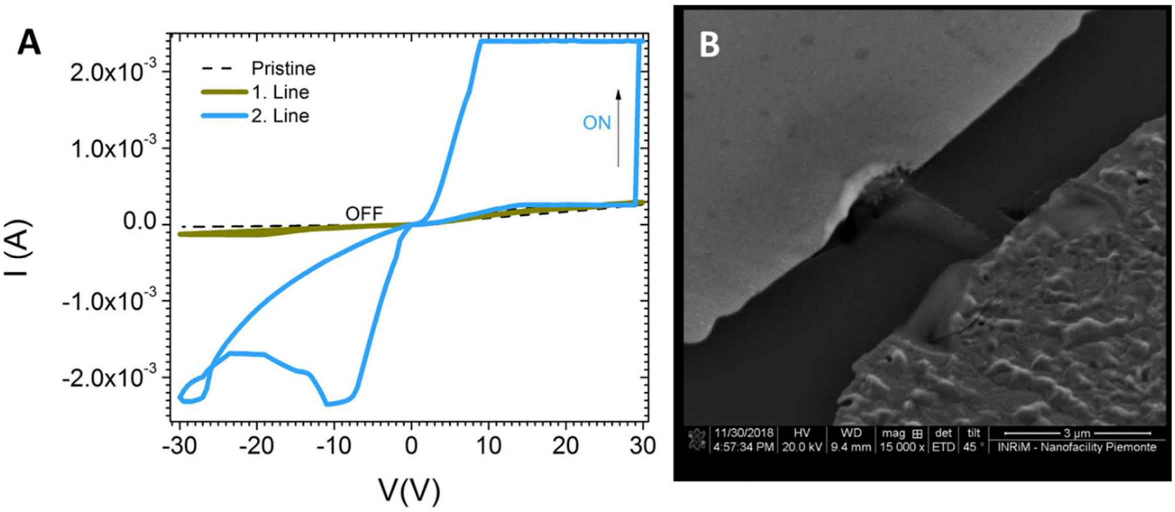

Figure 2. A. I-V curves of the TiO_2 single crystal acquired after two irradiation lines at the maxium photon flux highlighting a resitive switching phenomenon. **B.** SEM image of the irradiated region between the electrodes.

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