ESRF	**Experiment title:** Determination of the mechanisms of X-ray nanopattering in TiO2	**Experiment number**: MA-4883
Beamline: ID16B-NA, ID21	**Date of experiment**: from: 11/02/2022 to: 21/09/2022	**Date of report**: 23/09/2022
Shifts: 9+15	**Local contact(s)**: Valentina Bonino, Eduardo Villalobos	*Received at ESRF:*

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Report:

Material modifications induced by X-ray irradiation are often considered as undesirable side effects in applications involving high brilliance sources such as 4th generation synchrotrons. However, they can also be exploited for local tuning of electronic properties of materials such as superconducting Bi-2212 [1,2,3] and semiconducting oxides like rutile TiO_2 [4,5].
Regarding TiO_2, an increase of the device conductivity can be measured upon irradiation of a gap separating two metal electrodes deposited on top of a rutile single crystal. This increase in conductivity can be ascribed to an increase in the concentration of oxygen vacancies, which are n-dopants in this material [5].
To verify this, we irradiated different portions of TiO_2 and $SrTiO_3$ samples at ID16B, with a ≈60x60 nm^2 beam at the energy of 17.5 keV, which is known to be able to modify this material from previous experiments performed in similar conditions.
In particular, micrometric sized regions were irradiated both in the gap between the metal electrodes and far away from the electrodes. These relatively large regions were meant to be subsequently investigated by means of XANES at ID21.
We were expecting a reduction of Ti^{4+} to Ti^{3+} as a consequence of the introduction of oxygen vacancies, which should result in a shift of the Ti K edge in the irradiated regions of the sample.
Thereore, XANES maps were collected at ID21 to check differences in the edge position between irradiated and non-irradiated points, but no clear difference could be seen, as reported in Figure 1.
This could be due to the too high penetration depth of X-rays at this energy, which is possibly much larger than the thickness of modified material.

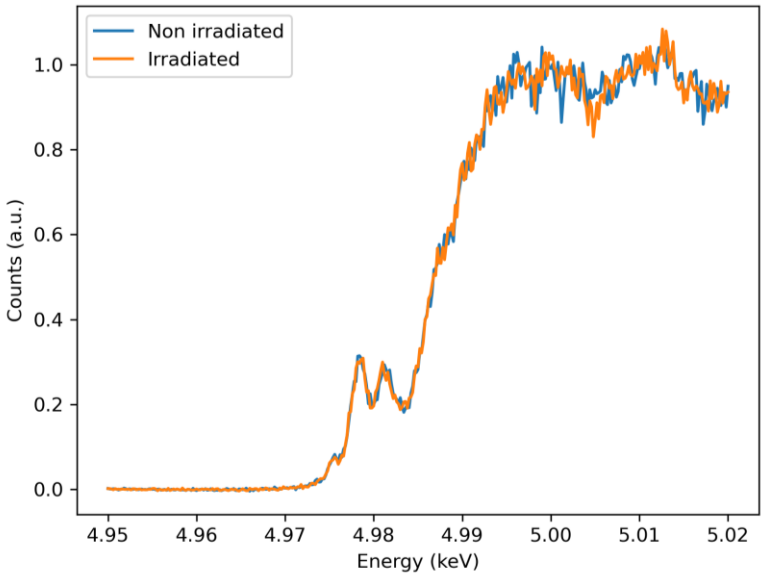

Figure 1: Comparison between XANES spectra collected in a non-irradiated point of the sample and an irradiated point.

Since no apparent change is visible, we are still performing a more in depth analysis.
During this experiment, the effect of temperature was also investigated by irradiating some samples at 8 K at ID16B, in order to see differences with respect to room temperature and between different materials.
Indeed, according to some FEM thermal simulations we performed, heating effects should be more pronounced in $SrTiO_3$ with respect to TiO_2, and the temperature gradients should be much higher at low temperature with respect to room temperature because of the lower heat capacity of materials.
Indeed, from subsequent AFM measurements, a greater surface damage was detected in $SrTiO_3$ irradiated at low temperature with respect to TiO_2, which seems to confirm the hypothesis that heating effects could play a role in material damage.

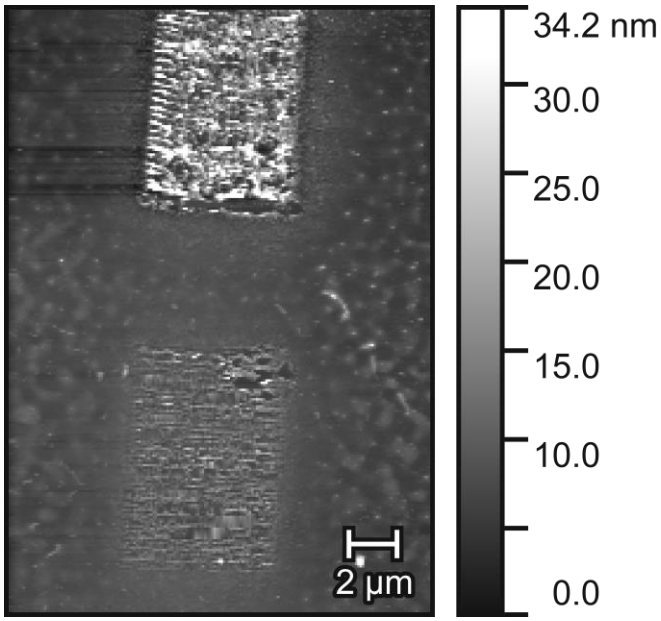

Figure 2: AFM image showing two areas of a $SrTiO_3$ sample irradiated at low temperature with different exposure times, namely 5 s/point (top) and 1 s/point (bottom)

References

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