EUROPEAN SYNCHROTRON RADIATION FACILITY

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Experiment Report Form

	Experiment title: *Structural UHV-characterization of Anatase (001) and (100) TiO_2-film surfaces with water pressure.*	**Experiment number**: CH-5660
Beamline:	**Date of experiment**: from: 27 October 2020 to: 03 November 2020 from: 10 March 2021 to: 12 March 2021	**Date of report**: 26 April 2021
Shifts:	**Local contact(s)**: Maurizio De Santis	*Received at ESRF: 26 April 2021*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

Objectives and summary of the expected results

The main objectives of the experiment were: (i) to measure the structure of the anatase(001)-(4x1)/(1x4) reconstruction and compare it with that of the (1x1) bulk structure. (ii) To follow the structural surface evolution with water pressure up to 10^{-6} mbar. (iii) To measure the average surface structure of anatase(001) film.

In the periode 10-12 March 2021 we also measured the STO - CTRs of the 4 nm thick anatase-TiO_2/STO film.

Expected results: (ia)To solve the surface of the anatase(001)-(4x1)/(1x4) rescontruction. (iia) To follow the surface structure's changes with water pressure and (iiia) To solve the average bulk structure of the anatase(001) film.

Results and conclusions of the study

Objectives (i) and (iii) were carried out succesfully.
Objective (ii) was not reached because the water pressure was not high enough to produce structural changes on the surface of the anatase(001) film. The experimental intensities with and without water dose remained identical. The time saved due to the omission of this part was used to measure 3 anatase(001) films prepared under different conditions and with different thicknesses [Objective (i)]:

(a) Anatase(001) film prepared by PLD: 80 nm

(b) Anatase(001) film prepared by MBE: 8 nm
(c) Anatase(001) film prepared by MBE: 4 nm.
(d) An extra data set for the case (c) was measured at the anatase/STO interface. More than 10 SrTiO3(001)-CTRs were measured with the new objective to describe the strain at the STO interface produced by the TiO2 film.

For cases (a) to (c), more than 15 anatase(001) film CTRs (with residual STO contribution or negligible in most of their CTRs) and 7 fractional order rods from the (4x1)/(1x4) superstructure were measured for each case, accounting for more than 3000 non-equivalent reflections for each sample. The surface quality of all samples was previously inspected with AFM, LEED and STM. See the representative figures below:

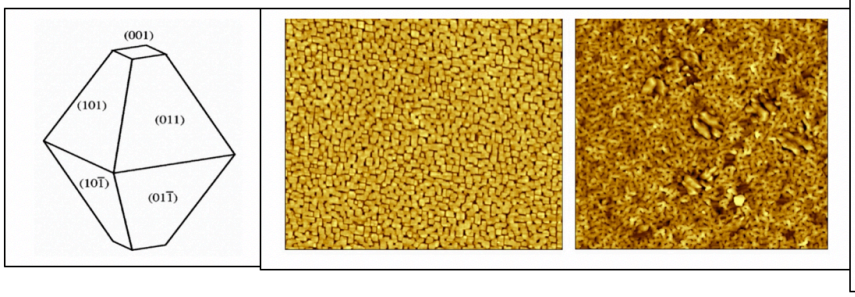

Figure 1. *Left.* Anatase crystal morphology. *Middle.* AFM of anatase(001) surface- Lateral grain size is larger than 100 nm. *Right.* Anatase(100) surface. Grain size ~100 nm. Inplane growth direction is along (110) +/- 6.5º. So, eight domains are present on the surface.

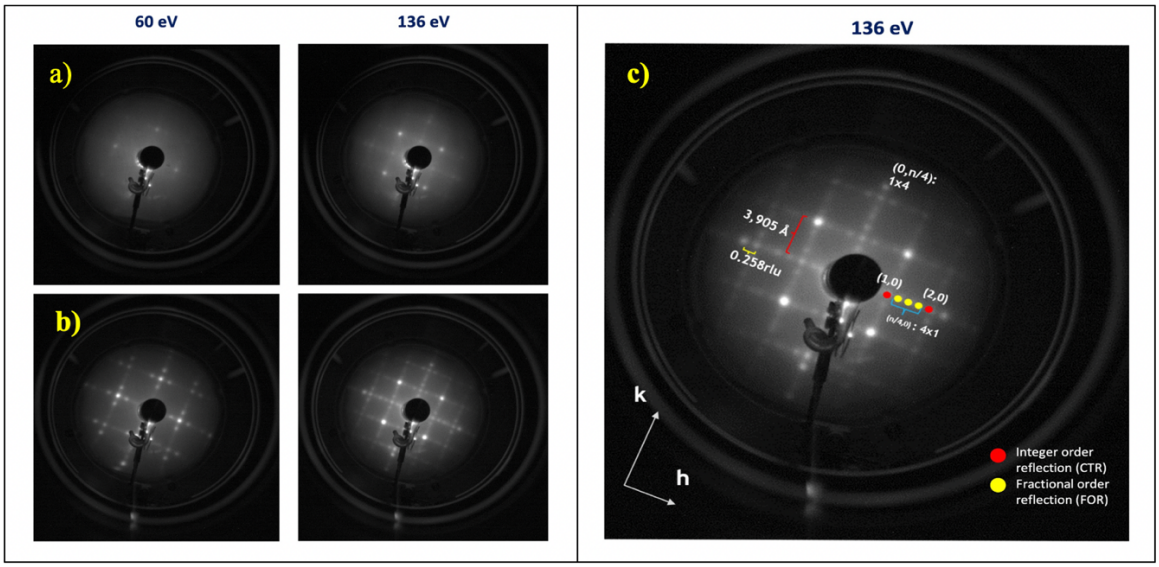

Figure 2. LEED images corresponding to a sample of 8 nm thickness. a) at two electron energies (60 and 136 ev) as prepared. b) After 3' Ar^+ sputtering, 600 eV, Isample 3 μA + annealing at 700°C in 10^{-6} mbar O2. C) Zoom figure showing the STO CTRs (brighter peaks) FORs. The relation between STO spacing and superstructure peaks (3.905/0.258 = 15.1 Å) gives the periodicity of the superstructure,

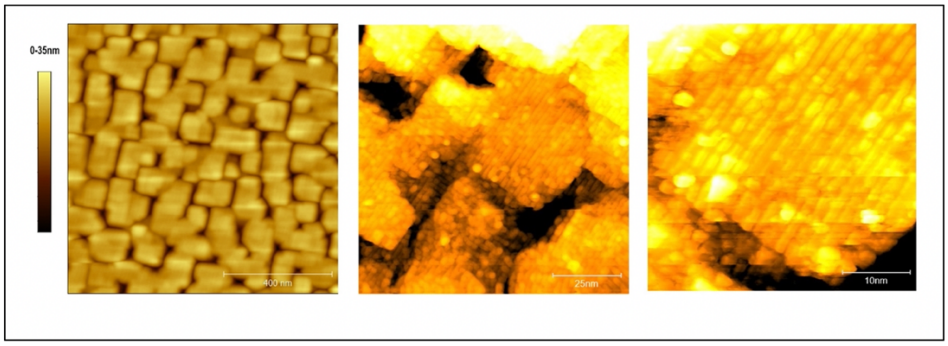

Figure 3. AFM image (left: 80 nm thick) and STM images (middle and right: zoomed, 8 nm thick). The distances between stripes correspond to the lattice spacing of the (4x1)/(1x4) reconstruction.

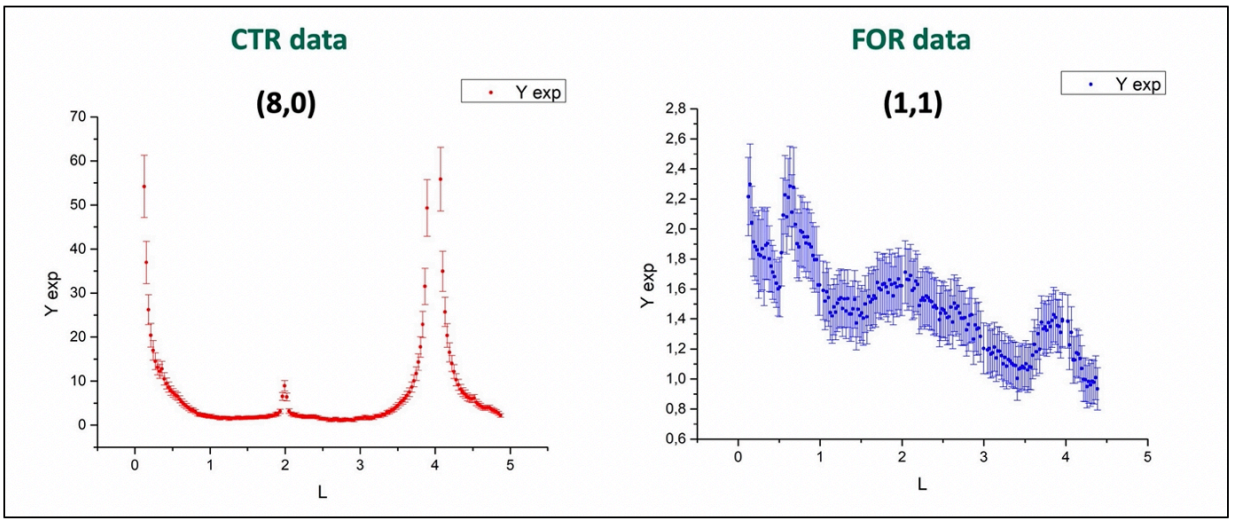

Figure 4. Left: (8,0,L) CTR of anatse(001) film (80 nm thick) and (11,L) FOR of the (4x1) superstructure domain. 3 full data sets of similar quality were measured for anatase thicknesses of 80, 8 and 4 nm.

The effect of water at low pressures was examined in all of the samples without success. Moreover, the Bragg reflections of the 80 nm thick film were measured in the full range defined by the energy of the selected beam.

A full data set of STO-CTRs at the TiO2/STO interface were also mesured during the period 10-12 March 2021. The objective was to take advantage of the small mismatach between TiO2 and STO(001) lattice parameters to measure the strain induced on the surface of the STO substrate by the TiO2 film.
15 non independent CTRs plus several equivalents ones were measured in order to determine the influence of TiO2 at the interface between both.

The analysis of the (4x1)/(1x4) anatae(001) superstructure recostruction is still in progress, however, a first model has been obtained from the analysis of one of the samples. It is compatible with a combination of a missing oxygen layer at the topmost TiO_2 surface with a missing row, as the STM images of figure 3 indicate. At this moment, we are still analysing the other two superstructure data sets, interface and average film structure of the films. We hope to finish this job as soon as possible for its publication. This job is part of the phD work of Adrian Crespo, who could not participate in the experiment due to restrictions imposed to the users at the ESRF during the experiment (only one user per beamline was permitted at that period of time).