

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	Experiment title: Structure of 2x1-OH intermediate in the surface dissolution of TiO ₂ (110) by SXRD	Experiment number: SI-2012
Beamline:	Date of experiment: from: 06/11/09 to: 24/11/09	Date of report: 25/02/10
Shifts: 18	Local contact(s): Jerome Roy	<i>Received at ESRF:</i>
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Report:

The interaction of TiO₂(110)(1x1) with H₂O has been the subject of significant recent activity because it is a model photocatalyst for water splitting. It is now generally accepted that dissociation can occur, but only at oxygen vacancies under typical *UHV* conditions [1,2]. At higher H₂O partial pressures it is hypothesised that a higher degree of surface hydroxylation occurs, and even weakly bound bi-layer structures, involving hydrogen-bonded molecular H₂O, may be present at room temperature, but currently there is a lack of experimental evidence. Salmeron's recent high pressure *PES* measurements [3] indicate that water only dissociates at oxygen vacancies creating bridging hydroxyls (*OH_{br}*). These *OH_{br}* act as Brønsted acid sites that anchor water molecules. The new complex then acts as a new anchor site with a lower acidic character. As more water molecules adsorb, the acidic character decreases and the overlayer structure tends towards a water or ice bulk like structure. Very recently, we have discovered that immersion of TiO₂(110)(1x1) in ultra-pure liquid water for a short time results in the formation of an ordered 2x1 overlayer. *UHV STM* images of this phase (known henceforth as TiO₂(110)(2x1)-H₂O_{dip}) suggest that it is comprised of *OH_{br}*. The goal of this experiment was to quantitatively confirm, or otherwise, this preliminary conclusion.

SXRD data were acquired from TiO₂(110)(2x1)-H₂O_{dip} on *ID32*, employing a *UHV Baby* chamber [4] mounted on the diffractometer in *EHI*. The sample was prepared in the ESRF's Surface Characterisation Laboratory (*SCL*). Clean substrate preparation involved repeated cycles of Ar⁺ bombardment and annealing in *UHV* to approximately 700°C. Sharp (1x1) patterns were obtained with low energy electron diffraction (*LEED*) and scanning tunneling microscope (*STM*) images of the surface showed a well-ordered, single phase (1x1) termination. Auger electron spectroscopy (*AES*) showed no contamination within the detection limits. To form the (2x1) overlayer, the sample was dipped in ~ 20ml of ultra-pure, deoxygenated H₂O for

approximately 15s. To avoid surface contamination/UV-induced modification this procedure was performed in a glove bag filled with Argon, illuminated only by red light. Post dip, the sample was immediately returned to the *UHV* system and transferred to the *Baby* chamber under vacuum.

SXRD measurements were all performed with the sample at room temperature, employing a photon energy of 18 keV. A complete dataset of 830 non-equivalent reflections along 20 *CTRs* were measured during the beam time. A selection of the crystal truncation rod (*CTR*) data from $\text{TiO}_2(110)(2\times 1)\text{-H}_2\text{O}_{\text{dip}}$ are displayed in Figure 1. This figure compares the intensity profiles of rods acquired from $\text{TiO}_2(110)(1\times 1)$ in *UHV* (blue, filled circles) [5] and $\text{TiO}_2(110)(2\times 1)\text{-H}_2\text{O}_{\text{dip}}$ (red, open squares). Clearly, the exposure of $\text{TiO}_2(110)(1\times 1)$ to H_2O by dipping strongly modifies the geometry of the topmost $\text{TiO}_2(110)$ surface layer(s). Interestingly, in the case of the previously measured $\text{TiO}_2(110)(1\times 1)\text{-H}_2\text{O}_{\text{liq}}$ interface [6], similar changes are also observed, which have been interpreted as due to the presence of two differently relaxed surface domains. Real space imaging of this interface is currently being undertaken to enable more complete understanding, and compare with images of $\text{TiO}_2(110)(2\times 1)\text{-H}_2\text{O}_{\text{dip}}$.

The analysis of the data measured in this experiment is ongoing.

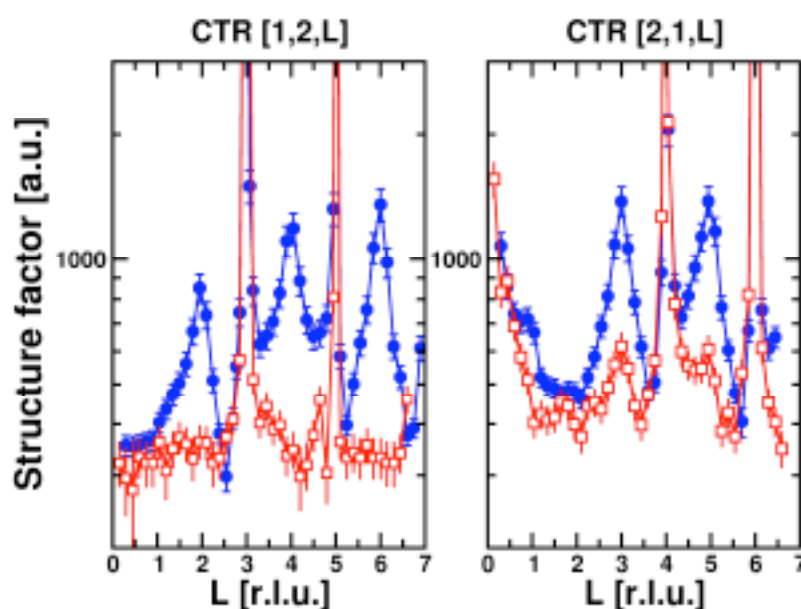


Figure 1: *l*-scans (1,2,*l*) and (2,1,*l*) acquired from $\text{TiO}_2(110)(1\times 1)$ in *UHV* (blue, filled circles) [5], and $\text{TiO}_2(110)(2\times 1)\text{-H}_2\text{O}_{\text{dip}}$ (red, open squares).

References

- [1] I.M. Brookes, C.A. Muryn and G. Thornton, Phys. Rev. Lett. 87, 266103 (2001).
- [2] R. Schaub, P. Thosttrup, N. Lopez, E. Lægsgaard, I. Stensgaard, J. K. Nørskov and F. Besenbacher, Phys. Rev. Lett. 87, 266104 (2001).
- [3] G. Kettler, S. Yamamoto, H. Bluhm, K. Andersson, D.E. Starr, D.F. Ogletree, H. Ogasawara, A. Nilsson and M. Salmeron, J. Phys. Chem. C 111, 8278 (2007).
- [4] http://www.esrf.eu/UsersAndScience/Experiments/StructMaterials/ID32/Preparation_Labs/R2P2System.html
- [5] G. Cabailh *et al*, Phys. Rev. B, 75, 241403 (2007).
- [6] ESRF Experiment SI-1718 (report date, 14/08/08).