

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: The structure of the TiO ₂ (110)-H ₂ O interface	Experiment number: SI-1899
Beamline: ID32	Date of experiment: from: 22/4/2009 to: 28/4/2009	Date of report: 26/8/09 <i>Received at ESRF:</i>
Shifts: 18	Local contact(s): Jerome Roy	
Names and affiliations of applicants (* indicates experimentalists): G. Thornton* and H. Hussain* <i>Chemistry Department and LCN, University College London, UK</i> R. Lindsay* <i>Corrosion and Protection Centre, University of Manchester, UK</i> X. Torrelles* <i>Institut de Ciència de Materials de Barcelona (CSIC), Spain</i> G. Cabailh* <i>Institut des Nanosciences, CNRS, Paris, France</i> O. Bikondoa* <i>Physics Department, University of Warwick, UK</i>		

Report:

$\text{TiO}_2(110)\text{-H}_2\text{O}$ has been the subject of significant recent activity, with much of the attention surrounding whether or not H_2O adsorbs dissociatively, hydroxylating the (110) surface. It is now generally accepted that dissociation can occur, but only at bridging oxygen vacancies ($\text{O}_{\text{br-vac}}$) under typical ultra high vacuum (*UHV*) conditions, forming so called bridging hydroxyls, *i.e.* $\text{H}_2\text{O} + \text{O}_{\text{br-vac}} \rightarrow 2\text{OH}_{\text{br}}$ [1]. At higher H_2O partial pressures it has long been presumed that there is more extensive surface hydroxylation. Recent high pressure photoelectron spectroscopy (*PES*) measurements [2] indicate, however, that this supposition is incorrect. It was determined that even at high relative humidity (close to 100 %) water still only dissociates at oxygen vacancies, forming a submonolayer coverage of OH_{br} . Furthermore, it was proposed that these species nucleate the formation of an ordered bi-layer of molecular water. The goal of this experiment was to quantitatively determine the geometry of this $\text{TiO}_2(110)\text{-H}_2\text{O}$ interface as a function of H_2O partial pressure, including confirmation, or otherwise of the ordered H_2O bi-layer.

SXRD measurements were performed on *ID32*, employing a *UHV Baby* chamber [3] mounted on the diffractometer in *EH1* (*N.B.* The *Baby* chamber was modified to incorporate a turbo molecular pump to enable data acquisition above *UHV*). The sample was prepared in the *ESRF's* Surface Characterisation Laboratory (*SCL*), and then transferred to the *Baby* chamber under vacuum. 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. We note that the *Baby* chamber employed initially was severely contaminated (almost certainly with oil), and so unusable. Thus we had to assemble a second *Baby* chamber during the beam time. This unforeseen setback significantly curtailed the amount of

beam time available for measurements; only 4.5 shifts were exploited for data acquisition. Nevertheless, as shown below, we were able to demonstrate the feasibility of this study.

SXRD measurements were all performed with the sample at room temperature, employing a photon energy of 18 keV. Initially, data were recorded from the $\text{TiO}_2(110)(1 \times 1)$ substrate in *UHV* to ensure the integrity of the surface through comparison with earlier results [4]. Diffraction intensity along three crystal truncation rods (CTRs) was acquired (*i.e.* $(0,1,l)$, $(2,1,l)$, $(1,2,l)$), using rocking scans in which the sample is rotated about its surface normal while scattered X-ray intensity is measured. Next H_2O vapour was admitted to the chamber and further diffraction data were recorded at a series of H_2O partial pressures ranging from $\sim 1 \times 10^{-6}$ mbar to ~ 10 mbar. At each partial pressure, given the limited time, only l -scans along the three CTRs acquired in *UHV* and two control reflections (rocking scans) were measured. However, these data are sufficient to demonstrate that the surface structure is modified by the presence of H_2O in the gas phase. Figure 1 shows the $(0,1,l)$, $(1,1,l)$ and $(2,1,l)$, l -scans measured for the $\text{TiO}_2(110)$ surface in *UHV* and at H_2O partial pressures of 1×10^{-3} mbar and 10 mbar, demonstrating that there is some variation in the diffracted profiles. Further beam time is required to obtain a more complete dataset to enable a quantitative assessment of the evolution of the $\text{TiO}_2(110)\text{-H}_2\text{O}$ interface as a function of H_2O partial pressure.

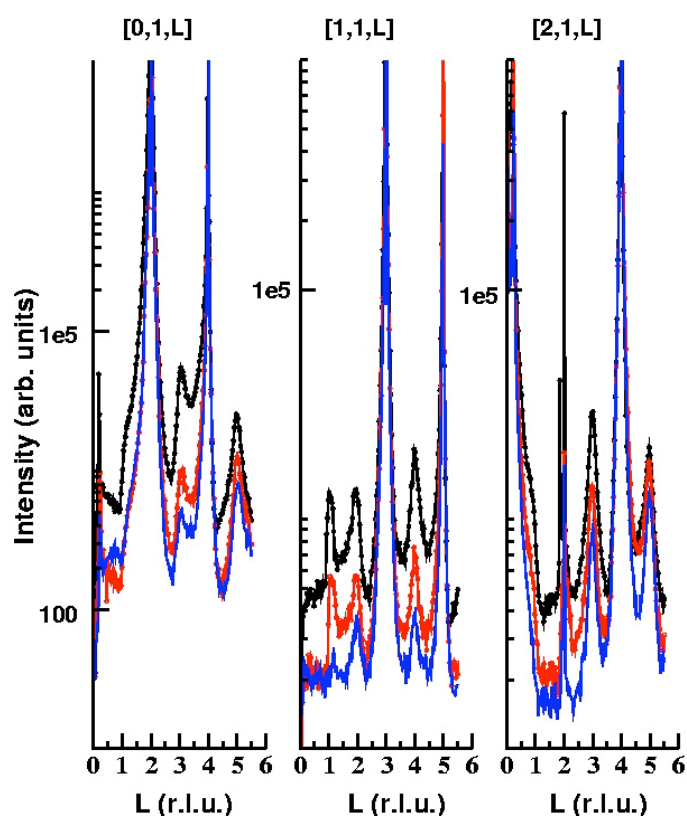


Figure 1: l -scans $(0,1,l)$, $(1,1,l)$ and $(2,1,l)$ acquired from the $\text{TiO}_2(110)$ surface in *UHV* (black) and the $\text{TiO}_2(110)\text{-H}_2\text{O}$ interface at H_2O partial pressures of 1×10^{-3} mbar (red) and 10 mbar (blue).

References

- [1] C.L. Pang *et al*, Chem. Soc. Rev. 37, 2328 (2008).
- [2] G. Ketteler *et al*, J. Phys. Chem. C 111, 8278 (2007).
- [3] www.esrf.eu/UsersAndScience/Experiments/StructMaterials/ID32/Preparation_Labs/SurfaceLab.html
- [4] G. Cabailh *et al*, Phys. Rev. B, 75, 241403 (2007).