



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: A quantitative determination of the surface structure of TiO ₂ (011)2x1	Experiment number: SI-1637
Beamline: ID32	Date of experiment: from: 5/12/2007 to: 11/12/07	Date of report: 29/2/08
Shifts: 18	Local contact(s): Jerome Roy	<i>Received at ESRF:</i>

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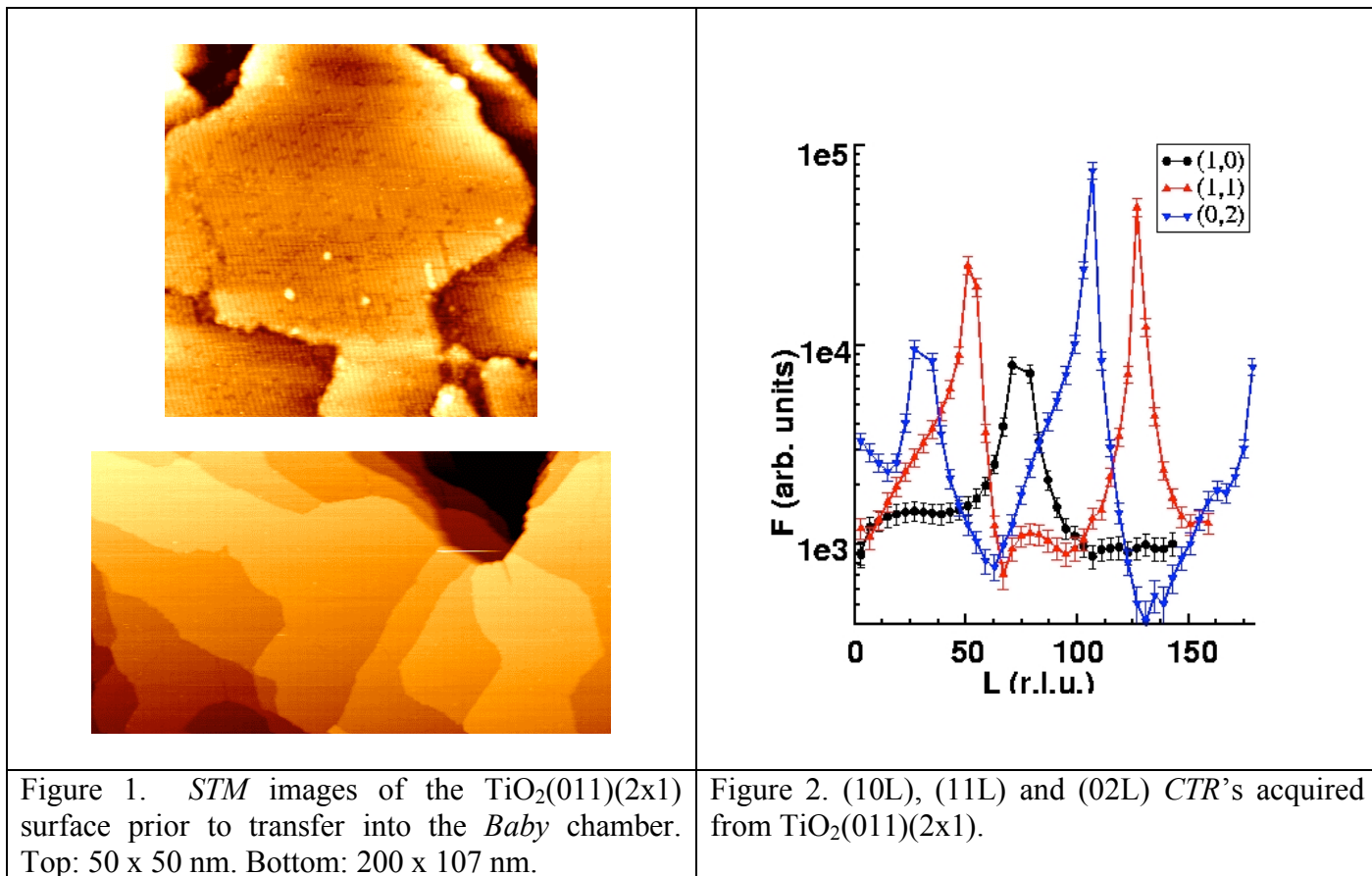
Report:

Reports of the higher photo-activity of {011} oriented surfaces of rutile TiO₂ (*e.g.* Refs. 1,2) have motivated researchers to investigate the atomic scale origin of this phenomenon. Diebold *et al* have been at the forefront of this effort, conducting fundamental surface studies to probe the geometric structure and reactivity of TiO₂(011) [3-6]. They have found that this surface exhibits a (2x1) reconstruction, which *ab initio* calculations predict to consist of added rows decorated with one-fold coordinated oxygen atoms, forming titanyl groups (Ti=O) [3]. These species have not been observed on other *model* TiO₂ surfaces, and it is hypothesised that they may be the source of the enhanced photo-activity. Currently, however, evidence for these titanyl groups is far from definitive, and a very recent study [7] has proposed an entirely different structure for TiO₂(011)(2x1), involving microfacets of {111} orientation rather than a 2D array of Ti=O moieties. Given this uncertainty, we have undertaken a surface X-ray diffraction (*SXRD*) study to directly determine the atomic scale geometry of the TiO₂(011)(2x1) surface.

SXRD measurements were performed on *ID32*, employing a *UHV Baby* chamber mounted on the diffractometer in *EHI*. The sample was prepared in the *ESRF*'s Surface Characterisation Laboratory (*SCL*), and then transferred to the *Baby* chamber under vacuum. Preparation involved repeated cycles of Ar⁺ bombardment and annealing in *UHV* to approximately 1150 K. A *UHV*-scanning tunnelling microscope (*STM*) facility, together with low energy electron diffraction (*LEED*) and Auger electron spectroscopy (*AES*), were exploited to ensure that the sample was prepared correctly. Typical *STM* images of the surface, following preparation, are displayed in Fig. 1. They clearly show a well-ordered, single phase (2x1) termination. Essentially identical images were also acquired subsequent to completion of the *SXRD* measurements, indicating that there was no appreciable degradation of the surface during data acquisition.

SXRD data were collected at room temperature ($h\nu = 17.7$ keV), using rocking scans in which the sample is rotated about its surface normal while scattered X-ray intensity is measured. For a given (*h,k*)-integer these rocking scans were performed at different *l*, enabling profiles of scattered intensity versus perpendicular

momentum transfer, known as crystal truncation rods (*CTR*'s), to be compiled. Fractional-order rods (*FOR*'s) were also acquired similarly. Two reflections, namely (1,0,4) and (1/2,0,3), were recorded at regular intervals to monitor sample degradation. No significant changes were observed throughout the duration of the experiment.



A large amount of data was acquired during the beam time, comprising 26 non-equivalent *CTR*'s, and 50 non-equivalent *FOR*'s. Example *CTR*'s are displayed in Fig. 2. Currently, structure determination is proceeding, employing the usual trial and error approach. It is expected that the large dataset will enable a reliable, high precision solution to be obtained, resolving the uncertainty about the geometry of $\text{TiO}_2(011)(2 \times 1)$.

References

1. J.B. Lowekamp *et al*, J. Phys. Chem. B 102, 7323 (1998).
2. T. Ohno *et al*, New J. Chem. 26, 1167 (2002).
3. T.J. Beck *et al*, Phys. Rev. Lett. 93, 036104 (2004).
4. C. Di Valentin *et al*, J. Am. Chem. Soc. 127, 9895 (2005).
5. T.J. Beck *et al*, Surf. Sci. 591, L267 (2005).
6. O. Dulub *et al*, Surf. Sci. 600, 4407 (2006).
7. T. Kubo *et al*, J. Am. Chem. Soc. 129, 10474 (2007).