



## 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:**Elucidating the high temperature 1x2/1x1 phase transition on TiO<sub>2</sub>(110) with surface X-ray diffraction**Experiment number:**

SI-1845

**Beamline:**

ID03

**Date of experiment:**

from: 24/6/2009 to: 30/6/2009

**Date of report:**

26/8/09

**Shifts:**

18

**Local contact(s):**

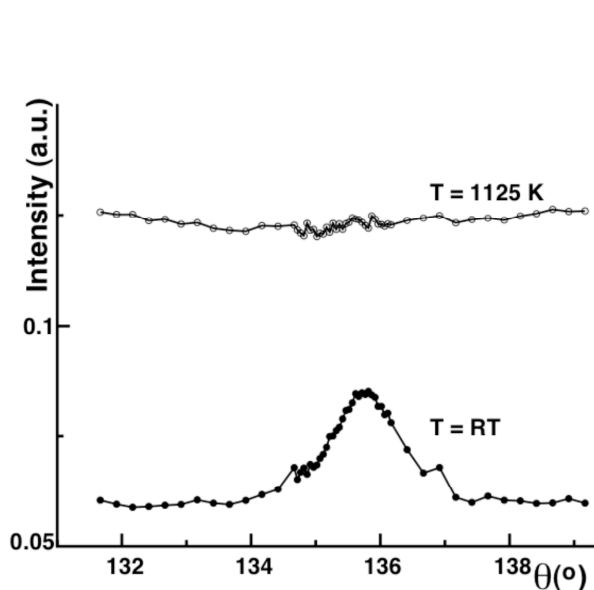
Andrea Resta

*Received at ESRF:***Names and affiliations of applicants (\* indicates experimentalists):****R. Lindsay\****Corrosion and Protection Centre, University of Manchester, UK***X. Torrelles\****Institut de Ciència de Materials de Barcelona (CSIC), Spain***G. Cabailh\****Institut des Nanosciences, CNRS, Paris, France***G. Thornton\* and H. Hussain\****Chemistry Department and LCN, University College London, UK***O. Bikondoa\****Physics Department, University of Warwick, UK***Report:**

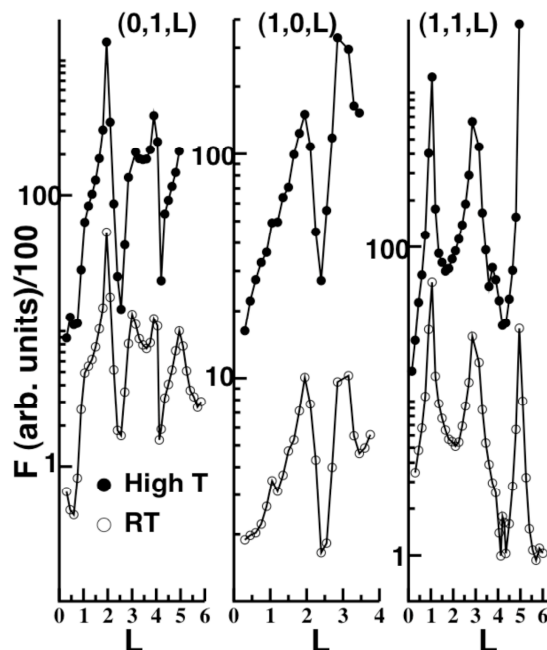
TiO<sub>2</sub>(110) is the prototypical metal oxide surface for fundamental surface studies. At room temperature this substrate typically displays either a (1x1) or (1x2) surface unit cell, with the latter being present on more highly reduced (oxygen deficient) samples [1]. Quantitative structure determinations have been conducted for both of these phases, and the atomic coordinates of surface selvedge atoms are known rather precisely [2-4]. Further to these room temperature phases, McCarty and Bartlet have found a high temperature (1x1) termination, henceforth referred to as TiO<sub>2</sub>(110)-HT-(1x1), which appears upon heating a sample exhibiting a (1x2) reconstruction to around 1050 K [5-7]. As yet, no real insight into the geometry of this TiO<sub>2</sub>(110)-HT-(1x1) phase has been gained, which is essential for mechanistic understanding of the (reversible) 1x2/1x1 phase transition. The objective of this experiment was to quantitatively determine the geometry of TiO<sub>2</sub>(110)-HT-(1x1), employing surface X-ray diffraction (SXR).

Initial sample preparation was undertaken at UCL (London, UK), employing an ultra high vacuum scanning tunnelling microscope (UHV-STM) facility. Cycles of Ar<sup>+</sup> bombardment and annealing were conducted to generate clean and highly ordered surfaces. Three samples displaying (1x2) reconstructions were prepared. In addition, a (1x1) terminated sample was produced. SXR measurements were conducted on ID03, employing the UHV vessel/diffractometer in EH2. Samples were inserted into the UHV environment using the load-lock facility, and underwent Ar<sup>+</sup> bombardment/annealing to remove surface contamination arising from atmospheric exposure during transport from UCL. Surface cleanliness and order were monitored by Auger and SXR measurements, respectively. In particular, fractional order diffracted X-ray reflections were recorded to determine the presence of the (1x2) reconstruction. Once satisfied with the quality of the room temperature (1x2) phase, the substrate temperature was increased in steps to search for the 1x2/1x1 phase transition to enable SXR data from the TiO<sub>2</sub>(110)-HT-(1x1) structure to be acquired.

None of the pre-prepared (1x2) samples proved to be suitable for  $\text{TiO}_2(110)\text{-HT-(1x1)}$  SXRD measurements. No 1x2/1x1 phase transition was observed for the first sample, and the  $\text{TiO}_2(110)\text{-HT-(1x1)}$  phase on the other two samples was unstable. These problems are believed to be due to the substrates being too reduced (oxygen depleted); McCarty and Bartlet indicate that beyond a certain degree of bulk reduction the 1x2/1x1 transition disappears [6]. In contrast, *in situ* (*i.e.* on the beamline) formation of the (1x2) reconstruction through reduction of the pre-prepared (1x1) sample gave rise to formation of a stable  $\text{TiO}_2(110)\text{-HT-(1x1)}$  termination. Presumably, this difference is simply a result of a lower degree of bulk reduction. Room temperature STM images acquired following SXRD measurements demonstrated that the pre-prepared (1x1) surface had become essentially entirely (1x2).



**Figure 1:** Rocking scans of the  $(1.5,0,0.6)$  fractional order reflection with the  $\text{TiO}_2(110)$  substrate at room temperature and 1125 K.



**Figure 2:** Experimental CTR data acquired from  $\text{TiO}_2(110)\text{-HT-(1x1)}$ , along with room temperature  $\text{TiO}_2(110)(1x1)$  data from Ref. 3.

SXRD data from the pre-prepared (1x1) substrate following *in situ* (1x2) preparation are shown in Figures 1 and 2. The presence of the temperature induced 1x2/1x1 phase transition is demonstrated in Figure 1 by the complete loss in intensity of the  $(1.5, 0, 0.6)$  fractional order reflection at a substrate temperature of 1125 K. Crystal truncation rod (CTR) data from  $\text{TiO}_2(110)\text{-HT-(1x1)}$  are displayed in Figure 2. Unfortunately, reflections (81 non-equivalent) along only these three CTRs were measured due to a lack of remaining beamtime following successful substrate preparation. In comparison a total of 625 non-equivalent reflections from 15 CTRs were acquired in our determination of the geometry of room temperature  $\text{TiO}_2(110)(1x1)$  [3] (Figure 2 also displays equivalent CTR data from this dataset). Thus further beamtime is required to obtain a more complete dataset to facilitate a reliable and precise structure determination.

## References

1. U. Diebold, Surf. Sci. Rep. 48, 53 (2003).
2. R. Lindsay *et al*, Phys. Rev. Lett. 94, 246102 (2005).
3. G. Cabailh *et al*, Phys. Rev. B, 75, 241403 (2007).
4. M. Blanco-Rey *et al*, Phys. Rev. Lett. 96, 055502 (2006).
5. K.F. McCarty and N.C. Bartlet, Phys. Rev. Lett. 90, 046104 (2003).
6. K.F. McCarty and N.C. Bartlet, Surf. Sci. 527, L203 (2003).
7. K.F. McCarty and N.C. Bartlet, Surf. Sci. 540, 157 (2003).