EUROPEAN SYNCHROTRON RADIATION FACILITY

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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

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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

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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.

ESRF	**Experiment title:** **Structure determination of Cr_2O_3(0001) as a function of oxygen pressure**	**Experiment number**: SI - 878
Beamline: ID03	**Date of experiment**: from: 02/7/03 to: 08/7/03	**Date of report**: 20/12/04
Shifts: 18	**Local contact(s)**: Hyojung Kim	*Received at ESRF:*

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Report:

A number of state of the art *ab initio* theoretical calculations have been performed to explore the geometric structure of *model* metal oxide surfaces as a function of ambient conditions. Recently, two such studies have been concerned with Cr_2O_3(0001) [1,2], examining the impact of oxygen partial pressure and substrate temperature. The results are not in complete agreement. Specifically, at 300 K, Wander *et al* [1] conclude that this surface exhibits three distinct structures, namely *–Bulk-Cr-3O-Cr*, *-Bulk-Cr-3O-Cr=O*, and *–Bulk-Cr-3O-Cr-Cr-3O* terminations, as the oxygen pressure increases, whereas Wang *et al* [2] predict that the *–Bulk-Cr-3O-Cr-Cr-3O* phase is always the most stable structure. The goal of this study was to experimentally probe the geometric structure of Cr_2O_3(0001) as a function of oxygen pressure at approximately 300 K, using the well-established technique surface X-ray diffraction (*SXRD*).

The experiment was performed on *ID03*, employing an ultra high vacuum/high pressure (*UHV*/*HP*) chamber, in tandem with a high precision vertical diffractometer [3]. An X-ray wavelength of 0.79 Å was utilised for the diffraction measurements. Data were accumulated using so called *rocking scans*, in which the sample is rotated about its surface normal while the scattered X-ray intensity is recorded. Such scans were performed for a given integer (*h*,*k*) as a function of *l*, providing profiles of scattered intensity, I_{hk}, versus perpendicular momentum transfer, which are known as crystal truncation rods (*CTR*'s).

Initially, following *in situ* surface preparation, involving a series of Ar^+ bombardment and annealing cycles, a set of *CTR*'s was acquired from the Cr_2O_3(0001) surface under *UHV* conditions. The goal of these measurements was to determine the structure of the *UHV-surface*, comparing

these results with previous experimental and theoretical work [1,4-6]. Oxygen was then admitted to the *UHV/HP* chamber, and a pressure of approximately 190 mbar was maintained, whilst diffraction data were collected. Under these conditions the $Cr_2O_3(0001)$ surface was found to be very unstable, as evidenced by the significant diminishment in the intensity of reference reflections over a short time period. A possible explanation for this surface instability is the presence of reactive O_3 species, generated by the X-ray beam.

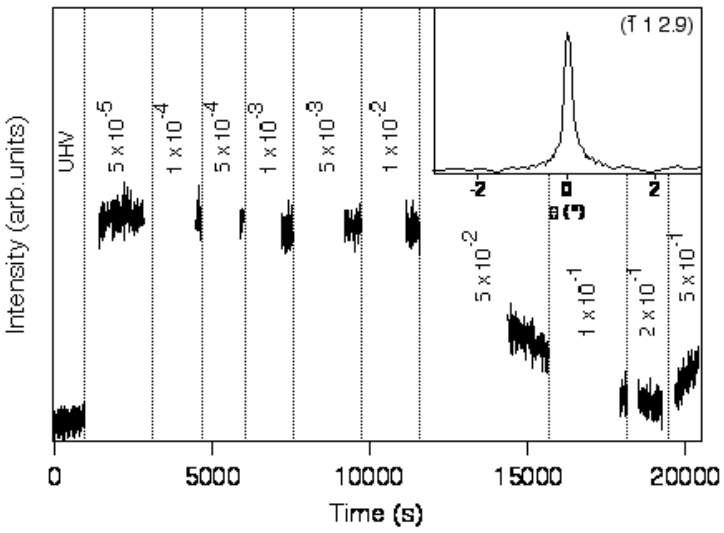

Figure 1. Variation in the intensity of ($\bar{1}$ 1 2.9) reflection as a function of oxygen partial pressure(mbar)/time. The inset displays a rocking scan through the ($\bar{1}$ 1 2.9) reflection. All of the data were recorded at room temperature.

To avoid this problem of surface degradation all further work focussed on significantly lower oxygen partial pressures. Figure 1 displays the intensity variation of the ($\bar{1}$ 1 2.9) reflection as a function of pressure/time. We note that this reflection was empirically selected on the basis of preliminary measurements indicating that it is sensitive to changes in oxygen partial pressure. It can be clearly seen that on going from an *UHV* environment to an oxygen partial pressure of $5x10^{-5}$ mbar the intensity increases significantly, and then remains approximately constant for several decades of pressure. This observation strongly suggests a change in the surface geometry. *CTR*'s were recorded at $1x10^{-2}$ mbar to enable the structure of this *10^{-2}-surface* to be elucidated. As the oxygen partial pressure is increased above $1x10^{-2}$ mbar further structural changes are indicated. The intensity of the ($\bar{1}$ 1 2.9) reflection decreases and attains a minimum at around $1x10^{-1}$ mbar, before beginning to increase again at an oxygen partial pressure of $5x10^{-1}$ mbar. Given the limited experimental time no *CTR*'s were acquired at these higher pressures. The reversibility of the *UHV-surface/10^{-2}-surface* structural change was also probed by recording diffraction data following pumping down of the chamber back to *UHV*. No clear evidence for or against a reversible phase change was found. This result indicates that the observation of structural variation with oxygen partial pressure may be a result of kinetics rather than thermodynamics

In summary, we have shown that the surface structure of $Cr_2O_3(0001)$ does vary with oxygen partial pressure. Currently, we cannot be certain that the structures observed are the lowest free energy geometries. Analysis of *CTR*'s from the *UHV-surface* and *10^{-2}-surface* to determine their structures is ongoing. This work is progressing somewhat more slowly than anticipated, due to the presence of multiple grains within the sample, which complicated data reduction procedures.

References

[1] A. Wander *et al*, *to be published.*
[2] X.-G. Wang and J.R. Smith, Phys. Rev. B 68, 201402(R) (2003).
[3] P. Bernard *et al*, Rev. Sci. Instrum. 70, 1478 (1999).
[4] F. Rohr *et al*, Surf. Sci. 372, L291 (199).
[5] Th. Gloege *et al*, Surf. Sci. 441, L917 (1999).
[6] A. Rohrbach *et al*, Phys. Rev. B 70, 125426 (2004).