

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: Investigation of charging effects in thin metallic films by X-ray reflectivity and grazing incidence diffraction.	Experiment number: HE-3003
Beamline:	Date of experiment: from: 24.06.2009 to: 30.06.2009	Date of report: 01.09.2009
Shifts: 18	Local contact(s): Alexei Vorobiev	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Alexey Dobrynin, Institut Néel, CNRS, Grenoble Patrick Warin, INAC, CEA, Grenoble Alain Marty, INAC, CEA, Grenoble Dominique Givord, Institut Néel, CNRS, Grenoble		

Report:

The purpose of the experiment was to directly visualize electric charging of thin metallic films by means of X-Ray reflectivity. When an E-field is applied to a metallic film, the concentration of conduction electrons at the film's surface is changing, which is equivalent to the formation of an additional layer at the top of the film, with density different from that of the main film. Numerical simulations and preliminary test measurements demonstrated the feasibility of synchrotron X-Ray reflectivity for revealing this effect, as it was described in detail in the proposal.

For this experiment, several Pt and Al films were prepared, with thickness 15 or 350 nm, deposited on 200 μm and 500 μm thick single crystalline MgO 110 substrates with a 5 nm Ti buffer layer in between. The voltage was applied to the samples in two different ways. The first approach is by using an electrolyte cell, where the studied film is used as one of the two electrodes. Two electrolyte solutions were used: carbonate propylene and ionic liquid (1-Butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide). The second approach is by applying voltage through a solid-state barrier. For the latter we used thin films of parylene C, deposited by chemical vapor deposition. The thickness of the barriers was 450-500 nm. Thin (10 nm) top Pt electrodes were then deposited on top of the barriers by sputtering. The supported E-field was up to $3.5 \cdot 10^8 \text{ V/m}$.

Fig. 1 shows two fragments of reflectivity curves for the MgO / Ti 5 nm / Pt 15 nm sample, immersed in carbonate propylene, taken under applied voltages of -1 V, 0 V, +1 V. The voltages were switched at every angle during the scan. The two sets of curves on the left and on the right of Fig. 1 were taken at different time slots. Apparently, there is a clear difference between the reflectivity curves, taken under different voltages. However, there is a lack of reproducibility of the reflectivity curves taken under the same voltage, but at different time periods. This time-related deviation is of the same order of magnitude as the expected effect, which complicates analysis of the results. Longer waiting times (up to 160 s, as opposed to usual 10 s) after voltage switching improve reproducibility of the measurements, although some uncertainty remains. We refer this effect to the formation of electrolytic double layer, which takes long time in carbonate propylene.

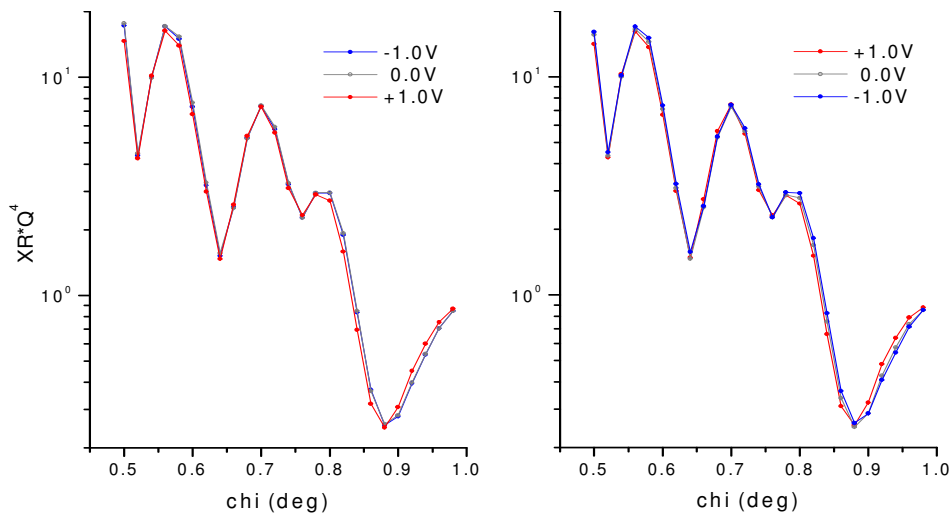


Fig.1

Fragments of reflectivity curves for sample MgO / Ti 5 nm / Pt 15 nm, taken under different applied voltages (different colors) and at different time slots (left and right figures)

In the case of the ionic liquid there was not much difference between the normalized reflectivity curves taken at different time slots, because there is no double layer formation in this liquid. Fig. 2 shows reflectivity curves from sample MgO / Ti 5 nm / Pt 350 nm. However, we haven't been able to collect statistically reliable data in this case because of the poor stability of the beam at ID 10B.

Ti15-Pt350 - ionic liquid

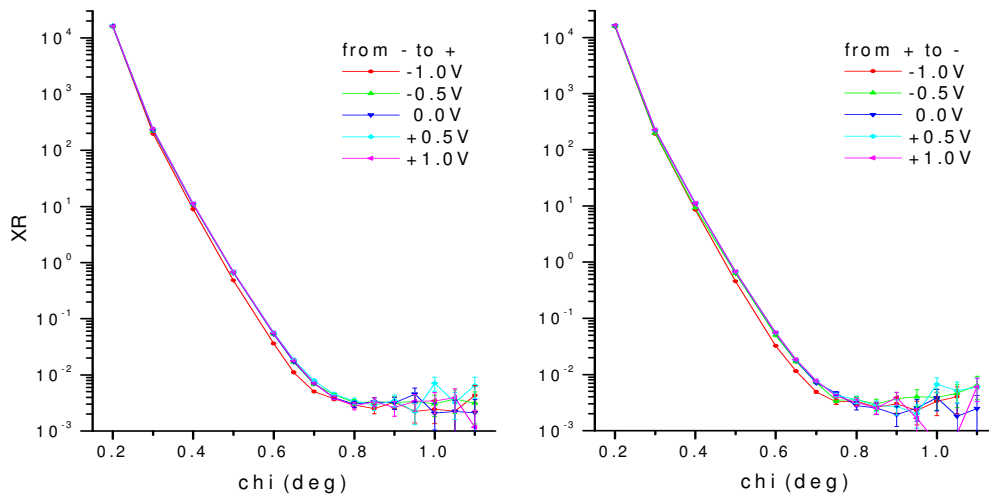


Fig. 2

Fragments of reflectivity curves for sample MgO / Ti 5 nm / Pt 350 nm, taken under different applied voltages (different colors) and at different time slots (left and right figures)

For the samples with the solid state barriers we arrived at the following conclusions. 1) The top barriers are too rough and too thick, which complicates obtaining good reflectivity signal from the studied surface of the film. 2) Although high E-field can be applied initially through the barrier (180 V for a 500 nm barrier), parylene C is being burned by the 22 keV X-Ray beam, so that in about 10-15 min after exposing the sample to the X-Ray, the barriers get broken. The latter is the biggest problem for the planned experiment, which could be avoided by using some very fast detector, which would allow collection of necessary amount of data in very short time periods. Different energies could be tried as well, in order to minimize the damages created to the parylene barrier from X-Rays.

The major problem during the whole experimental session was the very poor stability of the beamline optics. Under such conditions it was impossible to collect reliable and reproducible full reflectivity curves. Due to time lost for beam alignment we couldn't start with the initially planned crystal truncation rod diffraction measurements. Thus, so far we can only confirm qualitatively the feasibility of the proposed approach for revealing electric charging of thin metallic films. Based on the experience gained, for the next proposal we will limit ourselves to electrolyte experiments with the ionic liquid and, in case of a reasonable beam stability, carbonate propylene (which will require more measuring time due to long waiting time after every voltage switch). The samples to be investigated will be Pt and Pd thin films deposited on 500 μm thick MgO substrates, since we have found that it is impossible to use Al films as electrodes in the electrolyte cell probably due to oxidation of the films surface. Grazing incidence diffraction measurements, which are expected to bring quantitative and element-specific information during charging of the films, are pending.