EUROPEAN SYNCHROTRON RADIATION FACILITY

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ESRF

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.

ESRF	**Experiment title:** Structure of the Helmholtz Double Layer	**Experiment number**: SI-1096
Beamline: ID15A	**Date of experiment**: from: Feb 16, 2005 to: Feb 28, 2005	**Date of report**: March 2005
Shifts: 36	**Local contact(s)**: Veijo Honkimaki	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

Before the run, we decided it was pointless to look at metal substrates because none had been prepared flat enough for the high-energy reflectometer. Heavy metals have the problem that the solution structure makes almost no change to the reflectivity. Thin films have the additional problem of two surfaces, leading to strong oscillations of the reflectivity. The part of the curve most sensitive to the solution would be the dips, where the two sides cancel out, but which are hardest to measure accurately.

Silicon was the best choice from the reflectivity standpoint, even if the electrochemistry is more challenging. The low density of Si means that we are more sensitive to the structure of the adjacent solution. Fortunately the good electrical contacts (both to the electrolyte and to the external potential) can be made to Si by using "H-terminated" surfaces that are reproducibly made by dipping in 50% HF for 1 minute followed by buffered NH_4F (ph4) for 3 minutes. The complications to the electrochemistry of of a semiconductor (SC) electrode are:
i) the "flat band" potential, E_FB, is more relevant than the zero-charge potential, E_ZC, although these are similar. Most of the potential drop in a semiconductor-water interface occurs inside the SC in the form of "band bending". Relatively little change of surface charge state can be induced by the applied potential, which connects to the Fermi level.
ii) light-induced effects are strong due to photo-excitation across the band gap. An n-type semiconductor (our case) acts as a photo-anode, so has to be kept dark in the positive potential region. A p-type semiconductor acts as a photo-cathode.

The substrates were pre-cleaned using the RCA method, following the recipe of Alexander Reitzle (Ulm, 2003):
i) 2 hours reflux in boiling isopropanol (80C)
ii) 15 minutes in alkaline peroxide (NH_3:H_2O_2:H_2O, 1:1:5)
iii) stripping the resulting oxide in 50%HF for 1 minute

iv) 15 minutes in acid peroxide (HCl:H_2O_2:H_2O, 1:1:5)
The resulting surface has a well-defined sacrificial oxide that can be removed by a final HF-step just before use.

The samples were mounted in the EC cell of Frank Renner, that captures the top-hat shaped 20mm substrates at the top of a teflon post, sealed by clamping against an O-ring. The back contact was made with In-Ga eutectic. The cell was a gas-sealed glass bulb of 40mm diameter gravity-filled with electrolyte through side tubes from a gas bubbled drip-feed solution. Counter and reference electrodes, connected to the potentiostat, entered from the side. Some trouble was encountered draining the solution because of the narrow teflon tubes, which led to some spills. The cell was therefore redesigned for use with the toxic fluoride electrolytes (see below).

The ID-15 undulator beam at 70.5keV was colimated by 0.5x0.5mm entrance slits and focused by 200 compound refractive lenses (CRLs) made of Be. The resulting focus was about 20 microns at the sample. The new MPI Stuttgart reflectometer tilted the sample to an angle alpha_i in front of a detector table, 2m away, inclined at an angle of vtth=2xalpha_i. The 0.1mm(v)x0.4mm(h) detector slits were prealigned every 0.1 degrees of vtth and a least-squares regression used to maintain alignment of the specular ridge.

Initial experiments were with 0.1M H_2SO_4 electrolyte at potentials -1.0V, -0.7V, -0.5V and -0.45V vs Ag/AgCl, all negative of the nominal E_FB (-0.44V). Clear oscillations were found in the reflectivity, strongest near 0.3\AA^{-1}, that indicated the formation of some sort of film with thickness in the range of 20\AA. The oscillations were found to be time dependent but only weakly potential-dependent. They were clearly induced by the X-ray beam because they could be reset completely after a small sideways translation of the sample. The changes were irreversible, resulting in a series of parallel lines written on the electrode at the end of the experiment, as the position scan in Fig 1 shows.

The focusing CRL optics were therefore removed from the beam and the experiments resumed with 0.1mm(v)x2mm(h) entrance slits and 0.1mm(v)x3mm(h) detector slits. About the same reflected intensity resulted, but on a much enlarged background and consequently worse statistics. Presumably because the area of sample illuminated by the x-ray beam was much larger, the beam-damage effects were no longer observed. Again no potential dependence of the reflectivity was found for the 0.1M H_2SO_4 electrolyte.

Next an ionic solution of 0.5M K_3PO_4 at pH 3 was used as electrolyte, again at a series of potentials, -1.0V, -0.7V, -0.5V, -0.3V and -0.1V. Featureless close-to-ideal reflectivity resulted in all cases indicating no change of the solution structure at the resolution level of the measurement (Q_{max}=0.8\AA^{-1}). Analogous experiments in K_2SO_4 and KCl electrolytes showed similar results.

Without any clear result on potential dependence in conventional electrolytes, we redesigned the experiment to work with acidified fluoride electrolytes. We were obliged to remove the tube feed system and large volume cell for safety reasons; fluorides are toxic and can release dangerous HF fumes when acidified. The new cell design kept the total volume to 10ml and had a simplified loading/unloading procedure that minimised contamination and waste products, but it did not allow degassing of the solutions.

Since the last step of preparation of the hydrogen-terminated Si(111) surface is a concentrated solution of ammonium fluoride, acidified to pH4, we considered that interfaces of similar chemical composition might be sufficiently stable systems for our measurements, so we made electrolytes from 1M CsF acidified with HF for our initial tests. The highest purity (99.99%) reagents were available for this purpose.

Our initial tests were at a potential of -0.7V, similar to that used for the H_2SO_4 experiments, but there was a significant (negative) current. The interface was found to be stable for one scan, but when the potential was moved to -1.0V (vs Ag/AgCl) there were dramatic changes, later attributed to formation of hydrogen bubbles decorating the interface. Because of the high absorption of the 1M CsF solution, the bubbles had a big effect on the data.

Later it was found that the surface could be partly regenerated by application of 40% (2M) NH_4F, which is the last preparation step for the H-terminated Si(111) surface. The 1M CsF electrolyte was too absorbing to measure far out along the reflectivity curve, so the concentration was reduced to 0.1M and the potential was started at -0.4V near to the potential of zero charge. Under these conditions the reflectivity of the interface was measured, as shown in the figure, but still found to evolve in time. The shape is roughly what is expected for the Helmholtz layer of ions.

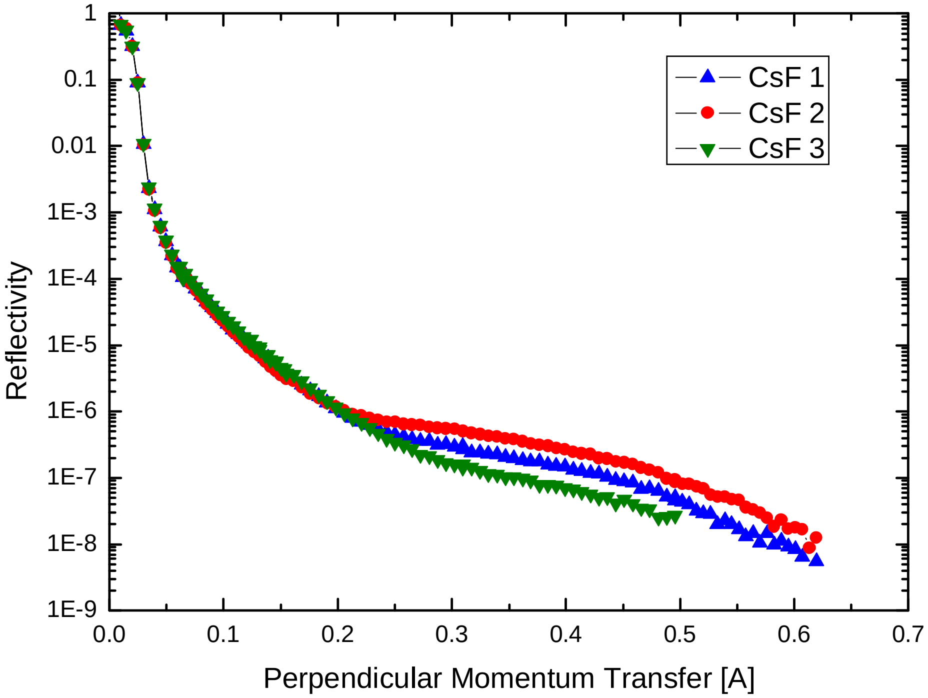

Figure. Measured reflectivity of a 0.1M CsF solution in contact with a hydrogen-terminated silicon substrate at a potential of -0.464V (vs Ag/AgCl). Curves are numbered in time sequence, spaced about one hour apart.