

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 via the User Portal:

<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

Reports supporting requests for additional beam time

Reports can 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:

Changing of the chemical properties through monolayer deposition investigated by Resonant Surface X-ray Scattering

Experiment number:

28-01-975

Beamline:

BM28

Date of experiment:

from: 20/6/2012 to: 3/7/2012

Date of report:

3/10/2013

Shifts:

36

Local contact(s):

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Received at ESRF:

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Report:

We have performed *in-situ* resonant surface x-ray scattering experiments on the Cu(001)-halide, Au(001)-halide and Au(001)-Cu-halide electrochemical system to to probe the charge transfer and nature of the chemical bonding for these systems.

The samples were aligned at energy below the Cu K-edge and Au L3-edge for the copper and gold electrodes respectively. The Au(001) and Cu(001) crystals were indexed to the conventional *fcc* unit cell with the (0, 0, *l*) direction along the surface normal ($a^*=b^*=c^*=2\pi/a$, where $a=4.078 \text{ \AA}$ and $a=3.615 \text{ \AA}$, for Au(001) and Cu(001) respectively) and aligned with the (0 0 2) and (1 1 1) Bragg reflections.

For both the Cu(001)-c(2x2)-Cl and Cu(001)-c(2x2)-Br superstructure the intensity on the (0 1) superstructure rod at L=0.2 was recorded in vertical geometry while varying the Energy through the Cu K-edge and the results are shown in Fig 1. At L=0.2 a shift in the Cu-K edge of about $3.5 \pm 0.5 \text{ eV}$ is observed for the Br and Cl superstructure.

In addition for the Cu(001)-c(2x2)-Br superstructure the intensity at the superstructure rod at different L

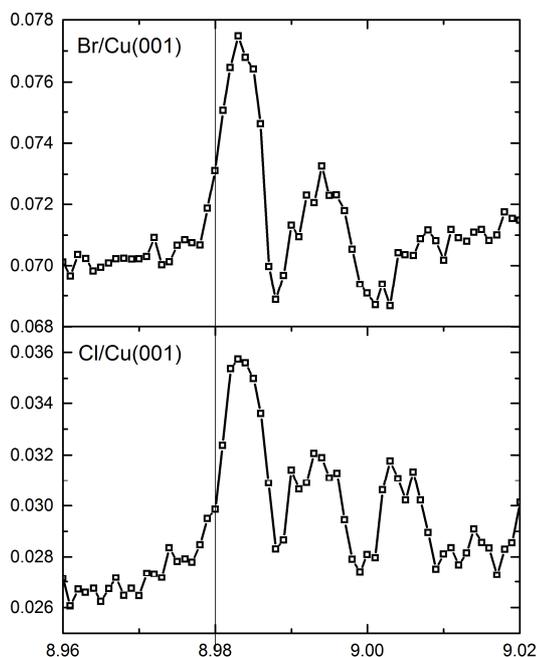


Fig.1 Intensity at the (0 1 0.2) for the Cl- and Br-adlayer on Cu(001) while varying the energy through the Cu K-edge.

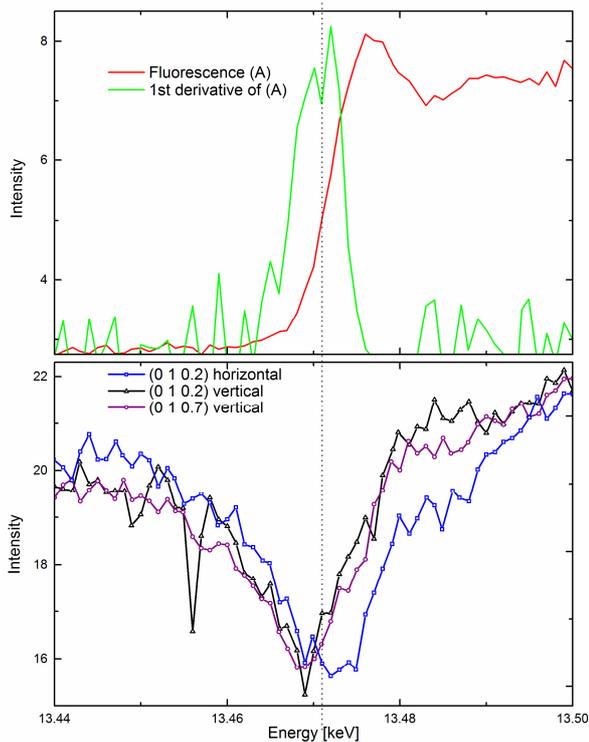


Fig. 2 Fluorescence (top) and Intensity of the superstructure rod for Br on Cu(001) in different polarisation of the beam (bottom) while scanning the Br edge.

bromide adsorption on Au(001)

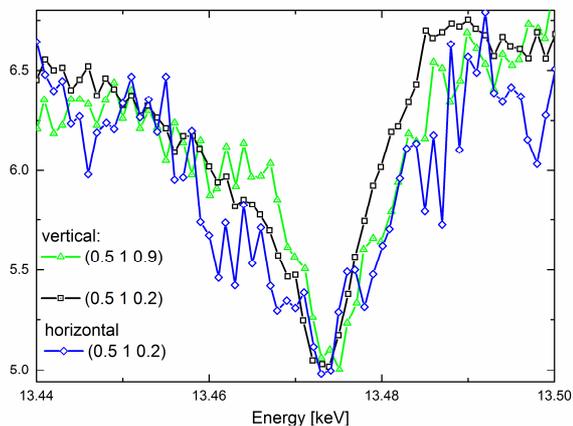


Fig. 3 The intensity at the Br superstructure position on Au(001) while scanning the Br edge at different L and for different polarisation of the x-ray beam.

was recorded while scanning through the Br K-edge. Although for the Br K-edge the fluorescence data was recorded in parallel to the resonant Surface Diffraction Intensities at specific points in reciprocal space in contrast to the Cu fluorescence which fluorescence arises from the Br ions in solution and adsorbed on the surface. The position of the fluorescence therefore does not give the exact position of the Br edge. To be able to distinguish the effect of the charge transfer between the adsorbed Br ion and the electrode surface, for the Br in all cases the resonant surface diffraction data had to be recorded in vertical and horizontal geometry. Such data is shown in Fig 2 on the superstructure rod at different L positions. The in-plane position at $L=0.2$ (for which the angle between the surface normal and the polarization of the x-ray beam is 7°) was recorded in horizontal and vertical geometry. A clear shift of the Br K-edge towards smaller values of $\Delta E=3.0\pm 0.5\text{eV}$ can be observed.

In comparison to the halide adsorption on Cu(001) resonant surface X-Ray diffraction data for the was recorded. Bromide forms a $c(\sqrt{2} \times 2\sqrt{2})R45^\circ$ superstructure on Au(001) in a potential range between 0 and 0.4 V vs Ag/AgCl in 10 mM KBr + 0.1 M HClO₄. Resonant Surface X-ray Diffraction was recorded on the (0.5 1) superstructure rod at different L values in horizontal and vertical geometry at a potential of 0.3 V by scanning the x-ray energy through the Br K-edge (Fig 3.). No shift in the X-ray edge (as compared to Br on Cu(001)) can be observed. Specifically, no difference in the the position can be observed at (0.5 1 0.2) in horizontal and vertical geometry.

Preliminary studies for the Br-Cu-Au(001) system on the Br and Cu edge were done. These were however too noisy to allow qualitative or quantitative analysis due to the restricted time of the experiment.