

## 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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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***

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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.



	<b>Experiment title:</b> The influence of a corrosion inhibitor and a brightener on the anodic selective dissolution of Cu <sub>3</sub> Au(111)	<b>Experiment number:</b> SI-1725
<b>Beamline:</b> ID32	<b>Date of experiment:</b> from: 07.02.2008 to: 15.02.2008	<b>Date of report:</b> 05.03.2009  <i>Received at ESRF:</i>
<b>Shifts:</b> 18	<b>Local contact(s):</b> Dr. Jörg Zegenhagen	
<b>Names and affiliations of applicants</b> (* indicates experimentalists): Dr. Frank Renner* Dr. Sascha Hümann* Mr. Genesis Ankah* Dr. Aparna Pareek Max-Planck Institut für Eisenforschung, Dusseldorf, Germany		

## Report:

The selective dissolution of Cu from Cu<sub>3</sub>Au(111) in presence of anionic additives e.g. bromide and iodide as well as under the influence of decanethiols was studied by in-situ X-ray diffraction. The experiment was performed at the undulator beamline ID32 at the European Synchrotron Radiation Facility (ESRF).

## Experimental:

The in-situ X-ray diffraction experiments were performed using Cu<sub>3</sub>Au (111) single crystal. Prior to the experiment, the sample surface was prepared in UHV by several sputter-anneal cycles. The cleanliness and chemical order of surface was verified by Auger electron spectroscopy and low-energy electron diffraction. The in-situ X-ray diffraction experiments were carried out in a customized thin-film electrochemical cell with the common three electrode setup [1]. The EC cell (Fig. 1) contains connections for the working electrode (sample, WE), the counter (CE) and reference electrodes (REF), and for supply (IN) and outlet of electrolyte (OUT). After UHV preparation and characterization, the sample was quickly transferred under ambient conditions into the electrochemical cell. Sample surface was then covered by a X-ray transparent Mylar Foil, sealing the electrochemical cell. Therefore, during the in-situ X-ray experiments, the sample surface was exposed only to a few mm thin films of electrolytes.

To check the influence of corrosion brightener, electrolyte was prepared by making 10mM KBr solution in 0.1M H<sub>2</sub>SO<sub>4</sub>. In addition, for checking the influence of heavier halogenide we also prepared 1mM KI solution in 0.1M H<sub>2</sub>SO<sub>4</sub>. To check the influence of corrosion inhibitor thiols, the decane thiols were adsorbed on the Cu<sub>3</sub>Au (111) surface and thiol adsorbed Cu<sub>3</sub>Au (111) crystal was exposed to 0.1M H<sub>2</sub>SO<sub>4</sub>.

In our *in situ* cell, the CE (a Pt wire), and the Ag/AgCl REF are arranged below the sample surface plane. The sample represents the WE and is held in place inside the electrochemical cell by under pressure with the help of an aspiration hole in the sample holder underneath the WE. This way of mounting assures clean electrochemical conditions and allows an easy exchange of the disk like WE. The sample was immersed into the electrolyte solution inside the cell at a cathodic potential, negative of the expected anodic onset of Cu dissolution (100 mV vs Ag/AgCl).

The energy of the synchrotron beam was chosen as 22 KeV. The incident angle has been chosen such that to lie about 20%–30% above the respective critical angle. The scattering vector  $q$  is defined as  $q = k_f - k_i$ , where  $k_i$  and  $k_f$  are the incoming and diffracted wave vectors, respectively. To describe the reciprocal space of the  $\text{Cu}_3\text{Au}$  crystal, and the scattering vector  $q$ , a surface unit cell was adopted, which can be described with two unit vectors  $a_1$  and  $a_2$  lying in the surface plane and the third unit vector  $a_3$  pointing along the surface normal ( $a_1 = a_2 = 2\sqrt{a_0} = 531$  pm,  $a_3 = 3\sqrt{a_0} = 650$  pm,  $\alpha = \beta = 90^\circ$ , and  $\gamma = 120^\circ$ ). This leads to a hexagonal reciprocal lattice unit cell of size  $a_1^* = a_2^* = 13.670$  and  $a_3^* = 9.666$  nm<sup>-1</sup>, and  $\alpha = \beta = 90^\circ$ , and  $\gamma = 60^\circ$ . Indices  $H$ ,  $K$ , and  $L$  are given in the reciprocal lattice units (r.l.u.) normalized to the three  $\text{Cu}_3\text{Au}$  (111) reciprocal lattice constants.

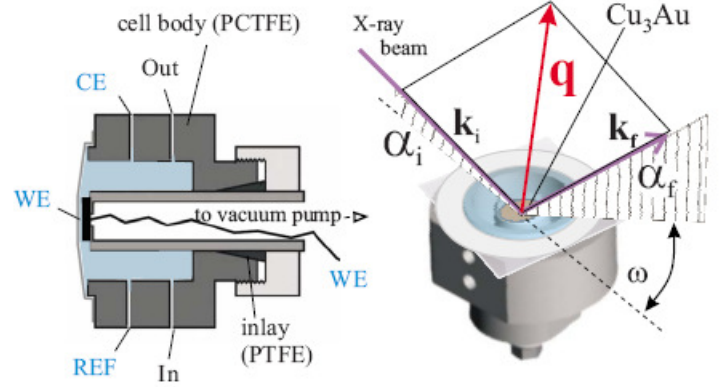


Fig. 1. Sketch of the *in-situ* X-ray diffraction electrochemical cell. A Mylar foil traps a thin film of electrolyte above the sample. In this way, the absorption of the incoming ( $k_i$ ) and diffracted ( $k_f$ ) x-ray beam inside the electrolyte is limited.

## Selective dissolution of Cu from $\text{Cu}_3\text{Au}$ (111) under the influence of Br and I anions:

Fig.2 shows several in-plane ( $H$ ,  $K$ ) and out of plane ( $L$ ) scans measured with  $\text{Cu}_3\text{Au}$  surface in the deaerated 0.1M  $\text{H}_2\text{SO}_4$  + 10mM KBr (top) and with the deaerated 0.1M  $\text{H}_2\text{SO}_4$  + 1mM KI (bottom) as electrolyte. During the measurement, potential was increased in steps. The in-plane ( $H$ ,  $K$ ) scans were measured in (1, 1) direction. In our earlier studies [1,2] with 0.1M  $\text{H}_2\text{SO}_4$  as electrolyte, it was observed that on increasing the potential, above +100 mV an additional in-plane Bragg peak at (1.9, 1.9, 0) appears close to the substrate fundamental peak (2, 2, 0.03), which was due to the formation of ultra-thin passive Au layer. With further increase in potential, this ultra-thin passive layer transforms into thick Au islands leading to the shift in peak towards Au bulk peak position (1.84, 1.84, 0). In 0.1 M  $\text{H}_2\text{SO}_4$ , the potential at which this ultra-thin passive Au layer transforms to the thicker Au islands is 400mV. With the addition of chloride additives (1mM HCl), this transformation potential shifts to lower values [3]. Here, in the current investigation, by the addition of bromide and iodide additives, we

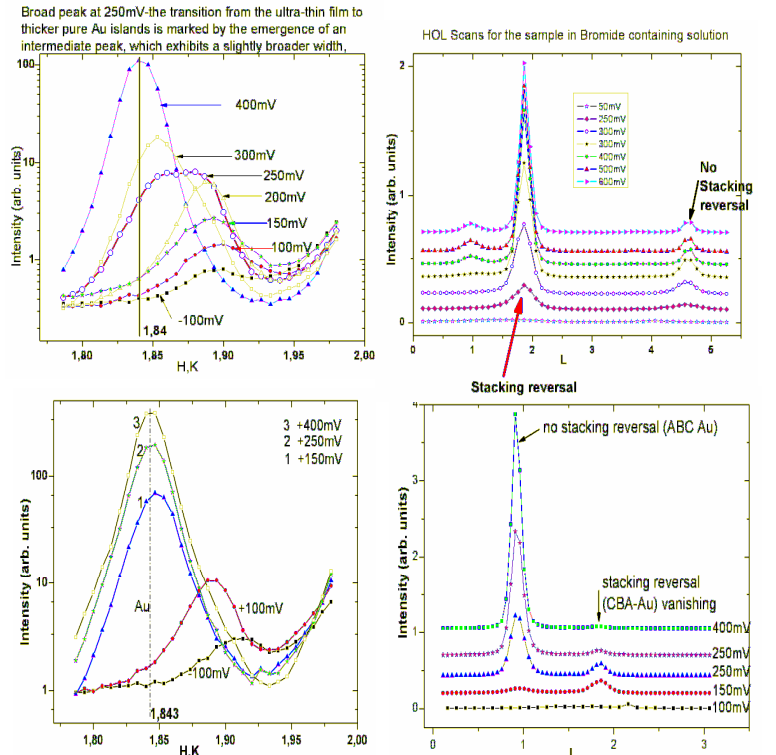


Fig. 2 Selective dissolution of  $\text{Cu}_3\text{Au}$  (111) surface as seen during in-situ X-ray diffraction. (Left to right: In-plane scans, out of plane scans showing stacking reversal scheme, Top: with bromide, Bottom: with iodide).

observe the similar phenomenon at even lower potentials. The addition of halogenides clearly promotes the selective dissolution of Cu from Cu<sub>3</sub>Au. In presence of bromide additive, the transformation potential at which the ultra-thin Au passive layer transforms to the Au islands is shifted to 300mV, whereas in presence of iodide additive, this transformation even occurred at 150mV. Furthermore, from the out of plane scans (Fig.2), we could track the changes in stacking sequence of the Cu<sub>3</sub>Au (111) surface (ABC) to that of ultra thin Au passive layer (CBA) and reversion to original stacking in case of thicker Au islands (ABC). By comparing the effect of two anionic additives (bromide and iodide), we observed the stacking reversal only in the case of iodide, whereas, in the case of bromide, the CBA stacking coexists with the ABC stacking sequence even after the transformation of ultra-thin Au passive layer to thicker Au islands.

### Selective dissolution of Cu from Cu<sub>3</sub>Au (111) under the influence decane thiols:

Fig.3 shows several in-plane (H, K) and out of plane (L) scans measured with decanethiol covered Cu<sub>3</sub>Au (111) surface in the deaerated 0.1M H<sub>2</sub>SO<sub>4</sub> as electrolyte. In contrast to halogen additives, the presence of decane thiol increases the potential at which the ultra-thin passive layer transforms to thicker Au islands, hence inhibiting the corrosion of Cu<sub>3</sub>Au (111) surface. The out of plane scans also confirm this observation, as the CBA stacking sequence of thin passive layer does not revert even after 400mV. These measurements show that with the decanethiol modified Cu<sub>3</sub>Au (111) surface, the Au-rich passive layer persists even at 500mV.

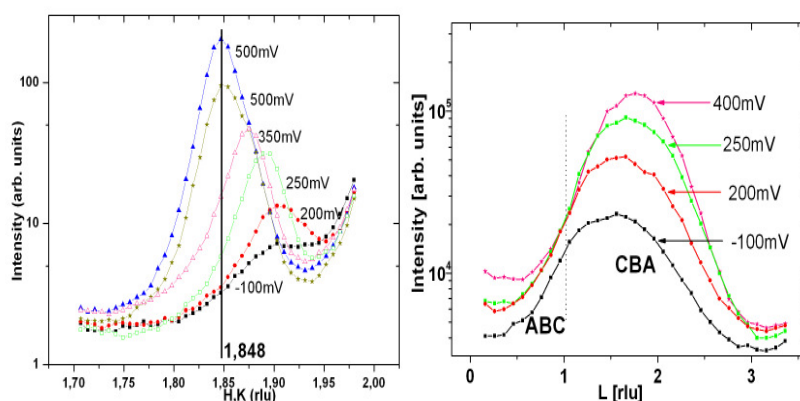


Fig. 3 Effects of a decanethiol-modified surface. From these, we can conclude that for potentials up to 500mV, a twinned Au-rich layer persists.

From the above experiments, we conclude that the addition of halogenides promotes the corrosion of Cu<sub>3</sub>Au (111) surface, while the presence of decane thiol on the surface of Cu<sub>3</sub>Au inhibits the selective dissolution of Cu. A manuscript comprising these results is in preparation and will be submitted in future.

### References

- [1] F.U.Renner et al., Phys. Rev. B 77, 235433 (2008)
- [2] F.U.Renner et al., Nature 439, 707 (2006).
- [3] F.U.Renner et al., Electrochemistry Comm. 9 (2007) 1639.