



	<b>Experiment title:</b> X-ray surface scattering studies of Au and Cu electrochemical dissolution	<b>Experiment number:</b> SI-1823
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<b>Shifts:</b> 18	<b>Local contact(s):</b> Jérôme Roy	<i>Received at ESRF:</i>
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## Report:

The electrochemical dissolution of Au in Cl-containing solution was studied by *in-situ* SXS. Elucidating the dissolution mechanism of noble metals is important for both industrial applications and fundamental understanding.

We investigated the atomic-scale dissolution behavior as a function of electrode potential. The experiments were performed at beamline ID32 ( $E_{\text{ph}} = 22.5$  keV) using a “hanging meniscus” transmission cell with minimized cell resistance and nearly unrestricted mass transport, which allows to combine *in-situ* surface x-ray diffraction studies of rapid structural changes simultaneously with high quality electrochemical measurements.

As shown in Fig. 1, x-ray intensity oscillations are found at the (1, 0, 0.1) reflection upon increasing the potential into the regime of active dissolution, indicating a layer-by-layer dissolution mechanism, confirming our previous results (SI-1639). However, the layer-by-layer dissolution is accompanied by a constant roughening of the surface which is indicated by a decay in the intensity at the anti-Bragg position, which could not be recovered. This roughening made further investigations of the dissolution and also of the homoepitaxial deposition process on the surface impossible.

Additionally, in continuation of our investigation of the Cu(001) surface in  $\text{Cl}^-$  and additive containing electrolytes and motivated by the large industrial importance of copper on-chip connections fabricated by electroplating (e.g. Cu dual damascene technique for ULSI chips) the Cu(001) surface has been investigated in Cl and additive containing electrolyte.

In the electrolytes ( $\text{HCl} + \text{H}_2\text{SO}_4$ ) used for former experiments, radiolytic effects associated with the sulfur ions strongly affected the surface roughness of the sample, therefore the sulfuric acid was in this experiment replaced by sulfate free electrolyte, consisting of a mixture of sodiumperchlorate and perchloric acid. The concentrations were chosen in a range where the surface is not oxidized in the applied potential range and where the total chloride free surface is accessible at a potential not too close to the hydrogen evolution.

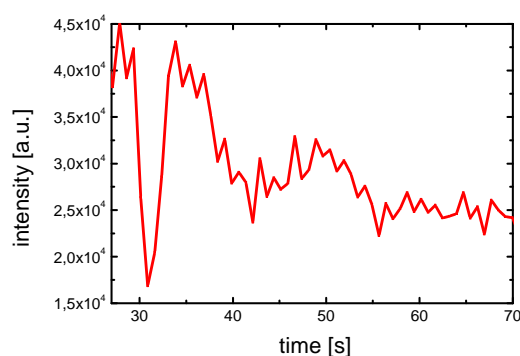
In a first step the Cu(001) surface exposed to an electrolyte with a low chloride concentration (0.01 mM  $\text{HCl} + 1$  mM  $\text{HClO}_4 + 0.1$  M  $\text{NaClO}_4$ ) was studied to exclude radiolytic effects. These studies were done by recording the intensities of the (1, 1, 0.1) anti-Bragg position of the Cu(001)-CTR during potential step experiments and potential scans. No effect of the x-ray beam could be observed. Then an electrolyte with a higher chloride concentration (0.1 mM  $\text{HCl} + 0.9$  mM  $\text{HClO}_4 + 0.1$  M  $\text{NaClO}_4$ ) was used to study the dynamics of the order-disorder transition of the  $c(2 \times 2)$  superstructure. The potential dependent intensity at

the (2, 0, 1) and (1, 1, 0.1) anti-Bragg positions of the CTR was recorded during potential scans at different rates and at selected potentials by rocking scans. Two different effects could be observed. Surprisingly, the intensity at negative potentials close to the hydrogen evolution differ for both anti-Bragg positions, indicating the existence of a superstructure in this range of potential.

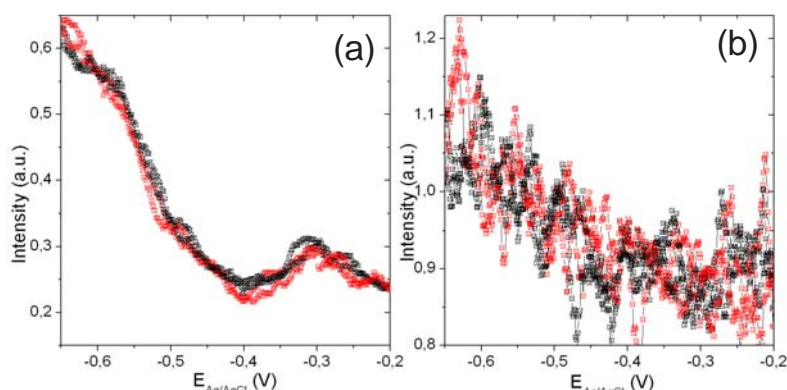
The existence of this superstructure was meanwhile also confirmed by *in-situ* STM studies by our group, which will help to identify the symmetry. The intensity decrease of the intensity at (2, 0, 1) shows a scanrate dependent hysteresis, which is not seen on the (1, 1, 0.1) position, indicating interesting ordering dynamics. A closer investigation by surface X-ray diffraction of the superstructure is planned to better understand its atomic structure and formation.

The time and potential dependent intensity behaviour of the Cl superstructure rod and of the anti-Bragg position at the order-disorder transition give information about the dynamics of the superstructure formation and lifting. In former experiments in PEG free electrolyte (Si-1530) the intensity of the superstructure rod and at the anti-bragg position showed an almost neglectable hysteresis when scanning through the order-disorder transition of the  $c(2 \times 2)$  superstructure, indicating a fast diffusion of the Cl to the surface as well as a fast ordering process of the superstructure

In addition, studies of the potential dependent intensity of the  $c(2 \times 2)$  superstructure rod at (1,0,0.1) in PEG containing electrolyte (Si-1722) revealed a scan rate dependent hysteresis reflecting the inhibiting effect of the PEG. However, from this data it could not be concluded if the PEG is affecting the diffusion of the Cl ions to the surface or the ordering of the Cl ions to form the superstructure. We therefore recorded during this experiment the intensity at the anti-Bragg position (1, 1,0.1) in electrolytes without (Fig. 2a) and with PEG (Fig. 2b). In both cases no significant hysteresis could be observed, indicating that the diffusion towards the electrode surface is not affected by the additive. Combined with the previous results, this indicates that PEG decelerates the ordering of the Cl-dynamics, but not the diffusion of Cl through towards the surface. However due to a surface roughening observed in PEG containing electrolyte, these results show large statistical errors which made a more detailed study of this effect difficult. For a more quantitative conclusion, further measurements with improved statistics are planned.



**Figure 1** The diffracted intensity at the (1,0,0.1) anti-Bragg reflection during the dissolution of the Au(111) surface at constant potential of 1.0V. The observed oscillations in intensity indicate layer-by-layer dissolution.



**Figure 2** The recorded diffracted intensity at the (1,1,0.1) (conventional bulk coordinates) anti-Bragg position of the Cu(001) surface recorded at 10mV/s in chloride containing perchloric acid (a) and in chloride and PEG containing perchloric acid. No hysteresis is visible when scanning through the order-disorder transition.