

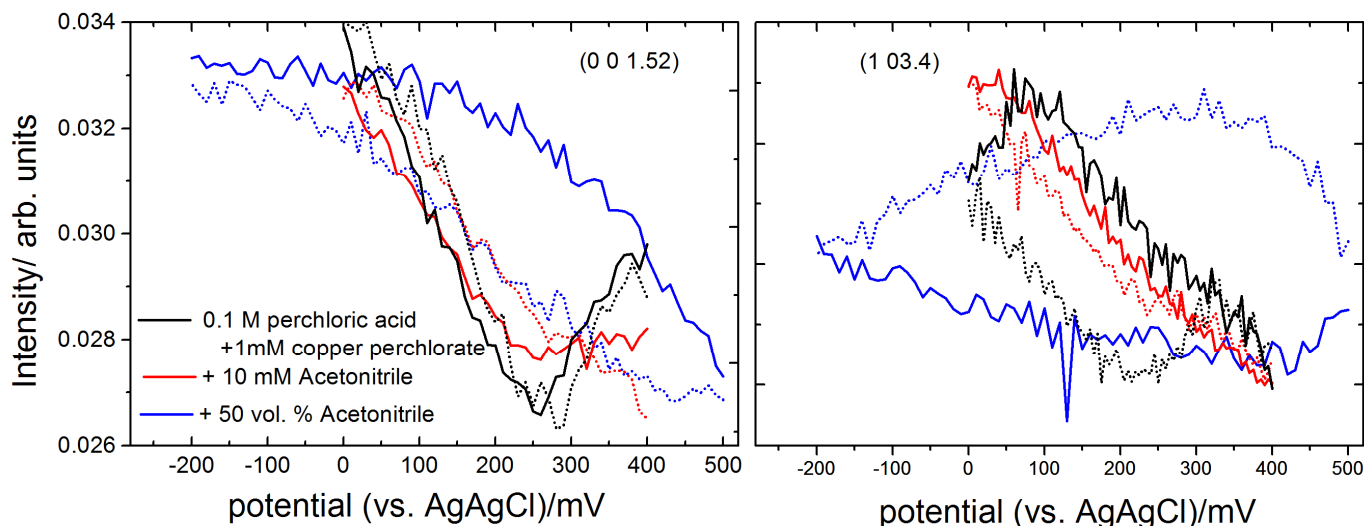


	<b>Experiment title:</b> Electrodeposition of Copper from water-nonaqueous solvent mixtures	<b>Experiment number:</b> <b>28-01-1055</b>
<b>Beamline:</b> <b>BM28</b>	<b>Date of experiment:</b> from: 16.04.2014 to: 22.04.2014	<b>Date of report:</b> 1.10.2015
<b>Shifts:</b> 18	<b>Local contact(s):</b> Paul Thompson	<i>Received at ESRF:</i>
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## Report:

The general aim of the experiment was to probe the electrodeposition of copper in acetonitrile and acetonitrile-water mixtures onto gold single crystals by surface X-ray diffraction (SXRD).

In aqueous solution, electrodeposition and the influence of spectator species is known to control the atomic arrangement during growth through the effect of additives and adatoms. At an applied potential above the potential for bulk deposition, a monolayer of copper is stabilised on the gold electrode through so called underpotential deposition (*upd*). In addition in non-aqueous (aprotic) solvents the Cu(I) ion, which does not exist in aqueous solution, is stabilised for water contents up to 20 vol. % and this is believed to be the origin of the change of the Cu upd process from a one step to a two step mechanism. We investigated Au(111) and single crystal surfaces in water acetonitrile mixtures with concentrations of 0 mM, 10 mM and 50 vol. % acetonitrile in perchlorate containing solutions.



**Figure 1** X-ray voltammograms at two positions in reciprocal space, (0 0 1.52) is the anti-Bragg position on the specular crystal truncation rod (CTR), sensitive to any electron density change/reordering normal to the surface. (1 0 3.4) is a position on the non-specular CTR sensitive to any ordering with the same in-plane symmetry as the electrode surface. The scan from positive to negative (line) and from negative to positive (dotted line) potentials are shown for each solution and position.

In a first step Cu *upd* on the Au(111) surface has been characterised in acetonitrile free 0.1 M perchloric acid + 1mM perchloric acid. The deposition of the Cu underpotential layer could be observed at negative potentials, whereas at positive potentials the gold surface remains copper free while scanning the potential. (Note: a detailed structural dataset has been obtained but due to a misalignment of the diffractometer chi-circle from the Beamline alignment only the data at constant Q is reliable).

Upon the addition of 10mM Acetonitrile and the 50vol. % Acetonitrile a difference in the formation of the Cu upd layer could be observed (Fig. 1). Without Acetonitrile in solution the onset of the copper deposition can be observed at about 250 mV clearly visible on the specular crystal truncation rod (CTR). In comparison, on the non-specular CTR a hysteresis in the ordering (the positive and negative scan don't overlay) reflects the slow ordering process of the Cu layer. Upon addition of 10 mM Acetonitrile the hysteresis on the non-specular CTR disappears indicating an improved ordering process. Upon further addition of Acetonitrile (50 vol. %) a totally new behaviour is observed. This time the hysteresis is much larger, which could reflect a very slow process either due to surface alloying and/or a slow replacement reaction of an adsorbate. Further experiments will be required to identify the origin of this process.

A full set of CTRs were recorded at specific potentials for the characterisation of the structure. The CTRs in 0.1 M perchloric acid + 10 mM Acetonitrile are shown in Fig. 2 together with the ratios of the Intensity measured at different potentials. The onset of the formation of the Cu upd layer can be seen on the (1 0 L) CTR. The data could be best fitted with simple adlayer model with a Cu coverage of 1/3. Remarkably the specular CTR shows a more pronounced change in intensity upon stepping the potential into the Cu deposition region. This change is due to structural changes on the electrolyte side of the interface and can be modelled by a layering of the electrolyte [1]. The origin of this structural change remains unclear; it could be either due to the organic solvent, as has been observed in non-aqueous ionic-liquids, or due to copper being non-specifically adsorbed at the interface. Further investigation of the system will have to be carried out and a structural analysis in combination with spectroscopic techniques is required.

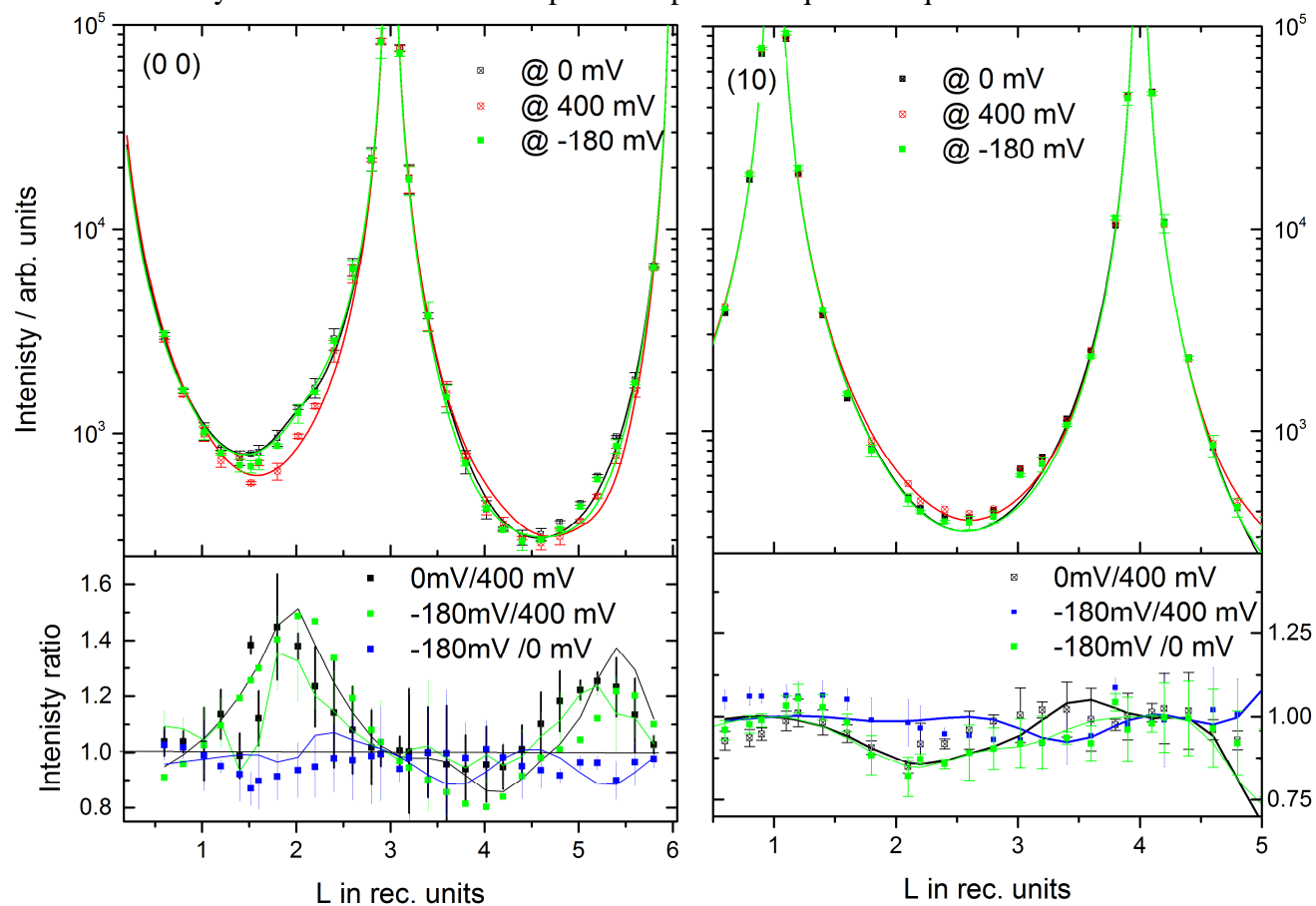


Figure 2 Crystal truncation rods measured at different potentials of the Au(111) surface in 0.1 M HClO<sub>4</sub>+1mM Cu(ClO<sub>4</sub>)<sub>2</sub>

Additional structural data for the 50 vol% was obtained and is currently under analysis.