



	<b>Experiment title:</b> Initial Electrochemical Corrosion of Cu <sub>3</sub> Au(111)	<b>Experiment number:</b> SI-861
<b>Beamline:</b>	<b>Date of experiment:</b> from: 06.11.2002                      to: 12.11.2002	<b>Date of report:</b> 05.11.2003
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**Report:**

The prototypical binary alloy Cu<sub>3</sub>Au exhibits in its ordered phase a cubic, fcc-like lattice with Cu, the electrochemically less noble constituent, occupying the face centred sites. In contrast to Cu, pure Au is stable in aqueous electrolytes within the whole potential range of stability of water itself, i.e., hydrogen evolution and oxygen evolution at the limiting negative and positive potentials, respectively.

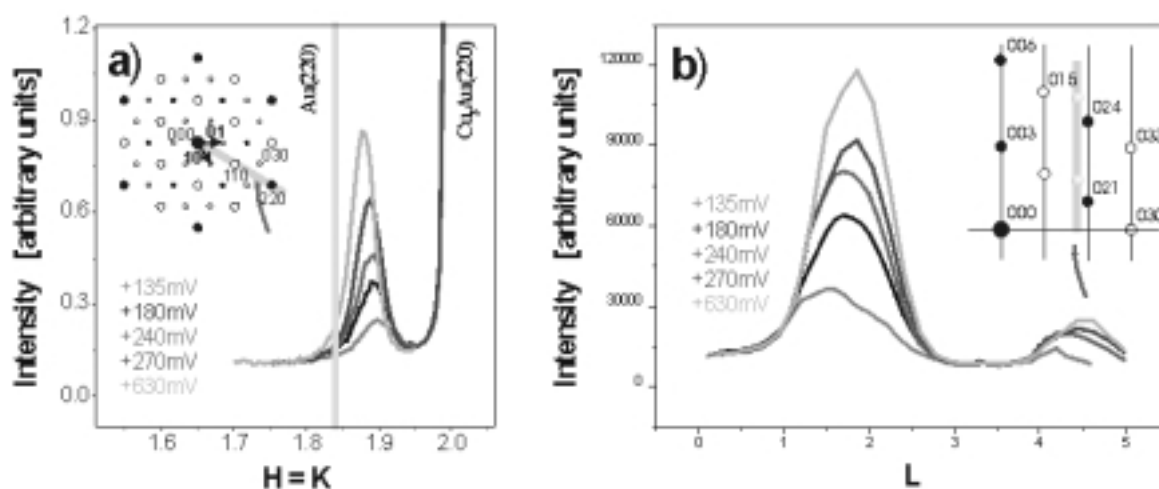


Figure 1: Inplane (a) and out-of-plane (b) diffraction scans for the growing ultrathin layer on Cu<sub>3</sub>Au

To learn about the details of the corrosion and passivation behaviour of Cu-Au alloys in acidic, aqueous solution we performed a GID experiment at the beamline ID32. For labelling the diffraction peaks we use a hexagonal surface unit cell for the  $\text{Cu}_3\text{Au}$ , in which case the  $l$ -direction is normal to the surface. The reciprocal lattice is shown in the inset of Figure 1a+b. The X-ray Cell [1] with the mounted  $\text{Cu}_3\text{Au}(111)$  crystal was filled with deaerated 0.1M  $\text{H}_2\text{SO}_4$  solution under a controlled potential of  $-150\text{mV}$  (vs.  $\text{Ag}/\text{AgCl}$ ), close to hydrogen evolution. At this stage of the experiment we could only observe the  $\text{Cu}_3\text{Au}$  Bragg reflections, indicating an unaltered surface structure. After increasing the potential above the equilibrium potential of Cu (and the equilibrium potential of Au being much further away), a new peak was observed with a lattice constant in between the values expected for pure Au and  $\text{Cu}_3\text{Au}$ , which is understood by epitaxial strain and/or alloyed Cu atoms in a thin layer that is in principle depleted of Cu and enriched in Au. The new layer is aligned with the  $\text{Cu}_3\text{Au}$  substrate, with the  $\{111\}$  face of the new layer being parallel to the  $\text{Cu}_3\text{Au}(111)$  surface and the in-plane  $[1-10]$  direction being parallel to the in-plane  $[-110]$  direction of  $\text{Cu}_3\text{Au}$ . Thus, it has grown with a different stacking sequence compared to the fcc-like substrate, ACB instead of ABC.

By stepwise further increasing the potential we can now follow the growth of this new layer, as is shown in Figure 1. The intensity in the in-plane peak (Figure 1a) as well as in the  $l$ -scans (Figure 1b) is growing. While the FWHM of the in-plane peaks is decreasing, indicating the lateral growth of islands, the FWHM of the  $l$ -scans is staying nearly constant. From the  $\text{FWHM} \approx 1$  for this forming layer (Fig.1b) a constant thickness of about 3ML can be estimated. This means, islands of constant thickness grow laterally, eventually covering the whole surface as a protective layer.

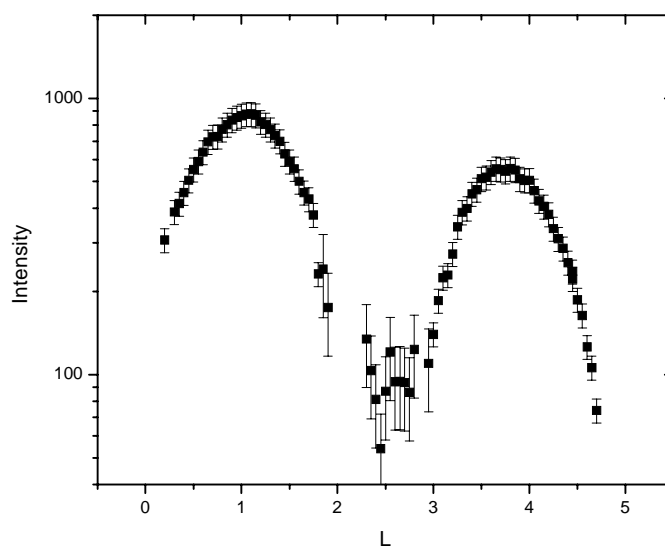


Figure 2: Intensity along the  $(1.9\ 0\ L)$  Rod (new layer rod) obtained by integration of transversal rocking scans.

Crystal Truncation Rod (CTR) Intensity of the substrate was recorded and an increased roughness in comparison to a previous UHV measurement of the clean surface has been seen. Interestingly, this roughness, which is already present at cathodic potentials, i.e. before the initial Cu dissolution and though originating from the in air transfer of the sample, does not increase with further Cu dissolution in the potential range below the critical Potential..

At a potential of  $+270\text{ mV}$  vs. a  $\text{Ag}/\text{AgCl}$  reference electrode the intensity on the rod was sufficient to record the integrated intensity rod shown in Figure 2. Also the  $(0\ 1.9\ L)$  and the  $(1.9\ 1.9\ L)$  intensity was recorded. A preliminary modeling with help of the ROD program initiated by E.Vlieg suggests that Cu atoms are still contained in this ultrathin layer. The analysis has to be completed.

[1] see e.g. J.Zegenhagen, A.Kazimirov, G.Scherb, D.M.Kolb, D.-M. Smilgies, R.Feidenhans'l, *Surf.Sci.* **352-354** (1996) 346.

[2] E.Vlieg, *J.Appl.Cryst.*33 (2000), 401.