



Experiment title:

The influence of surface mobility on the selective dissolution of Cu₃Au

Experiment number:

SI-913

Beamline:

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Local contact(s):

Dr.S.Warren

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Names and affiliations of applicants (* indicates experimentalists):

F.U. Renner*, ESRF, BP220, 38043 Grenoble Cedex, France

A. Stierle*, MPI für Metallforschung, Heisenbergstraße 3, 70569 Stuttgart, Germany

A.Reicho*, MPI für Metallforschung, Heisenbergstraße 3, 70569 Stuttgart, Germany

J.Zegenhagen*, ESRF, BP220, 38043 Grenoble Cedex, France

Report:

The prototypical binary alloy Cu₃Au 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.

In experiment SI-861 we observed the growth of an initial ultra-thin Au-rich layer at low overpotentials (of the Cu dissolution). At elevated potentials thicker (about 3nm thick) islands were observed. The transition potential was about 400 mV vs Ag/AgCl. These Au or Au-rich layers passivate the Cu₃Au crystal and the dissolution currents are very small after their formation until a critical potential is reached and massive Cu dissolution takes place, with the formation of a thick porous Au layer. The critical potential for Cu₃Au in 0.1M H₂SO₄ is about 800 mV vs Ag/AgCl. The passivation layers turned out to grow initially with a lattice constant different from Au, but the final thicker islands were growing at exactly the Au position. The

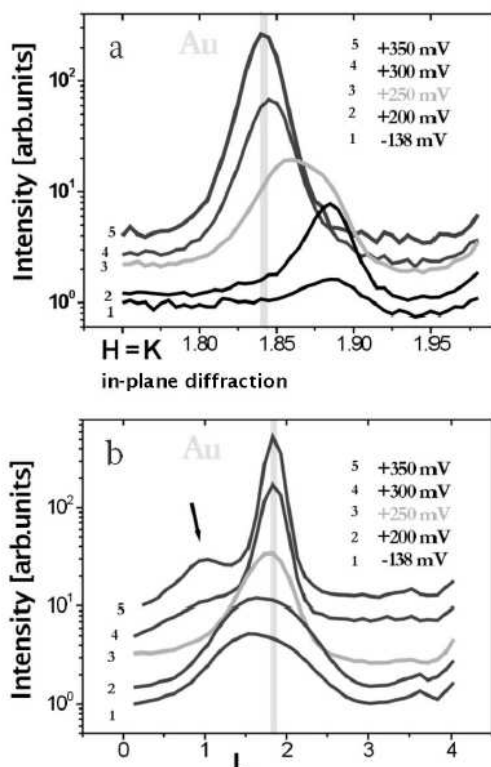


Figure 1. HK and L-scans at the reciprocal positions of the formed passivation layers.

initial ultra-thin layer is thus different from bulk Au, which can be understood by either strain and intermixing of Cu, but also by a possible different structure of an ultra-thin layer from a bulk structure. All Au/Au-rich layers grew with their 111 plane parallel to the Cu₃Au(111) surface and with an in-plane orientation of the structure rotated by 60° (120°) with respect to the substrate. This means that the 111 layers of the respective fcc-like structures change their stacking sequence.

In continuation to experiment SI-861 we studied the before observed structural evolution of the surface of Cu₃Au(111) under the influence of an additive of 5mM of HCl. We observed the same layers, i.e. the growth of an ultra-thin layer at low (Cu) overpotentials and thicker islands, showing Bragg peaks at exactly the position expected for a pure Au crystal with the respective orientation (Fig.1). With the HCl additive in the solution the transition takes place nevertheless at lower potentials (now about 250 mV) than observed for the case without Cl⁻. Also the observation of the twin domain within the passivation layer was now observed already at about 300 mV.

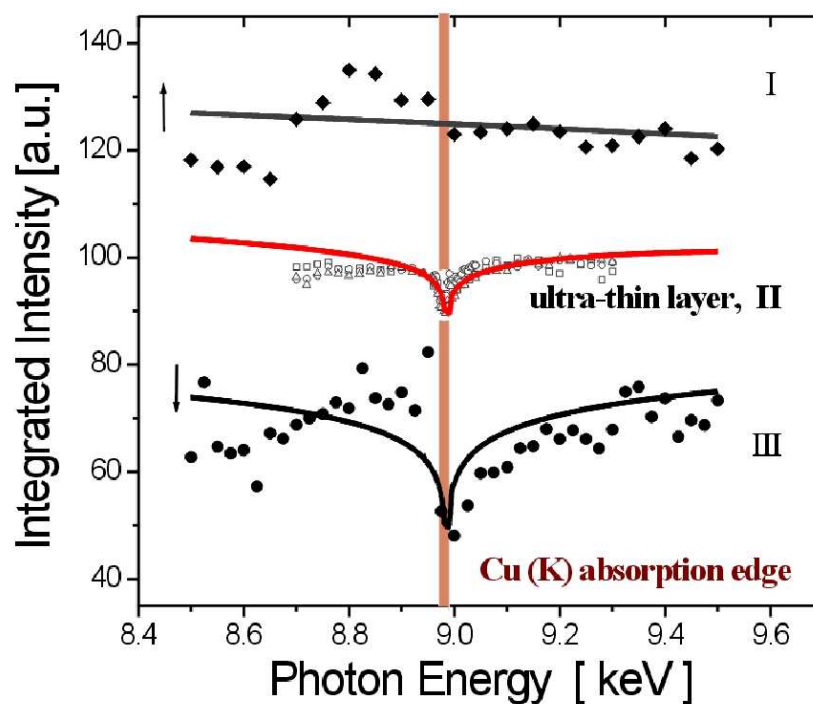


Figure 2. A resonant diffraction experiment reveals a Cu content of about 40% in the ultra-thin layer.

In addition to the Cl-experiments, we performed resonant diffraction on a sample without Cl⁻ in the solution. For one such sample we could reveal a Cu content of about 40% in the ultra-thin layer, while the thicker Au layers at elevated potentials showed no sign of a Cu content, as expected. For the substrate the measurement reproduced a Cu content of 75%. The integrated diffraction intensities of the respective measurements are shown in Fig.2. Nevertheless we experienced major difficulties in finding a reliable setting of the beamline optics.

We must state here that also the respective time that we stayed at a certain potential, i.e. the time we allowed for the growth of the passivation layer at certain potentials also influences the growth characteristics. For further experiments we have therefore to take care to compare the growth with similar time-potential evolutions.