Study of Initial Corrosion of Cu$_3$Au(111) at ID32, ESRF

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Motivation

Adlayers and thin films, very often only nm or single monolayers thick, influence to a great extent the properties and technical aspects of metal surfaces. Examples are heterogenous catalysis or corrosion and passivation. Corrosion of binary alloys serves as a model process to understand features of more complicated compound metal characteristics like in this case the dealloying of metal alloys. The combination of electrochemistry methods and surface sensitive X-ray diffraction (SXRD) gives in-situ structural details for a "real" system. With SXRD we can look "in" the surface and learn more about fundamental details of important processes. Corrosion is mostly electrochemical in nature and must be understood on an atomic scale. In addition a well defined control of the electrochemical potential allows us to trigger the onset of the process, here corrosion, under study. In electrochemistry the electrochemical potential of adlayer and surface atoms can be easily controlled by the potential applied.
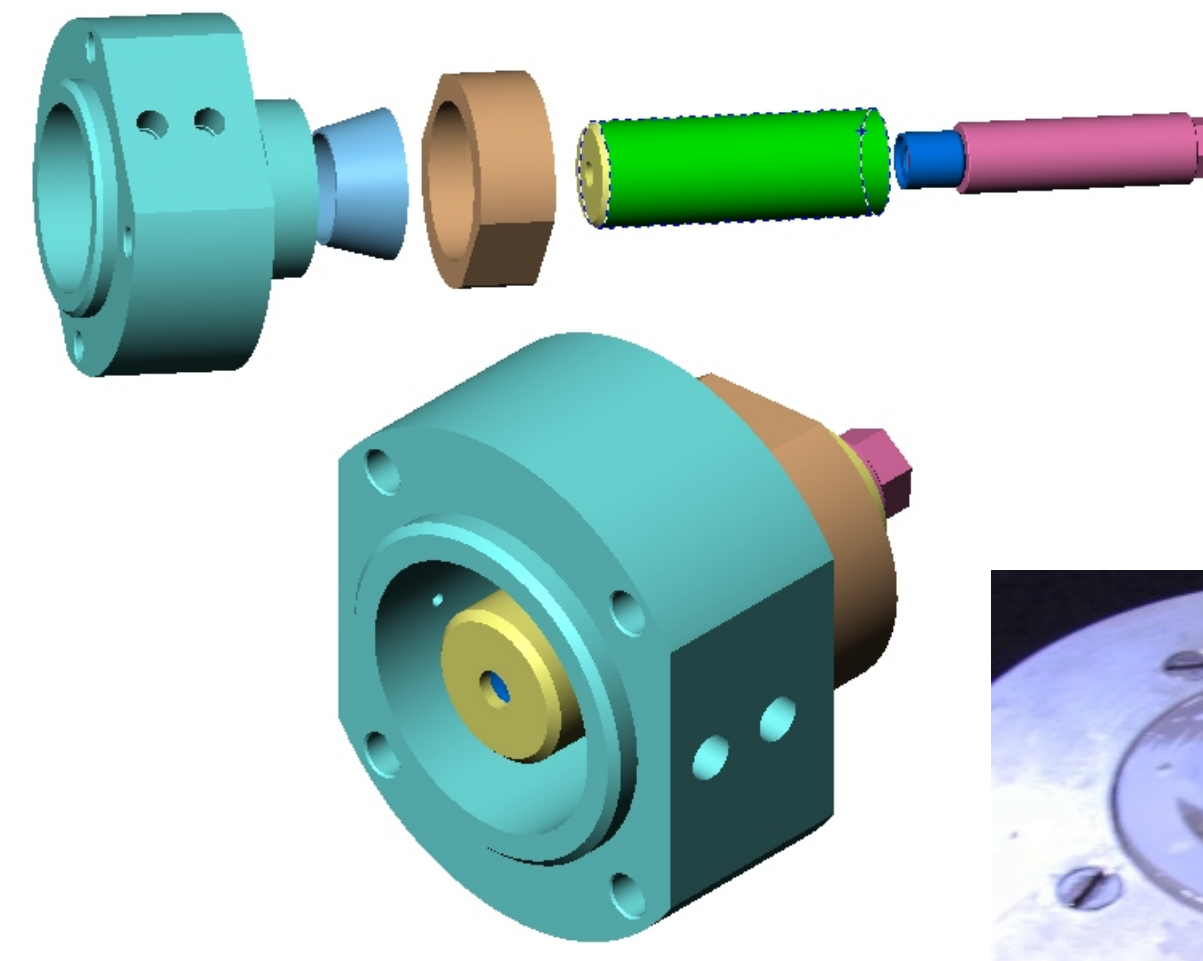
Equipement

For electrochemical surface diffraction X-ray studies new user-friendly X-ray Cells were designed. They are manufactured out of Kel-F and Teflon and connected to the electrolyte supply bottle, reference electrode etc...,via commercially available (HPLC) connectors. The cell design was accomplished in collaboration with F.D'Anca and R.Felici from INFM-OGG, Grenoble.
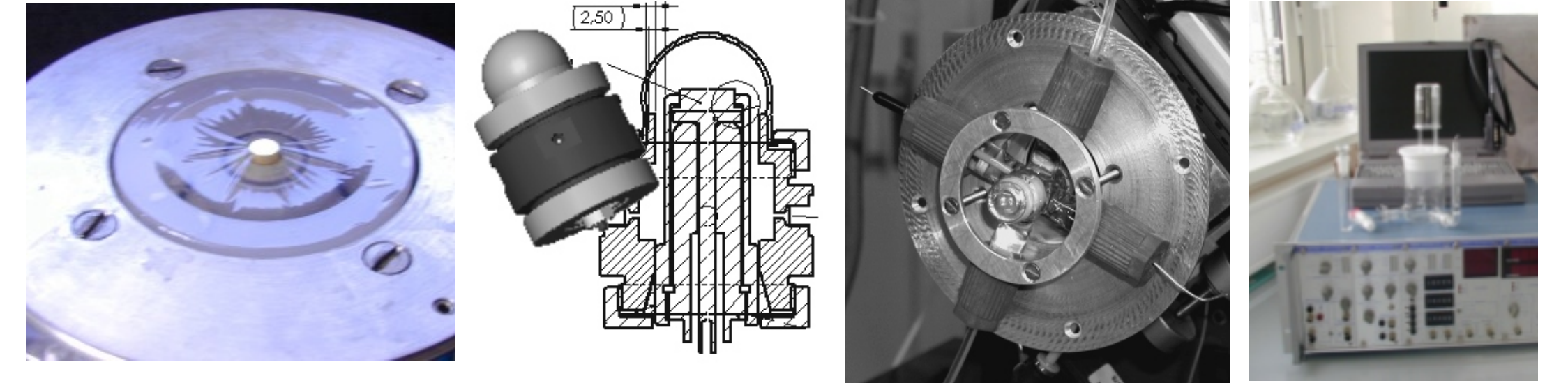
What happens during electro-corrosion of Cu$_3$Au(111) ?

In Voltammetry you vary the potential applied at the sample and then measure the current. For the curves on the left first a potential is applied at the sample at which no dissolution even of the more reactive component is expected (1) and the onset of hydrogen evolution reaction is observed. The peak at (2) is interpreted to be the initial dissolution of Cu from the Cu$_3$Au surface. The decrease of the current in region (3) points to the formation of a passivating surface layer. Reaching the critical potential E$_c$ a massive onset of current is observed. Here massive Cu dissolution takes place. When decreasing the potential from the critical potential to region (1) a corresponding peak to (2) is not observed (4) and in addition the hydrogen onset potential is shifted now to a more negative value (5). This indicates that the surface composition and structure has changed. In a second cycle the peak (2) is missing.
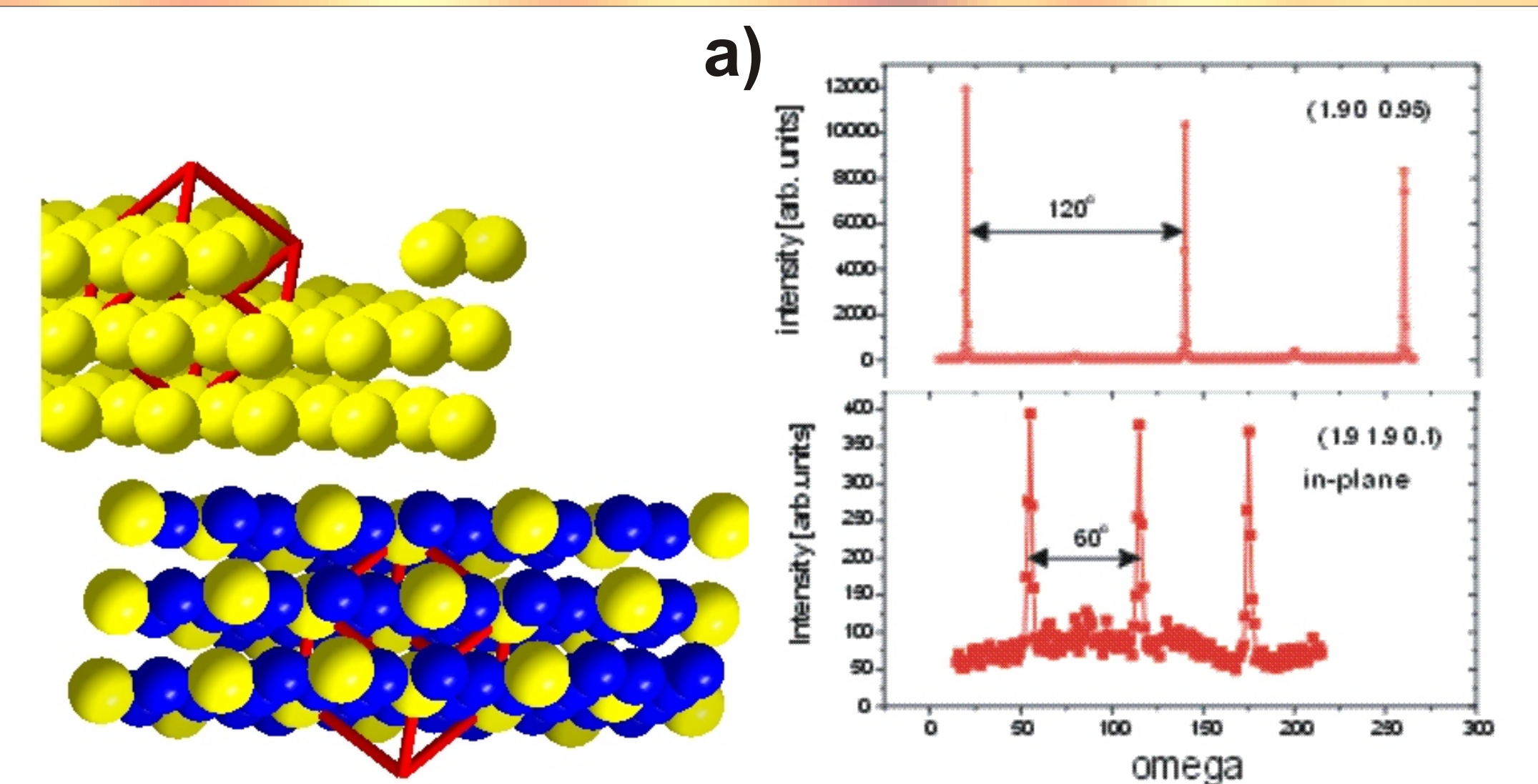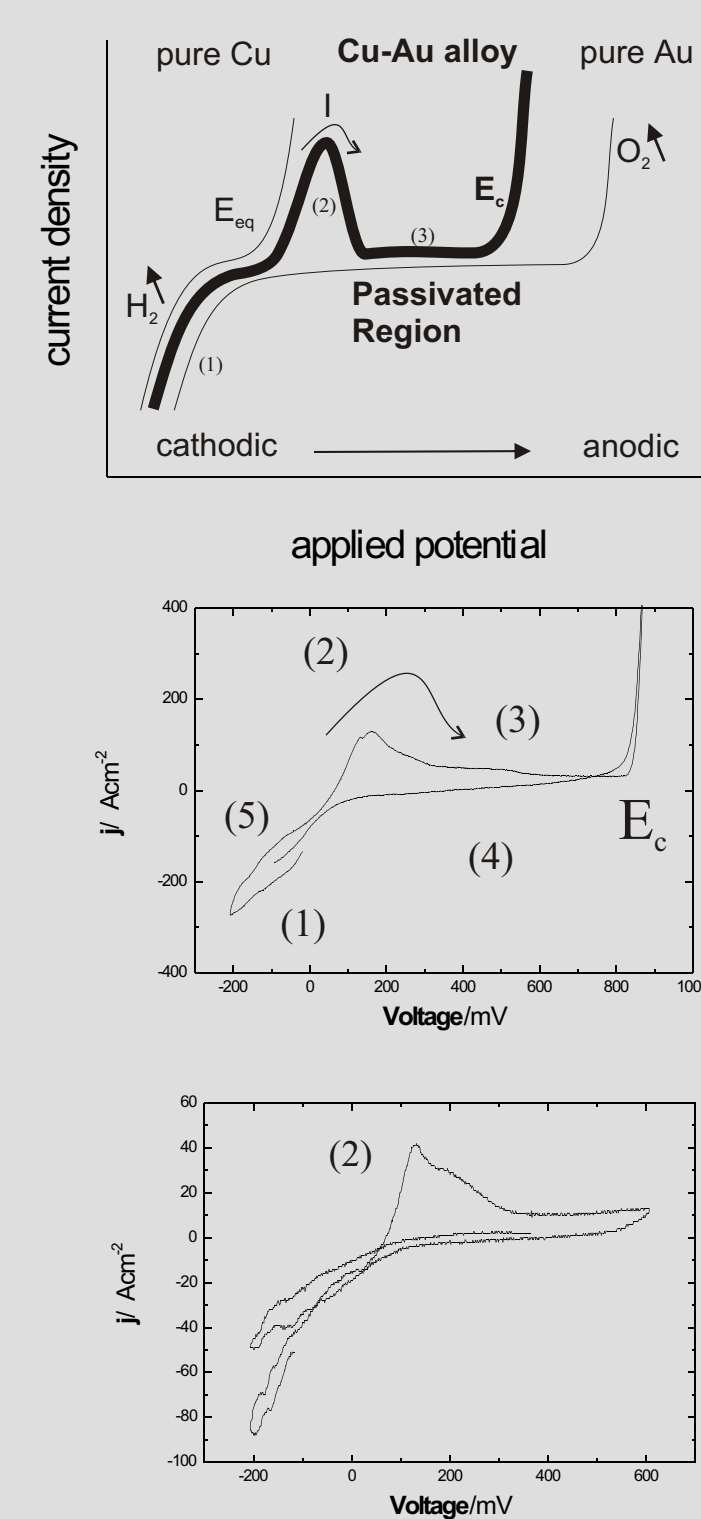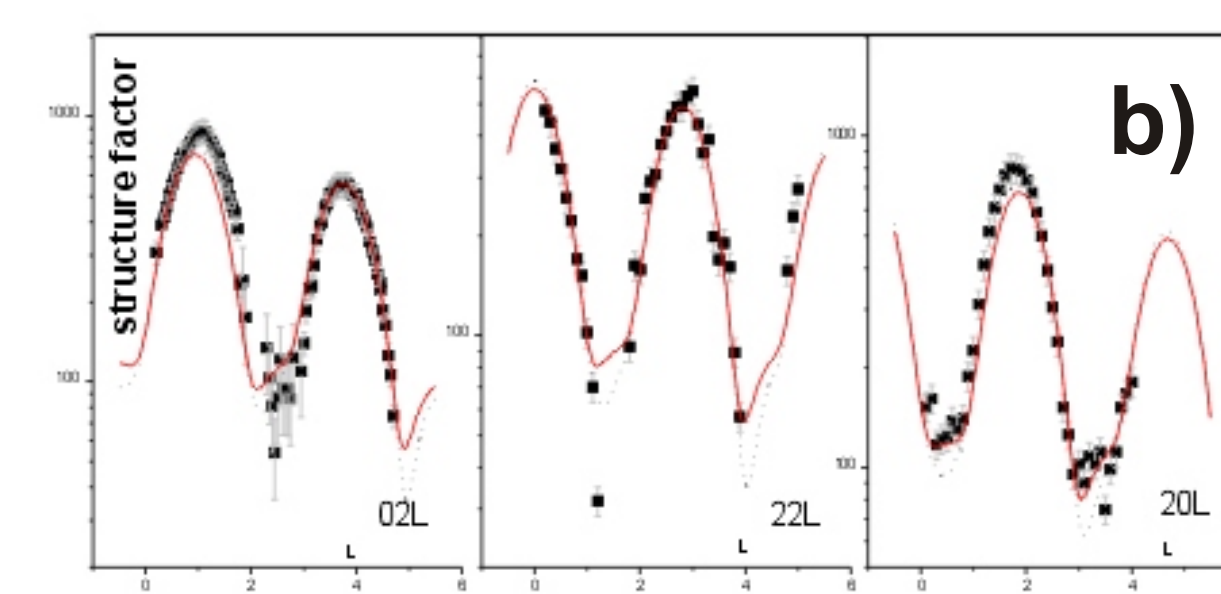

Figure 1: initial growth of an ultra-thin layer

Figure 1: We could follow the growth of an ultrathin film on top of our Cu3Au(111) substrate after we turned the potential to values positive of the Nernst potential of Cu/Cu^{2+}, i.e. to a potential where we expect Cu dissolution. If we compare the width of the growing in-plane peaks (~0.05) in **a)** with the L-scans (~1.0) in **b)** (L is perpendicular to the surface) and the fact that (hkl)=003 is the layer distance perpendicular to the surface we can estimate a thickness of islands of ~3 monolayers!

Figure 2
Structural Details of ultra-thin Layer

a) The rocking scans on the in-plane peak shown in Figure 1a (bottom) and of the maximum position of the peak of the L-scan of Figure 1b(top) shows, that the ultra-thin layer has the three fold symmetry of a fcc-like stacking expected for Au. If we in addition compare the peak positions with the substrate positions we realise that the orientation is of the ultra-thin Overlayer is turned by 180° (anti-parallel alignment/interface stacking fault)

Figure 2b shows an intensity profile, taken by measuring integrated intensities along L of the thin layer peak as in Fig.1b (thin layer rod). A model calculation (with ROD, E.Vlieg) reveals more structural details: The layer is 2.5 mono-layers thick (i.e. a not fully occupied third layer) and some (~6%) atoms sit on "hexagonal" positions (most likely at the non-coherent interface). We could not distinguish if there are still Cu atoms in the thin layer.

In **Figure 2c** we plotted the in- and out-of-plane values of the atomic layer distances obtained from different measurements (e.g. from Figure 1a+b, points 1-4) and we see that the initial thin layer (red squares) is stressed. The yellow line is expected for biaxially strained bulk Au(111) but most points most likely (still or again) with some Cu content. The stars describe the thicker islands that are observed for more elevated potentials.
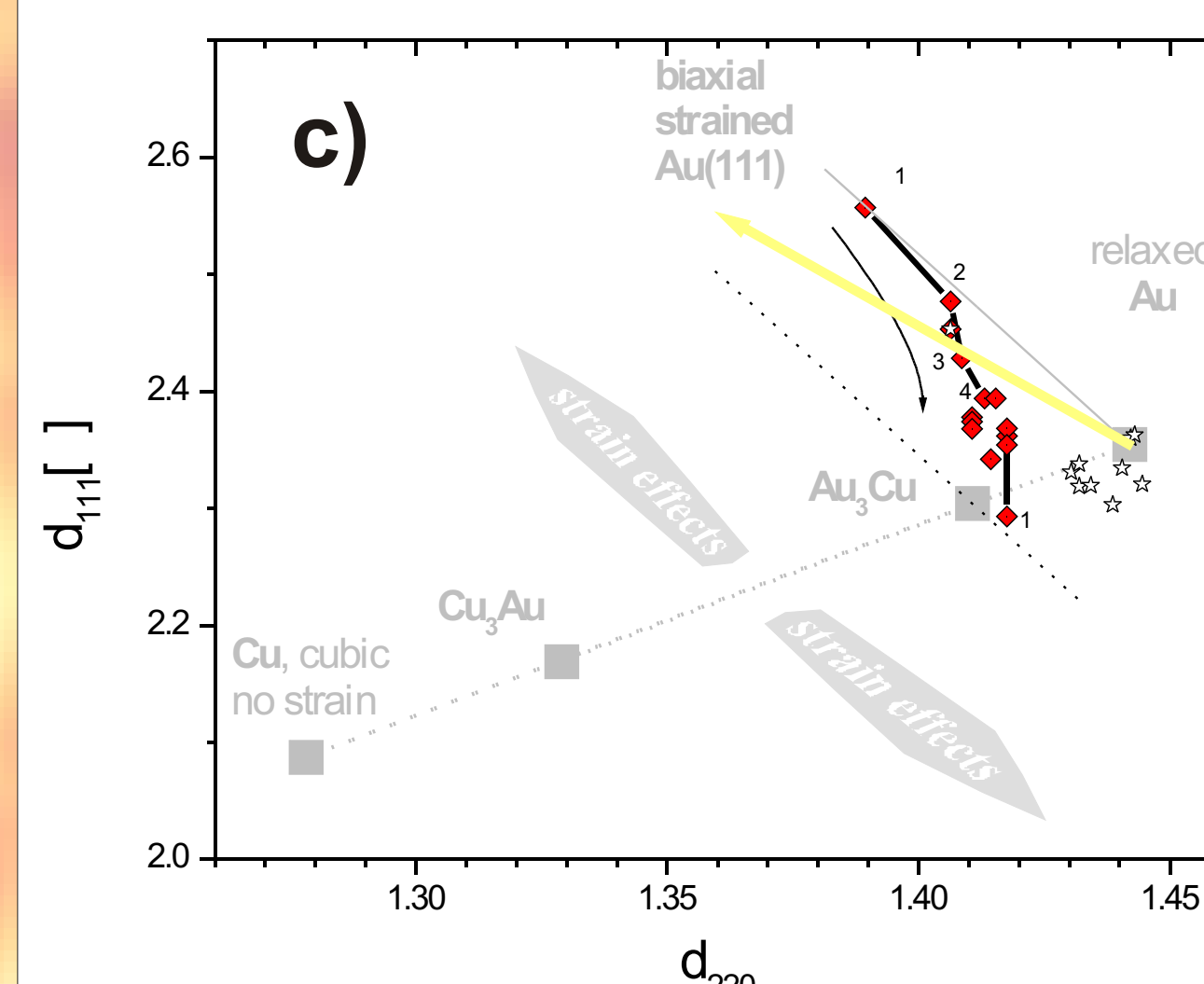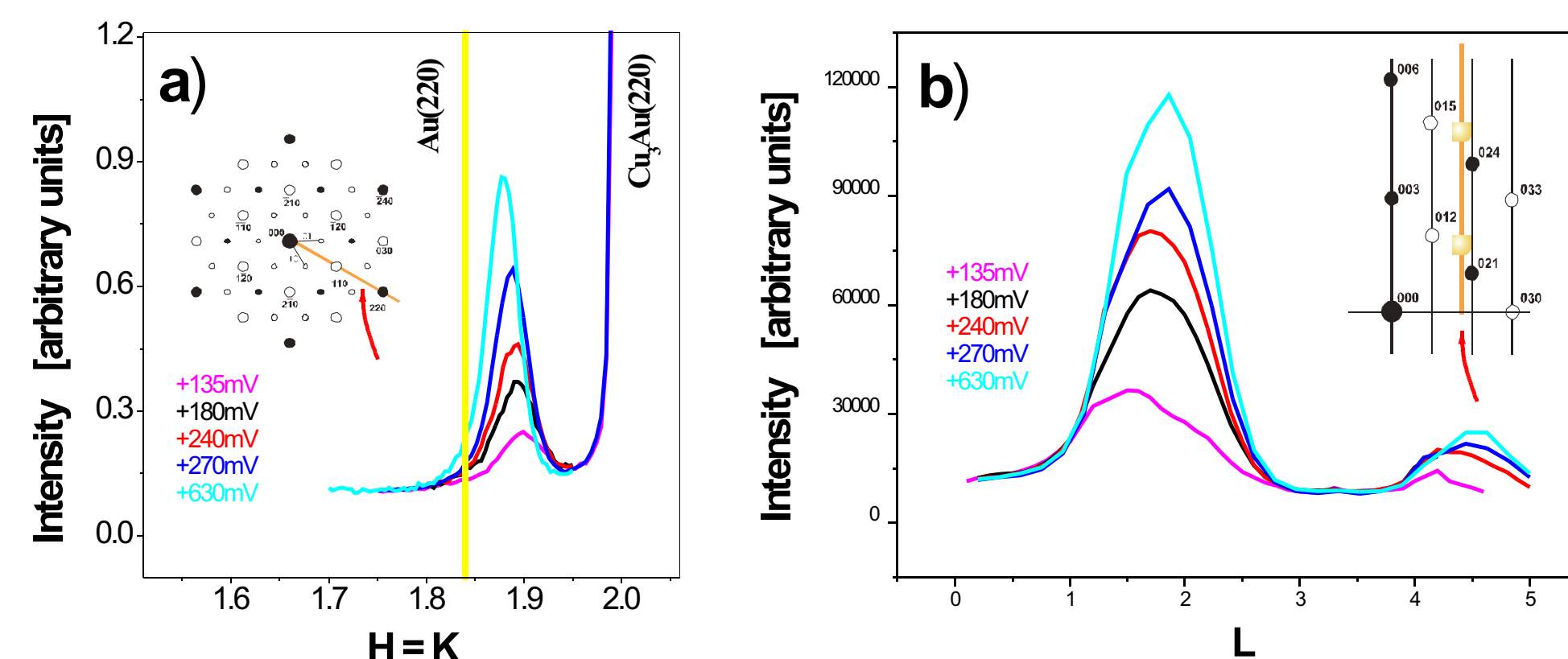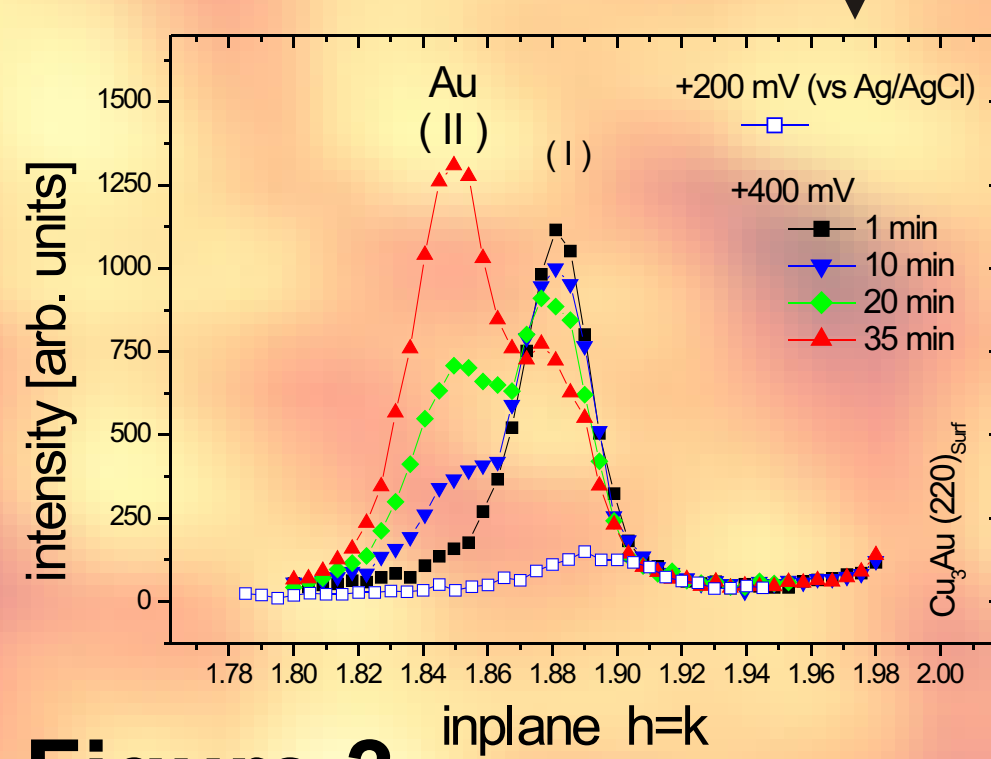
Figure 3
Further Growth

At position (I) the 3ML film is growing at lower potentials of the selective dissolution of Cu from Cu$_3$Au(111). At higher potentials pure Au islands emerge at position (II). Compare also Fig.2c

Figure 4: Ex-situ AFM: Thick Au-Island Structure

An ex-situ AFM study shows a regular arrangement of flatt islands (height color range from 0-10 nm). The top image shows the substrate Cu$_3$Au after UHV preparation.
In the middle the surface after ca. 10 min of Cu dissolution at extended potentials, but below the critical potential E$_c$, is depicted.
The 2D FFT image reveals now a certain length-scale, an average island distance. The islands are densely packed, the auto-correlation (AC) image shows a hexagonal order.After several hours of measurement the surfaces exhibit a porous microstructure. The order is still visible but on a now longer lengthscale.
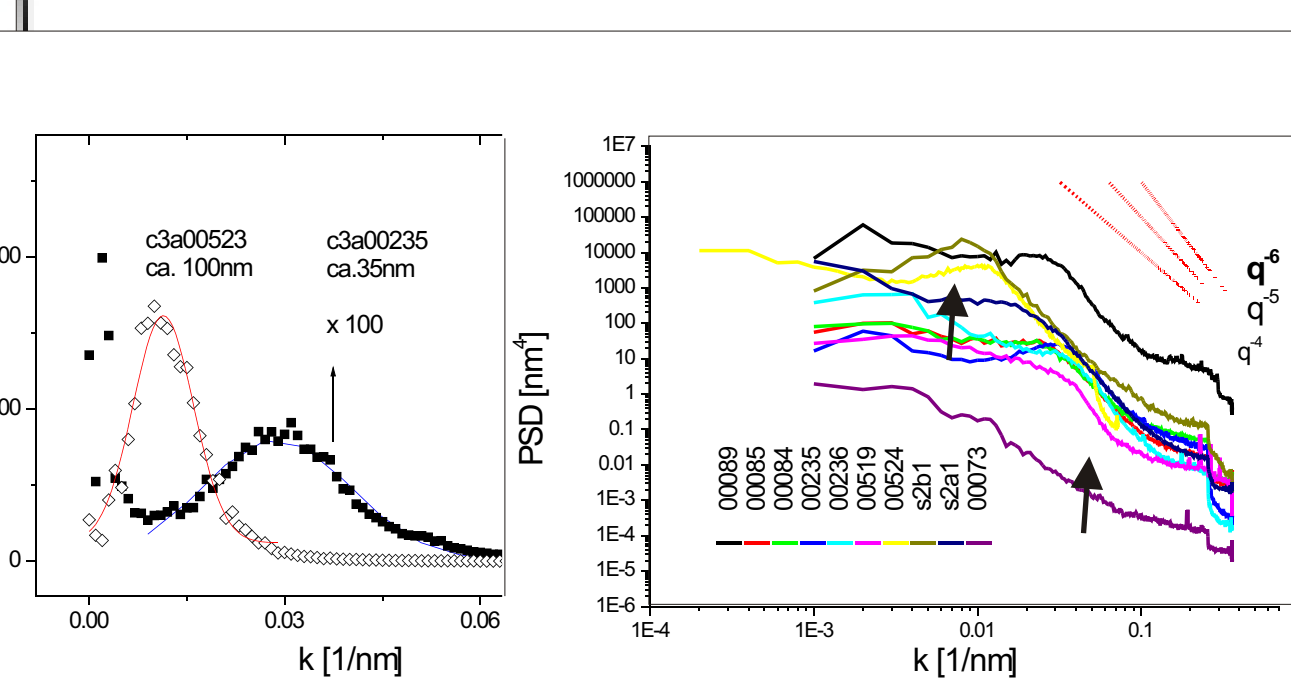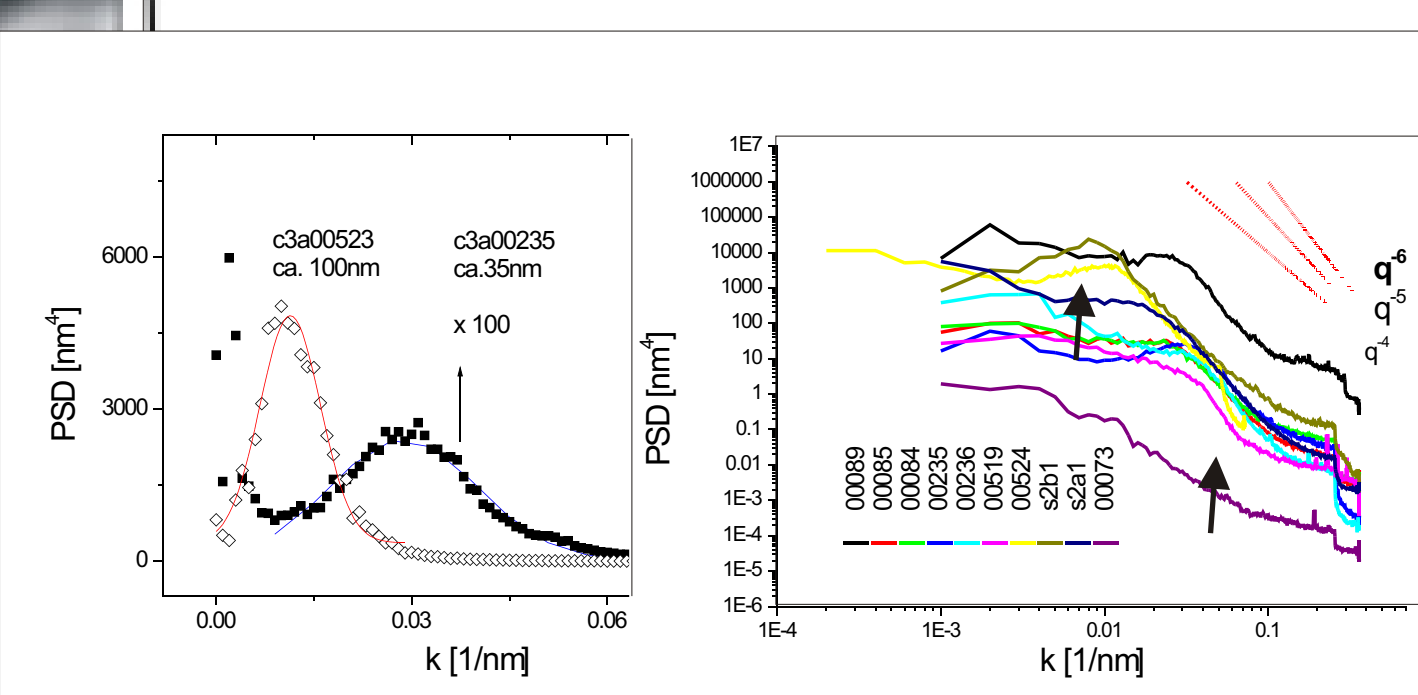

Figure 5: Quantitative AFM Analysis

The microstructure of the surface developes from a surface densely packed with islands, to a porous interface region. The peak in the power spectrum indicates the average island or ligament distance. Shown are Power Spectral Density(PSD) plots (linear and logarithmic).

Conclusion and Outlook

We could follow in-situ the selective dealloying of Cu3Au(111) and observe structural details of a first developing ultra-thin layer and in a later stage, with applying an elevated potential, the development of thicker Au islands on the surface. The ultra-thin layer and the Au islands grow epitaxially with an anti-parallel alignment. SXRD helps us to reveal the structure of the surface in depth and provides an extended knowledge of the process of dealloying. We could observe an initial behaviour that is quite different from the development of the later emerging porous structure. AFM showed an existing order in the evolving surface structures.
SXRD in combination with electrochemistry is a unique tool to study corroding systems in electrolyte solution.