



**Experiment title: In-situ grazing incidence X-ray diffraction study of the hetero-epitaxial growth of Cu on Au(111) substrate by electrochemistry**

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We have developed and tested a new spectroelectrochemical cell derived from the 3 electrodes standard cell<sup>[1]</sup> which enables optimal electrochemical conditions during X-ray diffraction measurement<sup>[2]</sup>. The intensity X-ray beam supplied by ID32 at high energies (around 20 KeV) provides the way to cross the 20 mm water path with enough photons to surface diffraction studies with good statistics within one second. This cell replaces advantageously the thin electrolyte film cells<sup>[3]</sup> which are limited by the capillar electrolyte film that strongly affects the electrochemical control of the interface. The gold surfaces are the model system in electrochemistry for fundamental studies, on the surface reactivity correlated with the desorption/adsorption of different anions. Controlling the substrate/electrolyte interface is one of the key points for the electro-deposition and for the growth of thin single-crystal films for further applications such as magnetic thin films, industrial coating, oxidation, environment.

The Au( 111) surface undergoes a phase transition between a bulk-like terminated at positive potentials and an incommensurate phase  $(23 \times \sqrt{3})^{[3-5]}$ , obtained at negative potentials (vs. potential of zero charge sulphate calomel electrode SCE). The sulphate ions play a key role in this transition. We have performed intensity measurements on a diffraction rod in out-of-plane condition, where the sensitivity to the surface structure is maximum. Fig 1-a presents the (0 1 0.45) peak intensity as a function of the potential for different scan rates. The transition occurs around 0.45 V and a high sweep rate seems to round the transition but no significant shift of the transition potential is observed. The electrochemical response to be compared with these scans is presented in (b). The peaks (1) and (2), attributed to sulphate desorption and adsorption respectively<sup>[4]</sup>, are correlated to the changes observed in the Au surface structure, which indicates that the surface structure modifications are mostly likely induced by the interaction of the sulphate ions with the substrate. Crystal truncation rods were measured and the full data set is being analysed.

The underpotential deposition (UPD) of Cu on Au(111) and Au(100) have being also investigated. The scans were performed from 0.8 V, where no Cu is adsorbed, to 0 V, where the massif Cu deposition starts, and back to 0.8 V<sup>[6]</sup>. The

changes observed during the potential sweep are produced by the surface structure modifications, which are dependent on the substrate orientation (Fig. 2). For Au(111) one intensity drop is observed for potentials around 0.25 V followed by the stabilisation of an ordered phase below 0.18 V, which is compatible with a stable Cu structure  $(\sqrt{3} \times \sqrt{3})^{[6]}$ . For the (001) orientation (fig. 2-b), the evolution is more complicated. The (1 - 1 0.2) intensity decays around 0.30 V and then grows up again, following the same pattern in the reversal processes. This indicates the existence of at least two different stable structures before the full Cu monolayer is completed. The (0, 0, 1.6) reflectivity shows that the surface starts to get rough in the beginning of the Cu deposition and evolves to less rough surface at 0 V, where is expected the completion of the Cu monolayer. The structural analysis using the rod measurements is in progress. The last part of our "test" for the cell performed at ESRF was its capability for the in situ studies of thin film deposition beyond the monolayer. Little is known concerning the morphology during the thin films deposition by electrochemistry. The intensity changes of the Cu (220) bulk reflection as a function of deposition time is shown in 3. An epitaxial relation is observed between the Cu film and the substrate, with the Cu film being completely relaxed from the very beginning of the deposition. The inset of fig. 3 shows the transversal scans for the Cu bulk peak and for the bare Au surface. The similarity on the coherent domain size between the Cu bulk and the Au surface indicates a two dimensional growth of the Cu film. One problem, observed during the measurements, was the interaction of the X-ray beam with the electrolyte, likely producing radicals in the electrolyte which oxidises the Cu deposit producing its removal.

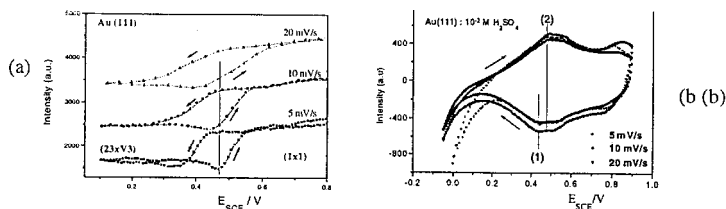


Fig. 1. (a): Intensity change for the (0 1 0.45) peak as function of the applied potential. (b) Corresponding voltammograms.

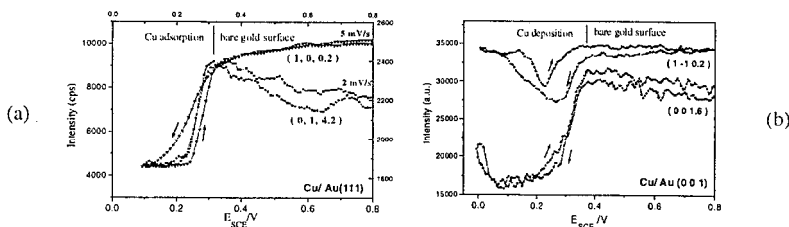


Fig. 2. Intensity change during Cu deposition as function of the applied potential. (a) Au(111); (b) Au(001).

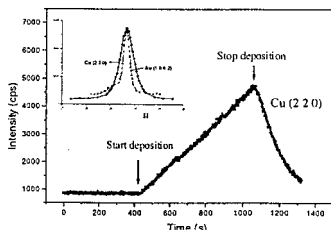


Fig. 3. Intensity change at the expected fully relaxed Cu (2 2 0) position as function of deposition. The inset shows the transversal scans at the Cu peak compared with the gold surface peak.

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