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## An *Ex Situ* Reflection Mode XANES Study of Underpotentially Deposited Copper Monolayers

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**Abstract:** Reflection mode XANES was performed *ex situ* on a copper monolayer underpotentially deposited onto a polycrystalline gold electrode. According to calculations based on reference substances, the thickness of the adsorbate layer was 0.21 nm and its oxidation state was close to +1. The *ex situ* spectra were found to be very similar to the previously published *in situ* data indicating that the adsorbate layer on the electrode surface does not significantly change after the removal from the electrolyte. The results showed that the reflection mode XAS is well suited for the study of adsorbate systems.

### 1. Introduction

Underpotential deposition (UPD) is a simple electrochemical method for the formation of thin adsorbate layers on electrode surfaces [1]. UPD deposits can form ordered submonolayers up to monolayer structures. To our knowledge, all previous x-ray absorption studies on UPD layers were performed by detection of the fluorescence radiation (e.g. [2-6]). However, the reflection mode XAS i.e. the variation of the x-ray reflectivity in the vicinity of an absorption edge can also be used in order to obtain the desired information. Previous calculations have shown that this detection mode should have a submonolayer sensitivity [7]. In contrast to the fluorescence detection, the measured x-ray reflectivity can simply be correlated to the absolute amount of the adsorbate present on the surface. Additionally, the evaluation of the x-ray reflectivity spectra yield the roughness of the electrode surface. The aim of this preliminary work was to test the possibility of the grazing incidence reflection mode XAS to provide valuable spectra from adsorbate systems.

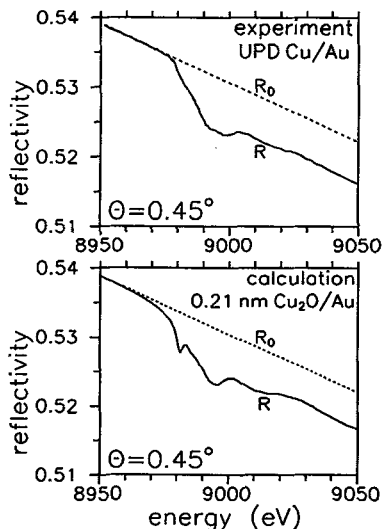
### 2. Experimental

The substrate for the copper deposition was a 100 nm thick gold layer vapour deposited onto a 3x5 cm<sup>2</sup> float glass plate. The electrolyte was 0.05 M H<sub>2</sub>SO<sub>4</sub> containing 1x10<sup>-3</sup> M CuSO<sub>4</sub>. The electrolyte was saturated with air during the deposition. The electrochemical potential at which the underpotential deposition was performed was +200 mV (vs. NHE); the electrode was held at this potential for 200 s and subsequently withdrawn from the electrolyte solution in order to perform the XAS measurement. The anodic stripping charge for a similar deposition performed directly before that used for the XAS measurement was 200  $\mu$ C, a value very near to that for a Cu<sup>+</sup> monolayer on Au(111) surface (190  $\mu$ C). The experiment was performed at the HASYLAB RÖMO 2 station (bending magnet) using the x-ray reflectometer build in our home laboratory [8] and a detector system consisting of three ionisation chambers. The reflection mode XAS measurement was performed at a glancing angle of 0.45 degrees i.e. in the vicinity of the critical angle for gold. The critical angle is the angle at which the step in the reflectivity curve has a maximum due to the adsorbed overlayer: This was additionally confirmed by numerical simulations for different Cu/Au systems. The irradiated electrode surface was about 1 cm<sup>2</sup> and the total integration time was 1 h with a mean DORIS current of 90 mA.

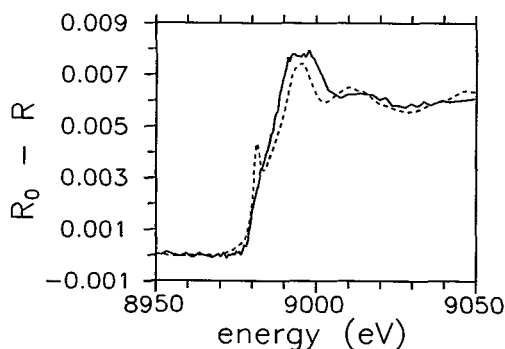
### 3. Results

The energy dependent x-ray reflectivity measured for the UPD copper monolayer on polycrystalline gold is shown in the upper part of figure 1. The lower part of this figure shows the spectrum calculated for a system consisting of 0.21 nm Cu<sub>2</sub>O on gold. The thickness of the copper oxide layer used for these calculations was chosen in order to achieve a best fit to the measured reflectivity step in the vicinity of the Cu absorption edge; The thickness of a Cu<sub>2</sub>O monolayer is 0.22 nm. The calculations started with the data obtained in the transmission mode with Au and Cu foils and CuO and Cu<sub>2</sub>O reference substances. Using these reference data, the real part of the complex, energy dependent refractive index  $n(E)=1-\delta-i\beta$  was obtained by Kramers-Kronig transform [9]. The x-ray reflectivities for layer system consisting of copper species on gold were calculated using the recursive algorithm described in [10].

The comparisons of the background subtracted measured spectrum with the spectrum calculated for the system  $\text{Cu}_2\text{O}/\text{Au}$  is shown in figure 2. The best fit to the measured spectrum was obtained with the assumed rms (root mean squared) surface roughness of 2.4 nm. The most striking feature of the measured spectrum is the absence of the edge peak at about 8982 eV which is characteristic for metallic copper and copper(I)-oxide. This indicates that no metallic copper or copper(I)-oxide bulk phase has formed on the gold surface. However, according to the position of the measured reflectivity edge (figure 2) the *ex situ* oxidation state of the copper atoms adsorbed on the gold surface is close to +1, a result very similar to that found *in situ* by Tadjeddine *et al.* [3]. Additionally, the similarity of the *ex situ* spectrum showed in figure 2 with published spectra measured *in situ* [3,6] suggest that the adsorbed copper monolayer does not significantly change after removal from the electrolyte: This is probably due to co-adsorbed sulfate ( $\text{SO}_4^{2-}$ ) or bisulfate ( $\text{HSO}_4^-$ ) ions [11] which seem to preserve copper adatoms from further oxidation.



**Figure 1:** Reflectivity measured *ex situ* in the vicinity of the Cu-K-edge for the UPD copper layer on gold (top) and the calculation for the system consisting of 0.21 nm  $\text{Cu}_2\text{O}/\text{Au}$  (bottom).



**Figure 2:** Direct comparison of the measured (solid) and the calculated (dashed) reflectivity edges from figure 1.

#### 4. Conclusions

- monolayer sensitivity with XAS in the reflection mode can be easily achieved;
- the comparison of the reflectivity data with calculations yields the amount of the adsorbate and its oxidation state;
- the *ex situ* oxidation state of the copper adatoms on polycrystalline gold surface is close to +1;
- the adsorbate system on the electrode surface seems to be preserved after the emersion of the electrode from the electrolyte;
- *ex situ* results are very similar to those obtained by *in situ* measurements on Au(100) and polycrystalline Pt.

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