



Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	Experiment title: XAS Studies of Electrodeposition, Surface Alloying and Self-Assembled Monolayers	Experiment number: CH 1179
Beamline: ID26	Date of experiment: from: 5/11/01 to: 13/11/01	Date of report:
Shifts: 18	Local contact(s): Dr. Thomas Neisius	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):
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Report:

The primary aim of the experiment was to establish the local environment of Zn when deposited onto an Au(111) electrode surface in a single monolayer film. Typically, the surface concentration of Zn atoms on the Au(111) was 1.5×10^{14} atoms cm^{-2} , established via measurements of cyclic voltammograms (CVs), an example of which is in figure 1 (peaks towards the cathodic end of the CV correspond to adsorption and deposition of the monolayer). Once the monolayer was well established by holding the potential slightly beyond that required for deposition, the zinc phosphate electrolyte was largely withdrawn from the cell, to remove any contribution from the solution to the signal (although enough for potential control remained), and the XAS experiments were undertaken.

This experiment had been attempted previously at other synchrotron facilities and the relative quality of the spectra was evident (figure 2 – ID26 vs station 7.1, SRS, Daresbury). In addition to a low level of noise, the oscillations are clearly identified and they continue to high k for such a low concentration of Zn. This clarity extends into the Fourier Transform (FT) of the background subtracted data (figure 3). Three peaks are observable above the noise at approximately $r = 1.93, 2.80$ and 3.78 \AA respectively. Preliminary analysis by fitting to the FT in EXCURV98 has shown that there is reasonable agreement with a model in which the Zn

atoms sit in a three-fold hollow site on the Au surface (the second shell) with three oxygen atoms forming a pseudo three-fold hollow site above them (the first shell). The third shell could be tentatively attributed to phosphorous (bonded to the oxygen atoms) backscattering to the Zn and a diagram of the model is displayed in figure 4.

Figure 1: CV of Zn on Au(111) in phosphate buffer

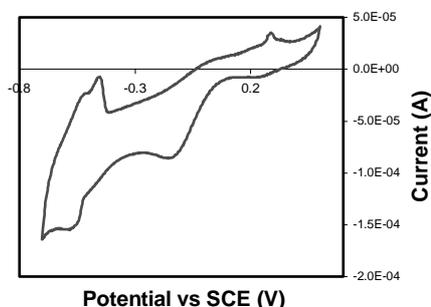


Figure 2: Comparison of raw EXAFS for ID26 (1) vs 7.1 (2)

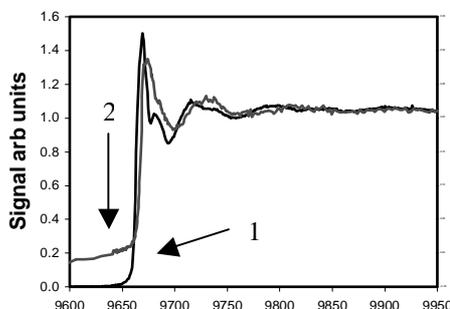
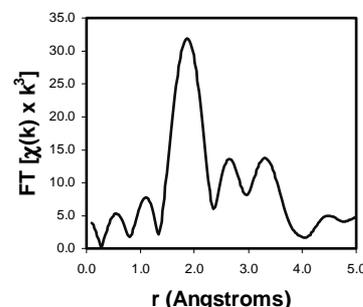


Figure 3: FT in R-space for UPD monolayer EXAFS



Unfortunately, a monochromator glitch is present at $k = 8.5$, whereas the EXAFS oscillations continued to $k = 10$ and beyond. This additional data at high k could not be used in analysis as everything from the inconsistency onwards required removal prior to analysis. Correction of the fault would permit a larger range of the EXAFS to be used and give greater confidence in the assignment of a third shell and a more complex structural model. Prior to investigation of UPD monolayer, reference control spectra were collected for Zn in aqueous solution (10mM and 0.1mM $\text{Zn}(\text{ClO}_4)_2$), since the local structure around the Zn is well known. Well-defined EXAFS oscillations were observed for 250 eV beyond the Zn edge.

Figure 4: A model for the local environment of Zn in the UPD monolayer

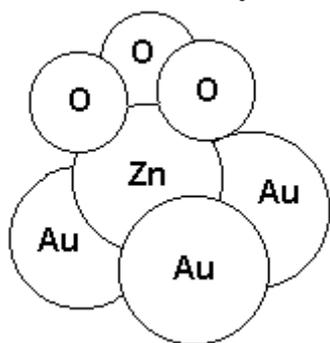


Figure 5: Pre-edge background subtracted alloying XAS spectrum

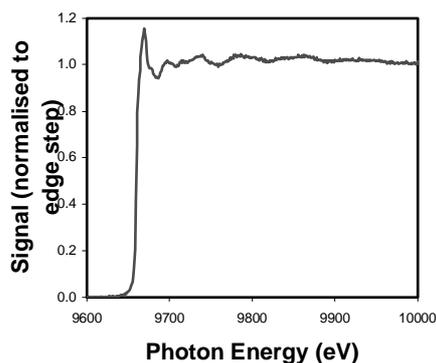
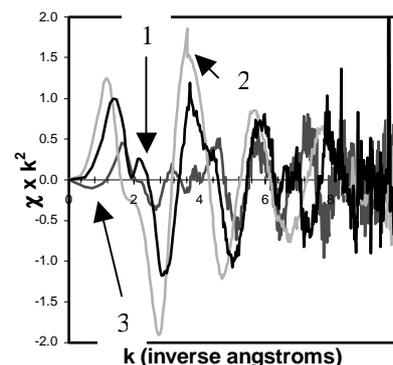


Figure 6: k^2 weighted EXAFS comparison (1 – UPD, 2 – Alloy, 3 – Soln.)



The outcome of the alloying experiments was very encouraging, although there was insufficient time to investigate the system to the full. Alloying was induced by maintaining the potential of the cell well into the bulk region, for example as far as -0.8V vs SCE, for some time before the electrolyte was withdrawn from the cell. The extent of alloying was calculated from electrochemical measurements, but the structure of the alloy can only be probed via EXAFS and figure 5 shows the raw EXAFS after alloying for 1 hour. Background subtraction of this data and Fourier Transform into real space shows two distinct peaks. As yet, analysis of the

spectra (which also suffered from the mono glitch) has not provided a satisfactory identification of the local environment of the Zn atoms within the alloy or the identity of the backscattering atoms (although it is expected that they will be Au or perhaps Zn).

What makes the alloying experiment so intriguing is that increased polarisation times appear to affect the degree of alloying and, we believe, the overall structure. In fact, the Au(111) evaporated onto Tempax glass samples employed in this experiment show marked differences in their CVs to those obtained for Au single crystals. Equally, the nature of the alloy developed in single crystals of different crystallographic orientation (Au(110), for example) is found to vary. We hope to extend the experiment to investigate these features in future beamtimes at the ESRF. Figure 6 shows a comparison of the k^2 weighted, background subtracted, data for the Zn / Au alloy against the 'solution' and 'UPD monolayer' spectra. The variation in the EXAFS for each of the Zn environments formed under the different conditions is evident.

The role of the counter-ion in the electrolyte upon the structure of the Zn UPD monolayer and Zn / Au alloy was also considered briefly towards the end of the experiment. Bromide ions, which are more strongly adsorbed onto Au than phosphate, were added to the electrolyte and the procedures for the study of UPD monolayer and alloy structure repeated. Significant differences in the EXAFS were observed in comparison to the data described previously, but only a small number of spectra could be recorded and, therefore, the statistical noise was high.

Data recorded during the course of CH1179, has proved very encouraging. The combination of high flux, reliable focus and beam stability and high detection efficiency available on ID26 make the station ideally suited to the study of monolayer films prepared by underpotential deposition (UPD). The EXAFS spectra collected were of high quality and compared very favourably with experiments run at the SRS in Daresbury and HASYlab in Hamburg. Due to our investigation of the UPD and alloying systems, the final section of our experiment, study of metal UPD through SAMs adsorbed onto gold electrodes, was untried. This experiment will be undertaken as part of our experiment scheduled on ID26 during June 2002.