XMaS the UK-CRG	**Experiment title:** Surface x-ray diffraction studies of Au electrodes: the electrodeposition of Nickel	**Experiment number:** 28-01-17
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Shifts: 18	**Local contact(s):** Dr. Simon Brown	*Received at XMaS:*

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Report: Introduction

The main emphasis of this run was to begin our studies of metal surfaces in an electrochemical environment. Initially the Au(111) crystal was studied, with two separate electrolytes, each generating an interesting result. The first was a measurement of the voltage dependence of the surface relaxation, which showed a parabolic form, mimicking the surface energy dependence. In the Ni deposition experiments, initial growth of Ni led to the appearance of scattering features, which were similar to those for the Au reconstruction, but modified by the inclusion of Ni atoms. Both points are treated separately below.

General Experimental Method

The experimental methods involved in these measurements are described in detail in ref. [1] and in the original application for beamtime [proposal number 28-01-17]. Briefly, however, the Au(111) surface was prepared by flame annealing, then placed in an electrochemical cell. The cell was then covered with a polypropylene window, and filled with modified Watts electrolyte (containing H_3BO_3, HCl, and $NiSO_4$) for the Ni studies, and dilute sulphuric acid (0.1 M H_2SO_4) for the surface expansion measurements. The polypropylene film can be deflated to trap a thin layer of electrolyte on the crystal surface, and allow x-ray measurements. However, on this run we were able to conclude that the Ni content of the thin layer region depletes, necessitating periodic reinflation of the film.

Results: (I) Surface Relaxation

Fig. 1 shows the voltage dependence of the scattered intensity at the position (1 0 3.5) on a crystal truncation rod (CTR), for Au(111) in sulphuric acid. At this position (the low **q** side of a Bragg peak) the x-ray intensity is directly related to the surface expansion of the crystal. In this particular measurement the electrode potential was cycled using a potentiostat, and appears to

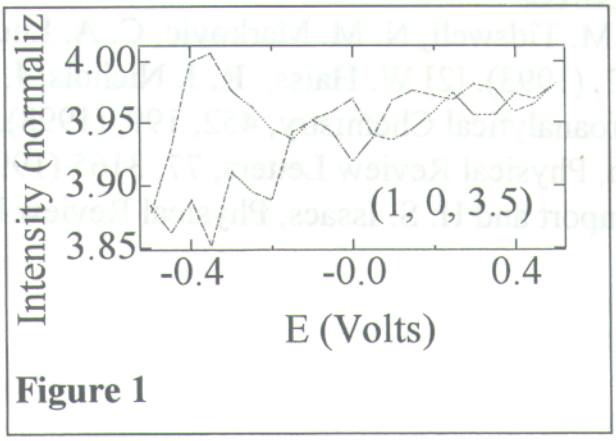

Figure 1

show a parabolic dependence, centred around the potential of zero charge (PZC). The hysteresis of the plot is purely due to the partial forming, and lifting of the reconstruction, which has fairly slow kinetics. Interestingly, manipulation of the Lippmann equation for the surface energy γ, of a metal predicts a parabolic dependence of γ on the electrode potential, but recent results suggest that the surface stress has a linear dependence [2]. The inference is, that surface stress and surface energy are not linearly related, and that our measurements of surface expansion are primarily giving us information on the surface energy changes. It would, therefore, be interesting to quantify and study the kinetics of the surface expansion, and compare the results with those of surface stress in similar systems [2].

Results: (II) Ni deposition

The main panel of Fig. 2 shows two scans in the <110> reciprocal space direction. The triangular points represent data taken at an electrode potential of 0.35 V, and the circular points at -1.0 V. The peak at 0.00 in both plots, is due to the Au(111) CTR. At this position the x-ray intensity is largely dependent on the surface layer of the crystal. The first plot at positive potential (+0.35 V), shows a single large peak due to the ordered Au surface. In the second plot (-1.0 V), the CTR peak has decreased in intensity and another peak has appeared at (1.02, 0.02 , 0.2). The scattering is very similar to that observed for a reconstructed Au surface. The inset plot however, shows the time dependent growth of the right hand peak, with intensity still increasing after 1200 seconds. In comparison, previous studies of the Au(111) reconstruction [4] showed that the reconstruction formed in approximately 20-120 seconds. The order of magnitude difference suggests a possible growth process, due to Ni deposition. In addition an energy scan on the right-hand peak showed a step change in intensity at 8.36 keV, (the K absorption edge for Ni), giving a strong indication that if the peak is due to a reconstruction, then it also incorporates Ni. A mixed reconstruction has been suggested by the STM studies[3]. Further measurements of the CTR's and some energy scans around the Ni edge will clarify the exact nature of this surface layer, which forms the transition layer between the Au lattice and a deposited Ni film.

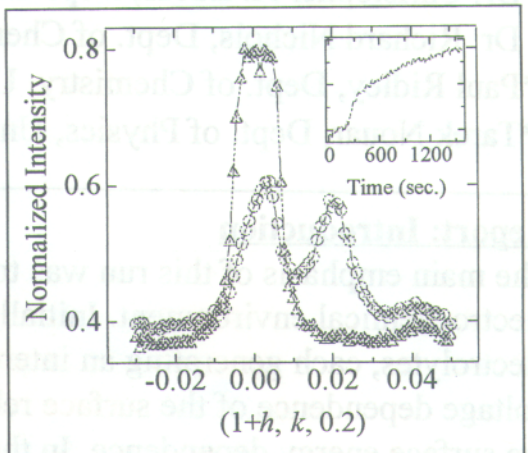

Figure 2

References

[1] I. M. Tidswell, N. M. Markovic, C. A. Lucas and P. N. Ross, Physical Review B, 47, 16542, (1993). [2] W. Haiss, R. J. Nichols, J. K. Sass, K. P. Charle, Journal of Electroanalytical Chemistry, 452, 199, (1998). [3] F. A. Moller, O. M. Magnussen, and R. J. Behm, Physical Review Letters, 77, 3165 (1996). [4] Jia Wang,B. M. Ocko, A. J. Davenport and H. S. Issacs, Physical Review B, 46, 10321, (1992).