	Experiment title: The Effects of a Magnetic Field on the Structure at the Electrochemical Interface	Experiment number: 28-01-652
Beamline: BM28	Date of experiment: from: 29/10/03 to: 04/11/03	Date of report: 1/3/2005
Shifts: 18	Local contact(s): Laurence Bouchenoire	<i>Received at ESRF:</i>
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Report:

During the previous XMaS experiment in February 2003 we experienced technical difficulties with the temperature-controlled electrochemical cell (which have since been resolved) that led us to try studying the effects of applying a magnetic field across the electrode/electrolyte interface (in order for the beamline not to be completely wasted due to equipment failure). Although the concept of doing electrochemistry in magnetic fields is not new (Faraday performed experiments more than a century ago) research in this area has been particularly active over the last few years as it has been realized that it is possible to introduce an additional degree of freedom in controlling important electrochemical parameters. Most of this work has focussed on the effects of magnetic fields on the electrodeposition of metals, eg. Co, Ni. Despite this interest it is realized that there is no fundamental understanding of the effects of a magnetic field on the structure at the electrode/electrolyte interface (most studies have focussed on magnetohydrodynamic effects). In our experiment we examined a well-characterized electrochemical system; namely single-crystal Au(*hkl*) electrodes in sulfuric acid electrolyte. The results were surprising, figure 1, which shows the effect of applying a 0.5 T magnetic field along the sample surface normal for the reconstructed Au(001)-(5x20) and Au(111)-(23x√3) electrode surfaces; note in electrolyte the surface reconstruction can be reversibly formed/lifted depending on the applied electrode potential. The data is a measurement of the specular crystal truncation rod (CTR) from close to the origin to the first ‘anti-Bragg’ position and is shown as the ratio of 2

data sets measured in a 0 T and 0.5 T field. Closed circles are data from the Au(001) surface and open circles for the Au(111) surface. Preliminary modelling of the data suggested that the effect observed for the Au(001) surface was due to relaxation in the Au surface although the precise structure at the electrolyte side of the interface was not included in the model. What is clear, however, is that there was a pronounced effect for the Au(001) surface. In this follow-up experiment we aimed to perform a systematic study of the effect of an applied magnetic field on relatively well-understood electrochemical interfaces, namely, the low-index

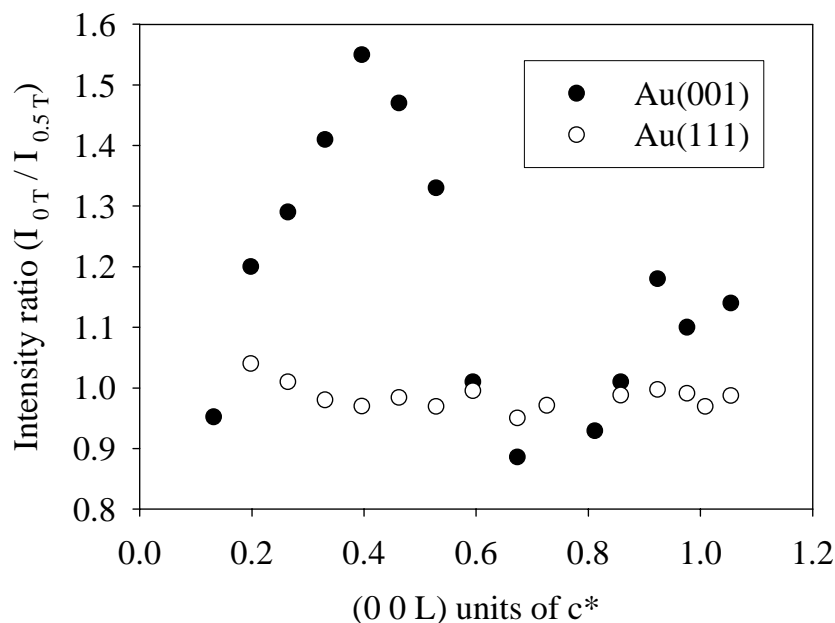


Figure 1. The ratio of two sets of CTR data measured with and without an applied magnetic field of 0.5 T along the sample surface normal.

Au(*hkl*) electrodes in simple alkaline (0.1 M KOH) and acid (0.5 M H₂SO₄) electrolytes. Unfortunately, during this experiment, it was impossible to reproduce the results shown in figure 1. The main conclusion was that the large changes observed for the Au(001) surface (in figure 1) were due to a magnetic field-induced movement of the sample holder, although when this was eliminated there were some small intensity changes which could be attributed to a ‘real’ magnetic field effect. The magnitude of the field-induced changes to the CTR scattering was too small to merit a detailed study. Despite these disappointing conclusions we were able to perform a systematic study of the low-index Au(*hkl*) electrode surface in alkaline (0.1 M KOH) solution. This work has led to a publication which has been submitted to Surface Science. The abstract is given below:

Structure Sensitivity of CO Oxidation on Gold Single Crystal Surfaces in Alkaline Solution: Surface X-ray Scattering and Rotating Disk Measurements

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Abstract:

A combination of *in-situ* surface X-ray scattering (SXS) and cyclic voltammetry (CV) measurements have been performed to determine the effect that the surface atomic structure of the low-index faces of Au single crystals has on carbon monoxide (CO) oxidation in alkaline solution. For the (111), (100) and (110) surface orientations, potentiodynamic measurements of the scattered X-ray intensity at key reciprocal lattice points have been employed to determine the potential window of stability for the reconstructed surfaces. By saturation of the electrolyte with CO, the effect that adsorbed CO has on the stability of the reconstructed surfaces has been investigated. The presence of CO acts to stabilize the surface reconstructions over a wider potential range, causing a positive shift in the potential for the lifting of the Au(111) surface reconstruction of ~200 mV. In the case of the (100) and (110) orientations, the adsorption of CO stabilizes the reconstruction over the entire potential range studied. The oxidation of dissolved CO was found to be structure-sensitive, with the activity decreasing in the order Au(110)-(1x2) > Au(100)-“hex” > Au(111)-(23x√3). The structure-sensitivity is correlated with the surface density of low coordinated sites.
