Electrochemical Roughening of Au(110) Single Crystal Electrodes

K.M. Robinson[1], *W.E. O'Grady*[1], *and I.K. Robinson*[2]

[1]Code 6170, Chemistry Division, Naval Research Laboratory, Washington, DC 20375, USA
[2]AT&T Bell Laboratories, Murray Hill, NJ 07974, USA

Abstract. The surface roughness of a Au(110) electrode was studied as a function of electrode potential. The electrode potential was cycled between the double layer region and the oxide and hydrogen regions. Measurements of the crystal truncation rod passing through the (111) reflection were made ex-situ. The results reveal that the surface roughness is not significantly changed by cycling the potential between the double layer and the oxide regions, (.3V - 1.4V vs. Pd/H_2, 0.1M $HClO_4$). The roughness is decreased when the potential is cycled into the hydrogen region, -0.4V.

1. Introduction

The surface structure of Au(110) single crystals has been frequently studied in vacuum [1-3]. The 1x2 reconstruction, which has been studied theoretically using embedded atom models [4,5], has repeatedly been observed by LEED [2] and x-ray diffraction [1]. The stability of the Au(110) surface was studied as a function of the electrochemical potential by LEED analysis [2]. It was reported that the Au(110) surface reconstruction was lifted by the oxidation of the surface, however these samples were vacuum prepared. In the work presented here, electropolished electrodes were examined as a function of potential. Recent work on flame-annealing of gold crystals has demonstrated that the roughness of these electropolished electrodes is sufficient to diminish the intensity of the scattering from the reconstruction [6]. Therefore, the roughness, and possible self-annealing, of the Au(110) electrode was studied.

The roughness of the Au(110) electrode was studied by measuring the crystal truncation rods, CTRs. These rods are described as lines of scattering perpendicular, in k-space, to the terminated surface passing through the bulk Bragg positions [7]. More precise details of CTRs are contained elsewhere [7,8]. A perfectly terminated flat surface would produce rods with a $1/\Delta q_z^2$ intensity dependence. Surfaces that are more rough deviate from the ideal dependence according to a roughness parameter, β, which is an estimate of the fractional occupancy of subsequent layers. The integrated intensities measured are fit to

$$|F(q_z)|^2 = N_1^2 N_2^2 \frac{(1-\beta)^2}{[1+\beta^2-2\beta\cos(q_z c)]} \frac{1}{4\sin^2(\frac{1}{2}q_z c)}$$

Springer Proceedings in Physics, Vol. 61 **Surface X-Ray and Neutron Scattering**
Eds.: H. Zabel and I.K. Robinson

where N^2_i are the crystal dimensions in the surface plane and c is the real space unit cell dimension in the surface normal direction.

2. Experimental

The preparation of the Au(110) electrode is discussed elsewhere [6]. Briefly, the surface is electropolished in a HCl:ethanol:glycol mixture at 4.5V [9]. This repeatedly produces a surface with a roughness parameter, $\beta = 0.56 \pm 0.08$. Chloride ion contamination from the electropolishing was removed by placing the electrode in boiling concentrated HNO_3. The electrode was emersed in 0.1M $HClO_4$ (Ultrex grade) under potential control at 0.3V (vs. Pd/H_2). The electrode potential was cycled, 25mV/sec, between the emersion potential, 0.3V, and two extremes, 1) oxide region, 1.4V, and 2) hydrogen region.

The electrode was removed from solution, under potential control, and mounted on a four-circle diffractometer and aligned according to bulk diffraction indices. Rocking scan measurements were made along the (1,1,*l*) truncation rod. The scans were background subtracted and integrated according to standard procedures [8]. Once the scan of the rod was completed, the crystal was re-emersed, or re-electropolished depending upon the desired experiment. The ex-situ nature of this work prevented any detail concerning the structural changes possibly caused by OH adsorption or reduction of the oxide layers. For details concerning these regions, in-situ scattering is necessary to be more electrochemically correct.

3. Results and Discussion

The data and best fits for the electropolished surface and the surfaces in the oxide and hydrogen regions are shown in figure 1. The data are averages of 5-7 separate electropolished and cycled samples. The electropolishing repeatedly produces roughness parameters of $\beta = 0.56 \pm 0.08$. There is no statistical difference

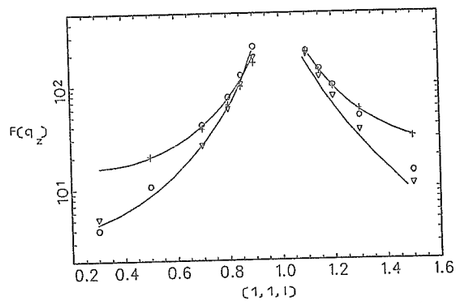

Figure 1: (1,1,*l*) truncation rod data for the electropolished surface (O), and the surfaces cycled into the oxide (∇) and hydrogen (+) regions. The solid lines are the best fit to the data.

between the electropolished roughness and the oxidized surface. This is in agreement with studies done on Au(100) crystals [6].

The data for the hydrogen region are fit with a roughness of $\beta = 0.27 \pm 0.09$. This decrease in the roughness supports observations in vacuum of self-annealing of Au crystals by repetitive cycling of the potential into the hydrogen production region [2,10]. There does appear to be a time-dependence to the smoothing of the surface, however after approximately 10 cycles (15 minutes), the roughness parameter remains constant so only data after 15 minutes were used in the fitting. There was no observation at any potential of the 1x2 reconstruction.

By assuming that upon reduction the gold atoms occupy (110) atomic positions, as opposed to a close-packed structure seen on Au(100), β can be related to an rms surface roughness by rms = $d_\perp \beta^{1/2}/(1-\beta)$ (for Au(110) $d_\perp$ = 1.44 Å). Michaelis etal. reported the reappearance of the 1x2 reconstruction after reduction of the oxide, however they did not cycle into the hydrogen production region [2]. The electropolished and oxidized samples have an rms = 2.5± 0.3Å which is very close to the Au-Au distance or one lattice distance. The surface cycled into the hydrogen production region has an rms = 1.0± 0.4Å which is very close to a half lattice distance. The rms values correspond to the presence, by electropolishing, and disappearance, by cycling the potential into the hydrogen region, of a missing row reconstruction, however the lack of any 1x2 surface scattering does not support this interpretation. One possible explanation would be small domains of 1x2 reconstructions, which are predicted by the embedded atom model [5]. These small domains would produce low intensity surface scattering on the order of the background noise. Future in-situ scattering work will aide in determining the driving mechanism for the self-annealing and the extent gold oxidation-reduction plays in the annealing.

This work is funded by the Office of Naval Research. KMR would like to acknowledge the support of the National Research Council Fellowship Program. In addition, we would like to acknowledge AT&T for the use of X16B and the NSLS which is funded by the Department of Energy.

References

[1] E. Vleig, I. K. Robinson and K. Kern, Surface Sci. 233 (1990) 248.
[2] R. Michaelis and D. M. Kolb, Surface Sci. Lttrs. 234 (1990) L281.
[3] E. van de Riet, H. Derks and W. Heiland, Surface Sci. 234 (1990) 53.
[4] L.D. Roelofs, S.M. Foiles, M.S. Daw and M.I. Baskes, Surface Sci. 234 (1990) 63.
[5] S.P. Chen and A. F. Voter, Surface Sci. Lttrs 244 (1991) L107.
[6] K.M. Robinson, I.K. Robinson and W.E. O'Grady, in preparation.
[7] I.K. Robinson, Phys.Rev. B 33 (1986) 3830.
[8] R. Feidenhans'l, Surface Science Reports 10 (1989) 105.
[9] J.L. Whitton and J.A. Davies, Steel Corrosion Mechanisms 111 (1964) 1347.
[10] D.M. Kolb and J. Schneider, Surface Sci. 162 (1985) 764.