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ELECTROCHEMICALLY INDUCED SURFACE ROUGHNESS ON Au(100) STUDIED BY SURFACE X-RAY DIFFRACTION

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Abstract—The surface of an electropolished Au(100) single crystal has been investigated by synchrotron X-ray diffraction. The crystal was examined after having swept the potential into the double layer of the oxide and hydrogen regions. The results show that there is very little change in the surface atomic roughness from the double layer through the oxide region. When cycled into the hydrogen region, where minimal H_2 production is measured, the surface becomes very rough. No evidence for inducing the (5 × 20) hexagonal reconstruction was observed.

Key words: Au(100) electrochemistry, surface structure, surface diffraction, synchrotron radiation.

INTRODUCTION

The surfaces of Au(100) single crystals have frequently been studied after electrochemical treatment under UHV conditions[1–3]. The (5 × 20) reconstruction has been observed by LEED[1, 2] and by X-ray diffraction[3, 4] and is described as a uniaxially incommensurate hexagonal surface layer. This reconstruction has been found to be stable after immersion in an electrolyte and after potential cycling in certain potential regimes[1, 5]. A recent study using *in situ* X-ray reflectivity and X-ray diffraction has shown the removal of the reconstruction with increasing positive potential and a possible recovery of the reconstruction in the hydrogen region[4]. These structural and morphological changes have all been observed on vacuum prepared or flame-annealed surfaces which induce the (5 × 20) reconstruction[2, 5, 6]. In this work we discuss the modification of an unreconstructed Au(100) surface brought about by changing the electrode potential.

EXPERIMENTAL

The Au crystals were studied by measuring crystal truncation and specular rods. Truncation rods are lines of X-ray scattering perpendicular to the terminated surface passing through bulk Bragg positions. The scattering vector **Q** is defined as $\mathbf{Q} = (q_z, \mathbf{q}_\parallel)$, where $q_z = c^*l$, and $\mathbf{q}_\parallel = a^*h + b^*k$. The vectors a^*, b^* and c^* are the reciprocal lattice vectors for the crystal surface and h, k, l are the Miller indices. For the specular rod, which is sensitive to the planes parallel to the surface, $h = k = 0$, while for truncation rods h and k have integer values. The vertical index is not constrained to be an integer due to the termination of the bulk crystal[7, 8]. For an ideally terminated smooth surface the intensity goes as $1/\Delta q_z^2$ from the bulk Bragg position. By allowing the termination to deviate from a perfectly smooth surface to a surface with fractional overlayer coverage, β, the intensity in q_z drops more rapidly than the ideal profile.

The truncation rod data are fitted to[7, 8]

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

where N_i^2 are the crystal dimensions in the plane, β is the roughness parameter, related to the rms roughness, $\sigma_{rms} = d_\perp \beta^{1/2}/(1-\beta)$ and c is the real space unit cell dimension in the surface normal direction. Fitting of the data to the rods involved using exponential q_z-dependent X-ray absorption and Debye–Waller factor corrections for $F(q_z)$[8]. These corrections merely adjust the baseline of the data and not the width of the rod in q_z. The specular rod, which is also known as the specular reflectivity[3, 4], can also be fit with a more rigorous expression which incorporates layer-by-layer deviations in density, displacement and fluctuation. To use layer-by-layer variables in the specular rod expression requires a smooth surface for a quantitative fit with reasonable (<25%) error. The error in the specular information is greatly increased for a rough surface ($\beta > 0.4$).

The preparation of the Au crystal has been described previously[6]. The sample (a disc of 4 mm diameter and 2 mm thick) was cut from a Au boule (Materials Research Corp.), with a rocking angle (111) <0.3° and aligned by Laue backscattering to <0.2°. The sample was electropolished in a 1:1:2 mixture of glycol:ethanol:HCl (conc) at 4.5 V[9]. This electropolishing technique removes atoms from the surface a layer at a time[6]. Once a strong surface diffraction intensity was measured from the electropolished surface, the sample was placed in boiling concentrated HNO_3 for 2–3 min to remove any residual Cl^- ions remaining from the electropolishing.

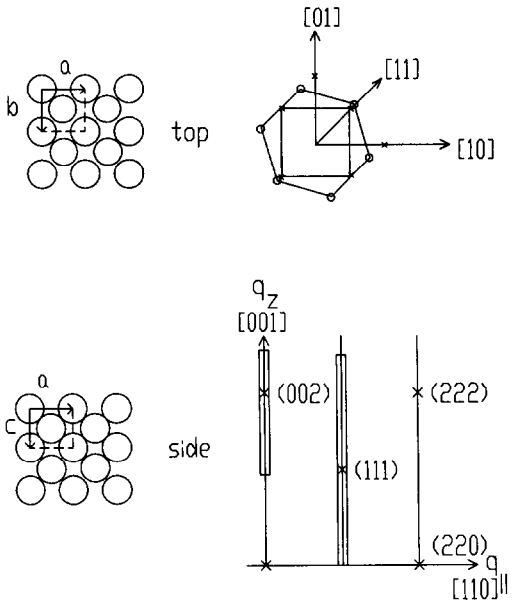

Fig. 1. The surface lattice in real and reciprocal space for Au(100). (×) Bulk Bragg positions and (○) surface diffraction positions from the 5 × 20 hexagonal reconstruction. The boxed in areas are the regions over which data were collected.

The crystal was transferred from the laboratory to the beamline in air and mounted in a standard four-circle diffractometer and aligned on the low index bulk diffraction peaks. The X-ray scattering was measured on beamline X-16B at the National Synchrotron Light Source, with fixed wavelength of 1.689 Å. The crystal truncation rods were measured by rocking the crystal through a series of (*hkl*) positions in *k*-space. A full set of scans consisted of measurements along the specular rod and a low index, usually the (111), truncation rod. The scattering indices from the crystal were defined according to a surface crystalline lattice analogous to LEED indices, shown in Fig. 1 for Au(100).

The first set of diffraction scans were carried out on the electropolished surface. Following these diffraction measurements, the sample was removed from the diffractometer, placed in an electrochemical cell where the potential could be scanned or stepped to the desired values. A standard cell shown in Fig. 2 was used. The electrolyte used was 0.1 M $HClO_4$ prepared from Baker Ultrex grade $HClO_4$ and triply distilled H_2O. The sample was always immersed at the same potential, +0.1 V (*sce*). All potentials were measured *vs* a palladium hydrogen (Pd/H_2) reference electrode and are reported here *vs* the saturated calomel electrode (*sce*). After immersion the potential was stepped at 25 mV s^{-1} to the terminal potential where the sample was carefully emersed from the cell under potential control, rinsed profusely with distilled H_2O and placed in the diffractometer. Three regions were studied: (1) the double layer region +0.1 to +0.5 V; (2) the oxide region +0.1 to +1.3 V (*sce*); and (3) the hydrogen region +0.1 to 1.3 to −0.5 V (*sce*) and +0.1 to −0.5 V (*sce*). Only the extreme potential regions were studied due to the *ex situ* nature of the experiments. *In situ* studies will be carried out to determine structural changes arising from oxygen adsorption and oxide growth.

RESULTS AND DISCUSSION

The specular rod (SR) and crystal truncation rod (CTR) data for the electropolished and the electrochemically modified surfaces are shown in Figs 3 and 4 together with the best fits to the data obtained from equation (1). The parameters obtained from the fitting and the surface roughness factor β are presented in Table 1.

The specular and crystal truncation rod data obtained for the sample treated in the double layer region (+0.1 to +0.5 V) are almost identical to those obtained for the electropolished surface indicating little or no change occurs in the surface structure as a result of the immersion and the following emersion at +0.5 V (*sce*). This is in good agreement with the UHV studies carried out by Kolb and Schneider[5]. Neither the electropolished sample nor the emersed sample gave any indication of a (5 × 20) reconstruction[3, 6] of the surface.

For the oxide region (+0.1 to +1.3 V) no significant perturbation from the initial electropolished surface were observed in the CTRs. However, the fitted data for the specular rods show a slight deviation in the surface roughness, Fig. 3a, which would arise from a density change in the topmost scattering layer. This change could be due to an oxide layer on the surface but at this time the quality of the data will not allow us to completely resolve the differences between the two surfaces.

Two different experiments were carried out when examining the effect of sweeping the potential of the electrode into the hydrogen region. In the first experiment the potential was swept from +0.1 V (*sce*) to +1.3 V (*sce*) and then immediately back to −0.5 V (*sce*) where it was emersed for the scattering experiments. In the second experiment the potential was swept from the immersion potential +0.1 V (*sce*) directly to −0.5 V (*sce*) where it was emersed for the scattering experiments. The data for the two hydro-

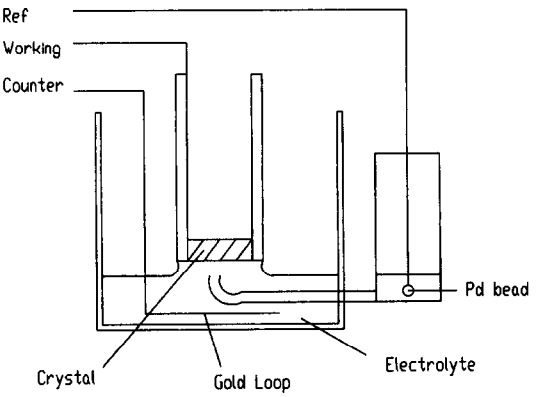

Fig. 2. Standard electrochemical cell used to cycle the Au(100) single crystal. The electrolyte, 0.1 M $HClO_4$, touched only the face of the crystal. The crystal was removed from this cell and mounted on a standard goniometer head for data collection.

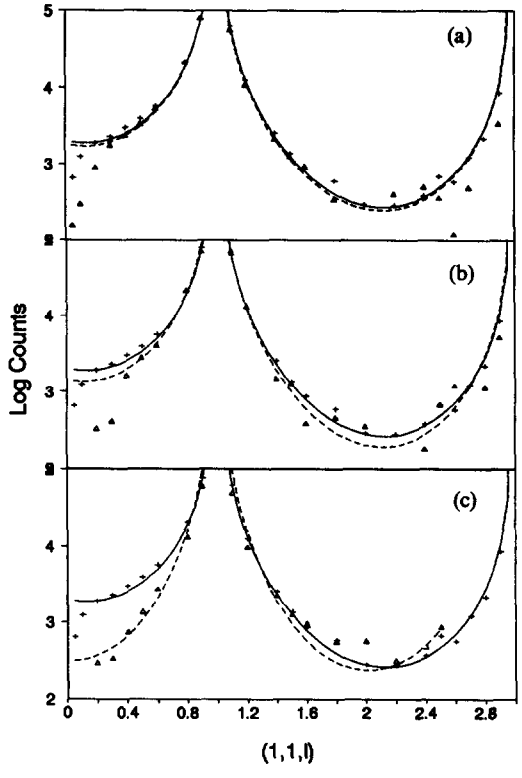

Fig. 3. (0,0,l) specular rod data (△) for the (a) oxide region, (b) hydrogen region (after oxide) and (c) hydrogen region (no oxide) compared with the electropolished sample (+). The lines are the best fits for the electropolished (——) and cycled surfaces (---).

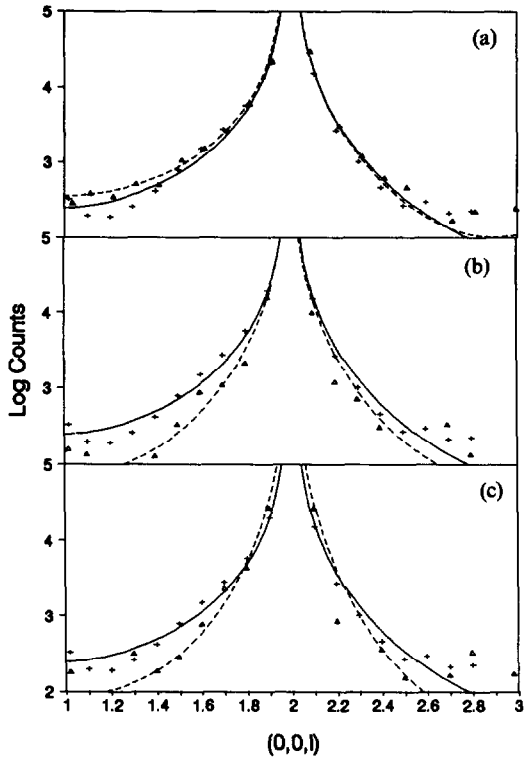

Fig. 4. (1,1,l) truncation rod data (△) for the (a) oxide region, (b) hydrogen region (after oxide) and (c) hydrogen region (no oxide) compared with the electropolished sample (+). The lines are the best fits for the electropolished (——) and cycled surfaces (---).

gen region experiments are very different from those observed for the electropolished or the oxidized surface. The specular rod data for the two surface treatments are shown in Fig. 3b and c and are compared with the electropolished sample. These data are best fitted with a model for an atomically rough surface and the results are shown in Table 1. The value of β indicates the surface roughness is the same within experimental error for both cases. On the other hand the crystal truncation rods shown in Fig. 4b and c compared with the electropolished surface show very different behaviors for the two treatments. The increase in the β value in Table 1 again indicates an increase in the surface roughness. However, the surface that was initially cycled into the oxide region prior to the hydrogen region (+0.1 to +1.3 to −0.5) shows a significantly lower value of β. SRs and the CTRs appear to give differing results for the two electrochemical treatments. The SRs are sensitive to the roughness of the crystallographic planes parallel to the surface. The surfaces produced by the electrochemical treatments have a termination which is atomically rougher than the initial electropolished surface and this roughness arises from taking the sample into the hydrogen potential region and is not due to the reduction of the electrochemically formed oxide layer. On the other hand the CTRs show a different result. The CTR measures the smoothness of the termination of a certain set of crystallographic planes at or near the surface. In this case the termination of the (111) places at the (100) surface is being monitored. The CTR shows that cycling the potential from +0.1 to +1.3 to −0.5 V (*sce*) produces a surface which is rougher than the electropolished surface but not as rough as the surface produced in sweeping the potential from +0.1 to −0.5 V (*sce*). If the SR and CTR from the +0.1 to +1.3 to −0.5 V (*sce*) data are compared it is seen

Table 1. Fitting parameters for the (0,0,l) and (1,1,l) truncation rods

	Electropolished	Oxide region	Hydrogen region (1)	Hydrogen region (2)
(0,0,l)				
β	0.25 ± 0.05	0.3 ± 0.05	0.7 ± 0.08	0.85 ± 0.1
$N_1^2N_2^2$	250	250	300	500
(1,1,l)				
β	0.3 ± 0.05	0.3 ± 0.05	0.45 ± 0.03	0.7 ± 0.06
$N_1^2N_2^2$	2.1	2.1	2.4	2.8

that the surface is slightly rougher from the CTR perspective and significantly rougher from the SR perspective. One possible explanation for this is that the metal which is deposited from the reduction of the initially formed oxide film forms a layer of metal on top of the terminated (111) planes which is roughened when the potential is stepped to -0.5 V (*sce*), leading to a large change in the β value for the SR. Since only one or two layers of the surface are perturbed in the oxidation[10] the termination of the (111) planes at the (100) surface as reflected in the CTR will only be slightly affected hence the small change in the β value for the CTR.

For the case where the potential is cycled directly from $+0.1$ to -0.5 V (*sce*) major changes of the same order of magnitude are observed for the β values obtained from both the SR and CTR. The β value of the SR obtained here is the same within experimental error as that obtained for the $+0.1$ to $+1.3$ to -0.5 V (*sce*). The β value for the CTR is significantly greater than that obtained from the $+0.1$ to 1.3 to -0.5 V (*sce*) cycle. Using the model proposed earlier it is suggested that the new layer of metal formed by the reduction of the oxide protects the (111) plane terminations and that this layer undergoes the primary rearrangement in this potential region. However when the potential is swept directly into the hydrogen region this protective layer is not formed and comparable roughness changes are observed for both the SR and the CTR. To understand the details of the rearrangements on this surface and to verify the presence of the "protective" metal layer and to determine the potential dependence of the disordering it will be necessary to carry out *in situ* experiments.

The full extent of the surface disordering has not yet been determined, however macroscopic observation of the Au(100) face after 5–10 min in the hydrogen region at $+0.5$ V (*sce*) showed severe pitting mixed with surface island growth. Recently, Izumi *et al.*[11] reported on the activation of gold electrodes in hydrochloric acid where X-ray diffraction data supported the growth of (111) facets on the (100) crystal surface. Faceting of this nature would register as an increased roughness on the CTRs as observed in the data presented here. They also observed similar behavior in $HClO_4$ after multiple cycles.

As was shown by Kolb and coworkers[1], it is possible to electrochemically remove the (5×20) reconstructed surface by cycling the potential in the anodic direction within certain limits, $> +0.35$ V (*sce*) for $HClO_4$ and $> +0.55$ V (*sce*) in H_2SO_4. They have also shown that it is possible to regenerate the (5×20) reconstruction surface by cycling the potential to -0.35 V (*sce*) in H_2SO_4. No mention was made of regenerating the reconstruction in $HClO_4$[1]. We have attempted to observe if the (5×20) surface structure could be induced by electrochemical means on the electropolished samples used in this study. The (5×20) reconstructed surface was not observed in any of the experiments described here.

In summary, the Au(100) electrode was observed to grow a Au layer of unknown structure upon reduction from the oxide state. No surface roughening was observed in the oxide region. When the potential is cycled into the hydrogen region, the surface of Au(100) is roughened. It was not possible to electrochemically induce the (5×20) structure on the electropolished Au(100) surface.

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