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LEED/ELECTROCHEMICAL ANALYSIS OF Au SINGLE CRYSTALS: STRUCTURAL EFFECTS OF POTENTIODYNAMIC CYCLING ON UHV PREPARED (111)-($\sqrt{3}$x22) and (100)-(5x20) SURFACES

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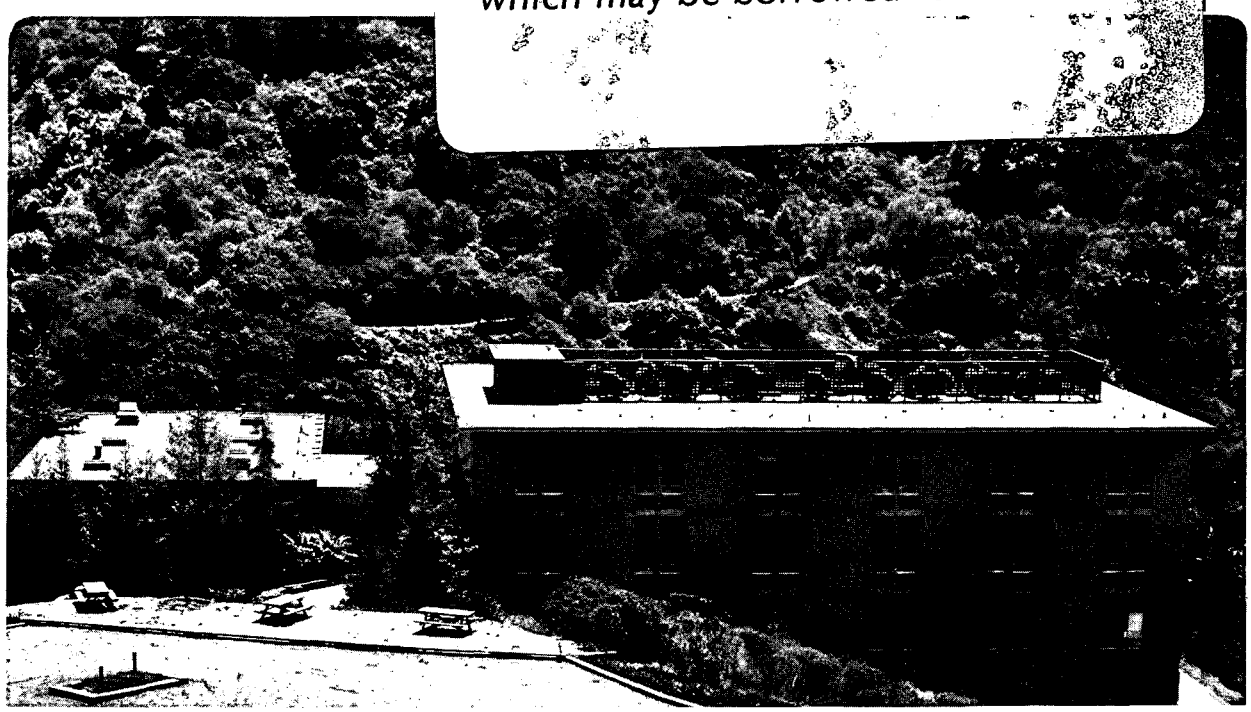

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LEED/ELECTROCHEMICAL ANALYSIS OF Au SINGLE CRYSTALS: STRUCTURAL EFFECTS OF POTENTIODYNAMIC CYCLING ON UHV PREPARED (111)-($\sqrt{3}$x22) AND (100)-(5x20) SURFACES

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ABSTRACT

Ultrahigh vacuum preparation (including Ar^+ sputtering and thermal annealing) of Au (111) and (100) single crystals yielded surfaces possessing incommensurate overlayer structures. The stability of these surfaces with respect to environmental changes and potentiodynamic cycling in aqueous HF electrolyte were studied in a coupled UHV-electrochemical system. The atomic-scale structural changes induced by either method were identified by Low Energy Electron Diffraction The incommensurate (5x20) overlayer structure on the (100) surface did not survive exposure to Ar gas/aqueous HF vapor environment, while the (111)-($\sqrt{3}$x22) overlayer was stable during this exposure. However, the conversion of the (111) surface to a 1x1 structure was achieved upon electrolyte contact. Thus the surfaces with either crystallographic orientation used for subsequent electrochemical analyses were those of a 1x1 nature. The characteristic cyclic voltammograms of both surfaces in 0.3 M HF are characterized by singular anodic film formation waves and sharp symmetric reduction waves. The difference in onset potential for the anodic waves was only 20 mV. Post-electrochemical LEED analyses suggested that profound structural changes were not induced by limited potentiodynamic cycling through oxide formation/reduction, consistent with the stable appearance of the linear sweep cyclic voltammograms. The voltammograms observed for the (111) and (100) surfaces in HF with added $HClO_4$ (up to 0.1 M) and 0.03 M $HClO_4$ were not appreciably different than those in aqueous HF alone. From the similar behavior observed with ion-bombarded (and not-annealed) surfaces, it appears that Au oxide formation/reduction is relatively insensitive to long-range order in these electrolytes.

INTRODUCTION

In studies whose aim is to correlate electrode surface structure with electrochemical phenomena (e.g. oxidation- reduction kinetics, electrocatalysis, metal deposition, etc.) it is necessary to begin experimentation with an electrode surface of known structure. It is natural, therefore, to consider the use of ultra high vacuum (UHV) techniques such as argon ion sputtering/high temperature annealing for surface preparation and Low Energy Electron Diffraction (LEED) for surface characterization. A number of laboratories have now developed UHV systems that facilitate preparation and subsequent electrochemical studies of well-defined single crystal electrodes [1-4].

For definitive studies of single crystal electrodes, it is not possible to use a single crystal electrode that has been cut to expose a particular crystallographic face, and been mechanically polished and/or electropolished and conclude that the electrochemistry observed is representative of the surface having the equilibrium structure for the chosen orientation. It has been shown in prior studies of platinum [4-6] that <u>in situ</u> electrochemical treatment to "clean" the surface such as by anodic cycling alters the surface structure from the one intended for study. In addition to anodic restructuring, there is the additional complication in the case of the electrochemically interesting Group

VIII noble metals (especially Au and Pt) that the equilibrium clean surface structures are not regular terminations of the bulk structure (they are reconstructed) [7-10]. Au is the most extreme example of this, where all the low index surfaces, even the (111) surface, is reconstructed [11,12]

In the case of gold, there are no methods known (with surface structure confirmed by surface diffraction) for producing clean, well-ordered surfaces that are regular terminations of the bulk lattice, i.e. so-called (1x1) structures. The reconstructed surfaces of gold are, therefore, the only known well-ordered structures which can serve as the starting surface for single crystal electrochemical studies. If clean conditions can be maintained during transfer of the crystal to the electrochemical environment from UHV, potentiodynamic cleaning is precluded and uncertainty about structural alteration due to electrochemical "cleaning" is reduced. In this way the potential for preserving the starting surface configuration to the instant of contact with electrolyte will be optimized.

In the case of the Au (111) surface, it has been shown that careful preparation of the surface yields an outermost atomic layer that is not commensurate with the bulk structure [11,12]. The LEED patterns obtained from this surface are characterized by three-fold symmetry and integral-order beams (in the normal (1x1) pattern) surrounded by hexagonal arrays of additional reflections aligned along <110>. The real-space structure that gives rise to this LEED pattern should be regarded as the equilibrium clean Au (111) surface

structure. In a preliminary communication [13] we reported observations of the UHV structure of Au (111) crystals prepared in our laboratory, the characteristic voltammetry for this surface, and the stability of the UHV structure to anodic cycling. We showed that it is very difficult to obtain a well-defined surface structure on Au (111) crystals, and suggested that most reports with Au single-crystals that have appeared in the electrochemical literature cannot be regarded as representative of a single well-defined surface structure. In particular, our voltammetry for Au (111) in dilute HF was very different from that reported previously by Hamelin et al. [14] (in dilute $HClO_4$) who did not use UHV surface preparation or LEED structure characterization. We suggested the difference was due to different surface structures due to the surface preparation methods. Hamelin recently responded [15] with a communication reporting voltammetry with flame annealed Au (111) samples that indicated the difference was not from surface structure but from the difference in electrolyte, i.e. dilute HF versus dilute $HClO_4$. In this paper, we report a further examination of the electrolyte effect on Au (111) voltammetry with UHV prepared surfaces. We find that the voltammetry for Au (111) in HF and $HClO_4$ are nearly identical, and that we could reproduce Hamelin's voltammetry only by the addition of Cl^- to $HClO_4$.

The clean annealed surface of Au (100) exhibits a well-known reconstructed LEED pattern first characterized by Fedak and Gjostein [16,17]. The (100) faces of iridium, platinum and gold all exhibit similar reconstructed LEED patterns which have the nominal

designation "(5x20)". In recent refined analysis by Van Hove et al. [18], there are subtle differences in the diffraction patterns between the metals, and even between the patterns observed with the same metal, e.g. Pt [19]. In the case of Au (100), Van Hove et al. suggest the definitive reconstructed surface is C(26x28) and not (5x20), but the basic real space structures are not very different, i.e. hexagonal overlayer on a square sublattice. Therefore, for our purposes here, and for convenience, we shall use the designation "(5x20)" in referring to the reconstructed surface throughout this paper.

In our previous study of Pt(100) [20], we reported that even exposure to the inert atmosphere in the transfer chamber caused the (5x20)->(1x1) transformation. Kolb et al. [21] used a combined UHV-electrochemical system to study this transformation on Au (100) and found that the (5x20) persisted even with immersion in electrolyte and with limited potential cycling. Kolb and Schneider [22] reported that the (5x20)->(1x1) transformation occurs at ca. 0.6 V (SCE) in 0.01 M $HClO_4$, about 0.5 V above the potential of zero charge (PZC) for the (5x20) surface. In cyclic voltammetry, this transformation was reported to produce a sharp anodic current peak caused by the sudden change in the PZC (the PZC for the (1x1) is reported to be ca. 0.4 V lower). Kolb and co-workers have reasoned that the transformation is caused by "incipient oxidation" of the surface, attributed to OH^- adsorption [23]. In this paper we report our study of the Au (100) surface in our combined UHV-electrochemical system [3] with results that differ

substantially from that of Kolb and co-workers.

EXPERIMENTAL

Single crystal rods were grown at Cornell (B. Addis) by the Czochralski method, and further refined by repeated recrystallization using the floating zone method; some crystals were also grown in-house from graphite crucibles using the Bridgeman technique. The rods were oriented using Laue back reflection, and the single crystals cut, mechanically polished down to 1 μm with diamond paste to within 0.5^{o} of the <111> and <100> planes respectively, and electropolished in cyanide [24a] following detailed instruction from Zehner [24b].

Following electropolishing, the crystals were mounted on Ta heating blocks on the UHV sample probe. The UHV/electrochemistry system has been described in detail previously [4]. The crystals were transferred into the UHV chamber/manipulator, where the surface was subjected to the usual ion bombardment/thermal annealing cycles. Surface cleanliness was monitored by Auger electron spectroscopy and surface structure determined using LEED.

Aqueous 0.3 M HF electrolyte was prepared using hydrofluoric acid (Ultrex, J.T. Baker) and ultrapure water (Harelco) in a Teflon reservoir. The solution was pre-electrolyzed using Au electrodes. Perchlorate anion concentration was adjusted, in certain experiments, by addition of aliquots of aqueous $HClO_4$, (double distilled $HClO_4$, GFS Chemicals). Perchlorate acid solutions were

not pre-electrolyzed in order to avoid Cl^- generation and were made using Ultrex $HClO_4$ (J.T. Baker). An Pd-H disk - Au ring assembly was used as the reference - counter electrode system onto which a 100 µl drop of electrolyte was delivered via PTFE capillary. The reference electrode was charged versus a polycrystalline Au wire which was also used subsequently in voltammetric experiments to aid in determination of electrolyte cleanliness. All potentials will be quoted with respect to the reversible hydrogen electrode (RHE, - 80 mV versus our Pd-H reference). Electrochemical manipulations were performed using the single crystal surfaces in the vacuum ante-chamber after backfill with argon (Matheson Research grade) which is pre-purified by passage through Ti sponge at 900°C (R.D. Mathis Inert Gas Purifier Model 100-P). The contact area of the electrolyte drop in the thin layer cell was approximately 0.3 - 0.4 cm^2 (only the center portion of the crystal is contacted). Standard electrochemical equipment was used to obtain the linear sweep cyclic voltammograms. After an electrochemical experiment was completed the electrolyte was withdrawn from the crystal surface in a controlled manner by overpressurization of the ante-chamber. Emersions were accomplished under potentiostatic control at potentials in the double-layer region (unless specified to the contrary).

RESULTS

Stability of the Reconstructed Surfaces

Both the (111)-($\sqrt{3}$x22) and (100)-(5x20) incommensurate surface structures were prepared in vacuo by argon ion sputtering (0.5 kV, $5x10^{-5}$ torr Ar) followed by annealing to approximately $350^{o}C$ for about 15 minutes. A number of these cycles were required to achieve sharp LEED patterns that matched the patterns reported in the literature for these surfaces [18]. In the case of the (111) surface, the appearance of additional reflections (Fig. 1a & b) about each of the primary beam reflections in indicative of the presence of a compressed hexagonal topmost atomic layer above the normal hexagonal second layer. The patterns obtained from our Varian LEED optics do not show the fine detail as well as do the (111) patterns obtained by Zehner [11] using modified Varian LEED optics. The difference in patterns is apparently both a result of optics and surface domain structure.

The single incommensurate overlayer on the (100) surface is also an hexagonal array, and the complicated LEED patterns observed (Fig. 2a & b) are a result of the superposition of this layer on the square array of atoms below. The multiple-split fifth-order spots observed result from the coincidence of hexagonal and square nets [16,17] and have been denoted as a 5x20 structure.

The first experiments performed on these surfaces involved their exposure to different environments in the vacuum ante-chamber and re-transfer to the UHV chamber for LEED analysis. Details of this type of experiment with Pt crystals were reported previously [3,20]. After transfer under vacuum and upon exposure to ultrapure Ar and aqueous HF (or $HClO_4$) vapor, it was observed (Fig. 2c & d)

that the surface reconstruction on the (100) surface was converted by atomic rearrangement to a 1x1 structure (atoms in a square mesh). This observation matches our previous experience with Pt(100) [20]. The Auger analysis of the surface concommitant with the LEED analysis is shown in Fig. 3a. We note that there is some finite carbon contamination on the surface accompanying the (5x20)->(1x1) transformation, but the level is very low, much less than ca. 10% of a monolayer. We tried dosing a clean (5x20) surface a with number of hydrocarbons (and carbon monoxide) and could not find any that produced either the (5x20)->(1x1) transformation or the observed C KLL Auger signal in Fig. 3a. We have also observed that a Au (100) crystal with a sharp (5x20) pattern can be left in our UHV system literally for days without a change in the LEED pattern.

When the same type of experiment was performed with the (111) crystal, the ($\sqrt{3}$x22) reconstruction was undisturbed in this same environment, even though it acquired the same characteristic amount of C KLL Auger signal as the (100) crystal. However, the ($\sqrt{3}$x22) surface did not survive electrolyte contact, irrespective of the potential of immersion, and rearranged to a <u>sharp</u> (1x1) pattern, as seen in Figs. 1c & d. We believe this is the only sharp (1x1) pattern ever reported for a (nearly) clean Au (111) surface. The surface after emersion does acquire some more carbon contamination than that acquired from just transfer, as seen from Fig. 3b. The contaminant increased the LEED background intensity, indicating it formed as a disordered adlayer. Based on our previous studies of Pt surfaces with our apparatus [3,20,25,26] we have concluded that this

contamination comes from the electrolyte layer left on the surface after emersion (in our system [26]) that is subsequently vacuum evaporated from the surface. Nonvolatile contaminants in the electrolyte become concentrated during evaporation and condense onto the surface, the amount condensing depending on the solution purity and the thickness of the electrolyte layer [26].

Thus, with the experimental apparatus used in this work, LEED analysis suggests that potentiodynamic cycling experiments involving the (111) or (100) surface were begun on surfaces that were not reconstructed, but in both cases were (1x1). The implications of this will be discussed in detail. It was noted that potentiodynamic cycling in the double-layer region in either HF or $HClO_4$ produced LEED patterns not very different than that from transferred surfaces.

Cyclic Voltammetry and LEED of the (111) Surface

With a freshly prepared annealed surface the anodic potential window opening experiment yielded the voltammograms shown in Fig. 4. The time varying positive displacement in the first five sweeps is due to oxidation of dissolved hydrogen in the electrolyte produced during charging of the reference electrode. In the oxide region, a steady state voltammetry was reached after a single cycle through a reversal potential of 1.75 V, e.g. the voltammetry remained stable for many cycles with the scan through the 20th cycle virtually identical to that observed on the first, as shown by comparison with the steady-state curve in Fig. 5. The potentiodynamic curve for (111) in HF is characterized by a single prominent wave in the oxide

region (1.42 V) and a reduction wave (1.08 V) that is sharp (FWHM = 75 mV) and symmetric. The anodic charge passed out to 1.75 V was determined by integration to be on the average about 250 $\mu C/cm^2$, corresponding to formation of about a monolayer of chemisorbed OH^-. If Au were to follow the same oxide formation process as Pt [20,25], oxidation beyond a monolayer OH^- is accompanied by place exchange and atomic-scale roughening of the surface. The development of roughness can be observed using LEED spot-profile analysis [20], by observing the width of LEED beams as a function of incident energy. At beam energies satisfying the Bragg condition for diffraction from planes parallel to the surface, $S_z d = \pi$, the LEED beams are sharp and insensitive to steps (roughness); at the out-of-phase energies, $S_z d$ = odd π, the LEED beams are most sensitive to steps. For Au (111), these beam energies were observed to be 54 eV and 110 eV (in-phase), and 80 and 145 (out-of-phase). As shown by comparison of Figs. 6 (a & c), with (b & d) the LEED beams at the out-of-phase energies of 80 eV and 145 eV did not show any spot broadening as a result of repeated cycling to 1.75 V. We concluded that there were no <u>irreversible</u> roughening processes on Au (111) accompanying oxide formation/reduction cycling (in HF or $HClO_4$) to an anodic limit of 250 $\mu C/cm^2$.

We attempted LEED analysis of surfaces emersed at oxide formation potentials, e.g. 1.2 - 1.7 V, in order to determine whether there were <u>reversible</u> roughening processes, i.e. disordered oxide formation with "annealing" oxide reduction. However, as we observed with Pt, all of the "oxide" formed on Au surfaces at a

charge < 300 $\mu C/cm^2$ is apparently discharged during emersion, since no oxygen signal was ever observed by Auger electron spectroscopy from an emersed Au crystal. The LEED patterns from Au (111) emersed at 1.2 - 1.72 V were sharp (1x1) patterns for all beam energies, but since there was no oxygen on these surfaces this observation cannot be related directly to the structure of the oxide.

Effect of Anion on Au (111) Voltammetry

Initially the effect of ClO_4 anion on the Au (111) voltammetry was observed by the addition of 0.1 M ClO_4^- to 0.3 M HF to a level of 1 - 10 mM $HClO_4$. There was only a slight effect observable at this level as a broadening of the anodic oxide formation peak. Subsequently, experiments were performed in 0.03 M $HClO_4$, with the resulting steady-state voltammetry shown in Fig. 7. In $HClO_4$, some features in the double-layer potential region of 0 - 0.6 V are more resolved than in HF, and the oxide formation peak is noticeably broadened and shifted anodically. There was, however, no evidence of the multiple peak structure reported by Hamelin [14] for Au (111) in $HClO_4$. We found, by trial and error, that we could only produce multiple anodic and cathodic peaks in the oxide potential region by the addition of Cl^- to either HF or $HClO_4$, as shown by the voltammetry in Fig. 8.

Cyclic Voltammetry and LEED of the (100) Surfaces

A series of experiments similar to those performed with the (111) surface were made with the (100) crystal. An unexpected striking similarity between the cyclic voltammograms of the (100) and (111) surfaces was observed in HF. The second, and also the

steady-state, cycle following anodic window opening to 1.7 V after immersion at 0.6 V is shown in Fig. 9. The potential of the anodic wave is only slightly (ca. 20 mV) cathodic to that for (111), with a sharper (FWHM = 35 mV) anodic peak and as sharp (FWHM = 75 mV) cathodic reduction feature. There are some additional subtle features following the principal anodic and cathodic peaks not seen on the (111) surface. The anodic charge passed to 1.7 V was 260 $\mu C/cm^2$, about 20% higher than the charge passed on the (111) surface to the same anodic potential.

The LEED analysis of the (100) following contact with electrolyte indicated the surface transformed from (5x20)->(1x1) regardless of the potential maintained during/after contact. The contacted, but not potentiodynamically cycled surface, exhibited LEED spot profile variations, i.e. alternate spot broadening [20], with beam energy which are indicative of stepped surfaces, e.g. as shown by Fig. 10 at 53 eV the (10) spots were sharp and the (11) diffuse, the reverse was true at 93 eV. The broadened spots exhibited featureless spot profiles, in contrast to the highly structured spot profiles we had observed with Pt (100) [20]. Uniformly broadened spots indicate a randomly stepped surface, and the width of spots at out-of-phase beam energies indicates a mean terrace width of about 10 atoms for the <u>uncycled</u> (1x1) surface. We attribute this roughness in the (1x1) surface to the difference in atomic density between a perfect (5x20) and a perfect (1x1) surface, ca. 20% [17,18]. Since the (5x20)->(1x1) occurs at room temperature, it is unlikely that the extra atoms from the hexagonal

overlayer can diffuse into the bulk, so that they lift on the (1x1) surface as adatoms, probably randomly nucleated into islands.

Potentiodynamic cycling through oxide formation to an anodic limit of 1.6 V did not appear to cause any further roughening of the surface, as shown by the identical sharpness of LEED spots in Fig. 11 for the cycled versus uncycled surface. However, at an anodic limit of 1.725 V, after 20 cycles the alternate spot broadening became more pronounced, as is clear in the LEED patterns in Fig. 11. The critical charge to cause the onset of roughening due to oxide formation/reduction processes appeared to be ca. 300 $\mu C/cm^2$, corresponding to the completion of a monolayer of OH^- and the formation of a significant fraction of a (+II) oxide layer (a complete +II oxide on a Au(100)-1x1 surface corresponds to 380 $\mu C/cm^2$). Interestingly, we comment that the LEED observable roughening of the (100) surface due to 20 cycles 0.2 - 1.725 V (in either HF or $HClO_4$) did not change the voltammetry.

Effect of Anion on (100) Voltammetry

A thermally annealed (100) crystal, prepared in UHV as indicated, and exhibiting the (5x20) reconstructed pattern, was transferred directly to the electrochemical cell and contacted with 0.03 M $HClO_4$ while potentiostatted at 0 V. The anodic window opening cycles are shown in Fig. 12. This experiment should be comparable to that reported recently by Kolb and Schneider [22], the only difference being the apparatus. The result, however, is quite different. The striking sharp feature at about 0.8 V (versus our reference electrode) reported by Kolb and Schneider was not observed

here, nor did we observe either irreversible changes in the fine structure at 0.2 - 0.4 V (near the PZC) when the anodic potential exceeded 0.8 V or an "incipient oxidation" current at 0.8 - 1.0 V. Kolb and Schneider attributed the anodic spike and the irreversible changes in voltammetry to the irreversible phase transition (5x20)->(1x1) caused by "incipient oxidation" at 0.8 - 1.0 V (versus our reference). In our experiments, we observed this transition to occur at contact with electrolyte (or even before contact), and we did not observe any oxidation process to occur at 0.8 - 1.0 V. The steady-state votammetry of (100) in 0.03 M $HClO_4$ was virtually identical to that in 0.3 M HF, and, as with the Au (111) surface, the voltammetry shows none of the multiple features in the oxide region reported by Hamelin and co-workers [14].

Effect of Disorder on Voltammetry

Since transfer of the reconstructed surface from UHV to contact with electrolyte may have produced a (1x1) surface structure, attempts were made to produce a well-ordered (1x1) surface in UHV prior to transfer. Exposure of the reconstructed surface to oxygen in the UHV chamber (50 L) produced a 5x1 pattern, instead of the (5x20) pattern, but there was no difference in voltammetry. Additional treatment of this surface using low energy (< 1 keV) argon ion sputtering yielded a surface that exhibited LEED patterns with an increase (factor of two) in spot widths at all energies. This surface was then subjected to potentiodynamic cycling in $HClO_4$ electrolyte. The voltametric trace shown in Fig. 13 is similar to the response of the annealed (100) surface, but the anodic wave is

considerably sharper (FWHM = 35 mV) than either of those for the (111) or (100) annealed surfaces. Extensive high energy (> 2 keV) argon ion bombardment that resulted in near-obliteration of the LEED pattern produced voltammetry like that observed from a polycrystalline surface, shown in Fig. 14.

DISCUSSION

The electrochemical structure- property relations found in this work differ significantly from all previously published work with gold single crystals. The reasons for these differences are explicable in one case and inexplicable in another. The voltammetry we found for both Au (111) and Au (100) in perchloric acid were completely different from those reported by Hamelin and co-workers [14], and we could find no evidence for the dramatic difference in the voltammetry of Au (111) in HF versus $HClO_4$ electrolytes Hamelin reported recently [15]. We did, however, find a dramatic effect of Cl^- anion on Au (111) voltammetry including the appearance of multiple peaks in the oxide formation potential region as reported by Hamelin for $HClO_4$. We conclude that the difference in results may be due in part to the presence of adventitious Cl^- anion in the $HClO_4$ solutions used in the latter's work.

The differences in results with Au (100) between our work and that of Kolb and co-workers [21,22] is not as readily explained. The stability of the (5x20) surface with respect to contact with electrolyte appears to be the central issue. They reported that the

(5x20) surface was preserved when contacted with electrolyte under potential control such that the potential never exceeded ca. 0.8 V (RHE). They observed a sharp anodic spike on the first anodic sweep of the voltammetry which they attributed to capacitive discharge due to the transition from (5x20) to (1x1) caused by "incipient oxidation" (at potentials well below the formal oxide formation potential region). We could not find any positive evidence confirming the stability of the (5x20) surface to contact with either HF or $HClO_4$ electrolyte at any potential. However, we were also unable to find definitive evidence that would preclude the possibility that the (5x20) is stable at some potential, since we analyzed the surface structure (by LEED) only after removal of the electrolyte, and we cannot eliminate the possibility that the transformation took place during the evacuation step. In fact, the indication of some carbon contamination of the surface by Auger analysis after emersion and evacuation of the crystal would support the possibility of impurity induced transformation during emersion. If that were the case, it is still unclear why we did not see the same voltammetry, since both experiments would have been initiated with the same (5x20) surface structure.

There are fundamental reasons to question the report of stability of the (5x20) reconstructed surface to contact with an aqueous ionic phase. The real-space structure of the reconstructed surface is an hexagonal overlayer on a square sublattice having atoms in positions that are not fcc lattice positions (incommensurate with the bulk). As might be expected for an

incommensurate structure, the energy difference between it and the bulk termination structure is not very large. The driving force for reconstruction from the lowering of surface tension due to close packing is counterbalanced by an energy increase due to large lattice misregistry. In their recent theoretical paper, Tomanek and Bennemann [27] concluded that in the fcc metals Ir, Pt and Au, the balance is such that the surface tension forces are stronger, and close packing of the top layer is favored, but by very small amounts of energy, e.g. the difference between the (100)-(5X20) and (1x1) is 0.06 - 0.09 eV depending on details in the overlayer structure. Tomanek and Bennemann also show how the bond energy from an adsorbate provides the energy to drive a transition to a (1x1) structure. In the case of Au (100), the required bond energy is extremely small, on the order of 0.1 to 0.5 eV, in the range of physisorption bonding. One would expect, therefore, that even contact adsorption with an aqueous ionic media would suppress reconstruction and drive the transformation from (5x20) to (1x1).

Why did Kolb and co-workers observe the reconstructed surface after contact with electrolyte? We can only conjecture at this stage until the experiments are repeated by others and a consensus emerges. We suggest that the crystal used by Kolb et al. may have contained silica and alkali metals from the polishing step. These metals are known to stabilize the reconstructed surface of the 3d transition metals [28] even at very low levels of surface concentration. In their previous work with their RHEED system, Kolb and co-workers rarely mention analysis of the surface by Auger

electron spectroscopy, and none of their publications actually shows Auger spectra. If Auger spectra are obtained, they appear to use the LEED optics, which have poor resolution for Si KLL features [29] and much lower sensitivity than CMA electron optics (which we used here). It is possible that the singular anodic features observed in Au (100) voltammetry by Kolb and Schneider correspond to oxidative dissolution of Si or Ca in the surface.

The voltammetric features for Au oxide formation and reduction were surprisingly insensitive to surface structure. There were very small differences between the curves for (100) and (111) surfaces, and sputtered but not-annealed surfaces produced nearly identical voltammetry to annealed surfaces. LEED spot profile analysis of low index Pt and Au surfaces indicates that low energy (< 1 keV) ion sputtering produces a randomly stepped structure that nonetheless has a high degree of short-range order, e.g. ordered domains of 3-5 atomic diameters. One would expect that surface processes that are sensitive only to local order would not display significant sensitivity to annealing. We did find that the Au oxide formation and reduction processes are relatively insensitive to surface annealing, and appear to be dependent only on local order. Local order is clearly very important to oxide formation/reduction kinetics as the voltammetric peak shapes for even sputtered surfaces were dramatically narrower than those for polycrystalline surfaces. The very narrow (FWHM = 75 mV) symmetric lineshape for the reduction wave suggests comparison with the autocatalytic thermal decomposition of anodically formed oxide on Pt(100) [24]. A model

for the electrochemical reduction of Au oxide employing features of our autocatalytic model for thermal decomposition of Pt oxide is currently in progress.

Potentiodynamic cycling through the oxide formation potential region forming approximately 250 $\mu C/cm^2$ of oxide per sweep did not appear to cause any roughening of either the Au (111) or Au (100) surface. This result is similar to our previous observations on Pt single crystals [20], where LEED observable roughening began when the anodic charge exceeded about 220 $\mu C/cm^2$ per sweep, i.e. a complete monolayer of chemisorbed OH^- had formed. In these metals, place-exchange appears to be the mechanism by which the transition from chemisorption of OH^- to a formal oxidation state of (+II) is accomplished. Thus, the surface structure of both metals appears to be stable to potentiodynamic sweeping to an anodic limit for chemisorption of a monolayer of OH^-.

Finally, we want to reemphasize a point made earlier in the presentation that the absence of LEED observable roughening of the surface after potentiodynamic cycling cannot be taken as evidence that the anodic layer formed at 200 - 250 $\mu C/cm^2$ is ordered. These anodic layers do not survive the process of emersion, evacuation and transfer to UHV, and we have not been able to make any direct observation of the structure of the layer. There is left open the possibility that the anodic layer is poorly ordered, and that place-exchange occurs even with chemisorption of OH^- since reduction might restore any displaced metal atoms to their original positions.

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FIGURE CAPTIONS

1. LEED patterns from Au (111) single crystal. Clean annealed reconstructed ($\sqrt{3}$x22) surface prepared in UHV: Beam energy of a) 54 eV and b) 145 eV. Emersed (1x1) surface obtained after 20 cycles to 1.7 V_{RHE} in 0.3 M HF: c) 54 eV and d) 145 eV.
2. LEED patterns from Au (100) single crystal. Clean annealed reconstructed (5x20) surface prepared in UHV: a) 53 eV and b) 133 eV.
   Surface obtained after transfer to ante-chamber and exposure to Ar gas/aqueous HF vapor environment: (1x1) structure at c) 53 eV and d) 133 eV.
   Emersed (1x1) surface obtained after 20 cycles to 1.6 V_{RHE} in 0.3 M HF: e) 53 eV and f) 133 eV.
3. Typical Auger spectra recorded from gold single crystal electrode surfaces: a) after transfer to ante-chamber and exposure to Ar gas/aqueous HF vapor and b) after oxidation/reduction cycling in HF electrolyte and emersion in the double-layer potential region.
4. Anodic potential window opening voltammetry for Au (111) in 0.3 M HF showing the first sweeps. The anodic displacement is a result of hydrogen oxidation. Steady-state voltammetry was achieved

after the first cycle through a reversal potential of 1.75 V_{RHE}. Sweep rate is 50 mV/s.

5. Complete cyclic voltammetry for UHV prepared Au (111) single crystal surface in 0.3 M HF showing the double-layer potential region. Sweep rate is 50 mV/s.

6. LEED patterns of potentiodynamically cycled Au (111) surface: Emersion at 0.6 V_{RHE} after cycling 20 times to 1.7 V in 0.3 M HF. (1x1) structure at energies of a) 54 eV, b) 80 eV, c) 110 eV, and d) 145 eV.

7. Cyclic voltammograms of the Au (111) single crystal surface in a) 0.3 M HF in the double-layer region, b) same surface after electrolyte change to 0.03 M $HClO_4$, c) complete voltammetry in $HClO_4$. Sweep rate 50 mV/s.

8. Addition of 1 mM NaCl to the electrolyte produced the voltammogram shown for the Au (111) single crystal surface. See text. Sweep rate is 50 mV/s.

9. Voltammetric curve for the UHV prepared Au (100) surface in 0.3 M HF electrolyte. Sweep rate is 50 mV/s.

10. LEED patterns of potentiodynamically cycled Au (100) surface: Emersion at 0.5 V_{RHE} after cycling 20 times to 1.6 V in 0.3 M HF: (1x1) structure at a) 53 eV, b) 78 eV, c) 93 eV and d) 133 eV.

11. LEED patterns of the Au (100) surface.

    Emersed at 1.6 V_{RHE}: a) 53 eV and b) 133 eV.

    Emersed after 20 cycles to 1.6 V in 0.3 M HF:

    c) 53 eV and d) 133 eV.

    Emersed after 20 cycles to 1.725 V in 0.3 M HF:

    e) 53 eV and f) 133 eV.

12. Cyclic voltammograms of the UHV prepared Au (100) surfaces in 0.03 M $HClO_4$: a) first sweeps in the double-layer potential region, and b) complete voltammogram. Sweep rate is 50 mV/s.

13. Ar^+ sputtering of the Au (100) single crystal surface produced the voltammetric curve shown. Sweep rate in the mixed electrolyte is 50 mV/s.

14. Cyclic voltammogram of polycrystalline Au in 0.3 M HF at 100 mV/s sweep rate.

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