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LEED/ELECTROCHEMICAL ANALYSIS OF Au SINGLE CRYSTALS: STABILITY OF THE UHV PREPARED SURFACES OF Au(111) AND (100) IN AQUEOUS ELECTROLYTE

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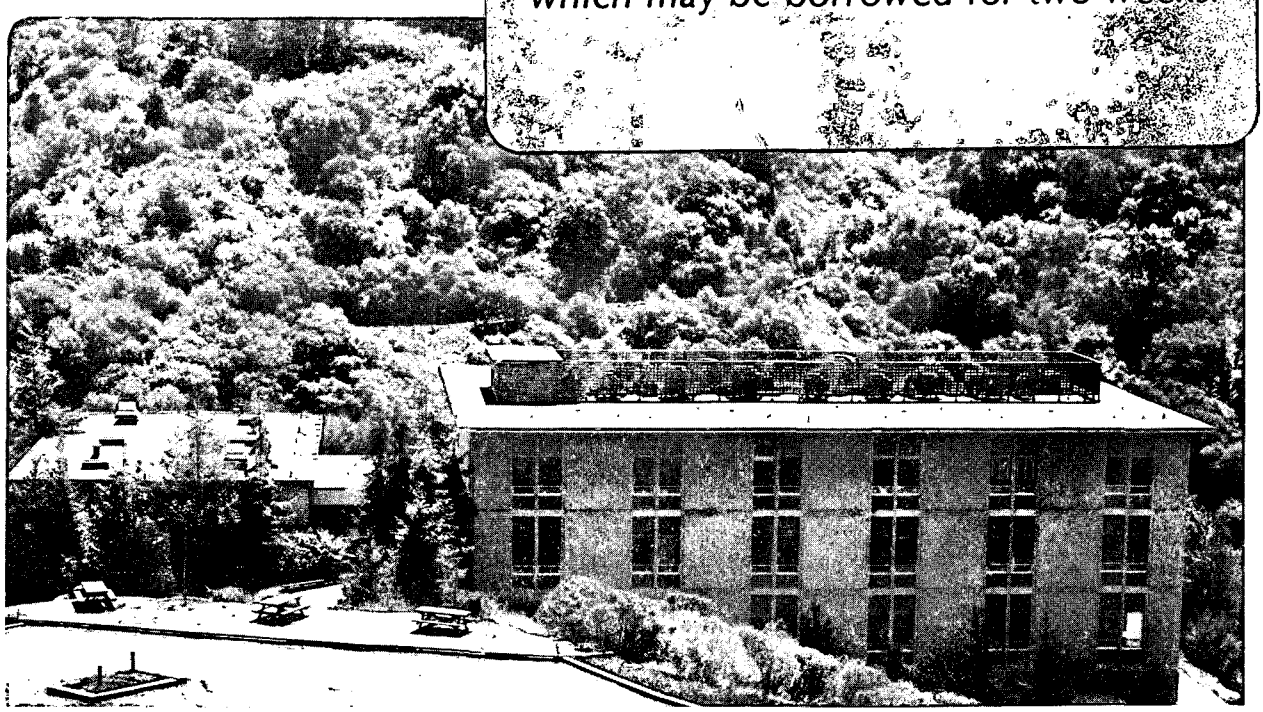

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LEED/ELECTROCHEMICAL ANALYSIS OF Au SINGLE CRYSTALS: STABILITY OF THE UHV PREPARED SURFACES OF Au(111) AND (100) IN AQUEOUS ELECTROLYTE

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ABSTRACT

Ultrahigh vacuum preparation (including Ar^+ sputtering and thermal annealing) of Au (111) and (100) single crystals produced reconstructed surfaces identified as (111)-(3x22) and (100)-(5x20) by previous workers. The stability of these reconstructed 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 (LEED). The (5x20) reconstruction on the (100) surface did not survive exposure to Ar gas/aqueous HF vapor environment, and transformed to the bulk termination (1x1) structure. The (111)-($\sqrt{3}$x22) overlayer was stable in the same environment, but transformation of the (3x22) structure to a (1x1) structure occurred upon electrolyte contact. Thus, the UHV reconstructed surfaces of either the (111) or (100) crystal were found to be unstable with respect to contact with aqueous electrolyte in our apparatus. The effect of adventitious impurities in the electrolyte on the stability could not, however, be precluded. LEED spot profile analysis indicated the (100)-(1x1) surface in contact with electrolyte initially has a nominally flat surface decorated with uniformly sized islands ca. 30 Å in diameter. Anodic oxidation of either the (100)-(1x1) or the (111)-(1x1) surface to a charge of ca. 250 $\mu C/cm^2$ (equivalent to a monolayer of OH^-) did not produce a change in structure observable by LEED. The critical amount of anodic charge to cause the onset of roughening observable by LEED was 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. Place-exchange appears to be the mechanism by which the transition from chemisorption of OH^- to formation of (+II) "oxide" is accomplished.

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 [3-6] 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 noble

metals (especially Au and Pt) that the equilibrium clean surface structures are not necessarily 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 are reconstructed [11,12], i.e. 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, need for 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. The stability of this reconstructed surface upon

exposure to different chemical environments has not been well studied. In particular, the stability to contact with electrolyte and the effect of applied potential is of interest to electrochemists. We report here a LEED study of the stability of the UHV-prepared Au(111) reconstructed surface in an electrochemical environment analogous to our previous study of the stability of Pt(111) [13].

The clean annealed surface of Au (100) exhibits a well-known reconstructed LEED pattern first characterized by Fedak and Gjostein [14,15]. 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. [16], there are subtle differences in the diffraction patterns between the metals, and even between the patterns observed with the same metal, e.g. Pt [17]. 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) [13], we reported that even exposure to the inert atmosphere in the transfer chamber caused the (5x20)->(1x1) transformation. Kolb et al. [18] 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 [19] 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 [20]. 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 with respect to both the voltammetry and the stability of the (5x20) structure.

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 m with diamond paste to within 0.5^o of the <111> and <100> planes respectively, and electropolished in cyanide [21a] following detailed instruction from Zehner [21b].

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 Grade, J.T. Baker) and a commercial ultrapure water (Harelco Chemicals) in a Teflon reservoir. The HF solution was pre-electrolyzed using Au electrodes. Perchloric acid solutions were not pre-electrolyzed in order to avoid Cl^- generation and were also made using Ultrex Grade acid. An Pd-H disk - Au ring assembly was used as the reference - counter electrode system onto which a 100 l 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 with ultra-pure argon [4]. 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, 5×10^{-5} torr Ar) followed by annealing to approximately 350°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 [11]. 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

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 sharp (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 [3,13,22,23] we have concluded that this contamination comes from the electrolyte layer left on the surface after emersion (in our system [23]) 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 [23].

Thus, with the experimental apparatus used in this work, LEED analysis suggests that neither the (111)-($\sqrt{3}$x22) nor the (100)-(5x20) surfaces are stable to contact with dilute HF or $HClO_4$ electrolyte regardless of the potential applied to the crystal during contact. This observation was not conclusive as the effect of impurities on the surface transformation could not be ruled out. Also, it is not possible, even in principle, to determine by LEED analysis when the transformation occurred, i.e. before contact with electrolyte or during removal, since one observes the structure only after the complete ("round-trip") sequence of events has occurred.

(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 [14,15] 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 [3,13]. 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) [3]. 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

Electrochemical Stability of the (111)-(1x1) Surface

The (111) crystal was subjected to repeated, e.g. ten cycles, potentiodynamic cycling in the potential region of 0.2-1.75V at a sweep rate of 50 mVs. After cycling, the potential was arrested at 0.6V, and the electrolyte was removed from the surface while potentiostated at 0.6V. The anodic charge passed out to 1.75V was determined by coulometry to be approximately 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 [13,22], 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 [13] 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. 4 (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 $\mu C/cm^2$.

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* ± 25 $\mu C/cm^2$ due to uncertainty in the area of the crystal contacted by electrolyte.

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 reversible 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.

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. 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. Emersion of the (100) crystal was also done at 0.6V. 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. Unlike the (111) surface, however, even the contacted, but not potentiodynamically cycled surface, exhibited LEED spot profile variations, i.e. alternate spot broadening [13] with beam energy which are indicative of stepped surfaces, e.g. as shown by Fig. 5 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) [13]. 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 uncycled (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% [15,16]. 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 are left on the (1x1) surface as adatoms, probably 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. 6 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. 6. 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 $\mu C/cm^2$).

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. 7. 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 electrode). 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.

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, i.e. a randomly stepped (100)-(1x1) surface. This surface was then

subjected to potentiodynamic cycling in $HClO_4$ electrolyte. The voltametric trace shown was essentially identical to the response of the annealed (100) surface. These experiments indicated to us that in our experiments the (5x20)->(1x1) transformation occurred at/or before the contact of the surface with electrolyte, and that the voltammetric curve shown in Fig. 7 is characteristic of the Au(100)-(1x1) surface.

DISCUSSION

The Au(111) surface has not been the subject of very many studies with modern LEED instruments, and we know of only one previous study of the ($\sqrt{3}$x22)->(1x1) transformation, that by Zehner and Wendelken [11]. They reported transformations of both the (100) - (5x20) and (110) - (2x1) reconstructed surfaces to the normal (1x1) structure upon dosing either with pre-dissociated oxygen, but similar treatment of the Au(111) produced no change in the LEED pattern. To our knowledge, the patterns in Fig. 4 are the first sharp (1x1) patterns ever reported for a Au(111) surface.

As we found in our previous study of Pt(100) [13], the reconstructed surface transforms to the normal (1x1) structure upon contact (or even upon exposure to the electrolyte vapor) with electrolyte. LEED spot profile analysis indicated that this Pt(100)-(1x1) surface is not a perfect surface, but rather is a nominally flat surface decorated with uniformly sized islands approximately 10 atoms in diameter (ca. 30 Å). A similar result was

obtained from the Au(100)-(5x20) surface. It seems likely that these islands form during the transformation due to the difference in atomic density between the (5x20) and (1x1) structures (the former being ca. 20% higher), with the "extra" atoms from the (5x20) structure nucleating on the surface to form islands. Recently, Behm reported [27] the direct observation by scanning tunneling microscopy (STM) of islands forming on the Pt(100) surface upon dosing the (5x20) surface with CO. The island size was typically 50 Å, in reasonable agreement with our estimate from LEED spot profile analysis.

The differences in results with Au (100) between our work and that of Kolb and co-workers [21,22] are not easily 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 <u>positive</u> 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 [24] 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 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 [25] 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 were obtained, they were apparently obtained using the LEED optics, which have poor resolution for Si KLL features [26] 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.

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 [13], 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. 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.

5. 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.

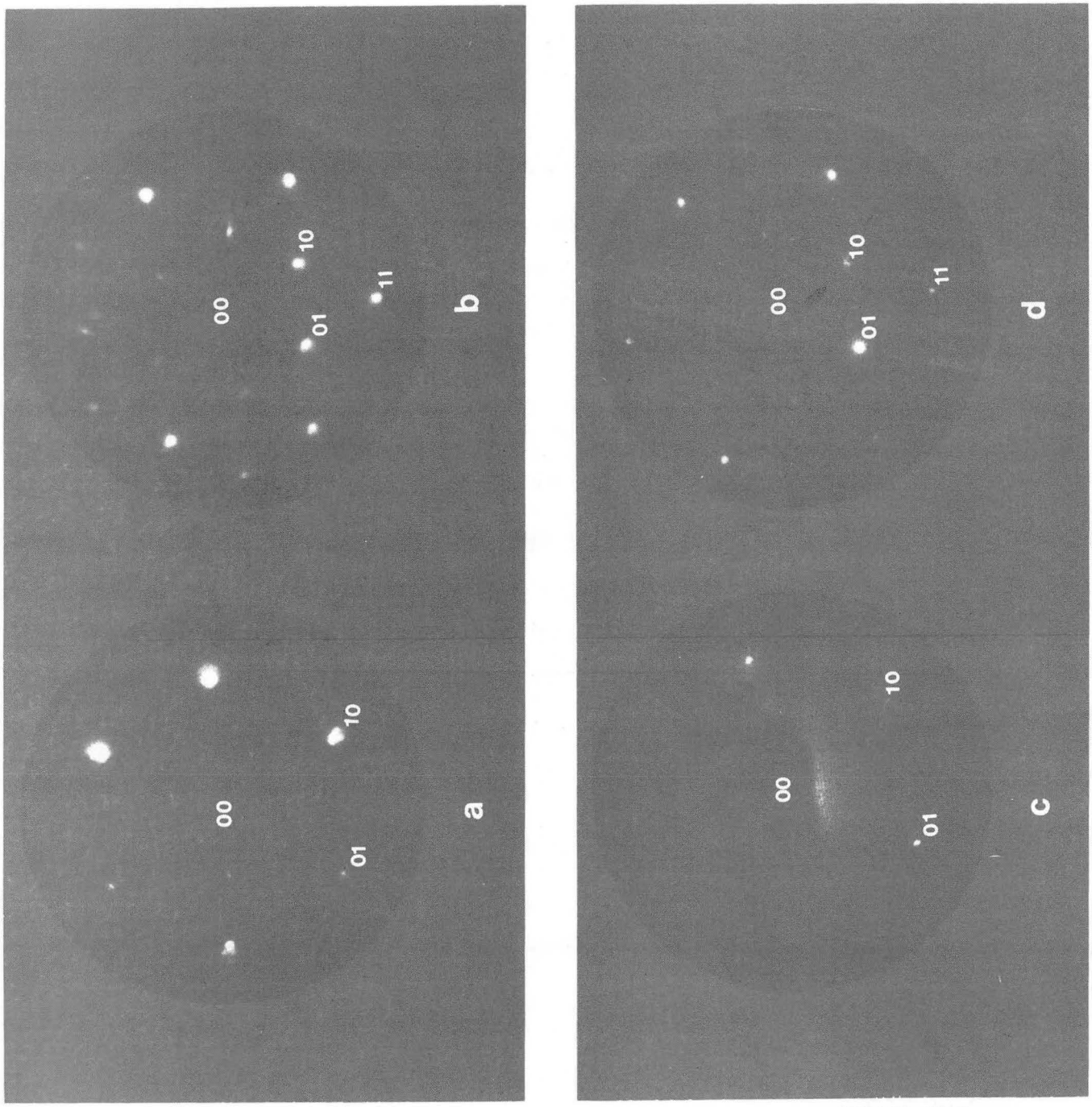
6. LEED patterns of the Au (100) surface.

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

   Emersed at 0.6 V_{RHE} after 20 cycles to 1.6 V in 0.3 M HF: c) 53 eV and d) 133 eV.

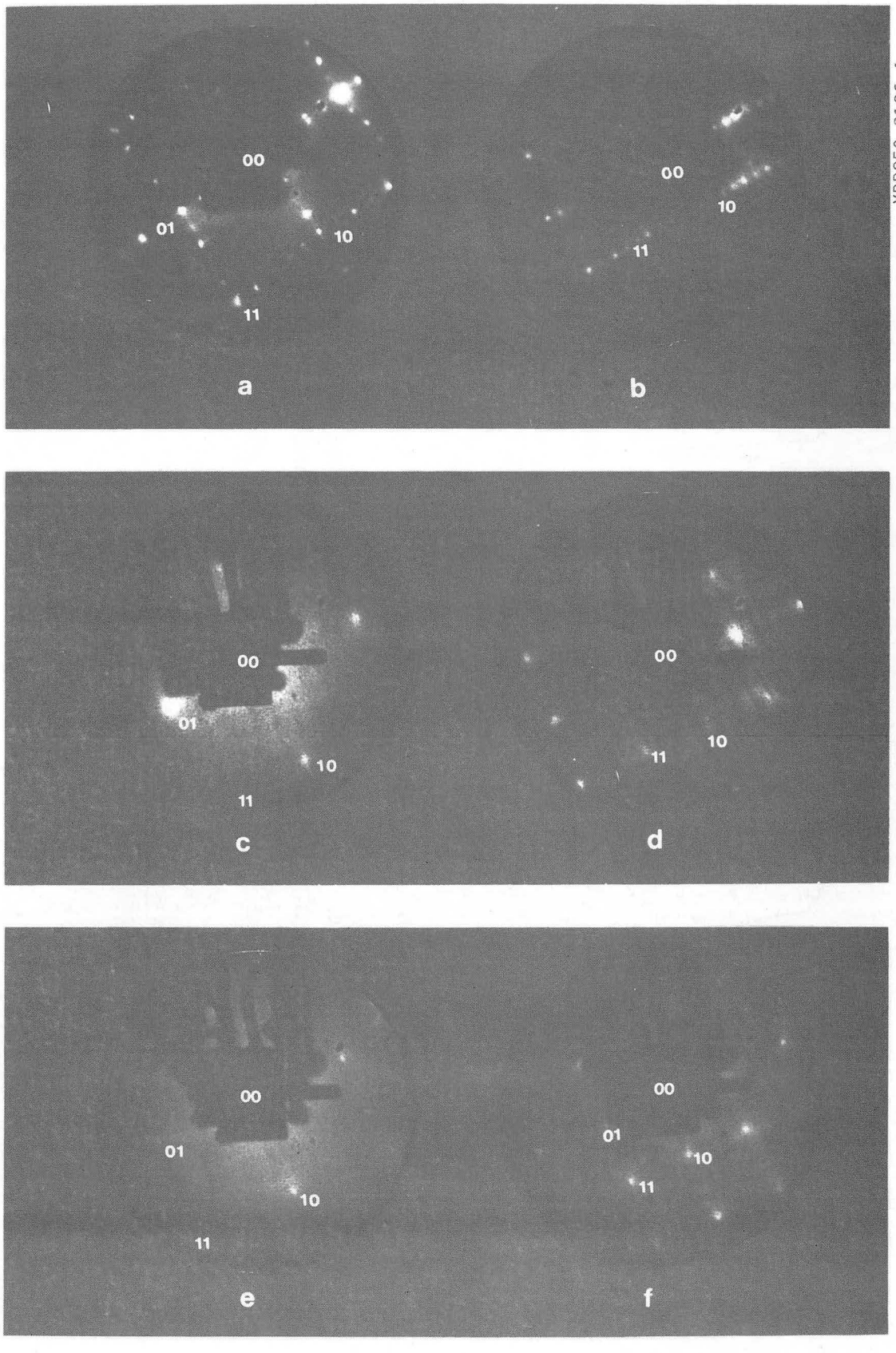
   Emersed at 0.6 V_{RHE} after 20 cycles to 1.725 V in 0.3 M HF: e) 53 eV and f) 133 eV.

7. 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.



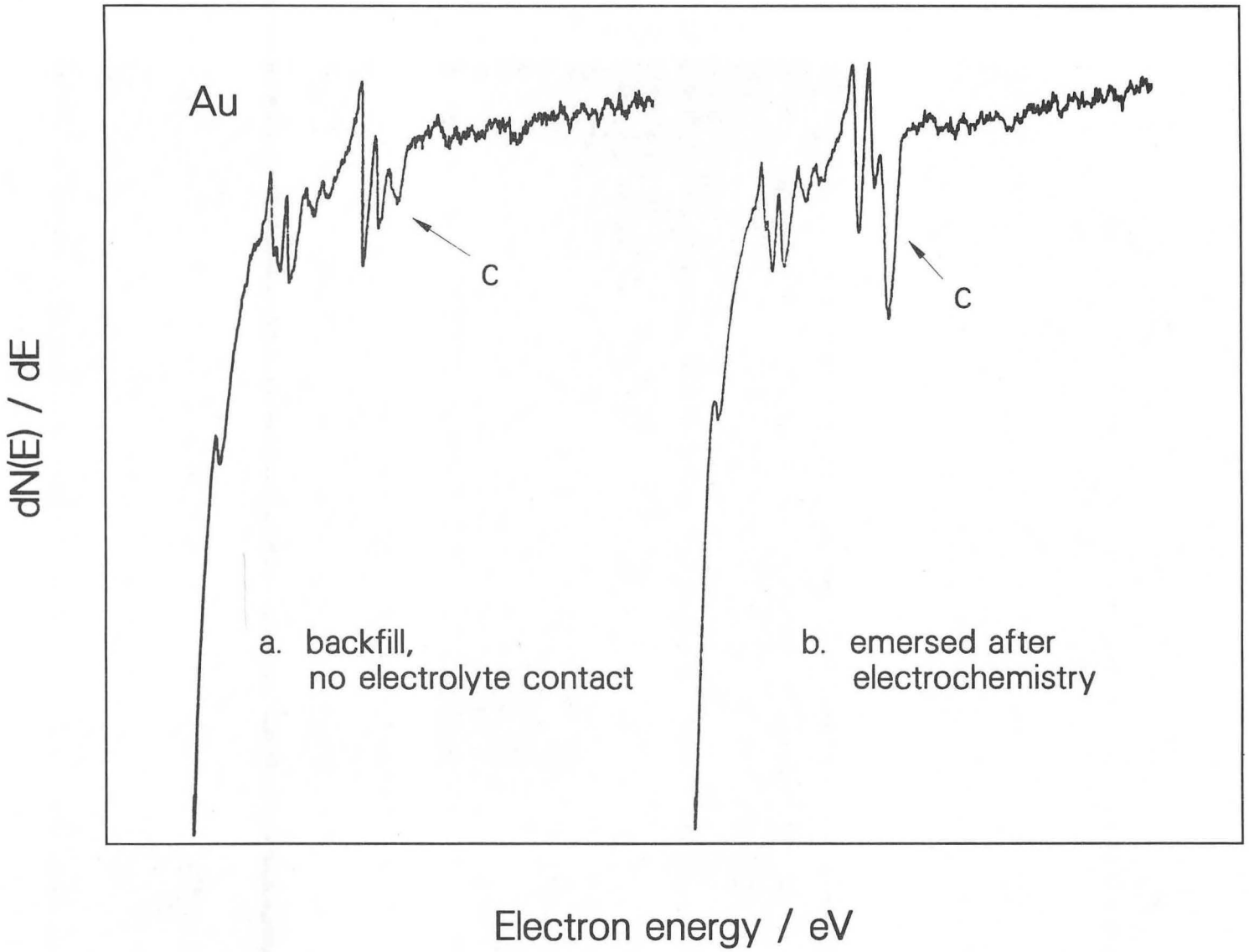
XBB851-280B

Fig. 1



XBB850-8186-A

Fig. 2



XBL 866-2255

Fig. 3

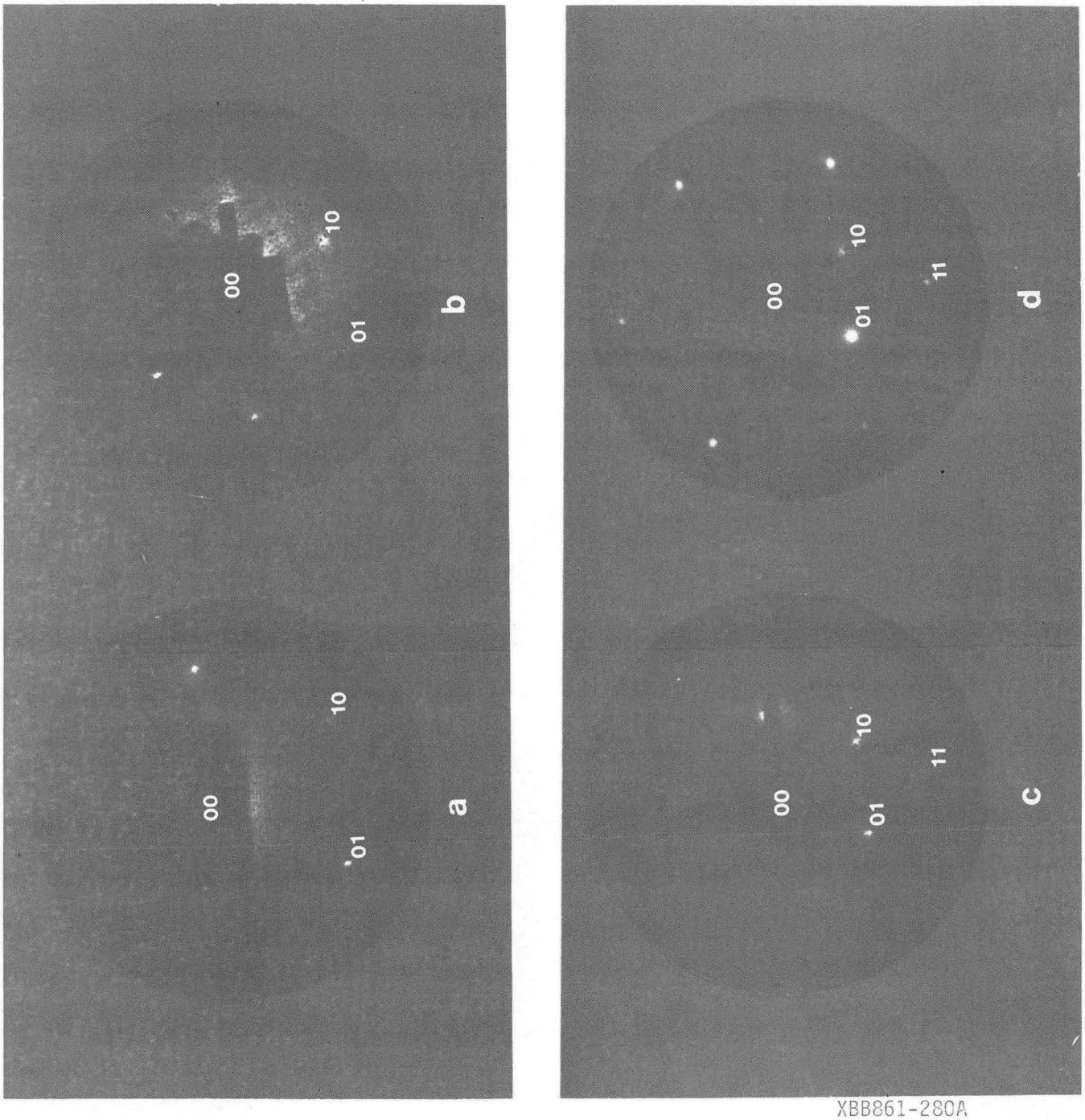


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Fig. 4

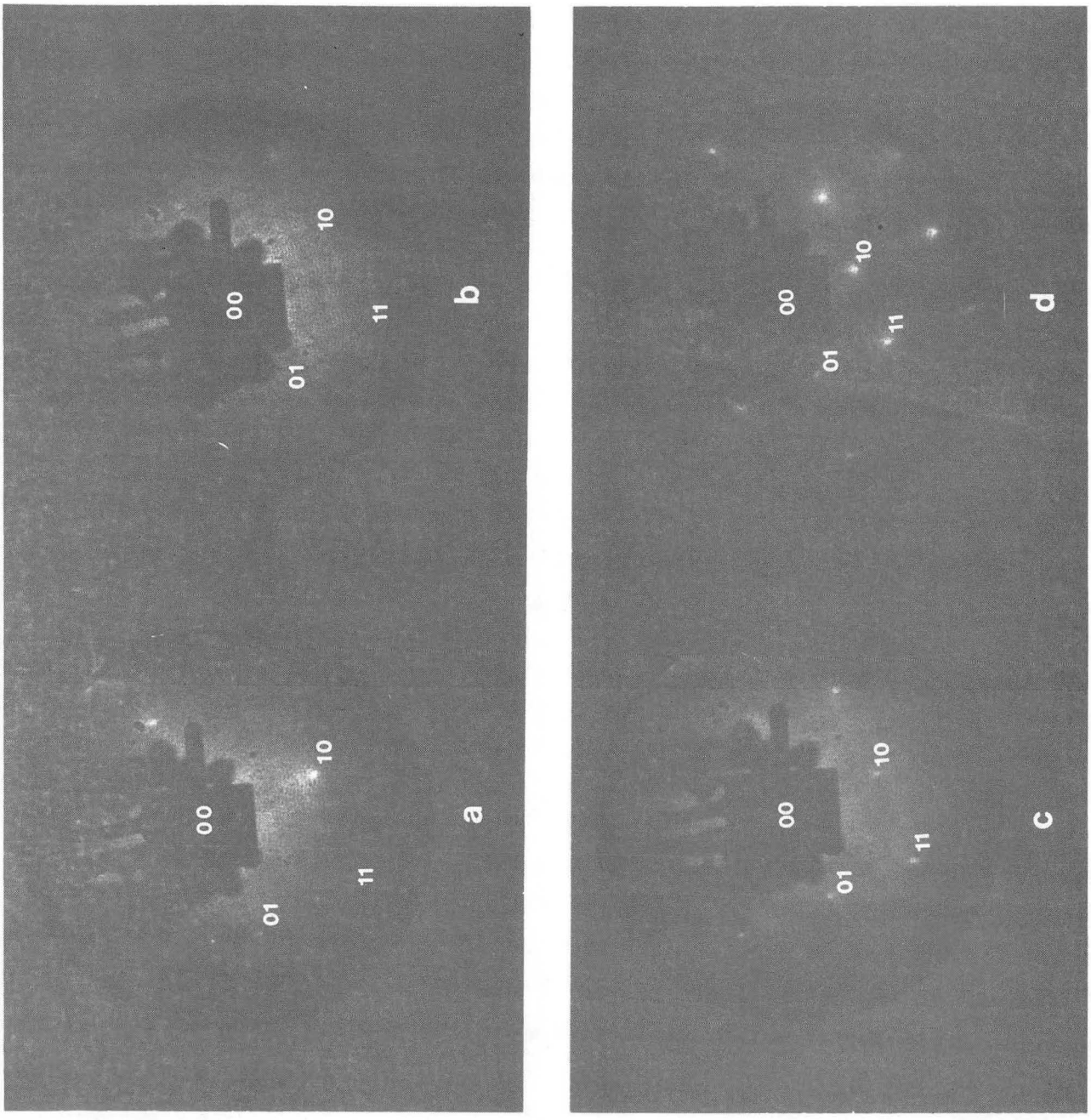

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Fig. 5

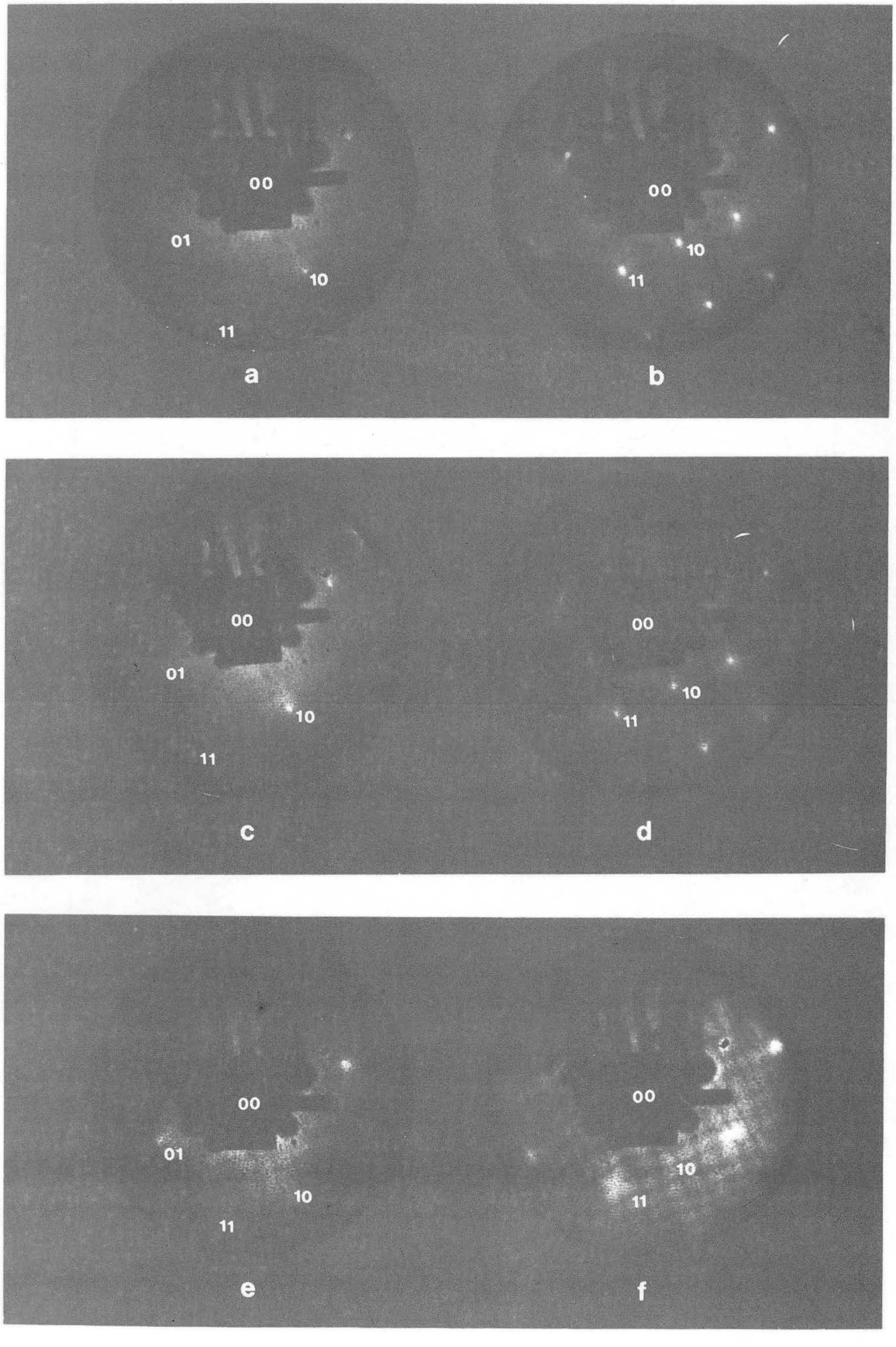

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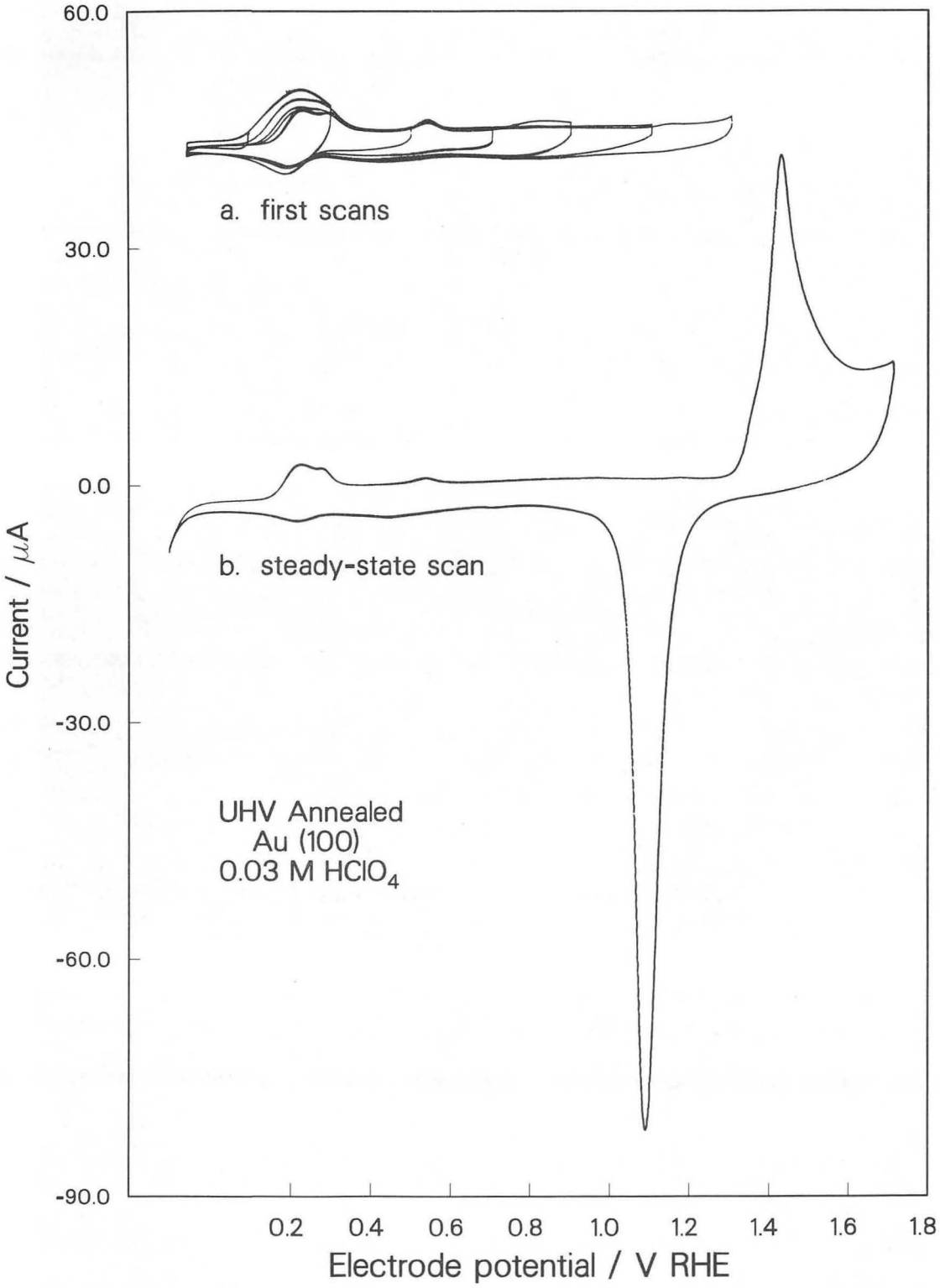
Fig. 6



XBL 866-2257

Fig. 7

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