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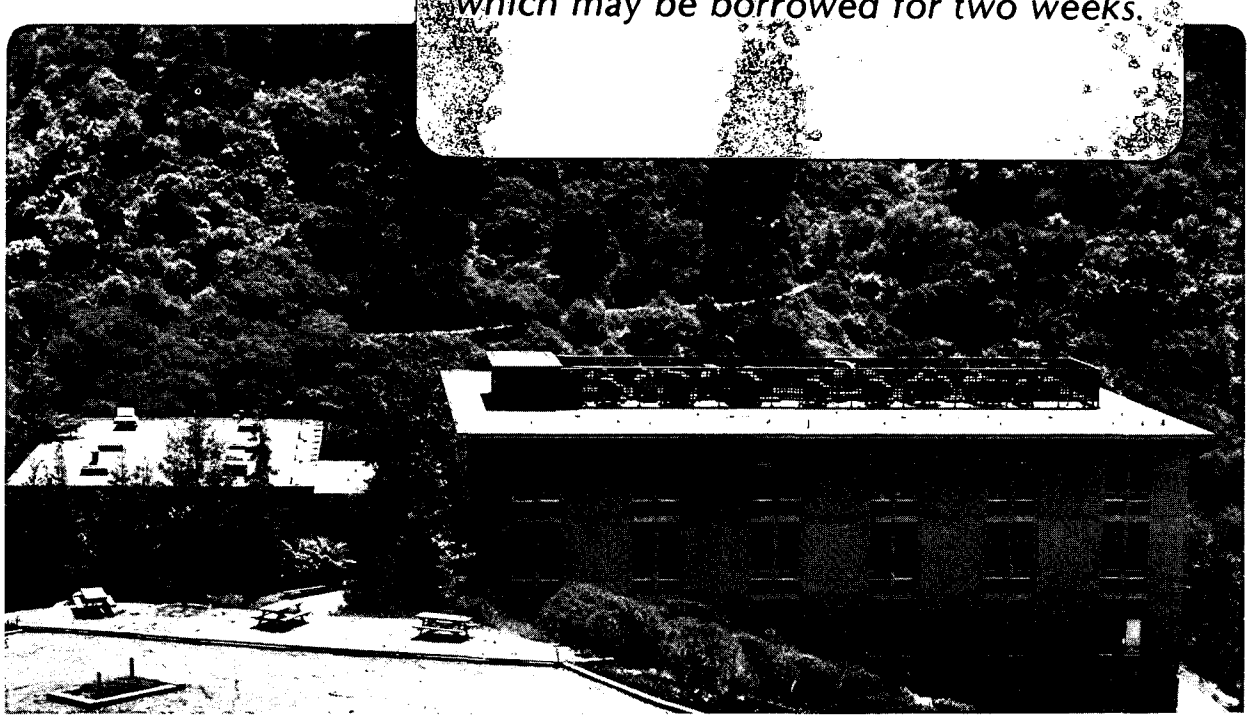

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ON THE IMPORTANCE OF SURFACE STRUCTURE IN ELECTROCHEMISTRY: THE WELL-DEFINED Au (111) SINGLE CRYSTAL ELECTRODE SURFACE

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ABSTRACT

A brief review is given of the preparative methods for producing a well-defined single crystal Au (111) surface for electrochemical studies. The Au (111) surface has been shown to reconstruct upon proper ultra-high vacuum preparation. LEED patterns and cyclic voltammetry of this surface are reported. Some conclusions are made on the importance of proper surface characterization (e.g. by LEED analysis) for Au single crystals, and the questionable validity of results found in the electrochemical literature for Au "single crystal" surfaces.

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 already 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, polish it mechanically and electrochemically 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 [5,6] that in situ 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 (reconstructed) [7-10]. Au is the most extreme example of this, where even the Au (111) surface is reconstructed.

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. This surface is the natural 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 equilibrium surface configuration will be optimized.

In this communication, we report 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 show that it can be very difficult to obtain a <u>well-defined surface structure</u> on Au (111) crystals, and we suggest that most reports with Au single-crystals that have appeared in the literature cannot be regarded as representative of known (well-defined) surface structures.

EXPERIMENTAL

Single crystal rods were grown at Cornell (B. Addis) by the Czochralski technique, and further refined by repeated recrystallization using the floating zone method. The rods were oriented using Laue back reflection, and the single crystals cut, mechanicaly polished down to 1 with diamond paste to within 0.5 degree of the [111] plane, and electropolished (in cyanide [13]) following detailed instructions from Zehner [14]. Following electropolishing, the crystals were mounted on Ta heating blocks on the UHV sample transfer probe. The UHV/electrochemistry system has been described in detail previously [3]. The crystal was transferred into the UHV chamber/holder, where the surface was subjected to the usual ion bombardment/thermal annealing cycles. Surface cleanliness was monitored by Auger electron spectroscopy and surface structure was determined using LEED.

RESULTS AND DISCUSSION

Early studies with LEED of the Au (111) surface have suggested that this surface exhibits its normal bulk-like atomic arrangements [15,16]. However, the published LEED photographs obtained during these studies exhibit large areas of intensity at the integral order reflection positions instead of sharp spots indicating that a poorly ordered outermost atomic layer existed. In these cases, inadequate surface preparation was likely. More recently, LEED patterns indicating a reconstructed Au (111) surface were reported by Zehner and Wendelken [12], which were obtained after argon

ion sputtering and high temperature annealing of single crystal surfaces that had been prepared using different pre-treatments [14] than those employed in the earlier studies [15,16]. For comparison, the LEED patterns at 54 eV are given in Fig. 1 for a series of different surface preparations. These patterns were obtained using modified Varian three-grid LEED optics; modifications to the Varian LEED gun were essential [14] to obtain the detail around the integral beam spots.

In all but the pattern given in part e, additional reflections are observed about the integral beam spots. This surface was only mechanically polished (with 0.3 alumina). The pattern given in part b of Fig. 1 corresponds to a surface of an epitaxially grown layer on mica. The preparations used for the other single crystal surfaces are given in the figure caption.

In our own work with the Au (111) single crystal surface, we have achieved LEED patterns that show (Fig. 2) additional reflections about the integral spots. However, the LEED patterns obtained after the first few sputtering/annealing cycles do not show additional reflections, but rather diffuse integral beam spots. In fact, the surface could have easily been mistaken as a result for a (1x1) structure (albeit a poor one). The patterns did improve with additional UHV treatments. The reconstruction was most easily attainable after the sputtered surface had been cycled oxidatively in dilute HF and returned to UHV for additional sputtering and annealing. We were not able to obtain the fine detail around the integral beams that were obtained by Zehner. We attribute this to deficiencies in our Varian LEED gun, which has too much angular dispersion to produce the coherence in the diffracted beams required for the large unit cells of the

incommensurate overlayer.

To date the structural models advanced for the reconstructed Au (111) surface have included a (1x23) structure [17] and a ($\sqrt{3}$x22) structure [18]. One structure giving rise to the LEED patterns of Fig. 1a was suggested by Van Hove, et al. [13] to be the superposition of three 120 degree rotated domains, each domain consisting of rectangular ($\sqrt{3}$x22) unit cells. A 4.55% uniaxial contraction of the hexagonal top layer in the [110] direction satisfies the observed diffraction pattern. Another domain-structure model was also proposed involving alternate strips of 11 atoms wide of different bulk structure termination, where half the strips have the normal fcc termination while for the others an hcp termination is achieved through slippage of the topmost layer to different hollow sites of the second layer. All the models for the reconstructed surface of Au (111) have in common the feature that they are incommensurate overlayer structures.

The LEED pattern given by Zehner for the mechanically polished surface (Fig. 1e) is not representative of the reconstruced surface that is obtained with careful surface preparation. It is clear from the work of Zehner that a diffuse integral beam LEED pattern for Au (111) is not representative of a (1x1) surface structure. In our work, mechanical polishing also resulted in a pattern with diffuse integral beams, and extensive UHV sputter/annealing did not improve the pattern significantly. We have concluded that mechanically polished Au (111) crystals do not give rise to any well-ordered surface structures.

Electrochemists, using Au single crystal electrodes, usually report that the surfaces were prepared by mechanical, electropolish, and thermal annealing. In one study [19], a LEED system was used to determine the

surface structure prior to use in the electrochemical cell. Following ion bombardment and annealing in UHV, they reported a LEED pattern with diffuse integral beam spots, which they concluded represented a (1x1) structure with a large number of defects. As we reported here, their LEED pattern is typical for a Au crystal with that pre-treatment history, but their contention that the surface was mostly (1x1) is not correct. The actual surface structure used in this kinetic study was, therefore, not well-defined, and the conclusions made therein with respect to structure-activity relations should be regarded with caution.

Some interesting voltammetric curves have been reported by Hamelin for various crystal orientations of gold [20-23]. The gold surfaces were prepared by mechanical polishing and electropolishing followed by annealing in a highly oxygenated methane flame [20]. Detailed analyses were presented in these papers of the effect of crystal orientation on kinetics of proton reduction [21] and the formation of lead upd [22,23]. The detailed analyses concerning the atomic nature of the surfaces studied were based on voltammetric experiments alone, presuming certain structure-property relations that are unproven. Figure 3 shows the voltammetry of Au (111) crystal following UHV preparation in our system. The time varying anodic displacement in the first five sweeps is due to oxidation of dissolved hydrogen left in the electrolyte from charging of the reference electrode. The anodic film formation/reduction process was characterized by a relatively sharp <u>single</u> peak, in contrast to the multiple peaks reported by Hamelin for Au (111) [21], but qualitatively similar to the peak-shape reported by Dickertmann, et al. [24]. After the voltammetry was completed to a potential just anodic of the oxide peak, the

crystal was emersed at 0.4V, transferred to UHV, and a LEED pattern obtained that indicated the surface structure was unaffected by this anodic treatment, i.e. that the voltammetry in Fig. 3 is characteristic of the UHV reconstructed (incommensurate overlayer) surface. It is not clear why our voltammetry for Au (111) is so dramatically different from that reported by Hamelin, but we suggest that different atomic arrangements were present on surfaces of the same nominal orientation. In our case, the voltammetry was representative of a well-ordered Au surface having one of the incommensurate overlayer structures sugested by Van Hove, et al. [18]. In Hamelin's case, the atomic arrangement was undetermined, but from our experience with Au (111) surfaces we have found that Hamelin's surface preparation usually produces a composite structure rather than a single well-ordered structure. We, therefore, suggest that detailed structure-property relations based on observations with single crystals of indeterminate surface structure are premature. With the evolution of LEED/electrochemistry systems, there may evolve a set of criteria by which one can deduce from some electrochemical property, e.g. the voltammetry "signature", what the surface structure must be. That criteria has, however, not yet evolved, and these results with Au (111), with its unexpected incommensurate overlayer surface structure, show how much research has to be done to derive these criteria.

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FIGURE CAPTIONS

Fig. 1. LEED patterns from clean Au (111) surfaces at a primary beam energy of 54 eV (courtesy of D.M. Zehner). The surface preparations before 500 eV argon ion sputtering and 400-600°C annealing were:

a) cyanide electropolish

b) epitaxially grown on mica

c) 1 min. aqua regia etch

d) 10 min. aqua regia etch

e) mechanically polished with 0.3 μ alumina

f) same as e after heating to approx. 750°C for several hours.

Fig. 2. LEED pattern from a clean reconstructed Au (111) surface at a primary beam energy of 54 eV.

Fig. 3. Cyclic voltammogram of the reconstructed Au (111) surface in aqueous 0.3 M HF for the anodic window opening at 50 mV/s. The steady state voltammetry was reached after the third cycle through the reversal potential of 1.5 V.

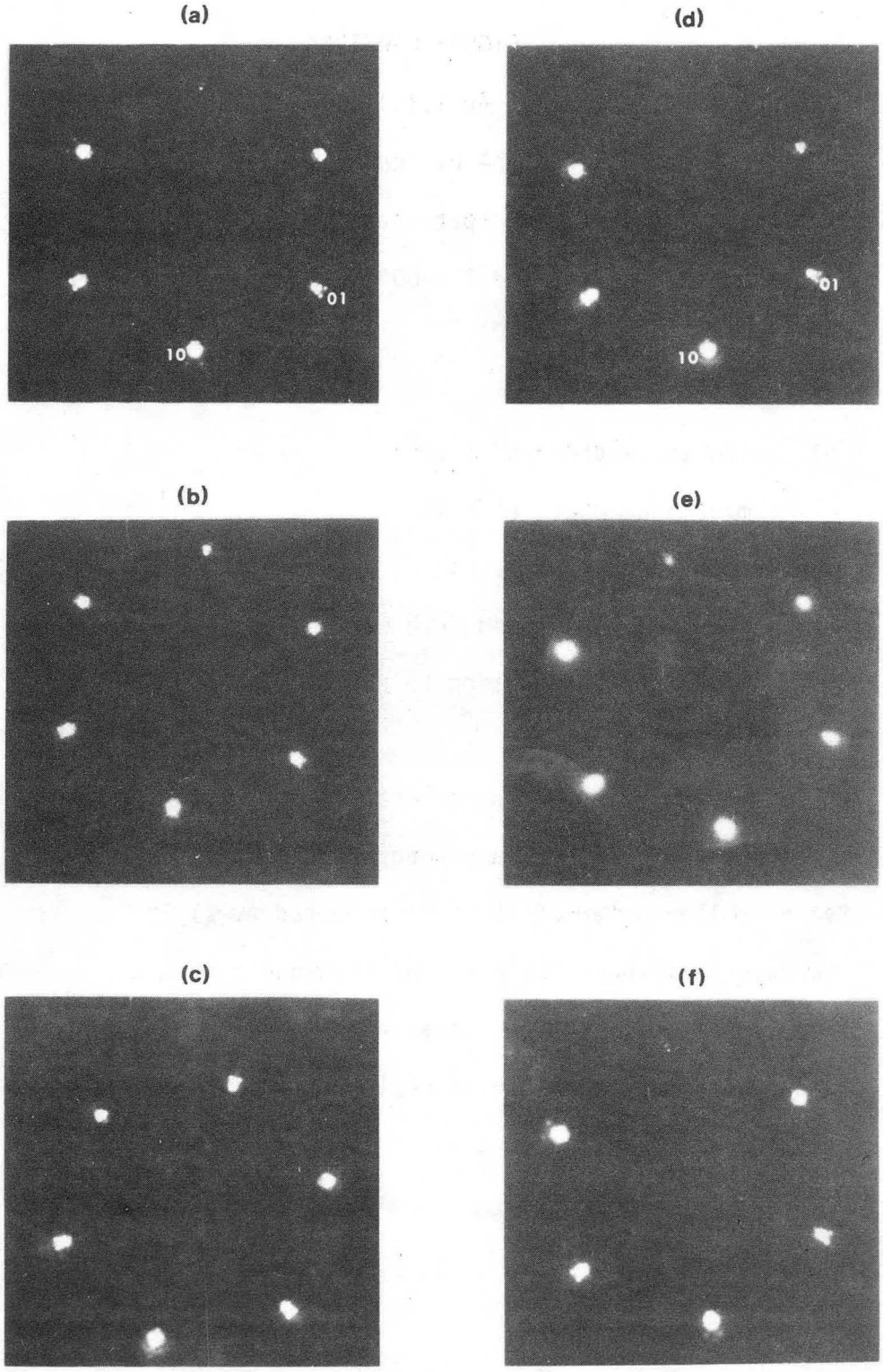

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Fig. 1

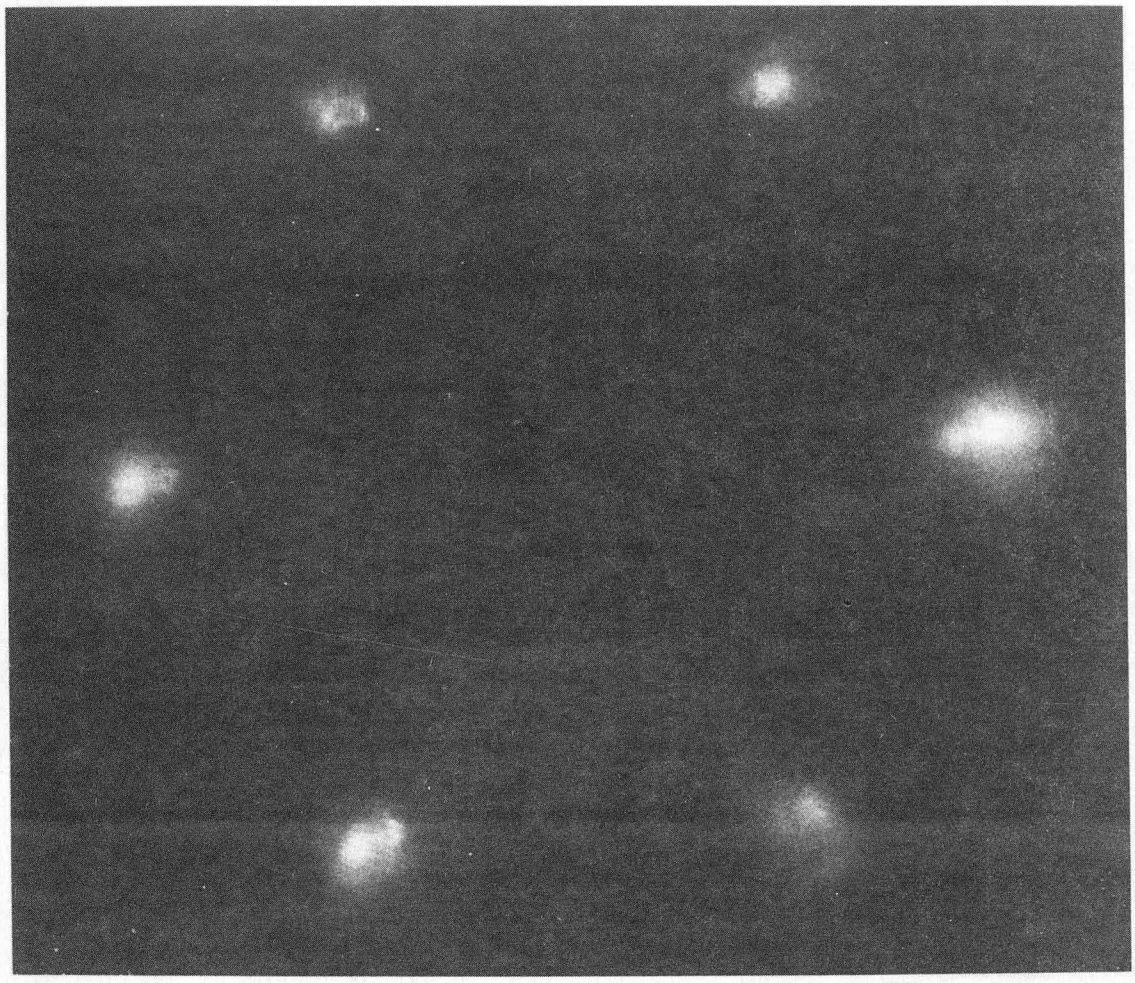

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Fig. 2

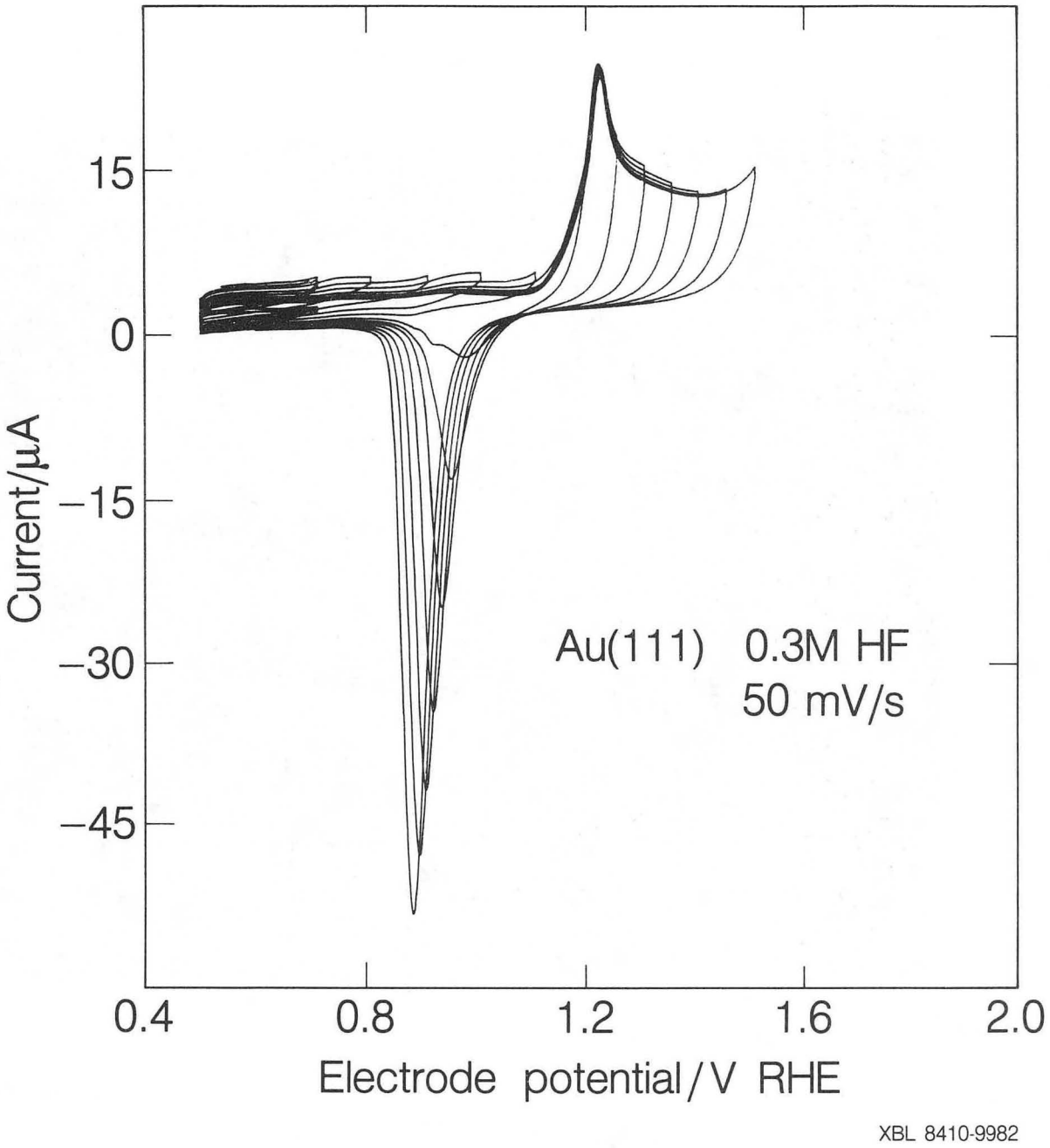

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Fig. 3

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