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POTENTIAL INDUCED STRUCTURAL TRANSFORMATIONS OF THE Au(100) AND Au(lll) SURFACES

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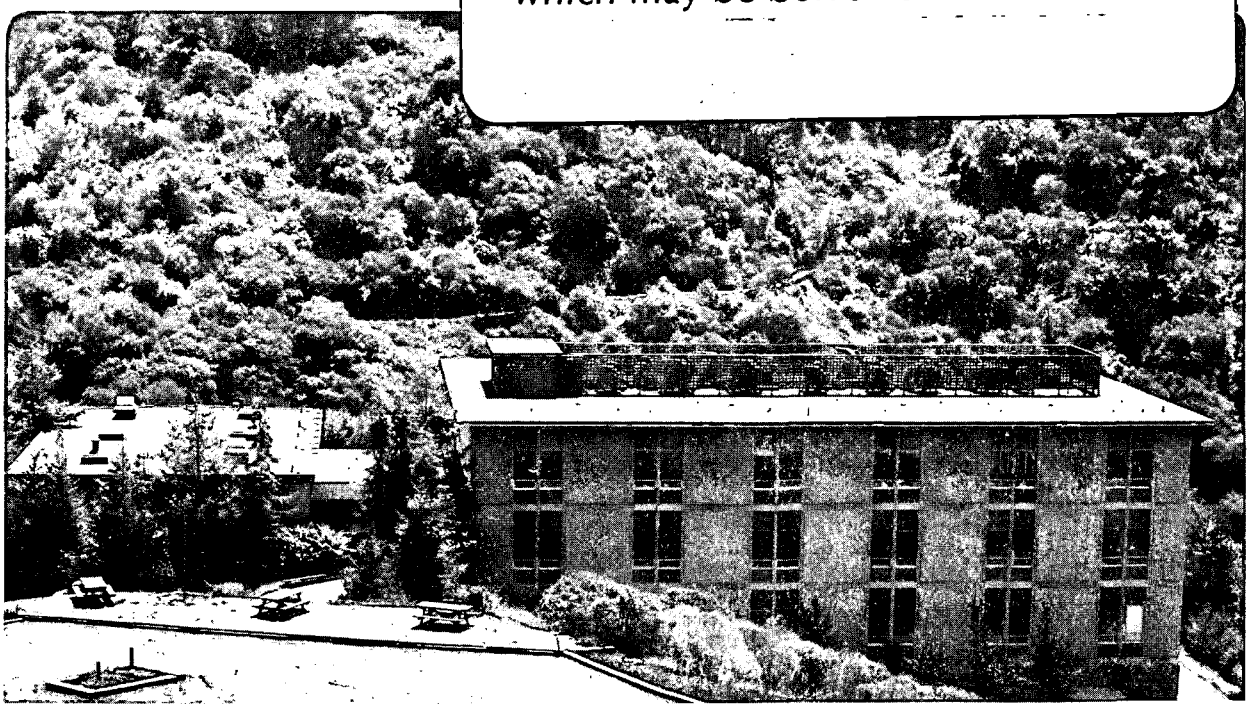

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POTENTIAL INDUCED STRUCTURAL TRANSFORMATIONS OF THE Au(100) and Au(111) SURFACES

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Ex-situ LEED analyses of emersed single crystal electrodes have provided direct observations of place-exchange during the anodic oxidation of both Pt [1,2] and Au [3] surfaces. These recent surface structure determinations have confirmed, and refined, the understanding of anodic oxidation and place-exchange developed from purely electrochemical methods [4,5]. It is now clearly understood that place-exchange is the mechanism by which more than a monolayer of OH-like species is accommodated onto the surface, i.e. more than 1e per surface atom of charge is injected into the surface. It is also clear from the LEED studies that place-exchange is an irreversible process, in which place-exchanged atoms do not find their way back to their original positions in the surface during cathodic reduction. Repeated cyclic oxidation-reduction with place-exchange produces accumulated displacement of atoms from the original atomically flat surface resulting in extensive atomic roughness. The anodically roughened surface can only be restored to the atomically flat structure via ex-situ thermal annealing.

The use of ex-situ LEED analysis to observe more subtle changes in surface structure has proven to be more problematic. In particular, the stability in electrolyte of the UHV reconstructed surfaces of Pt and Au

single crystals has not been well established. Two different groups [6,7] have observed the UHV 2x1 reconstruction of Pt(110) and Au(110) to be stable over a broad range of electrode potential, including some level of anodic oxidation. In previous studies of the Pt and Au (100) surfaces in this laboratory [1,3] we reported that the UHV (5x20) reconstructed surfaces are very unstable to contact with solution, and that there was no potential region (in acidic electrolyte) from which the electrode could be emersed in the reconstructed state. On the other hand, Kolb and Schneider [8] reported the observation of the (5x20) reconstructed surface Au(100) on electrodes emersed at cathodic potentials, e.g. -0.4 V vs. SCE in acidic electrolyte. In recent work at this laboratory, we have tried to reconcile these different observations. It appears that the observation of the (5x20) reconstruction depends critically on the state of charge of the electrode surface in the emersed state, i.e. excess ionic charge on the surface that raises or lowers the work function of the emersed electrode. The magnitude and sign of the excess ionic charge on the emersed electrode depends on the electrolyte being used, and on the experimental method used for emersion. It is not necessarily the case (in our experience) that the excess charge is quantitatively related to the potential of emersion, nor are the ex-situ observations of reconstruction necessarily representative of the structure of the surface in solution. For example, a Au(100) electrode emersed from 0.3 M HF has a small level of Cl impurity on the surface, detected by AES, that is probably due to specific adsorption of Cl^-, a known impurity (ca. 10-7 M) in our HF electrolyte. That the anion adsorption is specific is clear from the relatively wide potential region

of emersion (both positive and negative of the pzc) over which the AES signal was constant. The presence of Cl on the surface at the observed levels increased the work function of the emersed electrode vs. the clean electrode by ca. 0.1 eV, i.e. $\Delta\Phi$ = + 0.1 eV, at all potentials of emersion. Thus, even an electrode emersed at a very cathodic potential, e.g. - 0.4 V vs. SCE, in 0.3 M HF had a $\Delta\Phi$ > 0 due to Cl^- adsorption, and the LEED patterns were always (1x1). However, when K^+ or Cs^+ ion was added to the HF (to ca. 0.1 mM), the emersion at cathodic potentials resulted in K^+ or Cs^+ ion on the surface and a net $\Delta\Phi$ < 0. For example, for $\Delta\Phi$ = -0.5 eV, which resulted from very small quantities of Cs on the surface, the LEED pattern was characteristic of the (5x20) hexagonal reconstruction [9]. In the case of K^+ containing electrolyte, $\Delta\Phi$ = -0.5 eV occurred with larger coverages of cation (e.g. 0.25 ML) and produced c(2x2) spots superimposed on the (5x20) pattern. The coverage by alkali ions and the $\Delta\Phi$ did appear to increase linearly with increasing cathodic potential of emersion, as reported previously by D'Agostino and Hansen [10]. Thus, it seems at least probable that the (1x1) -> (5x20) transformation does occur at cathodic potentials in K^+ and/or Cs^+ containing electrolytes. However, we have not observed this transformation to occur in any pure acid electrolyte, probably due to specific anion adsorption that displaces H9O4+ from the surface and produces a $\Delta\Phi$ > 0 regardless of the potential of emersion.

Grazing incidence x-ray diffraction (GID) [11] presents the promise for in-situ analysis of the structure of electrode surfaces. The technique has been used in-situ to define the structure of UPD Pb on Ag(111) [12], but several groups, including ourselves, have encountered

difficulties using the technique with Au surfaces. In particular, GID appears to require optically flat surfaces, which are difficult to achieve with Au crystals. The work in our laboratory has concentrated on the use of Au(111) films evaporated on cleaved mica, analogous to the Ag(111) films used in other GID studies [12]. In our first phases of work, we have studied these Au(111) films using the same LEED/UHV apparatus as in our previous studies of Au(111) crystals [3], and supplemented these with GID analysis of emersed Au(111) films with thru-air transfer to a two-circle diffractometer on beamline VI at SSRL. In-situ studies using GID with a new four-circle diffractometer on beamline VI at SSRL are scheduled for the spring running of SSRL and results from those runs will be presented if available. The ex-situ analyses by LEED and GID of the (1x1) -> (5x20) transformation were in reasonable agreement with one another, and the results qualitatively similar to the results for Au(100), i.e. the reconstructed ($\sqrt{3}$x22) surface was observed only with emersion from K^+ and Cs^+ electrolytes, and not from pure acids, but the ($\sqrt{3}$x22) was observed at much more anodic potentials of emersion than for the (100) - (5x20).

Interestingly, both of the reconstructions on Au(111) and (100) represent a contraction of the Au-Au bond length for the Au atoms in surface layer, 4% and 6.5%, respectively. The contraction is probably induced by cathodic (relative to the pzc) potentials, and the contracted bond is stabilized on the emersed surface by the local charge density produced by the cations adsorbed on the surface. The larger contraction of the bond on the (100) surface may account for the reduced stability of this structure, and the need for a higher coverage by alkali cations to

stabilize it. Conversely, anions on the emersed surface stabilize the (1x1) structure, and possibly cause an as yet unobserved expansion in the Au-Au surface atom bond length. Charge density waves (solitons) produced by ion (cation or anion) adsorption appear to be the driving force for the (111)-(1x1) $\rightleftharpoons$ ($\sqrt{3}$x22) and (100)-(1x1)$\rightleftharpoons$(5x20) surface phase transitions.

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