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**IN SITU X-RAY SCATTERING FROM SINGLE
CRYSTAL ELECTRODE SURFACES**

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In Situ X-ray Scattering from Single Crystal Electrode Surfaces.

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Although it has been well known for many years that the room temperature surfaces of the *5d* metals reconstruct *in vacuo* [1], [e.g. all three low index faces of gold and the Pt(001) and (011) faces] the structure of the solution interface has remained a mystery due to the technical difficulties associated with probing the liquid/solid interface. We have used x-ray diffraction (principally x-ray reflection and diffraction) to study the metal/solution interface while the metal is held under potential control. This technique was recently used to probe the low index faces of gold in contact with acidic and neutral electrolytes [2, 3, 4]. These studies found that at sufficiently negative potentials the solution interface of all three low index gold surfaces could be induced to reconstruct. These reconstructions occurred at potentials for which anion adsorption on the surface was largely eliminated. In general, the reconstructed surfaces had structures which were quite similar to the UHV reconstructions.

Our work at SSRL extended the study of the reconstruction of the Au(001)/solution interface to alkaline electrolyte. In addition, we studied the interface of Pt(001) and Pt(111) with both acid and alkaline electrolytes. The vacuum interface of Pt(001) has a similar reconstruction to the Au(001) surface. In electrolyte, however, at potentials just above hydrogen evolution, platinum surfaces are covered by

an adsorbed state of hydrogen, a state which is not found on gold surfaces at similar potentials [5].

Gold Surface Reconstruction

Our studies of gold at SSRL have been used to contrast the reconstruction measured previously in acidic and neutral electrolytes with the reconstruction in alkaline electrolyte using x-ray reflectivity and grazing in-plane diffraction measurements.

In perchloric acid electrolyte (and vacuum) the (001) surface forms a distorted hexagonal overlayer rotated $\pm 0.8^\circ$ degrees from the [110] direction. In alkaline electrolyte, however, the reconstruction forms in smaller domains and is aligned along the [110] direction. These changes appear to be a consequence of the faster kinetics of the reconstruction formation and lifting in alkaline electrolyte.

The reconstruction of the (111) surface appears to be very similar in acidic, neutral, and alkaline electrolytes, although again the reconstruction forms more rapidly in the latter. Faster reconstruction formation is also found for the (011) surface in alkaline electrolyte, where the (1×3) reconstruction is formed. In vacuum the (1×2) surface reconstruction is favored. A previous study of this surface in perchloric acid [4] found that the reconstruction is potential dependent, with the (1×2) formed initially, and a

more complicated structure which is a combination of (1×2) and (1×3) reconstructions, formed at more negative potentials. In salt solutions, however, the (1×3) reconstruction only is observed. The explanation for these differences is unknown, but is probably a consequence of the very similar surface energies of the two different reconstruction. The (1×3) reconstruction seems to be favored if adsorbing anions are present in the electrolyte.

Platinum Surface Relaxation

Although the Pt(001) surface reconstructs in vacuum, and the Pt(111) surface reconstructs at elevated temperatures, neither of these surfaces was found to be reconstructed when placed in contact with an electrolyte. The x-ray reflectivity profiles were, however, found to be reversibly dependent on the potential (at sufficiently positive potentials, irreversible roughening of the surface occurs, due to oxide formation). Fig. 1 shows the cyclic voltammetry and the normalized scattering intensity changes occurring at two different places on both the specular reflectivity rod and a non-specular reflectivity rod as a function of potential for the Pt(001) surface in contact with 0.1M KOH electrolyte. In both cases the scattering below the Bragg peaks [positioned at (002) and (111)] show a increase of the scattering intensity as the potential is reduced below 0.3 V, while the scattering intensity above the Bragg peak shows the opposite behavior. This suggests that the top layer of platinum atoms are expanding away from the second layer as the potential is reduced. This effect occurs in the potential region between hydrogen evolution and 0.3 V (versus Pd/H reference electrode), where hydrogen adsorption is known to occur [5]. Fig. 2 shows two full truncation rods at two fixed potentials, 0.35 V, and 0.0 V. In both cases the scattering intensity lies below

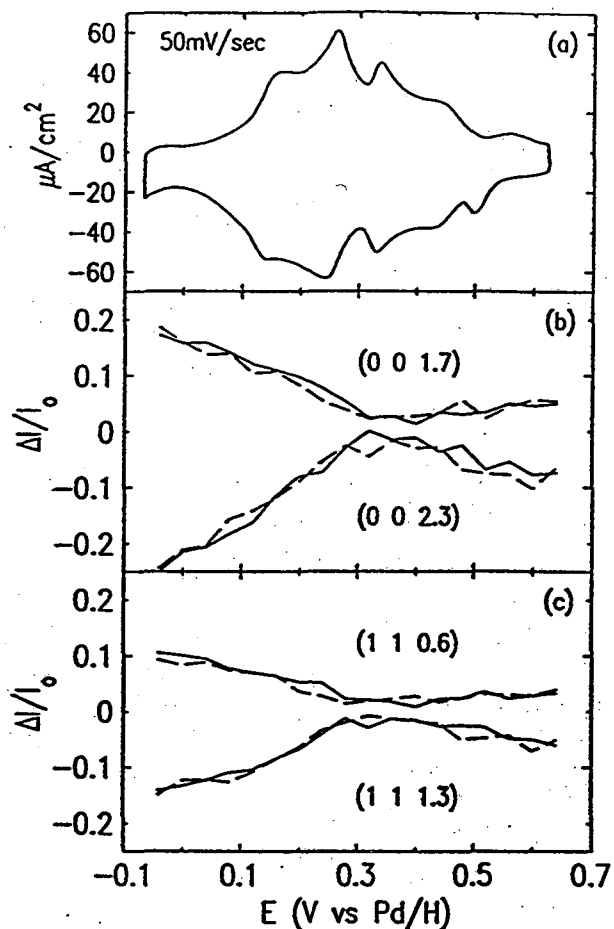


Figure 1: (a) Cyclic Voltammogram of the Pt(001) surface in 0.1M KOH electrolyte. The sweep rate was 50 mV/sec. (b) Changes in scattering intensity with potential at the (0 0 1.7) and (0 0 2.3) points on the specular rod. (c) Changes in scattering intensity with potential at the (1 1 0.6) and (1 1 1.3) points on the (1 1 L) non-specular rod. The solid(dashed) line shows the scattering on the positive(negative) sweep. The scan rate was approximately 4.5 mV/sec.

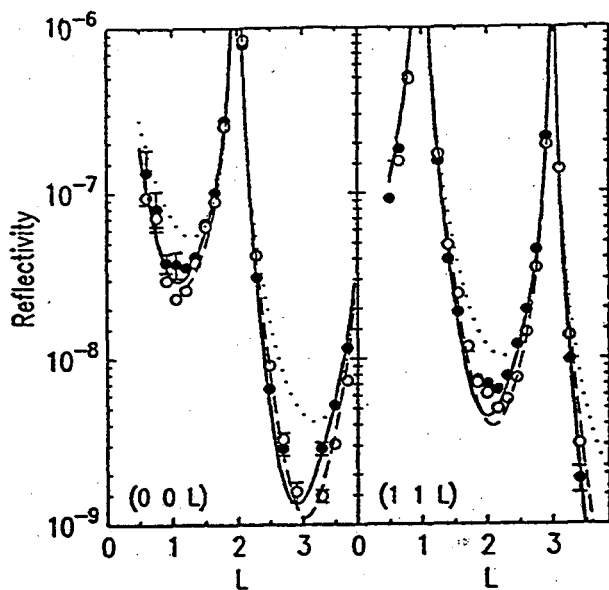


Figure 2: Scattering along the $(0\ 0\ L)$ rod (a) and $(1\ 1\ L)$ rod (b) at 0.0 V (closed circles) and 0.35 V (open circles). The dotted line shows the reflectivity expected from an ideal surface with bulk termination of the crystal. The solid and dashed lines show a model fit to the data at 0.0 V and 0.35 V respectively. The model is described in the text.

the expected scattering intensity for an ideal surface (dotted line), indicating that the surface is not sharp, most likely due to the presence of steps or islands of platinum on the surface. The model used to fit the data allowed the occupation and Debye-Waller-like disorder of the top metal layer to float, together with the top layer spacing (the distance between the first and second layers, d). The fits shown were obtained by using same parameters for the disorder and top layer occupation for both potentials and allowing d to float. For the surface at 0.35 V, the model indicates that d is $0.5 \pm 0.3\%$ larger than the bulk value. Previous vacuum studies of the (metastable) unreconstructed Pt(001) surface found d to be $0 - 0.2\%$ larger than the bulk value [6]. On changing the potential to 0.0 V, the expansion increases to $2.8 \pm 0.3\%$ of the bulk layer spacing, which is equivalent to an expansion of approximately 0.05\AA on changing the potential. We believe this is the first reported observation of this phenomenon. Unfortunately, no reliable studies of the structure of the H/Pt(001) surface in vacuum have been reported in the literature, so we are unable to determine whether this is a general effect or limited to the electrochemical interface. A similar change has also been observed for the Pt(001) interface with perchloric and sulfuric acids solutions, although the change in the top layer spacing was only about half the magnitude of the change in potassium hydroxide solution. The reason for the smaller change in acid electrolytes is unclear.

We have also studied the Pt(111) surface in contact with acid and alkaline electrolytes. Again the surface was not reconstructed in either electrolyte. The changes to the scattering in the hydrogen adsorption region were much smaller than found on the (001) surface, perhaps due to the much lower hydrogen coverage on this surface prior to hydrogen evolu-

tion. Reversible changes were also observed at higher potentials, in the potential region where the electrochemical "butterfly" feature is found (this electrochemical feature is characterized by a large pseudocapacitance of unknown origin). This change, however, cannot be associated with an expansion of the top layer spacing, and is probably due to the adsorption of anions. Studies of these and other related systems are ongoing.

Acknowledgments

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