Comment on "Monitoring the Transitions of the Charge-Induced Reconstruction of Au(110) by Reflection Anisotropy Spectroscopy"

The reflection anisotropy (RA) spectra of the Au(110)/electrolyte interface reported by Mazine and Borensztein (MB) [1,2] and in [3] show a very different dependence on the potential applied to the Au electrode. This can be most clearly seen by comparing the change in the RA spectrum in the two studies as the potential is varied from negative to positive values.

The comparison is complicated by the fact that MB plot the RA spectrum as $(r_{110} - r_{001})/r$ while we plotted $(r_{001} - r_{110})/r$. However, it is clear that in our results the maximum intensity observed at 2.5 eV in the spectrum occurs at the most negative potential and that the intensity of this feature is reduced as the potential becomes more positive. MB observe the reverse of this behavior. Both groups have checked the potential referencing in their experiments [4].

Since it is well known [5] that the Au(110) (1×2) to (1×1) phase transition occurs as the potential is changed from negative to positive values, the two groups have associated spectral features in the RA spectrum with the (1×2) and (1×1) reconstructions and used RA spectra to monitor the phase transition. However, because of the difference in their dependence on the potential, the spectral features identified with the two surface reconstructions are opposite in the two studies.

Currently RA spectra are not sufficiently understood that the character of the surface reconstruction can be deduced from the spectrum. In our work we identified the RA spectrum of the Au(110) (1×2) reconstruction from studies of clean surfaces in ultrahigh vacuum (UHV) in which the presence of the (1×2) reconstruction was established by low energy electron diffraction and scanning tunneling microscopy (STM). Our assignment is supported by the UHV study of Stahrenberg *et al.* [6] who comment that the spectrum they identify with the (1×2) reconstruction is similar to that identified with the (1×1) reconstruction by MB. Stahrenberg *et al.* [6] also showed that the changes in the RA spectra associated with the thermally induced (1×2) to (1×1) phase transition are consistent with our identification. However, in this context it should be noted that the thermally induced 1×1 phase observed in UHV is a disordered phase, while the 1×1 phase observed in an electrolyte is an ordered phase [4].

MB [2] discuss the potential range over which the phase transition occurs and suggest that in our experiments the spectra are influenced by the evolution of oxygen. This suggestion is not consistent with the results of our cyclic voltammogram, which is similar to that reported in [7]. We make clear in our paper that, relative to the saturated calomel electrode, the RA spectrum begins to change as the potential is increased positively from +0.2 V onwards. In making comparisons with STM results it is important to remember that STM provides a monitor of changes on a very small length scale while RAS monitors the (1×2) to (1×1) phase transition over a large area of ~ 1 cm^2. It is reasonable to expect that the potential range over which the transition is observed to occur will be wider in RAS than in STM since the phase change may well be completed in small areas before spreading to a large area, particularly if the transition is nucleated at many different sites and the resulting domain boundaries need to be removed in order for the phase change to cover the whole specimen.

We draw attention to a significant difference in the spectral shape in the region ~3.8 to 4.5 eV in the two studies. In UHV experiments we were able to correlate the strength of the signal in this region with the concentration of $\langle -110 \rangle$ monatomic steps. The difference suggests that such steps were more common in the specimen used by MB [2] than in our specimen. Such steps could have a strong influence on the 1×2 to 1×1 phase transition. This is also a region of the spectrum that is significantly influenced by surface disorder [8].

We conclude that an unambiguous identification of RA spectra with surface reconstructions at Au(110) electrodes in an electrochemical cell has not yet been established. It is likely that the difference between the two experimental studies arises from differences in the morphology of the Au surfaces.

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