Optical response of the Cu(110)/electrolyte interface

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Abstract. It is demonstrated that the angular variation of a positive peak at 2.2 eV in the reflection anisotropy spectrum (RAS) observed from the Cu(110)/electrolyte interface is consistent with its identification as a transition between surface states at the $\overline{Y}$ point of the surface Brillouin zone. The angular variation of a broad negative feature in the RAS spectrum is consistent with the major contribution to its intensity arising from transitions polarised along the principal axes of the Cu(110). The intensity of this feature varies with the potential applied to the Cu(110).

1. Introduction
The electronic structure of metal/electrolyte interfaces is expected to influence the performance of fuel cells and have an effect on important processes such as electrochemical deposition. Although it is difficult to study the electronic structure of such interfaces directly it has recently been shown that the optical technique of reflection anisotropy spectroscopy (RAS) \cite{1} has considerable potential in this field. In particular it has been shown that the RAS of the Au(110)/electrolyte \cite{1,2} and Cu(110)/electrolyte \cite{3} interfaces are similar to the RAS of clean (110) surfaces of these metals prepared in ultra high vacuum (UHV). In particular the RAS of the Cu(110)/electrolyte interface shows a feature at 2.2 eV that has been identified with a transition between surface states at the $\overline{Y}$ point of the surface Brillouin zone \cite{3}. In this work we show that the azimuthal angular variation of the intensity of this feature at 2.2 eV in the RAS spectrum of the Cu(110)/electrolyte interface is consistent with its identification with this transition between surface states. We also report the results of the angular dependence of a broad negative feature observed at ~4.3 eV in the RAS of this interface and its dependence on the potential applied to the Cu(110) electrode.

2. Experimental
The preparation of the Cu(110) crystal and its insertion into the electrochemical cell in an electrolyte of 10mM HCl in ultrapure water (Millipore 18MΩcm) has been described earlier \cite{3}. The electrochemical cell is a three-electrode cell using the copper as the working electrode, a platinum counter electrode and a silver/silver halide electrode as the reference electrode \cite{4}. All potentials quoted are referenced to this reference electrode. The RA spectrometer was of the Aspnes design \cite{5} and the measured RA signal from 1.5 eV to 5.0 eV is given by

$$\text{Re}(\frac{\Delta r}{r}) = \frac{2(r_{[1\overline{1}0]} - r_{[001]})}{(r_{[1\overline{1}0]} + r_{[001]})}$$

(1)

where $r_{[1\overline{1}0]}$ and $r_{[001]}$ are the reflection coefficients in the [1\overline{1}0] and [001] directions in the (110) surface respectively. The sum of these quantities is given by $r$ and the average by $\langle r \rangle$. The azimuthal angular variation of the specimen with respect to the direction of the incident light was performed...
using a rotating platform which ensured the same spot of the crystal was observed over the full 90° rotation.

3. Results
The RAS of the Cu(110) surface in 10mM HCl is shown in figure 1 as a function of the azimuthal angle, θ, in the plane perpendicular to the direction of the incident light. These spectra were obtained with a potential of -0.65 V applied to the Cu(110) electrode. The dependence of the RA spectrum on the applied potential has been reported previously [3] and it is clear that the adsorption of Cl begins at a potential of -0.40 V and that the Cu(110) surface is clean in the range -0.70 V to -0.55 V although it is possible that there are low levels of H adsorption at the more negative potentials. The optical axes of the Cu(110) surface are along [110] and [001] and the zero of θ used in the experimental results in figure 1 coincides with the [001] direction to ±10°. The inserts in figure 1 show the variation in the intensity of the peak at 2.2 eV and the broad feature at 4.3 eV as a function of θ. The results follow a cos²θ dependence as shown by the comparisons with theoretical curves. The difference in phase between the origins of the theoretical curves and the experimental results is consistent with an error in determining the origin of the experimental θ of 7°.

![Figure 1. RA spectra of Cu(110) in 10mM HCl at -0.65 V vs Ag/AgCl showing the angular rotation at 90° (◆), 75° (○), 60° (▲), 45° (×), 30° (□) and 15° (---) and 0° (+). The inset above shows the data points observed at 2.2 eV compared with a theoretical cos²θ curve and the inset below shows the data points observed at 4.3 eV compared with a theoretical cos²θ curve. In both curves the θ=0° of the theoretical curve has been shifted by 7° to bring it into coincidence with the experimental results.](image-url)
The dependence of the RAS of the Cu(110)/electrolyte interface on the applied potentials -0.7 V, -0.65 V, -0.60 V and -0.55 V is shown in figure 2. The results for the spectral range 2.0 eV to 2.5 eV encompassing the peak at 2.2 eV have been discussed earlier in detail [3]. The spectral region to low energy of 2.0 eV shows almost no dependence on the applied potential. The strong broad negative peak centred on ~4.3 eV becomes slightly broader and deeper as the potential is made more positive as shown in detail in the inset to figure 2.

![RA Spectra of Cu(110) in 10mM HCl at -0.7 V (solid line), -0.65 V (■), -0.6 V (∙ ∙ ∙) and -0.55 V (+) The inset shows the peak at 4.3 eV in more detail. There is a spurious weak feature ~2.7 eV in the spectra arises from a sharp peak in the output of the Xe lamp at this energy, which due to the less than perfect optical elements, does not cancel completely in the ratio $\Delta r/r$.](image)

4. Discussion

The RAS of the Cu(110)/electrolyte interface has been compared with the RAS of well prepared clean surfaces of Cu(110) in UHV [1,3,6-12]. The positive peak at 2.2 eV has been identified with a stronger feature observed from Cu(110) surfaces in UHV that arises from a transition between surface states at the $\bar{Y}$ point of the surface Brillouin zone [1,6,7]. This identification indicates that the peak is only excited by light incident along the [001] direction [6,7,13]. The azimuthal angular variation of RA spectra can yield considerable insight into the geometry of the optical response of surfaces [14-17]. For the Au(110)/electrolyte interface and for cytosine and adenine adsorbed at this interface [17,18] it has been shown that the RAS response collapses to close to zero across the whole spectrum when the incident plane polarised light is parallel to one of the principal axes in the surface. This implies that the dominant contributions to the RAS spectrum of Au(110) arise from transitions orientated along one of the principal axes [18]. For the absorbed molecules the angular variation of the RAS establishes that both adenine and cytosine are orientated essentially vertical to the Au(110) surface with the long
axis of the molecules aligned along one of the principal axes. It has been shown that the RAS of 9-
anthracene carboxylic acid [7] and 3-thiophene carboxylic acid [8] are influenced by the azimuthal
orientation of the stacked molecules on a Cu(110) surface in UHV. However there has been no
previous study of the azimuthal dependence of the RAS of the Cu(110) surface in either UHV or
liquid environments. The results of figure 1 show that as found for the Au(110)/electrolyte interface
[17,18] the RAS of the Cu(110)/electrolyte interface collapses to close to the zero across the spectral
range from 1.5 eV to ~3.5 eV. We will return to the spectral range above 3.5 eV later. An important
finding is that the intensity of the peak at ~2.2 eV shows essentially a cos2θ dependence. This is to be
expected if this peak arises from the transition between surface states at the Y point of the surface
Brillouin zone and the result is further confirmation of this assignment. In detail the theoretical cos2θ
curve has to be shifted by 7° in order to coincide with the experimental results. This indicates that the
experimental values of θ correspond to an origin 7° off the principal axes. This may explain why the
RAS in the region of the spectrum above 3.5 eV does not go to zero since it is difficult to find the
exact angle at which the spectrum will be a minimum. Alternatively this region of the spectrum could
contain weak contributions from transitions that are not orientated along one of the principal
directions. The insert to figure 2 shows that the broad negative feature centred on ~4.3 eV becomes
broader and more intense as the applied potential is increased from -0.70 V to -0.55 V. A similar
increase in intensity with a potential variation across this range was observed for the positive peak at
2.2 eV [3]. There is no clear explanation for either of these changes but they could result from the
desorption of H which could lead to a more ordered surface. This would be a similar affect to that
observed for the adsorption of CO impurities on the Cu(110) surface in UHV [19-21].

5. Conclusions
The RA spectral profiles of the positive peak observed at 2.2 eV from the electro-polished
Cu(110)/electrolyte interface show a cos 2θ dependence which is expected if this transition is
associated with a transition between surface states at the Y point of the surface Brillouin zone. The
broader negative peak at 4.3 eV shows a similar angular variation which indicates that this feature is
dominated by contributions that arise from transitions that are polarised along one of the principal axes
directions.

Acknowledgements
EEB is supported by a Ph.D. award funded by the UK Engineering and Physical Science Research
Council (EPSRC). This work was also support by an award from the UK Biotechnology and
Biological Science Research Council (BBSRC).

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