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Evidence for the observation of surface states at the Cu(110)/electrolyte interface

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Abstract – The reflection anisotropy (RA) spectral profiles of the interfaces between Cu(110) surfaces and H₂O, H₂SO₄ and HCl show a sharp positive feature at 2.2 eV that is identified with a transition between surface states at the \bar{Y} -point of the surface Brillouin zone. In HCl this peak is narrow, its position is independent of applied potential and its intensity grows with increasing potential. The RA spectra of these interfaces also show a broad negative feature at 4.2 eV similar to that associated with [001] steps on atomically rough Cu(110) surfaces in UHV.

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Introduction. – The electronic structure at the surface of an electrode and its dependence on the applied potential and the nature of the electrolyte has an important influence on electrochemical processes such as the electrochemical deposition of magnetic films and the behaviour of fuel cell catalysts. Progress in this field will advance the understanding of corrosion and facilitate the development of biocompatible materials. The field is also relevant to a number of problems in biophysics [1]. Despite recent advances [1,2] there is a need to develop the theoretical understanding of such interfaces and in particular to apply experimental techniques that will provide insight into the fundamental electronic structure of the electrical double layer that forms at the interface between the electrode and the solution [1].

An important question is whether surface states, which have been observed by a variety of experimental techniques on well-prepared single-crystal surfaces in ultra-high vacuum (UHV) [3–5], exist at metal/liquid interfaces. Such states are highly localised at the metal surface and since they are extremely sensitive to surface contamination in UHV [3–7] it might be expected that they would not exist at a metal/liquid interface. Early electroreflectance (ER) measurements [8–12] revealed anisotropic polarisation dependences in reflected light from noble-metal/electrolyte interfaces that were interpreted in terms of contributions from interband

transitions, the directional dependence of the surface conductivity and transitions between bulk states and surface states. Kolb *et al.* [13,14] obtained more direct evidence for the existence of surface states at Ag(100)/electrolyte interfaces by extending the ER technique into the infrared. It was later shown that these ER results are influenced by the concentration of the electrolyte and the presence of adsorbed species at the electrode [15]. This work established that optical probes of surface states have the potential to reveal useful information on the electronic structure of the electrical double layer and the progress of electrochemical reactions.

In ER the relative change in the reflectance of the surface, $\Delta R/R$, is measured along a single crystallographic direction as a function of the potential applied to the electrode and in order to increase sensitivity the applied potential is modulated at a high frequency, ~ 180 Hz, to give a derivative lineshape. It is usual to make a measurement at a single wavelength and to search for spectral features by scanning the linear bias potential.

In this work we make the first application of the surface optical technique of reflection anisotropy spectroscopy (RAS) to the study of the Cu(110) surface in liquids: in H₂O, H₂SO₄ and HCl. The technique has been extensively applied to the study of Au(110)/liquid interfaces [16]. RAS [17] is an optical technique that measures the difference in near-normal reflection of two orthonormal light polarisations incident normal to the surface as a function of photon energy. This geometry results in the

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cancellation of the optical response of the bulk of a cubic crystal by symmetry thus yielding the optical response of the surface. The RAS of the Cu(110) surface has been extensively studied in UHV and is a sensitive monitor of surface states [6,7,17–28]. In particular a strong feature at 2.1 eV is known to be associated with a transition at the \bar{Y} -point of the surface Brillouin zone between a filled surface state ~ 0.4 eV below the Fermi level and an empty state ~ 1.8 eV above the Fermi level. We observe this transition, at reduced intensity, at Cu(110)/liquid interfaces and explore its dependence on the potential applied to the Cu(110) electrode. This is the first identification of an optical transition between surface states at a metal/liquid interface.

Experimental. – A Cu(110) crystal of 8 mm diameter and 3 mm thick obtained from MaTecK Material-Technologie & Kristalle GmbH (Juelich, Germany) was used in all experiments and was prepared by electro-polishing in a 50% solution of phosphoric acid using the hanging-meniscus method for ~ 15 seconds with a positive voltage applied between the surface and a platinum disc submerged in H_3PO_4 . The Cu(110) surface was moved around whilst in contact with H_3PO_4 to ensure an even polishing of the surface. The Cu(110) surface was then rinsed with the electrolyte and transferred to the electrochemical cell with a droplet of the electrolyte on the surface to avoid oxidation in air. Experiments were performed in ultra-pure water (Millipore 18 M Ω cm) and in electrolyte solutions of 5 mM H_2SO_4 and 10 mM HCl in water and all solutions were degassed with argon before use. 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 [29] and all potentials quoted are referenced to this. The RA spectrometer was of the Aspnes design [30] and the measured RA signal from 1.5 eV to 5.0 eV is given by

$$\text{Re} \left(\frac{\Delta r}{r} \right) = 2 \frac{(r_{[1\bar{1}0]} - r_{[001]})}{(r_{[1\bar{1}0]} + r_{[001]})}, \quad (1)$$

where $r_{[1\bar{1}0]}$ and $r_{[001]}$ are the reflection coefficients in the $[1\bar{1}0]$ and $[001]$ directions in the (110) surface, respectively. The sum of these quantities is given by r and the average by $\frac{r}{2}$.

Results. – Figures 1(a) and (b) show, respectively, the RAS of a well-prepared Cu(110) crystal in UHV [22] and a similar well-prepared Cu(110) crystal in UHV following a thermal roughening treatment [25]. These spectral profiles have been discussed in detail previously [17–28]. Figures 1(c) and 1(d) show, respectively, the RAS of a Cu(110) crystal in H_2O and H_2SO_4 following the electro-polishing treatment described above. These spectral profiles are rather similar and show a positive peak ~ 0.25 eV wide centred on 2.2 eV followed by a steady fall into a strong negative peak centred on ~ 4.3 eV. These spectral profiles were unstable and both showed a steady

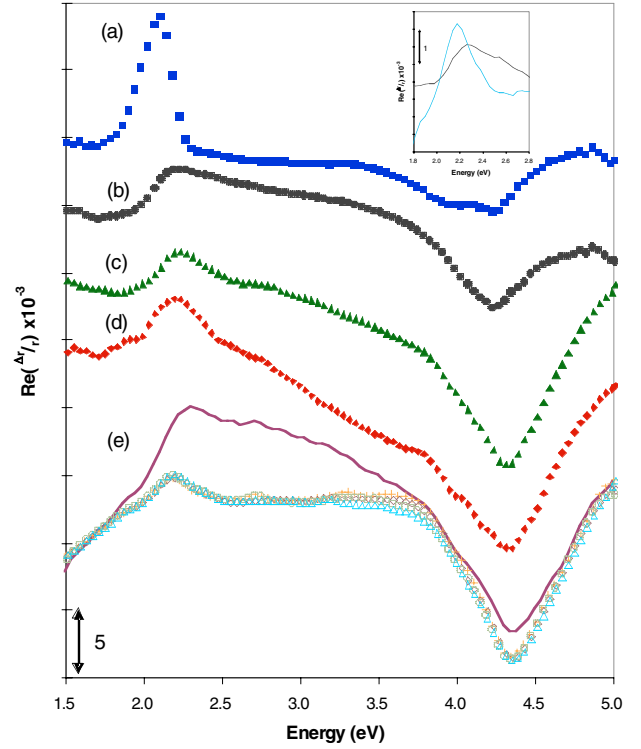


Fig. 1: (Colour on-line) RA Spectra of (a) Cu(110) in UHV (■), (b) thermally roughened Cu(110) in UHV (●), (c) Cu(110) in water (▲), (d) Cu(110) in 10 mM H_2SO_4 (◆) and (e) Cu(110) in 10 mM HCl at -0.35 V (solid line), -0.55 V (△), -0.60 V (○), -0.65 V (◇) and -0.70 V (+) vs. Ag/AgCl. The insert shows a comparison of a region of the spectrum of 1b and the 1e spectrum obtained at -0.55 V on the same expanded vertical scale.

increase in the width and intensity of the 4.3 eV negative feature with time. In H_2O this feature doubled in intensity over 90 minutes while in H_2SO_4 it increased fourfold over 90 minutes.

The RAS of the Cu(110) surface in HCl could be stabilised electrochemically and showed a strong dependence on the applied potential. The cyclic voltammogram of the Cu(110)/electrolyte interface (fig. 2) suggests that Cl^- adsorbs on the surface at -0.40 V when the potential was scanned in the positive direction and desorbs from the surface at -0.43 V when the potential was scanned in the negative direction. There is thus a small window in the applied potential below -0.50 V in which the Cl^- free Cu(110) surface can be monitored. Figure 1(e) shows the RAS profiles obtained at applied potentials of -0.70 V, -0.65 V, -0.60 V and -0.55 V which correspond to Cu(110) surfaces that are free of adsorbed Cl^- . These profiles show substantial overlaps and are difficult to distinguish on the scale of fig. 1(e). However all begin with a rising signal from 1.5 eV that reaches a peak at 2.2 eV, similar to that observed in H_2O and H_2SO_4 , and that then falls to yield a flat profile that eventually descends into the broad negative peak at 4.3 eV observed from the other surfaces. The region of the 2.2 eV peak is shown in more

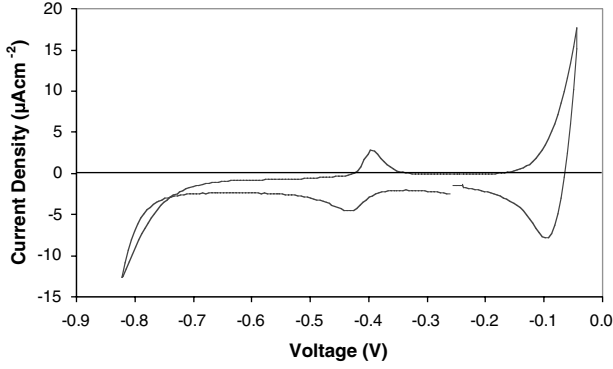


Fig. 2: Cyclic voltammogram of Cu(110) in 10 mM HCl recorded at a scan rate of 10 mVs^{-1} .

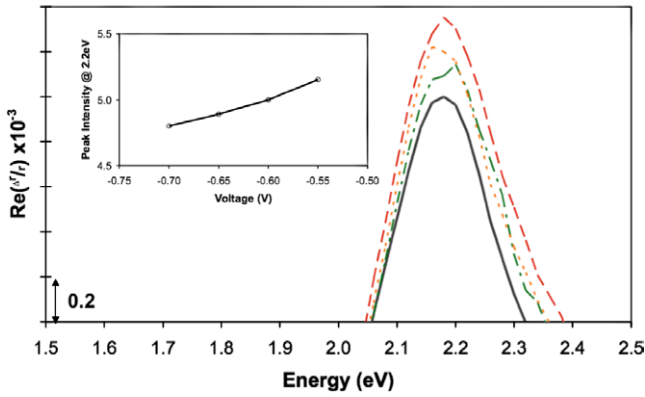


Fig. 3: (Colour on-line) RA spectra of Cu(110) in 10 mM HCl at -0.70 V (solid line), -0.65 V (— · —), -0.60 V (· · ·) and -0.55 V (— —) vs. Ag/AgCl. The inset shows the peak intensity at 2.2 eV as a function of applied voltage.

detail in fig. 3 together with an insert showing the increase in the intensity of this feature as the applied potential is made more positive. There is no change in the position of the peak as the potential is made more positive but the half width increases from $\sim 0.20 \text{ eV}$ to 0.25 eV . The RAS obtained at an applied potential of -0.35 V and corresponding to the surface with adsorbed Cl^- is shown by the full line in fig. 1(e). This rises from 1.5 eV to reach a stronger and broader peak at 2.3 eV than that observed from the Cl^- free surfaces and the profile then falls in intensity with a smoothly increasing curvature towards the negative peak at $\sim 4.4 \text{ eV}$.

Discussion. — The RAS of well-prepared Cu(110) surfaces in UHV (fig. 1(a)) has been extensively studied, is well understood and has been recently reviewed [6,7,17–28]. These surfaces show a strong positive, symmetrical, sharp peak at 2.1 eV , $\sim 0.25 \text{ eV}$ wide, and a broader negative bimodal feature at $\sim 4.2 \text{ eV}$. The major contribution to the intensity of the 2.1 eV peak is a transition between surface states at the \bar{Y} -point of the surface Brillouin zone though there are also contributions from surface modified interband transitions near the

\bar{X} -point of the bulk Brillouin zone and a “Drude” term associated with anisotropic free-electron transport in the surface [22,25,27]. The occupied surface state is $\sim 0.4 \text{ eV}$ below the Fermi level and increasing the temperature of Cu(110) in UHV causes a thermal depopulation of the state and results in a fall in intensity of the 2.1 eV peak [22,27]. This transition between surface states is also absent at room temperature from an almost uniformly roughened Cu(110) surface created in UHV by a thermal treatment (fig. 1(b)) and which results in a proliferation of narrow terraces ~ 5 to 15 nm wide separated by monatomic steps roughly aligned along the $[001]$ direction [22]. The transition between surface states does not occur on the roughened surface due to the confinement of the surface states on the narrow terraces which lifts the initial state above the Fermi level [22,23]. This spectrum, shown in fig. 1(b), thus reveals the profile of the weaker temperature-independent contributions to the spectrum which give rise to a weak asymmetrical feature at $\sim 2.3 \text{ eV}$ and a strong broad negative feature at 4.2 eV that is discussed later.

The peak observed at 2.2 eV in the RAS of the Cu(110) surface in H_2O , H_2SO_4 (fig. 1(c), 1(d)) and HCl at applied potentials below -0.50 V (fig. 1(e)) occurs in the same spectral region as the more intense symmetrical transition between surface states observed from the well-prepared Cu(110) in UHV (fig. 1(a)) and the weaker asymmetric peak observed from the roughened Cu(110) surface in UHV (fig. 1(b)). The inset to fig. 1 shows a comparison of the line shapes of the latter peak with the peak observed from Cu(110) in HCl (fig. 1(e)). The two features have a quite different lineshape. However the peak observed from Cu(110) in H_2O , H_2SO_4 and HCl has a very similar lineshape and linewidth (fig. 3) to the more intense feature associated with the transition between surface states observed from the Cu(110) surface in UHV (fig. 1(a)). It is 0.1 eV higher in energy, a shift which could arise from an overlap with the asymmetric spectrum of the other two contributions to the RAS in this region of the spectrum (fig. 1(b)), as found from some studies at high temperature [22], or from a difference between the UHV and liquid environments. Consequently we attribute the 2.2 eV peak observed from the Cu(110) surface under the liquids to a transition between surface states at the \bar{Y} -point of the surface Brillouin zone. We will return to a consideration of the intensity of this feature later.

We attribute the instability of the RAS profile observed from the Cu(110) surface in H_2O and H_2SO_4 to the high reactivity of the Cu(110)/liquid interface [31,32] and to the tendency of Cu to oxidise. The timescale of the experiments indicates that this process does not lead to an equilibrium structure over periods less than 90 minutes.

The strong negative feature observed at 4.2 eV from the roughened surface in UHV (fig. 1(b)) is associated with surface roughness and $[001]$ steps [22,28,33]. The shape and position of this feature is sensitive to details of surface roughness as illustrated by its temperature dependence:

there is a reversible shift in position between 4.2 eV and 4.3 eV at a roughening transition at ~ 1000 K [22]. The similarities between the RAS profiles of the thermally roughened Cu(110) surface and the surface in the three electrolytes between 3.5 eV and 5.0 eV suggests that the electrochemical polishing process produces an atomically rough surface and that this is the origin of the 4.3 eV feature. The high-temperature thermal roughening process will give the Cu(110) surface considerably more kinetic freedom than the electro-polishing process with the likely result that in the latter case the terraces are less uniform. We suggest that these differences in surface roughness explain why the 2.2 eV transition between surface states is present in the RAS of the Cu(110)/electrolyte interfaces but not in that of the thermally roughened surface. Its absence from the RAS of the thermally roughened surface is probably due to the depopulation of the initial state by surface confinement on the narrow terraces. Since we expect there to be a much wider range of terrace size on the electro-polished surface the initial state will be populated on some terraces this giving rise to the transition though at a reduced intensity when compared to the RAS of well-prepared surfaces in UHV. Support for this view is provided by *in situ* scanning tunnelling microscopy (STM) studies of the electro-polished Cu(110) surface. A $139\text{ nm} \times 139\text{ nm}$ region showed 11 terraces with widths ranging from 4 nm to 35 nm with 5 terraces of width 10 nm or less [34].

The attribution of the 2.2 eV feature observed from the Cl^- free Cu(110)/electrolyte interface, and to the interfaces with H_2O and H_2SO_4 , to the transition between surface states at the \bar{Y} -point observed in UHV is supported by a consideration of the results of ER studies. Early ER studies of the Cu(110) surface in electrolytes [9,10], in which the spectra are collected separately along the $[1\bar{1}0]$ and $[001]$ directions, reveal a sharp feature at 2.2 eV in the spectrum collected from each direction and a broad feature at ~ 4.4 eV from the spectrum obtained from the $[1\bar{1}0]$ direction. These features are clearly related to the difference spectra (eq. (1)) obtained in our RAS studies of the Cu(110) surface in H_2O , H_2SO_4 and HCl . In the ER studies these features were attributed to interband transitions and differences in the directional dependence of the surface conductivity. Transitions between d -band states and surface states have been observed in ER studies of interfaces between liquids and single-crystal Ag and Au surfaces. These studies show an increase in the energy of the transition as the applied potential, V , is varied in the positive direction of 0.9 eV V^{-1} for Ag(100) and 1.3 eV V^{-1} for Ag(111) [15]. This variation is interpreted as arising from the screening of the applied potential inside the metal which means that the d -bands will be much less affected by the potential than the surface states which are more responsive to the potential in the electric double layer [12–15]. Applying a potential thus results in a shift in the transition energy between d -bands

state and surface states. However a transition between surface states should be independent of the applied potential as we observe (fig. 3). An analysis of the ER results from the Ag/liquid interfaces [15] showed that the surface states were rather broad with widths of 0.6 eV to 0.8 eV. This inhomogeneous broadening is expected from considerations of the sensitivity of surface states, but not band states, to variations in the local potential in the electric double layer caused by fluctuations in the orientation of water dipoles [12,15]. Since RAS is a local probe a transition between surface states is not expected to be broadened by the variation in the potential in the electrical double layer since the initial and final surface states will experience the same local potential. This explains why the 2.2 eV peak has almost the same half width, ~ 0.25 eV, as the transition observed from surfaces in UHV (fig. 3).

We turn now to a consideration of the increase in the intensity of the 2.2 eV feature as the applied potential is increased in a positive direction. We have no clear explanation for these results. The intensity of a feature in an RA spectrum is dependent on the degree of anisotropy, the intrinsic intensity of the transition and the number of sites giving rise to the transition. The work of Sun *et al.* [6,7,35] shows that the intensity of this transition is very dependent on changes in surface anisotropy. It is difficult to see how a variation in the potential applied to the Cu(110) surface could change its anisotropy though it is possible that an increasing positive potential leads to the desorption of H impurities that disrupt the surface states in a similar way to the adsorption of CO on Cu(110) in UHV [6]. This would lead to an increase in anisotropy and an increase in the intensity of this feature as observed. We discount the possibility that the positive increase in the applied potential, which is expected to shift the initial surface state closer to the Fermi level, leads to a depopulation of the initial surface state since this would cause a fall in the intensity of the peak. We also note that the adsorption of Cl^- on the Ag(100) and Ag(111) surfaces leads to a decrease in the intensity of transitions between d -band states and surface states located above the Fermi energy [15]. It was suggested that this change is due to a change in the wave function of the surface state. There is also a surface state on Ag(100) that is just below the Fermi energy. Transitions from band states to this state are only seen when a positive potential shifts the state above the Fermi level when two features are observed which are attributed [15] to the formation of bonding and antibonding states separated by 1.25 eV arising from the formation of a chemical bond between the surface state and adsorbed Cl^- . This transition continues to be observed at Cl^- coverages of about half a monolayer. It is difficult to reconcile these observations with the results obtained on the Cu(110)/liquid interface (fig. 3). However, we note that the cyclic voltammogram (fig. 2) indicates that an increasing positive potential might lead to an increase in low levels of adsorbed Cl^- . If this gave

rise to more ordered structures, with larger terraces, this could increase the intensity of the 2.2 eV peak due to an increase in the population of occupied initial states or to a reduction in the scattering of the surface state wave functions. In the latter context it should be noted that very low levels of the adsorption of CO on the Cu(110) surface in UHV have a dramatic effect on the intensity of the RAS measurements of the transition between surface states due to the scattering of the surface state wave functions and that this scattering is extremely sensitive to the shape and uniformity of surface structures on the nanoscale [6,7,35].

Conclusions. – The RA spectral profiles of electropolished Cu(110) surfaces in H₂O, H₂SO₄ and HCl are very similar and show a sharp positive feature at 2.2 eV and a broad negative feature at 4.2 eV. The 4.2 eV feature is similar in profile, but at a slightly lower energy, to a feature observed on atomically roughened Cu(110) surfaces in UHV and associated with monatomic steps aligned along [001] directions. We identify the sharp feature at 2.2 eV with the transition between surface states at the \bar{Y} -point of the surface Brillouin zone that is observed in the RAS of well-prepared Cu(110) surfaces in UHV. The results of ER studies of transitions between band states and surface states indicate that, due to the screening of the bulk material from applied potentials and the variations in the local potential in the electrical double layer caused by fluctuations in the orientation of water dipoles, such transitions increase in energy with applied positive potentials and are inhomogeneously broadened to ~ 0.8 eV. This leads us to expect that the energy of a transition between surface states that is sensitive only to the local potential in the electric dipole layer should be independent of the applied potential and should remain rather narrow, as observed (fig. 3). We have no clear explanation for the rise in the intensity of this transition as the applied potential is increased.

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