

A LEED Fine Structure Study of Oxygen Adsorption on Cu(001) and Cu(111)*

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Abstract

LEED fine structure features are due to an interference between the measured beam (usually the specular) and a pre-emergent beam. This pre-emergent beam is internally reflected at the surface potential barrier and is subsequently diffracted by the substrate into the same direction as the beam under observation. As a result of the long-range image nature of the barrier potential, a rydberg-like series of peaks, converging on the emergence energy of the pre-emergent beam, is produced. Fine structure features, or threshold effects, occur at very low incident beam energies (typically <40 eV) and are extremely sensitive to the surface order of the crystal. The changes that occur to the fine structure features when atoms are adsorbed onto the surface contain information regarding the nature of the chemisorption process. In some cases it is possible to infer adsorption sites. In this work measurements are made of the fine structure features for the (001) and (111) surfaces of copper as a function of oxygen exposure. Analysis of these data shows that oxygen adsorption on Cu(111) takes place in a disordered manner and results in a roughening of the surface, while for Cu(001) the adsorption produces an ordered overlayer with oxygen atoms in the 2-fold bridge sites.

1. Introduction

One major area that the measurement and analysis of LEED fine structure has primarily been concerned with is refining estimates of the surface potential barrier shape. In particular, the position of the image plane and the degree of saturation of the barrier near the surface are the main items of interest. The other major area is the analysis of adsorption processes and the determination of adsorption sites. In this work we have used LEED fine structure measurements to investigate the initial stages of oxidation of two of the low index planes of copper.

2. Experimental

A high resolution LEED spectrometer, described previously (Thurgate and Hitchen 1985), was used to make measurements. The spectrometer consists of a 127° cylindrical deflecting analyser to monochromate electrons from a hot filament. The specularly scattered electrons were collected by a three grid retarding field analyser. The energy resolution of the system was 70 meV

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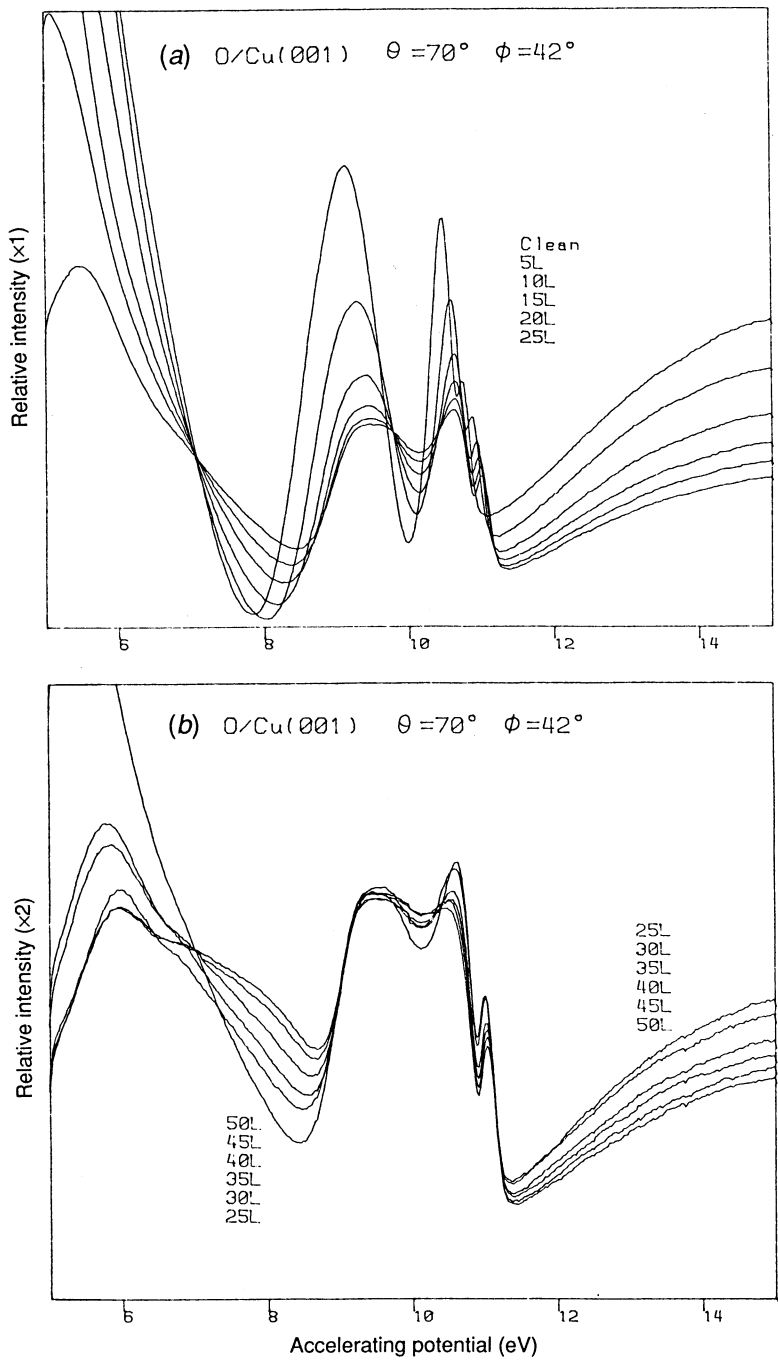


Fig. 1. Variation of LEED fine structure from Cu(001) with oxygen exposure for $\theta = 70^\circ$ and $\phi = 42^\circ$.

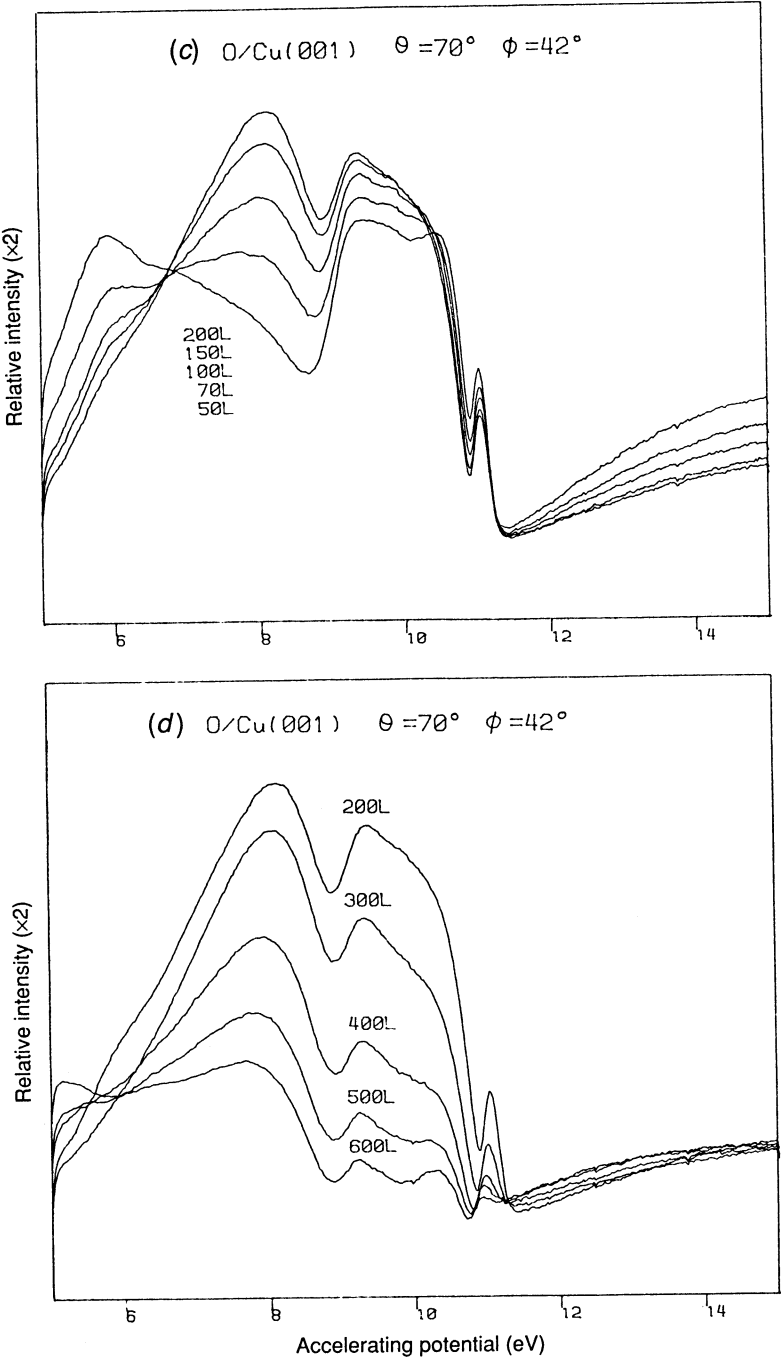


Fig. 1. (Continued)

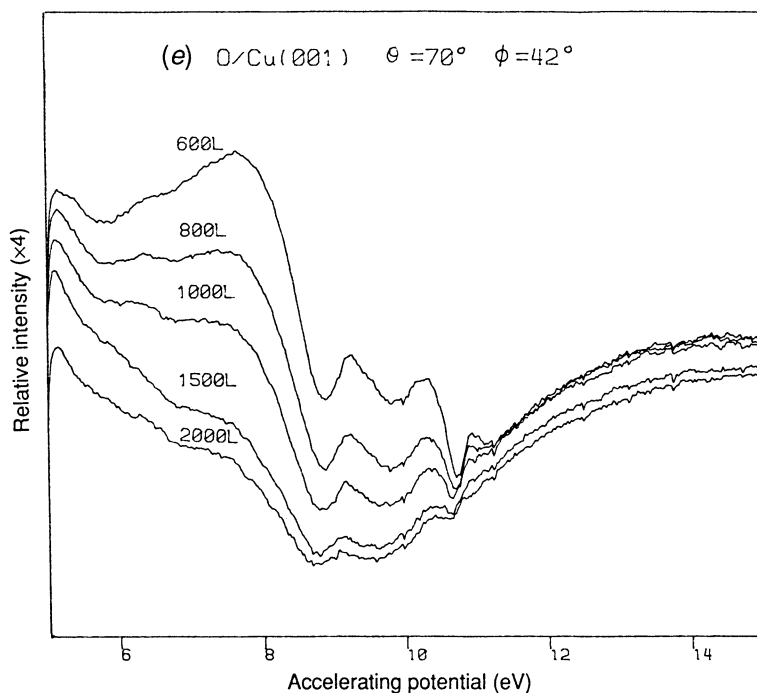


Fig. 1. (Continued)

and the angular resolution 1° . However, the apparent energy resolution for an intensity-potential (I/V) spectrum depends upon factors such as the incident beam conditions, the angular resolution and which pre-emergent beam is causing the fine structure (Hitchen and Thurgate 1988*a*). Both the angle of incidence and azimuth could be varied continuously. These angles were determined using techniques described previously (Hitchen and Thurgate 1988*b*).

The Cu(001) and Cu(111) samples were cut from a single crystal ingot after being oriented using a Laue X-ray backscatter camera. The samples were mechanically ground using silicon carbide paper and then mechanically polished with diamond paste. The final step involved electropolishing in a solution of orthophosphoric acid and water. The crystals were then placed in the UHV chamber and repeatedly ion bombarded and annealed until a clean, well ordered surface was produced, based on LEED and AES measurements.

3. Results and Discussion

Cu(001)

Figs 1 to 3 show the change in the fine structure, as a function of oxygen exposure, for the Cu(001) surface. Figs 1*a*–1*e* show the spectra obtained when near the $\langle 11 \rangle$ azimuth. For the clean surface a series of peaks due to the emergence of the $\bar{1}\bar{1}$ beam was seen. By an exposure of 300 L this had

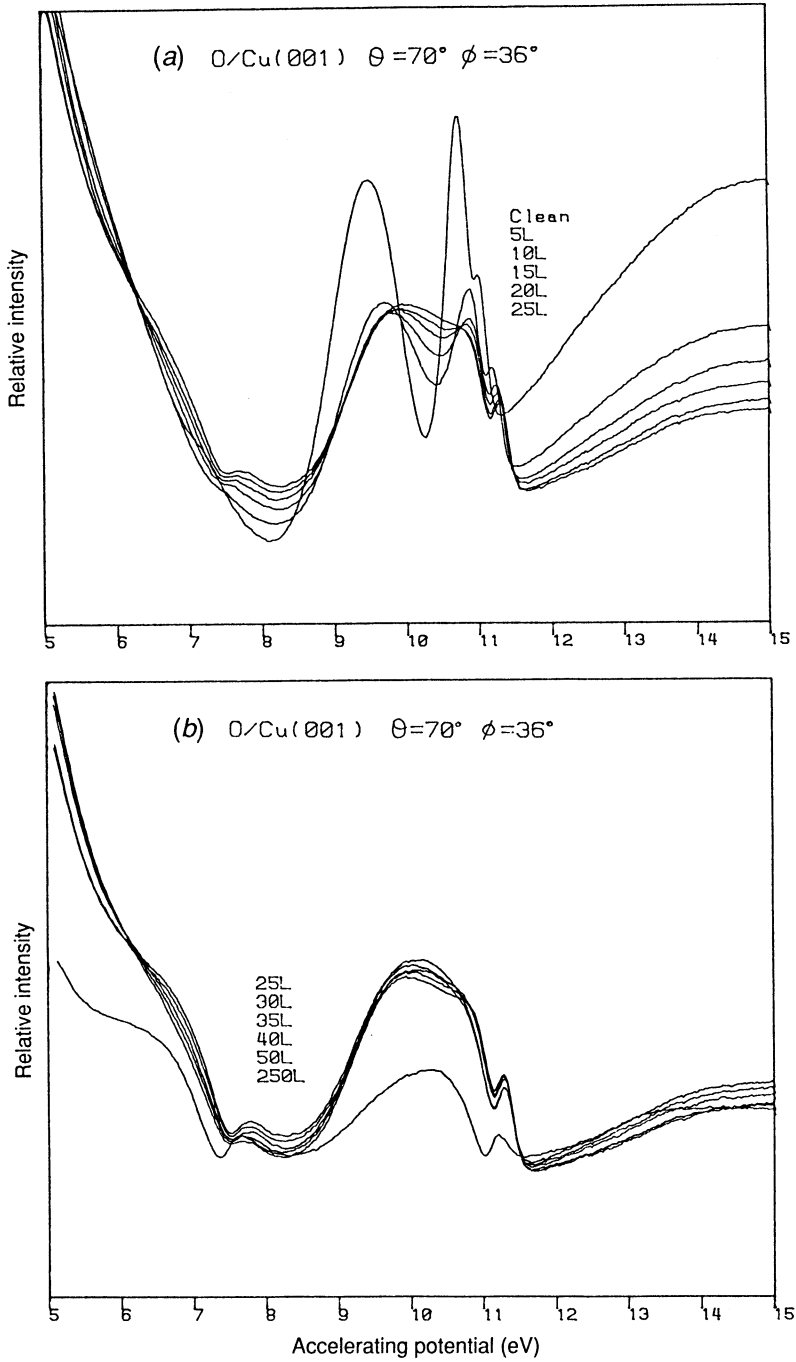


Fig. 2. Variation of LEED fine structure from Cu(001) with oxygen exposure for $\theta = 70^\circ$ and $\phi = 36^\circ$.

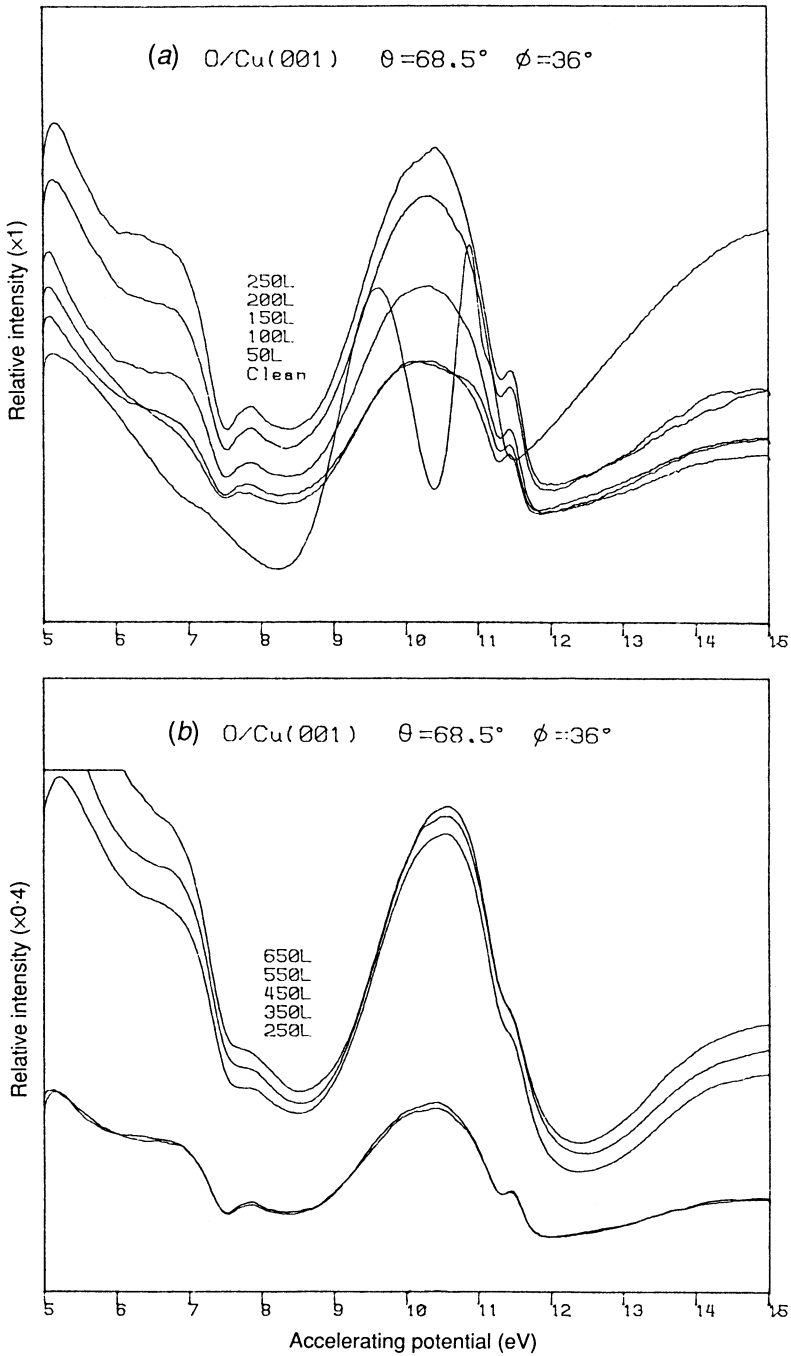


Fig. 3. Variation of LEED fine structure from Cu(001) with oxygen exposure for $\theta=68.5^\circ$ and $\phi=36^\circ$.

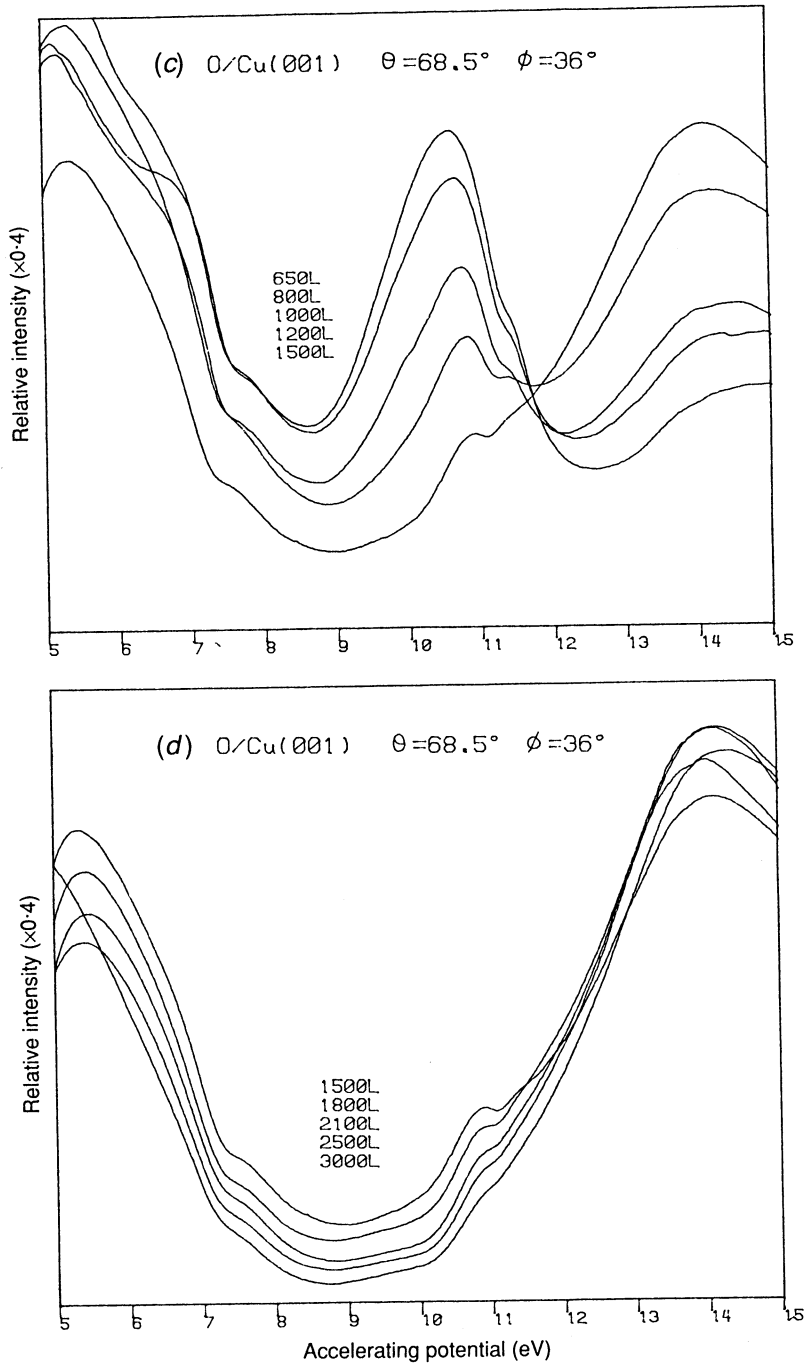


Fig. 3. (Continued)

transformed into a broad three peak feature. This was in fact the superposition of fine structure due to the $\bar{1}0$ and $\bar{1}\bar{1}$ beam emergences (Hitchen and Thurgate 1988*b*).

As the exposure increased from the clean surface, the $\bar{1}0$ feature initially increased in intensity and the $\bar{1}\bar{1}$ feature changed shape. At 50 L a 'hump' at 8 eV, due to the $\bar{1}0$ emergence, was visible. There was also a double peak centred around 10 eV. The lower energy peak was due to the $\bar{1}0$ emergence and the higher energy one to the $\bar{1}\bar{1}$ emergence. Further exposure resulted in an increase in intensity of the $\bar{1}0$ peaks relative to the $\bar{1}\bar{1}$ peaks, such that by 200–300 L the double peak structure was no longer observed. The spectrum now consisted of a broad three peak feature. At this exposure there was a maximum in the intensity of the peak structure.

Further exposure to oxygen resulted in a decrease in peak intensities. The $\bar{1}0$ peaks decreased relative to the $\bar{1}\bar{1}$ peaks so that by 600 L (Fig. 1*d*) the double peak structure centred around 10 eV was again visible. Exposure to more oxygen up to 2000 L (Fig. 1*e*) resulted in a general attenuation of the features with no significant changes in peak structure. These changes in the spectra indicate the presence of a structure phase change at an exposure of approximately 300 L.

Fig. 1 also shows a slight shift in the apparent emergence energy of the $\bar{1}\bar{1}$ feature, reflected by the position of the peak at about 11 eV, with oxygen exposure. This peak increased in energy rapidly up to 50 L (Fig. 1*b*), remained fairly constant from 50 to 200 L (Fig. 1*c*) and then decreased from 200 L up to the maximum exposure of 2000 L (Figs 1*d* and 1*e*). This change was simply a reflection of the change in work function. The trend of this change agreed with the measurements of other workers (Hofmann *et al.* 1978; Thurgate and Jennings 1983; Benndorf *et al.* 1979). These measurements showed that, for a temperature of 300 K, the work function increased to a maximum value at around 100 L and then slowly decreased with further exposure, for a temperature of 300 K. Increasing the temperature of the crystal shifted this maximum to lower exposures. This decrease in work function is said to be indicative of an incorporation of oxygen into the copper surface (Hofmann *et al.* 1978).

Figs 2*a* and 2*b* show the effect of oxygen adsorption at 9° from the $\langle 11 \rangle$ azimuth. At this angle the $\bar{1}0$ and $\bar{1}\bar{1}$ emergence energies were sufficiently different so that the fine structure associated with each no longer overlapped. There was a gradual change from the clean spectrum to that for the $c(2 \times 2)$ structure at about 250 L.

Figs 3*a*–3*d* show similar spectra at the same azimuth angle as Fig. 2 but over a larger range of oxygen exposures. Again there was a gradual change, up to an exposure of 350 L. In fact the spectra at 250 and 350 L were essentially identical (Fig. 3*b*). Between 350 and 450 L there was a sudden jump in intensity such that the $\bar{1}\bar{1}$ feature is about twice the size as that for the clean surface. This jump was not observed for the azimuth of Fig. 1. The most noticeable change in structure was for the small peaks at about 8 and 11.5 eV. In each case the peak was reduced in intensity relative to the larger features. In fact the 11.5 eV peak only appeared as a shoulder on the large peak at 10 eV. Further exposure to oxygen decreased the size of the fine structure until at

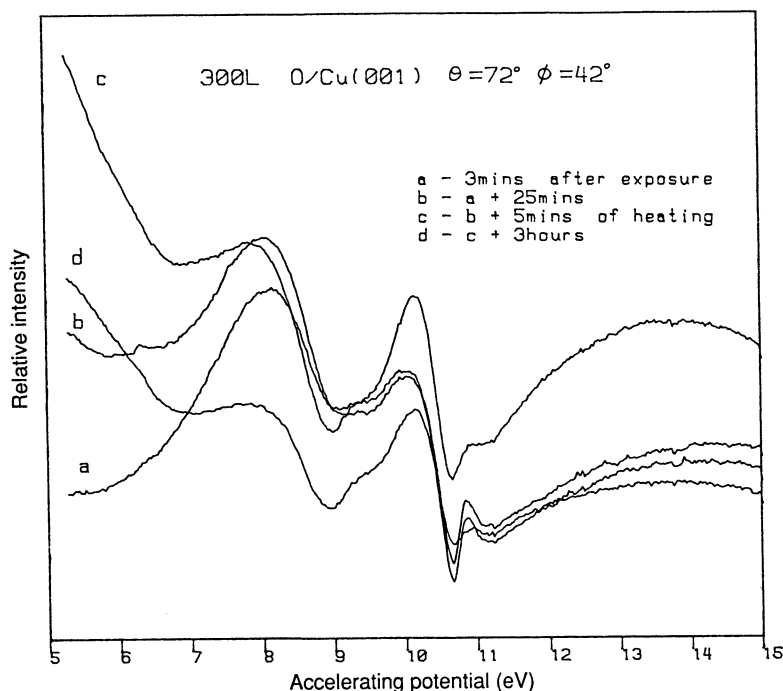


Fig. 4. Effect on LEED fine structure of heating oxygen exposed Cu(001).

3000 L it had all but disappeared (Fig. 3d). Again there seemed to be an overlayer phase change at around 350 to 450 L that coincided with the reversal of the work function change.

Finally, Fig. 4 shows the effect of heating the crystal after exposure to oxygen. Scan (a) was taken immediately after the clean surface was exposed to 300 L of oxygen. Note the well defined peaks at 8, 10 and 11 eV, due to the $\bar{1}0$, $\bar{1}1$ and $\bar{1}\bar{1}$ emergences respectively. Scan (b) was taken after the sample was left for 25 minutes and produced essentially the same result, apart from a change in slope between 5 and 7 eV. After 5 minutes of mild heating, to a dull red colour, there was noticeable change in structure, as shown in scan (c). The slope between 5 and 7 eV increased significantly, the peak at 10 eV increased in intensity and the peak at 11 eV reduced in intensity and was no longer well defined. Also, a new feature at about 9.5 eV, due to the $\bar{1}0$ emergence became apparent. Scan (d) was taken after a further delay of 3 hours and shows no change in structure from scan (c) apart from a reduction in intensity of the whole feature. The changes between scan (b) and (c) were similar in effect to the result of increasing oxygen exposure from 300 L, as shown in Fig. 1.

It would seem from the evidence presented that a stable overlayer phase, in which oxygen lies above the surface, was reached at an exposure of 300–400 L. Further exposure resulted in oxygen incorporation. This would account for the decrease in fine structure intensity if incorporation produced a rougher surface (Thurgate and Jennings 1985), perhaps by creating a rumpled surface as proposed by Hofmann *et al.* (1978).

However, the results reported here are more consistent with the results of an investigation of oxygen adsorption on Cu(001) by Scheidt *et al.* (1988). A summary of their work follows.

A spherical copper surface, centred on the (001) pole, was used to examine the effects of oxygen adsorption, temperature and step density on the LEED patterns and spot profiles. It was found that for the (001) pole a 4-spot pattern centred around the $(\frac{1}{2}, \frac{1}{2})$ positions was visible up to an exposure of 2000 L, a $c(2 \times 2)$ pattern was visible from 2000 to 6000 L and a $(\sqrt{2} \times \sqrt{2})R45^\circ$ pattern was seen for exposures larger than 6000 L. These observations were for a temperature of 300 K. When the clean surface was heated the transition from the 4-spot to the $c(2 \times 2)$ pattern occurred at lower exposures. At 420 K the $c(2 \times 2)$ structure was formed immediately and no 4-spot pattern was seen. Also, the $(\sqrt{2} \times \sqrt{2})R45^\circ$ structure could be seen for an exposure of only 360 L if the sample was annealed to 600 K afterwards.

Increasing the step density by translating the crystal from the (001) pole resulted in the 4-spot pattern disappearing and the $c(2 \times 2)$ spots becoming visible. The amount of translation depended upon oxygen exposure. For 100 L the transformation occurred 4 mm from the pole (corresponding to a surface misaligned by 4°), while for 1500 L it occurred at 0.5 mm (misaligned by 0.5°). In short, the transformation of the 4-spot pattern to the $c(2 \times 2)$ pattern was activated by an increase in either oxygen exposure, sample temperature or surface step density.

Spot profiles were also measured and from their shapes and the above results the following was concluded. For a smooth, well aligned Cu(001) surface molecular adsorption takes place at low oxygen coverages, followed by atomic $c(2 \times 2)$ adsorption in the 2-fold bridge position, followed by a $(\sqrt{2} \times \sqrt{2})R45^\circ$ structure at higher coverages. For misaligned or rough surfaces the molecular structure is absent and the atoms adsorb in the 4-fold hollow site for the $c(2 \times 2)$ structure.

This work by Scheidt *et al.* (1988) would seem to explain the differences reported by other workers in the observation of LEED patterns and the exposure at which they occur.

Previous observations (Thurgate 1982) with the crystal used in this LEED fine structure investigation reported that a plateau region occurred at around 300 L in a plot of oxygen Auger signal versus exposure. Also, a $c(2 \times 2)$ pattern with 'diffuse' half order spots was seen for an exposure of 300 L, similar to the pattern observed by Yang *et al.* (1983) at 600 L. It seems likely that this was in fact the 4-spot pattern as heating the crystal resulted in a sharpening of these 'diffuse' half order spots. This corresponded to the temperature activated transformation from a 4-spot to a $c(2 \times 2)$ pattern reported by Scheidt *et al.* (1988).

To investigate the adsorption site for oxygen, theoretical LEED calculations were carried out for a $c(2 \times 2)$ overlayer structure on a Cu(001) surface. The surface potential barrier model of Jones *et al.* (1984) was used in the LEED calculations. Three simple sites were trialled, namely the 1-fold on top position, the 2-fold bridge position and the 4-fold hollow position.

For each configuration a range of values for the overlayer height above the surface were used. These were centred on the equilibrium values determined from simple geometric considerations using a hard sphere model and atomic radii. A range of barrier positions were also used. In all cases there was no good match between the theoretical $c(2 \times 2)$ calculations and the experimental spectra for 300 L of oxygen exposure.

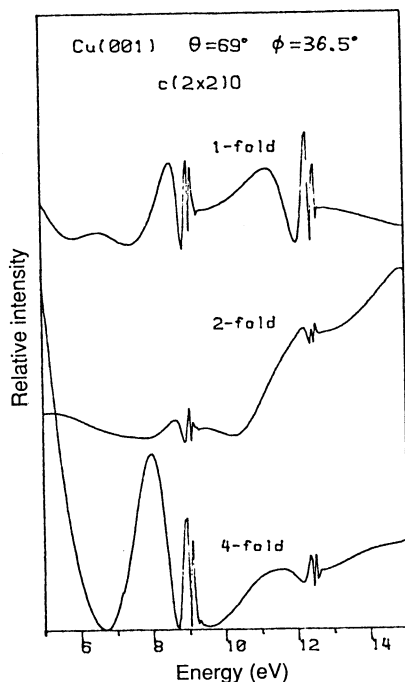


Fig. 5. Theoretical LEED I/V spectra for a $c(2 \times 2)$ oxygen overlayer on Cu(001).

Fig. 5 shows results typical of the calculated spectra for the three sites that were trialled. In each case barrier parameters of $z_0 = -2.5$ and $\lambda = 0.9$ were used. These are the optimal barrier parameters for the clean Cu(001) surface (Hitchen 1990). The overlayer heights above the surface were 3.70 a.u. for the 1-fold position, 2.65 a.u. for the 2-fold and 1.42 a.u. for the 4-fold position. Comparison with the experimental curves of Fig. 3 shows no match. This indicated that if 300 L corresponded to the $c(2 \times 2)$ structure then there was not a simple single adsorption site for the oxygen atoms.

Alternatively, a 300 L exposure may not have been indicative of the $c(2 \times 2)$ overlayer. Other workers (Scheidt *et al.* 1988) have reported values as high as 2000 L to produce the $c(2 \times 2)$ pattern. The 1200 L spectrum of Fig. 3c provides a qualitative match with the theoretical $c(2 \times 2)$ curve for the 2-fold bridge site. If in fact 1200 L does correspond to the $c(2 \times 2)$ overlayer then it is likely that adsorption takes place at bridge sites. The phase change at about 300 L may then have been due to molecular adsorption transforming to atomic adsorption.

Based on the results of Scheidt *et al.* (1988) it is most likely that in this fine structure work oxygen exposure initially resulted in molecular adsorption on the Cu(001) surface. This transformed into the atomic $c(2 \times 2)$ structure at about 300 L. This was reflected by the maximum in fine structure intensity, the decrease in the work function and the plateau in the oxygen Auger signal at this exposure. The fact that this transformation took place at 300 L indicated that the crystal used was slightly misaligned or rough. By 1200 L the $c(2 \times 2)$ overlayer was well established and comparison of the fine structure with theoretical calculations indicated that the favoured adsorption site was the 2-fold bridge position.

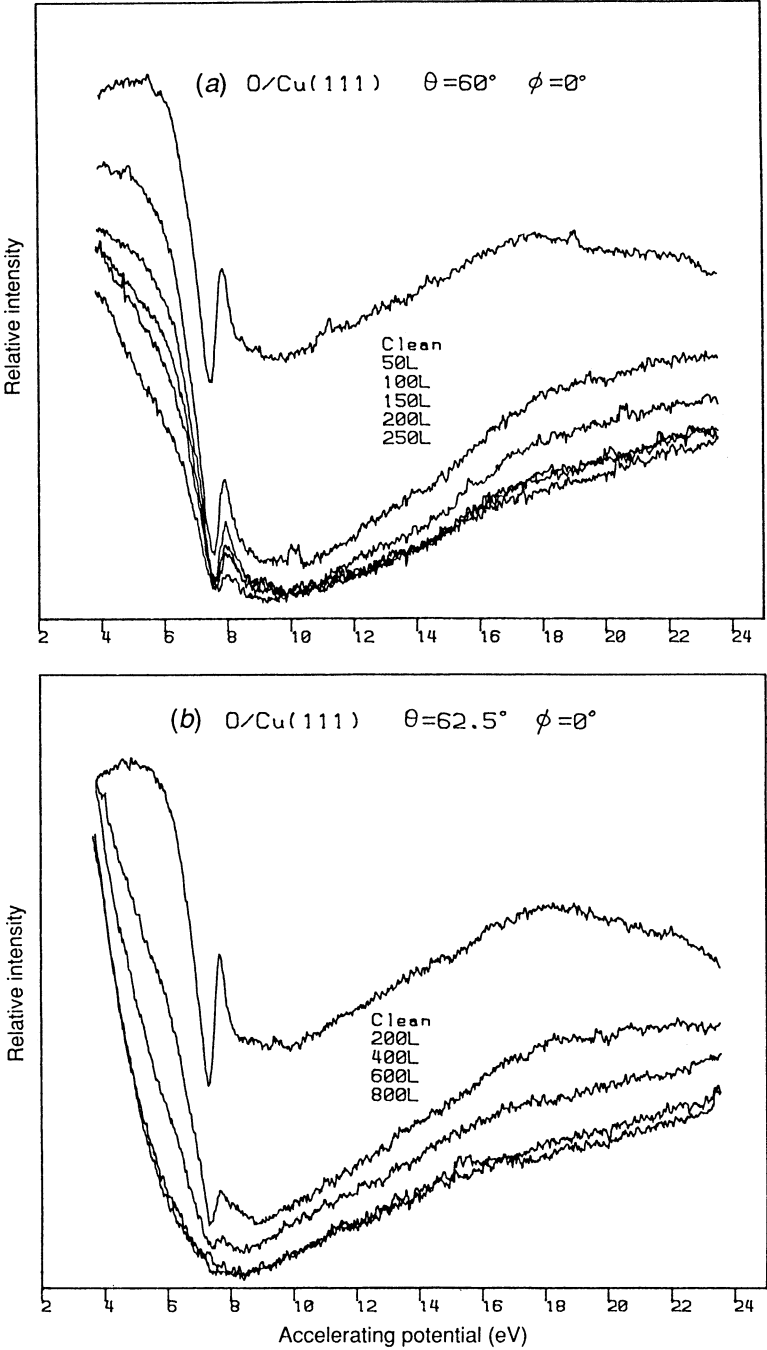


Fig. 6. Variation of LEED fine structure from Cu(111) with oxygen exposure for $\phi=0$: (a) $\theta=60^\circ$ and (b) $\theta=62.5^\circ$.

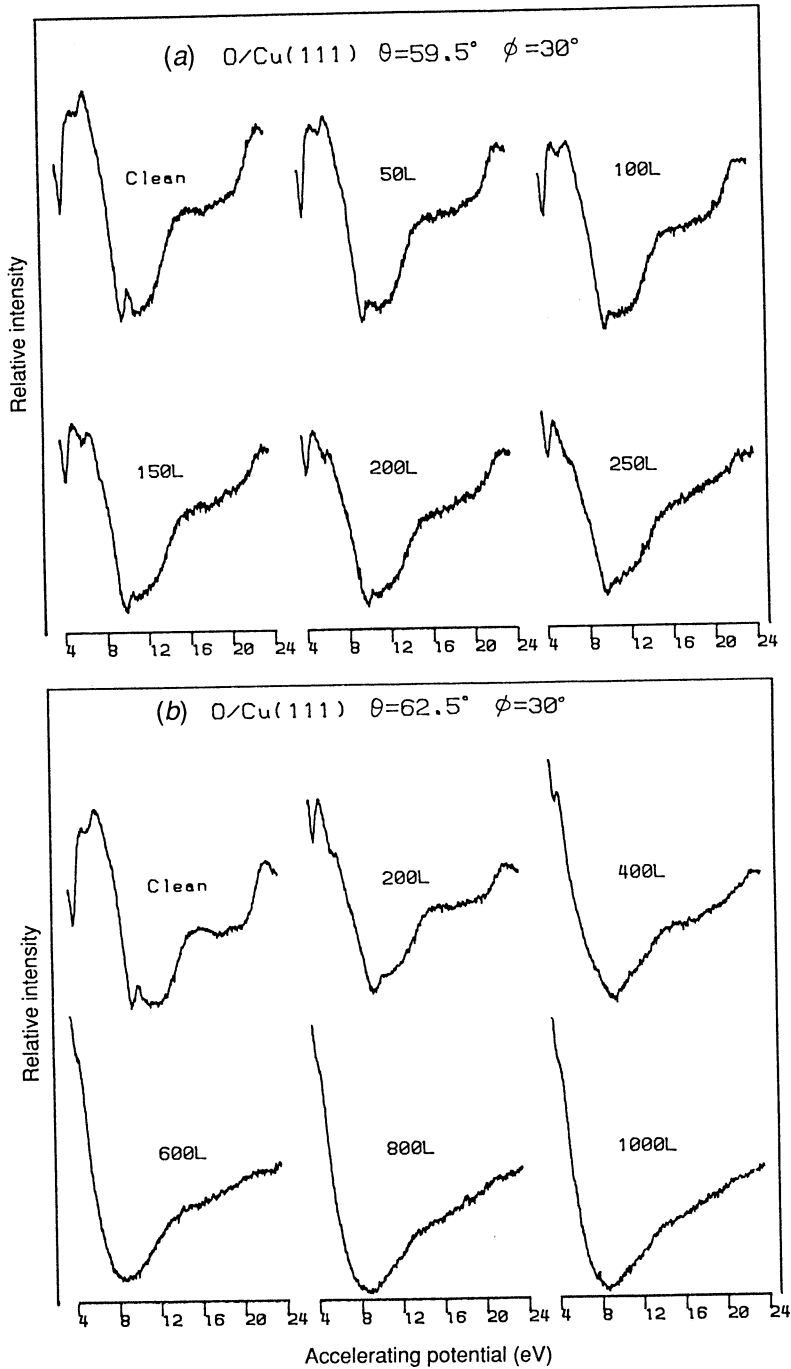


Fig. 7. Variation of LEED fine structure from Cu(111) with oxygen exposure for $\phi = 30^\circ$: (a) $\theta = 59.5^\circ$ and (b) $\theta = 62.5^\circ$.

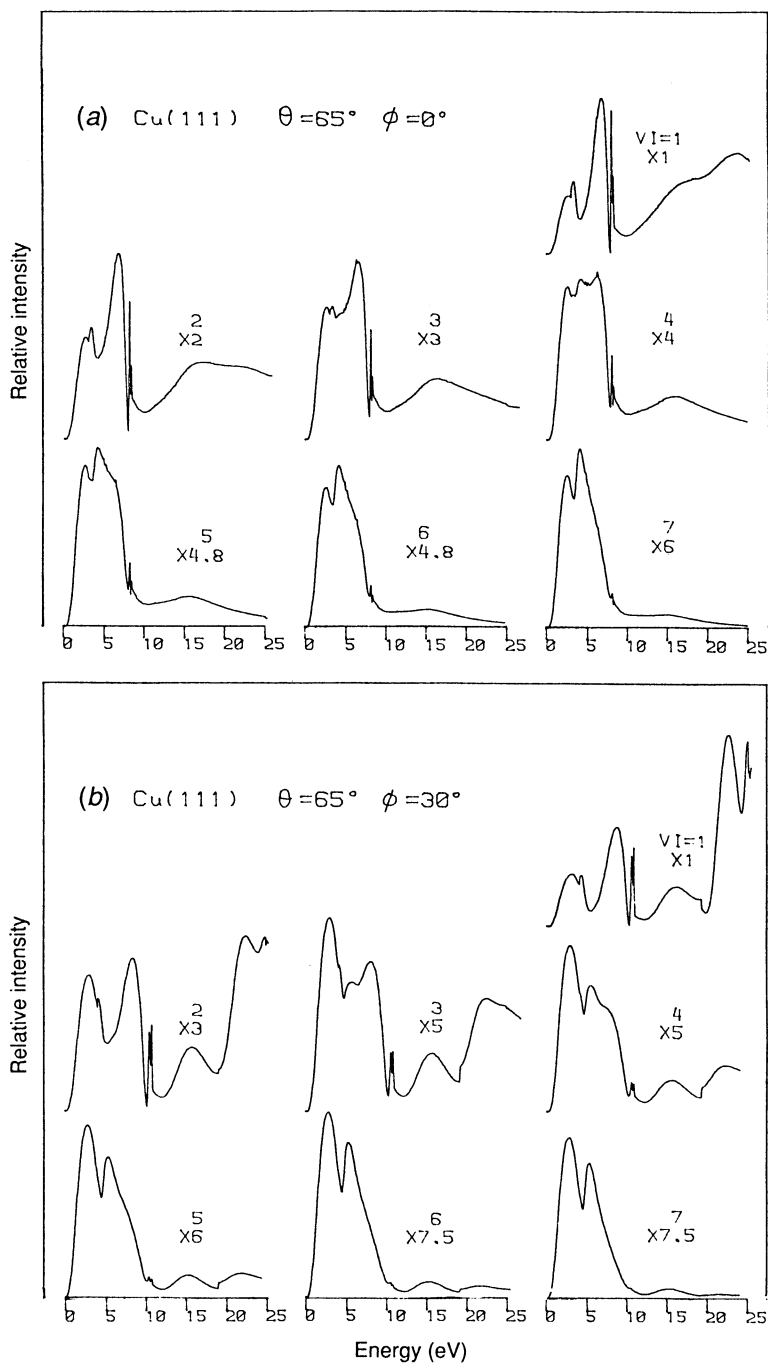


Fig. 8. Variation of theoretical LEED I/V spectra from Cu(111) with increasing barrier damping for $\theta = 65^\circ$: (a) $\phi = 0$ and (b) $\phi = 30^\circ$.

Cu(111)

Figs 6*a* and 6*b* show the changes that occurred in the spectra from the Cu(111) surface for measurements made on the $\langle 10 \rangle$ azimuth. There was a general attenuation of the fine structure features with no significant new features arising. By an exposure of 600 L the fine structure had completely disappeared.

Figs 7*a* and 7*b* show the effect that the adsorption of oxygen had on the fine structure for the $\langle 11 \rangle$ azimuth. Again there was an attenuation of the peaks. The double peak structure between 1 and 8 eV was the combination of a Bragg peak and a fine structure peak. The fine structure feature, with peaks at about 6 and 10 eV, is sitting on the side of a Bragg peak at about 5 eV. There was an alteration in the double peak structure at around 6 eV with the second peak of this double gradually disappearing by 250 L, i.e. the fine structure peak was losing intensity at a greater rate than the Bragg peak. By an exposure of 600 L the fine structure was no longer visible and even the Bragg peak had become only a 'shoulder'.

The changes in the fine structure indicated that oxygen exposure resulted in a disordered adsorption process that produced a roughening of the surface (Thurgate and Jennings 1985). This roughening could have been due to a disordered oxygen atom adsorption and/or surface reconstruction. It was not possible to differentiate between these models using the fine structure data.

The effect of oxygen exposure was reasonably well modelled by an increase in the barrier damping parameter VI . From the calculated spectra of Figs 8*a* and 8*b*, it can be seen that the fine structure changes as oxygen increased were accounted for by an increase in VI . Note that $VI=3$ corresponds to the clean spectrum. The major differences between theory and experiment arise from the fact that the substrate scattering was not adjusted by an increase in the bulk damping to simulate disordered adsorption. This would have reduced the intensity of the Bragg peak at 5 eV.

4. Conclusions

We have used LEED fine structure measurements as a basis for examining chemisorption. The way in which these fine structure features change as atoms adsorb onto the surface provides insight into the processes that are occurring there. For particular systems, such as O/Cu(001), it is possible to determine adsorption sites.

Acknowledgments

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