

## LOW ENERGY ION SCATTERING STUDY OF OXYGEN ADSORPTION ON A Cu{100} SINGLE CRYSTAL SURFACE

### Part II: Kinetics

Th.M. HUPKENS \*

*Fysisch Laboratorium der Rijksuniversiteit Utrecht, Princetonplein 5, 3584 CC Utrecht, The Netherlands*

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The kinetics of the  $O_2/Cu\{100\}$  system at room temperature have been studied with Low Energy Ion Scattering. Two measuring methods have been applied: 1) A method in which the coverage is measured as a function of oxygen exposure. In this method the influence of the ion beam is kept as low as possible. 2) A method in which the oxygen coverage is measured as a function of oxygen pressure, after an equilibrium is reached between adsorption and ion-induced desorption. In both methods the  $O^-$  recoil signal and the  $Ne^+|O$  reflection signal were evaluated. It is known from other scattering studies that at least two essentially different oxygen positions are involved at the Cu{100} surface. We tried to describe all experimental results with a model in which the two types of sites  $i$  become covered independently, with a sticking probability  $S(\theta_i) = S_{0i}(1 - \theta_i)$ . With this model it was possible to reproduce all experimental results using physically plausible parameter values, except for the  $Ne^+|O$  reflection signal when using method 2.

### 1. Introduction

The initial adsorption of oxygen on Cu{100} single crystal surfaces has been studied extensively using Low Energy Electron Diffraction and other surface sensitive techniques [1–22]. According to the LEED-patterns, at room temperature three successive adsorption stages can be discerned (see also ref. [24]):

- *stage A*: for small exposures a “four-spot” pattern, corresponding to small domains of an oblique net, is sometimes observed. This pattern has also been explained by phase–antiphase splitting of some spots of the subsequent structure.
- *stage B*: for exposures up to 0.1 Pa · s the four-spot pattern changes into the  $(\sqrt{2} \times \sqrt{2})R45^\circ - O$  structure.
- *stage C*: this structure gradually changes into the  $(\sqrt{2} \times 2\sqrt{2})R45^\circ - O$  structure for somewhat higher exposures ( $\sim 0.3$  Pa · s).

Note: in the literature different definitions of successive stages are used.

In contrast to the numerous studies on the surface characteristics for the fully developed super-structures, only a few studies on the *kinetics* of the  $O_2/Cu\{100\}$  system have been reported [14–16]. The results of these studies differ widely. In all studies it was assumed that only one type of oxygen site is involved at stage B and all conclusions were based on this assumption. How-

ever, according to recent ISS-studies [17,18,24] already at stage B more than one type of oxygen site is involved. Since the techniques that were used in the kinetics studies (AES, ellipsometry, work function measurements) are not “site sensitive”, the measured curves may also be explained by the combined signals of oxygen at different kind of sites, if suitable  $\theta$ -dependencies are chosen. To resolve this ambiguity, one has to apply techniques that make it possible to measure oxygen at the different kind of sites separately. This is – in principle – possible with low energy ion scattering, by using appropriate incidence directions, such that only those oxygen atoms at one type of site are “visible”. For the oxygen-covered Cu{100} surface this appears to be very difficult in practice, due to the  $90^\circ$  symmetry of this surface (see ref. [24]). Therefore, in the present study we did try to use a different approach, namely by using the different sensitivities of the various oxygen-related signals to the oxygen position, in a situation where oxygen atoms at both types of sites are assumed to be “visible” to the beam. It is well known from earlier work that the positive  $Ne^+|Cu$  scattering signal is not sensitive to deeper layers (especially at a scattering angle of  $\sim 45^\circ$ ), whereas the  $O^-$  scattering signal is rather sensitive to the second layer (see ref. [25]). The same difference in sensitivity should apply for the  $Ne^+|O$  scattering signal and the  $O^-$  recoil signal. Therefore one expects to find differences between the behaviour of both signals as a function of coverage if more than one type of oxygen site is involved. By varying the angles of incidence it may in principle even be possible to find the exact oxygen positions in this

\* Present adress: Kamerlingh Onnes Laboratorium der Rijksuniversiteit Leiden, Nieuwsteeg 18, 2311 SB Leiden.

way. However, the study presented in this paper is only intended to be exploratory. We shall show that it is possible to describe our experimental results by a simple two sites kinetics model. However, if more definite conclusions are desired, extensive time-consuming measurements of the kind presented here will have to be carried out.

## 2. Apparatus and target preparation

The apparatus has been described in ref. [30]. A provision was made to measure the height of several peaks in the energy-spectra quasi-simultaneously with our electrostatic energy analyser. Two Cu{100} samples were used, cut with an approximate deviation from the {100} plane of  $0.8^\circ$  (Cu{100} - 1) and of  $1.4^\circ$  (Cu{100} - 2) respectively. The samples were mechanically and electrolap polished just before they were mounted in the target manipulator.

## 3. Oxygen related signals

In fig. 1 an energy spectrum of an oxygen-covered Cu{100} surface, bombarded with 4 keV Ne<sup>+</sup> ions, is shown. In this spectrum three oxygen-related signals are visible: the O<sup>-</sup> and O<sup>+</sup> recoil peaks and the Ne<sup>+</sup>|O<sub>ad</sub> reflection peak. The fwhm of the O<sup>-</sup> recoil peak is independent of oxygen coverage. Only at high oxygen pressures an increasing background intensity at the high energy side of the peak is observed (see fig. 2). In the spectrum for positive ions a relatively high background is observed. This background varies approximately proportionally to the height of the Ne<sup>+</sup>|O<sub>ad</sub> peak, so only a small error is made in relative measurements, if the total height is taken instead of the peak height corrected for the background intensity. This was checked by plotting the heights of a Gaussian curve - fitted through the

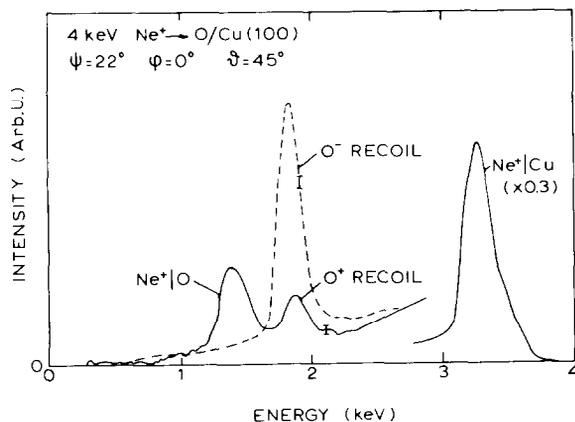


Fig. 1. Energy spectrum of an Ne-bombarded Cu(100) surface.

Ne<sup>+</sup>|O<sub>ad</sub> peak, corrected for background - together with the uncorrected peak height as a function of oxygen pressure. With both methods the same curve was produced.

The shape of the O<sup>+</sup> recoil peak, however, changed somewhat for high oxygen pressures. Besides, this peak is rather small compared to the background signal. Therefore this signal was not used any further.

## 4. Measuring methods

Two different measuring methods were used in this study:

### 4.1. The exposure method

In this method the oxygen-related signals are measured as a function of the exposures (Pa · s), i.e. of the amount of oxygen that is admitted to the surface. The influence of the ion beam on the adsorption process is as low as possible. The procedure is as follows:

- (1) The surface is cleaned by cycles of annealing and ion-bombardment.
  - (2) The ion beam is switched off.
  - (3) The surface is exposed to a certain amount of oxygen ( $L$ ).
  - (4) The oxygen is pumped away (time constant typically  $< 1-3$  s).
  - (5) The signal of Ne<sup>+</sup> ions scattered by the adsorbed oxygen atoms ( $Y_L^+$ ) as well as the O<sup>-</sup> recoil signal ( $Y_L^-$ ) are measured.
  - (6) The surface is further cleaned by ion bombardment.
- Care was taken to avoid damage to the surface by using small incidence angles.

The cycle is repeated, starting from point (2), with increasing exposures.

### 4.2. The pressure method (see ref. [26]).

This method involves the measurement of the peak heights  $Y_{eq}^+$  (Ne|O reflection) and  $Y_{eq}^-$  (O<sup>-</sup> recoil) when an equilibrium is reached between adsorption and ion-induced desorption at a given pressure. If no absolute calibration of the actual coverage can be made by using other techniques, these measurements have to be carried out until both signals reach a maximum, but in this case it appeared that the O<sup>-</sup> signal did not reach a maximum until impractically high pressures; even though  $Y_{eq}^+$  had reached a constant level.

## 5. Experimental results

The results for all measurements using the exposure method are shown in fig. 3a and 3b. The results ob-

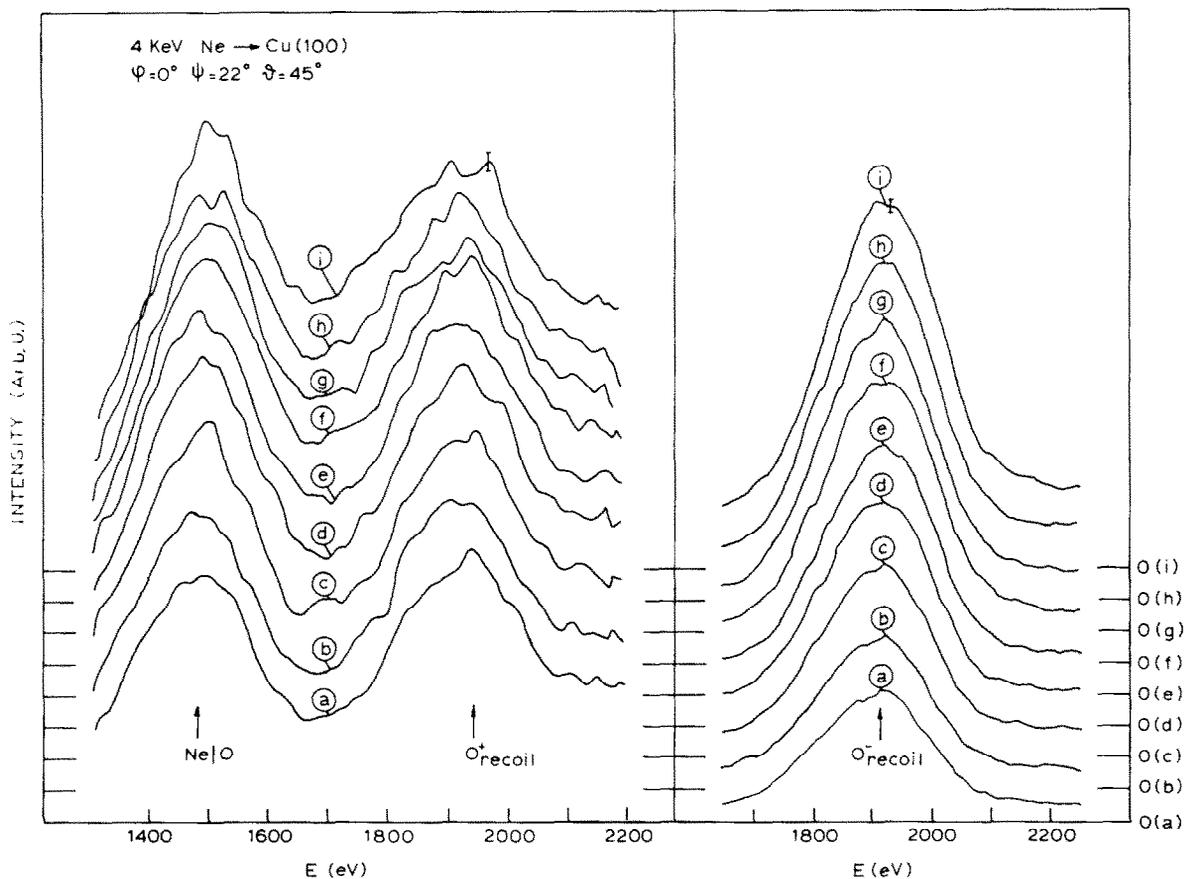


Fig. 2. Energy spectra for increasing oxygen pressure: 1)  $8.1 \times 10^{-6}$  Pa, b)  $1.3 \times 10^{-5}$  Pa, c)  $2.9 \times 10^{-5}$  Pa, d)  $6.5 \times 10^{-5}$  Pa, e)  $1.3 \times 10^{-4}$  Pa, f)  $3.3 \times 10^{-4}$  Pa, g)  $6.5 \times 10^{-4}$  Pa, h)  $1.3 \times 10^{-3}$  Pa, i)  $3.3 \times 10^{-3}$  Pa.

tained with the pressure method are shown in fig. 4a and 4b. One of these sets of data-points was composed of separate measurements using the time method (ref. [26]), with increasing oxygen pressures. Although in that case much higher ion doses were used, because the surface was cleaned after every data point that was measured, the measurement yielded the same result as with the usual pressure method. In both the exposure and pressure measurements no influence of the hot filaments of the pressure gauge and the quadrupole mass analyser on the adsorption rate could be detected.

The maximum  $O^-$  signal was not reached at the highest exposures that were used. We normalized the curves to the signal ( $Y_{\text{norm}}^-$ ) that corresponded to an exposure of  $0.1 \text{ Pa} \cdot \text{s}$ . It is known from the literature that the transition from the  $(\sqrt{2} \times \sqrt{2})R45^\circ$  to the  $(\sqrt{2} \times 2\sqrt{2})R45^\circ$  structure takes place at this exposure [16–18]. Furthermore at this exposure the  $\text{Ne}^+|\text{O}$  reflection signal reaches its maximum value.

## 6. Interpretation of the experimental results

Let us first assume that there is only one oxygen adsorption site involved. We define  $S'_0 = S_0/\theta_{\text{sat}}$  and  $\theta' = \theta/\theta_{\text{sat}}$ . Let us further assume that both  $Y^+$  and  $Y^-$  are proportional to the oxygen coverage. It is then possible to obtain reasonable fits with the experimental data of figs. 3a, 3b and 4a if the sticking probability is approximated by  $S'_0(\theta') = S'_0(1 - \theta')^{2.5}$  up to  $\theta' = 0.9$  and somewhat smaller for  $\theta' > 0.9$ .

The  $Y_{\text{eq}}^+$  signal (see fig. 4b) strongly deviates from the results of the other measurements. This measurement as it stands would be in agreement with a kinetic model leading to a  $S'_0(1 - \theta')$  relation, with  $S'_0 = 0.02$ . It is difficult to explain why the  $Y^+$  signal behaves differently when using different methods. It should be noted that for the  $\text{O}_2/\text{Cu}\{110\}$  system at room temperature excellent agreement was found between both measuring methods [26]. Furthermore there seems to be no simple explanation for the power of 2.5 in the  $S(\theta)$  relation. Although any simple  $S(\theta)$  relation can be obtained by a

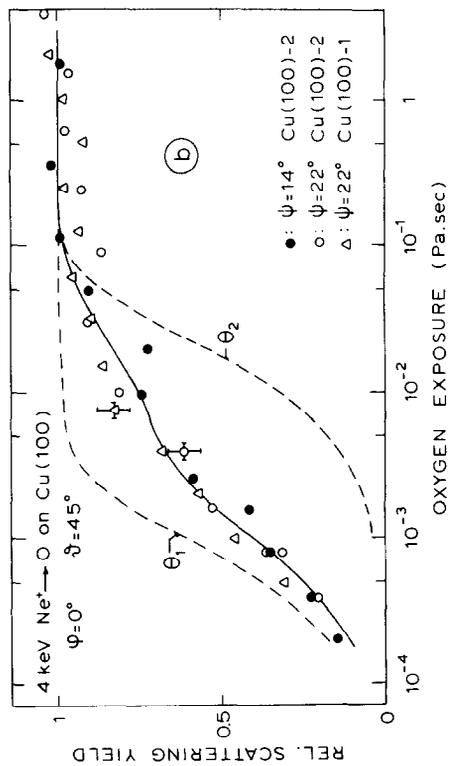
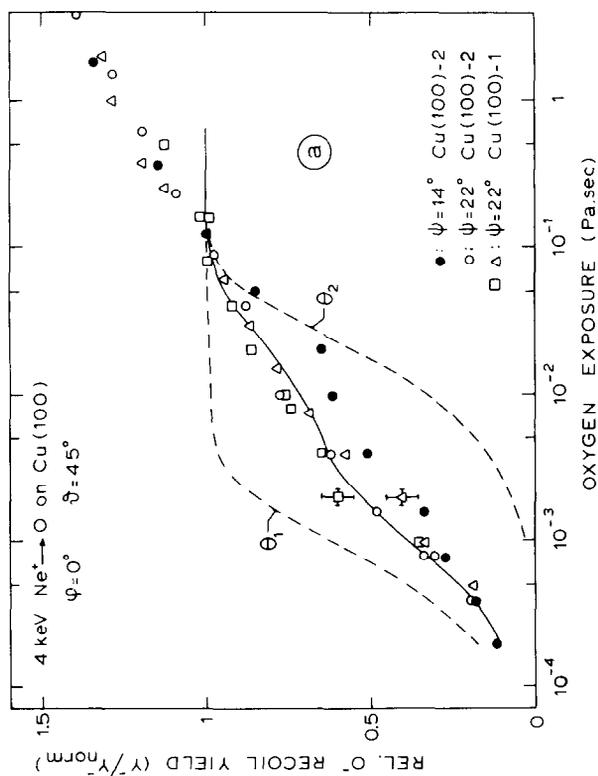


Fig. 3. Peak heights as a function of oxygen exposure, using the quasi-simultaneous technique. (a) the  $O_{recoil}$  signal, (b) the  $Ne^+ |O_{ad}$  reflection signal. The dashed curves represent the coverages of site 1 ( $\theta_1$ ) and site 2 ( $\theta_2$ ), according to our two-sites model. Solid curves: model calculations using the parameter values given in sect. 6.

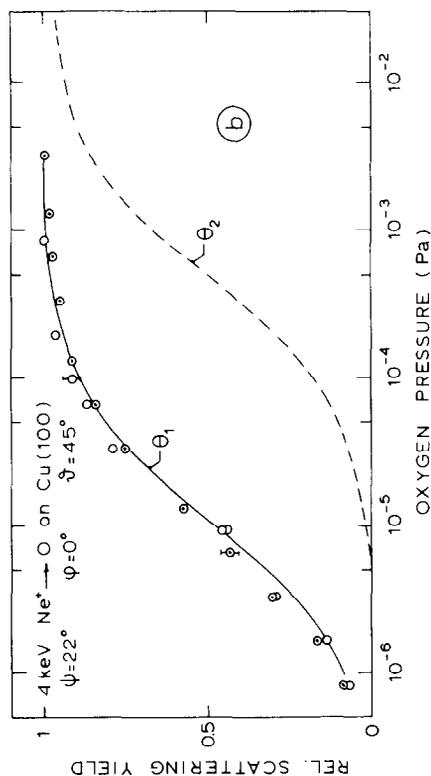
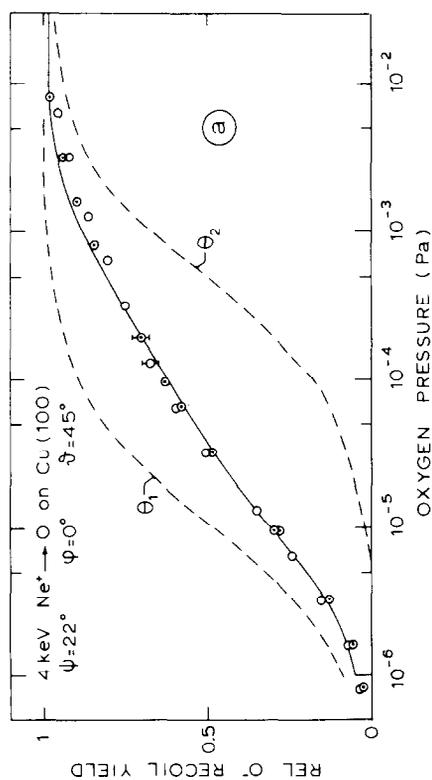


Fig. 4. Peak heights as a function of oxygen pressure, when an equilibrium is reached between oxygen uptake and ion-induced desorption. (a) the  $O_{recoil}$  signal, (b) the  $Ne^+ |O_{ad}$  reflection signal. The dashed curves represent the coverages of site 1 ( $\theta_1$ ) and site 2 ( $\theta_2$ ), according to our two-sites model. Solid curves: model calculations using the parameter values given in sect. 6.

sophisticated kinetic model, using many parameters (for instance the model introduced by King and Wells [29]), we shall show that by assuming two possible oxygen locations a much simpler kinetic model satisfies\*.

We make the following additional assumptions:

1) The relation between the measured signals  $Y$  and the respective relative coverages  $\theta_1$  and  $\theta_2$  for the two types of sites is given by

$$Y^-/Y_{\text{norm}}^- = \alpha\theta_1 + (1 - \alpha)\theta_2 \quad (1a)$$

and

$$Y^+/Y_{\text{max}}^+ = \beta\theta_1 + (1 - \beta)\theta_2, \quad (1b)$$

where  $\alpha$  and  $\beta$  are constants, and  $Y_{\text{norm}}^-$  is a normalization value that is reached at an exposure of  $0.1 \text{ Pa} \cdot \text{s}$ . At this exposure the transition from stage B to stage C takes place [16–18]. Furthermore at this exposure the  $Y^+$  signal reaches a maximum. For these reasons we believe that  $Y_{\text{norm}}^-$  corresponds to  $\theta_1 \approx \theta_2 \approx 1$ .

2) The two types of sites become covered independently, with a sticking probability  $S(\theta_i) = S_i(0)(1 - \theta_i)$  i.e. the sticking probability is proportional to the number of free adsorption sites. This relation was prompted by the results, that we obtained for the  $Y_{\text{eq}}^+$  signal and by the results for the  $\text{O}_2/\text{Cu}\{110\}$  system [26].

3) The ion induced desorption of oxygen from both sites takes place independently, with desorption cross section  $\sigma_1$  and  $\sigma_2$ .

With this model, good fits were obtained for all data, measured with the exposure method if the following parameter values are used (see figs. 3a, 4a):  $S_1(0)/S_2(0) = 25$ ;  $\alpha = 0.6$ ,  $\beta = 0.65$ ,  $S_1'(0) = 0.18$ . The coverages  $\theta_1$  and  $\theta_2$  are also indicated in the figures.

A good fit for the  $\text{O}_{\text{recoil}}^-$  signal, measured with the pressure method, could be obtained when using the same parameter values as given above, together with  $\sigma_2/\sigma_1 \approx 1.2$  (see fig. 4a). A value of  $\sigma_2/\sigma_1$  close to 1 is physically very plausible since sputtering is the main cause of ion-included desorption [26–28]. However, the  $\text{Ne}^+|\text{O}_{\text{ad}}$  signal, measured with the pressure method is described by the theoretical curve for  $\theta_1$ , i.e.  $\beta = 1$ . Thus it seems as if when using the exposure-method the positive signal measures oxygen at both sites, whereas when using the pressure method it only measures oxygen at sites 1. It should be noted that with any model

involving two essentially different oxygen sites, the discrepancy between the results of these two measuring methods cannot easily be explained. Therefore we did not try to modify our simple two-sites model (for instance by taking more complicated  $S(\theta)$  or  $Y(\theta)$  relations or by taking into account any interactions between the two types of sites). In order to resolve this problem one either has to find an explanation for the different sensitivity of the  $\text{Ne}^+|\text{O}_{\text{ad}}$  reflection signal in the exposure and pressure method, or one has to modify the adsorption model by introducing more essentially different adsorption sites.

If the adsorption model is modified by assuming a third possible oxygen position, one can easily obtain good fits with all experimental data presented here. However, the necessary parameter values seem to be rather unrealistic (for instance a factor of about 50 between two desorption cross sections would be necessary). This 3 sites model may possibly be modified by taking into account interactions between the three sites so that a good description of all available data is obtained. However, in view of the limited amount of data that cannot be explained by our “two site” model we decided not to search for more complicated models, involving more assumptions and fit parameters.

## 7. Discussion

In our previous paper on the adsorption of oxygen on  $\text{Cu}\{100\}$ [24] we concluded on the basis of the  $\text{O}^-$  recoil intensity for several incidence directions, that already at stage B at least two essentially different oxygen positions are involved. Despite the unresolved discrepancy between the  $Y_{\text{eq}}^+$  signal and the other signals, we believe that the kinetic measurements presented here also support the assumption that two or more oxygen sites are involved:

1) The discrepancy between the observed  $S(\theta') - (1 - \theta')^{5/2}$  relation with the  $(1 - \theta')^2$  relation mentioned in the literature is difficult to explain with a one-site model, whereas if two sites are involved, with LEIS different information is obtained than with other techniques so that no discrepancy arises.

2) Within a two-site model simple, physically reasonable kinetics are involved, whereas a one-site model would involve complicated “ad hoc”  $S(\theta)$  relations that have no physical basis.

3) Our  $Y_{\text{eq}}^+$  curve directly reflects the simple kinetics assumed for all sites.

In the literature it is well established [3,15] that gradual oxygen incorporation in the selvedge occurs at stage C. It is well possible that some incorporation takes place at stage B as well. If this incorporation mechanism can be described by an increasing number of adsorption sites (all in the surface or selvedge), the continuously increas-

\* In the literature a  $(1 - \theta')^2$  relation has been reported with  $S_0' = 0.02$  according to an AES-LEED Ellipsometry study [15] and  $S_0' = 0.06$  according to a work function study [16]. The  $(1 - \theta')^2$  relation that was claimed in this study was not determined very accurately – particularly not for room temperature adsorption – considering the poor fit of the data points with the calculated curves. Therefore it seems well possible that the measured adsorption curves in these studies are the result of other  $\theta$ -dependencies for each type of site if the signal is not sensitive to ‘sites’.

ing  $O^-$  recoil signal can be explained easily since this signal is sensitive to oxygen in the subsurface region (if no shadowing or blocking takes place). It is also simple to explain that the  $Ne^+ |O_{ad}$  reflection signal reaches a maximum, since this signal is completely insensitive to oxygen in the subsurface region.

It is, however, difficult to explain why the  $Y^+$  signal would have a different sensitivity to oxygen at different locations in both measuring methods. A different sensitivity could in principle result if adsorption takes place in domains with a lower symmetry than the surface symmetry. During ion-bombardment then, some orientation effects may be possible, which do *not* alter the adsorption kinetics to a large extent, but which do effect the "visibility" of oxygen in the  $Ne^+ |O_{ad}$  reflection signal. It is also possible that more than two oxygen positions are involved (these new positions are not necessarily essentially different with respect to the surface geometry). The behaviour of the  $O^-$  recoil signal for high exposures gives a clear indication that still more oxygen becomes incorporated in the selvedge. It is interesting to note that the absolute height of the  $Y_{eq}^+$  signal at saturation is of the same order of magnitude as was the case for the completely covered Cu{110} surface, whereas the highest  $O^-$  signal we obtained for Cu{100} was about a factor of three higher than it was for O/Cu{110}.

If we introduce three independent oxygen sites, it is possible to reproduce all our experimental data, however, physically not plausible parameter values are necessary. With a more complicated model, in which interactions between the three sites are taken into account it may be possible to explain all our experimental data using physically plausible values.

Because of the extra parameters that would be necessary in such a model and in view of the limited amount of data that could not be explained with our "two-site" model we decided not to search for more complicated models, until more specific knowledge can be obtained from other measurements.

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## References

- [1] R.N. Lee and H.L. Farnsworth, *Surface Sci.* 3 (1965) 461.
- [2] G. Ertl, *Surface Sci.* 6 (1967) 208.
- [3] G.W. Simmons, D.F. Mitchell and K.R. Lawless, *Surface Sci.* 8 (1967) 130.
- [4] T.A. Delchar, *Surface Sci.* 27 (1971) 11.
- [5] L. McDonnell and D.P. Woodruff, *Surface Sci.* 46 (1974) 505.
- [6] L. McDonnell, D.P. Woodruff and K.A.R. Mitchell, *Surface Sci.* 45 (1975) 1.
- [7] D.R. Lloyd, C.M. Quinn and N.V. Richardson, *Surface Sci.* 68 (1977) 419.
- [8] J.R. Noonan, D.M. Zehner and L.H. Jenkins, *Surface Sci.* 69 (1977) 731.
- [9] C.B. Duke, N.O. Lipari and G.E. Laramore, *Il nuovo cimento* 23B (1974) 241.
- [10] C. Benndorf, B. Egert, G. Keller, H. Seidel and F. Thieme, *J. Phys. Chem. Solids* 40 (1979) 877.
- [11] S.P. Holland, B.J. Garrison and N. Winograd, *Phys. Rev. Lett.* 43 (1979) 220.
- [12] S. Kono, C.S. Fadley, N.F.T. Hall and Z. Hussain, *Phys. Rev. Lett.* 41 (1978) 117.
- [13] C.S. Fadley, S. Kono, L.G. Petersson, S.M. Goldberg, N.F.T. Hall, J.T. Lloyd and Z. Hussain, *Surface Sci.* 89 (1979) 52.
- [14] F.H.P.M. Habraken, Thesis, University of Utrecht, (1980).
- [15] F.H.P.M. Habraken, C.M.A.M. Mesters and G.A. Bootsma, *Surface Sci.* 97 (1980) 264.
- [16] P. Hofmann, R. Unwin, W. Wyrobisch and A.M. Bradshaw, *Surface Sci.* 72 (1978) 635.
- [17] J.H. Onuferko and D.P. Woodruff, *Surface Sci.* 95 (1980) 555.
- [18] D.J. Godfrey and D.P. Woodruff, *Surface Sci.* 105 (1981) 459.
- [19] J.E. Boggio, *J. Chem. Phys.* 53 (1970) 3544.
- [20] D.T. Ling, J.N. Miller, D.L. Weissman, P. Pianetta, P.M. Stefan, I. Lindau and W.E. Spicer, *Surface Sci.* 95 (1980) 89.
- [21] A. Spitzer and H. Lüth, *Surface Sci.* 118 (1982) 121.
- [22] A. Oustry, L. Lafourcade and A. Escaut, *Surface Sci.* 40 (1973) 545.
- [23] H. Niehus and G. Comsa, *Surface Sci.* 93 (1980) L147.
- [24] Th.M. Hupkens, *Nucl. Instr. and Meth.*, preceding paper, this issue *Nucl. Instr. and Meth.* B9 (1985) 277.
- [25] A.G.J. de Wit, J.M. van Zoest and J.M. Fluit, *Surface Sci.* 126 (1983) 589.
- [26] Th.M. Hupkens and J.M. Fluit, *Surface Sci.* 143 (1984) 267.
- [27] E. Taglauer, G. Marin, W. Heiland and U. Beitat, *Surface Sci.* 63 (1977) 507.
- [28] P. Sigmund, *Phys. Rev.* 184 (1969) 383.
- [29] D.A. King and M.G. Wells, *Proc. Roy. Soc. (London)* A339 (1974) 245.
- [30] Th.M. Hupkens, Thesis, University of Utrecht (1983).