THE INFLUENCE OF LOW ENERGY ION BEAMS ON AN ADSORBING SURFACE

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Strong enhancement of the oxygen-chemisorption at a Cu(110) surface is measured during low energy (some keV) noble gas (Ne$^+$) ion bombardment. This phenomenon is independent of the coverage and is linearly related to the number of impinging ions per second. A model description of the oxygen adsorption on a Cu(110) surface is given: the model of dissociative adsorption via a mobile precursor state is extended to take into account the twofold symmetry of the surface. From a comparison of model calculations with the experimental results, model parameters can be estimated. The estimated parameters are in agreement with the adsorbate-structure deduced from LEED patterns. Ion-induced adsorption is discussed with the aid of this model.

1. Introduction

The adsorption of oxygen at pressures between $10^{-8}-10^{-4}$ Torr on Cu(110) has already been investigated with LEED [1–4], work function measurements [5] and ellipsometry combined with AES [6]. Some aspects of the adsorption of oxygen on Cu(110) surfaces were also studied with low energy ion scattering (LEIS). We determined the oxygen position on a Cu(110) surface with this technique [7,8]. The results showed the oxygen atom to be lying between two neighbouring surface atoms in a ⟨100⟩ row and about 0.6 Å below this row. Studies of sputtering of oxygen adsorbates by low energy noble gas ions (ion-induced desorption [9–11]) showed that the extent of adsorbed species removed by the ions is a sensitive function of the energy of the ions in the keV region [7,12].

In a previous paper we reported experimental results, obtained with LEIS, concerning the adsorption of oxygen on a Cu(110) surface during ion bombardment [13]. In the present paper we will compare the experimental results with results of calculations with a model in which it is assumed that the oxygen adsorbs dissociatively after a mobile precursor state on empty pair sites at the Cu(110) surface. The model used for the calculations is a modified version of the model used by King and Wells [14].

2. Experimental results

The sticking probability S for an oxygen molecule to become chemisorbed on a Cu(110) surface was determined from ion scattering signals consisting of noble gas ions (Ne$^+$) scattered by oxygen atoms on the Cu(110) surface [13]. Using different experimental methods the sticking probability for oxygen could be calculated from the measurements for two different cases, (i) the sticking probability for oxygen without
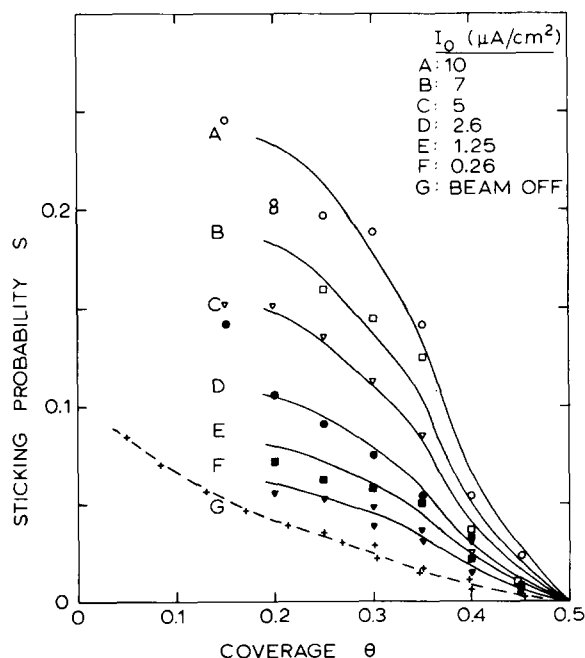

Fig. 1. The sticking probability S for oxygen on a Cu(110) surface during 4 keV Ne$^+$ ion bombardment at an elevation angle of incidence of 20° as a function of coverage θ. The different curves ($A-F$) correspond with different incident beam intensities I_0. Curve G gives the sticking probability measured without the influence of the ion beam.

X. TRAPPING. ADSORPTION AND EMISSION

the influence of ion bombardment (called "spontaneous" sticking probability) and (ii) the sticking probability during the ion bombardment (called "ion-induced" sticking probability, S_t [13]).

The "spontaneous" sticking probability was determined from measurements of ion scattering signals after a period of time T during which the beam was switched off [7,12]. From the signal as a function of T the sticking probability could be calculated (see fig. 1, dashed line).

The effect of ion-induced adsorption was found in experiments where the oxygen pressure was suddenly increased, with the ion beam on, until about 10^{-6} Torr. From the recorded ion scattering signal as a function of exposure time, the "ion-induced" sticking probability could be calculated taking into account the effect of ion-induced desorption [7,13].

In fig. 1 the experimental sticking probability curves are shown. The figure shows clearly that the sticking probability increases with increasing primary ion intensity I_0 ($\mu A/cm^2$). In fig. 2 the sticking probabilities for oxygen are plotted as a function of the primary ion intensity at fixed coverage θ. The sticking probability increases linearly with the ion intensity as is shown for different coverages. It appears that the relative increase in the sticking probability S_t

is nearly independent of θ: i.e.,

$$S_t(\theta) = S_0(\theta)(1 + \lambda i_0),$$

where i_0 is the ion current density (ions/cm^2 s) and λ is a proportionality factor. In fig. 1 the drawn curves are the best fits for the above-mentioned relation [with $\lambda = (5.5 \pm 1) \times 10^{-14}$ cm^2 s/ion].

3. Model calculations

In order to describe the experimental sticking probability profiles shown in fig. 1 model calculations were performed. King and Wells derived in ref. [14] an expression for the sticking probability for a diatomic molecule for the case of dissociative adsorption via a mobile precursor state. This expression reads

$$S(\theta) = \frac{\alpha f_a}{f_a + f_d}\left(1 + \frac{f'_d}{f_a + f_d}(\theta_f^{-1} - 1)\right)^{-1}$$

$$\equiv S_0[1 + K(\theta_f^{-1} - 1)]^{-1}, \qquad (1)$$

where α is the probability for a molecule to become physisorbed, f_a is the probability for the physisorbed molecule on a certain physisorption site to become dissociatively chemisorbed on empty sites, f_d is the probability for a physisorbed molecule to desorb from a physisorption site available for chemisorption and f'_d is the probability to desorb from a physisorption site which is not available for chemisorption, θ_f represents the fraction of empty nearest neighbour (nn) chemisorption pair sites, K is called the precursor state parameter.

The value of θ_f will depend on the degree of ordering in the adsorbed layer, i.e. on the interactions between the adsorbed atoms. For a surface with twofold symmetry the effect of ordering can be described by the parameters θ_{ee} and $\theta_{e'e'}$, which are the probabilities that nn chemisorption pair sites * in the directions are empty.

By means of the so-called quasi-chemical approximation it can be shown [15,16] that in the case of thermodynamic equilibrium

$$\theta_{ee} = 1 - \theta - \frac{2\theta(1 - \theta)}{[1 - 4\theta(1 - \theta)B_1]^{1/2} + 1}, \qquad (2)$$

where $B_1 = [1 - \exp(\omega_1/kT_s)]$ and ω_1 is the pairwise nn interaction energy in one of the surface directions (positive for attractive interactions). T_s is
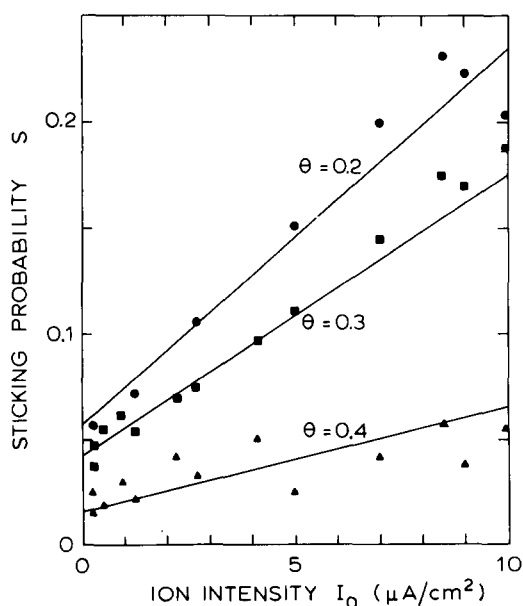

Fig. 2. The sticking probability S for oxygen on a Cu(110) surface during a 4 keV Ne$^+$ ion bombardment at an elevation angle of incidence of 20° as a function of beam intensity I_0. The curves are given for different coverages θ.

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* In the description given here, a chemisorption site is assumed to consist of one surface Cu atom.

the surface temperature. For $\theta_{e'e'}$ a similar expression is found, except that B_1 and ω_1 are replaced by B_2 and ω_2.

For the two-dimensional case the quantity θ_f can now be expressed as

$$\theta_f = \tfrac{1}{2}\theta_{ee} + \tfrac{1}{2}\theta_{e'e'} , \tag{3}$$

if the empty nn chemisorption pair sites in the two surface directions are assumed to be independent of each other.

In extreme situations ($B_1 = 0$, 1 or $-\infty$) it is easy to calculate θ_f from eqs. (2) and (3). An interesting example is the situation where $B_1 = 1$ and $B_2 = -\infty$ (i.e., there is considerable repulsive interaction in one direction and considerable attractive interaction in the other). Using eq. (2) for θ_{ee} and $\theta_{e'e'}$, we get

$$\theta_f = 1 - 1.5\theta \qquad \text{for } \theta \leq 0.5 , \tag{4a}$$

and

$$\theta_f = 0.5 - 0.5\theta \qquad \text{for } \theta \geq 0.5 . \tag{4b}$$

According to eq. (2) θ cannot be more than 0.5 if $B_1 = 1$, but if $\theta = 0.5$, eq. (4) yields $\theta_f = 0.25$; not zero. This inconsistency arises from the fact that θ_{ee} and $\theta_{e'e'}$ are taken to be independent.

We now introduce the dependence between the probability of finding empty nn pair sites in each direction by rewriting θ_f as

$$\theta_f = \tfrac{1}{2}g(\theta, \theta_{e'e'})\theta_{ee} + \tfrac{1}{2}g(\theta, \theta_{ee})\theta_{e'e'} , \tag{5}$$

where g is a function describing the fraction ($g \leq 1$) of empty nn chemisorption pair sites which are effec-

tively available for chemisorption when the dependence between θ_{ee} and $\theta_{e'e'}$ is taken into account.

The function g can be approximated by considering the different local environments of empty nn pair sites. When, for instance, the two sites of an empty pair of nn sites in direction 2 are part of four pairs of empty and filled nn sites in direction 1, and nn filled pair sites are not permitted in direction 1 (e.g., because of strong repulsions), then the empty pair of nn sites is not available for chemisorption. If nn filled pair sites are permitted in direction 1, then a certain fraction h of the mentioned empty nn pair sites is still available for chemisorption. This fraction h can be estimated to be the probability that a single filled site is part of a filled pair of nn sites. In view of these considerations an approximation of g has been attempted. In our calculations we used for g:

$$g(\theta, \theta_{ee}) = 1 - \frac{(1 - \theta - \theta_{ee})^5}{(1 - \theta)^4 \theta} . \tag{6}$$

With the relations (1), (2), (5) and (6) the ratio S/S_0 was calculated for different values of K, B_1 and B_2. In figs. 3 and 4 some of the calculated S/S_0 profiles are shown. For $K = 1$ eq. (2) becomes $S/S_0 = \theta_f$, which is equivalent to the Langmuir kinetic expression for dissociative adsorption. In this case the influence of the physisorbed state on the kinetics is negligible. Smaller values of K correspond to an increased possibility that molecules in the physisorbed state will migrate and larger values of K reflect an increased influence of f_d' [see eq. (2)]. When B_1 or B_2 is equal to 1, i.e., for complete order in one direc-
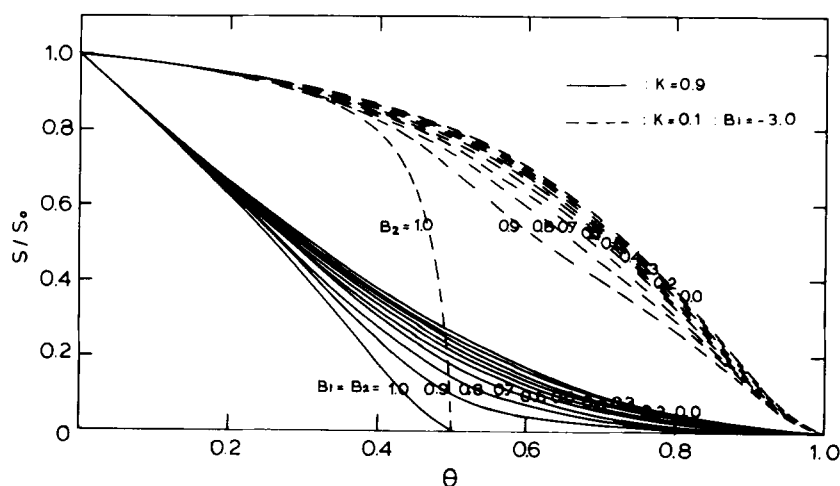

Fig. 3. Computed sticking probability curves for fixed values of the precursor state parameter K (=0.9 and 0.1) and various values of the short-range order parameters B_1 and B_2.
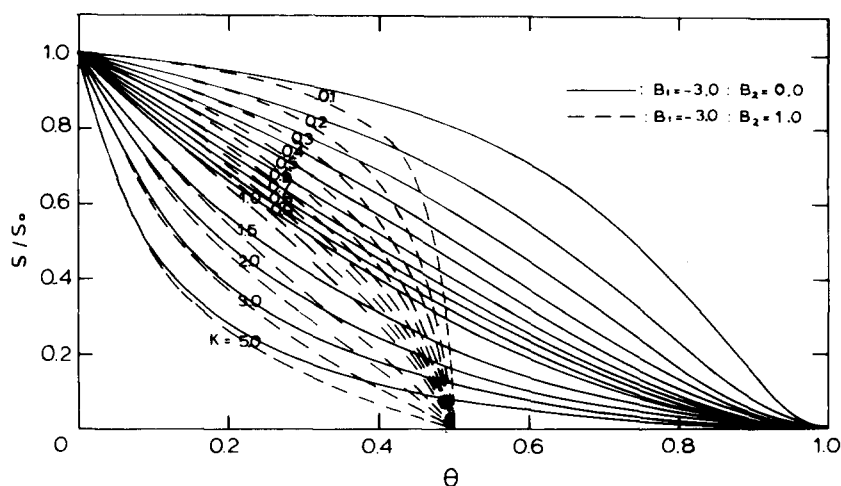
Fig. 4. Computed sticking probability curves for various values of the precursor state parameter K (= 0.1–5.0) and fixed values of B_1 (=–3.0) and B_2 (=0.0 or 1.0). The figure illustrates the effect of the precursor state parameter and the effect of the short-range order parameter B_2.

tion, the maximum coverage of a chemisorbed layer is half a monolayer. When $B_1 = B_2 = 0$ we arrive at the Kisliuk model [17] in which there is complete disorder in the chemisorbed overlayer.

4. Comparison of experimental results and model calculations

To explain the values of $S/S(0)$ obtained in the absence of ion beams (fig. 1) K values have to be taken larger than 1 (cf., figs. 3 and 4). Fig. 5 shows four reasonable fits with K from 2 to 3, B_2 equal to 1

and B_1 varying from 0 to $-\infty$. In view of the limited amount of our experimental data and the limited accuracy of these data, no further conclusions are warranted.

LEED patterns obtained for the adsorption of O_2 on Cu(110) show order in the ⟨100⟩ and disorder in the ⟨110⟩ direction; this may be attributable to (large) attractive interactions in the ⟨100⟩ direction ($B_1 \rightarrow -\infty$) and (large) repulsive interactions in the ⟨110⟩ direction ($B_2 \rightarrow 1$) (cf., ref. [6]). It should be pointed out that if B_2 was equal to 1 this would imply a maximum repulsion between nearest neighbours in the ⟨110⟩ direction and thus a maximum
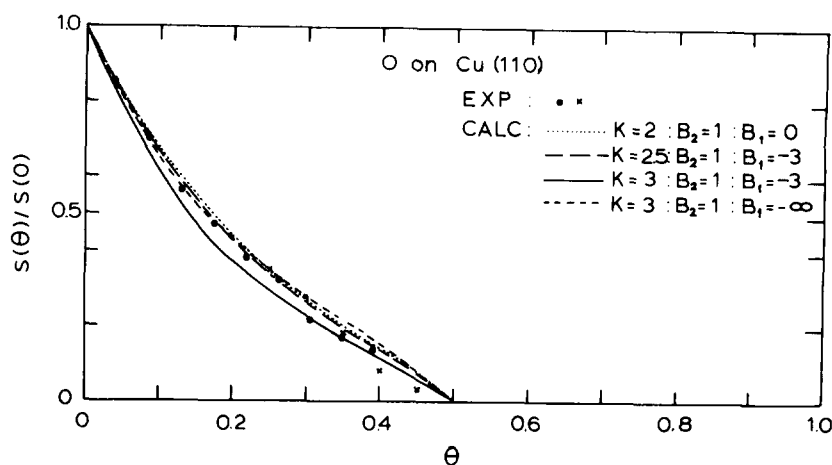

Fig. 5. Comparison between experimental and computed sticking probability profiles for oxygen on a Cu(110) surface for adsorption without the influence of ion beams. From the calculated curves the best fitting ones are shown.

coverage θ_{max} = 0.5. Note that our results (the model fits shown in fig. 5) are in agreement with the above interpretation of the LEED patterns.

The experimental results obtained with 4 keV Ne$^+$ ions (fig. 1) show an increased sticking probability and a slightly different shape of the S versus θ plot. Although the comparison with model calculations is hampered by a lack of experimental data at lower coverages the best fits show a tendency to lower K values, e.g., K between 0.3 and 1, $B_1 = -3$ and $B_2 = 1$. The smaller K-value for the ion-induced sticking probability profiles indicates an increase in the adsorption rate f_a and/or, eventually, a decrease in the desorption rates f_d and f_d' [see eq. (1)]. The increase in the ion-induced sticking probability with the ion intensity (fig. 2) may indicate an increase in the adsorption rate f_a too, but it may also indicate an increase in the condensation coefficient α by the ion bombardment.

The value of S_t extrapolated to a zero primary intensity (see fig. 2) appears to be twice as high as the "spontaneous" sticking probability (beam off) shown in fig. 1. This difference cannot be explained on the basis of our assumptions. Obviously, the relation $S_t(\theta) = S_0(\theta) (1 + \lambda i_0)$ is only valid for $I_0 > 0.3 \mu A/cm^2$ and (of course) for $S_t(\theta) \leqslant 1$.

The proposed model of the ion-induced oxygen adsorption for the above-mentioned range can be interpreted qualitatively by the idea of an "excited" surface area per incident ion, the extent of which depends on the travelling time of the incident ion in the uppermost surface layers and in which the adsorption rate and/or the condensation coefficient is (strongly) increased and the desorption rates of physisorbed oxygen are eventually decreased.

5. Conclusion

As far as the measurements of spontaneous adsorption are concerned, the used model of dissociative adsorption via a mobile precursor state can describe the measured sticking probability profiles. It is, however, obvious that sticking probability profiles have to be obtained at different surface temperatures (and/or gas temperatures), since f_a, f_d, f_d' and α can depend on temperature. Very recent ellipsometric results obtained by Habraken and Bootsma [6] have indicated that between 300–600 K the sticking probability is nearly independent of the surface temperature. A possible temperature dependence outside this range

can give more information about the model parameters.

Several investigations have still to be performed in connection with the ion-induced adsorption process. The primary energy dependence of the sticking probability needs to be investigated further, so that its influence becomes known and the proposed model for the induced adsorption can be checked. For the same reasons it is necessary to investigate the influence of the mass of the noble gas ion. A comparison between adsorption measurements obtained from experiments with and without ion bombardment, taking different target temperatures into account can also give information about the induced adsorption processes.

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