Surface Science 271 (1992) 340–348
North-Holland

surface science

Kinetics of the adsorption of atomic oxygen (N_2O) on the Si(001)2 × 1 surface as revealed by the change in the surface conductance

Herbert Wormeester, Enrico G. Keim and Arend van Silfhout
Faculty of Applied Physics, University of Twente, P.O.Box 217, 7500 AE Enschede, Netherlands

Received 16 December 1991; accepted for publication 12 February 1992

The adsorption behaviour of N_2O on the Si(001)2 × 1 surface at 300 K substrate temperature has been investigated by measuring in situ the surface conductance during the reaction process. For comparison we monitored in the same way the adsorption of O_2 on the same surface which ultimately leads to the flat band situation. The adsorption of atomic oxygen as released by decomposition of the N_2O molecule, in contrast with molecular oxygen, was found to result in an increase of the band bending. The difference in behaviour of the change of the surface conductance between the two solid–gas reactions can be explained by considering that the adsorption of O_2 will also remove deep-lying backbond states in addition to the dangling bond (DB) and dimer bond (DM) related surface states. It is well known that only the DB and DM surface states are affected by N_2O. The surface conductance measurements (SCM) presented in this paper complement our previous spectroscopic differential reflectivity measurements and Auger electron spectroscopic results for the system Si(001)2 × 1 + N_2O; we have found evidence that the second step of the proposed three-stage adsorption process of atomic oxygen can be divided into two substages. From our SCM data we could derive that the distance between the valence band edge and the Fermi energy of the clean Si(001)2 × 1 surface is 0.32 ± 0.02 eV, which is in agreement with previous photoemission results.

1. Introduction

Surface states can be characterized by various methods like photoemission [1–3], inverse photoemission [4], Auger electron spectroscopy (AES) [5,6] and scanning tunneling microscopy (STM) [7]. Exposing an atomically clean solid surface to a gas will usually result in changes in the density and position of its surface states. If one is interested in the adsorption kinetics, a study of the behaviour of surface states during the reaction using these experimental techniques may be less suitable. Because techniques commonly used in surface science depend on a rather strong interaction of probe and surface, processes at surfaces cannot be studied without unknown and therefore unwanted probe-induced effects. Therefore, in a typical experiment the measurement, which is to characterize the state of the surface states, is limited to a number of discrete stages. Even so, one should always be aware of probe-induced artefacts, such as dissociation of an adsorbed transient state by electrons [8,9]. In this paper we have studied the interaction of atomic oxygen with the Si(001)2 × 1 surface at room temperature. The atomic oxygen is released by the decomposition of N_2O at this surface and this reaction was found to be limited to the first-layer Si atoms [10], as confirmed by theoretical work [11]. The kinetics of this reaction is therefore well understood when compared, for instance, with molecular oxygen [12]. An electron beam, ion gauge or UV light, is likely to decompose the N_2O molecule before it reaches the surface because of a low bond dissociation energy (N_2–O = 1.677 eV [13]). This may lead to a different surface reaction as evidenced by the detection of nitrogen on the surface when the ion gauge filament was left on during the adsorption of N_2O [14]. In order to monitor the kinetics of the adsorption of atomic oxygen on the Si(001)2 × 1 surface one should therefore apply an in situ

0039-6028/92/$05.00 © 1992 – Elsevier Science Publishers B.V. All rights reserved

method without disturbing the reaction. The simplest and oldest in situ experimental technique in gas–solid interaction studies, although hardly used anymore, is the measurement of the change in surface conductance. Surface conductance measurements (SCM) provide information about changes in the difference in density of all occupied and unoccupied surface states, independent of their energy position relative to the Fermi level [15–19]. Its high sensitivity and accuracy allows the detection of changes in the difference between occupied and unoccupied states down to a variation in electron density of 10^{12} cm^{-2}. Moreover, electrical measurements are easy to perform and show a relatively high time resolution. From previous Auger electron spectroscopy (AES) and spectroscopic differential reflectometry (SDR) measurements [10,12] it is well known that the kinetics of the room-temperature adsorption of atomic oxygen on the Si(001)2 × 1 surface evolves in three distinguishable stages upto saturation, which occurs at about 0.85 monolayer (ML) oxygen coverage (θ). It is therefore expected that these stages also manifest themselves in the electrical measurements. It is the aim of this paper to demonstrate the applicability of SCM in the study of surface reactions by comparing the rather well understood adsorption of N_2O and O_2 on the Si(001)2 × 1 surface and to analyze the kinetics of the N_2O adsorption. The absolute value of the surface conductance is determined by the position of the valence band at the surface, i.e., the band bending (V_s). For the clean silicon surface this value is derived from the difference in surface conductance before and after exposing the clean Si surface to molecular oxygen up to apparent saturation coverage [20]. It is generally accepted that at the apparent saturation coverage a flat band situation results [19].

The joint property of occupied and unoccupied surface states as measured with SCM can also be measured in situ with optical techniques like SDR [10]. In contrast to SCM, SDR does not measure the difference between occupied and unoccupied states. In SDR it is the product of occupied and unoccupied states which determines the reflectivity at a specific photon energy for which optical transitions may occur between these states. Furthermore, the intensity of the optical transition depends on the optical transition matrix element. A relation between the change in the optical properties and the change in surface conductance is expected and can be derived with a simple model of the optical and electrical measurements as we will demonstrate in this paper.

2. Experimental

The experiments were performed in a stainless steel UHV system equipped with a single-pass cylindrical mirror analyser for AES and an arrangement for SCM measurements as described previously [15]. The base pressure in this system was in the mid 10^{-11} Torr region. For the SCM measurements, four titanium contacts were sputtered on the sample through a tantalum mask followed by a heat treatment at 1100 K. With secondary electron microscopy (SEM) and scanning Auger microscopy (SAM) the optimum thickness for these contacts, d_{Ti}, was determined to be 100 nm. With $d_{Ti} = 50$ nm, island formation was found to occur during the heat treatment. With 200 nm thick Ti contacts, the resulting silicide surfaces were not as optically flat as those having a d_{Ti} of 100 nm, as could be seen upon inspection by eye. Increasing the metal thickness to 1000 nm resulted in crumbling contacts [14]. With evaporated Ti contacts of 100 nm thickness essentially the same quality of contacts was obtained [21]. A block current of ± 100 μA with a frequency of 167 Hz was put on the outer pair of contacts, while the resulting potential was measured between the inner contacts of the sample. In this way nonlinear behaviour of the metal–semiconductor contact is eliminated. Use of an alternating current averages out any thermo- or photo-voltage effects resulting from a nonuniform sample temperature or illumination. The Si sample ($30 \times 8 \times 0.3$ mm^3) was made out of a 2000 $\Omega \cdot cm$ nominally flat p-type crystal (10^{13} B/cm^3) in the $\langle 001 \rangle$ orientation. The procedure for obtaining a clean Si(001)2 × 1 surface consisted of simultaneous ion-bombardment and annealing (SIBA) followed by annealing-only cycles as described previously [10]. Following this procedure

the intensity of the carbon peak was below the detection limit of the Auger spectrometer.

3. Electrical and optical measurements

The effect of band bending at the surface and its influence on the surface conductance has been described in various handbooks (see, e.g., ref. [16]). In order to make possible a comparison with SDR a short résumé is given. At equilibrium the surface charge density Q_{ss} trapped in the surface states is compensated by the space charge density Q_{ss} near the surface:

$$Q_{sc} = -Q_{ss} = \sum_a eN_{sa} f_{sa} - \sum_d eN_{sd}(1 - f_{sd}), \quad (1)$$

where e is the electron charge, N_{sa} the density of acceptor surface states with energy E_a and Fermi factor f_{sa}. In an analogous way N_{sd} is the density of donor surface states with energy E_d and Fermi factor f_{sd}. The summation includes all occupied (acceptor) and unoccupied (donor) states. Using Poisson's equation and the Fermi–Dirac distribution, the band bending (V_s) as a result of the number of acceptor and donor states can be calculated for a doped semiconductor [16]. At the clean silicon surface an accumulation of holes in the space charge layer (ΔP) is observed [17–19,22] and the surface conductance σ_s can then be written as

$$\sigma_s(V_s) = e\mu_{ps} \Delta P(V_s) = e\mu_{ps}\left(\sum_a N_{sa}^* - \sum_d N_{sd}^* \right), \quad (2)$$

$$N_{sa}^* = N_{sa} f_{sa},$$

$$N_{sa}^* = N_{sd}(1 - f_{sd}),$$

in which μ_{ps} is the mobility of the holes in the space charge layer. The exact magnitude of the surface mobility is a complicated problem since impurity atoms, dislocations, lattice vibrations, surface roughness and the density and occupancy of surface states may all effect μ_{ps}. It is therefore that μ_{ps} is replaced by the bulk mobility value μ_p which is only slightly larger. With a given surface conductance this leads to a band bending that is less than the actual value. However, Many and Goldstein [16] have shown that the deviation is

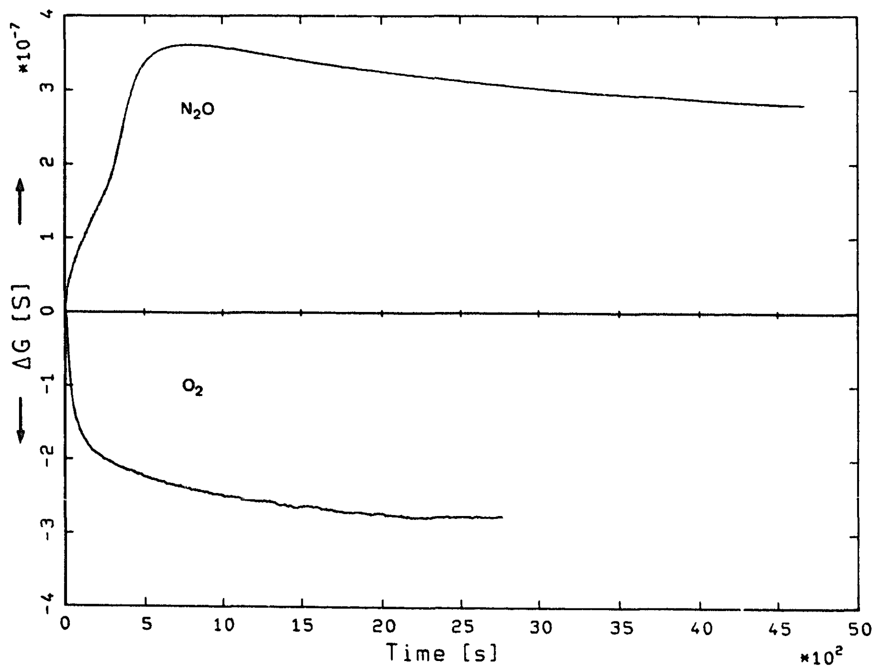

Fig. 1. Change of the surface conductance upon exposing the clean Si(001)2 × 1 surface to N_2O (upper curve) at a pressure of 1.25×10^{-4} Torr and O_2 (lower curve) at a pressure of 2×10^{-7} Torr.

small in the case the band bending is not too large. The contribution to the surface conductance by the charge carriers trapped in the surface states can be neglected. For the change in surface conductance upon adsorption (ΔG) one has in differential form:

$$\Delta G = \partial\sigma_s = e\mu_p\left(\sum_a \partial N_{sa}^* - \sum_d \partial N_{sd}^*\right). \quad (3)$$

In this equation, it is assumed that the surface mobility is not affected by the adsorption. The much larger change in the electron density-of-states and the relatively small value of the band bending justify this assumption.

Displayed in fig. 1 is the change in the conductance upon exposing the clean Si(001)2 × 1 surface to O_2 (lower curve) and N_2O (upper curve). The decrease in conductance upon the chemisorption of molecular oxygen can be attributed to the dominant removal of acceptor states. The shape of this curve is in agreement with early work on cleaved surfaces and wires of silicon [17–19]. Assuming a flat band situation at the apparent saturation coverage a band bending V_s = 65 meV can be derived, as depicted in fig. 2, where the relation between the quotient of the surface and bulk conductance is shown as a function of the band bending. The figure also provides evidence that our assumption of p-type conductance in the space charge layer (accumulation layer at the surface) is correct. The distance between the maximum of the valence band at the surface (the band edge) and the Fermi level, $(E_f - E_v)$, can therefore be estimated to lie at 0.32 ± 0.02 eV. This value is in good agreement with SCM [17–19] and workfunction measurements on Si(111) [22]. UPS measurements yield 0.35 ± 0.15 eV [2] and 0.40 eV [1] for $E_f - E_v$.

The chemisorption of atomic oxygen is, in contrast to molecular oxyen, limited to a bridge position between the first-layer silicon atoms [10–12,23] removing all the dimer and dangling bond surface states. In fig. 3 a side view of the reconstructed clean Si(001)2 × 1 surface is shown with the various adsorption sites named. It may be appreciated that in the case of atomic oxygen not all surface states are removed, in particular those related to the backbonds. In the following discussion we will regard all deviations from the bulk electronic structure as orginating from surface states. The different course of the surface conductance for the reaction of O_2 and N_2O with clean Si(001)2 × 1 (fig. 1) can be explained by a different degree of removal of the total number of surface states upon adsorption. Remarkable in fig. 1 is, however, the sign of the conductance change at saturation coverage. It can be seen that

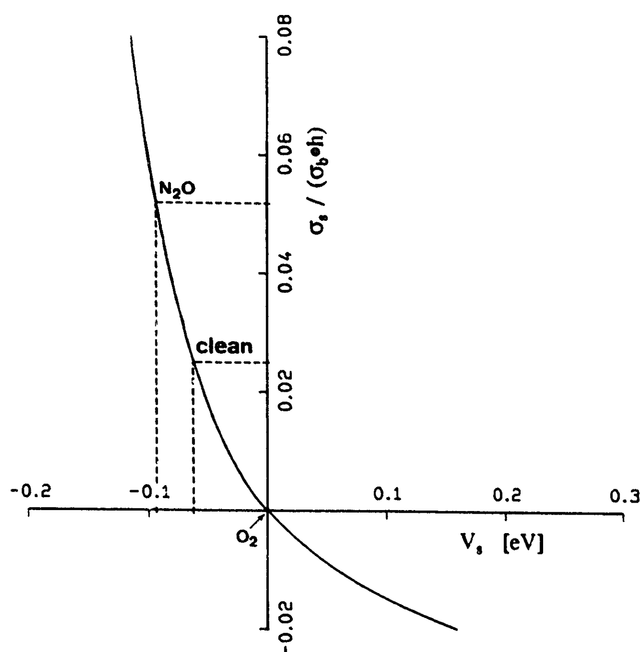

Fig. 2. Surface conductance as a function of the band bending V_s. The surface conductance is normalized to the bulk conductance (10^{13} B/cm^3) multiplied by the thickness of the sample (h). Indicated are the positions for the clean Si(001) 2×1 surface, the same surface exposed to a saturation dose of N_2O and to an apparent saturation dose of O_2 (100 L).

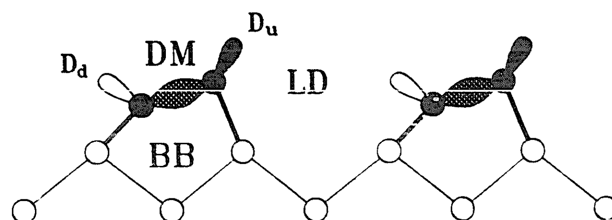

Fig. 3. Side view of the Si(001) surface with the (short) dimer site (DM), the long dimer site (LD) and the back bond (BB). Also shown are the up (D_u) and down (D_d) dangling bond.

the flat band situation is not achieved by the adsorption of atomic oxygen; the band bending has even increased to 0.095 eV, as pictured in fig. 2. A dominant removal of donor states instead of acceptor states must therefore occur in the case of atomic oxygen adsorption on Si(001). Incorporation of oxygen atoms into the backbonds as observed with the chemisorption of O_2 [6,24–26], on the other hand, must be interpreted with a dominant removal of acceptor states. As SCM measures the difference between the occupied and unoccupied states a creation of empty donor states cannot be ruled out. The results of our present comparitive study clearly reject the model for the chemisorption of N_2O on Si(001)2 × 1 in which incorporation of oxygen atoms into the backbonds can take place (like in the case of the adsorption of O_2) as proposed by Namiki et al. [27].

In contrast to the SCM results, optical SDR measurements do not show such a dramatic difference between the adsorption behaviour of atomic and molecular oxygen on Si(001)2 × 1 [10]. Also in the case of the Ge(001)2 × 1 surface no large difference between the optical spectra as a result of exposure towards O_2 and N_2O is observed, although the change in surface conductance was found to be twice as large for the adsorption of O_2, but with the same sign for the adsorption of N_2O [28,29]. The difference in the direction of the SCM kinetic curves between N_2O and O_2 on Si (opposite) and Ge (equal) can be explained by the different doping of the Ge (n-type) and Si (p-type) samples, which results in a different band bending at the clean surface. The discrepancy between the SDR and SCM measurements results on Si(001)2 × 1 can, to our opinion, be explained by the limited energy range in which the optical spectroscopy has been performed. SDR measurements of Keim et al. [10] concerning the adsorption of N_2O on Si(001)2 × 1 suggest an optical transition in the low-energy region, just outside the photon energy region recorded which is not observed in the O_2 SDR spectrum. The coverage dependence of this feature is the subject of further investigations. The immediate decrease of the surface conductance upon exposing the clean Si(001)2 × 1 surface to O_2 also suggests that, although at low coverages the adsorption mechanisms of N_2O and O_2 are thought to be quite similar [10,26], molecular oxygen adsorption must at this stage lead to the incorporation of oxygen at sites not feasible to the oxygen atoms as released by N_2O. The most likely site is the backbond between the first- and second-layer Si atoms. A comparative UPS study of the Si(001) surface saturated by exposing it to N_2O or O_2 would be very helpful. The study should be able to indicate which of the surface-related features still exist after the surface is covered with oxygen and disappear as the incorporation of oxygen atoms into the backbond takes place, since mainly filled acceptor states seem to be removed as observed with SCM.

In SDR the change in optical reflectivity R can be described by the dielectric three-layer model [30]. In this model the clean surface is described as a thin layer of surface states above an inert bulk. The surface states layer is removed by the adsorption of oxygen and is replaced by a thin silicon–oxygen layer which is optically transparent in the photon energy region studied (1.5–4.5 eV). Therefore the change in reflectivity recorded can be related only to the disappearence of the surface states of the clean surface [31,32]:

$$\frac{\Delta R}{R} = \frac{R_{\text{clean}} - R_{\text{ox}}}{R_{\text{ox}}} = \frac{8\pi}{c} \nu d_{\text{ss}} \operatorname{Im}\left(\frac{\epsilon_{\text{ss}} - \epsilon_{\text{b}}}{1 - \epsilon_{\text{b}}} \right), \tag{4}$$

in which ν is the frequency of the light reflected, d_{ss} is the thickness of the surface states layer and ϵ_{ss} and ϵ_b are the surface layer and bulk dielectric constant, respectively. Inserting the silicon bulk dielectric constant and taking into account that the imaginary part of ϵ_b is negligible in the photon energy region recorded, the derivative of the change in reflectivity can be written as:

$$\partial \frac{\Delta R}{R}(\nu) \sim -\nu d_{\text{ss}}\, \partial \operatorname{Im}(\epsilon_{\text{ss}}). \tag{5}$$

The imaginary part of the surface dielectric constant can be written in terms of the matrix element from the acceptor to the donor state M_{ad},

multiplied by the joint density of states $J_{ad}(\nu)$ [33].

$$\mathrm{Im}[\epsilon(\nu)] \sim \frac{1}{\nu^2} \sum_{a,d} M_{ad} J(\nu). \quad (6)$$

This joint density of states gives the density of pairs of states, one occupied the other empty, separated by an energy $h\nu$ [33,34]. Treating the transition matrix element as a constant during the adsorption process we can write, integrating over the whole optical spectrum:

$$\partial \int \frac{\Delta R}{R} \nu \,\mathrm{d}\nu \sim \partial \sum_k \left(\frac{\Delta R}{R}\right)_k \nu_k \sim -\sum_{a,d} M_{ad}\, \partial(N_{sa}^* N_{sd}^*)$$
$$\sim -\sum_{a,d} M_{a,d}[\partial(N_{sa}^*) N_{sd}^* + N_{sa}^*\, \partial(N_{sd}^*)]. \quad (7)$$

The integral over the light frequency is replaced by a summation over the frequency-weighted magnitude of the pronounced transitions (k) in the recorded spectrum [34]. From eqs. (3) and (7) it is evident that electrical and optical techniques measure comparable quantities. Electrical measurements provide the difference between occupied and unoccupied surface states while optical measurements give the total number of surface states. A graphical relation between the optical and electrical parameters which have been acquired during the adsorption of N_2O on Si(001)2 × 1 is given in fig. 4. The original optical data were taken from ref. [10] and have been modified in such a way so as to provide the property of eq. (7). The optical parameter is the sum of the differential reflectivity intensity, $\Delta R/R$, recorded at 2.90 and 3.85 eV photon energy, weighted by the corresponding photon energy $h\nu$. The optical data at $h\nu = 3.85$ eV correspond with the removal of the Si–Si dimers as the formation of bridge-bonded oxygen proceeds, the accompanying saturation of the dangling bonds is represented by the 2.90 eV data. Also indicated in this figure are the three adsorption stages which were found to be distinguishable for this reaction [10,12].

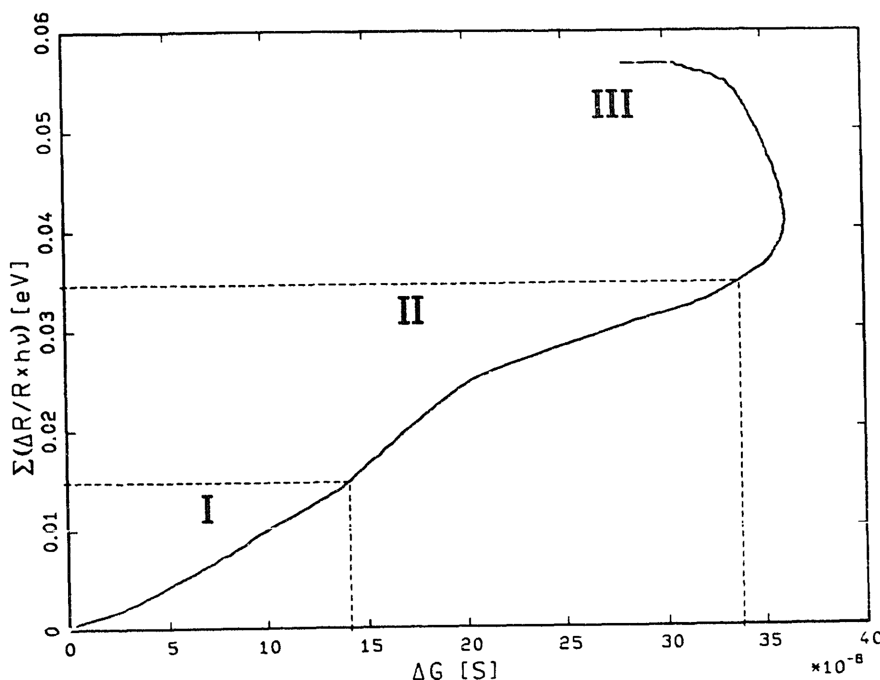

Fig. 4. Variation of the sum of the differential reflectivity intensity, $\Delta R/R$, recorded at 2.90 and 3.85 eV photon energy and weighted by the corresponding photon energy $h\nu$, as a function of the change in total conductance upon exposing the clean Si(001)2 × 1 surface to N_2O. The three stages of the adsorption process (see ref. [12]) are also indicated in this figure.

The first adsorption stage in fig. 4 consists of the formation of bridge-bonded oxygen on only the dimers, while in the second stage also bridging oxygen is formed by the attachment of the oxygen atoms with the two dangling bonds (D_u and D_d) of the first-layer Si atoms of two nearest-neighbour reacted dimers. This site is in line wit'ı the orientation of the dimers on the clean s rface and is also called long dimer site (LD) [26] although no actual dimer bond exists. As soon as at least one of the dimers on either side of this LD site has incorporated an oxygen atom in a dimer bridge site the long dimer site is prone to the uptake of an oxygen atom due to a more favourable geometric position position [10,12]. The rather straight lines in the first two stages in fig. 4 indicate a preferential removal of one donor state [34], although the rate of change of $\Sigma(\Delta R/R) \times h\nu$ (summed at the two frequencies) with ΔG is smaller at stage II. In order to discriminate between the reaction of the actual dimer site DM and the LD site, fig. 5 shows $(\Delta R/R) \times h\nu$ at 2.90 and 3.85 eV photon energy, both as a function of the change in total conductance. Fig. 5 shows more clearly that the first stage can be attributed almost solely to a change in the optical transition at 3.85 eV, which is due to a break-up of the (short) dimer bond as the formation of bridging oxygen takes place at this stage. The second stage can be clearly divided in two substages. The first part shows a take-up of oxygen in both DM (curve b) and LD (curve a) site as can be seen from a change in reflectivity at the characteristic transitions. Transitions in surface optics are in general rather broad and an overlap of the 2.90 eV transition with the feature recorded at 3.85 eV is not unlikely. A change in the reflectivity due to the removal of long dimer sites which have a mean energy of 2.90 eV may therefore lead to a notable change in the reflectivity in the region characteristic of the short dimer site around 3.85 eV. This may explain the final part of stage II, where the rate of change of reflectivity at 3.85 eV with ΔG goes to zero, normally indicating a reduction in the number of short dimer sites attacked by oxygen. At the be-

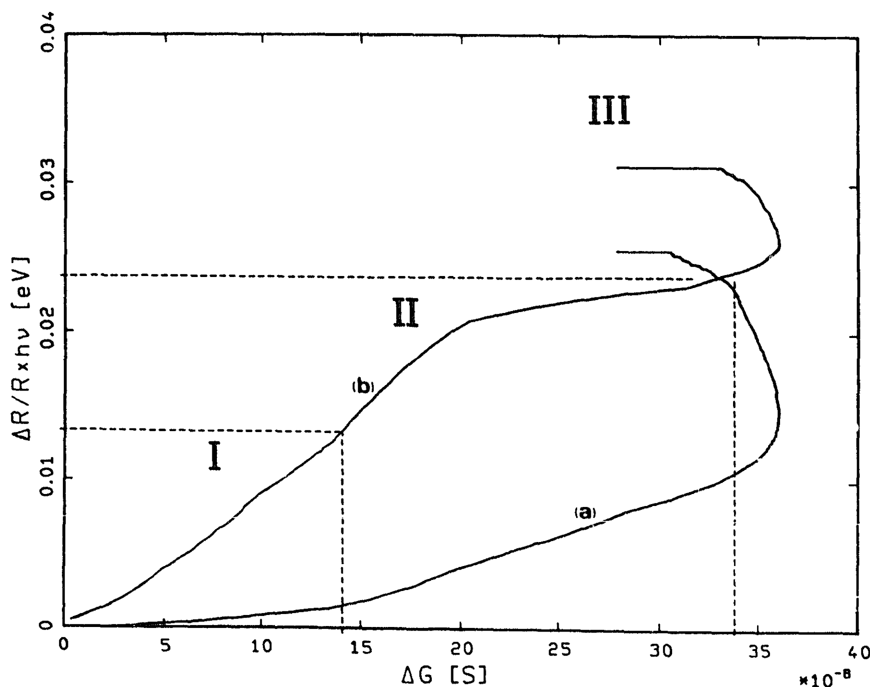

Fig. 5. Variation of the differential reflectivity intensity, $\Delta R/R$, recorded at (a) 2.90, and (b) 3.85 eV photon energy and weighted by the corresponding photon energy $h\nu$, as a function of the change in total conductance upon exposing the clean Si(001)2 × 1 surface to N_2O. The three stages of the adsorption process (see ref. [12]) are also indicated in this figure.

ginning of this second part of stage II already all dimer sites may be completely saturated. The overlap of the two optical transitions may also be the explanation for the small increase seen at 2.90 eV in stage I. It is therefore that stage II can be divided in two substages, the first one characterized by the incorporation of oxygen atoms in both the short and long dimer sites, the latter one by a preference for the long dimer site.

The SCM data in figs. 4 and 5 show in stage III a change in the removal from mainly donor to mainly acceptor states. In this stage mainly the LD sites in fig. 3 are liable to react as indicated by the optical parameter related to this site [10,12]. The small change in the optical parameter at 3.85 eV in fig. 5 may be partly due to the increase of the transition at 2.90 eV in the same way as in the final part of stage II. Whereas the optical data show saturation [10,12] the surface conductance still decreases a little at high N_2O exposures. This result provides supporting evidence for our idea that the optical spectra should be recorded in an energy region broader than was done in the present measurements in order to be compared satisfactorily with SCM measurements. From AES [5], UPS [24] and EELS [35] measurements, namely, surface states far below the Fermi energy were found to exist for the Si(001)2 × 1 surface. Their removal upon oxygen adsorption will certainly remain undetected within the optical photon energy region used (1.5–4.5 eV [10]). Not only the removal of surface states will lead to a change in reflection upon adsorption of a gas on the clean surface. States related to the incorporated oxygen atom will have their influence on spectra recorded over a broader energy region as can be deduced from the fact that the imaginary part of the dielectric constant of a silicon-oxide layer can no longer be neglected for photon energies above 4 eV. These oxygen-induced states with rather high binding energy have, however, been observed quite well with AES [10].

4. Conclusion

SCM shows a clear distiction between the process of molecular and atomic oxygen adsorption on the clean Si(001)2 × 1 surface. The three steps in the adsorption process of atomic oxygen are easily identified by comparing the results of optical and electrical measurements. The first part of the second stage shows clearly the incorporation of oxygen atoms into short as well as long dimer positions. In the second part the long dimer site is clearly more favourable for the uptake of O, indicating that all of the short dimer sites have been transformed into a bridge-bonded oxygen configuration. The atomic oxygen as released by the decomposition of N_2O on the Si surface is not able to penetrate the backbond positions. Therefore, not all of the surface states present at the clean surface are removed and a band bending still exists at saturation coverage. In contrast, exposure of the Si(001)2 × 1 surface to molecular oxygen is accompanied by the attack of the backbonds and ultimately leads to the unbending of the band. A value of 0.32 ± 0.02 eV for the distance between the valence band edge and the Fermi level could therefore be derived.

References

[1] P. Mårtensson, A. Cricenti and G.V. Hansson, Phys. Rev. B 33 (1986) 8855.
[2] F.J. Himpsel and D.E. Eastman, J. Vac. Sci. Technol. 16 (1979) 1297.
[3] L.S.O. Johansson, R.I.G. Uhrberg, P. Mårtensson and G.V. Hansson, Phys. Rev. B 42 (1990) 1305.
[4] F.J. Himpsel, Surf. Sci. Rep. 12 (1990) 1.
[5] A.G.B.M. Sasse, H. Wormeester, M.A. van der Hoef and A. van Silfhout, Surf. Sci. 218 (1989) 553.
[6] A.G.B.M. Sasse, H. Wormeester, M.A. van der Hoef and A. van Silfhout, J. Phys. (Condensed Matter) 1 (1989) 10175.
[7] Ph. Avouris, I.-W. Lyo and F. Bozso, J. Vac. Sci. Technol. B 9 (1991) 424.
[8] U. Höfer, P. Morgen, W. Wurth and E. Umbach, Surf. Sci. 211/212 (1989) 948.
[9] E.G. Keim and H. Wormeester, J. Vac. Sci. Technol., in press.
[10] E.G. Keim, L. Wolterbeek and A. van Silfhout, Surf. Sci 180 (1987) 565.
[11] P.V. Smith and A. Wander, Surf. Sci. 219 (1989) 77.
[12] E.G. Keim and H. Wormeester, Surf. Sci. 260 (1992) 23
[13] G. Herzberg, Electronic Spectra of Polyatomic Molecule (Van Nostrand, New York, 1966).
[14] E.G. Keim, unpublished results.

[15] H.J.W. Zandvliet and A. van Silfhout, Surf. Sci. 195 (1988) 138.
[16] A. Many, Y. Goldstein and N.B. Grover, Semiconductor Surfaces (North-Holland, Amsterdam, 1965).
[17] G. Heiland and H. Lamatsch, Surf. Sci. 2 (1964) 18.
[18] P. Handler, Appl. Phys. Lett. 3 (1963) 96.
[19] A.H. Boonstra, PhD Thesis, Eindhoven Technical University, 1967; Philips Res. Rep. 3 (1968).
[20] It is well known that the room-temperature adsorption of O_2 at the clean Si(001) and Si(111) surface involves a fast initial step followed by a continuous sorption stage which exceeds monolayer (ML) coverage. Between 50 and 100 L O_2 exposure ML coverage is usually achieved, which we will consider as apparent saturation. After this stage a further slow sorption of oxygen occurs.
[21] J.W.D. Martens, PhD Thesis, University of Twente, Netherlands, 1980.
[22] F.G. Allen and G.W. Gobeli, Phys. Rev. 127 (1962) 150.
[23] Y. Miyamoto and A. Oshiyama, Phys. Rev. B 41 (1990) 12680.
[24] G. Hollinger and F.J. Himpsel, Phys. Rev. B 28 (1983) 3651.
[25] L. Incoccia, A. Balaerna, S. Cramm, C. Kunz, F. Senf and I. Storjohann, Surf. Sci. 189/190 (1987) 453.
[26] X.M. Zheng and P.V. Smith, Surf. Sci. 232 (1990) 6.
[27] A. Namiki, K. Tanimoto, T. Nakamura, N. Ohtake and T. Suzaki, Surf. Sci. 222 (1989) 530.
[28] H.J.W. Zandvliet and A. van Silfhout, Surf. Sci. 211/212 (1989) 544.
[29] H.J.W. Zandvliet, E.G. Keim and A. van Silfhout, J. Vac. Sci. Technol. A 8 (1990) 2581.
[30] J.D.E. McIntyre and D.E. Aspnes, Surf. Sci. 24 (1971) 417.
[31] F. Meyer, E. de Kluizenaar and G.A. Bootsma, Surf. Sci. 27 (1971) 88.
[32] F. Meyer, Phys. Rev. B 9 (1974) 3622.
[33] F. Bassani and G. Pasori Parravicini, Electronic States and Optical Transitions in Solids (Pergamon, Oxford, 1975).
[34] H.J.W. Zandvliet and A. van Silfhout, Solid State Commun. 65 (1988) 1425.
[35] J.E. Rowe and H. Ibach, Phys. Rev. Lett. 31 (1973) 102.