

## Adsorption of oxygen on the Si(110)5×1 surface via interaction with O<sub>2</sub>

Enrico G. Keim, Arend van Silfhout, and Lambert Wolterbeek

Citation: *Journal of Vacuum Science & Technology A* **6**, 57 (1988); doi: 10.1116/1.574968

View online: <http://dx.doi.org/10.1116/1.574968>

View Table of Contents: <http://scitation.aip.org/content/avs/journal/jvsta/6/1?ver=pdfcov>

Published by the AVS: Science & Technology of Materials, Interfaces, and Processing

---

### Articles you may be interested in

[The adsorption and photodesorption of oxygen on the TiO<sub>2</sub>\(110\) surface](#)

*J. Chem. Phys.* **102**, 4657 (1995); 10.1063/1.469513

[Chemical titration of clean silicon surfaces with N<sub>2</sub>O and O<sub>2</sub>: Atomic nature of “5×1” reconstructed Si\(110\)](#)

*J. Vac. Sci. Technol. A* **8**, 2747 (1990); 10.1116/1.576661

[The adsorption of Cs and O<sub>2</sub> on a clean GaAs\(110\) surface under light illumination](#)

*J. Vac. Sci. Technol. A* **7**, 1563 (1989); 10.1116/1.576093

[Adsorption of atomic oxygen on the Si\(110\)5×1 surface via interaction with N<sub>2</sub>O](#)

*J. Vac. Sci. Technol. A* **5**, 1019 (1987); 10.1116/1.574176

[Abstract: Effect of surface structure on the adsorption of O<sub>2</sub> and H<sub>2</sub> on Pt\(100\): Comparison of the \(1×1\) and \(5×20\) configuration](#)

*J. Vac. Sci. Technol.* **14**, 445 (1977); 10.1116/1.569258

---



A PASSION FOR PERFECTION

PFEIFFER  VACUUM



### Customized cubical vacuum chambers

- Sizes 12" and 20"; ports and locations selectable
- Only 2 weeks production time
- Prices starting at \$5,900

Are you looking for a perfect vacuum solution?  
Please contact us!

# Adsorption of oxygen on the Si(110) $5 \times 1$ surface via interaction with O<sub>2</sub>

Enrico G. Keim, Arend van Silfhout, and Lambert Wolterbeek

University of Twente, Faculty of Applied Physics, P. O. Box 217, 7500 AE Enschede, The Netherlands

(Received 29 May 1987; accepted 19 September 1987)

Auger electron spectroscopy, low-energy electron diffraction, and differential reflectometry in the photon energy range 1.5–4.5 eV have been used to study the room-temperature adsorption of O<sub>2</sub> on the Si(110) surface with an initial  $5 \times 1$  superstructure. The reaction kinetics are complicated. Five adsorption stages can be discerned, the first stage (0–2 L) being remarkably fast with an initial sticking probability near unity. Our results suggest that the surface sites which constitute the higher-order reconstructions and possibly also defects, are highly reactive. In the second stage (2–200 L) the O<sub>2</sub> adsorption can be described by a dissociative process on the first-layer Si atoms, the sticking probability being about  $2 \times 10^{-3}$ . Incorporation of oxygen into the subsurface Si lattice and possibly also adsorption of a molecular oxygen species are the main processes of the third stage (200–1000 L). In the fourth stage ( $10^3$ – $4 \times 10^4$  L) O<sub>2</sub> adsorption completely removes the dangling bonds. This occurs at  $0.79 \pm 0.15$  monolayer oxygen coverage. The number of dangling bonds per  $5 \times 1$  unit cell (ten atoms) is thus eight or less. The fifth stage ( $> 4 \times 10^4$  L) comprises a slow further oxygen adsorption with a sticking probability of  $\sim 10^{-6}$ : oxygen mainly goes into a bridging position between two first-layer Si atoms in the uppermost chains of the ideal (110) surface. The optical spectrum indicates that the clean Si(110) surface probably has several types of (dangling bond) surface states.

## I. INTRODUCTION

The room-temperature adsorption of O<sub>2</sub> on the clean Si(110) surface has been studied with considerably less intensity than that on the other two low-Miller-index surfaces of silicon, although this surface is not without technological importance. The results of the few studies which have dealt with this adsorption process,<sup>1–3</sup> however, do not show favorable agreement with respect to the description of the O<sub>2</sub> adsorption kinetics in the submonolayer region. Very recently,<sup>4</sup> we have been able to show that the enormous discrepancy in the experimentally found initial sticking probabilities of O<sub>2</sub> on Si(110)<sup>1–3</sup> can mainly be attributed to the difference in the onset of the O<sub>2</sub> adsorption experiments. Another factor which may influence the O<sub>2</sub> adsorption behavior, is the reconstruction of the initial clean Si(110) surface. It is well known that this surface exhibits several reconstructions very critically depending on heat treatment, cooling rate, and preparation.<sup>5–10</sup> However, the experimentalists studying the O<sub>2</sub> adsorption on Si(110)<sup>1–3</sup> all used a different method of preparing their clean Si(110) surface. Moreover, they did not report on its superstructure.

The primary aim of the present paper is to give a more coherent picture of the initial stages of the room-temperature adsorption of oxygen on an atomically clean Si(110) surface. For that purpose we compare the interaction of this surface with N<sub>2</sub>O (Ref. 11) and O<sub>2</sub>. This approach has recently led to a substantial improvement in the understanding of the atomic nature of the oxygen covered Si(100) surface.<sup>12</sup> In Refs. 11–14 it has been shown that the room-temperature decomposition of N<sub>2</sub>O (into N<sub>2</sub> and O<sub>atomic</sub>) at the three low-Miller-index surfaces of silicon only occurs at those Si surface atoms with a broken bond. In this way an essentially abrupt interface between the saturated (mon)atomic oxygen adlayer and the underlying Si lattice

can be obtained. A comparative study, as mentioned above, can thus yield detailed information concerning the adsorption of O<sub>2</sub> on the clean Si(110) surface as to it being purely or partially dissociative, and the stage at which oxygen starts to penetrate into the Si subsurface.

The interaction of the clean Si(110) surface with O<sub>2</sub> has been studied in ultrahigh vacuum at 300 K by means of Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), and differential reflectometry (DR) in the photon energy range of 1.5 to 4.5 eV. With this combination of techniques it is possible to make an analysis of the geometric and electronic structure and the chemical composition of the surface layer.<sup>11–14</sup> The results are also compared with those of earlier works.<sup>1,11–15</sup>

AES was used (a) to check the surface cleanliness and (b) to measure the relative oxygen coverage on the Si(110) surface as a result of O<sub>2</sub> exposure. The fractional oxygen coverage in AES,  $\theta_{\text{AES}}$ , has been derived from the ratio of the measured oxygen *KLL* (510 eV) to the silicon *L<sub>23</sub>VV* (92 eV) Auger peak-to-peak (p-p) heights in the first derivative [ $dN(E)/dE$ ] of the energy distribution, i.e.,  $h_{\text{O}}/h_{\text{Si}}$ , using the procedure as outlined in Ref. 12 (see also Ref. 11). Information concerning the chemical bonding has been extracted from the Si *L<sub>23</sub>VV* Auger spectra in the energy range 50–90 eV. The LEED patterns were merely used as “fingerprints.” Figure 1 shows the LEED pattern of the clean Si(110) surface (see Sec. II). It shows a prominent  $5 \times 1$  superstructure, with faint streaks (indicative of higher-order reconstruction) and additional diffuse spots. The quality of our  $5 \times 1$  LEED pattern is good compared with that of Ref. 8. Each AES data point ( $h_{\text{O}}/h_{\text{Si}}$ ), Si *L<sub>23</sub>VV* curve, and LEED pattern was obtained after exposing the cleaned Si(110) surface to a single O<sub>2</sub> dose in order to avoid electron beam induced artifacts. O<sub>2</sub> was admitted into the reaction chamber in the pressure range  $10^{-9}$ – $10^{-4}$  Torr.

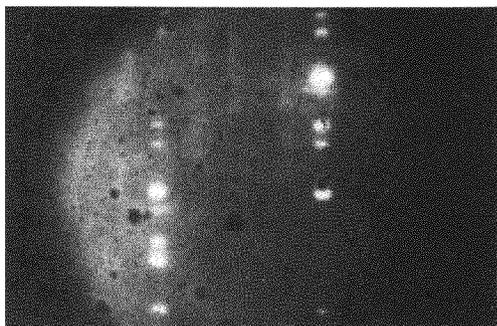


FIG. 1. LEED pattern of the clean Si(110)5×1 surface (105 eV).

DR has been used to monitor the adsorption of O<sub>2</sub> on Si(110) *in situ*. The relevant parameter is  $\Delta R/R$ , the relative change of the sample surface reflectivity.  $\Delta R/R$  is measured when the surface is allowed to change from an initial state (clean Si surface, containing  $\sim 10^{15}$  surface states per cm<sup>2</sup>) to a final state (the same surface covered by a fractional monolayer of oxygen and a reduced number of surface states). The corresponding expression<sup>1</sup> is

$$\Delta R/R = (R_{\text{clean}} - R_{\text{ox}})/R_{\text{clean}}, \quad (1)$$

where  $R_{\text{clean}}$  and  $R_{\text{ox}}$  are the overall reflectivities of the initial and final states of the surface, respectively. DR can provide information about the degree of oxygen coverage, the electronic structure of a clean silicon surface, and the change of this structure due to chemisorption.<sup>1,11-16</sup> The advantage of using DR over AES and LEED is that it allows one to study surface processes at any gas pressure and without electron beam induced surface effects.

## II. EXPERIMENTAL

For a detailed description of the cleaning recipe of the Si(110) surface (10 Ω cm boron doped *p* type, 10×30×0.2 mm<sup>3</sup>, purchased from Siltronix) by simultaneous Ar ion bombardment and annealing (SIBA), experimental setup (AES, LEED, and DR), principles of operation, gas handling, and procedures, we refer to Refs. 12, 14, and 17.

## III. RESULTS

### A. Reflectivity measurements

Curves (a)–(e) of Fig. 2 show the relative difference in reflectivity  $\Delta R/R(h\nu)$  before and after exposing a clean Si(110)5×1 surface to O<sub>2</sub> in five successive stages. The upper curve corresponds to the ultimate relative change in reflectivity upon O<sub>2</sub> exposure  $\Delta R/R^{O_2}(h\nu, \text{sat})$ . The bottom curve shows three peaks at 2.15, 3.10, and 4.1 eV, denoted as  $X'$ ,  $Y'$ , and  $Z'_1$ , respectively. Additional exposure (4.5 L) results in the appearance of a peak at 3.85 eV, in Fig. 2 denoted as  $Z'_2$ . Peaks  $X'$  and  $Y'$  remain at their initial position for exposures up to 12 L [curves (a)–(c)]. It seems that further exposure (> 12 L) leads to a shift in the maxima of peaks  $X'$  and  $Y'$ . At saturation [curve (e)] these peaks have merged into a broad peak, having its apparent maximum at  $\sim 2.6$  eV.

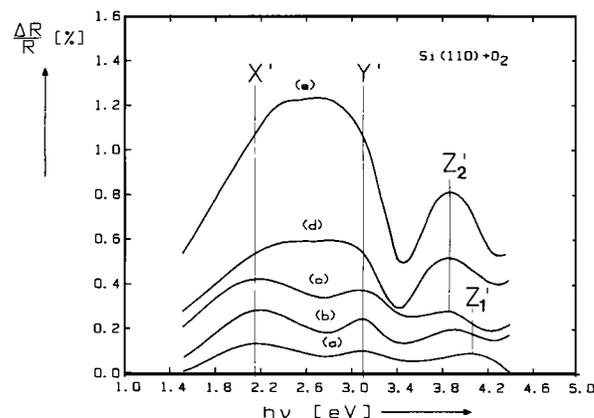


FIG. 2. The relative difference in reflectivity  $\Delta R/R(h\nu)$  before and after exposing a clean Si(110)5×1 surface to O<sub>2</sub>: (a) 1.5, (b) 6, (c) 12, (d) 170, and (e)  $\geq 4 \times 10^4$  L.

The relative change in reflectivity  $\Delta R/R$  at 2.15, 3.10, and 3.85 eV with O<sub>2</sub> exposure is depicted in Fig. 3 by curves  $X'$ ,  $Y'$ , and  $Z'_2$ , respectively. The inset shows  $\Delta R/R$  upon small O<sub>2</sub> exposure (0–20 L). We can, from this figure, determine that saturation occurs at an exposure of about  $4 \times 10^4$  L.

### B. AES and LEED measurements

Displayed in Fig. 4 is the converted  $h_{\text{O}}/h_{\text{Si}}$  ratio  $\theta_{\text{AES}}$  (see Sec. I) versus O<sub>2</sub> exposure. It can be seen that the oxygen uptake occurs in distinct stages.

During initial exposure (0–2 L), i.e., at  $0 \leq \theta_{\text{AES}} \leq 0.15$ , the diffuse spots and faint streaks observed in addition to the 5×1 LEED pattern (Fig. 1) rapidly disappear. At around monolayer (ML) coverage only a weak 1×1 pattern with very high background intensity is observed.

The sticking probability of O<sub>2</sub> as a function of the fractional oxygen coverage  $\theta_{\text{AES}}$ ,  $s_{\text{AES}}(\theta)$ , has been derived from the slope of the exposure curve in Fig. 4 using the expression

$$d\theta/dt = s_{\text{AES}}(\theta)(\nu P/N_0), \quad (2)$$

where  $\nu$  is a frequency factor ( $= 3.48 \times 10^{20} \text{ cm}^{-2} \text{ s}^{-1} \text{ Torr}^{-1}$ ),  $N_0 = 4.8 \times 10^{14}$  adsorption sites per cm<sup>2</sup> for an O<sub>2</sub>

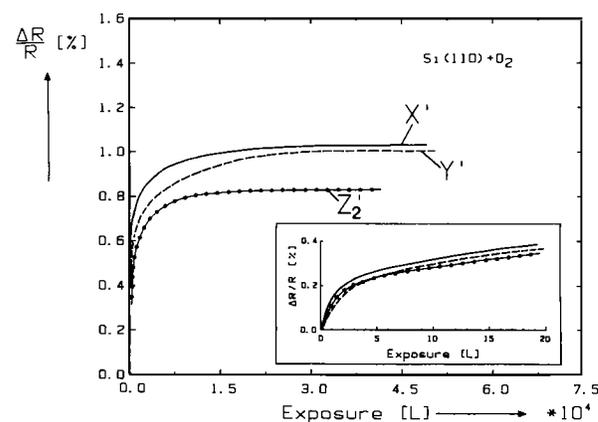


FIG. 3. The relative variation in reflectivity  $\Delta R/R$  vs O<sub>2</sub> exposure at  $h\nu = 2.15$  eV (curve  $X'$ ),  $h\nu = 3.10$  eV (curve  $Y'$ ), and  $h\nu = 3.85$  eV (curve  $Z'_2$ ). The inset shows the low-exposure behavior.

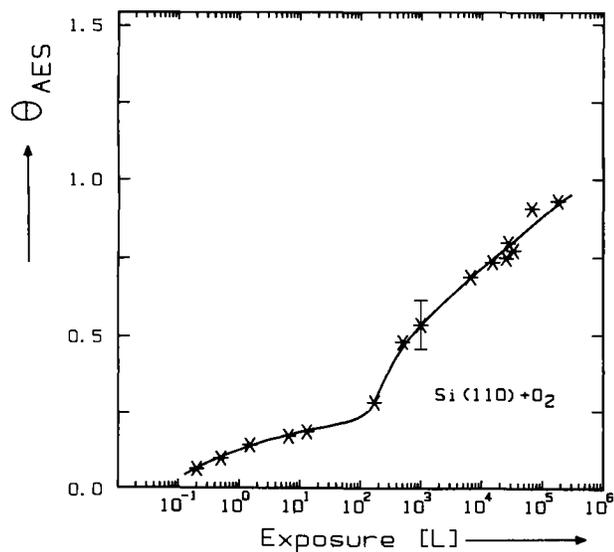


FIG. 4. The fractional oxygen coverage  $\theta_{\text{AES}}$  vs  $\text{O}_2$  exposure. Each data point is taken after new exposure to a freshly cleaned surface.

molecule on the (110) surface,  $P$  is the pressure in Torr, and  $t$  is the time in s.  $s_{\text{AES}}(\theta)$  is plotted versus  $\text{O}_2$  exposure in Fig. 5. From this figure, we conclude that the initial sticking probability is near unity.<sup>4</sup> At around ML coverage  $s_{\text{AES}}(\theta)$  has decreased to  $\sim 10^{-6}$ . It seems that slow sorption continues beyond ML coverage.

Curve (a) of Fig. 6 shows the actual  $L_{23}VV$  Auger spectrum of a clean Si(110)5×1 surface between 50 and 90 eV. This spectrum resembles that of a clean Si(100)2×1 surface,<sup>12,14,17</sup> the peak at 81 eV, however, being broader and less pronounced. Figure 6 further shows the Si  $L_{23}VV$  Auger spectra for several stages of the oxygen chemisorption on Si(110) up to about ML coverage [curve (g)]. These spectra show peaks at 62, 83, and  $\sim 70$  eV [starting to appear in curve (d)]. Recently,<sup>12</sup> it has been shown that the Si  $L_{23}VV$  Auger transition at 83 eV can be related to Si-O bond formation on the first-layer Si atoms since its p-p height [measured from the positive excursion at 79.5 eV to the negative end at 83 eV; see, e.g., curve (d) of Fig. 6] is linearly proportional to the total number of dangling and dimer bond orbitals which have disappeared upon exposing a clean

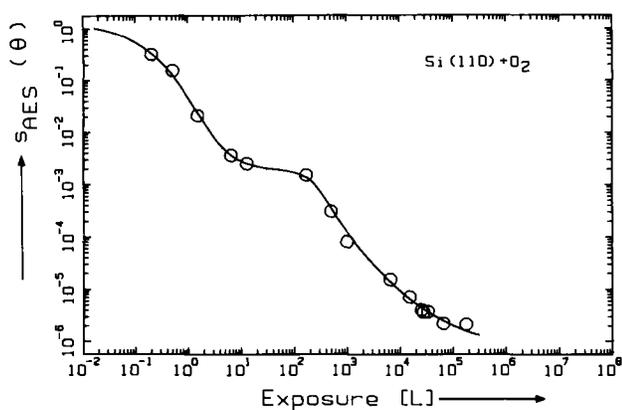


FIG. 5. The sticking probability of  $\text{O}_2$ ,  $s_{\text{AES}}(\theta)$ , as a function of exposure.

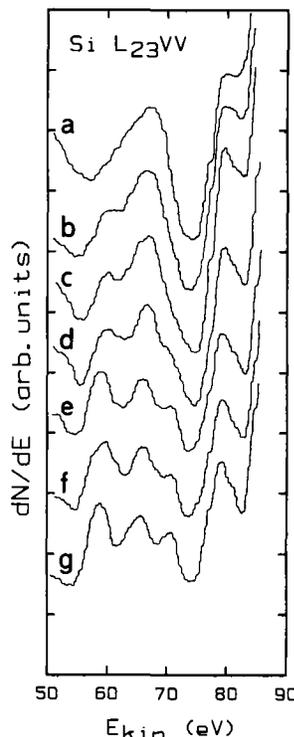


FIG. 6. Si  $L_{23}VV$  Auger spectrum of (a) a clean Si(110)5×1 surface, and the same surface exposed to (b) 13, (c) 170, (d)  $10^3$ , (e)  $2.7 \times 10^4$ , (f)  $7 \times 10^4$ , and (g)  $1.5 \times 10^5$  L  $\text{O}_2$ .

Si(100)2×1 surface to  $\text{N}_2\text{O}$  or  $\text{O}_2$ . Displayed in Fig. 7 is the p-p height of the SiO peak at 83 eV, denoted as  $h_{\text{SiO}}(83 \text{ eV})$  in arbitrary units (a.u.), versus  $\text{O}_2$  exposure. From Fig. 4 we derive that ML coverage occurs at an exposure of about  $6 \times 10^5$  L. At ML coverage  $h_{\text{SiO}}(83 \text{ eV}) = 22 \pm 1$  a.u. (by extrapolation). This is indicated by the arrow in Fig. 7. In this figure is also plotted  $h_{\text{SiO}}^{\text{N}_2\text{O}}(83 \text{ eV})$ , obtained after formation of a monatomic oxygen layer on the Si(100) surface via decomposition of  $\text{N}_2\text{O}$ ,<sup>12</sup> in this figure denoted by the asterisk. Its saturation value was found to be  $16 \pm 1$  a.u. At ML coverage the ratio  $h_{\text{SiO}}^{\text{N}_2\text{O}}(83 \text{ eV})/h_{\text{SiO}}(83 \text{ eV})$  is equal to  $0.73 \pm 0.04$ . This value is, within experimental error, equal to the ratio of the numbers of first-layer Si atoms at the Si(100) surface ( $N_1$ ) and of the Si(110) surface ( $N_0$ ), respectively, i.e.,  $N_1/N_0 = 6.8 \times 10^{14}/9.6 \times 10^{14} = 0.71$ . This result implies that around ML coverage (Fig. 4) practically all first-layer Si atoms have Si-O bonds (see also Sec. IV B).

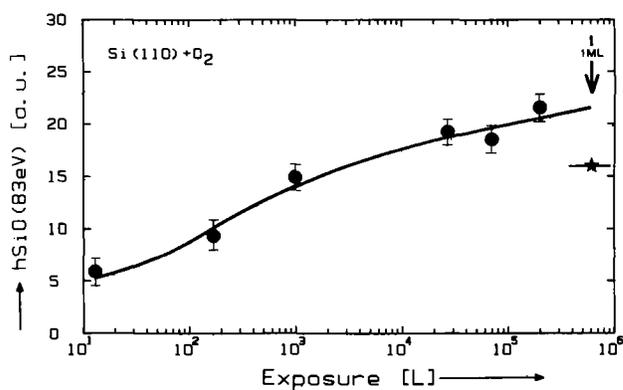


FIG. 7. SiO 83-eV Auger p-p height,  $h_{\text{SiO}}(83 \text{ eV})$  [arbitrary units], vs  $\text{O}_2$  exposure.

## IV. DISCUSSION

### A. Surface state transitions

Recently,<sup>18</sup> a preliminary microscopic calculation of the surface contribution to optical reflectivity has shown that, for the Si(110) surface, differential reflectivity structure in the range of 2 to 4 eV—usually attributed to transitions involving surface states—actually contains a large contribution of other transitions, yielding information not directly related to surface states, but rather to the surface geometry. Unfortunately, the authors of this study were not able to compare their calculational results with experiment, since polarization-dependent reflectance measurements on this surface, in contrast to the Si(111)2×1 surface,<sup>19,20</sup> have not yet been carried out. Surface excitonic effects and the Franz–Keldysh effect are not expected to contribute significantly to the optical spectrum for photon energies of 1.5 to 4.5 eV.<sup>12</sup> Because of the uncertainties in the assignment of peaks  $Y'$ ,  $Z'_1$ , and  $Z'_2$  (Fig. 2), we shall focus our attention in this paper on the relative change in reflectivity at 2.15 eV (peak  $X'$ ) with  $O_2$  exposure when we discuss the reaction kinetics (see Sec. IV B).

In view of earlier optical data<sup>1,11,21,22</sup> and a recent photoemission experiment<sup>9</sup> we assign the broad peak at 2.15 eV ( $X'$  in Fig. 2) to optical transitions from the broad filled band of dangling bond surface states near the top of the valence band<sup>9</sup> to empty bulk conduction-band levels. The fact that this surface state feature on Si(110)5×1 is relatively broad was attributed to disorder effects.<sup>9</sup> Evidence of higher-order reconstructions and partial disorder on the clean (110) surface is also given in our LEED picture (Fig. 1): it shows (weakly visible) streaks and diffuse spots in addition to the primary 5×1 LEED pattern which is reasonably clear. Peak  $X'$  might conceal a second and even a third peak around 2.7 eV (Fig. 2), since the maximum of peak  $X'$  [curves (a)–(c)] shifts towards higher photon energy, as estimated from the apparent maximum at ~2.6 eV in curve (e). Wierenga *et al.*<sup>1</sup> only recorded their  $\Delta R/R(h\nu)$  curve ( $1.0 < h\nu < 3.0$  eV) before and after adsorption of a monolayer of oxygen on the clean Si(110) surface. Their  $\Delta R/R(h\nu)$  curve is almost identical with our  $\Delta R/R^{O_2}(h\nu, \text{sat})$  curve [curve (e) of Fig. 2]. They interpreted the apparent maximum at ~2.6 eV as due to optical transitions from a filled dangling bond surface states band near the top of the valence band to empty bulk conduction-band levels. However, by recording  $\Delta R/R(h\nu)$  both as a function of photon energy and of exposure (Fig. 2) we must conclude that the actual maximum is not at 2.6-eV photon energy. The peak with its apparent maximum at ~2.6 eV [curve (e) of Fig. 2] seems to be composed of at least three peaks. As to the Si(110)5×1 surface exposed to  $N_2O$ ,<sup>11</sup> even a peak at 1.7 eV [ $X''_1$  in Fig. 1 of Ref. 11 (Ref. 23)] in  $\Delta R/R(h\nu)$  can be distinguished. Moreover, the peak at 2.15 eV ( $X''_2$  in Fig. 1 of Ref. 11) appears to be narrower than the corresponding one of this work ( $X'$  in Fig. 2). We believe that these peaks below 2.2 eV, i.e.,  $X''_1$  and  $X''_2$  in Fig. 1 of Ref. 11, are distinguishable and relatively narrow because of the site-specific decomposition of  $N_2O$  at the Si(110)5×1 surface<sup>11</sup>: in Ref. 11 we have shown that decomposition of the  $N_2O$  molecule only occurs at those sur-

face Si atoms which have an unsaturated dangling bond. Every stage of this reaction was found to involve oxygen atom attachment by the dangling bonds.  $O_2$  on the other hand, will, in general (Ref. 12, and references therein), interact with various surface sites, including the backbonds, as we shall show in Sec. IV B.

The other measured peaks in the  $\Delta R/R(h\nu)$  curves for the reaction of the Si(110)5×1 surface with  $N_2O$  ( $Y''$  and  $Z''$  in Fig. 1 of Ref. 11), differ slightly in photon energy from those for the same surface with  $O_2$  ( $Y'$  and  $Z'_2$  in Fig. 2). Furthermore, peak  $Z'_1$ , which can be clearly seen at low  $O_2$  exposures in curve (a) of Fig. 2, has not been observed in the  $\Delta R/R(h\nu)$  spectra of Ref. 11. We may therefore draw the conclusion that the binding state of atomic oxygen on Si(110), as released by  $N_2O$ , is different from the binding state of the oxygen species after exposing the same surface to  $O_2$ , even at low oxygen coverage. Moreover, we may speculate that peak  $Z'_1$ , which is prominent after low exposure [curve (a) of Fig. 2], can be related to an adsorption site highly reactive to the  $O_2$  molecule (see Sec. IV B). Nevertheless, further detailed experimental (photoemission, inverse-photoemission, and polarization-dependent surface reflectance measurements) and theoretical research on the Si(110)5×1 surface is needed to explain all the features in our optical spectrum (Fig. 2) satisfactorily.

### B. Reaction kinetics

Displayed in Fig. 8 is  $\Delta R/R$ , recorded at 2.15 eV (peak  $X'$  of Fig. 2), versus  $\theta_{\text{AES}}$ . This curve relates the removal of the dangling bond surface states by the adsorbed oxygen. The  $\Delta R/R$  recordings at 3.10 eV ( $Y'$ ) and 3.85 eV ( $Z'_2$ ) exhibit a behavior similar to that of Fig. 8 but are not shown here. The exposure regions are also indicated in this figure. From these data five adsorption stages can be distinguished.

The initial adsorption stage (0–2 L) is remarkably fast, the initial sticking probability being near unity (see Figs. 4 and 5 and Ref. 4). A possible explanation is that  $O_2$  mainly reacts with those (highly reactive) surface sites which constitute the additional higher-order reconstructions and/or defects on the clean Si(110)5×1 surface. We suggest that these surface sites can be related to peak  $Z'_1$  in curve (a) of

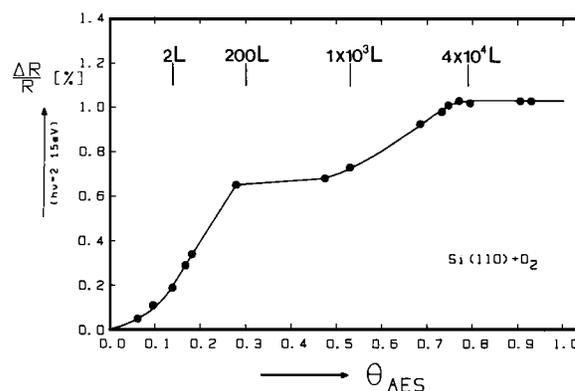


Fig. 8. The relative change in reflectivity  $\Delta R/R$  as a function of the fractional oxygen coverage  $\theta_{\text{AES}}$  at  $h\nu = 2.15$  eV (peak  $X'$  of Fig. 2). The boundaries of the five exposure stages are also designated in this figure.

Fig. 2, since this peak is only observed at low O<sub>2</sub> exposures (0–2 L). Additional evidence supporting this explanation is given by the results from LEED experiments. In this low exposure range, i.e., at  $0 \leq \theta_{\text{AES}} \leq 0.15$ , the diffuse spots and streaks, observed in addition to the prominent 5×1 LEED pattern (Fig. 1), were found to disappear rapidly, so that a “cleaner” 5×1 LEED pattern appears. This phenomenon is temporary since further O<sub>2</sub> exposure leads to a smooth removal of the 5×1 superstructure spots with an accompanying increase in background intensity (Sec. III B). In the low oxygen coverage region ( $0 \leq \theta_{\text{AES}} \leq 0.15$ ), the removal of the diffuse spots and streaks is accomplished more effectively using O<sub>2</sub> than using N<sub>2</sub>O.<sup>11</sup> This result is further evidence supporting our idea that the interaction of the Si(110)5×1 surface with N<sub>2</sub>O is site specific<sup>11</sup> as compared to that with O<sub>2</sub>.

In the 2–200 L exposure range, i.e., at  $0.15 \leq \theta_{\text{AES}} \leq 0.32$ , we found an almost constant sticking probability of  $\sim 2 \times 10^{-3}$  (Fig. 5) and a constant ratio  $\Delta R/R/\theta_{\text{AES}}$  (Fig. 8). This result is in favor of a model in which the oxygen adsorbs in a weakly bound precursor state, before it is dissociatively adsorbed at the surface.<sup>24–26</sup> Moreover, only first-layer Si atoms are involved in this reaction. Additional evidence in favor of this last remark is given in the Si L<sub>23</sub>VV Auger spectra: up to at least 170-L O<sub>2</sub> exposure these spectra [curves (b) and (c) of Fig. 6] do not give any indication that bulklike silicon oxide is formed at or below the surface, because of the absence of a peak at  $\sim 70$  eV in addition to those at 62 and 83 eV.<sup>27–29</sup>

During stage 3 (200–1000 L) incorporation of oxygen into the subsurface and possibly also molecular adsorption are the main processes since the rate of removal of the dangling bonds with exposure is very low compared to the rate of oxygen coverage (Fig. 8). Structure at  $\sim 70$  eV in the Si L<sub>23</sub>VV Auger spectrum can already be observed at exposures of 10<sup>3</sup> L [curve (d) of Fig. 6]. We may speculate that the grooves in an ideal Si(110) surface play an important role in this oxygen absorption stage.

Further exposure (10<sup>3</sup>–4×10<sup>4</sup> L), the fourth stage, leads again to the removal of dangling bonds. At an exposure of 4×10<sup>4</sup> L all dangling bonds have been removed (Figs. 3 and 8), the fractional oxygen coverage being  $0.79 \pm 0.15$  ML (Figs. 4 and 8). This result implies that the number of dangling (or broken) bonds per 5×1 unit cell (ten atoms) is at most eight, this number being about 40% larger than that found per (111)7×7 unit cell.<sup>14,30</sup>

The slow continuous increase in *h* SiO(83 eV) beyond 4×10<sup>4</sup> L (Fig. 7), stage 5, is an indication that oxygen now mainly establishes a bridging position between the first-layer Si atoms situated in the uppermost chains of the ideal (110) surface. In Sec. III B we arrived at the conclusion that practically all first-layer Si atoms have Si–O bonds at ML coverage since *h* SiO(83 eV) was found to be  $22 \pm 1$  a.u. Beyond ML coverage the formation of bridging oxygen between the first-layer Si atoms continues, since *h* SiO(83 eV) does not show saturation upon further O<sub>2</sub> exposure (Fig. 7).

Our results strongly suggest the existence of multiple-bonding configurations for oxygen on the Si(110) surface in the submonolayer region. This phenomenon has also been

found earlier for the adsorption of O<sub>2</sub> on the Si(111)<sup>13,14</sup> and Si(100)<sup>12,14</sup> surfaces. The results are essentially consistent with those of Hollinger and Himpsel.<sup>31</sup> Using high-resolution core level spectroscopy they showed that, at least for the (111) and (100) surfaces of silicon, multiple oxidation states persist into the submonolayer regime.

## V. CONCLUSIONS

The present study shows that the reaction kinetics of molecular oxygen at the Si(110)5×1 surface is complicated. Five stages can be discerned, the initial one being remarkably fast. Our results suggest that those surface sites which constitute the additional higher-order reconstructions and possibly also defects are highly reactive towards the O<sub>2</sub> molecule. Penetration of oxygen into the Si lattice and adsorption of a molecular oxygen species occur well below ML coverage. This has also been observed earlier on the Si(111)7×7 (Refs. 13 and 14) and Si(100)2×1 (Ref. 12) surfaces. We have found extra evidence supporting the idea that the SiO Auger peak at 83 eV can be exclusively related to Si–O bond formation on the first-layer Si atoms.<sup>11,12</sup>

The combined use of both atomic<sup>11</sup> and molecular oxygen<sup>this work</sup> has led to an improvement in understanding of the initial stages of the room-temperature adsorption of O<sub>2</sub> on the clean Si(110)5×1 surface. Moreover, we have found that the density of broken bonds per (110)5×1 unit cell is about 40% higher than that per (111)7×7 surface unit cell. This result suggests that the (110)5×1 surface unit cell does not differ significantly from the bulklike structural site.

<sup>1</sup>P. E. Wierenga, M.J. Sparnaay, and A. van Silfhout, Surf. Sci. **99**, 59 (1980).

<sup>2</sup>S. Tougaard, P. Morgen, and J. Onsgaard, Surf. Sci. **111**, 545 (1981).

<sup>3</sup>W. Ranke and Y. R. Xing, Surf. Sci. **157**, 353 (1985).

<sup>4</sup>E. G. Keim and A. van Silfhout, Surf. Sci. **186**, L557 (1987).

<sup>5</sup>F. Jona, IBM J. Res. Dev. **9**, 375 (1965).

<sup>6</sup>T. Sakurai and H. D. Hagstrum, J. Vac. Sci. Technol. **13**, 807 (1976).

<sup>7</sup>B. Z. Olshanetsky, S. M. Repinsky, and A. A. Shklyaev, Surf. Sci. **64**, 224 (1977).

<sup>8</sup>B.Z. Olshanetsky and A. A. Shklyaev, Surf. Sci. **67**, 581 (1977).

<sup>9</sup>P. Mårtensson, G. V. Hansson, and P. Chiaradia, Phys. Rev. B **31**, 2581 (1985).

<sup>10</sup>H. Ampo, S. Miura, K. Kato, Y. Ohkawa, and A. Tamura, Phys. Rev. B **34**, 2329 (1986).

<sup>11</sup>E. G. Keim, A. van Silfhout, and L. Wolterbeek, J. Vac. Sci. Technol. A **5**, 1019 (1987).

<sup>12</sup>E. G. Keim, L. Wolterbeek, and A. van Silfhout, Surf. Sci. **180**, 565 (1987).

<sup>13</sup>E. G. Keim and A. van Silfhout, Surf. Sci. **152/153**, 1096 (1985).

<sup>14</sup>E. G. Keim, Ph.D. thesis, Twente University of Technology, Enschede, 1986.

<sup>15</sup>P. E. Wierenga, Ph.D. thesis, Twente University of Technology, Eschede, 1980.

<sup>16</sup>P. E. Wierenga, A. van Silfhout, and M. J. Sparnaay, Surf. Sci. **87**, 43 (1979).

<sup>17</sup>E. G. Keim, Surf. Sci. **148**, L641 (1984).

<sup>18</sup>A. Selloni, P. Marsella, and R. del Sole, Phys. Rev. Lett. **52**, 1145 (1984).

<sup>19</sup>P. Chiaradia, A. Cricenti, S. Selci, and G. Chiarotti, Phys. Rev. Lett. **52**, 1145 (1984).

<sup>20</sup>S. Selci, P. Chiaradia, F. Ciccacci, A. Cricenti, N. Sparvieri, and G. Chiarotti, Phys. Rev. B **31**, 4096 (1985).

<sup>21</sup>F. Meyer, Phys. Rev. B **19**, 3622 (1974).

<sup>22</sup>F. Meyer, Surf. Sci. **56**, 37 (1976).

<sup>23</sup>Peak X<sub>1</sub>'' in Fig. 1 of Ref. 11 may be attributed to optical transitions from

the surface states band at  $\sim 0.8$  eV below the Fermi energy  $E_F$  (Ref. 9) to empty surface states in the gap. At the moment, however, there are no inverse photoemission data available which might give information concerning an unoccupied surface state in the gap.

<sup>24</sup>C. Kohrt and R. Gomer, *J. Chem. Phys.* **52**, 3283 (1970).

<sup>25</sup>It would be interesting to investigate if time-dependent effects of a molecular precursor [as observed for the dissociative adsorption of oxygen on Si(111) (Ref. 26) by means of x-ray and ultraviolet photoelectron spec-

troscopy] can also be perceived for the Si(110) surface.

<sup>26</sup>F. Höfer, P. Morgen, W. Wurth, and E. Umbach, *Phys. Rev. Lett.* **55**, 2979 (1985).

<sup>27</sup>C. Fiori, *Phys. Rev. Lett.* **52**, 2077 (1984).

<sup>28</sup>C. Fiori and R. A. B. Devine, *Phys. Rev. Lett.* **52**, 2081 (1984).

<sup>29</sup>C. Fiori and R. A. B. Devine, *Solid State Commun.* **51**, 441 (1984).

<sup>30</sup>E. G. Keim, *Surf. Sci.* (submitted).

<sup>31</sup>G. Hollinger and F. J. Himpsel, *Phys. Rev. B* **28**, 3651 (1983).