Coverage dependent interaction of N₂O and O₂ with Si(001)2×1 as monitored by the O KLL Auger intensity ratio

Enrico G. Keim and Herbert Wormeester

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

(Received 26 September 1991; accepted 9 December 1991)

The adsorption behavior of O₂ on Si(001)2×1 at 100 K sample temperature has been studied by measuring the intensity ratio of the KL_1L_1 and $KL_{2,3}L_{2,3}$ O Auger transitions α as a function of the fractional oxygen coverage in an attempt to solve a longstanding discussion whether this reaction also involves molecular chemisorption. Recent cluster calculations provided evidence that the bond distance between Si and O and between the two oxygen atoms in the O₂ molecule is a key parameter affecting the magnitude of α . By referring to the room temperature adsorption of N₂O on the same surface we have found evidence for the coadsorption of a metastable molecular oxygen species at advanced adsorption stages, a result which is essentially in agreement with previous experimental predictions and theoretical calculations.

I. INTRODUCTION

In the last decade a considerable progress has been made in characterizing the mechanism of oxygen adsorption on clean silicon surfaces.¹⁻¹⁰ The consensus that has emerged is that the final stable state of chemisorbed oxygen within the Si lattice is bridge bonded oxygen, Si—O—Si. It is well known, however, that at low oxygen coverage and/or low sample temperature transient species may be present. With respect to the identification of these species a breakthrough has been achieved by the research of Höfer and co-workers for the adsorption behavior of O₂ on Si(111)7×7.²⁻⁵ Using a number of experimental techniques, including x-ray induced Auger electron spectroscopy (XAES), they provided convincing evidence that the intermediate state, which is stabilized at liquid nitrogen temperature and at low coverages, can be characterized as a molecularly chemisorbed species, its molecular axis oriented parallel to the surface, which is a metastable precursor to the dominating dissociated bridge bonded oxygen. The results of Höfer *et al.*^{2,4,5} were essentially confirmed, very recently, by Avouris *et al.*¹⁰ using scanning tunneling microscopy (STM) and spectroscopy (STS).

For the Si(001)2×1 surface, on the other hand, the situation is less clear. From the pioneering electron energy-loss spectroscopy (EELS) measurements of Ibach *et al.*¹ it was proposed that on both the reconstructed Si(111) and Si(001) surfaces at substrate temperatures of 100 and 300 K chemisorbed O₂ is present, in particular at low oxygen coverage. Using EELS and x-ray photoelectron spectroscopy (XPS) Schaefer and Göpel^{11,12} were, however, not able to resolve intermediate molecular oxygen states. Very recent EELS and work function (WF) investigations on O₂/Si(001) at a sample temperature of 20 K by Silvestre and Shayegan¹³ gave an indication of a metastable chemisorbed peroxy bridging oxygen as an additional transient species. From a comparison of the room temperature adsorption behavior of N₂O and O₂ on Si(001) Keim *et al.*,⁶ employing Auger electron spectroscopy (AES), spectroscopic differential reflectometry (SDR) and low-energy electron diffraction (LEED), proposed that at coverages

(θ) below 0.5 monolayer (ML) molecular oxygen (O₂) adsorption can be described by a dissociative process on the first layer Si atoms. At intermediate adsorption stages ($\theta = 0.5$ —about 1 ML), they suggested that incorporation of oxygen into the Si subsurface and the adsorption of molecular oxygen occur simultaneously. To our knowledge no other experimental work exists in the literature which deals with the investigation of possible molecularly adsorbed oxygen species on Si(001). On the theoretical front, on the other hand, interesting results have been obtained showing that molecular oxygen dissociation and molecular chemisorption may coexist, in particular at low substrate temperatures and low oxygen coverages, but also at high θ .^{14,15}

In an attempt to solve a longstanding discussion whether the reaction of Si(001)2×1 with O₂ also involves molecular chemisorption we monitored this adsorption at a substrate temperature T_s of 100 K (which is needed to stabilize possible transient states^{1,2,4,5,13,16}) by measuring the intensity ratio of the KL_1L_1 and $KL_{2,3}L_{2,3}$ O Auger transitions α as a function of θ . With this ratio changes in the O KVV line shape can be quantized. From theoretical calculations¹⁷ it was found that the magnitude of α depends sensitively on the Si—O bond distance d_{SiO} and the O 1s core state. As d_{SiO} decreases the overlap of the oxygen wave functions with the silicon wave functions increases. This was found to lead to an increase of the probability of interatomic Auger electron emission processes, which can have a magnitude of the same order as intraatomic Auger transitions. Lowering the interatomic distance in an O₂ molecule d_{OO} was found to have the same effect. As a result the intensity of the O $KL_{2,3}L_{2,3}$ Auger transition will become higher,¹⁷ thus lowering α . A contraction of the O core hole wave function which occurs as the binding energy (BE) of the O 1s electron increases can lower the value of α as well.¹⁷ Our calculational results were in agreement with AES experiments, in which the room temperature adsorption of N₂O on the clean Si(001)2×1 surface was used as a model system.¹⁸ Our experimental results concerning this model system published previously⁶ indi-

cate that the adsorption of atomic oxygen (as released by the N₂O molecule) evolves in distinguishable stages. One of the most interesting results of our most recent AES study¹⁸ was that by measuring α as a function of θ , we found experimental evidence for an intermediate stable O adsorption state in a bridge bonded configuration on the dimer at low oxygen coverage ($\theta \leq 0.2$ ML), as proposed earlier from theoretical studies.^{19,20} This transient state is characterized by an O–Si bond distance which is about 0.25 Å larger than the corresponding one for the stable bridge bonded dimer configuration.^{19,20} Since the bond distance (d_{SiO} and d_{OO}) is a key parameter affecting the magnitude of α ,¹⁷ the question arises if α can be used to distinguish coexisting (metastable) minority species from the stable adsorbed oxygen configuration. For that purpose we measured O₂/Si(001)2×1 at $T_s = 100$ K and compared the $\alpha(\theta)$ values in the sub ML region with the corresponding values of the model system mentioned above.^{6,18}

In this paper we will illustrate the usefulness of α as a tool in O₂ adsorption studies which are directed towards the characterization of the oxygen adsorption geometry on clean surfaces of Si, provided that a reference system is available.

II. EXPERIMENTAL

Part of the low T_s O₂ adsorption experiments were performed some time ago in a stainless steel ultrahigh vacuum (UHV) system equipped with a retarding-field (RFA) four-grid LEED-Auger system (A) described previously.⁶ The most recent molecular oxygen adsorption experiments were performed in an UHV chamber (B) as described in Ref. 21, and equipped with a cylindrical mirror analyzer (CMA) for the AES measurements. The pumping systems in (A) and (B) are configured in a similar way; the base pressure of both systems was in the mid 10^{-11} Torr region. The procedures for gas handling, surface cleaning by simultaneous argon ion bombardment and annealing (SIBA) were identical to those described earlier.⁶ O₂ was admitted into the reaction chamber at pressures ranging from 5×10^{-9} to 5×10^{-8} Torr, N₂O from 10^{-5} to 10^{-4} Torr. No variation in adsorption behavior was observed in these gas pressure regimes. The fractional oxygen coverage θ was determined following the method of Keim²² in which the ratio of the O $KL_{2,3}L_{2,3}$ and the Si L_{VV} Auger peak to peak (p – p) heights, $h\text{O}/h\text{Si}$ (recorded in the first derivative of the energy distribution $\{dN(E)/dE$ in system A, and $d[E \cdot N(E)]/dE$ in system B}), at the saturation coverage of N₂O on Si(001) at $T_s = 300$ K is assumed to correspond with $\theta = 0.85 \pm 0.10$ ML. We note that the determination of the oxygen coverage in the sub ML region using these peaks may not provide the correct θ since the O $KL_{2,3}L_{2,3}$ peak intensity is modulated by the chemical bond. Nevertheless, we can determine an order of successive stages of oxidation from the O/Si p – p ratio. In system A (RFA) the Auger spectra were recorded using a primary beam energy of 2 keV, the angle of this beam being 10° with the plane of the Si surface, a primary current density of $50 \mu\text{A cm}^{-2}$, a modulation voltage of 9 V _{p – p} , a sweep rate of 1.0 eV/s and a lock-in time constant of 1 s. In

FIG. 1. The intensity ratio α as a function of the fractional oxygen coverage θ upon exposing the clean Si(001)2×1 surface at $T_s = 100$ K to O₂, in system A (*), and in system B (O). The filled circles connected by a line to guide the eye (dashed curve) represent the $\alpha(\theta)$ data obtained after exposing the same surface at $T_s = 300$ K to N₂O (data taken from Ref. 6).

system B (CMA) the Auger transitions were excited by an electron beam hitting the Si surface at normal incidence with a primary energy of 2 keV and a primary current density of about $1 \times 10^4 \mu\text{A cm}^{-2}$, 4 V _{p – p} modulation voltage, a sweep rate of 0.2 eV s^{−1} and a lock-in time constant of 3 s. Under these conditions the relatively low intensity O KL_1L_1 Auger peak could be resolved down to less than 0.05 ML oxygen coverage.¹⁸ The silicon samples ($10 \times 30 \times 0.3$ mm³ in system A and $8 \times 30 \times 0.3$ mm³ in system B) were made out of a 2000 Ω cm, nominally flat p -type crystal in the (001) orientation. Each set of AES data points, i.e., $h\text{O}/h\text{Si}$ and α at certain θ , was obtained after exposing the cleaned Si surface to a single O₂ dose in order to avoid unknown electron beam induced effects.

III. RESULTS AND DISCUSSION

Figure 1 [asterisks (*)] shows the intensity ratio α as a function of θ , recorded between 0.3 and 0.8 ML in system A. The open circles (O) represent the α values acquired in system B in the coverage range of $0.05 \leq \theta$ (ML) ≤ 1.2 . The figure also includes the $\alpha(\theta)$ data (filled circles) obtained by exposing the clean Si(001)2×1 surface at $T_s = 300$ K to N₂O (model system) published very recently.¹⁸ This data set will be used as a reference for the O₂ exposure measurements at $T_s = 100$ K (*, O).

We summarize the most important conclusions regarding our model system¹⁸: three distinct atomic oxygen adsorption stages can be discerned, the initial stage up to about 0.2 ML (I in Fig. 1), followed by the second ranging to $\theta = 0.6$ (II), and the final stage from 0.6 to 0.85 ML (III), a result which complements previous SDR measurements.⁶ The first stage can be characterized by the formation of bridge bonded oxygen at the dimers at low oxygen coverage ($\theta \leq 0.2$ ML) which occurs through an intermediate stable state in which d_{SiO} is about 0.25 Å

larger than the one in the stable bridge bonded dimer configuration. The continuous decrease of α can simply be attributed to a decrease of d_{SiO} since the BE of the O 1s photoelectron in this stage does not show a detectable shift.²³ At advanced stages, however, α is affected by changes in both d_{SiO} and O 1s core state. At these stages (II and III in Fig. 1) additional uptake of atomic oxygen occurs via attachment of the dangling bonds of the top layer Si atoms whose position has moved sufficiently to the *nn* first layer Si atoms of the reacted dimers forming the Si—O—Si configuration as well, and ultimately leading to a complete saturation of first the dimer and then the dangling bond orbitals. α at saturation ($\theta = 0.85 \pm 0.15$ ML) can therefore be assigned to a stable in-plane bridge bonded O adsorption geometry in which d_{SiO} ranges from 1.92 (Ref. 20) to 2.05 Å.¹⁹

Going back to the low T_s O₂/Si(001)2×1 adsorption results obtained in system B [(○) in Fig. 1] it can be seen that the α values at all stages are comparable to those of the N₂O data (filled circles) at more advanced adsorption stages (II and III), suggesting the existence of purely bridge bonded oxygen adsorbate geometries, i.e., bridge bonded oxygen at dimer sites and in between the *nn* reacted dimer sites.^{6,18} The O KVV Auger measurements performed in system A [(*) in Fig. 1], however, show a continuous increase of α as the adsorption proceeds, leading to a magnitude of about 0.15 at 0.75 ML oxygen coverage. By referring to the room temperature adsorption behavior of N₂O on Si(001)2×1, in particular at the initial stage (I in Fig.),¹⁸ and theoretical studies,^{14,15,17,19,20} the low T_s O₂ adsorption results [(*) in Fig. 1] indicate the existence of adsorbed oxygen species in which d_{SiO} increases with θ . In the case of a molecularly adsorbed oxygen species on Si(001), Barone *et al.*¹⁴ found several energetically favorable geometries of the chemisorption products with O—O bond lengths (d_{OO}) as large as or larger than the equilibrium bond length of an isolated O₂ molecule. Moreover, they found a relatively large distance between the oxygen and *nn* Si atom (d_{SiO}) ranging from 1.70 to 1.93 Å. In view of earlier experimental predictions⁶ and theoretical calculations^{14,15} (see also Sec. I), we therefore suggest that in this case at intermediate adsorption stages ($0.5 \leq \theta(\text{ML}) \leq 1.0$) adsorption of molecular oxygen occurs in addition to dissociative adsorption. In order to characterize the nature of the transient adsorbed oxygen species, it would be very useful to measure in the same experiment the BE of the O 1s electron, so as to obtain insight into the contribution of the core hole to α .¹⁷

Remains to explain the discrepancy between the recent (○) and previous (*) $\alpha(\theta)$ data in Fig. 1. Curves (a) and (b) of Fig. 2 show the O KLL Auger spectrum recorded at about 0.7 ML oxygen coverage obtained by exposing the Si(001)2×1 surface to O₂ at $T_s = 100$ K in system A and system B, respectively, and in which α is defined as the ratio of the indicated KL_1L_1 and $KL_{2,3}L_{2,3}$ *p-p* heights. It can be easily seen that α recorded at this coverage using the RFA (system A) is larger than that recorded in system B using the CMA. To our knowledge the only difference in experimental conditions between the low T_s O₂ adsorption

FIG. 2. O KLL Auger spectrum in the first derivative of the energy distribution $N'(E)$ recorded at a fractional oxygen coverage of $\theta = 0.75$ ML in system A [curve (a)], and at $\theta = 0.65$ ML in system B [curve (b)], by exposing the clean Si(001)2×1 surface at $T_s = 100$ K to O₂. α is defined as the ratio of the KL_1L_1 and $KL_{2,3}L_{2,3}$ *p-p* heights.

studies in system A and B is the magnitude of the primary current density of the excitation source (see Sec. II). In system A the total electron dose during the recording of the O KLL Auger spectrum was always lower than 10^{14} electrons/cm². In system B, in contrast, the dose often exceeded 10^{17} electrons/cm². This relatively high dose may inhibit the observation of a molecular transient species, both at intermediate coverages and in the early adsorption stage ($\theta \leq 0.2$ ML), due to a rapid electron beam induced decay. This result is in agreement with observations of Höfer *et al.*⁴ who investigated the adsorption of O₂ on Si(111)7×7, using about the same dose (3×10^{18} electrons/cm²). Our previous α data obtained in system A [(*) in Fig. 1], on the other hand, indicate that possible metastable molecularly adsorbed oxygen species can survive an electron dose of about 10^{14} per cm². Because of signal-to-noise ratio and stability considerations of the RFA, the determination of α at low T_s in system A was limited to about 0.3 ML oxygen coverage. Best results at low oxygen coverage [$0.05 \leq \theta(\text{ML}) \leq 0.2$] are obtained using a cylindrical mirror analyzer, as was also shown recently.¹⁸ One way to reduce the high primary current density is to modify the CMA so that it can operate in pulse count (PC) mode,²⁴ a subject which is part of our future research.

IV. CONCLUSIONS

By measuring the intensity ratio of the KL_1L_1 and $KL_{2,3}L_{2,3}$ O Auger lines α we have been able to show that

metastable adsorbed oxygen species coexist with the stable adsorbed oxygen adsorbate if the clean Si(001)2×1 surface at 100 K is exposed to O₂. Our results are essentially consistent with earlier experimental predictions and theoretical calculations which allow the coadsorption of molecular oxygen at advanced adsorption stages. Our results indicate that the observation of molecularly adsorbed oxygen species is feasible with a total electron dose of 10¹⁴ electrons/cm². Electron beam induced dissociation effects are likely to play a major role if this dose is exceeded.

- ¹H. Ibach, H. D. Bruchmann, and H. Wagner, *Appl. Phys. A* **29**, 113 (1982).
- ²U. Höfer, P. Morgen, W. Wurth, and E. Umbach, *Phys. Rev. Lett.* **55**, 2979 (1985).
- ³P. Morgen, U. Höfer, W. Wurth, and E. Umbach, *Phys. Rev. B* **39**, 3720 (1989).
- ⁴U. Höfer, P. Morgen, W. Wurth, and E. Umbach, *Phys. Rev. B* **40**, 1130 (1989).
- ⁵U. Höfer, A. Puschmann, D. Coulman, and E. Umbach, *Surf. Sci.* **211/212**, 948 (1989).

- ⁶E. G. Keim, L. Wolterbeek, and A. van Silfhout, *Surf. Sci.* **180**, 565 (1987).
- ⁷J. P. Pelz and R. H. Koch, *Phys. Rev. B* **42**, 3761 (1990).
- ⁸J. P. Pelz and R. H. Koch, *J. Vac. Sci. Technol. B* **2**, 775 (1991).
- ⁹I.-W. Lyo, Ph. Avouris, B. Shubert, and R. Hoffmann, *J. Phys. Chem.* **94**, 4400 (1990).
- ¹⁰Ph. Avouris, I.-W. Lyo, and F. Bozso, *J. Vac. Sci. Technol. B* **9**, 424 (1991).
- ¹¹J. A. Schaefer, F. Stucki, D. J. Frankel, W. Göpel, and G. J. Lapeyre, *J. Vac. Sci. Technol. B* **2**, 359 (1984).
- ¹²J. A. Schaefer and W. Göpel, *Surf. Sci.* **155**, 535 (1985).
- ¹³C. Silvestre and M. Shayegan, *Solid State Commun.* **77**, 735 (1991).
- ¹⁴V. Barone, F. Lelj, N. Russo, and M. Toscano, *Surf. Sci.* **162**, (1985).
- ¹⁵X. M. Zheng and P. V. Smith, *Surf. Sci.* **232**, 6 (1990).
- ¹⁶A. J. Schell-Sorokin and J. E. Demuth, *Surf. Sci.* **157**, 273 (1985).
- ¹⁷H. Wormeester, H. J. Borg, and A. van Silfhout, *Surf. Sci.* **258**, 197 (1991).
- ¹⁸E. G. Keim and H. Wormeester, *Surf. Sci.* **260**, 23 (1992).
- ¹⁹P. V. Smith and A. Wander, *Surf. Sci.* **219**, 77 (1989).
- ²⁰Y. Miyamoto and A. Oshiyama, *Phys. Rev. B* **41**, 12680 (1990).
- ²¹H. J. W. Zandvliet and A. van Silfhout, *Surf. Sci.* **195**, 138 (1988).
- ²²E. G. Keim and A. van Silfhout, *Surf. Sci.* **216**, L337 (1989).
- ²³A. Namiki, K. Tanimoto, T. Nakamura, N. Ohtake, and T. Suzuki, *Surf. Sci.* **222**, 530 (1989).
- ²⁴R. M. Tromp (private communication).