Chemical titration of clean silicon surfaces with N_2O and O_2 : Atomic nature of " 5×1 " reconstructed $\text{Si}(110)$

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Using spectroscopic differential reflectometry (SDR), Auger electron spectroscopy (AES), and low-energy electron diffraction (LEED) we have studied the room temperature adsorption behavior of N_2O and O_2 at the clean low-Miller index Si surfaces. Decomposition of the nitrous oxide molecule, resulting in Si-O bond formation, only occurs at the top layer Si atoms which have an unsaturated dangling bond. In this way it has been possible to determine the number of broken bonds at these clean reconstructed surfaces using AES. From a comparison of the site-specific adsorption of N_2O with the non-site-specific adsorption of O_2 we propose a model of the atomic nature of the $\text{Si}(110)$ surface showing a prominent 5×1 reconstruction which is in agreement with previously published LEED results and recent scanning tunneling microscopy (STM) and ultraviolet photoemission spectroscopy (UPS) work. This model is based on a reduction of dangling bonds which is due to the formation of adatoms. The model also includes a kind of rest atoms and atoms in nearest-neighbor top layer chains along the $[\bar{1}10]$ direction (*A* type). We have found that the ratio adatoms/rest atoms/*A* atoms per reconstructed unit cell determines the primary superstructure. This ratio also accounts for a more or less "apparent" coexistence of higher order reconstructions very often reported in LEED studies, their presence being in the form of streaks at various fractional order positions along the $[\bar{1}10]$ direction. A real coexistence of various reconstructions with partial order at the $\text{Si}(110)$ surface cannot be excluded as evidenced by STM, a result which makes it the most complicated low-Miller index Si surface to study. Complementary information concerning the energy position of the unoccupied surface states has been obtained from SDR. Our clean $\text{Si}(110)$ surface shows partial order along the $[\bar{1}10]$ direction, indicating the coexistence of 5×2 and 5×5 superstructures in addition to the observed prominent 5×1 LEED reconstruction. It has been derived that this surface has empty states at about 0.9 and 1.7 eV above the Fermi level (E_F). The occupied states at about 0.8 and 2.4 eV below E_F could be identified with rest atoms and *A*-type atoms, respectively.

I. INTRODUCTION

A. Atomic and molecular oxygen adsorption on low-Miller index Si surfaces: A review

In a recent series of papers we have shown that the combination of spectroscopic differential reflectometry (SDR), Auger electron spectroscopy (AES) and low energy electron diffraction (LEED) is very useful in studies concerning the initial oxidation behavior of N_2O and O_2 at the three low-Miller index Si surfaces.¹⁻⁶ These studies demonstrated that the combination of the site-specific decomposition of N_2O and the non-site-specific adsorption of O_2 is an important complementary tool in clarifying the electronic properties and structure of at least the $\text{Si}(100)2\times 1$ and $\text{Si}(111)7\times 7$ surfaces. By exposing the carefully cleaned $\text{Si}(100)2\times 1$ surface to nitrous oxide⁵ SDR has revealed several types of dangling bond (db) surface states in addition to the dimer bond state, which is in agreement with earlier experiments performed on the clean $\text{Si}(100)2\times 1$ surface using ultraviolet photoemission spectroscopy (UPS), Bremsstrahlung Isochromat Spectroscopy (BIS) and, more recently, by scanning tunneling microscopy (STM) (see, e.g., Ref. 5 and references therein). The significance of the use of nitrous oxide in studies dealing with the initial oxidation behavior of clean Si surfaces is that the N_2O molecule supplies only one

oxygen atom after the dissociative adsorption, i.e., N_2O (gas) $\rightarrow \text{O}_{\text{ad}} + \text{N}_2$ (gas),^{1,5,6} thus excluding the possibility of complex molecular adsorption if O_2 is used. From a comparison of the adsorption behavior of N_2O and O_2 we were able to show that the reaction of N_2O with the $\text{Si}(100)2\times 1$,⁵ $\text{Si}(111)7\times 7$,^{4,6} and $\text{Si}(110)5\times 1$ ¹⁻³ surfaces is very site-specific; Si-O bond formation occurs at the top layer Si atoms via attachment of the db's, and in the case of the 2×1 reconstructed $\text{Si}(100)$ surface also via attachment of the "dangling bonds" which constitute the dimer by breaking this dimer bond.⁵ In Refs. 1, 5, and 6 we have argued that the decomposition of the N_2O molecule demands very restrictive geometric conditions in order to reach the appropriate orientation, the bridge bonded geometry on $\text{Si}(100)$ being in favor of the "head-on" position as observed on $\text{Si}(111)$. According to our model of the dissociative reaction of N_2O on the $\text{Si}(100)2\times 1$ surface⁵ oxygen goes into a bridging position between top layer Si atoms in the initial oxidation stage by decomposing at the Si-Si dimer bonds, followed by atomic oxygen uptake via attachment of the db's of the top layer Si atoms whose position has moved considerably to the nearest neighbor (nn) Si atoms forming the Si-O-Si configuration as well. Since this reaction leads to a well-defined saturated monatomic oxygen layer, in the case of an ideal defect-free $\text{Si}(100)2\times 1$ surface, we have used

this reaction as a reference to calibrate the normalized oxygen Auger signal.⁵ Supporting evidence, in favor of the idea of having only Si-O bond formation at the top layer Si atoms, has been given both experimentally by high-energy resolution Auger electron spectroscopy (HRAES),^{1,2,5,7} and theoretically by semiempirical quantum chemical cluster calculations.⁸ Additional proof in favor of our model for the uptake of atomic oxygen (O) on an ideal clean Si(100) 2×1 surface as experimentally predicted in Ref. 5 has been given, very recently, from theoretical work on the adsorption of atomic oxygen at the 2×1 reconstructed Si(100) surface by Smith and Wander,⁹ employing the GAMESS self-consistent field (SCF) molecular orbital package.¹⁰ The applicability of our method, i.e., chemically "titrating" the various surface sites with an unsaturated broken bond using N_2O , has been demonstrated by studying the well-characterized Si(111) 7×7 surface for which we found 23 ± 4 db's per 7×7 unit cell (49 atoms),⁴ which is in agreement with the established 19 as revealed by STM.^{11,12} Moreover, it was found that this surface, covered with oxygen atoms, was fully passivating against additional O_2 exposure. The results mentioned above clearly illustrate that, using N_2O , a real adsorption of oxygen atoms (Si-O bond formation limited to the top layer atoms) can be achieved. They also show the importance of using nitrous oxide in studies dealing with the adsorption of oxygen on clean Si surfaces; *absorption* (incorporation of oxygen into the subsurface lattice) can be distinguished from *adsorption*.

In this paper we will demonstrate that the combination of SDR, AES, and LEED while chemically titrating the various surface sites with the combination of N_2O and O_2 at 300 K is an important complementary tool to STM in clarifying the structure of the clean reconstructed Si(110) surface which shows a prominent 5×1 LEED pattern. Previous SDR, AES, and LEED results concerning the adsorption of N_2O ¹ and O_2 ^{2,3} at this surface are discussed in view of recent STM work^{11,12} and ideas about the structure and electronic properties (STM and UPS¹³) of the clean reconstructed Si(110) surface. Various reconstructions have been observed for this surface, however, models for the superstructures proposed only explain one superstructure or part of it and seem to be incompatible with each other. Furthermore, a detailed description of its filled and empty surface state distribution is not available at the moment. In this paper it will be shown that the clean Si(110) surface with a primary 5×1 reconstruction exhibits a reduction in db density which is of the same order of magnitude as for the Si(111) 7×7 surface.⁴ A model based on an adatomlike superstructure consistent with STM and UPS investigations and including the various reconstructions is proposed (Sec. III A). Moreover, we provide complementary information about the electronic structure of this surface, i.e., the unoccupied surface states (Sec. III B).

B. The clean reconstructed Si(110) surface

On Si(110) a large number of ordered surface superstructures have been observed using LEED.^{14,15} Olshanetsky and Shklyayev,¹⁵ hereafter denoted as OS, obtained distinct LEED patterns resulting from different sample heat treat-

ments. They ascribed the various superstructures to distortions of the surface lattice potential. A description of the atomic nature of these reconstructions is however, difficult as long-range order effects are probed in LEED. STM, on the other hand, is able to reveal the surface structure in real space on an atomic scale. Very recent STM measurements by Becker, Swartzentruber, and Vickers¹¹ (BSV) and Neddermeyer and Tosch¹² (NT) show missing first layer chains and adatom structures on the reconstructed (110) crystal face of silicon. The very complicated " 16×2 " superstructure (" X ") which has been reported by a number of authors¹⁴⁻²¹ cannot be considered as a (110)-oriented Si surface. It was shown by Olshanetsky, Repinsky, and Shklyayev¹⁶ that such diffraction pictures are produced by faceted planes with the indices $(17\ 15\ 1)$, $(15\ 17\ \bar{1})$, $(17\ 15\ \bar{1})$, and $(15\ 17\ 1)$ which contain the 2×1 superstructure.

BSV, who observed a primary 5×1 LEED pattern, interpreted their STM measurements with the missing of two (out of five) first layer chains (tubes) per surface unit cell, the tubes being oriented along the $[\bar{1}10]$ direction. In the missing tubes they observed terrace structures, which were found to consist of two tetramers per unit cell. The individual protrusions of the tetramers were related to adatoms, in the STM image identified as unoccupied states. The unit cell was measured to be approximately $27.5 \times 16\ \text{\AA}^2$.

While their LEED image showed a 4×5 pattern with dominant 2×1 contributions, in STM NT observed a 2×5 periodicity of atomic building blocks. In this basic 2×5 unit cell, with an experimentally determined size of $11.7 \times 19.8\ \text{\AA}^2$, they could distinguish two types of adatoms and argued that 18 out of 20 db's are saturated by 6 adatoms, leaving 2 db's per unit cell unsaturated. The atomic position of the atomic features indicated that at least the second atomic layer is severely distorted compared to the ideal structure. From the heat treatment experiments on the Si(110) surface performed by OS we may consider the 4×5 reconstruction as the one with the lowest energy of all superstructures observed, a result which suggests that it is energetically unfavorable to saturate all db's with adatoms, leading to a periodicity along the $[\bar{1}10]$ direction; upon cooling the Si(110) surface OS initially observed fractional order along $[001]$, i.e., $(5 \times 1, 7 \times 1, 9 \times 1, 2 \times 1)$. Fractional order along $[\bar{1}10]$ leading to the 4×5 superstructure could only be achieved at a very low cooling rate.¹⁵

The existence of adatom and nonadatom sites at the clean Si(110) 5×1 surface is supported by our adsorption experiments¹⁻³ as will be shown in Sec. III A. Before these results are discussed we will first outline the AES calibration procedure which has been followed to obtain the fractional oxygen coverages reported in this paper (Sec. II).

II. EXPERIMENTAL

The N_2O and O_2 experiments were performed in a stainless steel ultrahigh vacuum (UHV) system with facilities for SDR, AES-LEED, ion bombardment, and residual gas analysis previously described in detail.⁵ The procedures for gas handling, surface cleaning by simultaneous argon ion bombardment and annealing (SIBA), and the SDR and AES-LEED measurements can be found in Refs. 1 and 2.

For the determination of the fractional oxygen coverage with AES, θ , as derived from the normalized oxygen Auger signal ($O_{KLL}/Si_{L_{VV}}$), using the system $Si(100)2 \times 1|N_2O$ as a reference,⁵ we refer to Ref. 4 in which a defect density of $15 \pm 10\%$ is assumed for the clean 2×1 reconstructed $Si(100)$ surface. This implies that saturation occurs at 0.85 ± 0.10 monolayer (ML) atomic oxygen coverage. All previously published fractional oxygen coverages concerning the interaction of N_2O and O_2 with the $Si(110)5 \times 1$ surface¹⁻³ have been corrected for the deviation from a monatomic oxygen layer in the case of an ideal defect-free $Si(100)2 \times 1$ surface⁵ using the calibration procedure as described in Ref. 4. If one wants to compare the θ values (for O_{ad}) for the three low-Miller index planes of Si one should therefore consider Ref. 4 and the present paper. We define 1 ML as one oxygen atom per surface Si atom [$= 9.58 \times 10^{14} \text{ cm}^{-2}$ for the unreconstructed $Si(110)$ surface]. All exposures are given in units of Langmuir ($1 \text{ L} = 1 \times 10^6 \text{ Torr s}$). We note that contamination of the Si surface with Ni can be ruled out in our experiments; the surface was considered to be clean when no elements other than Si could be detected.

III. RESULTS AND DISCUSSION

A. AES/LEED; atomic nature of " 5×1 " reconstructed $Si(110)$

We summarize the most important AES and LEED results: exposure of the $Si(110)5 \times 1$ surface to N_2O ¹ resulted in a saturation coverage of 0.36 ± 0.05 ML atomic oxygen as shown in Fig. 1, a stage at which the 5×1 LEED pattern was still visible with only a slight increase in background. Additional exposure of this apparently saturated surface to molecular oxygen ($\geq 1 \times 10^5 \text{ L}$) was accompanied by the disappearance of the fractional order spots and yielded a fully passivating surface at 0.60 ± 0.10 ML oxygen coverage. In

the initial adsorption stage, i.e., up to about 0.10 ML oxygen, the diffuse spots and streaks as observed in the LEED image of the clean $Si(110)$ surface (Fig. 2) disappeared, leading to a "cleaner" 5×1 pattern on a slightly increased background, a phenomenon which also was observed in the same coverage range if the same surface was exposed to O_2 .^{2,3} This result strongly suggests the removal of coexisting higher order superstructures due to the adsorption of oxygen at sites which form these superstructures. Adsorption of oxygen at defects in the initial stage cannot be the main reaction path since defects would not generate the relatively sharp streaks in the LEED image at fractional order positions (Fig. 2) disappearing upon adsorption. Exposing the clean $Si(110)$ surface to O_2 resulted in a slow sorption beyond ML coverage, indicating an *absorption* behavior. In Fig. 3(a) we present a schematic side view of the 5×1 reconstruction, as derived from the STM measurements of BSV, in which we will first focus our attention to the $[001]$ direction. Since this reconstruction has two missing tubes per unit cell, two of the three remaining must be nn. The Si top layer atoms with their db pointing towards the nn first layer chain are in Fig. 3(a) denoted as (A). Possibly some kind of dimer bond¹⁹ between nn (A) atoms may result. As argued by OS, the existence of and the distance between nn chains (double tubes) determine the order of the potential distortions in LEED resulting in LEED patterns with varying dimensions along the $[001]$ direction (5×1 , 7×1 , 9×1 , and 2×1). Moreover, from their sample heat treatment experiments, it can be seen that $Si(110)$ tends to a superstructure (at room temperature) without double tubes, i.e. 2×1 (and 4×5). Our adsorption measurements suggest that the N_2O molecule does not decompose at atom (A) since the 5×1 LEED pattern is still visible at saturation (0.36 ± 0.05 ML). Upon additional exposure to O_2 up to final saturation at 0.60 ± 0.10 ML oxygen coverage (Fig. 1), however, the

FIG. 1. The fractional oxygen coverage θ as a function of N_2O exposure. Each data point is taken after new exposure on a freshly cleaned surface. The result of additional exposure to O_2 ($\geq 1 \times 10^5 \text{ L}$) following N_2O exposure ($6 \times 10^6 \text{ L}$, i.e., at "initial" saturation), is also indicated in this figure by the dashed line. The figure has been adapted from Ref. 1; the coverage scale has been modified using the procedure as outlined in Sec. II. Further explanations are given in the text.

FIG. 2. LEED pattern taken from the clean $Si(110)5 \times 1$ surface (105 eV). The LEED photo was taken with the OLYMPUS OM4 camera with ZUIKO MC 3.5/50 mm macro lens. The top part of the photo indicates the weakly visible streaks at $1/5$ and $1/2$ order along $[110]$.

FIG. 3. (a) Schematic side view of the Si(110)5 $\times$ 1 substrate showing the missing $[\bar{1}10]$ tubes (adapted from Ref. 11). (b) Schematic representation of the reconstructed Si(110) surface (top view) showing various unit cells; 5 $\times$ 3 (model I), 5 $\times$ 5 (model II), and 5 $\times$ 4 (model III). Atoms located nearer to the surface are illustrated with the larger circles. Hatched circles represent adatoms, rest atoms are indicated by filled circles.

5 $\times$ 1 LEED pattern disappears. For a unit cell in which the $[001]$ direction has a repetition unit five times the surface lattice constant (5.45 Å)—see Fig. 3(a)—0.20 of the total number of db's is related to atom (A). It may therefore be argued that the extra amount of oxygen, 0.24 ± 0.10 ML, adsorbs at the double tubes since the removal of order along $[001]$ is possible by creating Si–O bonds with the (A) atoms via interaction with their db's thereby destroying the scattering centres for the LEED interference pattern. From Fig. 3(a) it can be seen that the missing tubes induce $\{111\}$ facet planes. On these planes two kinds of db's can exist; one is connected to a top layer Si atom, the other one to a second layer Si atom, in Fig. 3(a) denoted as (B) and (C), respectively. In analogy with the Si(111) 7 $\times$ 7 surface these $\{111\}$ facet planes may contain adatoms, saturating three db's to minimize the total energy. If the db's of two (B) atoms and one (C) atom are saturated an adatom is obtained which is different from the one after saturating the db's of one (B) atom and two (C) atoms. In STM^{11,12} adatoms at the Si(110) surface are observed as empty states, like the ada-

toms at the Si(111)7 $\times$ 7 surface.^{22–24} Upon surveying the literature a pure 5 $\times$ 1 reconstruction has, to our knowledge, never been obtained, and may, to our opinion, not be expected as will be argued below. LEED images,^{1–3,11,13,14} for example, always show more or less visible streaks at various fractional order positions along the $[\bar{1}10]$ direction in addition to the characteristic 5 $\times$ 1 (fractional) order spots. In an attempt to describe the real reconstructed Si(110) surface, we will therefore discuss a number of possible unit cells all retaining a repetition unit along the $[001]$ direction five times the surface lattice constant but with different repetition units along $[\bar{1}10]$. In all unit cells proposed [Fig. 3(b)], the second and third atomic layers are considered to have their ideal structure. In the first unit cell proposed is striven after a maximum reduction in db's. This can only occur if the $[\bar{1}10]$ direction contains a repetition unit which is at least three times the surface lattice constant. Displayed in Fig. 3(b) is a schematic model of a 5 $\times$ 3 unit cell showing the complete saturation of db's (model I), connected to (B) and (C), by adatoms. From the 30 db's which are originally present six are connected with (A), the remaining (24) have been saturated by adatoms. The result is a reduction from 24 to 8 db's leading to 0.27 ML of newly created adatom-adsorption sites. Decomposition of the N₂O molecule can occur at these adatom sites without seriously disturbing the LEED pattern along the $[001]$ direction. However, the calculated maximum atomic oxygen coverage of 0.27 ML is too small to account for the measured coverage, 0.36 ± 0.05 ML atomic oxygen. Moreover, there is a discrepancy in the length of the unit cell considered along the $[\bar{1}10]$ direction, 16 Å as measured by BSV and 11.52 Å as calculated [model I of Fig. 3(b)]. In order to solve this problem and from the fact that a 5 $\times$ 3 reconstruction has never been reported we must introduce “rest atoms” in addition to the adatoms. These rest atoms are likely to have a filled db state as a result of charge transfer from the unoccupied adatom db state. This type of rest atoms also appears in the model of NT although they did not mention it. In STM NT observed a basic unit cell with 2 $\times$ 5 periodicity for which they argued that 90% of its db's are saturated by adatoms. Ten percent of the db's had to be left unsaturated (denoted by us as rest atoms) in order to explain the observed STM image. This situation is schematically depicted in model II of Fig. 3(b) and corresponds to a 5 $\times$ 5 unit cell, or in the absence of double tubes, to a basic 2 $\times$ 5 reconstruction. In this model a third kind of adatom is introduced which is the result of saturation of the db's of three (C) atoms, leading to the omission of the type of adatom connected to one (B) atom and two (C) atoms [model I in Fig. 3(b)]. The width of the unit cell along the $[\bar{1}10]$ direction, 19.2 Å, is however, not in accordance with the value of BSV (16 Å) as expected for their “5 $\times$ 1” LEED pattern. We therefore suggest that they have measured a reconstruction as represented in model III of Fig. 3(b), the width being 15.36 Å, and based on the same types of adatoms as proposed by NT. In this situation it would generate a 5 $\times$ 4 LEED pattern with a streak at 1/2 integral order position along $[\bar{1}10]$, a result which does not conflict with our LEED experiments. The LEED photo in Fig. 2 shows, in addition to the characteristic 5 $\times$ 1 (frac-

tional) order spots, streaks at $1/5$ and $1/2$ order along $[\bar{1}10]$, indicating the coexistence of 5×1 , 5×2 , and 5×5 superstructures. This complex LEED pattern was also reported by BSV who only found first-order beams and streaks at various fractional order positions along the $[\bar{1}10]$ direction. The streaks and the diffuse spots in our LEED photo (Fig. 2) completely disappeared after about 0.10 ML oxygen coverage upon exposing the clean Si(110) surface to N_2O or O_2 ,^{2,3} indicating the removal of partial order along the $[\bar{1}10]$ direction. This is possible by creating Si–O bonds with the rest atoms via interaction with their db's thereby destroying the scattering centres for the LEED interference pattern. The quenching of these centres is accompanied by a slight increase in the diffuse background. The number of rest atoms (in model II and III) determined in this way (using AES) can only be a rough estimate. Since decomposition of the N_2O molecule does not significantly influence the 5×1 LEED pattern, even at saturation (0.36 ± 0.05 ML), it can be concluded that chemisorption of atomic oxygen at the double tubes, that is, Si–O bond formation with atom (A) [see Fig. 3(a)], is an unfavorable reaction path.

On geometric arguments we can understand why nitrous oxide prefers to react with adatoms and rest atoms. The length of an N_2O molecule is of the same order of magnitude as the Si–Si bond length in the chains and about twice that of O_2 . Considering the "open" structure at the missing tubes [Fig. 3(a)], Si–O bond formation can easily take place at adatoms (which are about 1 Å above the $[\bar{1}10]$ tubes of the substrate¹¹) and rest atoms. Whereas much theoretical work has been devoted to the chemisorption of (atomic) oxygen on the Si(111) and Si(100) surface, e.g., by applying the MNDO and MINDO method in the framework of a cluster approach (see Refs. 8 and 25 and references therein), and recently by employing the GAMESS SCF molecular orbital package to the adsorption of atomic oxygen on the 2×1 reconstructed Si(100) surface,^{9,10} similar calculations have, to our knowledge, not yet been performed at the (reconstructed) Si(110) surface. This is partly due to the fact that an adequate picture of the real reconstructed Si(110) surface, until the STM studies^{11,12} were published, was not available. These calculations might give clues about the reactivity of the various db states towards (atomic) oxygen. Experimentally, atom-resolved surface chemistry using STM^{24,26} as applied to the research of the adsorption behavior of N_2O and O_2 at the real Si(110) surface would be very helpful. Additional evidence that nitrous oxide decomposes preferentially at ad- and rest atoms is given by our SDR measurements, to be discussed later.

Molecular oxygen, on the other hand, can more easily penetrate the Si lattice. It can, e.g., break Si–Si bonds between the surface and subsurface layer before all db states are quenched, a well known phenomenon which is observed on the three low-Miller index surfaces of Si.^{2,5,6} In this way the surface is opened for slow further sorption which is most likely to occur at the $\{111\}$ facet planes of the Si(110) surface. The sorption of oxygen on the Si(110) surface, after about 0.10 ML oxygen coverage, ultimately leads to a complete removal of the db surface states.²

Table I shows the various fractional oxygen coverages (in

ML) per adsorption site as a function of the model of the unit cell considered [Fig. 3(b)]. The second column shows the experimentally determined oxygen coverages from AES.¹⁻⁴ From this table it can be seen that the inclusion of rest atoms in our model (II and III) results in a good agreement with our chemical titration results. The ratio adatoms/rest atoms/A atoms per reconstructed unit cell determines the primary superstructure and also accounts for a more or less "apparent" coexistence of higher order reconstructions very often reported in LEED studies. To our opinion, the real 5×1 reconstructed Si(110) surface cannot be described by one static model only; both LEED^{2,11,14,15} and STM¹¹ experiments strongly suggest a real coexistence of several superstructures with local order, which makes it the most complicated low-Miller index Si surface to study. When model II and III are combined to describe the real Si(110) surface showing a primary 5×1 reconstruction (Fig. 2), both the STM observations of BSV and NT, which are local measurements of a particular superstructure, as well as our chemical titration measurements, which indicate a coexistence of reconstructions, can be explained.

B. SDR; electronic structure of " 5×1 " reconstructed Si(110)

Up to now we only considered our previous AES and LEED results concerning the interaction of N_2O and O_2 with the Si(110) 5×1 surface in view of recent STM work and ideas about the structure of this surface. We have been able to derive a model for its surface structure which is consistent with this STM work and LEED studies. Upon surveying the literature, information about the electronic structure of the 5×1 reconstructed Si(110) surface is incomplete; UPS¹³ measurements show surface state features at about 0.8 eV and at energies lower than 1.5 eV (below E_F), the former exhibiting db state character and the latter being also present at the complicated faceted X surface,¹⁴⁻¹⁶ known as " 16×2 ", and very prominent. STM measurements by BSV show an occupied state at ≈ -1 eV (in agreement with the filled state found by UPS¹³) which is associated with the tube between the adatoms containing atom (B) (Fig. 3), and unoccupied states at about +1 and +2 eV which are related to adatoms. NT, on the other hand, observed V-

TABLE I. Fractional oxygen coverage, θ , (in ML) per adsorption site as a function of the model of the unit cell [I, II, and III of Fig. 3(b)] proposed. The second column shows the experimentally determined θ values from the AES measurements,¹⁻⁴ modified using the procedure as outlined in Sec. II. Decomposition of N_2O at the Si(110) surface terminates at 0.36 ± 0.05 ML atomic oxygen. Additional exposure to O_2 leads ultimately to saturation at 0.60 ± 0.10 ML oxygen. Further explanations are given in the text.

Adsorption site	θ (ML)			
	Experimental	Model I	Model II	Model III
Atom (A)	0.24 ± 0.10	0.20	0.20	0.20
Rest atom	0.10 ± 0.05	0.00	0.08	0.20
Adatom	0.26 ± 0.05	0.27	0.24	0.20
Total	0.60 ± 0.10	0.47	0.52	0.60

shaped contours in the case of tunneling from occupied states of the sample, while for tunneling into unoccupied states (voltage bias of +1 and +2 V) these V's carry a prominent protruding feature on the apex. The findings of NT are in favor of model II [Fig. 3(b)] in which V-shaped contours can be discerned. To our knowledge neither BIS nor spectroscopic STM measurements have been performed yet which give clues about the unoccupied surface state distribution. We will show that SDR can fill this gap without seriously disturbing the delicate clean surface before adsorption.

Adsorption studies are frequently performed to characterize the electronic structure of the clean surface, e.g., oxygen adsorption is used to generate a bulklike electronic structure in the surface region. The difference between the clean and adsorbed state serves to identify the electronic structure of the clean surface (see, for example, Refs. 1, 2, 5, 6, and 27–36). During oxygen adsorption the relative change of the sample surface reflectivity, $\Delta R/R$ (in SDR), is continuously followed.^{1,2,5,6,30–33} $\Delta R/R$ is measured when the surface is allowed to change from an initial state (clean Si surface, containing $\approx 10^{15}$ surface states per cm^2) to a final state (the same surface covered by a fractional ML of oxygen and a reduced number of surface states). The corresponding expression is

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

where R_{clean} and R_{ox} are the overall reflectivities of the initial and final states of the surface, respectively. By means of SDR the excitation of electrons from filled to empty states is investigated and information is obtained containing joint properties of both types of bands. In Ref. 5 we have argued that SDR, when applied in the photon energy region of 1.5–4.5 eV, essentially probes the surface states at the clean Si surface. The advantages of SDR are its essentially nonperturbing nature if the wavelength and intensity of the light

beam are properly chosen and its sensitivity for transitions originating from surface states up to the Fermi energy E_F .

In SDR the relation between the disappearance of surface states and the measured change in reflectivity is given by

$$\delta(\Delta R/R) \propto \sum (N_{\text{sd}}^* \delta N_{\text{sa}}^* + N_{\text{sa}}^* \delta N_{\text{sd}}^*), \quad (2)$$

in which N_{sd}^* is the number of surface donor states and N_{sa}^* the number of surface acceptor states (the Fermi factor included³⁵). A peak in the optical reflection spectrum can therefore arise from either the disappearance of acceptor states, donor states or both.

Curves (a)–(c) of Fig. 4 show the relative difference in reflectivity, $\Delta R/R(h\nu)$, before and after exposing a clean Si(110) 5×1 surface to N_2O at three successive stages. Curve (c) corresponds to the ultimate relative change in reflectivity with exposure. The fractional oxygen coverages (θ) as determined from AES measurements are also indicated in the figure. Curves (a)–(e) of Fig. 5 show $\Delta R/R$ before and after exposing a clean Si(110) 5×1 surface to O_2 at five successive stages. The upper curve corresponds to the ultimate relative change in reflectivity with O_2 exposure. The θ values are displayed on the right-hand side of the curves. Exposing the Si surface to N_2O leads to peaks at low photon energy $h\nu$ (below 2.5 eV), which have a high intensity relative to those at $h\nu > 2.5$ eV when compared to exposing the same surface to O_2 (Fig. 5). Additional exposure of the apparently saturated surface [curve (c) of Fig. 4] to O_2 results in an increase of the region around 3 eV [dashed curve of Fig. 4].

In Sec. III A we have argued that N_2O is not likely to adsorb at the nn (A) atoms since the 5×1 LEED pattern is still visible at saturation (0.36 ± 0.05 ML). Instead, we have found evidence that decomposition of the N_2O molecule takes place at adatoms and rest atoms. As rest atoms are likely to have a filled db state as a result of charge transfer

FIG. 4. The relative difference in reflectivity $\Delta R/R(h\nu)$ before and after exposing a clean Si(110) 5×1 surface to N_2O : (a) 1.8×10^5 , (b) 3.5×10^5 , and (c) $\geq 6 \times 10^6$ L. Additional exposure to O_2 ($\geq 1 \times 10^5$ L) results in the dashed curve. The fractional oxygen coverages (θ) are indicated on the right-hand side of the curves. The figure has been adapted from Ref. 1.

FIG. 5. The relative difference in reflectivity $\Delta R/R(h\nu)$ before and after exposing a clean Si(110) 5×1 surface to O_2 : (a) 1.5, (b) 6, (c) 12, (d) 170, and (e) $\geq 4 \times 10^4$ L. The fractional oxygen coverages (θ) are indicated on the right-hand side of the curves. The figure has been adapted from Ref. 2.

from the unoccupied adatom db state (Sec. III A) the acceptor state at about -0.8 eV, as revealed by UPS,¹³ can be associated with a rest atom, but also with atom (B) which is directly connected with an adatom, that is, those atoms which are associated with the $[110]$ tubes between the missing chains, as evidenced by STM.¹¹ The formation of Si-O bonds at adatoms and rest atoms will result in the removal of these acceptor states. In our optical reflection spectrum (Fig. 4) the intense peak below $h\nu = 2.5$ eV can therefore be attributed to optical transitions originating from the acceptor state at about -0.8 eV.

Going back to the optical reflection spectra (Fig. 4), it can be seen that in particular, the peaks at approximately 3.2 and 3.9 eV increase in intensity upon exposing the apparently with atomic oxygen saturated surface [curve (c)] to O_2 (dashed curve). From our AES and LEED results (Sec. III A) we found good reasons to assume that the extra amount of oxygen, 0.24 ± 0.10 ML, adsorbs at the double tubes containing the (A) atoms. The SDR results therefore strongly suggest that the peaks at about 3.2 and 3.9 eV (photon energy) can be assigned to optical transitions originating from the filled db state of atom (A) [Fig. 3(a)] which, according to STM,¹² is positioned at about -2 eV, UPS data¹³ reveal features at a binding energy of ≈ -2.4 eV. This acceptor state was very prominent in the faceted X reconstruction as evidenced by UPS.¹³ According to LEED^{15,16} and STM¹² such a superstructure is thought to consist completely of nn tubes without "missing" tubes. The optical transitions, which are observed as peaks in Figs. 4 and 5, are possible if we assume the existence of two donor states at about 0.9 and 1.7 eV above E_F associated with adatoms, which is reasonable since in our model [II and III in Fig. 3(b)] two kinds of adatoms [one saturating two (B) atoms and one (C) atom, the other saturating three (C) atoms] can be discerned. Moreover, our assumption does not conflict with the STM results performed by NT, who observed two kinds of protrusions with dissimilar height measured at positive sample bias (1 and 2 V) in V-shaped contours, clearly excluding model I [Fig. 3(b)]. In spectroscopic STM measurements, however, the two adatom db states as proposed by us (in model II and III) may be hard to distinguish because STM does not have k -space resolution. With optical methods like SDR, there is also no k -space resolution and only specific points in k space are measured but high energy resolution is easily obtained although the width between the energy levels of the surface states as derived tend to be too low.^{30,31} The transitions in SDR are threshold energy differences that need not to occur at the Γ point of the surface Brillouin zone which is emphasized in the tunneling spectrum. The transitions therefore give an indication of the minimum difference in energy between surface states. Since the electronic surface structure is changed upon adsorption of oxygen the positions of the peak maxima in an SDR spectrum may shift as a function of oxygen coverage. From our SDR measurements (Figs. 4 and 5) and the present STM^{11,12} and UPS¹³ results it is possible to derive a picture in which the surface state density is plotted as a function of the energy near E_F on the " 5×1 " reconstructed Si(110) surface as has been done in Fig. 6. The surface states transi-

FIG. 6. Densities of states and surface states transitions on the clean Si(110) surface showing a prominent 5×1 superstructure as a function of the energy around the Fermi level E_F . The figure has been composed of results from SDR (Figs. 4 and 5), STM (Refs. 11 and 12) and UPS (Ref. 13) work.

tions, as shown by the peaks in the curves of Figs. 4 and 5, are indicated by the arrows. Only careful spectroscopic STM and BIS measurements can yield more definite conclusions about the actual unoccupied surface state distribution.

When Figs. 4 and 5 are compared it can be seen that the interaction of the clean Si(110) 5×1 surface with O_2 , in contrast to that of the same surface with N_2O , leads to an equal increase of all peaks in the optical spectrum. This result is in agreement with the non-site-specific (complex) adsorption behavior of molecular oxygen on virtually any Si surface (see, e.g., Ref. 5 and references therein), i.e., dissociative and molecular adsorption, penetration of the subsurface Si lattice well below ML coverage and the removal of surface states all may occur simultaneously.

IV. CONCLUSIONS

By chemically "titrating" the clean Si(110) surface, showing a prominent 5×1 reconstruction, with N_2O and O_2 we have been able to describe its superstructure. It is based on structures containing adatoms and rest atoms and our description is consistent with LEED, UPS, and STM studies of this complex surface. Unoccupied states were identified and are attributed to adatoms, the occupied states could be identified with rest atoms and atoms in nn top layer chains. Our present paper demonstrates that the use of the combination of AES, LEED, and SDR while chemically "titrating" the various surface sites with (atomic) oxygen promises to be an important complementary tool in clarifying the electronic structure and atomic nature of at least the low-Miller index surfaces of Si. Similar research on the clean low-index planes of germanium using in addition spectroscopic ellipsometry, x-ray photoelectron spectroscopy (XPS), STM, and surface conductivity³⁴⁻³⁷ measurements is in progress in our laboratory.

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