Atomic nature of '5 × 1' reconstructed Si(110) as revealed by chemical titration with N₂O and O₂: AES and LEED results

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By comparing the site-specific adsorption of N₂O with the non-site-specific adsorption of O₂ at the clean Si(110) surface which shows a prominent 5 × 1 superstructure (both at 300 K), employing Auger electron spectroscopy (AES) and low energy electron diffraction (LEED), a model of the atomic nature of this surface has been derived which is in agreement with previous LEED and recent scanning tunneling microscopy (STM) work. The description of the real '5 × 1' reconstructed Si(110) surface 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 neighbour top layer chains along $\bar{1}10$ (A). It is the ratio adatoms/rest-atoms/A-atoms which determines the primary superstructure. The spatial variation of this ratio at the same Si(110) surface is examined, which cannot be excluded as evidenced by STM, and is found to itself account for the more or less visible streaks (or even spots) very often reported in LEED studies.

Studies in which a comparison is made between clean surfaces and the same after gas adsorption have been widely performed to gain information about the structure of the clean surface and its electronic properties. Recently¹⁻⁴, we have shown that a comparison between the adsorption of N₂O and O₂, studied by means of the combination of spectroscopic differential reflectometry (SDR), Auger electron spectroscopy (AES) and low energy electron diffraction (LEED), is very useful in studies dealing with the three low-Miller index surfaces of Si. At atomically clean Si surfaces, N₂O decomposes into N₂ (gas) and atomic oxygen, Si-O bond formation only occurring via attachment of dangling bonds (db's) and dimer bonds² of the surface layer atoms. It has been established that the system 'Si(100)2 × 1 surface exposed to N₂O at 300 K' can be used as a reference to determine the fractional oxygen coverage, θ , in AES^{2, 5-8}. Whereas for the clean reconstructed Si(111) and Si(100) surfaces the structure seems to be well resolved, which is mainly because of the application of scanning tunneling microscopy (STM)^{9, 10}, for the clean Si(110) surface the situation is far less clear. This is partly due to the fact that an adequate picture of the real reconstructed Si(110) surface, which is considered to be the most complicated low Miller index Si surface^{11, 12}, until STM studies were published^{13, 14}, was not available.

In this paper we will demonstrate that the combination of AES and LEED while chemically titrating the various surface sites with the combination of atomic (N₂O) and molecular oxygen (O₂) 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. The AES and LEED data discussed in this report are adapted from previous work^{3, 4, 15} and are reinterpreted in view of recent STM work^{13, 14} and ideas about the structure of the clean reconstructed Si(110) surface. For the determination of the fractional oxygen coverage with AES, θ , as derived from the normalized

oxygen Auger signal (O_{KLL}/Si_{LVV}), using the system Si(001)2 × 1 - N₂O as a reference², we refer to ref 5 in which a defect density of 15 ± 10 % is assumed for the clean Si(001) 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 N₂ and O₂ with the Si(110) 5 × 1 surface^{3, 4, 15} have been corrected for the deviation from a monatomic oxygen layer in the case of an ideal defect-free Si(001)2 × 1 surface² using the calibration procedure as described in ref 5. In this article we want to discuss the family of reconstructions containing 5 × 1 and 4 × 5 as these can be obtained by various heat treatments¹². Contamination of the Si(110) surface with Ni was not detected with AES. The effect of Ni is therefore less than one atom per unit cell and of no direct concern to the various types of adsorption sites upon reconstruction.

Table 1 summarizes the most relevant AES results and LEED observations of our chemical titration experiments. We will first focus our attention to the STM results of Becker *et al*¹³, hereafter denoted as BSV. They observed a primary 5 × 1 LEED pattern with streaks at various fractional order positions along $\bar{1}10$ and interpreted their STM measurements with the missing of two out of five first layer chains per unit cell, the chains being oriented along $\bar{1}10$. In Figure 1(a) we present a schematic side view of the 5 × 1 reconstruction as proposed by BSV as an explanation of their STM measurements. The Si top layer atoms with their db pointing (in off-normal directions) towards the nearest neighbour (nn) first layer chain are in Figure 1(a) denoted by A. As argued by Olshanetsky and Shklyayev¹² (OS), the existence of, and the distance between, nn chains determines the order of the potential distortions in LEED resulting in LEED patterns with varying dimensions along [001], e.g. 5 × 1. Since the 5 × 1 LEED pattern is still well visible at saturation after exposing the clean Si(110) surface to N₂O, that is at 0.36 ± 0.05 ML atomic

Table 1. Summary of the most relevant AES results and LEED observations concerning the chemical titration experiments of the $\sqrt{5} \times 1$ reconstructed Si(110) surface with N_2O and O_2 at 300 K^{3,4}. The fractional oxygen coverage, θ , has been adapted from refs 3 and 4 using the calibration procedure as outlined in ref 5. The first column shows the gas used, the second contains the θ data and displayed in the third column are the results of the LEED observations. 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

Gas	θ (ML)	LEED
-----	0	5×1 plus streaks at $1/5$ and $1/2$ order along $[\bar{1}10]$
N_2O	0.10 ± 0.05	streaks disappeared, 5×1 on slightly increased background
N_2O	0.36 ± 0.05	5×1 plus low background
additional O_2	0.60 ± 0.10	no pattern, high background

oxygen (Table 1), it is unlikely that Si-O bond formation takes place at the nn top layer chains via interaction of the A-type db's. On geometric arguments we can understand why nitrous oxide prefers to react at the missing chain sites. 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 chains (Figure 1(a)). Si-O bond formation can easily take place at adsorption sites in these missing chains. Additional exposure to O_2 , however, must be accompanied by the removal of the A-type db's. At this position we can account for the saturation behaviour of molecular oxygen after an additional 0.24 ± 0.10 monolayer. For a unit cell in which the $[001]$ direction has a repetition unit five times the surface lattice constant (5.45 Å)—see Figure 1(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 the interaction with their db's thereby destroying the scattering centers for the LEED interference pattern. Saturation of the additional O_2 indicates that only adsorption at first layer sites has occurred and that the previous N_2O exposure has blocked the incorporation of oxygen into subsurface sites. This is in contrast to the situation in which the clean Si(110) surface is exposed to molecular oxygen, leading to slow further adsorption beyond one ML⁴. This is possible, as argued for the Si(001) surface², by incorporation of oxygen into subsurface bonds. Also the 5×1 LEED pattern which is still visible after exposure to N_2O has completely disappeared after additional exposure to O_2 at 0.60 ± 0.10 ML oxygen (Table 1) as a result of a large change in the scattering centers responsible for the observed 5 repetition in the $[001]$ direction. In our opinion, the most likely candidates for these scattering centers are the nn first layer chains, the atoms A. Additional proof for this adsorption behaviour of O_2 is given by SDR experiments¹⁷.

Adatoms may explain the relatively low saturation coverage of 0.36 ± 0.05 ML atomic oxygen after N_2O exposure. This idea is supported by the STM measurements of BSV who observed terrace structures in the missing chains suggesting the existence of adatoms. If we aim at a maximum reduction of db's by

Figure 1. (a) Schematic side view of the Si(110) $\sqrt{5} \times 1$ substrate showing the missing $[\bar{1}10]$ chains (adapted from ref 13). (b) Schematic representation of the reconstructed Si(110) surface showing various models (I-III) for the unit cells considered. The triangles denote the atoms saturated by an adatom. The rest atoms with a db are indicated by filled squares (■).

saturation the db's in the missing chains, in model I of Figure 1(b) indicated by the triangles, this will naturally lead to a 5×3 reconstruction. From Figure 1(a) it can be seen that missing chains induce $\{111\}$ facet planes. On these planes two kinds of db's can exist; one is connected to a top layer atom, the other one to a second layer Si atom, in this figure denoted as B and C, respectively. There are three possibilities to create adatoms by saturating three db's, namely the db's of two B atoms and one C atom, one B atom and two C atoms, and three C atoms. Only the

first two combinations will result in a maximum reduction of db's as depicted in model I of Figure 1(b). From the 30 db's which are originally present 6 are related to 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. This value is, however, too small to account for the measured coverage, 0.36 ± 0.05 ML atomic oxygen (Table 1), although the additional uptake of oxygen, 0.24 ± 0.10 ML (Table 1), upon O_2 exposure after initial saturation by N_2O and leading to saturation at 0.60 ± 0.10 ML oxygen, compares favourably with the calculated number of A-type Si atoms per 5×3 unit cell, i.e. 0.20 ML. In order to solve this problem and from the fact that a 5×3 LEED pattern, which has never been reported, cannot explain the streaks at $1/5$ and $1/2$ order along $[\bar{1}10]$ (Table 1) we must introduce another type of atom. Supporting evidence is given by the STM measurements of Neddermeyer and Tosch¹⁴ (NT). While their LEED image showed a prominent 4×5 pattern, in STM NT observed a basic unit cell with 2×5 periodicity. They interpreted their measurements with two different sites. The first one saturating three C atoms should in their opinion be an adatom. The other kind of protrusion observed is also an empty state that also shows a resemblance to an adatom. In the case where both protrusions are adatoms, each saturating 3 db's, we have 6 adatoms per unit cell saturating 18 db's of the unreconstructed cell. This means that 2 db's per unit cell are not saturated by an adatom. The positions of the protrusions as resolved by NT indicate that if these are adatoms they are located at rather asymmetric positions. The basic unreconstructed lattice as shown in Figure 1(a) should therefore certainly have a large change in bond angle and distances in the first atomic layers as compared with the ideal structure. It is the inclusion of rest atoms in our model which makes it possible to obtain good agreement with our chemical titration results. This situation is represented by model II of Figure 1(b) and corresponds to a 5×5 unit cell, or in the absence of nn double chains, to a basic 2×5 reconstruction. It contains 0.24 ML adatoms and 0.08 ML rest atoms per basic unit cell, the sum being, within the bounds of experimental error, equal to 0.36 ± 0.05 ML atomic oxygen. The rest atoms in this model are separated by a distance equal to five times the surface lattice constant and may therefore be the source for the observed streaks at $1/5$ order along $[\bar{1}10]$ in LEED^{3, 4, 11, 13, 15, 16}. The observation of streaks instead of sharp spots suggests that the distribution is not very regular over large distances, which is in good agreement with the STM measurements of NT who observed an irregular distribution of the 2×5 unit cell over larger distances. Note that in model II the type of adatom connected to one B atom and two C atoms, which appears in model I, is omitted in favour of the adatom saturating the db's of three C atoms. Considering our N_2O titration results in the initial stage ($0 < \theta < 0.1$ ML), see Table 1, in which the streaks at $1/5$ and $1/2$ order along $[\bar{1}10]$ disappear, leading to a 'cleaner' 5×1 LEED pattern, it seems that there is a preference for the N_2O molecule to decompose at the rest atoms. By creating Si-O bonds with the rest atoms the scattering centres for the LEED interference pattern are destroyed. Additional evidence that nitrous oxide decomposes preferentially at ad and rest atoms is given by our SDR measurements¹⁷. Neither of the models (I and II) for the unit cell described above can, however, account for its width along $[\bar{1}10]$, 1.6 nm, as measured by BSV. Good agreement with respect to this width is obtained if we allow the basic unit cell to contain more rest atoms. We then arrive at a unit cell with a repetition unit along $[\bar{1}10]$ four times the surface

lattice constant containing 0.2 ML adatoms, 0.2 ML rest atoms and, like in the first two models, 0.2 ML A-type atoms. This model (III in Figure 1(b)) can also account for the streaks as observed in LEED (Table 1). It is very likely that the ratio adatoms/rest-atoms varies locally at the same reconstructed Si(110) surface under investigation. This may yield, when probed with STM, (locally) a well defined reconstruction with a repetition unit along $[\bar{1}10]$ 4 to 5 times the surface lattice constant. With LEED this partial order is observed as streaks or even as spots with varying relative intensity depending on the sample preparation; OS already showed the subtle influence of sample heat treatment on the LEED image. Upon (fast) cooling the Si(110) surface they initially observed fractional order along $[001]$, i.e. 5×1 , 7×1 , 9×1 and 2×1 . Fractional order along $[\bar{1}10]$ leading ultimately to the 4×5 superstructure could only be obtained at a very slow cooling rate¹². We may therefore consider the 4×5 reconstruction as the one with the lowest energy of all superstructures observed. This result also suggests that it is energetically unfavourable to saturate all db's with adatoms which is additional proof against model I of Figure 1(b).

In conclusion, by chemically titrating the clean '5 × 1' reconstructed Si(110) surface with N_2O and O_2 we have been able to describe its superstructure. It is based on structures containing adatoms and rest atoms. We have found that the ratio adatoms/rest-atoms/A-atoms per reconstructed unit cell determines the primary superstructure. The spatial variation of this ratio at the same Si(110) surface studied and the ratio itself account for a more or less 'apparent' coexistence of higher order reconstructions very often reported in LEED studies. In contrast to the atomically clean Si(100) surface, which usually shows a two-domain superstructure (2×1 and 1×2), domain walls are unlikely to exist at the clean reconstructed Si(110) surface as indicated by Figure 1(b) in which the transition from one unit cell into another goes smoothly, a phenomenon which is also evidenced by STM measurements. To our opinion, the real 5×1 reconstructed Si(110) surface cannot be described by one static model only. Both LEED^{3, 4, 11, 13, 15, 16} and STM^{4, 5} experiments strongly suggest a real coexistence of several superstructures with local order. When model II and III (Figure 1(b)) are combined to describe its atomic nature, both the STM observations of BSV and NT, which are local measurements of a particular superstructure, as well as our chemical titration experiments, which indicate a coexistence of reconstructions, can be explained.

The chemical titration method as described in this paper can only be a complementary tool for resolving the reconstruction of surfaces. However, the power of this global method for testing proposed models for a reconstruction should not be underestimated¹⁻⁸. A reduction of dangling bonds in the case of the Si(110) surface is quite likely as the number of saturation sites is below one ML. Moreover, any model proposed describing the Si(110) surface must account for the different observed adsorption behaviour of N_2O and O_2 accompanied with the changes in the LEED pattern. Especially the additional adsorption of O_2 after saturation by N_2O is a typical phenomenon of this surface that must be incorporated in any model.

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