

STM study of the C-induced Si(100)- $c(4\times 4)$ reconstruction

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(Received 12 June 2001; revised manuscript received 1 October 2001; published 28 February 2002)

We report a direct and reliable way to produce the Si(100)- $c(4\times 4)$ reconstruction by submonolayer deposition from a SiC source and subsequent annealing. Auger electron spectroscopy, low-energy electron diffraction, and scanning tunneling microscopy (STM) investigations reveal that a C amount equivalent to 0.07 monolayers (ML's) is sufficient to obtain full coverage of the $c(4\times 4)$ reconstruction. A deposition of 0.035 ML's C produces a $c(4\times 4)$ coverage of only 19%, indicating that C is not only present in the $c(4\times 4)$ areas, but also in the 2×1 areas. There is not enough C to make it a regular part of the $c(4\times 4)$ reconstruction and we therefore conclude that the $c(4\times 4)$ reconstruction is strain induced. We find that a combination of the mixed ad-dimer and buckled ad-dimer models explains all main features observed in the STM images. Images of freshly prepared $c(4\times 4)$ surfaces exhibit a decoration of approximately 50% of the unit cells, which is attributed to perpendicular ad-dimers. Long exposures (>20 h) to the UHV background gas quench these features and the $c(4\times 4)$ reconstruction appears as if more homogeneous.

DOI: 10.1103/PhysRevB.65.115321

PACS number(s): 68.35.Bs, 68.35.Dv, 68.35.Rh

I. INTRODUCTION

The Si(100)- $c(4\times 4)$ reconstruction was originally discovered by Thomas and Francombe¹ in early low-energy electron diffraction (LEED) experiments on Si surfaces prepared by molecular beam epitaxy (MBE). This was reproduced by Sakamoto *et al.*,² and later Müller *et al.*³ reported that this reconstruction also appeared when a clean Si(100) surface was annealed in vacuum. It turns out that this reconstruction has been formed with a wealth of methods; Si deposition,^{1,2,4,5} C deposition,⁶⁻¹¹ Ge deposition,¹² H exposure,¹³⁻¹⁹ C₂H₄ and C₂H₂ treatment,²⁰⁻²⁴ SiH₄/Si₂H₆ growth,²⁵⁻²⁹ annealing in vacuum,^{3,30-36} B deposition,³⁷⁻³⁹ and O or S treatment.⁴⁰⁻⁴² Several models for the reconstruction have been proposed: Pandey's π -bonded defect model,^{30,43} missing dimer,^{9,13} parallel ad-dimer,¹⁵ and mixed ad-dimer¹⁵ models, and it has been debated whether it is a pure Si reconstruction or if it contains any foreign species. There were some Auger electron spectroscopy (AES) investigations reporting a clean surface^{27,30,42} while others reported traces of C present on the surface.^{13,6} In recent years most investigations seem to support the idea that the reconstruction is C related^{7-9,19,22,24} and there have been some attempts to estimate the carbon concentration.^{6,7,9,20,22} Some have argued for reconstruction models containing an integer number of C atoms per unit cell while others claim that subsurface C and/or surface C produces the reconstruction indirectly—by strain or otherwise. Very recently models based on simple dimer rows with substitutional C atoms in various surface and subsurface positions were investigated theoretically.⁴⁴ Miki *et al.*⁶ estimated the carbon concentration with secondary-ion mass spectrometry (SIMS) and concluded that it was not large enough to have C atoms as a regular part of the reconstruction model, i.e., it corresponded to less than one C atom per $c(4\times 4)$ unit cell. Since they used reflection high-energy electron diffraction (RHEED) to monitor the reconstruction, there was, however, no determination of how large the fraction was of the surface that was $c(4\times 4)$ reconstructed. By using scanning tunneling microscopy (STM) one can easily obtain this fraction and thus cor-

relate it to the deposited amount of C.

In this paper we present a reliable and direct way to produce the Si(100)- $c(4\times 4)$ reconstruction and show that a small amount of carbon is sufficient for its formation. We have determined an upper limit for the amount of carbon needed to get a full coverage and conclude that this is not enough for having one C atom per each unit cell such that the C atoms would be a regular part of the reconstruction. The processes of forming the surface, as well as the changes of the surface when exposed to the residual gas of the UHV system, are discussed. We also discuss the models proposed for the reconstruction and find that a combination of the mixed ad-dimer model and the parallel ad-dimer model fits the data best.

II. EXPERIMENTAL DETAILS

The combined scanning tunnel microscopy (STM) and molecular beam epitaxy (MBE) system used consists mainly of three sections; the preparation chamber, the MBE chamber, and the STM chamber, separated by UHV valves. It sits on top of a support that has no contact with the laboratory floor to avoid vibrations. The MBE chamber contains an Auger electron spectrometer (cylindrical mirror analyzer, CMA), a rear-view LEED optics and several thermal evaporation sources, and its background pressure is $<5 \times 10^{-11}$ Torr. When doing quantitative measurements of the C coverage with AES, the sensitivity is sufficient to detect approximately 1% of a monolayer (ML). Throughout this paper, 1 ML of atoms corresponds to the density of atoms on an unreconstructed Si(100) surface, i.e., 6.78×10^{14} cm⁻². An IR pyrometer was used to measure the temperature of the resistively heated samples. All the depositions in this study were done using thermal sources, described elsewhere.⁴⁵ The background pressure in the chamber containing the home-built STM, was below 1×10^{-10} Torr and the STM itself is suspended in a two-level spring system, using eddy-current damping.⁴⁶ When necessary, some image processing was applied to improve the quality of the STM images. A least mean-square fitted plane was subtracted to produce flat im-

ages and averaging was occasionally applied to produce reliable line profiles. Usually, the averaging procedure used between 4 and 25 data points (taken from the same image frame) and the physical size of the area that these points were taken from was always less than half the characteristic features of the images. All images were taken in constant current mode with Pt/Ir tips, as cut from a 0.4-mm wire.

Phosphorus-doped ($1.7\text{--}2.3\ \Omega\ \text{cm}$) Si(100) substrates were used. They were prepared by chemical etching according to the Ishizaka-Shiraki procedure.⁴⁷ The samples were then inserted into the preparation chamber and heated to $600\ ^\circ\text{C}$ for several hours to remove any water or any other volatile species adsorbed onto the sample and sample holder. After this initial degassing, the samples were annealed using a procedure controlled by a computer to ensure low pressure and high reproducibility. The annealing cycles started at $650\ ^\circ\text{C}$ (in periods with a maximum annealing duration of 60 s) while the pressure was kept below 1×10^{-9} Torr. The temperature was increased stepwise up to $950\ ^\circ\text{C}$. The duration of the current pulses was adjusted to keep the pressure within range, and the time between the annealing pulses was always at minimum 60 s—and prolonged if the pressure was too high, i.e., higher than 1×10^{-10} Torr.

We measured the Si and SiC fluxes from the sources by using a thickness monitor. The rates used were in the range $0.01\text{--}0.03\ \text{\AA}/\text{s}$ and the deposition time was in the order of minutes. The background pressure during deposition from the Si and SiC sources was $<2\times 10^{-8}$ Torr and the sample was held at room temperature in all cases. Subsequent annealing was applied to form the $c(4\times 4)$ reconstruction, usually $600\ ^\circ\text{C}$ for less than 3 min. To vary the C concentration in the material flux, the Si and SiC sources were concurrently depositing Si and Si/C. The C atomic fraction in the flux from the SiC source was about 10%.

The C surface coverage was determined by using the *in situ* AES where the C/Si peak-height ratio, the electron mean free path and the C and Si sensitivity factors were taken into account. The carbon concentration in the flux from the SiC source was determined by depositing $1\ \text{\AA}$ on a clean Ge substrate and performing a quantitative AES analysis on the C, Si, and Ge peaks. The amount of C deposited was determined to be 0.07 ± 0.01 ML when depositing $1\text{-}\text{\AA}$ Si/C from the SiC source. The amount of C deposited during the Si/SiC co-deposition was confirmed (by AES measurements) to be half (i.e., 0.035 ± 0.01 ML) for half the time of deposition and the same rates for Si and SiC sources. These preparations resulted in oxygen-free surfaces as verified by the AES measurements.

The amount of C adsorbed from the background gases during deposition (25% CO , 2.5% CO_2 , and the rest H_2) was estimated by doing a dummy deposition on a clean Si sample with all parameters kept the same as for the real deposition, but with the sample facing away from the source. No adsorbed C was detected, as far as the AES could tell. When the $c(4\times 4)$ samples were exposed to the background pressure in the MBE chamber for periods extending up to days, nothing but the ion gauge, the ion- and turbopumps were running.

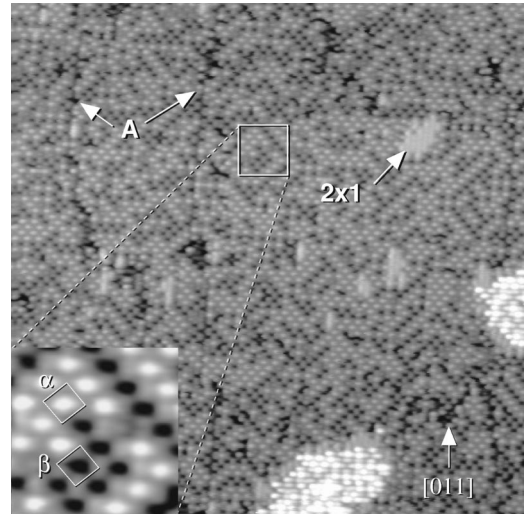


FIG. 1. Filled state STM image of a Si(100) surface with ~ 0.07 ML C deposited. $V_{tip}=2.0$ V, $I=210$ pA, $670\times 670\ \text{\AA}^2$. 98% coverage of $c(4\times 4)$.

III. RESULTS

A. SiC deposition

By depositing $1\ \text{\AA}$ from the SiC source and thus obtaining an equivalent amount of 0.07 ML C, we could get 98% surface coverage of the $c(4\times 4)$ reconstruction. The remaining 2% of the surface was covered by 2×1 reconstructed parts residing mainly at step edges or forming small islands, as seen in Fig. 1. The bright patches at the bottom and at the right side of Fig. 1 are $c(4\times 4)$ reconstructed areas on one atomic layer high terraces. In the inset in Fig. 1 there is a (low resolution) close-up showing the two main types of $c(4\times 4)$ unit cells, α and β , on this surface. In filled state images, the α cell seems to be occupied by a structural element in the center, while the β cell is unoccupied. There is also a small fraction of $\leq 5\%$ of the unit cells on this relatively freshly prepared surface that shows an intermediate contrast. This image was taken ~ 2 h after the preparation by annealing.

Beside the major differences between the central region of the α and β cells, there is an underlying height variation near the cell boundaries that seems to be the same for both types of cells. This will be further described below in connection with high-resolution measurements.

The main characteristic of the $c(4\times 4)$ reconstruction is that there is a highly ordered underlying $c(4\times 4)$ periodicity. Superimposed on this, there is a “decoration” of approximately 50% of the unit cells which are occupied by something appearing like a protrusion in the filled state images. By modifying the annealing procedure we have tried to achieve a phase separation between α and β unit cells. This has not been possible and the lateral distribution of the unit cells is close to random, with some tendency to form rows of the same type of cell along $\langle 010 \rangle$ directions.

We point out that the underlying $c(4\times 4)$ reconstruction extends coherently over large areas. The main defects are domain boundaries which in most cases are just $3.8\ \text{\AA}$ wide, i.e., the same width as a line of missing dimers on the 2

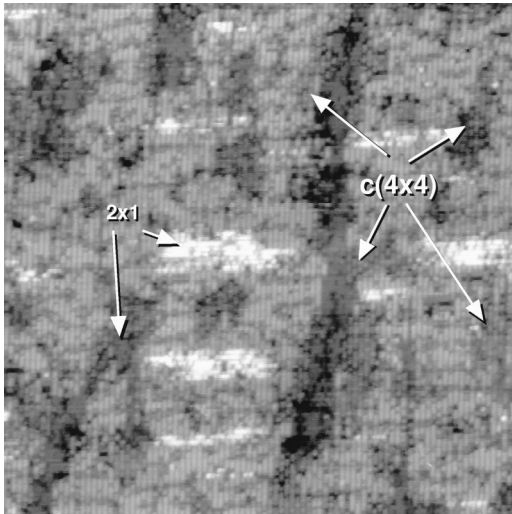


FIG. 2. Filled state STM image of a Si(100) surface with ~ 0.035 ML C deposited. $V_{tip}=2.0$ V, $I=210$ pA, $670 \times 670 \text{ \AA}^2$. The $c(4\times 4)$ phase covers 19% of the surface.

$\times 1$ reconstructed surface. The arrows A in Fig. 1 point to domain boundaries of the underlying $c(4\times 4)$ reconstruction that extend in the $[011]$ direction.

Using half the amount of carbon (0.035 ML in a 1- \AA -thick Si layer) in the deposition resulted in a surface with approximately 19% coverage of the $c(4\times 4)$ phase; see Fig. 2. This surface gives a much more fractured impression. The areas with $c(4\times 4)$ are small and they are not very well ordered, and the surface contains to a larger extent islands and depressions, reflecting an increased roughness. As pointed out in the image, there are 2×1 areas also on islands and in depressions.

In reference experiments we also studied the effects of deposition of 1 \AA pure Si. Annealing of this surface did not result in any changes of the 2×1 reconstruction into $c(4\times 4)$ reconstructed parts. The amount of C on the surface was in this case less than the AES detection limit.

B. Aging

When the $c(4\times 4)$ reconstructed surfaces were left in the UHV system for a long time (24 h up to three days), their appearances changed. The underlying $c(4\times 4)$ reconstruction did not disappear, but the amount of occupied sites (α) had seemingly decreased to only a fraction of the original 50%. In the example in Fig. 3, the α unit cells correspond to only $\sim 9\%$ of the surface. The domain boundaries were still present on the aged surfaces and did not disappear with subsequent annealing.

At first glance the $c(4\times 4)$ reconstruction seems more homogeneous after aging, but a closer examination, see Fig. 4, shows that there are now four types of unit cells. They are α , cells of the original occupied type that decrease in number by aging; β , the so-called unoccupied cells that seem to stay constant in numbers; γ , asymmetric unit cells in two variants, which appear to be half occupied; δ , unit cells with center height in between occupied and unoccupied ones. In order to unambiguously identify a unit cell as being of type γ or δ , high resolution STM images are required.

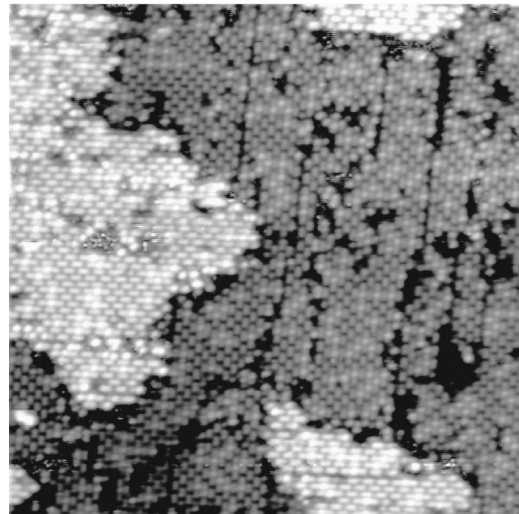


FIG. 3. Filled state STM image of a Si(100) surface with 0.07 ML C deposited, stored in UHV (5×10^{-11} Torr) for 24 h. $V_{tip}=1.3$ V, $I=100$ pA, $536 \times 536 \text{ \AA}^2$.

C. Annealing

The aged samples can be regenerated to show a surface with the as-grown characteristics by annealing at 730°C , as shown in Fig. 5. Our studies show that the aging process is reversible and that the original $c(4\times 4)$ reconstruction can be completely restored, i.e., essentially only containing occupied and unoccupied sites of nearly equal numbers.

Annealing at 750°C , on the other hand, results in large changes in the surface structure as shown in Fig. 6. One can observe the formation of some islands. Moreover, large parts of the surface have developed a 2×1 reconstruction. This is consistent with the results in, e.g., Refs. 15, 27, and 42, that the $c(4\times 4)$ reconstruction disappears irreversibly at about $730\text{--}750^\circ\text{C}$. Detailed studies of the islands show that their lateral sizes are smaller than the white areas in Fig. 6 which just reflect the size of high level Si terraces. The actual islands are approximately 10–20 \AA high and 100–200 \AA wide.

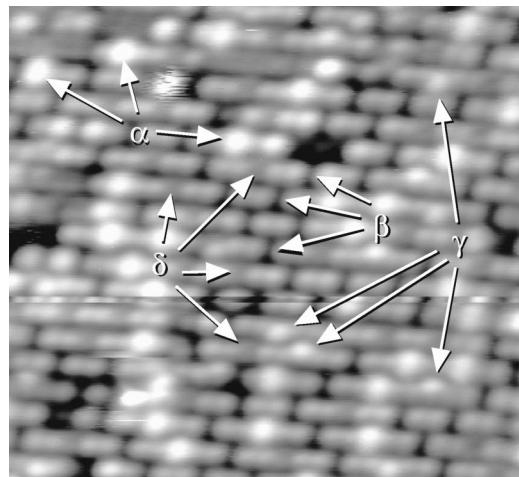


FIG. 4. Filled state STM image of a Si(100) surface with 0.07 ML C deposited, stored in UHV (5×10^{-11} Torr) for 24 h. $V_{tip}=2.0$ V, $I=90$ pA, $144 \times 132 \text{ \AA}^2$. The features α , β , γ , and δ are discussed in the text.

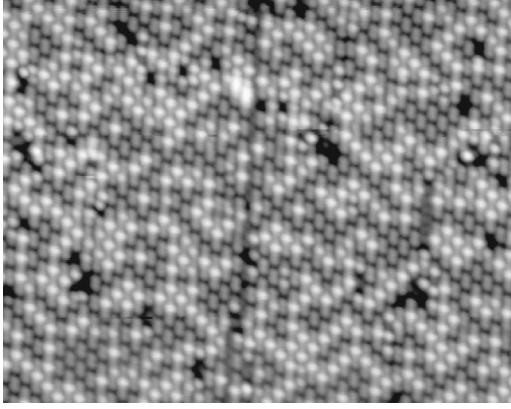


FIG. 5. Filled state STM image of a Si(100) surface with 0.07 ML C deposited, stored in UHV for 24 h and annealed to 730 °C. $V_{tip}=2.0$ V, $I=260$ pA, 353×281 Å².

Under the assumption that these islands consist of SiC, the corresponding amount of carbon was estimated to be approximately 0.10 ML, which is close to the deposited amount.

IV. DISCUSSION

A. C concentration vs coverage of the $c(4\times 4)$ reconstruction

It is not clear how the deposited carbon is shared between the $c(4\times 4)$ and the 2×1 areas. It has been reported that the concentration needed to get a complete coverage of $c(4\times 4)$ is $\frac{1}{2}$ or $\frac{1}{3}$ ML.^{7,8} We have now determined that an amount equivalent to 0.07 ML is enough to get full coverage of the $c(4\times 4)$ reconstruction, while 0.035 ML of C only gave 19% coverage. The deposited carbon can possibly go into four regions: (i) into the $c(4\times 4)$ areas; (ii) into the 2×1 areas; (iii) into SiC islands; and (iv) into the bulk. Going into the bulk can be dismissed by the results of Butz and Lüth,⁷ Stoffel *et al.*,²⁴ and others who reported a strong ten-

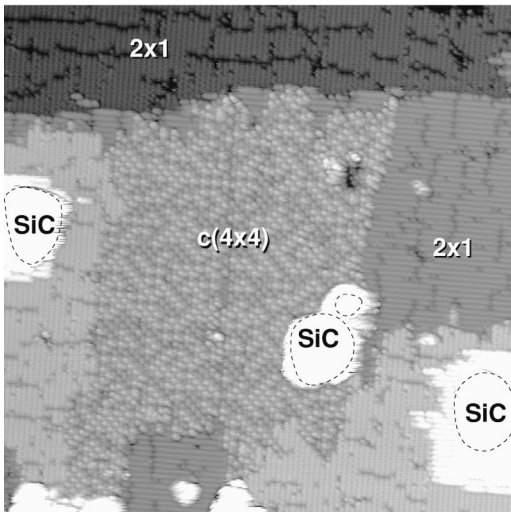


FIG. 6. Filled state STM image of a Si(100) surface with 0.07 ML C deposited and annealed to 750 °C. $V_{tip}=1.3$ V, $I=100$ pA, 700×700 Å².

dency for C to stay at or near the surface. Furthermore, the C bulk diffusion at the temperatures used in our experiments is negligible.⁴⁸

Option (iii) can be ruled out too, since there is evidence⁶ that SiC islands do not start to form below 730 °C. This is also consistent with our observation that islands, assigned to be SiC, are formed by annealing at 750 °C. Since we do not see any SiC islands below 750 °C, we must conclude that the major part of the deposited C is found near the surface and is shared between the $c(4\times 4)$ and the 2×1 areas. It is reasonable that the C concentration is higher in the $c(4\times 4)$ areas, but the question is if there is a complete depletion of C in the 2×1 reconstructed areas.

Our results indicate that there is a substantial amount of C in the 2×1 regions. Under the assumption that 0.07 ML is precisely enough to get a complete coverage over the surface and that there is no C outside the $c(4\times 4)$ areas, 0.035 ML should generate a coverage of 50% if there was a complete C separation. Anything less than 50% indicates that not all C is active in the formation of the $c(4\times 4)$ reconstruction. Our observation that 19% of the surface was $c(4\times 4)$ reconstructed thus indicates that there is an equivalent coverage of 0.027 ML C in the 2×1 reconstructed areas.

B. Models

There have been at least four models proposed for the $c(4\times 4)$ reconstruction: Pandey's π -bonded defect model,³⁰ missing dimer,^{9,13,49} parallel ad-dimer,¹⁵ and mixed ad-dimer.¹⁵ There are schematic views of the various models in Fig. 7.

Based on our result that 0.07 ML is a sufficient C coverage for a completely $c(4\times 4)$ covered surface, we can rule out the possibility that the C atoms are a regular part of the reconstruction. With one C atom per unit cell, the necessary C coverage would be 0.125 ML. From the lack of asymmetry in the images of α and β unit cells, and the fact that all models suggested so far are based on surface dimers, it would be necessary to have an even number of C atoms per unit cell if they were localized in the dimers, i.e., corresponding to at least 0.25 ML of C. Even with the assumption that either only α or only β cells contain the C atoms in dimers, there are not enough C atoms to explain how 0.07 ML can give a complete coverage of the observed 50-50 mixture of α and β unit cells.

The role of C must thus be different. There are enough C atoms to have one C atom in either each α or in each β cell. If these atoms are in some subsurface sites, it can result in symmetric unit cells. Since still approximately 50% of the unit cells do not contain any C atoms, it is reasonable to attribute the overall reconstruction to the long-range effect of strain, induced by the C atoms. Thus we support the conclusions drawn by Miki *et al.*⁶ that this is an impurity-induced Si reconstruction.

To support the discussion about the geometry of the $c(4\times 4)$ reconstruction, Fig. 8 shows filled and empty state images of a part with both $c(4\times 4)$ and 2×1 reconstructed areas. Height profiles along two lines in the filled state image show the relative height of various observed features. Figure

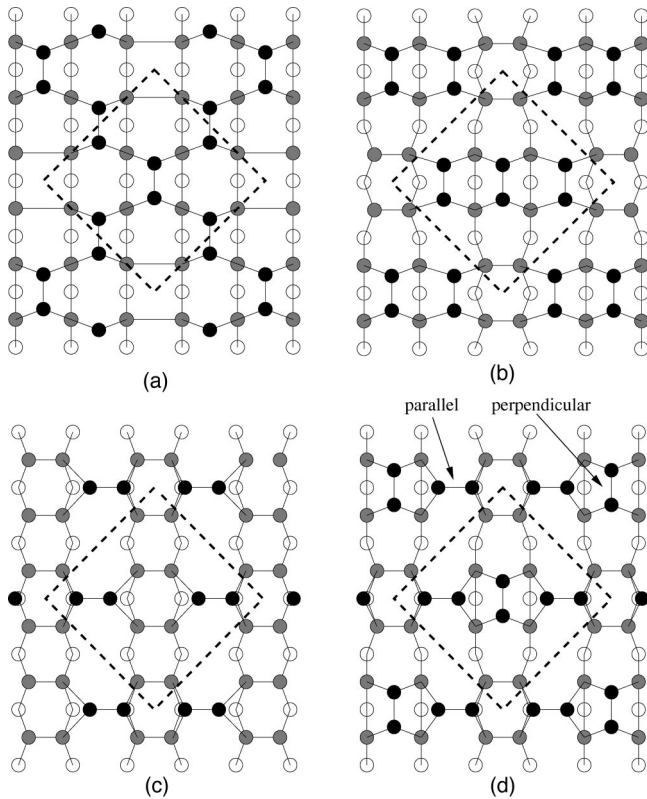


FIG. 7. Models for the $c(4\times 4)$ reconstruction: (a) Pandey's π -bonded defect model, (b) the missing dimer model, (c) the buckled parallel ad-dimer model, and (d) the mixed ad-dimer model.

9 shows high-resolution filled and empty state images where some internal structure of the units is easily observed.

By studying the STM images one can make the following observations:

(i) The occupied sites (in α unit cells) are of approximately the same height as the 2×1 dimer rows (within 20 pm) in filled state images [Figs. 8(c) and 8(d)].

(ii) The occupied sites split in the empty state images just as 2×1 dimers do [Fig. 8(b)].

(iii) The regions near the corners of the unit cells are about 35–40 pm lower than the occupied sites [Figs. 8(c) and 8(d)].

(iv) The feature at the corners of unit cells consists of a pair, which does not split perpendicular to the pair axis in the empty state images [Figs. 9(a) and 9(b)].

(v) The unoccupied sites (in β unit cells) are ~ 120 pm lower than occupied sites [Figs. 8(c) and 8(d)].

(vi) The features at the centers and the corners of the α and β unit cells (as defined in Fig. 1) are laterally aligned with the dimer rows at the same height level [e.g., along line A in Fig. 8(a)]. They are also aligned with the surrounding segments of dimer rows at the level below [Figs. 8(a) and 8(b)].

(vii) The fresh surface has approximately an equal amount of occupied and nonoccupied sites, ordered in nearly random fashion (Fig. 1).

First we note that the 20-pm and 35–40-pm differences are small enough to be electronic effects. However, it is not

plausible that the ~ 120 -pm difference between the occupied and unoccupied sites is a pure electronic effect, especially as there is no voltage dependence at all and the distance is not far from the Si(100) monolayer distance of 136 pm. This justifies the notions of occupied and unoccupied sites, since there are probably atoms missing on the unoccupied sites.

Based on the above observations we must rule out Pandey's π -bonded defect model [Fig. 7(a)]. In particular, we do not observe any features corresponding to the cross-linked dimers, it cannot explain why the corner region should only be 35–40 pm lower (and not ~ 136 pm) and it provides no clue to observation (vii).

Concerning the missing dimer model, one could argue that the first observations [(i) and (ii)] could be explained. Still, the STM images are not like that of a 2×1 surface with every fourth dimer missing. In Ref. 9, a modification of the missing dimer model containing 6 C atoms per unit cell was suggested. This model must also be ruled out since it requires a C coverage of 0.75 ML for a complete $c(4\times 4)$ reconstruction.

The buckled parallel ad-dimer model [Fig. 7(c)] misses the bright, splitting features of the α unit cells, but it can explain all features found in the β -cell regions, e.g., it explains observation (iv). Since the pairs discussed in (iv) are attributed (in this model) to a pair of dimers aligned along the pair axis, it is clear that these should not split perpendicular to their axes in empty state images. The lateral alignment of the $c(4\times 4)$ and 2×1 reconstructed areas [observation (vi)] can easily be explained in terms of the buckled parallel ad-dimer model since it is essentially a 2×1 reconstruction with two added dimers per $c(4\times 4)$ unit cell forming the pair structure in the unit-cell corners.

The mixed ad-dimer model [Fig. 7(d)] can explain the observed features related to the α unit cells. There are two types of dimers (parallel and perpendicular) that can give rise to the different levels [observation (iii)], the perpendicular and parallel ad-dimers should be on approximately the same level as the 2×1 rows [observations (i) and (iii)]. The perpendicular ad-dimers (at the unit cell center) are expected to split in the same manner as the 2×1 rows [observation (ii)]. Furthermore, Fig. 9 shows that at the corners of the unit cells there is a pair structure [observation (iv)] which is interpreted as the two parallel ad-dimers in the model. According to the electron-density calculations in Ref. 15, unlike for the perpendicular ad-dimers, one should not see a splitting of parallel ad-dimers in the empty state STM images, which is consistent with the experimental observations (ii) and (iv). More support for the model comes from the fact that these ad-dimers should, according to the model, be separated with alternating large and small distances on adjacent rows and this is exactly what we see, both in the empty and filled state images. Note that this structural element is common for the buckled parallel ad-dimer and the mixed ad-dimer model and the corresponding feature is observed in both α and β unit cells in the STM images.

To summarize, we find that the mixed ad-dimer explains all observations related to the α -unit cells. If the perpendicular ad-dimers are removed we get the buckled parallel ad-dimer model, which explains the features of the β -unit cells

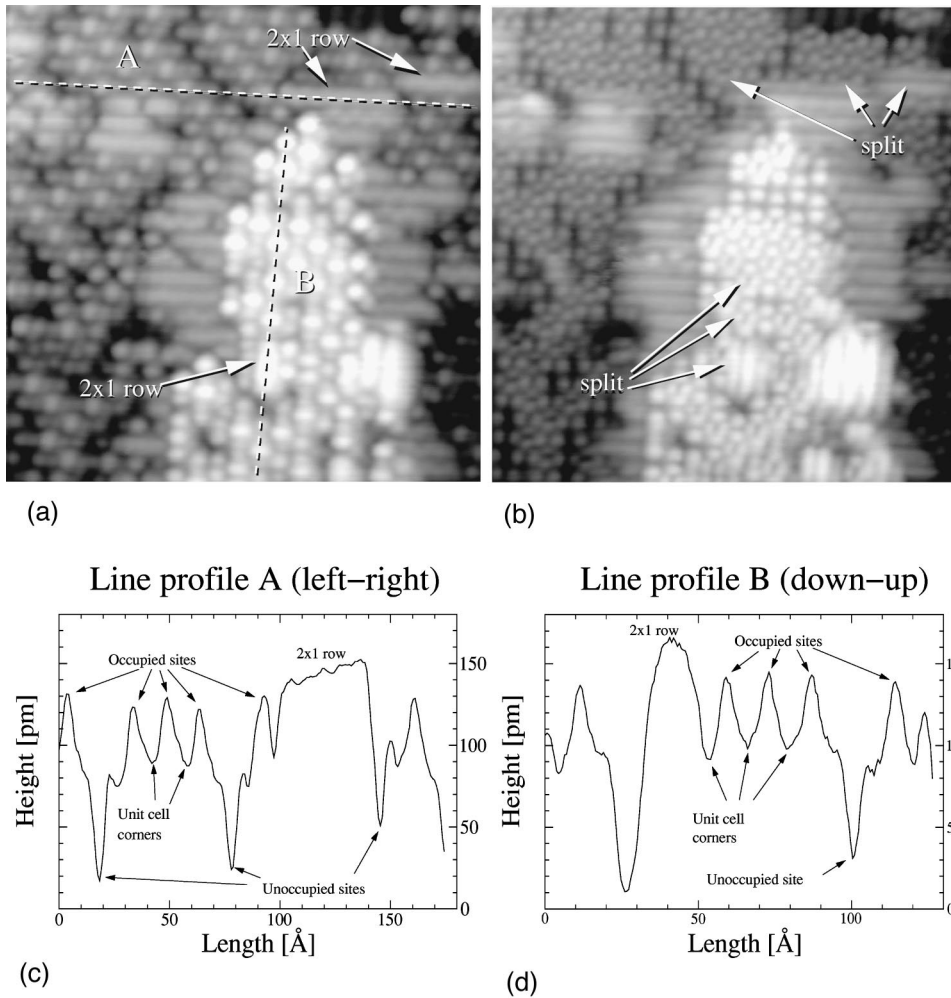


FIG. 8. Filled (a) and empty state (b) STM images, $V_{tip} = \pm 1.5$ V, $I = 150$ pA, $190 \times 190 \text{ \AA}^2$. (c) and (d) are the line profiles A and B in the filled state image.

and this is also consistent with the height difference between the center of α and β unit cells [observation (v)]. In agreement with previous studies¹⁵ we find that it has not been possible to observe more than approximately 50% of the unit cells of α type, while the rest are essentially β unit cells.

In total-energy calculations of $c(4 \times 4)$ models without C atoms,¹⁵ the mixed ad-dimer model and buckled parallel ad-dimer model both end up with a higher energy than the 2×1 buckled dimer surface, by 0.11 and 0.09 eV per 1×1 unit cell, respectively. If their relative energy difference stays ap-

proximately the same when strain is introduced by the carbon atoms and if they both have a lower energy than the correspondingly strained 2×1 surface, we will get a mixture of the mixed ad-dimer and the buckled parallel ad-dimer reconstruction. If one then considers the high temperatures at which the $c(4 \times 4)$ reconstruction is formed, there will be a certain amount of disorder explaining the mixture of the occupied and unoccupied perpendicular dimer sites found in the images. The observation that the annealing does not separate the $c(4 \times 4)$ areas into two phases (with and without perpendicular dimers) supports the idea that the experimentally realized $c(4 \times 4)$ reconstruction is a mixture of two structures which are very close in energy. It is also possible that there is a local strain compensation by the two types of unit cells resulting in a reduced energy of the mixture. Energy calculations for surfaces with various levels of strain may give more information to whether this proposal is correct or not, and may provide hints to why there seems to be a weak ordering of the perpendicular ad-dimers.

Concerning the very recently suggested dimer row-based models⁴⁴ with substitutional C atoms giving the $c(4 \times 4)$ periodicity we must conclude that, despite the low energies reported for some of these structures, there is no support for these models in the STM images. Since we find a total near-surface concentration that is less than one C atom per $c(4$

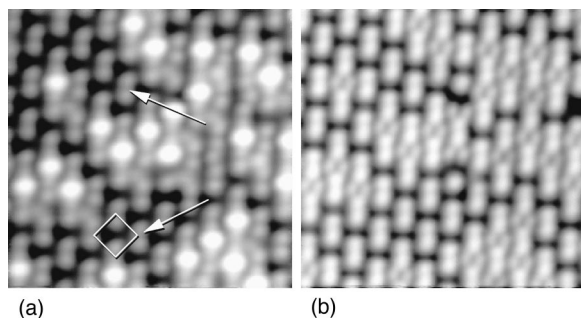


FIG. 9. Filled (a) and empty state (b) STM images, $V_{tip} = \pm 1.3$ V, $I = 100$ pA, $92 \times 90 \text{ \AA}^2$. Arrows point to corner positions of $c(4 \times 4)$ unit cells.

$\times 4$) unit cell, there is no basis for a model where an ordered distribution of C atoms is the origin of the $c(4\times 4)$ periodicity. For disordered distributions of C atoms that also are treated in Ref. 44 it is not at all clear what should be the reason for maintaining a $c(4\times 4)$ periodicity.

C. Aging

The increasing numbers of γ and δ unit cells with time in the UHV system is attributed to adsorption from the background gas. By comparing images before and after aging it is clear that it is mostly the α -unit cells that are affected by the contamination. The transformation to γ cells results in asymmetric filled state images and empty state images showing a split structure, very similar to the α cell. In the case of the δ unit cells it is not so clear that they also correspond to α cells that have been modified by the background gas. The evidence is indirect, since we do not find a decrease in the number of β unit cells with time.

Due to the gradual disappearance of the α unit cells, the filled state images of aged surfaces appear more and more homogeneous. It is interesting to note that STM images similar to our aged surfaces have been reported before, by Leifeld *et al.*,⁹ but they made no statement about the time in vacuum before the STM image was taken.

D. Dynamic process of creating $c(4\times 4)$

There are many ways to prepare the Si(100) surface to obtain the $c(4\times 4)$ reconstruction. Our experiments show that presence of carbon can induce the reconstruction and that it is sufficient with even less than one C atom per unit cell. It is plausible that this is a strain-induced reconstruction, coming from the tensile strain when C atoms are sitting in substitutional sites in the Si subsurface layers. If this is true, the reconstruction is not tied to C as a species, but to the smaller size of the carbon atom. Thus other atoms, smaller than Si, that occupy substitutional sites, may also induce $c(4\times 4)$ reconstructions. B is such an element and interestingly, it is reported to cause a $c(4\times 4)$ reconstruction on Si(100).^{37–39}

Reordering in one form or another appears, in many of the reported procedures, to be essential for the formation of this reconstruction:

The H experiments used atomic hydrogen to create a 1×1 surface, or exposed hot samples (up to 700 °C) to H. In the latter case, the hydrogen may start to act as an etchant, removing Si from the surface.^{13–19}

In the Si-MBE and Si_xH_y experiments growth changes the surface structure over time.^{1,2,4,5,25–29}

The hydrocarbon compounds (C₂H₄ and C₂H₂) crack at Si surfaces at elevated temperatures and leaves atomic hydrogen to modify the surface.^{20–24}

Oxygen treatment has also been used and when the SiO and/or SiO₂ leaves the surface, its morphology is changed.^{41,42}

Argon sputtering seems to help forming $c(4\times 4)$.^{31,50}

Electron irradiation (90 eV–2 keV) modifies the surface and causes a $c(4\times 4)$ reconstruction.⁵¹

The only case where there is no surface reordering of any sort, besides the diffusion, is the pure UHV-annealing cases. It is interesting to note that the preparation times for the reported cases are very long, from “a few hours”^{35,36} up to 220 h.³³

Since our results indicate that only a few percent of a monolayer of C is required on the surface to create the $c(4\times 4)$ reconstruction, it might be that several of the methods above that do not employ deposition of carbon directly, may still involve a small amount of C by some indirect contamination process.

It is clear from our experiments that it is not sufficient to only deposit Si on the surface and anneal. To get a uniform distribution of $c(4\times 4)$ it is required to have some sort of Si rearrangement and C deposition. It might be that surface reordering or amorphization helps the C atoms to diffuse into favorable positions in the subsurface layers while the Si atoms move around to find low-energy sites.

There were B-exposure experiments that reportedly failed⁷ creating the $c(4\times 4)$ reconstruction using elemental B, but succeeded when a H-containing carrier,^{37–39} such as B₂H₆, was used. Given the results above, the dissociated hydrogen in the latter experiment might have assisted the B atoms in finding subsurface substitutional sites by making the Si atoms more mobile, and thus giving the B atoms the opportunity of creating the strain needed to produce the reconstruction.

V. CONCLUSIONS

The formation of the Si(100) $c(4\times 4)$ reconstruction has been studied in experiments using co-deposition of Si and C atoms and post-annealing. It has been determined that 0.07 ML of C is enough to get a $c(4\times 4)$ reconstruction over the whole surface. This excludes the possibility that there is one or more C atoms per $c(4\times 4)$ unit cell. The freshly prepared $c(4\times 4)$ surface contains a blend of mainly two types of unit cells. The features observed in STM images are consistent with an underlying buckled parallel ad-dimer model that is decorated with perpendicular ad-dimers in approximately 50% of the unit cells. Thus our results are not compatible with, and do not support, either the missing dimer model or the dimer row-based model with substitutional C atoms.

From studies of surfaces with less than 0.07 ML of C it is found that the 2×1 reconstruction can be maintained with approximately 0.03 ML C. The formation of the $c(4\times 4)$ reconstruction is attributed to the increased tensile strain with increasing C coverage. We have not found any evidence that the C atoms are in the topmost layer and this is consistent with theoretical predictions that the C atoms at low concentrations prefer subsurface sites.^{44,52,53} It is likely that the $c(4\times 4)$ reconstruction is induced by the tensile strain of C atoms in a way that also would explain why the $c(4\times 4)$ reconstruction can be induced by B atoms as well.

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