

Formation of the 5×5 reconstruction on cleaved Si(111) surfaces studied by scanning tunneling microscopy

R. M. Feenstra and M. A. Lutz

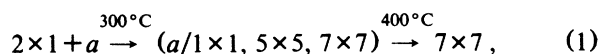
IBM Research Division, T. J. Watson Research Center, Yorktown Heights, New York 10598

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The transformation of cleaved Si(111) 2×1 surfaces into apparent 1×1 , 5×5 , and 7×7 structures has been studied with the scanning tunneling microscope. Two reaction paths are identified, one proceeding through a disordered adatom arrangement into the 7×7 structure, and the other proceeding directly from 2×1 into the 5×5 structure. Near a nucleation site (step or domain boundary), the first path is favored due to the abundance of adatoms on the surface, and far from a nucleation site the second path dominates.

It is well known that the lowest-energy structure for the Si(111) surface is a 7×7 reconstruction, having an atomic arrangement described by the dimer-adatom-stacking-fault (DAS) model.¹ Such a structure is obtained by preparing the surface at high temperatures ($> 600^\circ\text{C}$). Alternatively, if the Si(111) surface is formed by cleaving at room temperature, a 2×1 reconstruction is formed, with atomic arrangement given by the π -bonded chain model.² The transformation of this metastable 2×1 structure to the 7×7 structure, as a function of temperature, has been studied by a number of authors using mainly low-energy-electron diffraction (LEED).³⁻⁹ In the early work of Lander, Gobel, and Morrison, an intermediate 5×5 structure was observed.³ Subsequent workers did not observe this 5×5 structure, but in some cases they did observe an apparent 1×1 pattern in LEED which was correlated with the quality (i.e., step density) of the cleaved surface.⁴⁻⁶ Recently, the 5×5 structure has again been observed by two research groups.^{8,9} Theoretically, it is predicted that the 5×5 structure has a total energy only slightly above that of the 7×7 .¹⁰ Thus, it is of interest to consider the mechanism whereby the 2×1 surface transforms to 7×7 , and the reason for the appearance of the intermediate 5×5 phase.

This work is based on the use of the scanning tunneling microscope (STM). An obvious advantage of the STM over diffraction methods is its real-space atomic resolution, which allows a direct and specific identification of structures on the surface. In the present study this ability is important, since it allows us to focus in on individual nucleation sites on the surface (e.g., a step or a domain boundary). We find that there are two distinct reaction paths by which the surface transforms. In the first path, which can be viewed as a nucleation stage, the 2×1 surface becomes covered with adatoms (silicon atoms bonding on top of the surface), converting to a somewhat disordered arrangement containing simple adatom structures and small domains of 5×5 , 7×7 , and other DAS-related structures. This surface, which produces an apparent 1×1 LEED pattern,¹¹ subsequently orders forming the 7×7 structure. We express this reaction path as



where the symbol a refers to extra adatoms on the surface, and $a/1 \times 1$ denotes adatoms on a 1×1 surface. We have indicated in Eq. (1) an approximate onset temperature for each process, based on our own results and in agreement with Ref. 8. In the second path, which can be viewed as a growth stage, the transformation grows from small 5×5 domains, with the 2×1 surface transforming directly into a well-ordered 5×5 arrangement. At sufficiently high temperatures this 5×5 arrangement then transforms to the 7×7 structure. This second reaction path is written as



The occurrence of one or the other of these reaction paths at a particular surface location depends on the proximity to a nucleation site (step or domain boundary); near a nucleation site the first path is favored due to the existence of excess adatoms on the surface, and far from a nucleation site the second path dominates. Thus, a surface with few nucleation sites can transform into a well-ordered 5×5 arrangement, whereas a surface with many nucleation sites tends to form the 7×7 structure.

Measurements have been performed for annealing temperatures in the range 100 – 650°C , including an extensive set of observations as a function of time and temperature in the range 280 – 425°C . In this paper we discuss mainly the structures that are found, and kinetic results for transition rates will be presented elsewhere.¹² The studies were performed in ultrahigh vacuum, at a base pressure of less than 4×10^{-11} Torr. p -type silicon samples with resistivity of $0.1 \Omega \text{ cm}$ were cleaved in the $[2\bar{1}\bar{1}]$ direction. The results presented here are obtained from relatively flat portions of the cleaves, with a separation between steps of typically 500 nm . Annealing was performed by resistive heating of the sample. Temperatures were measured with a small Chromel-Alumel thermocouple (0.001 - or 0.002 -inch-diameter wire) pressed firmly against the cleavage face, with an estimated accuracy of $\pm 20^\circ\text{C}$. Relatively large STM images were acquired, with extensive surveying over the sample; typical images consist of 512×512 pixels extending over a total area of $250 \times 250 \text{ nm}^2$, and images as large as $2 \times 2 \mu\text{m}^2$ were used. All images presented here were acquired with a constant tunnel current of 1 nA , and sample-bias voltages in the range

1.5–2.5 V. Images are shown with a conventional grey scale, keyed to the surface height.

In Fig. 1 we present a typical STM image of a partially transformed Si(111) surface. Regions of differing structure are indicated in the figure. A 2×1 region is seen in the upper left-hand-side corner of the image, with π -bonded chains extending in the $[01\bar{1}]$ direction. The rest of the image consists of adatom-covered areas, with a height difference of $1.1 \pm 0.2 \text{ \AA}$ between corrugation maxima of the adatom covered and 2×1 areas. Within an uncertainty of a few tenths of an angstrom arising from possible electronic-structure effects, this observed difference is consistent with the model-height difference of about 1.3 \AA between DAS adatoms and 2×1 π -bonded chains.^{1,2} In Fig. 1 we see two well-ordered 5×5 areas, as indicated in the figure. The remainder of the image consists of disordered arrangements of adatoms. These disordered adatom arrangements form small structures of various symmetries, including simple adatom arrangements such as 2×2 and $c4 \times 2$, and partially ordered DAS structures. We do not discuss in detail here the well-known atomic arrangements which make up all of these adatom-related structures.¹ However, one important point is the difference between the simple adatom and the DAS structures: The former consists simply of adatoms arranged on a 1×1 surface, whereas the latter has, in addition to adatoms, stacking faults and dimers which delineate the unit cells.

One special structure is seen in Fig. 1, occurring at the boundary of the 5×5 and 2×1 regions, parallel to the 2×1 chains. Using the known atomic arrangements of these two structures (the DAS structure for the 5×5 region has been confirmed by STM spectroscopic measurements¹²), we can construct a model for this boundary. As illustrated in Fig. 2, the dimers which delineate the 5×5 unit cell can be conveniently bonded onto the 2×1 chains, forming an energetically favorable structure. The 5×5 and 2×1

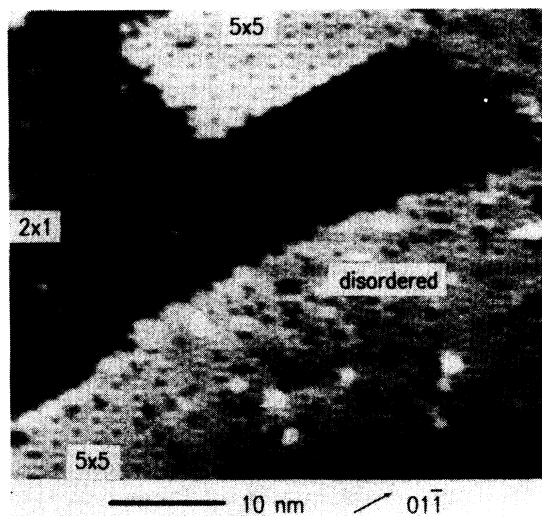


FIG. 1. STM image obtained from a Si(111) surface, annealed at 330°C for 900 s. The image gives a typical example of the structures formed during annealing, and regions of differing structure are indicated.

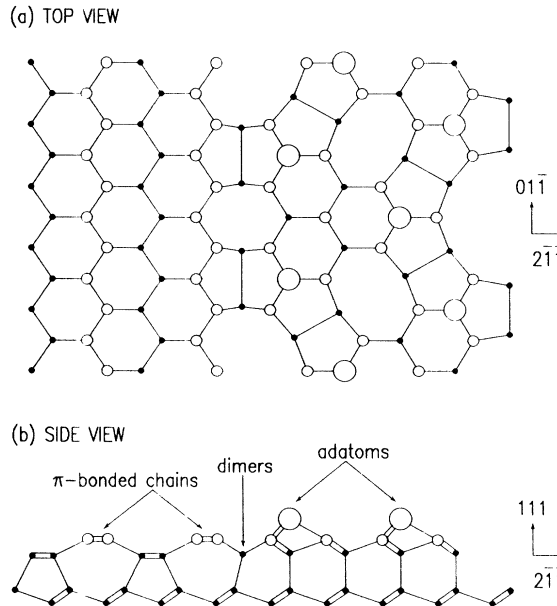


FIG. 2. Model of the structure formed at the boundary between the π -bonded chain 2×1 reconstruction (left-hand side) and the DAS 5×5 reconstruction (right-hand side).

structures have the same density of atoms as an ideal 1×1 bilayer, i.e., two atoms per 1×1 unit cell, whereas the 7×7 and simple adatom structures require 4.1% and 12.5% more atoms, respectively [a $(2m+1) \times (2m+1)$ DAS structure requires $9m^2 + 7m$ atoms for the adatoms plus top bilayer, compared with $2(2m+1)^2$ atoms for a 1×1 bilayer]. We argue below that this change in the atom density between the various structures provides an impor-

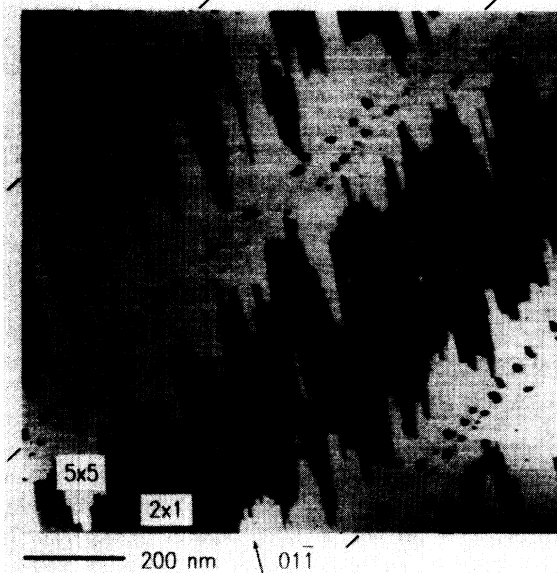


FIG. 3. Large-scale STM image obtained from a Si(111) sample, annealed at 425°C for 20 s. A series of domain boundaries in the original 2×1 structure are indicated by tick marks at the edge of the image, with the transformed regions growing out from those boundaries.

tant constraint in determining the structure formed on the surface.

To understand the growth of the 5×5 structure, it is necessary to image the surface over relatively large regions, as shown in Fig. 3. In that figure we observe a series of parallel lines, indicated by tick marks at the edge of the image. These lines are domain boundaries of the original 2×1 reconstruction. Domain boundaries in the 2×1 reconstruction can occur between different domain orientations, or between domains which are shifted $\frac{1}{2}$ unit cell in the $2 \times$ direction; the boundaries in Fig. 3 are of the latter type. The small black areas which appear along the domain boundaries are "holes" in the surface, one bilayer deep (0.314 nm). It is apparently energetically feasible to form such holes at the domain boundaries, and the holes act as a source of adatoms. Growing out from the domain boundaries is the transformed area of the surface, appearing white in Fig. 3. The remainder of the surface is 2×1 , appearing grey in Fig. 3. We see that, away from the domain boundaries, the transformed area grows in a well-ordered manner, forming "fingers" which extend along the $[01\bar{1}]$ chain direction of the 2×1 structure.

Expanded views of the type of transformed area seen in

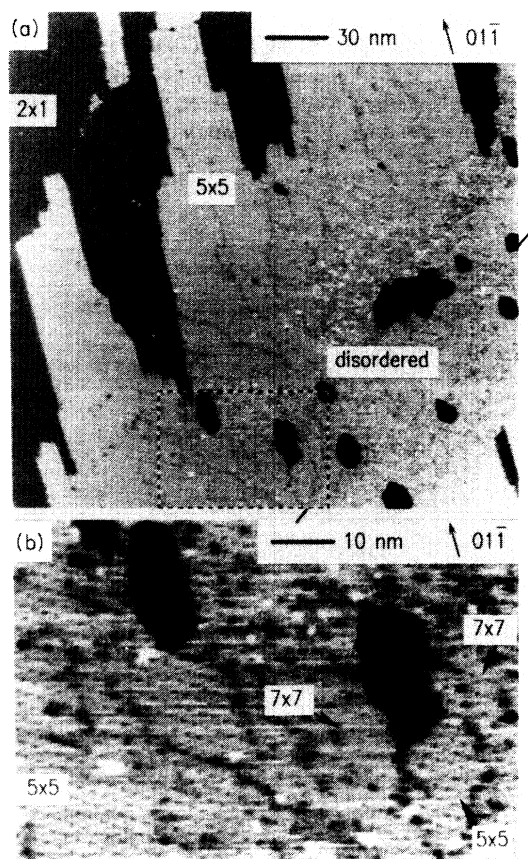


FIG. 4. Expanded views of the fingerlike transformed regions, obtained from the same sample displayed in Fig. 3. A domain boundary in the original 2×1 surface passes through the lower right-hand-side corner of image (a), as indicated by the tick marks. Image (b) shows an expanded view of the region marked by the dashed rectangle in (a).

Fig. 3 are displayed in Fig. 4. A domain boundary in the original 2×1 surface extends across the lower right-hand-side corner of Fig. 4(a), where several holes are visible. Growing out from the domain boundary is the transformed area. Far from the 2×1 domain boundary we see that the transformed fingerlike regions consist entirely of well-ordered 5×5 structure. The sides of the 5×5 fingers which are parallel to the 2×1 chains are well ordered, as depicted in Fig. 2, whereas the ends of the fingers are not so well ordered (cf. Fig. 1) and hence energetically less stable. Growth of the 5×5 regions proceeds from these less stable arrangements at the ends of the fingers. Near the original 2×1 domain boundary, considerable disorder is visible, with the surface structure consisting of a combination of simple adatom, 5×5 , and 7×7 arrangements, as seen in Fig. 4(b) and in Fig. 1. In terms of the reactions expressed in Eqs. (1) and (2), we interpret the transformation of the surface to proceed by Eq. (1) near the domain boundary where there is an excess of surface atoms, and then by Eq. (2) further away from the boundary where the number of atoms is a constant and equal to the ideal concentration of two atoms per 1×1 unit cell. With further annealing, the 5×5 regions grow over the remaining 2×1 surface. Annealing at higher temperatures ($\geq 600^\circ\text{C}$) finally transforms the entire surface into the 7×7 structure.

Additional evidence for the separation of the structural transformation into two reaction paths, as in Eqs. (1) and (2), can be obtained from the study of stepped surfaces. Qualitatively, we find that stepped regions of a sample form predominantly the 7×7 structure, whereas non-stepped regions form the 5×5 structure as seen above. This observation can be quantified by observing the fraction of 5×5 or 7×7 , as a function of separation from a step. The results of such a study, compiled from a set of 12 high-resolution images acquired side by side over the surface, is shown in Fig. 5. Figure 5(a) shows the surface-height-versus-lateral-scan distance, formed from a cross sectional cut across the middle of each image. Several monoatomic steps, and one larger step, are ob-

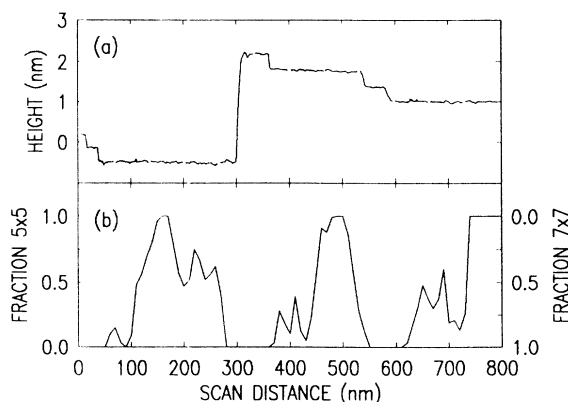


FIG. 5. Compilation of data from 12 high-resolution STM images acquired side by side over a Si(111) surface, annealed at 410°C for 100 s. (a) Surface height (the zero is arbitrary), taken from cross-sectional cuts through the middle of each image. (b) Fraction of the surface consisting of 5×5 or 7×7 reconstructions.

served. The total observed surface area is then divided into regions of 10-nm width, and the fractional area of 5×5 and 7×7 is measured in each region (the sum of these equals unity, neglecting the few percent of disordered area). The results are shown in Fig. 5(b). We see that the formation of 7×7 is highly correlated with the occurrence of a step, and ≥ 100 nm from the steps the surface is completely 5×5 . As above, we interpret this behavior as arising from an excess number of silicon atoms near a step edge transforming the surface according to Eq. (1), whereas further from a step edge the surface behaves according to Eq. (2).

In conclusion, we have studied the transformation of the 2×1 structure on cleaved Si(111), through intermediate disordered and 5×5 states, into the 7×7 structure. We find that there are two reaction paths, one proceeding through a disordered phase into 7×7 , and the other proceeding directly from 2×1 into 5×5 and then to 7×7 . The first case requires an increased density of surface

atoms over and above that of the ideal surface, and that reaction path is observed near nucleation centers which act as a supply of adatoms. In the second case, the number of atoms is conserved between the 2×1 and the 5×5 structures, and we observe what appears to be a direct transition from one to the other. Given that the nucleation of the transformed surface produces both 7×7 and 5×5 domains, then the remarkable fact is that the subsequent growth strongly prefers the 5×5 over the 7×7 . We attribute this preference simply to the surface-atom density, which is identical for the 2×1 and 5×5 structures. Other effects, such a strain, could suppress the growth of the 7×7 regions, but we find that possibility unlikely considering that the 7×7 structure is seen both as small domains and as the final equilibrium phase on the surface. Thus, we conclude that the number of atoms on the surface acts as a *kinetic barrier* in determining the surface structure: 7×7 is formed when a sufficient number of atoms are available, and 5×5 is formed otherwise.

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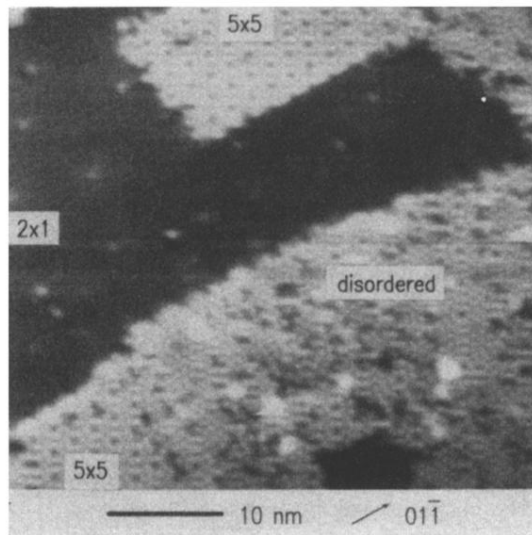


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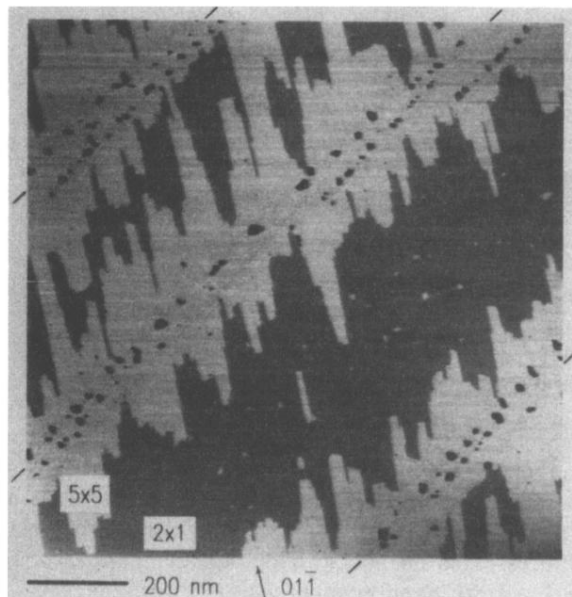


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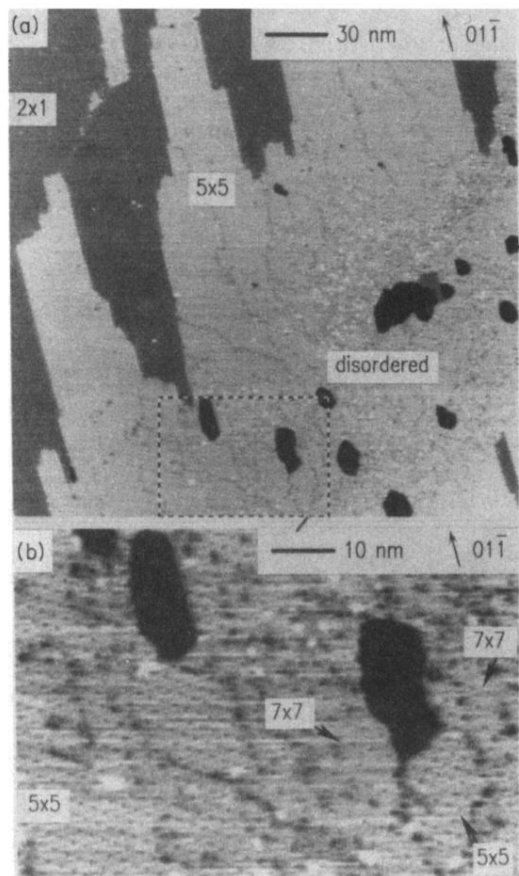


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