High Atom Density in the "1×1" Phase and Origin of the Metastable Reconstructions on Si(111)

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We report unambiguous atomic scale evidence demonstrating that the atom density in the "1×1" high temperature phase of Si(111) is ~6% higher than the 7×7. Such evidence is provided by scanning tunneling microscopy observation of excess adatom density and related island formation on surfaces prepared by a novel method which provides a low step density. The presence of the excess adatom density is also correlated to the observation of areas of metastable reconstructions, i.e., 9×9, 2×2, $c2\times4$, and $\sqrt{3}\times\sqrt{3}$, much larger than previously reported and for the first time, the existence of metastable 11×11 on Si(111).

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Si(111) is one of the most studied semiconductor surfaces. It has been established, both experimentally [1–5] and theoretically [6–8], that the surface has a 7×7 reconstruction of Takayanagi type [9] which disorders at around 870 °C to a high temperature phase commonly referred to as "1×1" [2,3]. However, there are still two important questions about this surface which remain unanswered. First, even though the existence of the high temperature 1×1 phase has been known for years, the exact nature of the phase is far from clear [10–13]. At the heart of this problem is the fundamental issue of whether the 1×1 is a denser or less dense phase relative to the 7×7. Recently, there have been suggestions that the 1×1 phase has higher atom density than the 7×7 [14]. However, there has been so far no direct atomic scale experimental confirmation. The second question is related to the formation of reconstructions other than 7×7 on Si(111). In 1986, using scanning tunneling microscopy (STM), a host of new reconstructions, i.e., 9×9, 5×5, 2×2, $c2\times4$, and $\sqrt{3}\times\sqrt{3}$ were reported on laser-annealed clean Si(111) [15]. Even though only a little more than one unit cell of each of the new reconstructions were reported, a puzzling question is what causes these metastable reconstructions to form. More recently it has been suggested that atomic density in the reconstruction is important in stabilizing the growth of the 5×5 structure on cleaved surfaces [16].

When the temperature of a Si(111) surface is slowly lowered from above the transition temperature, the 7×7 nucleates at the top of step edges and grows across terraces [17,18]. Recently, it has been suggested that the structural transition results in a net displacement of the step edges [14]. The implication is that the high temperature phase has higher density and that the excess atoms, released when the lower density 7×7 forms, diffuse to the step edge. If this explanation is correct, then it should be possible to trap the excess atoms on the terraces by a rapid quench. For this to succeed, the time it takes to quench to low temperature must be shorter than the time it takes for the adatoms to diffuse across the terraces to the steps. However, the ultrafast cooling rates achieved using laser annealing are not desirable, as such fast cooling prohibits the formation of the 7×7 [15]. The best way to trap the adatoms on the terraces, yet still allow the 7×7 to form, is to quench surfaces with *large terrace widths*, at a moderate speed. The surfaces quenched in such fashion should also allow us to reexamine the various metastable reconstructions that have been reported previously [15].

In this Letter, we show that the atom density of the "1×1" phase is indeed higher than that of the 7×7, by using a novel yet simple sample preparation method. The same sample preparation method allows us to obtain surfaces with non-7×7 reconstructions which we argue are stabilized by the presence of higher-than-normal atom density on the surface during the quench.

The experiments were performed in a UHV system with a base pressure of 2×10^{-11} Torr, equipped with a homemade scanning tunneling microscope. To achieve a fast cooling rate, we reduced the thermal mass of the heater by heating with a dc current through a Si wafer. The second benefit of dc heating is that the "electromigration" effect can be used to control the step structure on the surface [18–22]. Nominally flat Si(111), *n*-doped wafers, $15\times3\times0.4$ mm^3 in size, were installed in vacuum without chemical precleaning, degassed at 700 °C, then cleaned by flashing to 1250 °C for 1 min. The samples were then quickly cooled to 900 °C and quenched from this temperature to below 250 °C with a cooling rate of ~100 °C/s by cutting off the heating current. Using a dc current in the step-down direction during the flash resulted in formation of terraces of width beyond the maximum 6 μm field of view. These terraces contained trapped single-height steps at an average separation of about 2 μm. Such surfaces with wide terraces were used in this experiment. Temperature was measured using an infrared pyrometer.

Figure 1(a) shows a 4500 nm×4500 nm scan of a surface quenched from 900 °C. It is evident that in addition to the dark triangular regions, which close-up images show to contain a well-ordered 7×7, there are regions which appear to have overlying "clouds" on the surface.

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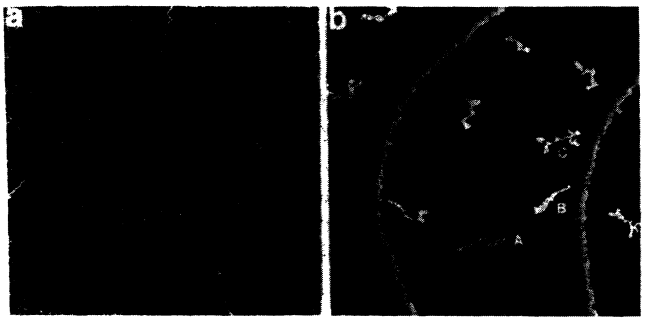

FIG. 1. STM images of area 4500 nm×4500 nm. (a) After quench from 900 °C showing dark 7×7 triangular domains and regions with clouds of adatoms that have a brighter gray scale. Depletion zones near step edges are also evident. Terrace on the left of a step is higher than that on the right. (b) After annealing at 600 °C following quench. The formation of islands on the surface provides clear evidence that the atom density of 1×1 is higher than that of the 7×7. The sample biases are all +2 V.

Images with greater resolution show a disordered atomic structure, approximately 1.5 Å in height above the 7×7 in the cloudy regions. Near the steps [Fig. 1(a)], there is a depletion zone without such cloudy structure, and atomically resolved images show that the reconstruction within the zone is entirely 7×7. This suggests that any adatoms initially found near the step edges diffused to the step and were incorporated into an ordered layer. The width of the depletion zone seen in Fig. 1(a) measures ~2200 Å. Thus the minimum width of a terrace needed to trap the Si adatoms, at this cooling rate, is ~4400 Å. On a uniformly stepped surface, this would correspond to a miscut angle less than 0.04°. To confirm that the cloudy regions present in Fig. 1(a) contain Si adatoms, surfaces such as the one shown in Fig. 1(a) were annealed at 600 °C for 2 min. The resulting surface exhibits formation of islands as shown in Fig. 1(b). These results provide direct evidence that the "1×1" phase has higher atom density than the 7×7 phase. From the 6% coverage of the islands [23], we estimate that the "1×1" density is about 10%–11% more than the bulk-terminated 1×1 atom density.

These results shed new light on the nature of the high temperature 1×1 phase. It has long been recognized that this phase is disordered [10–13], which is confirmed by recent observations showing extensive atomic motion [24,25]. A simple model for the disordered surface is a sea of adatoms on the bulk-terminated substrate with step edges as the source of adatoms. Our observed density difference of 0.10–0.11 double layer would correspond to an adatom density of 0.2–0.22 monolayer. This is comparable to the maximum entropy configuration of a disordered lattice gas with nearest-neighbor repulsions on a triangular lattice [26].

The excess atom density found on large terraces after the quench also appears to be related to the formation of nonequilibrium reconstructions. Atomically resolved STM images show that island *A* in Fig. 1(b) has a 2×1 reconstruction, island *B* represents a mixture of 5×5 and 7×7, while island *C* consists entirely of 7×7. Detailed analysis of these island structures will be published elsewhere [22]. Here, we note only that both the 2×1 and the 5×5 have lower atom density than the 7×7 and are also observed during growth [22,27,28] (see Table I). Atomically resolved images (not shown) of "cloudy" areas in Fig. 1(a) reveal that underneath the adatom cloud the surface layer consists of 9×9, 2×2, and *c*2×4 reconstructions [22]. However, the disorder makes the imaging of the surface layer very difficult. Surface structures in such regions can be better examined on the annealed surfaces on which the density of disordered adatoms in the cloud is much less due to the formation of islands. Figure 2(a) shows a scan taken from the same surface as in Fig. 1(b). Each large dark triangular-shaped area (~3000 Å in size) represents a single domain of 7×7 formed when the surface was quenched from high temperature. In the cloudy regions, there are alternating dark and bright small triangles (~300 Å in size). These features must have developed when the sam-

TABLE I. The atomic density of the different reconstructions of Si(111) is compared with that of the bulk-terminated (1×1) structure.

Surface reconstruction	Density (atoms/unit cell)	% difference relative to 1×1	References
1×1	2	0	
2×1	2	0	[16], this work
5×5	2	0	[15,16,27], this work
7×7	2.08	4.1	[4,5], this work
9×9	2.12	6.2	[15,34], this work
11×11	2.15	7.4	This work
13×13	2.17	8.3	This work
"1×1"	2.20–2.22 (measured)	10–11 (measured)	This work
2×2, *c*2×4	2.25	12.5	[15], this work
$\sqrt{3}\times\sqrt{3}$	2.33	16.7	[15], this work

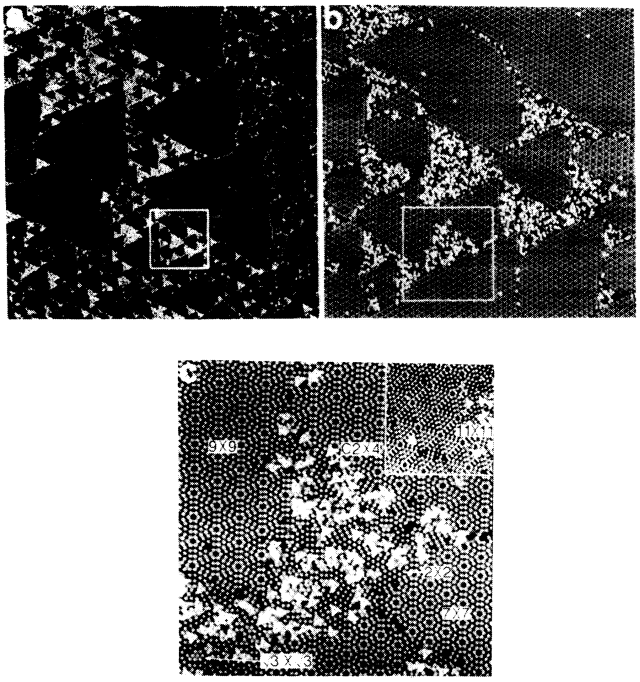

FIG. 2. (a) STM smaller area scan (750 nm×750 nm) of the surface shown in Fig. 1(b). In addition to large 7×7 triangular domains, there are many small triangular regions in the high atom density regions. (b) A close view (150 nm×150 nm) of the area indicated in (a) by the square box. Three different types of regions are evident, i.e., 7×7, 9×9, and the regions appear to have a large number of adatoms on the surface. (c) Atomically resolved image of an area, 45 nm×45 nm, in (b). Atomic features of 7×7, 9×9, 2×2, $c2\times4$, and $\sqrt{3}\times\sqrt{3}$ can be seen clearly. The relative coordinates of the different reconstructions in the image demonstrate that the adatoms in 2×2, $c2\times4$, and $\sqrt{3}\times\sqrt{3}$ are at T_4 sites. Inset in (c) demonstrating, for first time, the existence of 11×11 on Si(111). The sample bias is −2 V for (a) and (b) and +2 V for (c).

ple was reannealed at 600 °C, as on the surfaces without reannealing such small triangles are absent. A close-up image of the area consisting of small triangles is shown in Fig. 2(b). The 7×7 domains appear as ordered areas with small diamond-shaped units. The unit cell consists of a dark and a bright triangle under the imaging condition of −2 V sample bias, a result of a stacking fault in half of the cell [4,5]. In addition to the 7×7, several 9×9 domains, as large as 71 unit cells, are also present on the surface. The third type of region present (bright triangles) appears to consist of randomly distributed adatoms. A change of sample bias voltage from −2 V to +2 V and larger magnification as shown in Fig. 2(c) show that the structure of these regions consists of 2×2 and $c2\times4$ in the surface layer with some adatoms on top of the surface. Apparently, the image with negative bias condition is more sensitive to the adatoms on the surface while positive bias makes the structures in the surface layer more pronounced. A more careful inspection of Fig. 2(c) reveals that there are also small regions of $\sqrt{3}\times\sqrt{3}$ as indicated at the lower left part of the image. With the aid of a negative biased image of the same area (not shown), the image in Fig. 2(c) also allows us to identify that the adatoms in 2×2, $c2\times4$, and $\sqrt{3}\times\sqrt{3}$ occupy T_4 sites, as expected from theoretical calculations [29,30].

The inset in Fig. 2(c) shows six units of the previously unreported 11×11 reconstruction that was found from a region similar to that of Figs. 2(a)–2(c). On a different part of the same surface we have also observed 13×13 structure. However, only a little more than half a unit cell was found.

Table I lists the atom densities for all the reconstructions that have been observed on Si(111). A striking correlation is that the observed metastable (non-7×7) reconstructions in the surface layer, namely, 9×9, 11×11, 2×2, $c2\times4$, and $\sqrt{3}\times\sqrt{3}$, all have higher density than the 7×7. (Reconstructions that have lower atom densities than 7×7, such as 5×5 and 2×1, were never found in the surface layer, only as islands on top of the surface layer.) Given these observations, it is reasonable to deduce that the metastable structures in the surface layer form to accommodate high densities of adatoms trapped during the quench. This is similar to Feenstra and Lutz's previous conclusion that the low density 5×5 structure forms from the 2×1 due to a low density of atoms present on the surface [16,31]. The process in which the metastable reconstructions are formed can then be understood as follows: During the phase transition, the 7×7 and 1×1 structures are known to coexist [17]. Thus, when 7×7 is first formed on the terrace, it can simply push the excess atoms aside to regions that are still in the 1×1 phase, creating an abnormally high atom density in the regions. During the quench, such regions order locally into a surface layer with high density reconstructions and an adatom layer on top which appears as a layer of cloud in the STM images. When the surface is reannealed at moderate temperature, there is sufficient atomic mobility to allow the system to lower its energy by creating more ordered structure, subject to the constraint of the high atom density in the region imposed by the limited diffusion length. To accommodate the atoms, 9×9 becomes favorable and excess atoms (see Table I) are further pushed into the remaining cloudy region, creating an even higher atom density in this region. As a result, reconstructions with even higher atom densities such as 2×2, $c2\times4$, and $\sqrt{3}\times\sqrt{3}$ are formed in these regions [32]. Experimentally, additional adatoms were only observed on top of the regions that have 2×2, $c2\times4$, and $\sqrt{3}\times\sqrt{3}$ reconstructions following annealing. This mechanism is also consistent with previous observation of some of these reconstructions during growth where the high atom density was achieved through supersaturation [27,33,34].

To understand how the formation of metastable structures is driven by an excess atomic density, we consider the formation of the 9×9 in an area A on the surface

having an atom density so that it can be completely filled with 9×9. An alternative configuration for the surface with the same density of atoms is to fill the area with 7×7, leaving a triangular 7×7 island on top, as the 7×7 atom density is smaller than that of the 9×9. For the 9×9 to be more favorable thermodynamically, we need to have $AE_9 < AE_7 + LE_s$, where $E9$ and $E7$ are the surface energy per 1×1 unit cell for the 9×9 and 7×7. E_s is the step energy per unit cell length for 7×7 island edges and L is the length of the island edge. The length of the island edge is approximately $L = \alpha\sqrt{A}$, where $\alpha = [36(D_9 - D_7)/\sqrt{3}D_1]^{1/2} = 0.659$, and where D_9, D_7, and D_1 refer to the atom density per 1×1 unit cell for 9×9, 7×7, and 1×1. Thus $E_9 - E_7 < \alpha E_s/\sqrt{A}$. It becomes clear that when the atom density is high in a given area and the area is small, it is possible to have the formation of 9×9 preferred over the 7×7, simply because it is costly to create a step (island edge). This simple equation not only explains the formation of 9×9 in our experiment, it also provides an insight into the fact that the size of 9×9 is always much smaller than that of the large 7×7 regions. If we use the estimate of $E_s = 0.465$ eV/unit cell length [35] and let $A = 81N$, where N is the number of 9×9 unit cells in area A, we get $E_9 - E_7 < 0.034/\sqrt{N}$ eV. Experimentally, as many as 71 units of 9×9 have been found in a single domain. Using this number, we estimate that $E_9 - E_7 < (0.004$ eV$)/(1\times1$ cell). This value is of the same order of magnitude as the calculated energy differences between other Takayanaki structures [$\sim$(10 meV)/(1×1 cell)] [7,8]. The same idea can easily be used to argue for the formation of other reconstructions we have observed in the surface layer. Since the observed sizes for 11×11, 2×2, c2×4, and $\sqrt{3}\times\sqrt{3}$ are all much smaller than that of the 9×9, we can conclude that the surface energies for these reconstructions should be higher than that of 9×9.

In conclusion, we have provided indisputable experimental evidence demonstrating that the atom density in the high temperature 1×1 phase for Si(111) is about 6% higher than the 7×7, and this is about 10%–11% higher than the bulk-terminated 1×1. Our sample preparation method enabled us to generate areas of 9×9, c2×4, and $\sqrt{3}\times\sqrt{3}$ larger than have been seen before by removing the steps which otherwise act as sinks for excess atom density. Through examination of the relative locations of these reconstructions, we were able to conclude from the experimental data that these non-7×7 reconstructions are stabilized by the artificially created abnormally high atom density on the surface. Simple energetic arguments are shown to be consistent with such a conclusion.

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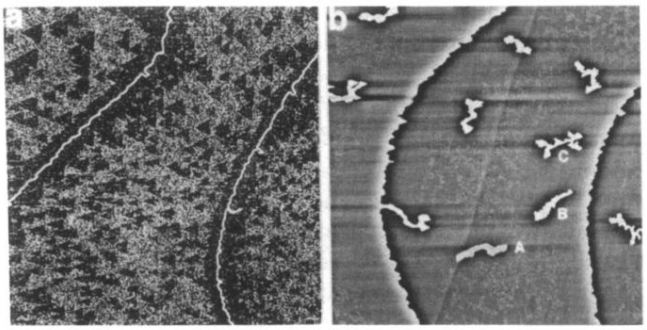

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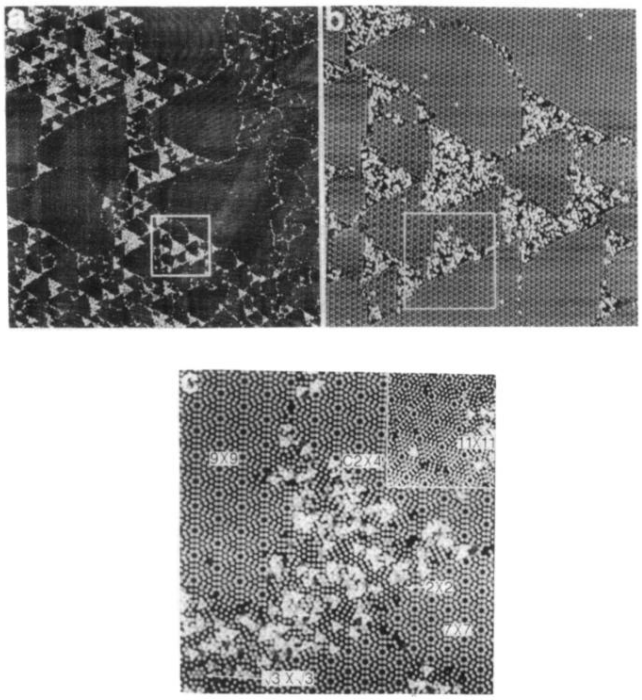

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