

Reexamination of the Si(111)3×1-Na reconstruction on the basis of Si atom density and unit cluster determination

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Using scanning tunneling microscopy, features of the Si(111)3×1-Na reconstruction have been found, namely, Si atom density of 4/3 ML and a unit cluster that shows up in STM images as a group of four protrusions forming a ($\sqrt{3}a \times 1a$) rectangle. These findings led to the reexamination of the atomic arrangement of a Si(111)3×1 phase. As a result, a double- π -bonded chain model is proposed. The model incorporates two Si π -bonded chains in faulted-unfaulted orientations connected through Na atoms. [S0163-1829(98)01631-2]

In the last decade a 3×1 reconstruction induced by Ag and alkali metals on the Si(111) surface has been an object of extensive investigations by many groups by an abundance of surface sensitive techniques, e.g., reflection high-energy electron diffraction,^{1,2} low-energy electron diffraction (LEED),³ Auger electron spectroscopy,³⁻⁶ scanning tunneling microscopy (STM),⁷⁻¹³ ion-scattering spectroscopy,^{14,15} x-ray diffraction,¹⁶ photoemission spectroscopy (PES),¹⁷⁻²⁰ and theoretical calculations.²¹⁻²³ As a result, many features of a Si(111)3×1-metal (Me) structure have been well established. The principal findings are as follows: (1) Si(111)3×1 reconstruction is plausibly very similar for all metals and is predominantly a Si(111) substrate reconstruction.³ (2) The absolute metal coverage for this phase is 1/3 monolayer [1 monolayer (ML)= $7.8 \times 10^{14} \text{cm}^{-2}$].^{5,14} (3) The Si(111)3×1-Me surface is semiconducting.^{11,17-19} (4) π -bonded chains formed by top Si atoms are present on this surface.¹⁷⁻¹⁹ However, the atomic structure of a Si(111)3×1 surface still remains controversial. Several structural models have been proposed^{3,6,8,10,11,17,19,21} (see Table I). Two of them, namely, the Seiwatz model^{6,19} containing fivefold Si rings separated by empty channels (denoted simply as “... 500500...”) and the extended Pandey model^{17,21} containing alternating sevenfold, sixfold, and fivefold Si rings (denoted “... 765765...”) are considered to be the most plausible candidates now.^{18,22-24} The common feature of these models is the presence of a π -bonded chain represented by sevenfold or fivefold Si rings; the most basic dif-

ference is in the value of top Si atom density, which equals 2 ML (or 0 ML) for the extended Pandey model and 2/3 ML for the Seiwatz model.

Accurate determination of Si atom density in the Si(111)3×1-Na phase conducted in the present work from Si mass transport balance yields the value of 4/3 ML. As one can see in Table I, *no* known model fits this value. Another essential result of the present study is an elucidation of the Si(111)3×1-Na unit cluster, which shows up in STM images as a group of four protrusions forming a ($\sqrt{3}a \times 1a$) rectangle, where $1a=3.84\text{\AA}$, the surface period of Si(111)1×1. These findings provide insight into the structure of a Si(111)3×1 phase. As a result, a double- π -bonded chain model is proposed, which is in agreement with our results and known literature data.

TABLE I. Me coverage and Si density for the proposed models of Si(111)3×1 reconstruction.

Ring structure	Me coverage	Si density	Ref.
... 500500 ...	2/3 ML	2/3 ML	8
... 500500 ...	1/3 ML	2/3 ML	6,19
... 550550 ...	1/3 ML	1 ML	10
... 660660 ...	~0.01 ML	5/3 ML	3
... 750750 ...	1/3 ML	5/3 ML	17
... 666666 ...	2/3 ML	2 ML	11
... 765765 ...	1/3 ML	2 ML	17,21

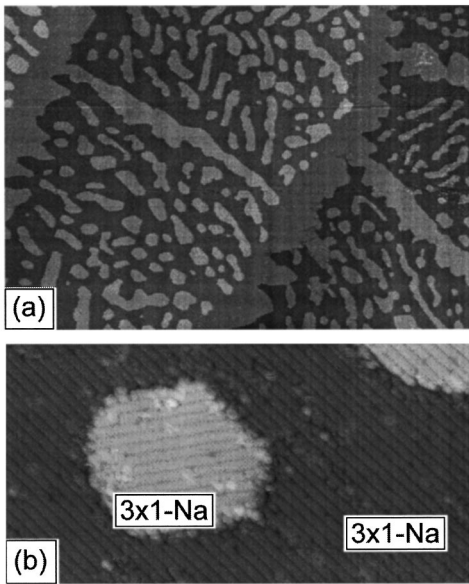


FIG. 1. (a) Typical large-scale ($7000 \times 5000 \text{ \AA}^2$) filled state ($V_t = +2.5 \text{ V}$) STM image of a Si(111) 3×1 -Na surface. (b) The same surface at a greater magnification ($500 \times 250 \text{ \AA}^2$). Both islands and terraces have a 3×1 -Na reconstruction.

Experiments were carried out in the UHV chamber with a base pressure of $1.1 \times 10^{-8} \text{ Pa}$ equipped with STM (“Omicron”) and LEED systems. The substrates used were P-doped Si(111) wafers with high resistivity. Atomically clean Si(111) surfaces were prepared *in situ* by heating to $1250 \text{ }^\circ\text{C}$ after the samples were first outgassed at $600 \text{ }^\circ\text{C}$ for several hours. The Si(111) 3×1 -Na surface was produced by Na deposition from chromate dispensers (SAES Getters Inc.) onto the Si(111) 7×7 surface held at $300\text{--}400 \text{ }^\circ\text{C}$. For STM observations, electrochemically etched tungsten tips cleaned by *in situ* heating were employed.

For elucidation of a surface phase structure, the knowledge of the exact value of top Si atom density is believed to be of the same importance as the determination of the absolute coverage of adsorbate. If Si atom density in the Me/Si(111) surface phase differs from that in the Si(111) 7×7 surface, which contains 102 Si atoms per 7×7 unit cell, i.e., about 2.08 ML, then the formation of this phase is accompanied by a surface Si mass transport. In recent STM studies,^{12,13} indication of such a behavior was found for the $(7 \times 7) \leftrightarrow (3 \times 1)$ -Na transition. In the present work, we have also observed that an initially flat Si(111) 7×7 terrace transforms upon Na adsorption into the two-level system of monoatomic 3×1 -Na islands (upper level) on the 3×1 -Na (lower level) terrace (see Fig. 1). In Fig. 1, the long stripes of the 3×1 -Na phase connected to the upper terrace are associated with the 3×1 -Na growth along the antiphase domain boundaries of the initial Si(111) 7×7 surface, while the 3×1 -Na islands are the result of a random nucleation.

Measurement of the fraction of surface area covered by 3×1 -Na islands (S) allows us to determine Si atom density (Θ_{Si}) in the Si(111) 3×1 -Na surface phase. The surface between islands (lower level), which occupies an area fraction of $(1-S)$ is a source of Si atoms for the 3×1 -Na island (upper level) and it supplies $(1-S)(2.08 - \Theta_{\text{Si}})$ [ML] of Si. This Si amount is accumulated in 3×1 -Na islands and, thus,

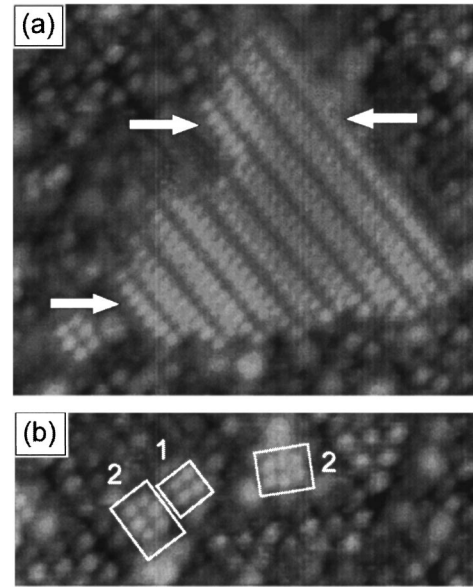


FIG. 2. (a) $165 \times 140 \text{ \AA}^2$ STM image ($V_t = +1.8 \text{ V}$) of a 3×1 -Na island surrounded by a $\delta\text{-}7 \times 7$ -Na phase. The edge rows of the island in which half of protrusions are missing are indicated by arrows. A nucleus of a 3×1 -Na phase is seen in the lower left corner. (b) $165 \times 65 \text{ \AA}^2$ STM image showing three 3×1 -Na phase nuclei (in frames), one of which contains a single unit cluster (labeled 1) and two are built of 2 unit clusters (labeled 2).

equals $S(\Theta_{\text{Si}} - 0.08)f$ [ML]. From a Si mass balance, one can easily obtain that

$$\Theta_{\text{Si}} = 2.08 - 2S.$$

In the present experiment, to maximize the surface area suitable for island area evaluation and to minimize the influence of the steps on Si mass transport, Si samples with nominal zero miscut were used. Actually, the typical terrace width was in the range from 3000 to 7000 \AA , which fits perfectly the above requirements. The measurements were conducted for a set of Si(111) 3×1 -Na samples prepared at various growth conditions. In all measurements, the fraction of surface area occupied by islands appears to be 0.35 ± 0.02 . Si atom density (Θ_{Si}) in Si(111) 3×1 -Na is consequently $1.38 \pm 0.04 \text{ ML}$.

In principle, Si atom density in the ideal Si(111) 3×1 -Na phase can be $1/3, 2/3, 1, 4/3, 5/3$ and 2 ML i.e., from 1 to 6 Si atoms per 3×1 unit cell. The experimentally obtained value shows definitely that the Si(111) 3×1 -Na phase has a Si atom density of $4/3 \text{ ML}$. One can see in Table I that the structural models proposed for Si(111) 3×1 reconstructions incorporate different Si atom densities, namely, $2/3, 1, 5/3,$ and 2 ML . However, no model consistent with the present result, i.e., having Si atom density of $4/3 \text{ ML}$ has emerged as of yet.²⁵

Close inspection of high-resolution STM images reveals a feature of the Si(111) 3×1 structure that has been previously overlooked. Let us consider the STM image in Fig. 2(a). It was acquired at the early stage of Si(111) 3×1 -Na phase formation and shows a 3×1 -Na island surrounded by the so-called $\delta\text{-}7 \times 7$ -Na phase.²⁶ In agreement with the reported STM data, Si(111) 3×1 -Na shows up in filled states

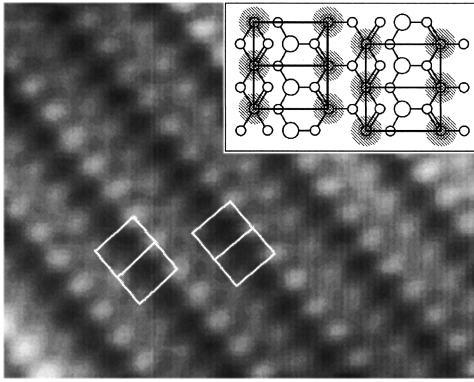


FIG. 3. High-resolution ($70 \times 55 \text{ \AA}^2$) filled state ($V_t = +1.8 \text{ V}$) STM image of a Si(111) 3×1 -Na surface phase. The arrangement of unit clusters in a 3×1 structure is shown by rectangles superimposed with STM image and illustrated schematically in the inset.

as an array of zigzag rows of protrusions parallel to the $[1\bar{1}0]$ direction, which are separated by dark channels. It has been assumed conventionally that this zigzag chain is a main structural element of Si(111) 3×1 structure and is associated with a π -bonded chain of surface Si atoms. However, one can see that in the edge rows of the 3×1 -Na island [marked by arrows in Fig. 2(a)] half of protrusions forming a regular zigzag chain is missing in obvious contradiction with the conventional interpretation of 3×1 STM images. We believe that this observation implies that the main structural element of Si(111) 3×1 reconstruction is not a zigzag chain but rather a unit cluster that shows up as a group of 4 protrusions forming ($\sqrt{3}a \times 1a$) rectangle. Thus, the structural arrangement of a Si(111) 3×1 -Na surface is essentially a stacking of rectangular unit clusters into rows with a shift between adjacent rows by half of period ($a/2$) along $[1\bar{1}0]$ direction (see Fig. 3).

Further inspection of STM images proves that the unit cluster is more than simply a result of an arbitrary choice of the structure unit cell. We have found that the nuclei of a Si(111) 3×1 -Na phase are always built of one or two of these unit clusters. For example, a 3×1 -Na nucleus containing 2 unit clusters is clearly seen near the Si(111) 3×1 -Na island in the low left corner of Fig. 2(a). Two nuclei built of two unit clusters and one nucleus containing a single unit cluster are shown in Fig. 2(b). The similar nuclei were found to be distributed randomly all over the surface with a number density of $\sim 10^{12} \text{ cm}^{-2}$. So, the unit cluster can be considered as a kind of ‘‘quantum’’ of Si(111) 3×1 -Na surface phase.

The obtained results, namely, determination of $4/3 \text{ ML}$ Si density and observation of 3×1 -Na phase unit cluster demand reexamination of the Si(111) 3×1 -Na surface structure, as all previously reported models are in obvious contradiction with these findings. We propose a model of the Si(111) 3×1 -Na structure shown in Fig. 4. This model can be defined as double- π -bonded chain ($D\pi C$) model, since it incorporates two π -bonded chains ($4/3 \text{ ML}$ Si) connected through Na atoms ($1/3 \text{ ML}$). The occurrence of the π -bonded chains in alternating faulted-unfaulted orientations results in the required rectangular appearance of the 3×1 -Na phase unit cluster as shown in Fig. 4. Moreover, as

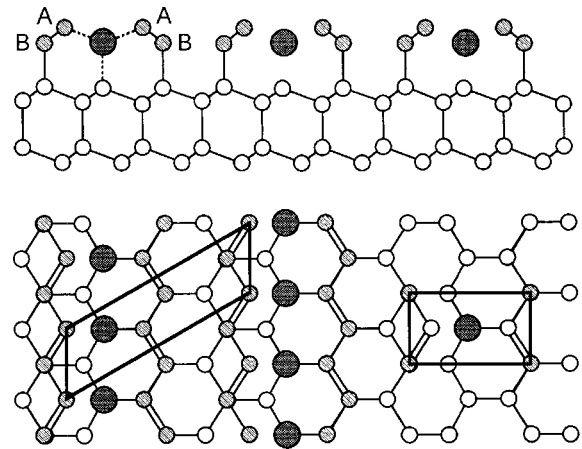


FIG. 4. Structural model of Si(111) 3×1 -Na reconstruction (open circles are Si atoms of the bulk, hatched circles are Si atoms of the reconstructed layer, dark circles are Na atoms) 3×1 unit cell and unit cluster are outlined. Two types of surface Si atoms are labeled *A* and *B*.

one can see in Fig. 3 two rows of protrusions forming zigzag chain have slightly different apparent heights. Since according to the model they belong to the faulted and unfaulted Si π -bonded chains, their apparent height difference is much like that of Si adatoms in the faulted and unfaulted unit-cell halves in filled state STM images of the Si(111) 7×7 surface.

PES data of Ref.17 indicate that in 3×1 -Na phase there are two types of surface Si atoms with different electronic character and the number of Si surface atoms of each type is comparable. In the present structural model, these two types of Si atoms are represented by surface Si atoms forming π -bonded chain. Half of them are bonded to Na atoms (labeled *A* in Fig. 4) and the others are bonded to Si atoms of a bulklike Si(111) plane (labeled *B* in Fig. 4).

‘‘On-top’’ location of protrusions in the Si(111) 3×1 -Na phase [determined from STM images with coexisted Si(111) 7×7 and Si(111) 3×1 -Na regions] and relative spacing between protrusions strongly indicate that the protrusions in 3×1 -Na STM images correspond to the type-*B* Si atoms of the $D\pi C$ model (see inset in Fig. 3). The fact that type-*A* Si atoms and Na atoms are not seen in the filled state STM images is believed to be associated with the peculiarities of the electronic structure of Na/Si(111) surface. For instance, it has been reported that individual alkali atom on the Si(111) 7×7 surface shows up as depression in filled state STM images.¹⁴

The data of the present study do not provide a sufficient basis for the determination of Na-atom location. However, the significant difference in the work function reported for Si(111) δ - 7×7 -Na and Si(111) 3×1 -Na surface phases in Ref. 17 implies that the location of Na atoms in the 3×1 -Na phase should differ from the adatom position known for δ - 7×7 -Na phase. So, Na atoms as imbedded in the top Si double layer (see Fig. 4) can be considered as a plausible suggestion.

In conclusion, we have reexamined the atomic structure of the Si(111) 3×1 -Na surface as our experimental results ($4/3 \text{ ML}$ Si atom density in the 3×1 -Na phase and existence of the rectangular-shaped unit cluster of 3×1 -Na phase) ap-

peared to be in conflict with the previously reported structural models. We have proposed a double- π -bonded chain model that incorporates two π -bonded chains in faulted-unfaulted orientations connected through Na atoms. The $D\pi C$ model even in a present draft form accounts successfully for most if not all available data. However, the further refinement of the model is needed. The determination of atom exact positions and bonding geometries is a complicated problem and it requires additional experimental and theoretical efforts. We believe that the proposed model is valid for the other $\text{Si}(111)3\times 1\text{-Me}$ reconstructions and is useful for understanding of their structure peculiarities. For instance, it can be expected that in the case of Me atoms with a large atomic radius the size of a unit cluster should be increased along $[11\bar{2}]$ direction. As a result, the interaction

between the outer Si atoms of the adjacent rows (labeled B in Fig. 4) should take place resulting in a long-range reordering. This is indeed the case for Cs and Ag adsorbates, which are known to induce $\text{Si}(111)6\times 1$ reconstructions.

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²⁵From PES data, Okuda *et al.* (Ref. 17) estimated the number of Si atoms to be about 4 in the surface unit cell ($\Theta_{\text{Si}}=4/3$ ML) in agreement with the result of the present work. However, the models considered in Ref. 17 have 2/3, 5/3, and 2 ML Si atom density.

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