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Scanning tunneling microscopy of the 7×7 to 3×1 transformation induced on the Si(111) surface by Na adsorption

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Using scanning tunneling microscopy (STM), the process of the Si(111)3×1-Na phase formation induced by Na adsorption on the Si(111)7×7 samples with a terrace width of 3000–6000 Å has been studied. The STM monitoring of the successive stages of the 7×7 to 3×1 transformation enables us to elucidate its main regularities. The redistribution of Si atoms in a top Si(111) layer has been found to play a critical role in the Si(111)3×1-Na growth mode. As a result of the Si redistribution, initially flat Si(111)7×7 terrace converts into the two-level system of the 3×1-Na islands on the 3×1-Na terrace. From the quantitative consideration of the Si mass transport balance, the top Si atom density of the Si(111)3×1-Na phase has been determined to be 4/3 monolayer. [S0163-1829(98)02535-1]

I. INTRODUCTION

Formation of the Si(111)3×1 reconstruction as a result of alkali-metal adsorption on a Si(111) surface has been the subject of numerous investigations.[1–17] The interest to this system is twofold. On the one hand, the alkali-metal/Si submonolayers exhibit the extraordinary chemical and electronic properties[4,5] that show promise for the device applications. On the other hand, alkali metals have a simple electronic structure and do not form silicides and, thus, are considered to be a handy prototype for the study of atom adsorption on solid surfaces in general. However, in spite of the seeming simplicity, the geometric and electronic structure of the Si(111)3×1 surface is still controversial.[15,16] Understanding of the mechanism of the Si(111)3×1 phase formation is also far from complete. Considerable Si mass transport detected at the 7×7 to 3×1 transformation[11,13] complicates essentially the issue.

In this paper, we report on the results of the scanning tunneling microscopy (STM) study of the 7×7 to 3×1 transformation induced by Na on a Si(111) surface. The samples with terraces of 3000–6000 Å width have been used. From the step-by-step observation of the successive stages of the transformation, the main regularities of the Si(111)3×1-Na phase formation have been determined. It has been found that the process is controlled primarily by the redistribution of Si atoms in the Si(111) surface layer. From the data obtained, the top Si atom density of 4/3 monolayer (1 ML$=7.8\times10^{14}$ cm^{-2}) has been determined for the Si(111)3×1-Na phase and a complete Si mass transport balance has been established for the 7×7 to 3×1 transformation.

II. EXPERIMENT

Experiments were carried out in the ultrahigh vacuum chamber with a base pressure of 1.1×10^{-8} Pa equipped with STM (‘‘Omicron’’) and low-energy electron diffraction (LEED) systems. The substrates used were P-doped Si(111) wafers with high resistivity and nominally zero miscut. Atomically clean Si(111) surfaces were prepared *in situ* by heating to 1250 °C after the samples were first outgassed at 600 °C for several hours. After this treatment, a sharp 7×7 LEED pattern was observed and STM images corresponded to a well-ordered Si(111)7×7 surface. Si(111)3×1-Na surface was produced by Na deposition from the

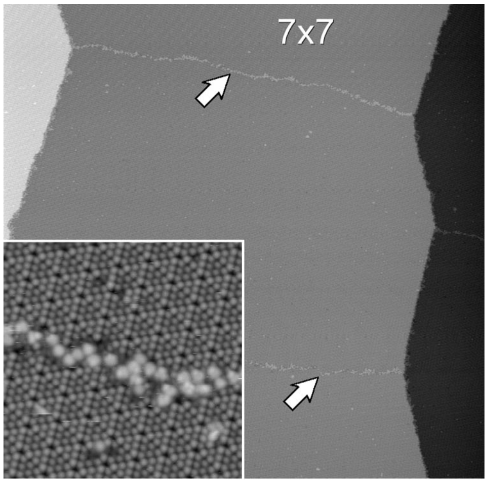

FIG. 1. 4000×4000 Å^2 filled state ($V_t=+2.5$ V) STM image of a Si(111)7×7 sample surface prior to Na deposition. The arrow indicates the 7×7 antiphase domain boundary that is shown in the inset at a greater magnification (scale 250×250 Å^2).

thoroughly out-gassed chromate dispensers (SAES Getters, Inc.) onto the Si(111)7×7 sample heated by dc current to a desired temperature from the range of 300–400 °C. For STM observations, electrochemically etched tungsten tips cleaned by *in situ* heating were employed.

III. RESULTS AND DISCUSSION

A. General features of the 7×7 to 3×1 transformation

STM image of the as-cleaned Si(111)7×7 surface prior to Na deposition is shown in Fig. 1. The sample surface displays large terraces of a typical width in the range from 3000 to 6000 Å separated by monoatomic steps. (In all images shown, the down-step direction is from left to right). The surface structure is the well-ordered Si(111)7×7 reconstruction. The feature of the surface that appears to be essential for the 7×7 to 3×1 transformation is the presence of the 7×7 antiphase domain boundaries (marked by the arrow in Fig. 1 and shown also at a greater magnification in the inset in this figure). These boundaries run across the terrace and are separated by a typical distance of 1000–3000 Å.

Figure 2 presents a set of the large-scale (7000×7000 Å^2) STM images of the Si(111) sample surface acquired successively at the various stages of 7×7 to 3×1 transformation. The very early stage of a Na deposition is illustrated by Fig. 2(a). One can see that 7×7 to 3×1 transformation starts from the step edges, while no 3×1-Na domains appear on the remaining area of the 7×7 terraces. The only exception is 7×7 antiphase domain boundaries where chains of the triangular-shaped 3×1-Na islands form. The high-resolution STM observations reveal that the remaining Si(111)7×7 has undergone a transformation also: it converts upon Na adsorption to a so-called $\delta7\times7$-Na structure.[1,18]

With a further Na deposition [Figs. 2(b) and 2(c)], the 7×7 to 3×1 transformation proceeds via the propagation of the $7\times7/3\times1$ boundary across the terrace in the up-step direction. In this process, a flat 7×7 surface "splits" into the two-level system of the one-atomic layer height islands (upper level) residing on the terrace (lower level). As illustrated by Fig. 3, the islands and the terrace surface both display the Si(111)3×1-Na reconstruction.

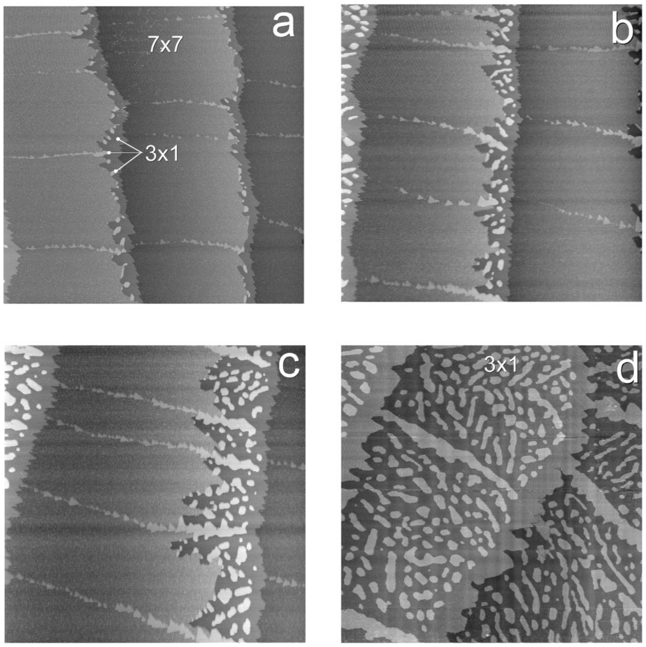

FIG. 2. 7000×7000 Å^2 filled state ($V_t=+2.5$ V) STM images showing a Si(111) surface at different stages of the 7×7 to 3×1 transformation induced by Na adsorption. Na deposition time is (a) 3 s, (b) 15 s, (c) 30 s and (d) 180 s.

The 7×7 to 3×1 transformation is completed when no 7×7 regions are left at the sample surface. As a result, a surface like that shown in Fig. 2(d) is formed. One can see that the chains of the triangular-shaped 3×1-Na islands nucleated along domain boundaries of the original 7×7 surface evolve finally into 3×1-Na stripes. The other area of the terraces is occupied by the randomly distributed 3×1-Na islands of arbitrary shape. One can notice also the "denuded zone"[19] (free of islands) near the step edge (note that the "denuded zone" forms only at the side of the upper terrace).

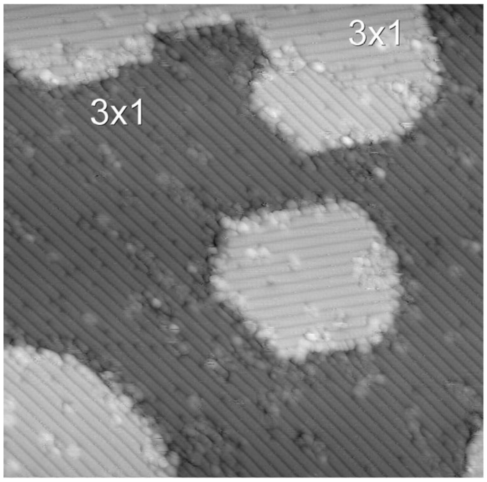

FIG. 3. 500×500 Å^2 filled state ($V_t=+2.5$ V) STM image showing that in the converted region both islands and terrace display the 3×1-Na reconstruction.

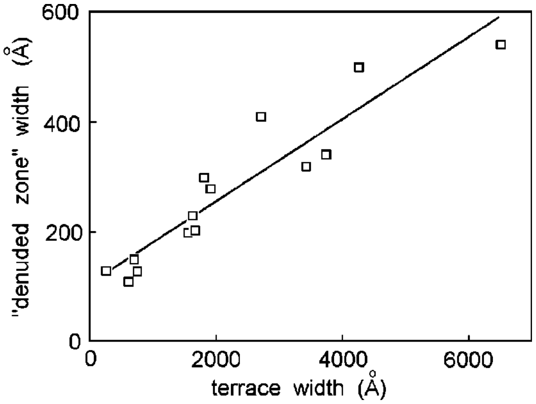

FIG. 4. The denuded zone width as a function of the terrace width converted into the 3×1-Na.

In the following sections we would like to discuss the above observations in greater detail.

B. 3×1-Na growth on the 7×7 terrace

The above listed results show definitely that the 7×7 to 3×1 transformation takes place primarily at the $7\times7/3\times1$ boundary, which acts as a front of transformation. As a result, the $7\times7/3\times1$ boundary moves at a constant rate (for the fixed growth conditions) from a step edge leaving behind the 3×1-Na terrace with the 3×1-Na islands. The island number density and their average size are statistically the same all over the 3×1-Na terrace, i.e., these values do not depend on the moment of island formation. This means that the formed 3×1-Na islands remain unchanged (i.e., they do not increase in size) and that no new 3×1-Na islands nucleate at the 3×1-Na terrace.

The island formation is a direct indication on the Si mass transport as a consequence of the difference in the top Si atom density of the Si(111)3×1-Na phase and that (2.08 ML) of the Si(111)7×7 surface. Most Si atoms released at the destruction of the 7×7 surface layer become redistributed between the 3×1-Na terrace and the 3×1-Na islands adjacent to the $7\times7/3\times1$ boundary. However, the growth of the denuded zone near the step edge indicates that some released Si atoms have another destiny: they migrate over the 3×1-Na terrace until becoming incorporated into the 3×1-Na phase at a step edge, thus, increasing the width of the denuded zone.

Figure 4 shows the denuded zone width plotted vs the width of an area occupied by the 3×1-Na phase. (Denuded zone width is defined here as a mean distance from a step edge to the nearest island; 3×1-Na area width is defined as a mean distance from a step edge to the nearest $7\times7/3\times1$ boundary. The 3×1-Na area width includes, evidently, distance covered by advancing the $7\times7/3\times1$ boundary from the initial position of a step edge and the denuded zone width.) Linear dependence of the plot indicates that a fraction of Si atoms that escape from the reaction zone at the $7\times7/3\times1$ boundary is constant. This value is believed to be governed by an equilibrium density of the free Si adatoms on the Si(111)3×1-Na surface. These Si adatoms can migrate easily over the 3×1-Na surface for relatively long distances (at least, up to 6000 Å as one can conclude from Fig. 4).

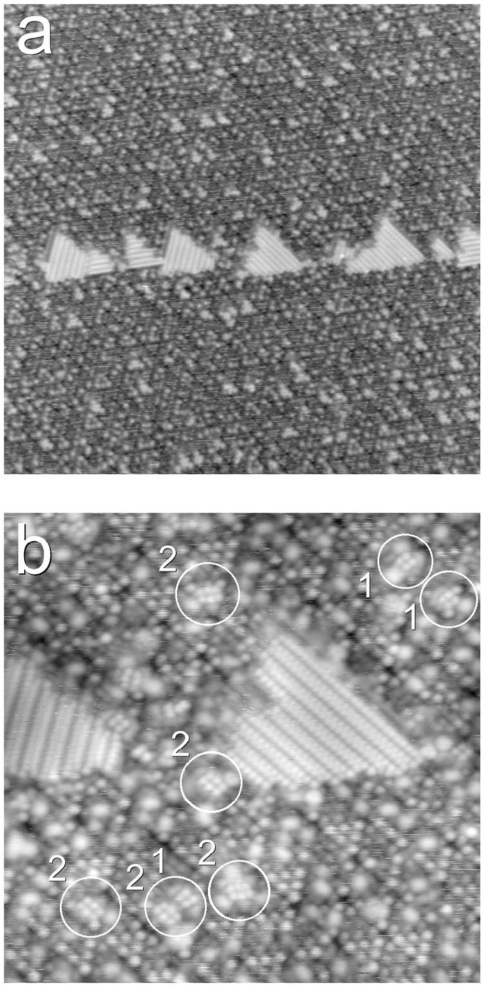

FIG. 5. (a) 1000×1000 Å^2 filled state ($V_t=+2.5$ V) STM image of a chain of the triangular-shaped 3×1-Na islands formed along the 7×7 domain boundary. (b) The 3×1-Na island shown at a greater magnification (scale 200×200 Å^2). Small 3×1-Na domains consisting of a single unit cluster (labeled 1) and of two unit clusters (labeled 2) are present on the surface, which is a mixture of the 7×7 and $\delta7\times7$ reconstructions.

C. 3×1-Na growth at the 7×7 domain boundary

Formation of the triangular-shaped 3×1-Na islands along the 7×7 domain boundary (Fig. 5) represents an additional channel for the 7×7 to 3×1 transformation. Forming at the very early stage of a Na deposition, these islands do not change in size until the advanced front of the 7×7 to 3×1 transformation approaches them. This time-dependent island growth is believed to be the sequence of the nonmonotonous supply of the Si atoms required for the formation of the 3×1-Na islands: the source of silicon for the initial island growth becomes rapidly exhausted and the resumption of island growth becomes possible only when Si atoms released from the $7\times7/3\times1$ transformation front can reach an island. The noticeable island growth occurs when the transformation front approaches the island at a distance of a few hundred Å indicating that the Si adatom mobility on the 7×7 surface is about an order of magnitude lower than on the 3×1-Na one.

It seems difficult to conclude definitely what is a source of silicon for the initial growth of the 3×1-Na islands at the 7×7 domain boundaries. We can list several possible can-

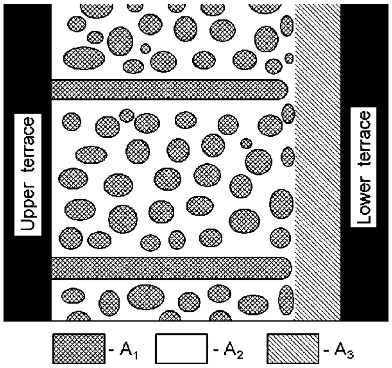

FIG. 6. Schematic representation of the Si(111)3×1-Na sample morphology [compare with the STM image in Fig. 2(d)]. Surface area occupied by the 3×1 islands A_1 (see text) is cross-hatched; surface area of the 3×1 terrace between islands A_2 is blank; denuded zone A_3 is shaded. The upper (left) and the lower (right) terraces are shown in black and are excluded from consideration.

didates: (i) the groups of the Si atoms at the 7×7 boundaries that show up as bright protrusions in the STM images (Fig. 1, inset), (ii) the Si atoms liberated in the transformation from the Si(111)7×7 surface to the Si(111)δ7×7-Na one,[20] (iii) two-dimensional gas of the free Si adatoms that are not incorporated into 7×7 (DAS) structure. However, there is a lack of convincing evidence to favor any one among them as the most plausible.

Close inspection of the high-resolution STM images of the δ7×7-Na surface has revealed a presence of the extremely small domains of the 3×1-Na structure. The domain of minimal size shows up in the STM image as a group of four protrusions forming a $(\sqrt{3}a\times 1a)$ rectangle. We define it as the 3×1-Na unit cluster. These domains cannot be described in conventional terms of the unit cells because neither one unit cluster [labeled 1 in Fig. 5(b)] nor a group of two unit clusters [labeled 2 in Fig. 5(b)] constitute the integer number of the 3×1 unit cells though these clusters are evidently the fragments of the Si(111)3×1-Na reconstruction. The detailed description of the accordance of the unit cluster to a plausible model of the 3×1-Na atomic structure is given elsewhere.[21] These 3×1-Na domains appear at the very early stage of a Na deposition with a number density of $\sim 10^{12}$ cm^{-2}. It should be noted that they do not evolve at further Na deposition and, thus, produce negligible effect on the 7×7 to 3×1 transformation.

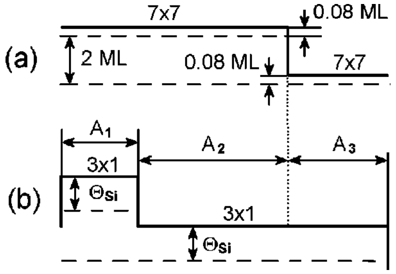

FIG. 7. Schematic illustration for balance of the Si mass transport at the 7×7 to 3×1 transformation: (a) top Si layer of the 7×7 surface prior the transformation; (b) top Si layer of the 3×1 surface after the transformation. The location of the ideal Si(111) double layers are shown by dashed lines. Dotted line shows the position of the step edge at the Si(111)7×7 surface prior to the transformation.

D. Si mass transport balance and top Si atom density of the 3×1-Na phase

Quantitative consideration of the Si mass transport involved in the 7×7 to 3×1 transformation enables us to determine a top Si atom density of the Si(111)3×1-Na phase. Let us define the terrace area occupied by the 3×1-Na islands as A_1, the terrace area between islands as A_2, and the area of the denuded zone as A_3 (see Fig. 6). Before transformation, the whole terrace area (A_1+A_2) is covered by a Si(111)7×7 reconstruction. 7×7 DAS structure contains 102 Si atoms per 7×7 unit cell, i.e., it has a top Si atom density of about 2.08 ML. Thus, the whole 7×7 terrace contains a Si amount of $2.08(A_1+A_2)$ [see Fig. 7(a)]. Upon the 7×7 to 3×1 transformation, this Si amount becomes redistributed between the 3×1-Na islands, the 3×1-Na terrace, and the 3×1-Na denuded zone [see Fig. 7(b)]. If Θ_{Si} is the Si atom density of the 3×1-Na phase, then the 3×1-Na terrace area between islands accumulates Si amount of $\Theta_{\mathrm{Si}}A_2$. Since 3×1-Na islands are one double Si(111) layer above the terrace, they consume a Si amount of $(2+\Theta_{\mathrm{Si}})A_1$. Si amount accommodated by the denuded zone is $\Theta_{\mathrm{Si}}A_3$ of which 0.08 ML Si is a contribution from the original Si(111)7×7 surface of the lower terrace. Thus, from the Si mass balance

$$2.08(A_1+A_2)=(2+\Theta_{\mathrm{Si}})A_1+\Theta_{\mathrm{Si}}A_2+(\Theta_{\mathrm{Si}}-0.08)A_3,$$

one can easily obtain

$$\Theta_{\mathrm{Si}}=\frac{2.08-2S+0.08r}{1+r},$$

where $S=A_1/(A_1+A_2)$ and $r=A_3/(A_1+A_2)$.

In the present experiment, the Si samples with nominal zero miscut were used to maximize the surface area suitable for island area evaluation. The actual terrace width was in the range from 3000 to 6000 Å, which perfectly fits this requirement. Measurements were conducted for a set of the Si(111)3×1-Na samples prepared at various growth conditions. For all cases, the fraction of the surface occupied by islands appears to be $S=0.335\pm0.005$ with a very low scattering of the data. The ratio r has been determined from the slope of the plot in Fig. 4, taking into account that this slope presents in fact the $A_3/(A_1+A_2+A_3)$ ratio. The linear best fit of the data in Fig. 4 gives $r=0.079\pm0.005$. These data yield the value of 1.31 ± 0.03 ML, i.e., 4/3 ML, for the Si atom density (Θ_{Si}) in the Si(111)3×1-Na phase.

IV. CONCLUSION

Using step-by-step scanning tunneling microscopy observations of the Si(111) surface structure and morphology evolution during Na adsorption, the main regularities of the 7×7 to 3×1 transformation have been determined and the Si(111)3×1-Na phase formation mechanism has been proposed as follows.

The alkali-metal coverage in the Si(111)3×1 phase is known to be 0.33 ML and the results of the present study show that the top Si atom density in this phase is 1.33 ML.

At Na deposition, Na atoms adsorb all over the Si(111)7×7 surface converting it to the Si(111)δ7×7 one. Taking into account that the δ7×7 has a Na saturation coverage of about 1 ML,[18] one can see that the Na amount accumulated provides the principal possibility for the 7×7 to 3×1 transformation to take place in any arbitrary point of a surface. However, this transformation actually starts only from the step edges and at the 7×7 domain boundaries.

The 7×7 to 3×1 transformation starting from the step edges proceeds via a continuous motion of the 7×7/3×1 boundary leaving behind the 3×1-Na islands on the 3×1-Na terrace. The first stage of an elementary act of the 7×7 to 3×1 transformation is the destruction of the 7×7 DAS structure. At this stage, 2.08 ML of Si [top Si atom density of the Si(111)7×7] is liberated. From this Si amount, 1.33 ML becomes incorporated at once in the 3×1-Na surface phase of a terrace. About 8% of the remaining 0.75 ML Si escapes from the reaction zone and migrates in the form of the Si adatoms over the 3×1-Na terrace until reaching a step edge. These Si atoms constitute finally the top Si layer of the 3×1-Na denuded zone near the step edge. The other Si amount of about 0.69 ML diffuses onto the δ7×7 area. Suppressed mobility of the Si adatoms on the δ7×7 surface and continuous motion of the 7×7/3×1 transformation front lead to an increase in the Si adatom density in the vicinity of the 7×7/3×1 boundary. As a result of the Si adatom supersaturation, the 3×1-Na islands nucleate and grow incorporating these Si atoms.

The mean size and number density of 3×1-Na islands are the result of the competition between two processes, namely, the Si adatom migration on the δ7×7 surface and the 7×7/3×1 boundary motion [the rate of the latter process being determined mainly by the rate of the Si(111)7×7 destruction]. Both processes are thermally activated but are expected to have different activation energies. Thus, by changing the growth temperature, one can change the mean size and the number density of the islands. Our results (not presented here) show that, with decreasing temperature, the island number density decreases and their size consequently increases.

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[19] The term denuded zone is used conventionally to define the area near the step edge where the probability for adatoms to stick to the step is higher than to meet each other to form a new island. The formation mechanism of the Si(111)3×1-Na islands is found to be essentially different from the above one. So, we use here the term ‘‘denuded zone’’ only to define the area near the step edge that is free of islands.

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