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## Regular arrangement of nanometre-scale clusters by surface strain on stabilized Cl/Si(111)

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### Abstract

The dynamic processes during halogen etching at a Si(111) surface were observed at atomic resolution using a scanning tunnelling microscope (STM) at high temperature. It was found that after the thermal desorption of chlorine atoms, the metastable '1 × 1' structure and the 7 × 7 structure coexisted at a relatively low temperature. The narrow strips of the metastable '1 × 1' structure within the 7 × 7 structure tended to be straight, presumably because this minimizes the strain energy induced by the reconstruction. At the same time, silicon atoms diffusing on the surface appear to be trapped on the boundary strips, where nucleation occurs to form silicon clusters. After the sample had been cooled to room temperature, the silicon clusters were still regularly aligned. Our results indicate that the dynamics of the reconstruction from the '1 × 1' to the 7 × 7 structure leads to the straightening of the boundary, resulting in the regular alignment of silicon clusters. The formation mechanism of the clusters appears to be related to the stabilization of the surface by halogen adsorption, because such a pattern was not formed upon thermal treatment of Si(111) without chlorine adsorption. The simple thermal treatment presented here may provide a new approach to the assembly of regular arrangements of nanometre-scale silicon clusters.

### 1. Introduction

Silicon nanocrystals buried in dielectric materials have attracted considerable interest due to their potential application in future electronic devices [1]. As the miniaturization of electronic devices approaches the nanometre scale, beyond the limits of optical lithography, alternative methods to fabricate nanostructures on silicon surfaces are required. It is possible to control silicon cluster formation with the assistance of carbon monoxide, silane/disilane and

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hydrogen gases. In these cases, nucleation of silicon atoms takes place at voids on the oxide layer and at corners of the step edges [2–6]. These clusters, however, appear not to be uniformly aligned.

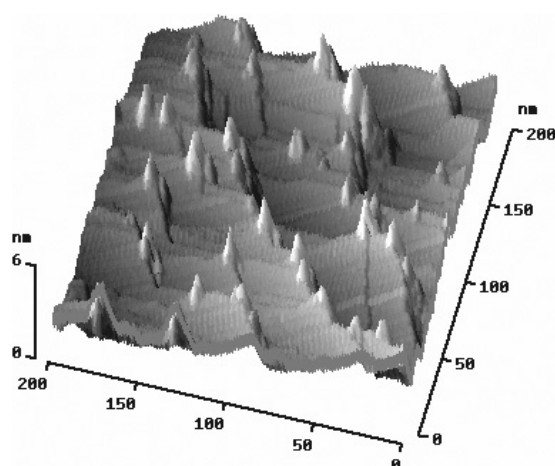
A low-energy electron microscopy (LEEM) study in the absence of gas exposure showed the formation of patterns of triangular domains during thermal reconstruction from  $1 \times 1$  to  $7 \times 7$  due to reconstruction strain [7, 8]. Here, we describe the utilization of halogen desorption kinetics to form a regular arrangement of silicon nanoclusters on a Si(111) surface. The kinetics of the etching process with chlorine, bromine and iodine has been widely studied in terms of the atomic structure [9, 10], island/cluster formation [11] and reconstruction strain [12]. It is recognized that the reaction is qualitatively the same among these halogen species as regards the surface structure [13] although the desorption barriers of the silicon halides are different [14]. When halogen is adsorbed on a Si(111) surface, an unreconstructed  $1 \times 1$  structure can stably exist [15], and reconstruction from  $1 \times 1$  to  $7 \times 7$  takes place at a lower temperature [13, 16] than on a clean surface [17]. As the halogens are removed upon heating, a thermal process with halogen may provide a simple method to fabricate nanometre-scale silicon structures on silicon surfaces.

Scanning tunnelling microscopy (STM) can be utilized for manipulation of single atoms [18]. The electric field applied with the tip can control the diffusion of silicon atoms on an annealed surface [19], and the electric current from the probe tip to the heated silicon surface produces a symmetric mound or a pit at nanometre scale [20–22]. Nevertheless, this approach is not suitable for mass production. On the other hand, combined use of etching, deposition and lithography has been proposed to have potential technological application [23, 24]. In this type of fabrication, strain dynamics and diffusion kinetics lead to the spontaneous appearance of patterns at specific nucleation sites through surface reconstruction.

Irrespective of homo- or hetero-epitaxy, the mechanism of the growth process at high temperature is governed by match/mismatch at the interfaces, step motion, surface diffusion or reconstruction. In the case of halogen etching, the kinetics of halogen atoms on silicon surfaces has been examined mainly through room temperature observation with STM [9, 25, 26]. However, the kinetics at high temperature has not been clarified. Step motion on a vicinal surface and reconstruction at high temperature are known to change the surface morphology [27, 28]. Our previous report [30] described the novel formation of silicon clusters on halogen-adsorbed silicon surfaces. On a step-rich surface of a vicinal slope ( $\sim 5^\circ$  towards the  $[10\bar{1}]$  direction, for example), the clusters (typically 8 nm in diameter and 2–4 nm in height) are predominantly formed at the apexes of the step edges, as can be seen in STM images such as that in figure 1, observed at room temperature. The clusters grow at the edges of multiple steps whose height is more than  $\sim 1.5$  nm, just like a step-bunched surface. These clusters may not simply grow at the apexes, but rather may pin the step motion during heating. The process was suggested to be governed by diffusion and step retreat. Here, we address another important factor, local strain associated with the surface reconstruction, and discuss the mechanism initiated by the halogen on the surface.

## 2. Experimental details

We used a normal (111) sample in the following experiments. A specimen was cut from a commercial n-type (P-doped) Si(111) wafer with a resistivity of a few to a few tens of  $\Omega$  cm, and mounted on a molybdenum holder in an ultra-high vacuum chamber at a pressure of about  $10^{-8}$  Pa. A clean surface with wide terraces was prepared by repeated direct current heating up to  $\sim 1400$  K. The surface was dosed with chlorine gas generated in an electrochemical cell of AgCl. The operations of heating and gas exposure were done carefully so as to maintain a



**Figure 1.** STM images of aligned clusters on a vicinal Si(111) surface observed at room temperature. Nanoclusters can be seen at apexes of the step edges. They are aligned in the direction of the white arrow. The tunnelling current was 0.1 nA, and the sample bias was +2.5 V.

vacuum pressure of less than  $10^{-6}$  Pa. The surface was observed with an STM (JEOL, JSTM-4500XT). During STM observation at high temperature, the sample was heated by applying direct current. The temperature of the surface was monitored with an IR radiation thermometer at temperatures higher than 773 K, and the current-to-temperature relation [31] was calibrated at temperatures up to 923 K. The temperature was controlled by means of digital regulation of the sample current. The error in the temperature was estimated to be within  $\pm 10$  K. The time required to scan a frame was 8–30 s.

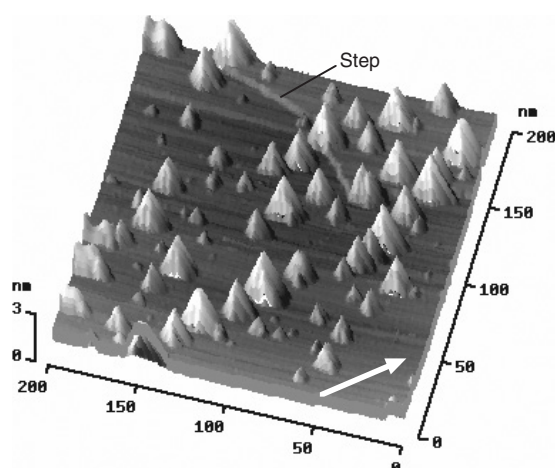
### 3. Results and discussion

#### 3.1. Aligned clusters on the terrace

In the present study, the sample was processed each time from the clean Si(111)- $7 \times 7$  dimer-*adatom*-stacking-fault (DAS) surface with saturation coverage of Cl at room temperature. The coverage was estimated to be 1.62 monolayers (ML) by means of x-ray photoemission spectroscopy<sup>2</sup>, where 1 ML corresponds to the adsorption of 49 atoms in a  $7 \times 7$  unit cell [32].

Figure 2 shows a STM image observed at room temperature after heating the sample to 873 K for about 20 min. This treatment leads to desorption of most of the chlorine atoms on the surface [14, 30]. In the image, obtained at room temperature, only one step is seen. Some clusters can be seen at the step edges, while many more are apparent on the wide terrace. The clusters are aligned in the direction indicated by the white arrow. The average spacing between them is about 30 nm. Compared with the step-rich surface (as in figure 1), where the regular alignment can be explained in terms of diffusion and step retreat [30], there must be another mechanism leading to the formation of the self-organized pattern of clusters on the terrace, because the step density is too low to affect the motion of the clusters. To elucidate the mechanism of this regular cluster arrangement on the terrace, in the following section we will focus on reconstruction on the surface from the viewpoint of strain near the surface.

<sup>2</sup> In the reference, the value is noted to be 1.89 monolayers based on a definition of one-to-one adsorption to 42 rest-atoms per unit cell.



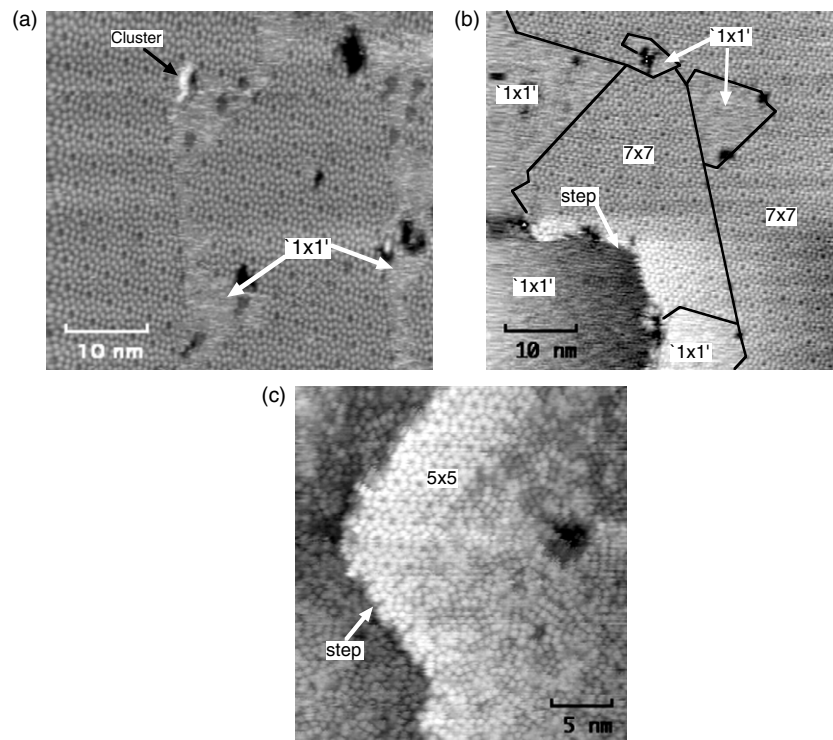
**Figure 2.** STM images of aligned clusters on a normal Si(111) surface observed at room temperature. Clusters formed on a wide terrace are aligned in the direction of the white arrow. The tunnelling current was 0.1 nA, and the sample bias was +2.5 V.

### 3.2. Equilibrium between '1 × 1' and 7 × 7 structure

We observed the evolution of surface morphology during high-temperature treatment in order to examine the mechanism of cluster alignment on the terrace at 873 K over 40 min. In figures 3(a) and (b), there are 7 × 7 DAS areas as well as structureless areas with blurred contrast. The structureless areas observed at high temperature may remain after quenching to room temperature. An image, obtained at room temperature after brief heating, is shown in figure 3(c). There is no periodic structure except for the 5 × 5 region near the step. It is considered that molecular or radical species migrate on the 1 × 1 surface at high temperature in these structureless areas, which are referred to as '1 × 1'. The diffusion rate would be too fast to allow resolution of the structure with conventional STM [20, 33]. The '1 × 1' structure reconstructs to 7 × 7 structure, starting from the upper terrace at the step edge. During high-temperature observation, 5 × 5 or 9 × 9 structures were temporarily observed near the periphery of the 7 × 7 domains, indicating that the reconstruction to 7 × 7 took place through such metastable periodic structures. The lifetimes of the metastable structures on the heated sample were estimated to be no more than a few seconds, because even quick scans rarely gave a clear image of these structures.

In contrast to a clean surface after quenching [34], DAS structure did not emerge inside the wide '1 × 1' terrace in the case of the chlorine-adsorbed surface. This difference suggests that chlorine influences the reconstruction process even after the desorption of chlorine atoms. The desorption of SiCl<sub>2</sub> occurs at 820 K and higher, and it continues for several minutes [14]. During heating near 873 K, silicon chloride diffuses on the surface and the surface may be partially chlorine-terminated. The occurrence of active migration is likely because desorption is caused by associative (second-order) reaction of the surface species chiefly at the step edges [9, 35]. The residual chlorine keeps the surface structure more stable before reconstruction [13]. The transit of chloride species may change the surface structure, and finally the diffusive species collapses into the clusters.

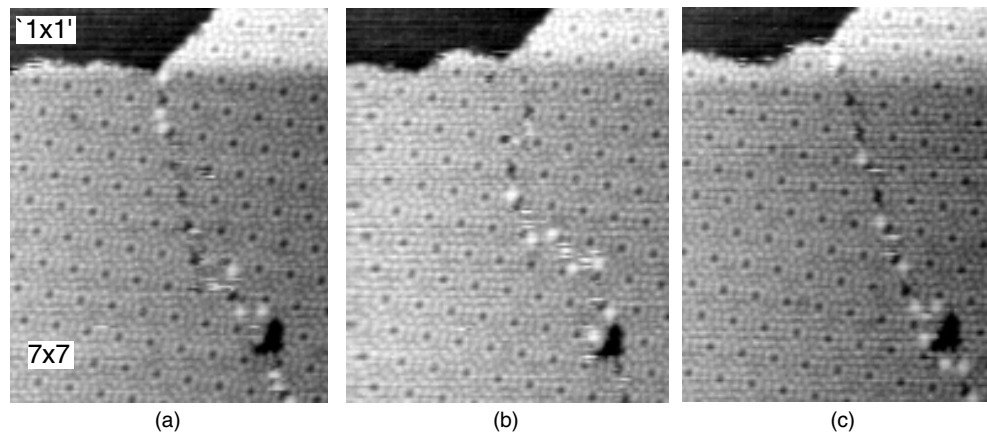
The 7 × 7 areas were preferentially observed at the upper terrace near the step, and they grew inwards inside the terrace [16]. The tendency for reconstruction to occur from the upper side at the step is the same as on a clean surface in this temperature range [28, 36]. The



**Figure 3.** (a), (b) Si(111) surface observed while maintaining a chlorine-saturated surface at the temperature of 873 K for 40–42 min. The region of  $7 \times 7$  structure grew from the step edge on the upper side. Structureless areas are seen (designated as ' $1 \times 1'$ '), together with  $7 \times 7$  DAS areas. The ' $1 \times 1'$ ' areas form stripes inward from the terrace (a), becoming very thin near the step (b). The thin structureless areas, which appear like phase boundaries of the  $7 \times 7$  domains, are indicated with black lines (see text). The tunnelling current was 0.1 nA, and the sample bias was +2.5 V. (c) The Si(111) surface observed at room temperature after heating a chlorine-saturated surface at 873 K for 5 min. Heating to this temperature for this period almost exhausts the chlorine, which is etched out as silicon chloride [14]. In addition to the  $5 \times 5$  area on the upper side at the step edge, an atomically resolved ' $1 \times 1'$ ' surface can be recognized. The tunnelling current was 0.1 nA, and the sample bias was +1.0 V.

width of the structureless strip in the images decreased at high temperatures, and the reduction rate was greater at higher temperature. The structureless region tended to become a narrow strip, as in figure 3(a), and was frequently reduced to two-dimensional dislocations in the DAS structure [37, 38], especially near the step. The ' $1 \times 1'$ ' areas tended to reshape into triangular form due to reconstruction to  $7 \times 7$  [37–39]. The remaining triangles were often connected with a domain boundary (derived from the strip) between different phases of adjacent  $7 \times 7$  regions, emphasized in (b). After a sufficient heating time, the ' $1 \times 1'$ ' areas converged to a certain size, which diminished as the temperature was increased. These results did not depend on the duration of the heating (at least up to several hours), whether triangular domains or strip domains were observed.

Compared with the clean Si(111) surface, the growth process of the reconstructed  $7 \times 7$  domains on the terrace is quite similar [36, 40] but the rate is rather small [33]. ' $1 \times 1'$ ' areas (structureless regions in the images) remained on the surface after hours of heating, while this was never observed on the surface without chlorine. The remaining unreconstructed triangular



**Figure 4.** Si(111) sample cooled from 913 to 773 K. Images were successively obtained at 773 K. The area of the image was  $25 \times 30 \text{ nm}^2$ , the sample bias was about +2.8 V, and the tunnelling current was 0.8 nA. The three images were taken successively at intervals of  $\sim 20$  s. Changes in the step shape and the domain boundary were recognized, while small clusters emerge/disappear at the boundary.

regions, as seen in figure 3(b), were very stable even at high temperature. The area of the regions converged to a fraction that was dependent on the temperature. The result of optical measurement of second harmonic generation (SHG) is consistent with imperfect recovery of the dangling bonds of the DAS structure [41]. The nanometre-scale co-existence of  $1 \times 1$  with  $7 \times 7$  structures is possible because of the stabilization of the  $1 \times 1$  structure by chlorine adsorption. As quite a small amount of remaining chlorine (or chloride) is bound to the  $1 \times 1$  region [42], the attack of the diffusing species at the step edge cannot occur once the  $1 \times 1$  area becomes narrower. This explains the stabilization of the surface and the undetectable desorption in the temperature range. A cluster can be seen in figure 3(a) in the  $1 \times 1$  area, since mobile silicon atoms nucleate preferentially at regions where  $7 \times 7$  DAS is broken. Thus, the formation of the clusters is understood. Next, the reason why the clusters are formed in a regular arrangement will be discussed.

### 3.3. Nucleation of diffusing Si

Sometimes no clusters were observed at various temperatures, as depicted in figures 3(a) and (b), when the temperature was raised. However, the width of the  $1 \times 1$  region was reduced at high temperature. In order to investigate the origin of the cluster arrangement in figure 2, we reduced the sample temperature to 773 K after sufficient heating at 913 K, at which the  $1 \times 1$  region looks like the phase boundary of  $7 \times 7$  domains. In figure 4 this quenched surface is seen to have a step, whose lower side consists of the  $1 \times 1$  structure. The shape of the step apparently changes, indicating detachment/attachment of silicon atoms diffusing on the surface [33, 43]. The boundary strip of two  $7 \times 7$  domains grows from the concave corner of the step into the terrace. The shape of the boundary changes from curved (a), to irregular (b) and finally straight (c). The relaxation of the surface strain may drive boundary straightening along the DAS perimeter parallel to the dimer row. At the boundary between out-of-phase  $7 \times 7$  domains, there is a large energy due to atomic mismatch in the stacking-fault layer and disorder of the corner-hole symmetry [44]. At very high temperatures the boundary exhibits undulating and bending segments [39, 45], because the lateral disorder around the

bending boundary induces excessive strain. The surface strain around the boundary appears to be gradually relaxed from the step edge through the straightening of the boundary regions.

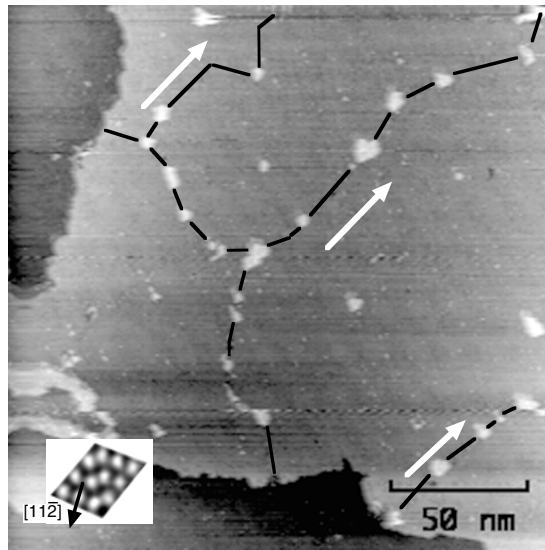
Small protrusions can be seen along the boundary region at high temperature (figure 4). Their height is less than that of a single diatomic step, indicating that they represent accumulations of silicon atoms on the surface. Their shape changed continuously, presumably because silicon atoms can be expelled from them and reattached to them. As long as these clusters were relatively small, they could change their positions. Some horizontal scratches are seen near the boundary. These are traces of the rapid migration of silicon adatoms [46]. No scratches were observed on the terrace far from the boundary, indicating that the diffusion rate is higher than the scanning speed under equilibrium conditions. The velocity near the domain boundary may be slower. The diffusion barrier to the lateral motion (related to the diffusive velocity) is known on a DAS surface [47], but not on the  $1 \times 1$  structure. We consider that the potential near the irregular boundary is lower than on the flat terrace, because the density of the diffusive species is higher there. This is consistent with the high density of small clusters in ' $1 \times 1$ ' areas on a Br-adsorbed surface at room temperature [42]. In the case of the Si-deposited or quenched clean Si(111) surface at high temperature, the clusters were more frequently found in ' $1 \times 1$ ' than  $7 \times 7$  areas, and were trapped near the narrow boundary [33]. When the surface was cooled, excess silicon atoms or chloride species over the maximum density of the two-dimensional equilibrium may condense preferentially at the boundary or the step. The density of silicon atoms in the top-most layer of the ' $1 \times 1$ ' surface is higher than that of DAS structure at a  $7 \times 7$  surface (only 12 Si adatoms per unit cell). When ' $1 \times 1$ ' reconstructs to  $7 \times 7$ , the extra silicon atoms would be expelled. This would give rise to an increase in the surface density of mobile silicon atoms. In contrast, the silicon atoms deposited onto a heated clean surface are distributed randomly on the surface, and uniform deposition at high temperature generates triangular islands with monatomic layer height [48].

The structure of the wide terrace observed at 663 K is shown in figure 5. The sample was heated at 913 K for a sufficient time, and then cooled to 663 K within a few seconds. The surface on the terrace was mostly covered with  $7 \times 7$  DAS structure. To clarify the domain boundaries, segmented lines are drawn in the figure. Small protrusions with a diameter of about 5–8 nm are found to be located preferentially at the apexes of the connected lines. The lines tend to be directed along the substrate lattice (white arrows). Their height is  $\sim 0.3$  nm, corresponding to a single diatomic layer height. Slow cooling from the aligned seeds (figure 5) allows the clusters grow in that direction. The two effects, alignment of ' $1 \times 1$ ' regions into straight phase boundaries and nucleation of the diffusive species inside ' $1 \times 1$ ' areas, are cooperative, causing large clusters to become fixed at the apex of the boundaries. The cluster size (the bottom area and the height) depends on the rate of temperature reduction, but the relationship remains to be quantitatively determined.

### 3.4. Stability of the clusters

The clusters and islands are volatile at high temperature [43], and the clean surface immediately transforms to a  $7 \times 7$  structure [33]. Pyramidal clusters can be formed on the clean surface by the effect of the current or the electric field from the STM tip. This is because the activation energies of detachment/attachment at the step edges ( $1.5 \pm 0.1$  and  $1.3 \pm 0.2$  eV, respectively) [43, 49] are reduced by 0.1–0.4 eV when the current and the bias voltage satisfy certain conditions [22]. However, our measurements are made far from such conditions. Indeed, clusters were observed on a cooled surface without scanning at high temperature [30]. Thus, we conclude that the clusters are formed by the condensation of the two-dimensional vapour concomitantly with the growth of reconstructed  $7 \times 7$  areas due to the reduced barrier





**Figure 5.** Si(111) sample cooled from 913 to 663 K. The  $7 \times 7$  domain boundary is emphasized with segmented lines. The boundary tended to be oriented in the direction of the arrows. The image is slightly distorted due to thermal drift. To show the crystalline direction of the substrate, a magnified image of the  $7 \times 7$  DAS structure is shown in the inset.

to diffusion by chlorine. The stable clusters are considered to be formed by accumulation of silicon adatoms attached to the edge of the islands or piled on the plateau of the clusters, rather than at the irregular and mobile ' $1 \times 1$ ' boundary. In these areas, metastable facets, such as  $[331]$ ,  $[122]$ , would be formed to reduce the surface energy [22]. The shape of the present clusters is pyramidal [30], similar to those formed with the STM tip by Ichimiya *et al* [22]. However, in the present case the clusters are formed simply as a result of thermal treatment at relatively low temperatures from 673 to 773 K, owing to the involvement of chlorine. Recently, it has been suggested, based on molecular dynamics calculation, that the formation of a silicon dome including chlorine atoms is possible during stacking-fault reconstruction at high temperature [50]. Their collapse has an activation energy of 1.6 eV [49], so that they may be resistant to thermal treatment.

In successive observations (figure 5), some boundary lines changed their orientation. As indicated in figure 4, this is presumably due to straightening of the domain boundary from the step edge to the terrace (indicated by the white arrows in figure 5). The length of the segmented straight lines was 20–40 nm, which may reflect the tolerance to strain accumulation at this temperature. This would be the reason why the clusters are placed at regular distances. Spacing between the clusters would be determined by the initial nucleation sites and the interaction between the clusters mediated by the strain in the substrate. After the clusters had grown large, we did not observe any further motion. The immobile clusters, once formed, may have become crystalline epitaxial to the substrate. The critical size of clusters was determined not only by the temperature but also by the width of the boundary.

Our previous report dealt with cluster formation due to the pinning of step retreat [30], which is different from the present case on the wide terrace. These clusters may not simply grow at the apexes, but rather may pin the step motion during heating [30] through a mechanism similar to step bunching. Step pinning occurs not only on a clean surface but also on an oxygen-covered [5, 6] or chlorine-adsorbed surface. This regular alignment suggests interaction

between the steps and the seeds of the clusters at the step edges [4], while in the current case on the terrace, the clusters are seeded at positions that relax the strain of the substrate. With the aid of photolithography, regular alignment of bunched steps is possible through artificial pinning of step motion [24]. We show here that regular arrangement of clusters can take place on the wide terrace without such elaborate treatment.

#### 4. Summary

Reconstruction of Si(111) surfaces was observed at the atomic level *in situ* at high temperature. Si clusters were formed in the process of chlorine-assisted etching. In contrast to the regular  $7 \times 7$  structure generated from a completely clean surface [43], clusters formed at the domain boundaries of  $7 \times 7$  derived from '1  $\times$  1' strip (corresponding to structureless regions in STM images) remained at high temperature, and grew through Si diffusion. This process, as well as step motion, is essential for self-organized patterning. We suggest that the results presented here may provide a clue to a novel approach for assembly of nanometre-scale patterned structures using simple thermal processes.

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#### References

- [1] Tiwari S, Wahl J A, Silva H, Rana F and Welser J J 2000 *Appl. Phys. Lett.* A **71** 403–14
- [2] Palermo V and Jones D 2004 *Appl. Surf. Sci.* **226** 191–6
- [3] Mizushima I, Koike M, Sato T, Miyano K and Tsunashima Y 1999 *Japan. J. Appl. Phys.* **38** 2415–8
- [4] Fujita K, Kusumi Y and Ichikawa M 1997 *Surf. Sci.* **380** 66–74
- [5] Johnson S, Markwitz A, Rudolphi M and Baumann H 2004 *J. Appl. Phys.* **96** 605–9
- [6] Johnson S, Markwitz A, Rudolphi M, Baumann H, Kuo P Y, Blaikie R and Mücklich A 2005 *J. Appl. Phys.* **97** 094301-(1–4)
- [7] Hannon J B, Hibino H, Bartelt N C, Swartzentruber B S, Ogino T and Kellogg G L 2000 *Nature* **405** 552–4
- [8] Hibino H, Homma Y, Hu C W, Uwaha M, Ogino T and Tsong I S T 2004 *Appl. Surf. Sci.* **237** 51–7
- [9] Reviewed by Aldao C M and Weaver J H 2001 *Prog. Surf. Sci.* **68** 189–230
- [10] Pechman R J, Wang X S and Weaver J H 1995 *Phys. Rev. B* **52** 11412–23
- [11] Grube H and Boland J J 1998 *Surf. Sci.* **407** 152–61
- [12] Itchkawitz B S, McEllistrem M, Grube H and Boland J J 1997 *Surf. Sci.* **385** 281–93
- [13] Itchkawitz B S, McEllistrem M T and Boland J J 1997 *Phys. Rev. Lett.* **78** 98–101
- [14] Shudo K, Kirimura T, Tanaka Y, Ishikawa T and Tanaka M 2006 *Surf. Sci.* **600** 3147–53
- [15] Eves B J and Lopinski G P 2005 *Surf. Sci.* **579** L89–96
- [16] Feltz A, Memmert U and Behm R J 1994 *Surf. Sci.* **307–309** 216–22
- [17] Ino S 1977 *Japan. J. Appl. Phys.* **16** 891–908
- [18] Example as pioneer works, Huang D, Uchida H and Aono M 1994 *J. Vac. Sci. Technol. B* **12** 2429–33  
Uchida H, Huang D, Grey F and Aono M 1993 *Phys. Rev. Lett.* **70** 2040–3
- [19] Tokumoto H, Miki K, Morita Y, Sato T, Iwatsuki M, Suzuki M and Fukuda T 1992 *Ultramicroscopy* **42–44** 816–23
- [20] Iwatsuki M, Kitamura S and Sato T 1992 *J. Japan. Soc. Appl. Phys. (Oyo Butsuri)* **61** 1161–4 (in Japanese)
- [21] Sudoh K and Iwasaki H 2000 *Japan. J. Appl. Phys.* **39** 4621–3
- [22] Hayashi K and Ichimiya A 2001 *Japan. J. Appl. Phys.* **40** 5109–15
- [23] Ogino T, Hibino H, Homma Y, Kobayashi Y, Prabhakaran K, Sumitomo K and Omi H 1999 *Acc. Chem. Res.* **32** 447–54

- [24] Ogino T 1997 *Surf. Sci.* **386** 137–48
- [25] For example, Avouris Ph, Lyo I W, Bozso F and Kaxiras E 1990 *J. Vac. Sci. Technol. A* **8** 3405–11
- [26] Sakurai S and Nakayama T 2002 *Japan. J. Appl. Phys.* **41** 2171–5
- [27] Suzuki M, Hibino H, Homma Y, Fukuda T, Sato T, Iwatsuki M, Miki K and Tokumoto H 1993 *Japan. J. Appl. Phys.* **32** 3247–51
- [28] Hibino H, Fukuda F, Suzuki M, Homma Y, Sato T, Iwatsuki M, Miki M and Tokumoto H 1993 *Phys. Rev. B* **47** 13027–30  
Hibino H and Ogino T 1995 *Appl. Phys. Lett.* **67** 915–7
- [29] Hibino H, Fukuda T, Suzuki M, Homma Y, Sato T, Iwatsuki M, Miki K and Tokumoto H 1993 *J. Vac. Sci. Technol. A* **11** 1640–3
- [30] Shudo K, Kirimura T, Kaneko N, Takahashi M, Tanaka Y, Ishikawa T, Tanaka M, Nakagawa H and Asakura S 2004 *Surf. Sci.* **566/568P1** 425–9
- [31] Ichikawa T and Ino S 1981 *Surf. Sci.* **105** 395–428
- [32] Whitaman L J, Joyce S A and Yarmoff J A 1990 *Surf. Sci.* **232** 297–306
- [33] Hwang I S, Ho M S and Tsong T T 2001 *J. Phys. Chem. Solids* **62** 1655–71  
Hwang I S, Ho M S and Tsong T T 1999 *Phys. Rev. Lett.* **83** 120–3
- [34] Shimada W, Tochihiro H, Sato T and Iwatsuki M 2000 *Japan. J. Appl. Phys.* **39** 4408–11  
Shimada W, Tochihiro H, Sato T and Iwatsuki M 1999 *Surf. Rev. Lett.* **6** 995–1001
- [35] Shirao T, Shudo K, Tanaka Y, Nakajima T, Ishikawa T and Tanaka M 2003 *Japan. J. Appl. Phys.* **42** 593–6
- [36] Miki K, Morita Y, Tokumoto H, Sato T, Iwatsuki M, Suzuki M and Fukuda T 1992 *Ultramicroscopy* **42–44** 851–7
- [37] Tochihiro H, Shimada W, Yamamoto H, Taniguchi M and Yamagishi A 1998 *J. Phys. Soc. Japan* **67** 1513–6
- [38] Hoshino M, Shigeta Y, Ogawa K and Homma Y 1996 *Surf. Sci.* **365** 29–37
- [39] Toshino T, Kumamoto K, Kokubun K, Ishimaru T and Ohdomari I 1995 *Phys. Rev. B* **51** 14594–7
- [40] Osakabe N, Tanishiro Y, Yagi K and Honjo G 1981 *Surf. Sci.* **109** 353–66
- [41] Shudo K, Sasaki M, Tanaka M and Shirao T 2003 *Solid State Commun.* **127** 203–8
- [42] Grube H and Boland J J 1998 *Surf. Sci.* **407** 152–61
- [43] Ichimiya A, Tanaka Y and Hayashi K 1997 *Surf. Sci.* **386** 182–194  
Ichimiya A, Tanaka Y and Ishiyama K 1996 *Phys. Rev. Lett.* **76** 4721–4
- [44] Fouchier M and Boland J J 1989 *Phys. Rev. B* **57** 8997–02
- [45] Ohdomari I 1992 *Appl. Surf. Sci.* **56–58** 20–6
- [46] Sato T, Kitamura S and Iwatsuki M 2000 *J. Vac. Sci. Technol. A* **18** 960–4
- [47] Sakurai S and Nakayama T 2002 *J. Cryst. Growth* **237–239** 212–6
- [48] Köhler U, Demuth J E and Hamers R J 1989 *J. Vac. Sci. Technol. A* **7** 2860–7
- [49] Ichimiya A, Hayashi K, Williams E D, Einstein T L, Uwaha M and Watanabe K 2000 *Phys. Rev. Lett.* **84** 3662–5
- [50] Kobayashi R and Nakayama T 2004 *Thin Solid Films* **464/465** 90–4