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Dynamic growth steps of $n\times n$ dimer–adatom–stacking-fault domains on the quenched Si(111) surface

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Dynamic growth steps of Si(111)-$n\times n$ dimer–adatom–stacking-fault (DAS) domains in the 1×1 matrix have been investigated on quenched Si(111) surfaces, with high-temperature scanning tunneling microscopy. It has been found that both growth and annihilation of $n\times n$ DAS domains occur with a single $n\times n$ stacking-fault (SF) half cell as the building unit. Not only 7×7, but also 9×9 DAS domains have been observed to gradually expand on the quenched surface above 450 °C. Every type of $n\times n$ DAS domains grows with a successive addition of single SF half cells to a $n\times n$ DAS domain side. Structural transformation of 7×7 and 11×11 SF half cells into 9×9 SF half cells occurs at a 9×9 domain side, to form a large 9×9 DAS domain on the quenched Si(111) surface.

I. INTRODUCTION

The 1×1↔7×7 phase transition is one of the most important surface phenomena and the growth mechanism of the 7×7 domain on the Si(111) surface has been studied extensively by a variety of techniques.[1–3] How the 7×7 dimer–adatom–stacking-fault (DAS) (Ref. 4) domains grow in the 1×1 matrix is an especially interesting scientific subject.

So far, several experimental works have been performed for the real-space observation of the 1×1→7×7 phase transition to reveal the dynamic aspect of the transition.[5–9] For example, a reflection electron microscopy study by Osakabe *et al.* revealed that the 7×7 DAS domain nucleated at the upper edge of the steps and expanded towards the inner side of the terraces.[5] Telieps and Bauer found that triangular 7×7 DAS domains nucleated, not only at the step edges, but also on the terraces of the quenched Si(111) surface, using low-energy electron microscopy.[6] We also have observed the quenched Si(111) surfaces in atomic scale at high temperatures above 500 °C, using high-temperature scanning tunneling microscopy (STM), and investigated a variety of unique features in the 7×7 DAS domain growth. Our previous experimental results are summarized as follows: (1) The 7×7 DAS domains grow in the triangular shape with a single stacking-fault (SF) half cell as the building block.[7] (2) The corner holes play an important role in forming SF half cells.[8] (3) The growth of 7×7 DAS domains resembles that of thin film and the critical domain size between expansion and shrinking exists for the 7×7 DAS domain growth.[9] In spite of these many discoveries about the 1×1→7×7 phase transition, there still remain some important questions to be made clear for the complete understanding of the growth mechanism of $n\times n$ DAS domains. One of the questions to be clarified is the atomic scale nucleation mechanism of a 7×7 DAS domain. How the 7×7 DAS domains nucleate and grow to form large domains in the 1×1 matrix is not known. The other is the growth mechanism of $n\times n$ DAS domains other than the 7×7 DAS domains. It is interesting to compare the growth steps of 7×7 and $n\times n$ ($n\neq 7$) DAS domains and to study the similarity in the growth process. Yang and Williams previously reported that various $n\times n$ ($n=7$, 9, 11, and 13) DAS domains were formed on the quenched Si(111) surface.[10] However, an atomic scale growth mechanism of $n\times n$ DAS domains is not clear yet.

In this paper, we report dynamic growth steps of $n\times n$ ($n=7$ and 9) DAS domains on a quenched Si(111) surface observed *in situ* at above 450 °C, using high-temperature STM. On the quenched surface, the 1×1→$n\times n$ ($n=7$ and 9) DAS phase transition proceeds gradually, which enables us to ‘‘see’’ the growth mechanism of $n\times n$ DAS domains. The following results have been obtained in our present STM observation. Single SF half cells of $n\times n$ DAS structures nucleate and collapse in the 1×1 matrix. The $n\times n$ DAS domain expands with successive addition of SF half cells to a domain side on the quenched surface. The growth of the 9×9 DAS domain has been found to be the same as that of the 7×7 DAS domain, which indicates that the atomic scale mechanism of $n\times n$ SF half cell nucleation and the subsequent growth are the same, except for the size of the single SF half unit.

II. EXPERIMENT

All the experiments were performed in an UHV chamber with a base pressure of $<1\times10^{-10}$ Torr, pumped with an ion getter pump. A high-temperature STM unit was used in our experiment (JEOL JSTM-4000XV). The samples were cut from 40 Ω cm *n*-type, *p*-doped epitaxial wafer (10-μm epitaxial layer on a 0.2-mm floating zone substrate, supplied by KOMATSU Electronic Metals Co., Ltd.) into 7×2×0.2 mm^3. The samples were introduced into a vacuum chamber after chemical cleaning and HF treatment, then degassed at 500 °C for 12 h, and finally flushed repeatedly to 1200 °C by resistive heating. Clear STM images of Si(111)-7×7 surfaces were obtained over the whole surface after the above sample heating. The Si(111) surfaces were then heated resis-

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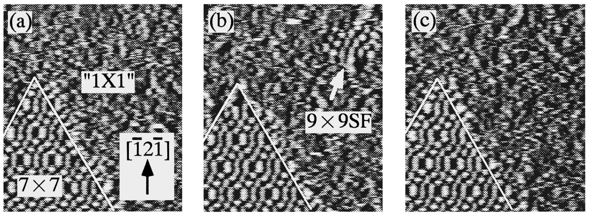

FIG. 1. Quenched Si(111) surface observed at around 490 °C. Successive STM images show the nucleation process of the 9×9 DAS structure in the 1×1 matrix. The images of (b) and (c) were taken 15 s and 45 s after (a), respectively. The 9×9 DAS structure is formed in a single SF half cell in the 1×1 matrix, as pointed out by the arrow in (b). The single 9×9 SF half cell has disappeared in (c).

tively up to 1100 °C, using two dc current supplies and subsequently quenched to 400 °C by turning off the heating current of one of the two dc current supplies. The *in situ* STM observations were performed at above 450 °C.

The sample temperature was determined by a power-temperature relationship below 600 °C and was cross checked by an infrared pyrometer above 600 °C. STM images were acquired in the constant height mode with a sample bias of +1.0 V (empty state) and a current of 0.3 nA, with a scanning speed of 15 s per an image of 50×50 Å^2 size. All of the STM images were recorded on video tapes.

III. RESULTS

A. Nucleation of *n*×*n* DAS domains

Figure 1 shows the Si(111) surface at around 490 °C, after the quenching of the clean Si(111) surface from 1100 °C to 400 °C. Both a triangular 7×7 DAS domain and the disordered 1×1 matrix appear. Detailed structures of the triangular 7×7 DAS domain and the 1×1 matrix were described elsewhere.[7,11] Figure 1 shows the nucleation process of the 9×9 DAS structure in the 1×1 matrix. Successive STM images of Fig. 1 were taken on the same 1×1 area, which is verified by the large 7×7 DAS domain appearing in the lower left-hand corner of the images. In Fig. 1(a), only a 7×7 DAS domain is present on the quenched Si(111) surface. Then, a single SF half cell of the 9×9 DAS structure suddenly nucleates in the 1×1 matrix, as pointed out by the arrow in the image in Fig. 1(b), which was acquired immediately after Fig. 1(a). The nucleated SF half cell again collapses in 30 s after Fig. 1(b), as shown in Fig. 1(c). These results indicate that the DAS structures nucleate as single SF half cells in the 1×1 phase. We have observed not only a single 9×9 SF half cell but also single SF half cells of 7×7 and 11×11 DAS structures in the 1×1 matrix. Hence, single *n*×*n* SF half cells are possible to nucleate in the 1×1 matrix. The collapse process of the single SF half cell shown in Fig. 1(c), however, provides the evidence that a single SF half cell is not stable enough to survive at around 490 °C. Therefore, it would be natural to think that various single *n*×*n* SF half cells repeatedly form and collapse in the 1×1 matrix on the quenched Si(111) surface at high temperatures.

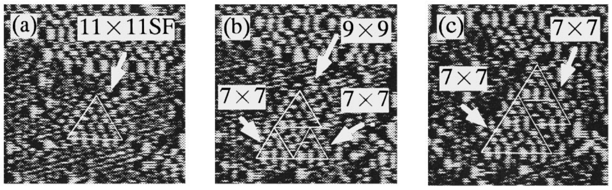

FIG. 2. Formation process of a small 7×7 DAS domain observed at around 450 °C. A single SF half cell of the 11×11 DAS structure is present on the surface in (a). A successive addition of single 7×7 SF half cells at the side of the nucleated SF half cell results in the formation of a small 7×7 domain, as shown in (b) and (c). The single 11×11 SF half cell transforms into the 7×7 SF half cell in (c). The images of (b) and (c) were taken 240 s and 720 s after (a), respectively.

Figure 2 illustrates a series of STM images showing a formation process of a small 7×7 DAS domain in the 1×1 matrix. In Fig. 2(a), a single SF half cell of the 11×11 DAS structure is present on the surface at around 450 °C. At this temperature lower than that in Fig. 1, the growth of SF half cells is slow and the 11×11 SF half cell was kept in the 1×1 matrix during our STM observations. In Fig. 2(b), we see that a DAS domain composed of one 9×9 and two 7×7 SF half cells are formed by sharing corner holes. It is interesting to note that the 11×11 SF half cell transformed into a 9×9 SF half cell. Figure 2(c) shows that the formation of a small 7×7 DAS domain consisted of five SF half cells of the 7×7 DAS structure in the 1×1 matrix. Namely, the 9×9 SF half cell transformed into the 7×7 SF half cell at first and then two SF half cells of 7×7 DAS structure were newly added to the upper right side of the domain of three 7×7 SF half cells. Comparing Fig. 2(a) with Fig. 2(c), it is clear that the SF half cell of the 11×11 DAS structure finally transformed into the 7×7 SF half cell in the 1×1 matrix. This indicates that a *n*×*n* SF half cell with *n* greater than 7 is able to transform into the SF half cells of other sizes at high temperatures. It will be shown later that a large 9×9 DAS domain is constructed by the transformation of 7×7 and 11×11 SF half cells into 9×9 SF cells.

B. Growth of *n*×*n* DAS domains

Dynamic growth features of large domains of 7×7 and 9×9 DAS structures are shown in Figs. 3 and 4, respectively. On the quenched Si(111) surface, not only 7×7 DAS domains, but also 9×9 DAS domains, were observed to be formed in the triangular shape. It is noted, however, that the formation of the 9×9 DAS domain rarely occurred on the quenched surface, i.e., almost all of the DAS domains that we have found in the 1×1 matrix were the triangular 7×7 DAS domains. Both domains gradually expanded on the surface above 480 °C. Figures 3 and 4 clearly show that each domain grows in the same way in the 1×1 matrix, where the subsequent addition of single SF half cells to a side of the triangular *n*×*n* DAS domain one by one leads to the expansion of both domains. These results indicate that the formation of single SF half cells is essential for constructing *n*×*n* DAS domains, and completely explains our recent result that triangular 7×7 DAS domains are always surrounded by the SF half cells on the quenched Si(111) surface.[7] This feature of *n*×*n* DAS domain formation sup-

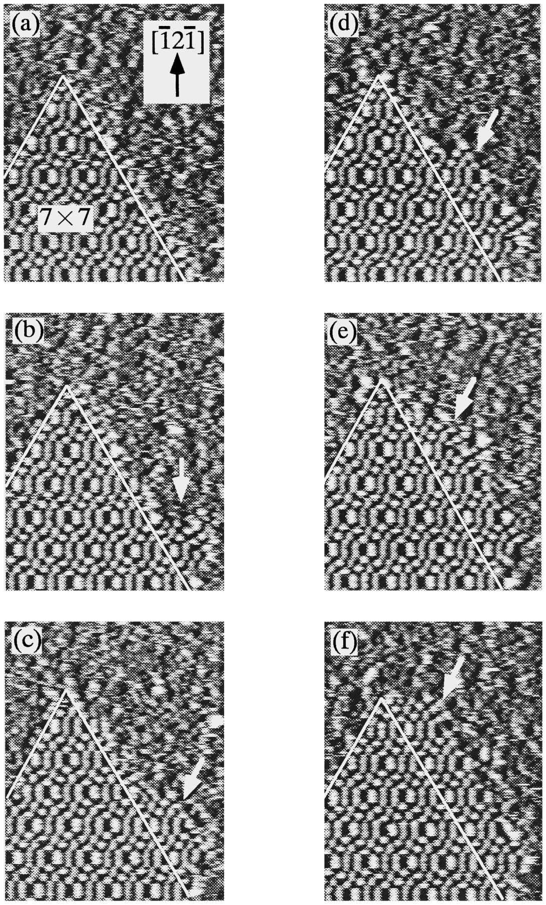

FIG. 3. A series of STM images acquired at around 490 °C showing the growth of a 7×7 DAS domain. Subsequent addition of single 7×7 SF half cells to a side of the 7×7 DAS domain one by one leads to the expansion of the 7×7 DAS domain, as pointed out by the arrows. Each elapsed time after (a) is 15 s in (b), 45 s in (c), 60 s in (d), 75 s in (e), and 120 s in (f).

ports also the nucleation model of an $n\times n$ DAS structure suggested previously by Ohdomari,[12] which predicts that the SF half cell plays a leading role in forming $n\times n$ DAS domains. In Fig. 4(b), a single SF half cell of the 7×7 DAS structure is observed to nucleate at a side of the 9×9 DAS domain and finally transform into the 9×9 SF half cell. We have also found a single 9×9 SF half cell at a side of a 7×7 DAS domain. Hence, it is general that various $n\times n$ SF half cells nucleate at a side of the DAS domains sharing corner holes.

Figure 5 shows the growth of a 9×9 DAS domain on the surface at around 450 °C. In Fig. 5(a), a small 9×9 DAS domain is initially formed on the quenched Si(111) surface, with several 7×7 and 11×11 SF half cells adjacent to the domain. Successive observation of this surface enabled us to see the dynamic growth process of the 9×9 domain. According to Figs. 5(b)–5(d), all of the 7×7 and 11×11 SF half cells subsequently transformed into the 9×9 SF half cells, which results in the formation of a large 9×9 DAS domain [Fig. 5(d)]. It is extremely interesting to note that movement of a corner hole position causes the transformation of the 7×7 and 11×11 SF half cells and the number of SF half cells in the region delineated by the white line is

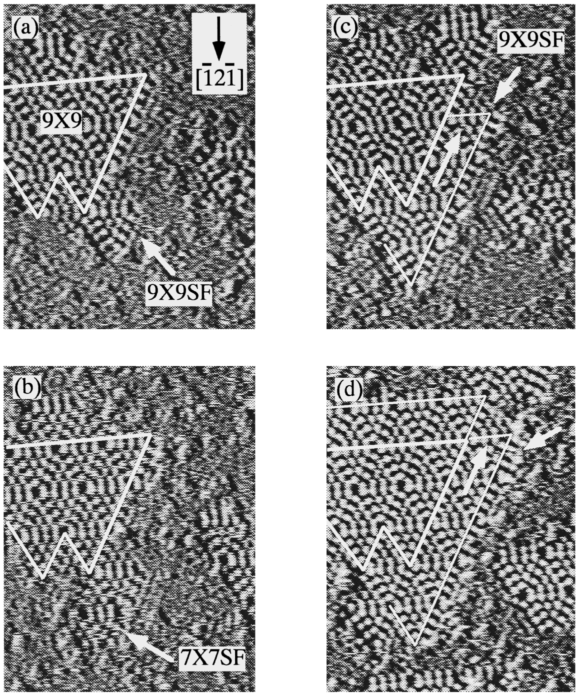

FIG. 4. STM images acquired at around 480 °C showing the growth of a 9×9 DAS domain. The 9×9 DAS domain grows in the same way on the surface as the 7×7 DAS domain with continuous formation of single SF half cells at the domain side, as pointed out by the arrows. A single 7×7 SF half cell nucleates at the domain edge in (b) and finally transforms into a 9×9 SF half cell in (c). Each elapsed time after (a) is 45 s in (b), 105 s in (c), and 240 s (d).

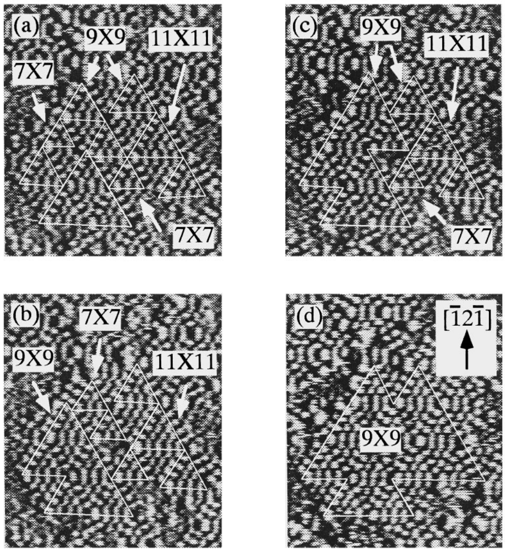

FIG. 5. Growth process of a 9×9 DAS domain observed at around 450 °C. Several SF half cells of 7×7, 9×9, and 11×11 DAS structures are initially formed on the surface in (a). Structural transformation of the 7×7 and 11×11 SF half cells into the 9×9 SF half cells results in the formation of a large 9×9 DAS domain on the surface in (b)–(d). The images of (b), (c), and (d) were taken 90 s, 210 s, and 300 s after (a), respectively.

preserved in Figs. 5(a)–5(d). This indicates that the frame of a SF half cell is determined by the corner hole position.

IV. DISCUSSION

A. Similarity in growth mechanism of $n\times n$ DAS domain with different n

From Figs. 1–3, we understand all stages of 7×7 DAS domain growth in the 1×1 matrix. At the beginning, a 7×7 DAS domain nucleates as a single SF half cell in the 1×1 matrix and a large domain is finally built up by continuous addition of 7×7 SF half cells to the nucleus by sharing the corner holes, as shown in Figs. 2 and 3. Figures 1 and 3 exhibit a growth feature that the stability of a 7×7 DAS domain depends on the domain size, i.e., a single SF half cell collapses in the 1×1 matrix, as shown in Fig. 1(c), while in Fig. 3, a large 7×7 DAS domain survives and grows. These phenomena can be explained by critical nucleus size of the 7×7 domain reported previously by us.[9] Our experimental equation on the temperature dependence of critical nucleus predicts that the domains composed of more than three SF half cells are stable at 490 °C and should expand, while the domains smaller than three SF half cells should collapse. This prediction explains our experimental results in Figs. 1 and 3.

Here, we shall discuss the formation process of $n\times n$ DAS domains with an n other than 7. On the quenched Si(111) surface, formation of various domains of 7×7, 9×9, 11×11, and 13×13 DAS structures has frequently been observed in STM.[10] The $n\times n$ DAS structures with n larger than 7 have interior adatoms, which is an important distinction from the 7×7 DAS structure. In Figs. 3 and 4, we showed the growth of 7×7 and 9×9 DAS domains on the quenched surfaces. According to these figures, both domains grow in exactly the same way, i.e., by adding the SF half cells to a side of the domains. This indicates that the existence of the interior adatoms do not influence the growth process of DAS domains. Thus, it can be expected that the $n\times n$ DAS structures with n larger than 9 also have the same growth process obtained for the 7×7 and 9×9 DAS structures. In this connection, we observed single $n\times n$ SF half cells, with $n=11$ and 13 in the 1×1 matrix, as shown in Fig. 2(a) and in Ref. 8.

B. Change in the SF half cell size and unification of cell size

In Figs. 2, 4, and 5, SF half cells transform into both larger and smaller SF half cells at the sides of 7×7 and 9×9 DAS domains. For example, in Fig. 4, the 7×7 SF half cell transforms into the 9×9 SF half cell at a domain side, while Fig. 2 shows that the 11×11 SF half cell changes to a 7×7 SF half cell. At an $n\times n$ domain side, the formation of SF half cells with different n is possible, as shown in Figs. 3–5. Figure 4(b) is a good example of size mismatch, i.e., a 7×7 SF half cell is formed at the 9×9 domain side. Size mismatch produces domain boundaries at a domain side in the growth of an $n\times n$ DAS domain. Obviously, the domain boundaries are not stable energetically. Therefore, rearrangement of domain size to eliminate size mismatch becomes favorable.

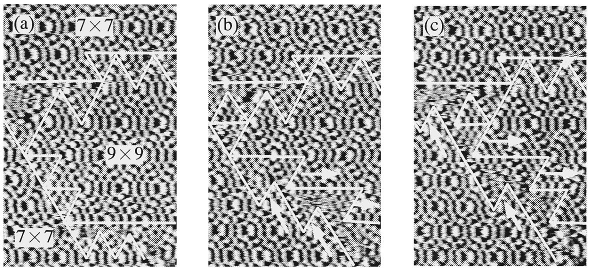

FIG. 6. Successive STM images observed at around 520 °C. In (a), a 9×9 DAS domain is formed on the surface, surrounded by the 7×7 DAS domains. The 9×9 DAS domain shrinks following the expansion of the 7×7 DAS domain in (b) and (c).

The growth of a large 9×9 DAS domain, due to rearrangement of $n\times n$ SF half cells with $n=7$, 9, and 11, is typically shown in Fig. 5. The white line in the figure represents the boundary between the 9×9 DAS domain and the SF half cells with 7×7 and 11×11 structures. The growth of the 9×9 DAS domain shown in Fig. 5 is regarded as the process where the length of the white line becomes shorter. In Fig. 5(a), the boundaries between different SF half cells have many mismatches in the positions of corner holes. These mismatches generate many dangling bonds on the surface. Recently, it was reported that structural distortion was induced at the boundary between different structures of 7×7 DAS domains and the 1×1 matrix.[13] The region shown in Fig. 5(a), which contains many SF half cells of different sizes, is considered not to be favorable energetically. In contrast, Fig. 5(d) shows that structural transformation of 7×7 and 11×11 SF half cells into 9×9 SF half cells results in the formation of a large 9×9 DAS domain, where all the corner holes inside the 9×9 domain are shared by each of the 9×9 SF half cells. Accordingly, the 9×9 DAS domain in Fig. 5(d) is more favorable than the region in Fig. 5(a). Thus, SF half cells tend to change their sizes to eliminate mismatch. The fact that the adjustment of corner hole position causes the unification of the SF half cell size reveals that movement of the corner hole position induces a change of the SF half cell size. It was previously suggested that the formation of corner holes is closely related with the presence of surface oxygen atoms.[12] Hence, we dare to consider that movement of surface oxygen atoms induces change of SF half cell size.

C. Stability of $n\times n$ DAS domains

As shown in Fig. 4, the 9×9 DAS domain nucleates and grows in the 1×1 matrix. This indicates that the 9×9 DAS structure is energetically more stable than the 1×1 matrix at the temperature around 480 °C. Similarly, the experimental result that various $n\times n$ DAS domains with $n=5$, 7, 9, 11, and 13 are formed on the quenched Si(111) surface[7,10] suggests the stability of these $n\times n$ DAS domains, compared with the 1×1 matrix. On the surface covered with various $n\times n$ DAS domains, there must be domain boundaries between different structures. In fact, we have found the domain boundaries formed between 7×7 and 9×9 DAS domains on the quenched surface at around 520 °C, as shown in Fig. 6. Figure 6 shows that a 7×7 DAS domain grows by adding

SF half cells to a side of the domain, while a 9×9 DAS domain shrinks by losing 9×9 SF half cells. We previously reported that the 5×5 DAS domain also was replaced by the 7×7 DAS domain on the surface at above 500 °C.[11] These results provide direct evidence that the 7×7 DAS structure is the energetically most stable structure on the Si(111) surface. Therefore, it is concluded that all of the metastable $n\times n$ DAS domains formed on the quenched Si(111) surface are replaced by the 7×7 DAS domains at the end.

V. CONCLUSION

We have studied the nucleation and growth process of $n\times n$ DAS domains on the quenched Si(111) surfaces at above 450 °C, using high-temperature STM. The $n\times n$ DAS domain nucleates as a single SF half cell in the 1×1 matrix. The successive addition of a single SF half cell to a side of the single SF half cell or small DAS domain results in the growth of a large domain. Unification of $n\times n$ SF half cell size occurs frequently at the boundaries of $n\times n$ domains, with different n in order to eliminate mismatch. All of the metastable $n\times n$ DAS domains ($n\neq 7$) formed on the quenched Si(111) surface do not survive, but transform into the most stable 7×7 DAS domains at the end.

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