Formation and annihilation of various stacking-fault half units in dimer–adatom–stacking-fault structures on quenched Si(111) surfaces

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The formation and annihilation of a stacking-fault (SF) half unit in dimer–adatom–stacking-fault (DAS) structure on the Si(111) surface have been investigated quantitatively by the scanning tunneling microscopy observations of the quenched surface at several temperatures ranging from 380 to 500 °C. It has been revealed that the formation rate of the SF half unit increases with the number of corner holes shared with the preexisting DAS domain and decreases with the size of the SF half unit. The annihilation of the SF half unit sharing one corner hole becomes more frequent than its formation at higher temperatures. From the Arrhenius plots, the activation energies for the formation and the annihilation have been deduced to be around 1.5–1.7 eV and 2.4 eV, respectively.

Si(111) dimer–adatom–stacking-fault (DAS) reconstruction is one of the most studied subjects in semiconductor surfaces. The DAS model proposed by Takayanagi *et al.*[1] is a widely accepted atomic arrangement of the most stable 7×7 structure as well as the metastable structures with the periodicity of $n\times n$ (n is odd). A variety of the experimental techniques has revealed the dynamical process of the $1\times1 \rightarrow$ DAS structural phase transition. It has been found that the DAS domain nucleates preferentially at step edges but also inside terraces, and grow in a triangular shape with the vertices pointing in $\langle\overline{112}\rangle$ direction.[2,3] Our high-temperature scanning tunneling microscopy (STM) observations of quenched Si(111) surfaces have shown that the growth of the DAS domain is dominated by the formation of stacking fault (SF) half units with sharing corner holes with the preexisting SF units[4,5] and that the critical domain size between expansion and shrinkage exists for the growth of 7×7 DAS domains.[6] Recently, it has been reported by several STM works that the formation of a SF half unit proceeds through the step-by-step size change of the SF half unit.[7–9] In spite that almost full understanding has been obtained concerning the qualitative features of the $1\times1\rightarrow$ DAS phase transition except the atomic-scale mechanism of the DAS formation, the quantitative information on the rate or the activation energy for the formation of the DAS structure has not been derived yet. These information will be important for the theoretical investigation of the atomic-scale dynamics, although only a few theoretical works using Monte Carlo[10] or extended Huckel molecular orbital[11] methods have been performed so far because of the limitation due to the large unit cell of the DAS structure.

In this paper, we report the rate and the activation energy for the formation and annihilation of SF half units determined by *in situ* STM observations of a quenched Si(111) surface at several temperatures ranging 380–500 °C. In this temperature range, the DAS domain growth is slow enough to see the appearance and disappearance of individual SF half units with the real-time STM. Further, the atomic-scale STM observations enable us to classify the SF half units according to the number of corner holes shared with the preexisting DAS domain and the size of the SF half unit. In this work, not only the quantitative data have been provided, but also the dependence of the rate and the activation energy on the number of shared corner holes and the SF size have been investigated. The formation process of the SF half unit and the growth process of the DAS domain will be discussed based on the data acquired for the following processes: (1) the formation of the SF half units sharing different number of corner holes, (2) the formation of $n\times n$ SF half units with different n, and (3) the annihilation of the SF half units.

The STM experiments in this work are the same in our recent work.[9] The details of the experimental conditions and procedures were described in Ref. 9.

Figure 1 shows the typical STM images of the first and the last in a sequential STM images of the quenched Si(111) surface acquired at (a) 500, (b) 440, and (c) 380 °C. The bottom images of (a′),(b′), and (c′) were taken 924, 1091, and 3326 s after the respective top images in the same surface area. The boundary edges between the DAS and 1×1 regions in the top images are shown by solid white lines in both of the top and bottom images, and new edges of the expanded DAS region by broken lines in the bottom images. In the top images, only a part of the surface is covered with the DAS region, and the high-temperature 1×1 phase remains in the large area. During the STM observations, the DAS domains gradually expanded into the 1×1 area. As can been seen in Fig. 1, the growth rate of the DAS domain largely depends on the temperature. The number of newly formed SF half units is 70 in about 15 min at 500 °C in (a), 15 in 18 min at 440 °C in (b), and 8 in 55 min at 380 °C in (c).

Figure 2 shows a series of the STM images obtained at 500 °C in the area surrounded by the black line in Fig. 1(a). The 7×7 DAS domain in the right side of the images was enlarged by the one-by-one addition of 7×7 SF half units sharing corner holes with the preexisting DAS domains, as indicated by the arrows. It should be noted that the formation of SF half units takes place with sharing various numbers of

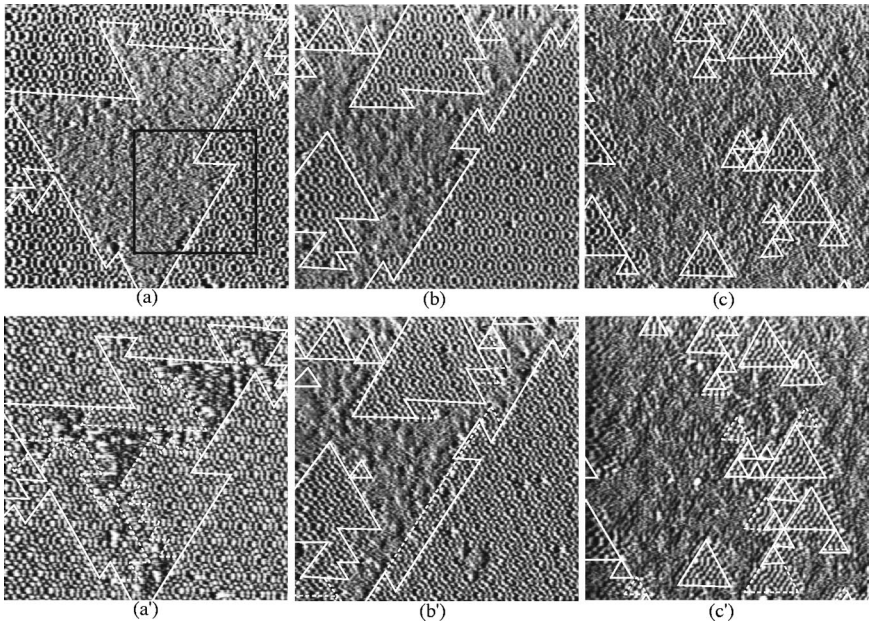

FIG. 1. Typical STM images of a quenched Si(111) surface acquired at the temperatures of (a) 500, (b) 440, and (c) 380 °C. All the images of 50×50 nm^2 were acquired with a constant height mode and a sample bias voltage of +1 V. The bottom images of (a′), (b′), and (c′) were taken after 924, 1091, and 3326 s from the respective top images. The solid white lines show the edge of the DAS domain in the top images, and the broken lines the edge of the domain in the bottom images. The faster growth of the DAS domains at the higher temperature can be clearly recognized.

corner holes; one in (c), two in (e) and (f), and three in (b). The annihilation of SF half units, as shown in Fig. 2(d), and the formation of the metastable SF half units such as 5×5 and 9×9 were also observed in our successive STM images.

To begin with, the formation rates of 7×7 SF half units have been measured as a function of the number of shared corner holes. The corner hole we call here implies an apex of a SF triangle, not necessarily a perfect ''hole'' on the surface. Figure 3 shows the Arrhenius plots of the formation rate of 7×7 SF half units sharing 1–3 corner holes. The formation rate was determined by dividing the number of the occasion of the formation by the total existing time of the formation site. It is found in Fig. 3 that the formation rate depends on the number of shared corner holes; it becomes lower for the 7×7 SF half unit sharing less corner holes at all temperatures. The activation energy for the 7×7 SF formation determined from the Arrhenius plots in Fig. 3 is listed in Table I together with the pre-exponential factors. It is found that the 7×7 SF formation is produced with the activation energy of around 1.5–1.7 eV. In the previous work, using a simple growth model of a DAS domain and assuming the frequency factor to be a general value of 10^{13}s^{-1}, we estimated the activation energy for the SF formation to be 2.4 eV.[12] However, the formation rate itself, which is determined by the previous activation energy and frequency factor in the Arrhenius equation, is almost the same with the present value. As shown in Table I, the activation energy for the 7×7 SF formation also varies with the number of shared corner holes; it becomes lower for the SF formation with sharing more corner holes. The dependence of the rate and activation energy for the formation on the number of the shared corner holes indicates that corner holes play a leading role in the formation process of the SF half unit.

The importance of the corner holes to the formation of SF half units was first predicted by one of the authors (I.O.).[13] He proposed the model for the formation mechanism of the 7×7 structure, in which the SF region nucleates from the corner holes. Our previous STM work showed a single SF half unit sharing one corner hole at a side edge of a 7×7 domain, which indicates the formation of the SF half unit from a corner hole.[4] Miyake *et al.*[14] and Koike *et al.*[15] also have pointed out the important role of the corner holes based on the STM results. The formation of a SF half unit without sharing corner holes, i.e., the appearance of a single SF half unit in the disordered 1×1 region, was also observed in our high-temperature STM observations, but its formation rate is

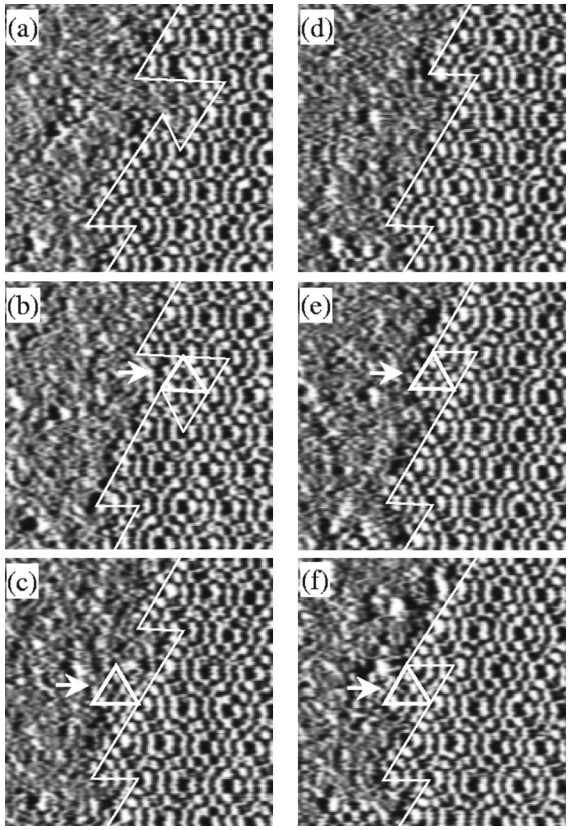

FIG. 2. Successive STM images (16×16 nm^2) taken every 8.8 s at 500 °C in the surface area indicated by the black line in Fig. 1(a). 7×7 SF half units were added to the preexisting DAS domain sharing one corner hole in (c), two in (e) and (f), and three in (b), as pointed by the arrows. The disappearance of the 7×7 SF half unit sharing one corner hole were also observed in (d).

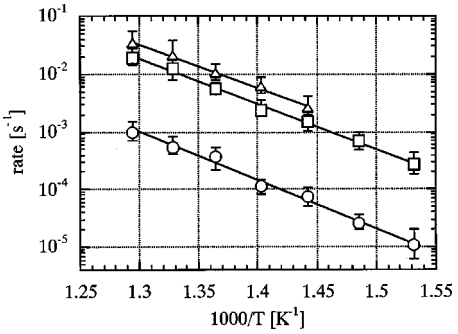

FIG. 3. Arrhenius plots for the formation rate of 7×7 SF half units sharing one (○), two (□), and three (△) corner holes. The formation rate is higher for the SF half units sharing more corner holes. The activation energy and the preexponential factor are listed in Table I.

quite low compared to that with sharing corner holes. The formation with sharing corner holes was observed about 1600 times in total, whereas the formation without sharing corner holes was only 15 times. Note that the number of the sites for SF formation without sharing corner holes is much larger than that with sharing one corner hole. The preferential nucleation of the SF half unit at the corner hole site might be similar to the preferential nucleation of DAS domains at the step edge. These are considered to be caused by the easy formation of strained dimers or the easy movement of a Si atom from an UF site to a SF site. The leading role of the corner hole would be the key to understanding the nucleation mechanism of the SF region.

Next, we focused on the formation of SF half units with different sizes. In our STM observations, SF half units with the sizes of 5×5–15×15 were observed. Among them, the formation rates were measured for the 5×5 and 9×9 SF half units sharing two corner holes. Figure 4 shows the Arrhenius plots of their formation rates together with that of the formation rate of the 7×7 SF half unit sharing two corner holes. Only three plots for the formation of the 5×5 SF half unit are obtained because of the rareness of its formation. 5×5 domains consisting of more than three 5×5 SF units were not observed at all inside the terraces, excluding around the void created by an STM tip, and the 5×5 SF formation with sharing two corner holes took place only at the edge of DAS domains composed of 7×7, 9×9 or 11×11 SF half units. On the other hand, large 9×9 domains composed of more than forty 9×9 SF units were observed, and the formation took place one after another along the side of the 9×9 domains sharing two corner holes. Note that the favorable DAS size is different between on the terraces and at the step edges, which has been discussed elsewhere.[9]

In Fig. 4, it is found that the formation rate becomes higher for the smaller SF half unit at all temperatures. Recently, several STM works[7–9] have revealed the formation process of the SF half unit sharing one corner hole, in which small size of the SF half unit nucleates from one corner hole at first and then the SF region expands step by step. This process agrees with the result of the higher formation rate for the smaller SF half unit. Further, it would be suggested that the SF formation with sharing two corner holes proceeds from one corner hole through the size changes as well. The activation energy for 9×9 SF formation are shown in Table I. For the formation with sharing two corner holes, the 9×9 SF half unit has a little smaller activation energy than the 7×7, but the dependence of the activation energy on the SF size cannot be definitely concluded from this result.

Finally, the annihilation of the SF half units has been investigated. In our high-temperature STM observations at 380–500 °C, the annihilation was not observed for the SF half units sharing two and three corner holes at all but frequently for the SF half units sharing one corner hole and the SF half units isolated in the 1×1 region. This is thought to be due to the decrease in the peripheral length of the DAS domain upon the annihilation of the latter SF half units, as we reported previously.[16] The annihilation rate has been determined for the 7×7 SF half unit sharing one corner hole by dividing the number of times for observing the annihilation by the total existing time of the SF half unit sharing one corner hole. Figure 5 shows the Arrhenius plot of the annihilation rate together with that of the reverse change of the formation with sharing one corner hole, and the activation energy and pre-exponential factor are listed in Table I. It is revealed from Fig. 5 and Table I that the annihilation rate is higher than the formation rate and that the activation energy for the annihilation is higher than that for the formation. In our previous STM work,[6] the critical size of the DAS domain upon the nucleation has been explained on simple nucleation and growth theory, in which the Gibbs free energy change is given as a sum of the energy gain due to the transition to the stable DAS phase and the energy loss due to the strain at the periphery of the domain. The energy gain due to the transition decreases as the temperature increases, which is considered to be the reason why the annihilation is more frequently observed than the formation at higher temperature.

Although the annihilation rate is higher than the formation rate, some of the SF half units sharing one corner hole changed the number of the shared corner hole from one to two by the formation of a new SF half unit at the adjacent site and survived. In our observations at 380 °C, 36% of the SF half units sharing one corner hole disappeared, whereas the rest of 64% survived. On the other hand, at the higher

TABLE I. Activation energy and preexponential factors for the formation and annihilation of SF half units.

		Number of shared corner hole	Activation energy (eV)	Preexponential factor (s^{-1})
Formation	7×7 SF	1	1.67 ± 0.31	$10^{7.9\pm2.2}$
		2	1.54 ± 0.16	$10^{8.3\pm1.6}$
		3	1.49 ± 0.52	$10^{8.3\pm3.6}$
	9×9SF	2	1.45 ± 0.29	$10^{7.5\pm2.0}$
Annihilation	7×7SF	1	2.42 ± 0.28	$10^{14.7\pm2.0}$

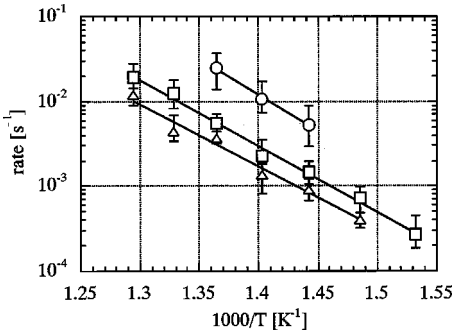

FIG. 4. Arrhenius plots for the formation rate of SF half units with the sizes of 5×5(○), 7×7(□), and 9×9(△) sharing two corner holes. The formation rate is higher for the SF half units with the smaller size. The activation energy and the preexponential factor are listed in Table I.

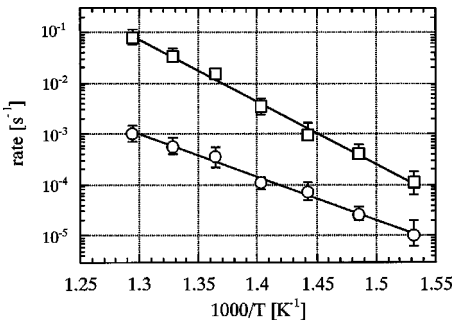

FIG. 5. Arrhenius plots for the formation (○) and annihilation (□) rates of SF half units sharing one corner hole. The annihilation takes place at higher rates than the formation at all the temperatures, and the temperature dependence of the annihilation rate is larger than that on the formation rate. The activation energy and the preexponential factor are listed in Table I.

temperature of 500 °C, only 30% of the SF half unit survived and contributed to the subsequent growth of the DAS domains. As a result, the configurations of the DAS domains at the high and low temperatures are different. The boundaries between the DAS and 1×1 regions at 500 °C are more straight compared to those at 380 °C, as can be seen in Figs. 1(a) and 1(c). Namely, it can be said that the periphery of the DAS domains becomes shorter at higher temperature. As seen in our previous STM study,[4] the periphery of the domains is more straight at 600 °C, where the SF half unit sharing one corner hole was not observed at all with STM due to its very short lifetime. It can be concluded from the STM results that the annihilation of the SF half units largely affects the growth of the DAS domains.

In conclusion, *in situ* STM observations of the Si(111) quenched surface at 380–500 °C has revealed the following findings in the kinetics of the DAS domain growth. (1) The formation rate of the SF half unit depends on the number of shared corner holes and the size of the SF half unit; it becomes higher for the SF half unit sharing more corner hole and the SF half unit of the smaller size. This can be explained by the formation process of the $n\times n$ SF half unit in which a small SF unit nucleate from a corner hole and expands its size step by step. (2) The SF half units is produced with the activation energy of around 1.5–1.7 eV, which also depends on the number of shared corner holes. It decreases as the SF half unit shares more corner holes, which suggests that the corner hole plays an important role in the formation of the SF half unit. (3) The annihilation of SF half unit sharing one corner hole has higher rate and higher activation energy, 2.4 eV, than the reverse process of the formation. This affects the growth of the DAS domain, that is, the growth proceeds with the shorter periphery of the domain at higher temperature.

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