Interactions of Br with Si(111)-7 \times 7: Chemisorption, step retreat, and terrace etching

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The dissociative chemisorption of Br_2 on Si(111)-7×7 and the effects of spontaneous etching have been studied with scanning tunneling microscopy as a function of temperature, flux, and fluence. At room temperature, the Si surface retains the 7×7 reconstruction, and bias-dependent imaging reveals Br bonding to adatom and rest-atom dangling-bond sites. For $700 \le T \le 900$ K, terrace etching involves Si removal from adatom sites and conversion to a 1×1 periodicity that is stabilized by Br. In this temperature range, bilayer step flow etching dominates and Si removal is fastest along $\langle 1\overline{10} \rangle$. Regrowth structures derived from six-membered Si rings terminated by Br appear near the bilayer steps. They are more common near steps that descend along $[\overline{1}\,\overline{1}2]$ than those that descend along $[1\overline{2}1]$ or $[\overline{2}11]$, a distribution that reflects differences in the atomic scale bonding at the steps. Step flow continues at 1000 K but terrace pitting is also activated. This produces triangular bilayer pits bounded by $\langle 1\overline{10} \rangle$ edges. Analysis yields the ratio of the rates of formation of terrace pits and step kink formation, giving a difference in activation energies for these processes of 0.8 eV. Flux-dependent studies at 1000 K show that pit sizes and densities vary dramatically, an effect related to the mean Br content on the terrace. No such dependence was observed at 900 K because pits could not be formed and the terraces were inactive once converted to 1×1 . At 1100 K, etching produces disordered vacancy clusters in the adatom layer. The presence of small ordered domains amidst randomly distributed adatoms is attributed to facile local removal. In all cases removal proceeds in a layer-by-layer fashion because of the striking anisotropy in etching energetics.

I. INTRODUCTION

Investigations of the spontaneous etching of semiconductor surfaces by molecular halogen beams have provided important insights into surface chemical processes. In turn, those insights have been helpful in modeling the more complicated environments prevalent in halogen plasma etching.¹ In particular, they offer an understanding of the mechanisms and energetics of etching with respect to the formation and evolution of volatile species. Recent studies of etched surfaces using atomic resolution scanning tunneling microscopy (STM) have contributed to the overall understanding of etching by revealing the morphology of the surface before and after modification.²⁻⁵ For example, investigations of Si(100)after 2×1 have demonstrated that spontaneous etching occurs via Si removal at steps and the creation of single-layerdeep etch pits on terraces. For Si(100)-2×1, distinct etching pathways have been identified from analysis of STM images, and it has been possible to deduce etching energetics and kinetics.⁶

The bonding configurations of Si(111)-7×7 are more varied than those of Si(100). Etching of this surface with oxygen^{7,8} has been characterized by material removal from steps and the formation of bilayer pits on terraces. Also observed were metastable 5×5 and 9×9 domains when the exposed layer could reconstruct. STM studies of wet-etched Si(111) (Refs. 9–11) showed directional anisotropies as well as terrace pitting and step retreat. STM investigations of the interaction of beams of Cl₂ with Si(111)-7×7 (Refs. 4 and 12–14) have emphasized chemisorption dynamics leading to preferred bonding sites and

the initial formation of volatile species.

Here, we have used STM to examine the interaction of molecular bromine with Si(111)-7×7 at $300 \le T \le 1100$ K. We discuss chemisorption at 300 K to identify the adsorption sites. Temperature-, flux-, and fluence-dependent studies indicate etching from the Si adatom layer and transformation from the 7×7 reconstruction into a Br-stabilized 1×1 structure. We also found step retreat characterized by directional anisotropies, regrowth structures involving six-membered Si rings, and terrace roughening due to flux-dependent pitting. From quantitative analysis of bilayer pit distributions near steps, we determined the difference in activation energies for pit formation and step kink formation.

II. EXPERIMENT

The experiments were performed in an ultrahigh vacuum chamber equipped with a Park Scientific Instruments Autoprobe VP AFM/STM. The base pressure of the system was 5×10^{-11} Torr. Silicon wafers oriented to within 0.3° of (111) and miscut along [112] were rinsed in ethanol prior to introduction into the vacuum chamber. The wafers were degassed at 875 K for several hours and flashed to 1475 K for 1–2 min. This procedure produced clean, well-ordered Si(111)-7×7 with defect densities $\leq 1\%$. Sample temperatures were monitored with an optical pyrometer and were typically controlled to ± 10 K. Electrochemically etched tungsten tips were cleaned using electron bombardment. Scan dimensions were calibrated against the size of the Si(111)-7×7 unit cell and

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the height of bilayer steps. The STM micrographs shown here were acquired in a constant current mode at room temperature with sample bias between -4 V and +3.5V. The images were not corrected for thermal drift.

An electrochemical cell made by doping a AgBr pellet with $CdBr_2$ was used as a Br_2 source. An applied voltage caused diffusion of halogen ions to a Pt mesh electrode where they combined and desorbed as Br₂. During exposure the sample was ~ 3 cm from the mesh electrode. During operation of the cell, the chamber pressure remained below 1×10^{-10} Torr. Stable cell currents of 2 to 120 μ A were used, releasing ~6.2×10¹² to $\sim 7.5 \times 10^{14}$ molecules/sec. Bromine exposures were done under conditions of constant flux, with fluences expressed in units of mAs. In most cases, the samples were cooled rapidly to room temperature immediately upon terminating the flux. For high-temperature studies, it is likely that Br was lost during sample cooling after exposure via etching and measurements of absolute Br concentrations at specific conditions of etching were not viable. Under our experimental conditions, fluences of 1.0 mAs corresponded to approximately 1×10^{15} molecules/cm² (dangling bond density for the 7×7 reconstruction is 3.04×10^{14} cm⁻²). Note, however, the sticking coefficient will depend on surface conditions and temperature, and the etching of Si(111)-7 \times 7 produces a 1 \times 1 unit cell with a higher number of surface bonds $(7.83 \times 10^{14} \text{ cm}^{-2})$.

III. CHEMISORPTION AT 300 K

In this section, we focus on the dissociative chemisorption of Br_2 at 300 K and compare to results for H- and Cl-Si(111)-7×7. For reference, Fig. 1 shows top and side views of the 7×7 unit cell of Si(111) according to the



FIG. 1. Schematic of Si(111)-7 \times 7 unit cell showing (a) top and (b) side views. The side view in (b) follows the long axis of the unit cell. The faulted half of the unit cell is on the left and the unfaulted on the right. The 19 dangling bonds per unit cell are derived from adatoms in the top layer (12), exposed rest atoms in the next layer (6), and exposed bulk atoms at corner holes (1). The dashed lines denote unit-cell boundaries defined by dimer rows. Nucleation of the 7 \times 7 reconstruction at a step edge exposes these dimer rows.

model of Takayanagi *et al.*¹⁵ Each of the 12 Si atoms in the adatom layer (large solid circles) is a dangling-bond site. These adatoms can be distinguished as corner and center adatoms according to their proximity to the corner holes, as labeled. There are 42 rest atoms in the next layer, six of which are dangling-bond sites (shaded circles). There is also a dangling bond in the highest bulk layer at each corner hole, giving a total of 19 dangling bonds per unit cell. The dashed lines outlining the unit cell locate the dimer-chain walls of the reconstruction. These walls give rise to stacking faults in alternate halves of the unit cell.

Figure 2 shows occupied state micrographs acquired at different sample bias voltages after 0.1-mAs exposure at room temperature, corresponding to $\sim 1.0 \times 10^{14}$ Br atoms/cm². The same 7×7 unit cell is outlined in each image to show that the reconstruction is not disturbed by chemisorption. At the highest bias (-3.5 V on the sample), the image is speckled with bright features that we associate with Br adsorption at Si adatom positions. The number of such features increases with exposure. Their presence as single spots indicates dissociative chemisorption. This is consistent with on-top reaction of Br with Si(111)-7 \times 7 deduced from x-ray standing wave measurements.¹⁶ At lower sample bias, the bright spots tend to disappear and darker regions emerge. As discussed by Boland and Villarrubia^{12,13} for Cl-Si(111)-7 \times 7, the occupation of Si dangling bonds reduces the electron density near E_F so that adsorption sites appear dark relative to unreacted sites when imaged at low magnitude bias. At higher magnitude biases, bonding states (negative sample bias) or antibonding states (positive sample bias) formed by the interaction of the Br 4p orbitals and the Si adatom dangling bonds can be accessed and the sites appear bright.

Coverage-dependent adsorption studies were undertaken to determine whether there were preferential adsorp-



FIG. 2. 135×135 -Å² images after 0.1-mA s exposure to Br₂ at 300 K showing the same area with sample bias voltages recorded in the insets. The same unit cell is outlined in each. Br is observed to adsorb at adatom and rest-atom dangling-bond sites. Most dark areas seen at low magnitude bias were bright at high magnitude bias. The arrow indicates a dark area that did not become bright at higher bias.

tion sites within the 7×7 unit cell. This was motivated by the observation by Avouris and Wolkow¹⁷ that corner adatoms tend to be less reactive than center adatoms. Such preferred bonding could be due to the different coordination of corner and center adatoms with respect to rest-atom dangling bonds and to dimers that induce strain (Fig. 1). With images like those in Fig. 2, we were able to quantify Br adsorption with site specificity as a function of exposure. It should be noted that although tip-induced effects were rare (such as displacement of a Br atom from one site to another during scanning), we took special care to exclude such events in our analysis. The statistical distributions indicated equal occupancy of corner and center adatoms and an overall scaling with exposure. We found no preference for adsorption near missing adatoms or steps. Hence, thermally activated diffusion of Br is insufficient to allow sampling sites of higher chemical activity. Processes associated with molecular dissociation, Si-Br bond formation, and motion driven by the release of the condensation energy need not yield equilibrium structures (thermochemical data give 1.9 eV for a Br-Br bond and 3.6 eV for a Si-Br bond).

The distribution of Cl on Si(111)-7 \times 7 has been used by Yan, Jensen, and Kummel¹⁴ to distinguish between precursor-mediated reaction and direct-activated reaction. After exposing Si(111)-7 \times 7 to Cl₂ beams having energies of 0.05-0.44 eV, they deduced that beams with energies of ≤ 0.11 eV produced islands of Cl-terminated Si and a background of Cl bound to Si adatoms. Island formation was attributed to a physisorbed precursor state that allowed Cl₂ to diffuse sufficiently to reach the growing islands where dissociation would occur. Island structures were not observed for beams with an energy of ~ 0.44 eV but dissociative chemisorption led to center adatom occupation twice that of the corner adatom occupation. In our experiments, we find equal occupancy of corner and center adatoms with no indication of island formation after impingement of Br₂ at near-normal incidence from a thermal source (temperature ~ 400 K). Our results indicate direct dissociative chemisorption on Si(111)-7×7 with no mobile precursor state. This could be due to a lower barrier to dissociation of Br₂ relative to Cl₂ (Cl-Cl bond strength 2.5 eV compared to 1.9 eV for Br-Br). Boland and Villarrubia¹² found that Cl adsorbed at center and corner adatoms with equal probability. They noted that their source produced a significant amount of atomic Cl, which they expect to react without ample site sampling, though again the chemisorption energy itself would activate hopping until thermalization was achieved.

Inspection of Fig. 2 shows dark areas at low bias that do not become bright at high bias. An example is indicated by the arrow. These features show no site selectivity, although the total area of the dark features scaled with exposure. It may be that they reflect adsorption in the rest-atom layer. Avouris and Wolkow¹⁷ found that the rest atoms were more reactive than the adatoms because the special coordination of the adatoms hinders dangling-bond saturation. Halogen adsorption in this rest layer would reduce the local electron density near the Fermi level and would affect tunneling conditions. This could account for the dark patches at low bias. However, bright spots at higher bias would not be seen since the tip cannot directly probe these next-layer atoms. Bonding to rest atoms of Si(111)-7×7 has been suggested for Cl based on electron energy loss spectroscopy,¹⁸ for H based on infrared spectroscopy,¹⁹ and for NH₃ from STM analysis.¹⁷ Adsorption at rest atoms was not discussed for STM studies of Cl-Si(111)-7×7 (Refs. 12 and 13) or H-Si(111)-7×7.²⁰

Saturation coverage for Si(111)-7×7 was achieved with ~ 1.5 -mA s fluence at 300 K. This corresponds to 3×10^{14} Br atoms/cm², assuming that all dangling bonds in adatom, rest-atom, and corner hole sites are satisfied (19 per unit cell). Under these conditions, *I-V* curves showed a gap approximately between -3 V and +1 V so that atomic resolution imaging was not possible in this bias range. Images obtained outside of this range resembled those for the clean surface since Br saturated the adatom dangling bonds. This surface was sufficiently passivated that atomic resolution was possible after allowing the sample to reside in the chamber for over 12 h (clean surfaces degrade after ~ 6 h at 6×10^{-11} Torr). Heating to 1100 K for 10 min restored a clean surface.

IV. SPONTANEOUS ETCHING

Heating to 500-650 K during Br₂ exposure leads to a conversion to a 1×1 structure after ≥ 3 mA s fluence and suitable annealing (15-20 min) with minimal etching, as confirmed by temperature programmed desorption results on Si surfaces.²¹ During this process, bilayer islands are formed that have a characteristic dimension of 10-30 Å. They reflect the accumulation of atoms that had originally constituted the adatom layer. Adatoms not contributing to island formation are consumed by healing dimer chain walls of the reconstruction. After exposures in this temperature range, we observed no evidence for etching such as terrace pit formation or step edge roughening. Equivalent results have been discussed by Boland and Villarrubia^{12,13} and by Owman and Mårtensson²² for Cl- and H-Si(111)-7 \times 7, respectively. As noted, the driving force for the 7×7 reconstruction is lost when the Si dangling bonds are saturated by halogens or hydrogen. Conversion to the Br stabilized $(111)-1 \times 1$ structure is accomplished by thermally activated transport and this requires the long anneals reported above.

Spontaneous etching of Si(111) can be observed during exposure at $700 \le T \le 1100$ K. As discussed below, distinct pathways were identified that resulted in step retreat (dominant for 700-900 K), terrace pitting (1000 K), and surface disordering (1100 K). Each temperature regime is characterized by different sensitivities to Br₂ flux and fluence.

A. Fluence dependence and step retreat at 900 K

Figure 3(a) shows a surface etched using a flux of 20- μ A Br₂ at 900 K. The fluence, 0.6 mA s, was about onetenth that needed to reach steady-state terrace morphology. Crossing the image is a bilayer step descending along [112] due to wafer miscut (by convention, we refer to bi-

layer steps by their descending direction). After etching, such steps were characterized by irregularities that averaged ~ 200 Å in length, in contrast to the straight steps observed for clean surfaces. The irregularities tend toward triangular shapes defined by $[1\overline{2}1]$, $[\overline{2}11]$, and [112]step segments with those of $[1\overline{2}1]$ and $[\overline{2}11]$ nature accounting for more than 90% of the total step length. Also evident is an island on the lower terrace, labeled I, that represents a terrace remnant. Such islands were formed when a peninsula was isolated by etching. Their average separation along the steps was $\sim 2 \ \mu m$. Their distance from the parent step, no more than 1500 Å, established a lower limit to the amount of step retreat. The islands were subject to etching from their edges and eventually were consumed. It is likely that the peninsula that produced the island of Fig. 3(a) was quite large. The beginning of island formation is indicated by the bold arrow



FIG. 3. Etching at 900 K proceeds via step retreat and Si adatom removal (flux 20 μ A; fluence about 10% of that needed to achieve steady-state terrace appearance). (a) Step profiles are defined by triangular peninsulas with step-down directions indicated. The island *I* represents the remnant of a back-cut peninsula. The bold arrow indicates where Br etching has exposed a $[11\overline{2}]$ step so that a small island may develop. (b) Terrace image for an area far from a step showing changes in the original surface layer. Dark areas are missing adatoms. Four intact corner holes are connected and shown in the inset. Features denoted *X* probably represent SiBr_x moieties that did not desorb. All exposed dangling bonds are terminated by Br.

of Fig. 3(a), though the resultant island would be small and short lived.

The image of Fig. 3(b) shows that the terraces of Fig. 3(a) were irregular with a large number of randomly distributed adatom vacancies. (This image was obtained for an area that was far from a step so that it represents changes in the original surface.) Despite the vacancies, the 7×7 reconstruction persisted (a unit cell is drawn connecting four intact corner hole sites). Bias-dependent imaging revealed that the dark patches were missing Si adatoms, not Br adsorption sites, in contrast to what was observed after room-temperature chemisorption. The remaining Si adatoms were Br terminated and appeared as bright spots. The dark areas never represented more than a few adatom vacancies, and no defects were found in the exposed rest-atom layer. From the surface of Fig. 3, we estimate that 0.9×10^{14} adatoms/cm² (~45% of the adatom layer) were removed under conditions where steps have retreated ≥ 1500 Å ($\geq 7.8 \times 10^{14}$ atoms/cm² removed from bilayer steps). This indicates that removal at bilayer steps is at least 8 times that of terrace adatom removal. Occasionally, bright objects were found on the terraces, labeled X in Fig. 3(b). They could be due to SiBr, species that were unable to desorb when the sample was quenched. Similar features for Si(100) exposed to Br₂ and I_2 were attributed to residual silicon halides.^{3,23} For I-Si(100), photoemission confirmed the emergence of a Si²⁺ oxidation state after suitable exposure.²³

Figure 4 shows the effects of higher fluence on terrace etching at 900 K. The bright spots represent residual Si adatoms, labeled A. The exposed rest-atom layer is atomically resolved as a local 1×1 structure, saturated by Br. About twice as many adatoms have been removed in Fig. 4(a) relative to Fig. 3(b), scaling well with exposure. The outlined unit cell shows the persistence of the 7×7 periodicity. The dark lines in the image correspond to cell boundaries defined by dimer rows of the reconstruction. Atomic resolution images of the Br-bonded rest atoms are similar to those for Cl-Si(111),¹³ H-Si(111),²² and NaOH wet-etched Si(111).²⁴ Also evident are sites where Si atoms are missing from the rest-atom layer, labeled V for vacancy. These vacancies are almost exclusively located near unit-cell edges where, from Fig. 1, there are dimer rows in the next layer. This indicates that Br weakens Si back bonds and that removal near dimer rows is easiest where Si-Si bonds are strained.

Figure 4(b) shows a surface exposed to five times the fluence of Fig. 4(a) when the number of remaining adatoms is ~50% of that of Fig. 4(a). The fact that the adatom removal did not scale with fluence reflects a reduction in halogen sticking coefficient on the Br-rich 1×1 terrace. Moreover, the conversion from 7×7 to 1×1 requires consumption of atoms from the adatom layer. Most of the surface of Fig. 4(b) has converted to 1×1 , and only a few stacking faults (S) remain, as observed for a Cl-covered Si(111)-7×7 surface that had been annealed.¹² For Fig. 4(b) the residual halogen coverage is nearly 7.8×10^{14} cm⁻² while the saturated surface of Fig. 4(a) has 6.4×10^{14} Br/cm². While Si atoms are also removed from the 1×1 layer, the resulting vacancies remain isolated, indicating insufficient mobility at 900 K



FIG. 4. Images of terrace areas far from steps after etching at 900 K with greater fluence than in Fig. 3 (flux 20 μ A). (a) After 1.2-mAs exposure most of the adatoms (A) are gone, leaving the rest-atom layer with Br bonding that stabilizes the local 1×1 -like structure. The dark lines provide evidence of the presence of the dimer rows of the original 7×7 cell. Vacancies in the rest-atom layer are denoted V. (b) After 6 mAs, the terrace has transformed increasingly to a Br-terminated 1×1 structure although some dimer rows persist and give rise to stacking fau!ts (S). The Br concentration is close to saturation on the terraces since only the steps act as sites where Br is lost.

in the presence of Br to form larger pits. Occasionally, vacancies are found in pairs, as indicated by the V in Fig. 4(b). The atomic scale morphology represented in Fig. 4(b) is unchanged for longer exposures. Hence, continuous etching at 900 K is characterized by terraces that have Br-terminated 1×1 character with a few vacancies and residual adatoms. The dominant pathway for Si removal is via step retreat. Despite the abundance of Br, the barrier against pit formation is too great to allow pits to form. As discussed below, this ceases to be the case at 1000 K.

B. Regrowth structures and step profiles

For Si(100)-2×1, etching is accompanied by the formation of regrowth islands that nucleate from liberated, mobile Si atoms.^{2,3} These islands exhibit dimer rows analogous to those observed during Si homoepitaxial growth on Si(100)-2×1.²⁵ Here, we report the development of ring-shaped clusters during etching at 900 K. They are concentrated near steps where 1×1 regions are exposed. Such regrowth structures have not been observed previously for Si(111). As shown in Fig. 5(a), the ring structures, denoted R, appear as atomically resolved six-membered rings on the upper and lower (1×1) terraces.

Regrowth structures should reflect the tendency to minimize the number of dangling bonds. Of the possible geometric arrangements, six-membered rings represent the smallest structures that allow fourfold coordination of each Si atom when terminated with Br. Figure 5(b) depicts the proposed ring structure. Image analysis shows that each ring atom is situated above a Si atom on a 1×1 area. The height of these rings above the Br-terminated terrace is ~2.6 Å while bilayer steps are 3.2 Å (measured for two Br-terminated terraces or for two clean terraces). Hence, the rings are not consistent with bilayer structures that would extend the Si bulk lattice. These rings are rarely seen on upper and lower terraces more than 100 Å from steps, indicating that they are etched away as steps retreat.

Analysis shows that regrowth rings form $\simeq 5$ times more frequently near steps descending toward [112] than those that descend toward [211] or [121]. Figure 5(c) demonstrates that bonding at these two steps is quite different. One type has two dangling bonds and dimerizes along the edge, denoted S_D , while the other has one dangling bond extended from the step, denoted S_N . The extra row of atomic features along both steps in Fig. 5(a) is due to Br adsorption, and the position of the Br atoms relative to the 1×1 positions of the upper terrace indicates the step type. The fact that both step types show one Br per Si atom confirms the Si dimerization depicted in Fig. 5(c).

Since the terraces near the two step types are equivalent, the greater density of rings near S_D steps indicates greater release of Si from those steps. Anisotropic etching with easier removal at S_D steps relative to S_N steps can be rationalized in terms of bond strength arguments. Br adsorption on the dimers of S_D steps is analogous to adsorption on Si(100)-2 \times 1 dimers where the dimer π bond is broken and the σ bond and backbonds are weakened. Above ~ 850 K the dominant etch product is SiBr₂.²⁶ We propose that one Si atom of an S_D step-edge dimer escapes into the gas phase upon SiBr₂ formation while the other can be released onto the surface, analogously to Si(100).³ Volatile products can be formed more readily at S_D edges since there are only two back bonds and SiBr_2 -like bonding is achieved when the σ bond is broken. Such dimer etching is observed at steps at 900 K. Volatile species formation at S_N steps has a higher activation energy since it requires attack of the three back bonds. Hence, kink formation limits the etching of S_N steps. However, once an atom is removed from an S_N step, that kink is readily etched because atoms on both sides of the kink have two dangling bonds.

The step profiles for the surfaces shown in Figs. 4 and 5, and for those obtained after > 6-mAs exposure, revealed the same distribution and average size of peninsulas evident in Fig. 3. More than 90% of the step length is comprised of S_N steps although the sample miscut would



FIG. 5. (a) Etching near steps at 900 K produces regrowth structures (R) that consist of Si₆ rings to which Br is bonded. The inset shows the ring structure. Rings are more abundant near S_D steps than near S_N steps. Br termination at step sites indicates rebonding characteristics of the steps. (b) Schematic of rings as six Si atoms back bonded to the surface and bonded to neighbors. Fourfold coordination is achieved by Br termination. (c) Schematic of the two types of close-packed steps on Si(111)-1×1. S_D steps descend along [112], [$\overline{121}$], or [211] while S_N steps descend toward $[11\overline{2}]$, $[1\overline{2}1]$, or $[\overline{2}11]$. Each Si atom has one dangling bond at S_N steps. Atoms at S_D steps dimerize and the dangling bonds are saturated with Br. The steps of clean Si(111)-7 \times 7 are defined by linear structures that are locally analogous to the S_D step due to dimer chain walls. Kink formation at an S_N step involves removal of an atom that had three back bonds. This kink can then flow along the step as atoms with only two back bonds are removed. Etching of an S_D step is more facile and involves breaking the dimer bond to form a SiBr₂ unit with two back bonds.

yield S_D steps. This again indicates S_N steps are more stable upon Br adsorption than S_D steps. Significantly, the mechanisms for step etching remain similar even though the surface converts from 7×7 to 1×1 . For Si(111)-7 \times 7, bilayer steps are bounded by unit-cell edges with the dimer chains atoms each contributing one dangling bond at the step. These dimer chains create segments that are like S_D steps except for the presence of adatoms on the terraces. As adatoms are removed, the bonding in the exposed areas is like that of the 1×1 areas, differing only by the influence of the dimer chain walls that create stacking faults. There is no evidence of preferred removal of the faulted half of unit cells at steps edges. Rather, stacking faults are healed easiest at step edges so that the S_D -like dimer chains are removed so that etching exposes S_N steps. The further removal of adatoms and conversion to 1×1 facilitates step flow, but the atomic considerations regarding kink formation, S_D etching, and S_N stability remain the same.

C. Pit morphologies at 1000 K and etching energetics

Etching at 1000 K continues to involve adatom removal, terrace conversion to a 1×1 structure, and step retreat, as at 900 K. It differs from etching at 900 K, however, in that bilayer pits with distinctive shapes are also formed and these pits grow laterally. The pit sizes and densities depend on the flux because the flux determines the mean Br concentration achieved under conditions where there is Br loss via etching. At 900 K, Br loss was less profound, the mean concentration could reach saturation, and there was a weak dependence on flux. Analysis of the STM images makes it possible to assess the energetics of pit formation, step kink formation, and kink flow at 1000 K.

Figure 6 shows images of a surface exposed at 1000 K to a flux of 20 μ A for a fluence of 1.6 mA s. This image is representative of intermediate-state etching in that further exposure increased the pit density somewhat. (Steady-state etching at 1000 K as a function of flux will be discussed in Sec. D.) The surface is characterized by macroscopically irregular steps and bilayer terrace pits P. The step irregularities are triangular, as at 900 K, but the mean separation is smaller and the deviation from linearity is larger. Pit boundaries are defined locally by three equivalent S_N steps, as indicated in Fig. 6(b) and shown schematically in Fig. 6(c). The average pit has a characteristic dimension of 1250 Å (distance from pit apex to base). Remnants of upper terraces are often observed, having been created during terrace retreat and the possible breakthrough of a pit with a retreating step.

Pit formation is observed only after there has been local transformation to the 1×1 structure. Hence, the first stages of terrace etching are like those at 900 K with adatom removal and stabilization by Br of the 1×1 structure. We propose that pits are initiated when two neighboring vacancies are created in the top layer as, for example, atoms numbered 1 and 2 in Fig. 6(c). This produces an atom with two dangling bonds on the second layer [atom 3 in Fig. 6(c)] so that a volatile SiBr₂ unit can form. Subsequently, another top-layer atom is vulnerable [atom 4 in Fig. 6(c)]. This series of events would produce a bilayer pit with four vacancies bounded by six second-layer atoms each having one dangling bond. The span of such a pit is indicated by the dashed boundaries. Further



FIG. 6. Etching at 1000 K produces peninsulas at steps and bilayer pits (P) on terraces. (a) Denuded zones (DZ) are regions of reduced pit density near steps. Their width indicates how far the steps have retreated in the time necessary to form a terrace pit. Analysis reveals the energy difference for the rate-limiting step (see text). (b) Pits are triangular and are bounded by S_N steps. Etching occurs along the step by kink formation and kink flow. (c) Schematic showing a triangular bilayer pit bounded by S_N steps. The lengths of the three step edges are less than 10 Å on Si(111) whereas those in the images are much larger. Numbers 1–4 indicate a sequence of removal events that would lead to the initiation of a bilayer pit bounded by the dashed lines. We propose that this represents the rate-limiting step for pit formation.

growth requires removal of a boundary atom from the top layer or the second layer. Doing so would create a kink that exposes two dangling bonds on neighboring Si atoms. Removal of these kink site atoms is then relatively facile and the kink flows until the pit again assumes a triangular shape bordered by second-layer atoms, each with one dangling bond. The formation of a new kink allows the pit to grow again. At this stage, the pit resembles the one depicted in Fig. 6(c) with boundaries defined by S_N edges. We propose that the rate limiting step for terrace etching is the creation of two neighboring vacancies on the locally 1×1 surface followed by the creation of kinks so that the pit can grow. Each step involves removing a Si atom that had three back bonds. The energy barrier associated with such events is reflected by the low density of bilayer pits. The competing channel that removes Si and Br is associated with step flow.

Once a triangular pit is formed, etching at the S_N steps is limited by kink formation. Indeed, the same process limits step etching since this initial removal of a Si atom with three back bonds exposes neighboring atoms with only two back bonds. High-resolution images of large pit boundaries and terrace steps show that kinks are separated by an average of ~150 Å. Thus, the S_N steps that define large pits are multiply kinked. We expect that pits smaller than ~ 150 Å will be etched at a slower rate since the number of sites available for kink formation (and thus the probability of forming a kink) is smaller. For larger pits, size considerations would be minimal since their bounds are indistinguishable from step edges. Since most pits were significantly larger than 150 Å, the result that pits grow and steps retreat at nearly the same rate is understandable.

Examination of Fig. 6(a) indicates that denuded zones (DZ) develop on terraces near ascending steps, as characterized by the small number of pits within a distance w_{DZ} of a step. This distance is defined by the point at which the linear density of pits (along the step direction) is 90% of the maximum linear density. Since a retreating step exposes new areas of the surface where pits can form, the denuded zone width is related to the ratio of the rates of step retreat to pit formation. For the surface of Fig. 6, the denuded zone width w_{DZ} was ~1300 Å. Etching under different conditions gives the same value, as discussed below.

The rate limiting step for pit creation involves the formation of neighboring vacancies followed by an edge kink [Fig. 6(c)]. The growth of established pits and steps requires removal of one step atom with three back bonds (kink creation), followed by atom removal along the step (kink flow). The rate of step flow is then measured as the number of kink events per unit step length per unit time and the rate of pit initiation is measured as the number of pits created per unit step length per unit time. Since $w_{\rm DZ} \sim 1300$ Å and the distance between rows is 3.2 Å, then at least 400 kink formation events must have occurred before pit initiation could form in that area. However, step "irregularities," such as kinks and peninsula vertices, interrupt the linear continuity of edges, and kink flow is terminated when such features are encountered. Thus, the number of "irregularities" per unit step length must be taken into account. Similarly, the linear density of pits at the edge of the denuded zone must be taken into account. From STM analysis we found that there are ~ 120 step "irregularities" within the average spacing between pits. Given this result, approximately 48 000 (400×120) kink events occurred before the three events leading to pit initiation could be accomplished.

Scaling the number of step kink events (48 000) to the number of removal events needed to initiate the pit (3) gives a ratio of the rates of step kink formation to terrace pit formation, k_k/k_p , of ~16000. Rates can be related to activation barriers by Arrhenius relations so that $k_k = \sigma_k \exp[-E_k / kT]$ and $k_p = \sigma_p \exp[-E_p / kT]$ where σ_k and σ_p are the rate constants and E_k and E_p are the activation energies. In principle, the rates will depend on the diffisivity of Br, the activation and deactivation channels for the volatile species, and the desorption of volatile species. Analyses of Cl etching of Si(100) indicated that the rate-limiting step involved volatile species desorption⁶ and that is likely to be the case here as well. This is supported by results obtained under different conditions of Br flux and, therefore, mean surface concentration. We can simplify by assuming that the rate constants, σ_k and σ_p , are approximately equal since both depend on removal of a Si atom that had three back bonds. We note that step and terrace atoms are not equivalent past their first neighbors, but the difference between the rate constants may be small. Accordingly, $k_k / k_p = \exp[-(E_k - E_p) / kT] = 16\,000$ so that the barrier difference between kink and terrace pit formation at 1000 K is $E_p - E_k = 0.8 \text{ eV}$.

As a check, surfaces were etched to various fluences at 1000 K, again with a flux of 20 μ A. The pit and step irregularity density increased with fluence but the distribution of pits near ascending steps was unchanged and the denuded zone width did not vary. The effect of fluence was to increase the mean Br coverage until balance was achieved between the arrival and loss of Br. [Unfortunately, absolute Br coverages could not be measured because Br was lost during sample cooling to room temperature.] When this steady-state condition was reached, a morphology was achieved where further exposure resulted in the same pit size distribution and density. Thus, new pits were formed at the same rate as older pits were engulfed by retreating steps. While the higher Br concentration allowed for more pit formation events, there was a corresponding increase in step etching.

D. Flux dependence at 1000 K

Figures 7 and 8 show surfaces etched at 1000 K with fluxes of $5-80 \ \mu$ A to achieve steady-state morphologies (total fluences exceeded 6 mA s but longer exposures gave the same morphology). Inspection shows that the pit shape, size distribution, and density were flux dependent. This indicates that the Br arrival rate was important.

Figure 7(a) shows that bilayer pits were formed on the terraces for $5-\mu A$ flux (density 1.9×10^9 cm⁻²). These pits averaged 250 Å across. The pit and step edge profiles were highly irregular and triangular shapes were difficult to identify. Areas below steps were decorated



FIG. 7. $1.0 \times 1.0 \ \mu\text{m}^2$ images of surfaces etched at 1000 K to steady-state morphology using fluxes of (a) 5 μ A and (b) 10 μ A. High Br concentrations are difficult to achieve for fluxes $\leq 5 \ \mu$ A so that pits in (a) are irregular due to continual reconstruction of exposed areas. Residual concentrations using higher fluxes are conducive to 1×1 ordering so that pits in (b) are bounded by S_N steps yielding a triangular shape.

with remnant islands that were absent for distances \geq 1000 Å from these steps. This indicates that they were removed as their parent steps treated. Figure 7(b) shows that triangular pits were formed at a flux of 10 μ A (density 2.2×10^9 cm⁻²). The average pit size was 1000 Å. Analysis shows that the pits and steps of Fig. 7(b) were bounded by S_N edges. The difference in appearance for the 5- and 10- μ A results can be understood in terms of the Br concentration of the surface. One of the effects of Br is to stabilize the S_N steps and the 1×1 surface. When present in insufficient concentration, as at 5 μ A and below, the surface is able to reconstruct locally and there is no longer a distinction between S_N and S_D steps. Thus, edges are continually reordering during etching and are highly irregular. Surfaces etched using 10 μ A and above always show triangular pits bounded by S_N steps.

Figure 8 shows the dependence of pit diameter and density on flux for surfaces etched to steady-state morphology at 1000 K. A flux of 20 μ A produced pits with sizes that averaged 1300 Å (density 3.9×10^9 cm⁻²).²⁷ Etching with 40 μ A resulted in an average pit size of 2100 Å (density 5.6×10^9 cm⁻²). At this point, there was significant pit-pit and pit-step coalescence, and pitting had started in the next layer. Etching at 80 μ A yielded much smaller average pit sizes (600 Å) and a dramatic increase in density (2.8×10^{10} cm⁻²). A great many pits contacted neighboring pits or steps and the terraces appeared nearly half eroded. These size and density data

are summarized in Fig. 8(d) for fluxes of $2-80 \ \mu$ A. It should be noted that pit size and density data can be skewed by pit coalescence. However, the triangular shape of pits enabled us to identify portions of large pits that had originally nucleated as individual pits and then grew together. When such identification was possible we counted each portion as a separate pit and estimated their sizes accordingly.



FIG. 8. $2.0 \times 2.0 \ \mu m^2$ images of surfaces etched at 1000 K to steady-state morphology using fluxes of (a) 20 μ A, (b) 40 μ A, and (c) 80 μ A. The etchant arrival rate affects local Br concentrations resulting in flux-dependent pit sizes and densities. (d) Pit density and size are plotted vs flux. Steady-state Br concentrations increase with flux so that pit formation is more probable at higher fluxes. Pit sizes increase with flux also due to higher Br concentrations and higher yield step etching. The decline in pit size for fluxes greater than 40 μ A indicates effects of terrace width (see text).

These results demonstrate that the concentrations needed for attack of Si back bonds on terraces are difficult to achieve at low flux. The accumulation of Br depends on the flux, the fluence, the sticking coefficient, and the rate of Br loss through etching. From Fig. 8(d), the trend is that higher pit densities are the result of increased flux at 1000 K. This is analogous to the situation during growth where island nucleation is governed by local concentration and the free energy barrier associated with an analysis converting to a nucleus. At high flux, the area that the mobile species can sample is small due to the arrival of new species. This supersaturation increases the likelihood of forming a stable island. At low flux, mobile species are able to reach accommodating sites at steps or, if the steps are widely separated, then island formation can ultimately occur. This preferred thermodynamic path is frustrated if the diffusion length is low and the degree of supersaturation is high.

For etching at 1000 K, the rate of Br accumulation on the terrace increases with flux. This increases the change of pit formation. Here, the higher-energy barrier for removing Br (and thereby Si) via pit nucleation is the counterpart to the free-energy barrier associated with island nucleation and growth. At low flux, Br is lost via the lower-energy pathway (kink formation and kink flow) and the concentration on the terrace is insufficient to yield conditions conducive to pit formation. At very low flux, below 5 μ A, there is also competition with reconstruction of the Si surface, and etching involves different pathways. During local reconstruction, step reordering takes place since there is no edge favorability (all edges are S_D -like steps on reconstructed areas). Thus, resulting edge profiles are highly irregular.

The data of Fig. 8(d) demonstrate that the pit density D_p is a nonlinear function of the Br flux I_B . Indeed, $D_p \propto I_B^x$ where x is between 2 and 3. This is reasonable since pit initiation depends on multiple removal events, each of which depends on the local concentration (flux). In addition, vacancies are susceptible to annihilation via refilling with adatoms. The probability for such an annihilation event would depend on the adatom density and diffusivity, and these should decrease as the flux increases since more Br is available at higher fluxes. However, if we assume that each independent terrace removal event [as those numbered 1 and 2 in Fig. 6(c)] depends linearly on flux, then pit creation should go as the square of the flux. In addition, a kink creation event is required to conform to our description of pit initiation (as stated above), and this increases the flux dependence. Taking this into account as well as adatom-vacancy recombination, the net functional dependence of pit formation on flux approaches a cubic form, consistent with the data of Fig. 8(d).

The growth of a bilayer pit is governed by the relative rates of kink formation and kink flow. The kink formation rate is proportional to the number of available sites, i.e., pit edge length L in addition to I_B . When a pit is small, less time is required for a kink to advance across the entire edge than to form a new kink. Experimentally, this is deduced from the average kink-kink separation of ~150 Å. At some critical pit edge length, L_c , the times required for kink flow and kink formation become equal. If kink formation depends linearly on I_B , then pit growth, dL/dt, is governed by $dL/dt \propto I_B L$ for $L < L_c$ and $dL/dt \propto I_B L_c$ for $L \geq L_c$. Thus, small pits will grow exponentially with time for a given flux, $L \sim \exp(I_B t)$, since the growth rate increases with L. When the pit edge length exceeds L_c , the growth rate loses its dependence on L, and growth will become linear with flux and time. In this regime, $L \approx L_c + kL_c I_B t$. This is equivalent to step retreat. Such a dependence on the difference in energy needed to produce a kink and to propagate a kink explains the decrease of average pit size for high Br fluxes shown in Fig. 8(d). Moreover, at high flux as the rate of step retreat increases, the terraces are exposed for a shorter time before they are swept away. In this regime, pit growth is suppressed since step retreat annihilates pits before they achieve sizes corresponding to the exposure time and etch rates. The result is a decrease in average pit size because of reduced growth time.

Denuded zone widths can be calculated for each of the conditions of Figs. 7 and 8. Interestingly, $w_{\rm DZ}$ remains constant over the range of fluxes studied. In addition, the ratio of step irregularities per step length to pits per step length remained constant at ~120 for these conditions. These observations imply that the relationship between terrace pitting and step kink formation was unaffected by flux. This is reasonable since the Br arrival rate was uniform near steps and on terraces and, while the etching rate is faster at higher flux, the rate of step kink formation events and terrace removal events should scale equally with flux.

E. Terrace disordering at 1100 K

For Si(111), there is a first-order transition from the 7×7 to the 1×1 structure at ~ 1125 K.²⁸⁻³⁰ Hence, etching at 1100 K will still occur under conditions where there is a tendency to reconstruct to 7×7 but there is also facile removal. For these surfaces, little Br was observed after cooling, and the morphology is consistent with fast local removal of adatoms.

Figure 9(a) shows that the steps remain relatively straight and that bilayer pits are not formed after exposure at 1100 K to 1.2 mAs at 20 μ A. Indeed, the periodicity and roughness of the steps is nearly that of the clean surface. Thus, while steps are susceptible to etching at 1100 K, the high temperature and absence of Br promotes sufficient Si diffusion that etch-induced step irregularities are annihilated and the step length is minimized. The absence of terrace pits indicates that local Br concentrations needed for pit nucleation cannot be achieved. Results from studies at different flux and fluence at 1100 K confirm that terrace pits were not formed.

The expanded scale image of Fig. 9(b) shows adatoms (A), vacancies (V), and small clusters (C). The adatoms seem randomly distributed, but small 7×7 and 5×5 domains can be seen occasionally. The surface then reflects etching with the tendency to reconstruct to reduce the dangling-bond density. The persistence of intact corner holes [indicated by arrows in Fig. 9(b)] suggests that the corner holes act as seeds for the growth of

domains. Significantly, the largest domains (up to 150 Å) were concentrated at step edges, consistent with the nucleation of the reconstruction for the clean surface at steps. Comparison to results for oxygen, where the etching of Si(111)-7×7 produced 5×5 , 7×7 , and 9×9 domains,^{7,8} indicates that Br etching is characterized by a more disordered distribution of adatoms.

The adatom vacancies in Fig. 9(b) appear as dark areas. The formation of vacancy patches that range in size from 1 to 15 missing adatoms is associated with the accumulation of adatoms in small domains. These areas expose the rest-atom layer (local 1×1). The disordered nature of the terraces most likely inhibits the transport of material over large distances. The cluster features in Fig. 9(b)



FIG. 9. (a) Large area of a surface etched at 1100 K showing that steps remain straight and no terrace pitting is observed. (b) Atomic detail after etching at 1100 K showing that adatoms (A) are distributed in a disordered fashion although small ordered domains can be seen, as indicated by the arrows. Vacancy clusters (V) and Si clusters (C) can be seen. (c) Etching to steady-state morphology at 1000 K, as in Fig. 8(a), followed by annealing at 1000 K for five min (without additional Br) yields a morphology similar to etching at 1100 K. Ordered domains have nucleated at the steps on upper terraces. A 5×5 region is indicated and shown in detail in the inset.

represent 4–7 atoms that are back bonded to the surface and bonded to each other. The atoms that constitute these clusters are imaged at a different contrast than adatoms due to their unique bonding configurations. Many of the clusters consist of six atoms arranged similarly to the regrowth structures, discussed in Sec. B although bias-dependent imaging indicates that the clusters are not Br terminated. Clusters are observed in equal numbers regardless of their distance from steps, so they are probably not regrowth structures directly formed from liberated Si, as were the regrowth rings seen at 900 K.

Figure 9(c) shows a surface that was initially etched to steady-state morphology with 20 μ A at 1000 K, as in Fig. 8(a) and then annealed for 5 min at 1000 K after the Br source was turned off. The resulting morphology can be compared to that of Figs. 9(a) and 9(b). In particular, structures equivalent to those produced by etching at 1100 K are present after annealing at 1000 K a surface etched at 1000 K. Steps are macroscopically straight but showed segments of $[1\overline{2}1]$, $[\overline{2}11]$, and [112] edges, and no bilayer pits were observed. Terrace adatoms showed no long-range ordering, but 5×5 and 7×7 domains had nucleated on upper terraces at step edges. A 5×5 domain is evident in Fig. 9(c) and is detailed in the inset. No Br was detected on the adatom layer. Substantial diffusion was accomplished and healing of pits and reordering of steps was promoted as residual Br was lost during the anneal at 1000 K.

F. Comparison to Br etching of Si(111)-2×1

It is instructive to compare the flux, fluence, and temperature dependencies of surface morphology for spontaneous etching of Si(111)-7×7 to those for Si(100)-2×1. Chander *et al.*^{2,6} and Rioux *et al.*³ found that Siremoval proceeded via step flow with overall layer-by-layer removal for $700 \le T \le 1100$ K. They showed that residual Br concentrations for steady-state surfaces approached 1 ML for $T \le 900$ K but then decreased markedly at 1000 K with no Br remaining for 1100 K. Such general behavior is maintained for Br etching of Si(111)-7×7.

Comparison of the present results to those for Si(100) shows that there are striking differences with regard to terrace pit formation. For Si(100)-2×1, terrace pits were seen for temperatures as low as 600 K, although significant pitting was observed only for temperatures at and above 800 K. These pits were initiated as single dimer vacancies and were aligned along dimer rows (aspect ratios $\sim 9:1$). Quantitative modeling of the pit shapes allowed Chander et al.⁶ to deduce the differences in energy barriers for etching along the dimer rows versus branching. Average pit sizes increase with temperature to 1000 K where pits as large as 2000 Å along the long axis were observed. For Si(100), the steady-state morphology showed little dependence on the flux. Here, we have shown that terrace pitting occurs on Si(111)-7 \times 7 only for temperatures near 1000 K, and pits were quite large (200-4000 Å). This significant difference reflects the difference in energy associated with removal of dimer atoms from Si(100)-2 \times 1 terraces (two back bonds) relative to terrace atoms of $Si(111)-1 \times 1$ (three back bonds). Kink formation, which is the rate-limiting process for step etching of $Si(111)-1 \times 1$, also involves breaking these back bonds. The formation of kinks on $Si(100)-2 \times 1$ has a much lower energy.

V. SUMMARY

We have used STM to study the interaction of Br_2 with Si(111)-7×7 for $300 \le T \le 1100$ K. The conclusions are summarized schematically in Fig. 10. Chemisorption is dissociative, and Br atoms bond at adatom and rest-atom sites at room temperature. Exposures at 500-650 K result in the transformation to a Br-terminated 1×1 surface where the halogen saturates the dangling bonds and there was not etching. Exposures at 700-1100 K result in spontaneous etching. At 900 K, the terraces are converted to 1×1 with Br saturation but no pitting. The steps are the active sites for etching during the initial stages of Si removal and especially following 1×1 conversion. The steps establish specific atomic structures with triangular appearance. Etching is faster at S_D steps, and this is rationalized by step rebonding characteristics and the lower energy needed to remove Si atoms with two back bonds compared to that needed to create a kink in an S_N step.



FIG. 10. (a) Summary of surface characteristics and dominant etching pathways as a function of temperature. (b) Schematic of the dynamic processes involved during etching at 1000 K, showing uniform Br arrival but consumption at steps to set up concentration gradients. This makes terrace pitting difficult near steps. Terrace pits are formed when local Br concentrations are high. Pit formation consumes Br and reduces the chance for pit formation nearby.

Fast etching at steps gives rise to Br-terminated Si₆ rings as regrowth structures. Etching at 1000 K leads to large-scale pitting on terraces as well as step flow etching. The pits are a single bilayer deep and show characteristic S_N bounds. The average pit size and pit density increase under conditions of increased flux, demonstrating the role of etchant arrival rate and its surface concentration on morphology. Figure 10(b) summarizes the dynamics involved with Br arrival, diffusion, and consumption. Throughout the exposure, the etchant arrival rate is uniform. Br is consumed as Si atoms at steps are removed. This produces triangular peninsulas. The loss of Br at the steps sets up a concentration gradient relative to the terrace concentration, the magnitude of which depends on the Br diffusivity. At low flux and high temperature, this gradient is small while at high flux it is higher. This concentration gradient also changes on upper terraces as steps sweep by. Si atoms released from steps are captured by the advancing front of Br. In addition, pits can be formed in regions where high Br concentrations have been achieved. Pit formation consumes Br, and the pits act as Br sinks, leading to a reduced chance for pit formation nearby. Subsequent pit growth proceeds via step re-

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treat. For high flux, the probability of achieving high local concentrations increases and pits are formed more easily. The fast arrival of additional Br inhibits diffusion of the etchant (just as high fluxes inhibit diffusion during growth), resulting in shorter diffusion lengths than for low fluxes. Thus more pits can be formed. Etching at 1100 K leaves a Br-free surface with straighter steps reminiscent of the clean surface. On the terraces, Si adatoms are packed randomly amidst small 7×7 and 5×5 domains because etching is local and disruptive. Efforts to locally reconstruct during Br attack result in complicated local bonding configurations. Etching proceeds in a layer-by-layer fashion under all conditions studied here because of the difference between step kink formation and pit formation, 0.8 eV.

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FIG. 1. Schematic of Si(111)-7 \times 7 unit cell showing (a) top and (b) side views. The side view in (b) follows the long axis of the unit cell. The faulted half of the unit cell is on the left and the unfaulted on the right. The 19 dangling bonds per unit cell are derived from adatoms in the top layer (12), exposed rest atoms in the next layer (6), and exposed bulk atoms at corner holes (1). The dashed lines denote unit-cell boundaries defined by dimer rows. Nucleation of the 7 \times 7 reconstruction at a step edge exposes these dimer rows.



FIG. 2. 135×135 -Å² images after 0.1-mAs exposure to Br₂ at 300 K showing the same area with sample bias voltages recorded in the insets. The same unit cell is outlined in each. Br is observed to adsorb at adatom and rest-atom dangling-bond sites. Most dark areas seen at low magnitude bias were bright at high magnitude bias. The arrow indicates a dark area that did not become bright at higher bias.



FIG. 3. Etching at 900 K proceeds via step retreat and Si adatom removal (flux 20 μ A; fluence about 10% of that needed to achieve steady-state terrace appearance). (a) Step profiles are defined by triangular peninsulas with step-down directions indicated. The island *I* represents the remnant of a back-cut peninsula. The bold arrow indicates where Br etching has exposed a $[11\overline{2}]$ step so that a small island may develop. (b) Terrace image for an area far from a step showing changes in the original surface layer. Dark areas are missing adatoms. Four intact corner holes are connected and shown in the inset. Features denoted *X* probably represent SiBr_x moieties that did not desorb. All exposed dangling bonds are terminated by Br.



FIG. 4. Images of terrace areas far from steps after etching at 900 K with greater fluence than in Fig. 3 (flux 20 μ A). (a) After 1.2-mAs exposure most of the adatoms (A) are gone, leaving the rest-atom layer with Br bonding that stabilizes the local 1×1 -like structure. The dark lines provide evidence of the presence of the dimer rows of the original 7×7 cell. Vacancies in the rest-atom layer are denoted V. (b) After 6 mAs, the terrace has transformed increasingly to a Br-terminated 1×1 structure although some dimer rows persist and give rise to stacking faults (S). The Br concentration is close to saturation on the terraces since only the steps act as sites where Br is lost.



FIG. 5. (a) Etching near steps at 900 K produces regrowth structures (R) that consist of Si₆ rings to which Br is bonded. The inset shows the ring structure. Rings are more abundant near S_D steps than near S_N steps. Br termination at step sites indicates rebonding characteristics of the steps. (b) Schematic of rings as six Si atoms back bonded to the surface and bonded to neighbors. Fourfold coordination is achieved by Br termination. (c) Schematic of the two types of close-packed steps on Si(111)-1×1. S_D steps descend along [112], [121], or [211] while S_N steps descend toward [112], [121], or [211]. Each Si atom has one dangling bond at S_N steps. Atoms at S_D steps dimerize and the dangling bonds are saturated with Br. The steps of clean Si(111)-7 \times 7 are defined by linear structures that are locally analogous to the S_D step due to dimer chain walls. Kink formation at an S_N step involves removal of an atom that had three back bonds. This kink can then flow along the step as atoms with only two back bonds are removed. Etching of an S_D step is more facile and involves breaking the dimer bond to form a SiBr₂ unit with two back bonds.



FIG. 6. Etching at 1000 K produces peninsulas at steps and bilayer pits (P) on terraces. (a) Denuded zones (DZ) are regions of reduced pit density near steps. Their width indicates how far the steps have retreated in the time necessary to form a terrace pit. Analysis reveals the energy difference for the rate-limiting step (see text). (b) Pits are triangular and are bounded by S_N steps. Etching occurs along the step by kink formation and kink flow. (c) Schematic showing a triangular bilayer pit bounded by S_N steps. The lengths of the three step edges are less than 10 Å on Si(111) whereas those in the images are much larger. Numbers 1–4 indicate a sequence of removal events that would lead to the initiation of a bilayer pit bounded by the dashed lines. We propose that this represents the rate-limiting step for pit formation.



FIG. 7. $1.0 \times 1.0 \ \mu m^2$ images of surfaces etched at 1000 K to steady-state morphology using fluxes of (a) 5 μ A and (b) 10 μ A. High Br concentrations are difficult to achieve for fluxes $\leq 5 \ \mu$ A so that pits in (a) are irregular due to continual reconstruction of exposed areas. Residual concentrations using higher fluxes are conducive to 1×1 ordering so that pits in (b) are bounded by S_N steps yielding a triangular shape.



FIG. 8. $2.0 \times 2.0 \ \mu m^2$ images of surfaces etched at 1000 K to steady-state morphology using fluxes of (a) 20 μ A, (b) 40 μ A, and (c) 80 μ A. The etchant arrival rate affects local Br concentrations resulting in flux-dependent pit sizes and densities. (d) Pit density and size are plotted vs flux. Steady-state Br concentrations increase with flux so that pit formation is more probable at higher fluxes. Pit sizes increase with flux also due to higher Br concentrations and higher yield step etching. The decline in pit size for fluxes greater than 40 μ A indicates effects of terrace width (see text).



FIG. 9. (a) Large area of a surface etched at 1100 K showing that steps remain straight and no terrace pitting is observed. (b) Atomic detail after etching at 1100 K showing that adatoms (A) are distributed in a disordered fashion although small ordered domains can be seen, as indicated by the arrows. Vacancy clusters (V) and Si clusters (C) can be seen. (c) Etching to steadystate morphology at 1000 K, as in Fig. 8(a), followed by annealing at 1000 K for five min (without additional Br) yields a morphology similar to etching at 1100 K. Ordered domains have nucleated at the steps on upper terraces. A 5×5 region is indicated and shown in detail in the inset.