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Adsorption site preference of Br on Si(111)-7×7

M. Tanaka,* K. Shudo, and M. Numata†
Department of Physics, Faculty of Engineering, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku,
Yokohama 240-8501, Japan

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The site preference of the bromine (Br) atom adsorption process on Si(111)-7×7 at room temperature was investigated. The density of the reacted adatom bonds of dimer-adatom-stacking fault structure and the total coverage were determined by means of surface differential reflectivity and thermal desorption spectroscopy, respectively. Partial coverage on the rest atoms was then obtained. At the initial stage below 0.1 ML, Br atoms are adsorbed selectively on dangling bonds at the Si adatoms, but not on those at the rest atoms. Above 0.1 ML, dibromide species are formed at the adatoms even when half of the adatom dangling bonds remain intact. The observed site preference of Br atoms is quite different from that of Cl atoms, which are adsorbed randomly on the dangling bonds at both the adatoms and the rest atoms, and form dichloride only after about 80% of the adatoms and the rest atoms are covered. This study provides direct evidence of the adsorption site preference and suggests pattern formations of Br adsorbates on Si(111).

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I. INTRODUCTION

Halogen gas is widely used to etch semiconductor surfaces and is a promising candidate tool to fabricate nanometer-scale structures.[1] Different halogens have different ionic radii and different electron affinities, so that they will react with a semiconductor surface in different ways; for example, the sticking probabilities, the desorption rates, and their temperature dependences will be different. Understanding the chemical trend of halogen reactivity is crucial to optimize the conditions for nanostructure formation. In this study, we focus on the adsorption process, especially on the adsorption site preference, which may be available for atomically controlled surface modification, site selective etching, and so on.

On Si(100), it has been already reported that halogen atoms have site preference in the adsorption process. For example, a patterning of larger halogen (Br or I) adsorbates was found in the form of a stable $c(4\times 2)$ structure at 0.5 monolayer (ML).[2,3] This phase involves adsorption on non-neighboring dimers under certain conditions at elevated temperature. At high coverage in Br adsorption, a (3×2) structure in which Si dimer rows alternate with atom vacancy lines is favored as a result of desorption of volatile SiBr_2.[4,5] The roughening under which dimer vacancies, dimer vacancy lines, pits, and Si regrowth are observed occurs at temperatures below the threshold for $\mathrm{Si}X_2$ $(X=\mathrm{Cl},\mathrm{Br})$ desorption.[6–8] Si epitaxial growth on Br-Si(001) produces an ordered Si overlayer chain.[9] The results of these scanning tunneling microscope (STM) studies were interpreted in terms of repulsive interaction both experimentally and theoretically.[10,11] However, this simple picture is not enough because the influence of adsorption on the properties of the underlying substrates should be taken into account. Patch formation on Cl-Si(001) was then explained by an attractive interaction between anticorrelated bare dimers on Si(001).[11]

Thus reaction on the Si(001) surface is preferentially studied in connection with industrial applications, but reaction on the Si(111) surface is also of interest because the dimer-adatom-stacking fault (DAS) structure has a variety of sites with different chemical reactivity.[13] The halogen adsorption on Si(111) has been examined using various methods. It is known that chlorine atoms first react with Si adatom sites to form monochlorides and remove dangling bond states near E_F at low coverage,[14,15] while further exposure produces SiCl_2 and SiCl_3 species.[16,17] However, interaction between adsorbates has not been well studied on Si(111). The STM study on halogen molecule adsorption at room temperature[18] showed that a Cl_2 molecule with 0.05 eV translational energy tends to be adsorbed on center adatoms to form a single chloride or a pair of chlorides. The neighboring pair of adsorbates seemingly suggests an attractive interaction between adsorbates. On the other hand, significant I-I interaction was seen at high coverage as the binding energy decreases in x-ray photoemission spectra.[19] Furthermore, in the previous paper,[20] we compared adsorption and desorption processes of Br atoms with those of Cl on Si(111) and found that the Br process yields a higher sticking probability on adatom dangling bonds, a higher breaking probability of adatom back bonds, and a lower desorption energy. These results suggest a repulsive interaction between Br adsorbates on Si(111). Thus interactions of opposite directions were reported so far.

The underlying interaction in the adsorption on Si(111) may be different from that on Si(100) because of different surface structure. The distance between center adatoms on Si(111) is 0.69 nm and much longer than 0.38 nm of the distance between dimers on Si(001). The latter is rather close to the distance between the adatom and the bare rest atom on Si(111). However, the authors of Ref. 18 assumed that the adatoms are the exclusive adsorption sites, and they proposed dissociative adsorption on the adatom-restatom pair contrarily in their previous paper.[21] The adsorption on the rest atoms is therefore crucial to discuss interaction between adsorbates on Si(111). Rest atom dangling bonds on Si(111) can hardly be accessed by a STM, so that we proposed to combine two experimental methods in order to obtain direct evidence for the adsorption site preference on Si(111), i.e., surface differential reflectivity spectroscopy (SDR) and thermal desorption spectroscopy (TDS).[22] Using this method, we found that Cl atoms are adsorbed randomly on the dangling bonds at both the adatoms and the rest atoms at the initial stage, and that they preferentially form dichloride at the adatoms at the expense of the Cl atoms on the rest atoms after the onset of back bond breaking.[23]

The question to be addressed in this study is therefore the behavior of different halogen atoms as regards adsorption on the adatom and the rest atom of Si(111), that is, whether or not the site preference in Br adsorption is different from that in Cl adsorption. The adsorption process of bromine on a Si(111)-7 × 7 surface was investigated by means of SDR and TDS using the same approach as in Ref. 22. Densities of saturated adatom dangling bonds and broken adatom back bonds were determined from SDR, and these densities yield the partial coverage on the adatoms. Total coverage was determined from TDS. Partial coverage on the rest atoms is then calculated from the total coverage and the partial coverage on the adatoms. These coverages on different adsorption sites reveal the adsorption site preference of Br atoms on Si(111). The result is compared with that for Cl atoms, and the origin of the site preference is discussed.

II. EXPERIMENT

A specimen of $5\times18\times0.38$ mm^3 cut from a B-doped p-type Si(111) wafer 10–15 Ω cm was cleaned in an ultrahigh vacuum chamber at a base pressure of 2×10^{-8} Pa. It was ohmically heated to 1420 K for several seconds and then slowly cooled. The 7 × 7 structure of the surface was confirmed by low-energy electron diffraction. Bromine gas was generated with a AgBr electrochemical cell doped with $CdBr_2$ (5 wt %).[24] The electrochemical cell produces more atoms than molecules.[25] Actually, no trace of Br_2 species was detected with a quadrupole mass spectrometer during the bromine gas exposure. Moreover, it was revealed that atoms play essential roles in the adsorption of halogens generated with this kind of source.[20,22]

The experimental setup for SDR has been described in detail in Ref. 22. Light from a halogen tungsten lamp was polarized horizontally and separated into a probe beam and a reference beam. The p-polarized probe beam was introduced into the vacuum chamber and was incident on the surface at an angle of 70° from the surface normal. The specularly reflected probe beam and the reference beam were introduced via optical fibers to a grating-spectrograph. The spectra of both beams were detected with a dual photodiode array, and the intensity of the reflected spectrum was normalized with respect to the reference spectrum. Differential reflectivity is defined as $\Delta R/R=(R_a-R_c)/R_c$, where R_a and R_c are the reflectivities of the adsorbed and the clean surfaces, respectively. Spectral features of halogen adsorption on adatom dangling bonds and breaking of adatom back bonds were identified for the Cl-adsorbed surface[22] from the calculation of the $\Delta R/R$ spectrum of the hydrogenated 7 × 7 surface.[26] Densities of saturated dangling bonds and broken back bonds were thus determined from SDR.

The total coverage was determined by means of TDS. TDS spectra were measured with a quadrupole mass spectrometer located in front of the specimen. The target mass was 107, due to $SiBr^+$ ions generated from $SiBr_2$ species. The heating rate was 10 K/s. It was found that about 10% of the Br atoms are desorbed around 600 K and about 90% are desorbed around 1000 K when the coverage is above 60% of the saturation.[27] The former component arose from polybromides, the amount of which could not be evaluated quantitatively. Accordingly, the specimen was annealed at 673 K for 3 min before the TDS measurement in order to eliminate polybromides. Thus the total coverage was calculated from the area of the $SiBr^+$ desorption spectrum between 770 and 1170 K, as the additional 10% is taken into account when the coverage is above 60% of the saturation. The saturation of TDS is normalized to 1.35 ML (=66/49), where 36 Br atoms are on the adatoms and 30 Br atoms are on the rest atoms.

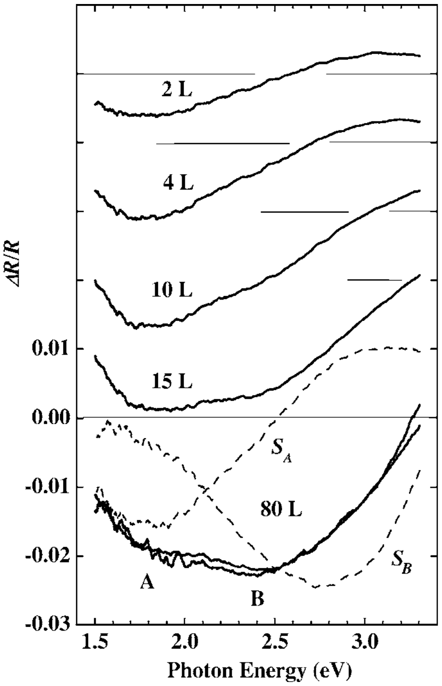

FIG. 1. Variation of p -polarized reflectance spectra during Br adsorption at 313 K. Exposure is indicated in the unit of langmuir (L). The feature A originating from the adatom dangling bonds develops first, and the feature B from the adatom back bonds appears later. Each $\Delta R/R$ spectrum is well reproduced by a linear combination (aS_A+bS_B) (gray line) of two component spectra S_A and S_B (dashed lines) representing the features A and B, respectively.

III. RESULTS AND DISCUSSION

Figure 1 shows typical SDR spectra in the visible range at room temperature. The Br exposure is expressed in the unit of L ($1\ \mathrm{L}=1.33\times10^{-4}$ Pa s). The $\Delta R/R$ spectra have two features, negative peaks A and B located at 1.8 and 2.4 eV, respectively. Peak A appears first and peak B appears later. The procedure for the analysis of the spectra is described in detail in the previous paper.[20] The features A and B arise mainly from adatom dangling bonds and adatom back bonds of the DAS structure, respectively.[26] SDR is thus insensitive to the dangling bonds at the rest atoms because the filled

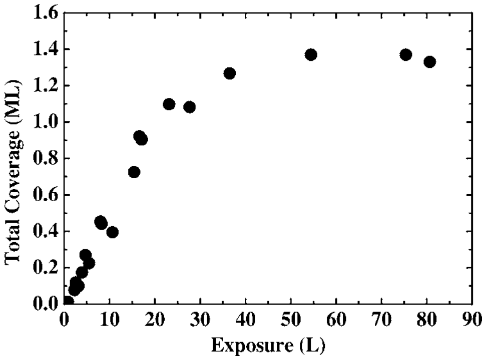

FIG. 2. Relationship between the total coverage and the exposure.

dangling bond states of the rest atoms are clearly below the filled dangling bond states of adatoms.[28,29] The feature A appears when Br atoms are adsorbed on the adatom dangling bonds, that is, monobromide is formed on the adatoms. The feature B appears when Br atoms break the adatom back bonds, that is, dibromide or tribromide is formed on the adatoms. Each $\Delta R/R$ spectrum is well reproduced by a linear combination (aS_A+bS_B) of two component spectra S_A and S_B, representing the features A and B, respectively. In other words, each spectrum can be decomposed into a dangling bond contribution and a back bond contribution. These contributions to the saturated spectrum (80 L) are shown by dashed lines in Fig. 1. The gray line shows the sum of both contributions and agrees well with the experimental curve.

The coefficients a and b are proportional to the densities of saturated dangling bonds and broken back bonds, respectively. There are 12 adatom dangling bonds in the 7×7 unit cell, so that is normalized to 0.24 ML (=12/49), whereas b is normalized to 0.49 ML (=24/49) because two of three adatom back bonds for each Si adatom are breakable. At each exposure, the SDR spectrum was first measured and coefficients a and b were determined. The TDS spectrum was then measured so as to determine the total coverage θ. The obtained relationship between the total coverage and the exposure is shown in Fig. 2. This uptake curve is more structureless than that for I adsorption, where I-I interaction was found at high coverage.[18]

Based on the total coverage in Fig. 2, the densities of saturated dangling bonds and broken back bonds are plotted against the total coverage in Fig. 3(a). The result of Cl adsorption[23] is shown in Fig. 3(b). Open circles represent the density of saturated dangling bonds, whereas closed circles represent the density of broken back bonds. The errors in Fig. 3 were evaluated from several measurements. Gray lines are drawn as a visual guide. Apparently, Br and Cl adsorption follow different lines, which reveals a chemical trend in the adsorption processes. It has already been found that both the sticking probability on adatom dangling bonds and the breaking probability of adatom back bonds for Br adsorption are higher than those for Cl adsorption.[20] With the aid of TDS, the development of the adsorption process can be seen more quantitatively in relation to the total coverage in Fig. 3. This figure shows how many Br atoms are adsorbed on adatom dangling bonds and how many Br atoms break adatom back bonds when a specified number of Br atoms is adsorbed. The chemical trend found in Fig. 3 is as follows. First, the density of saturated dangling bonds (open circles) for Br adsorption increases with a slope of 1 below 0.1 ML, then the slope decreases, becoming almost saturated above 0.6 ML. On the other hand, the slope for Cl adsorption is about 2/3 below 0.3 ML, becoming saturated at around 0.6 ML. Second, the onset point of the density of broken back bonds (closed circles) for Br adsorption, that is, the onset of dibromide formation, is about 0.1 ML. The density increases monotonically with a slope of about 0.4 up to saturation. On the other hand, the onset for Cl adsorption is about 0.3 ML, and the density increases with a slope of about 1.0 up to 0.6 ML and about 0.25 above 0.6 ML.

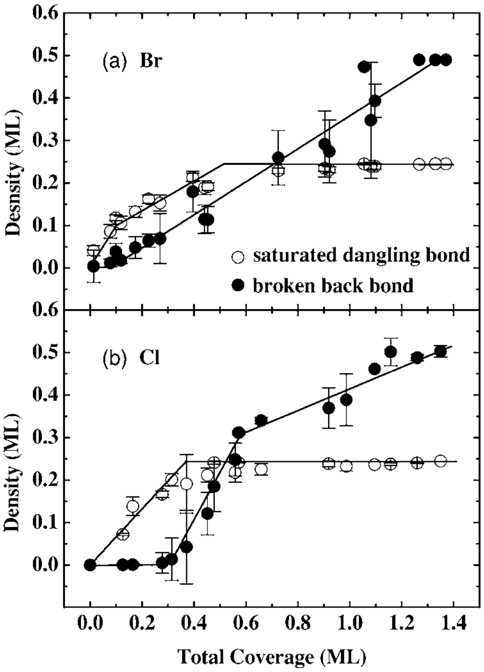

FIG. 3. Density of saturated dangling bonds a (open circles) and that of broken back bonds b (closed circles) determined from SDR vs total coverage determined from TDS. Part (a) is for Br and (b) for Cl. Gray lines are shown merely as visual guides.

We consider that the adatoms and the rest atoms are the main adsorption sites for the following reasons. Halogen atoms can be adsorbed on the dangling bonds of the corner holes, but the partial coverage on the corner holes is negligible, being 1/49=0.02 ML at most. Adsorption on the dimers can be also excluded because there is no experimental evidence that halogen atoms break the dimer bonds. In the meantime, two types of dangling bond appear upon breaking of the adatom back bonds. We hereafter call one of them "new dangling bonds at the adatoms" and the other "emerging dangling bonds at the rest atoms". They should be distinguished from "native dangling bonds at the rest atoms" on the clean surface. SDR measurements cannot identify whether the halogen atom is adsorbed on new dangling bonds at the adatoms or on emerging dangling bonds at the rest atoms. However, the latter is unlikely, because there is no evidence for asymmetric polyhalide in the STM observations.[15] For example, when a Br atom breaks a back bond of monobromide at the adatom, a dibromide is formed at the adatom and the emerging dangling bond at the rest atom remains intact. Consequently, the partial coverage on the adatoms is evaluated as $a+b$. The partial coverage on the rest atoms is then calculated as the difference between the total coverage and the partial coverage on the adatoms, $\theta-(a+b)$. If all the adatoms form trihalides at saturation, the partial coverages on the adatoms and the rest atoms can be as large as $12\times 3/49=0.73$ and $(6+12\times 2)/49=0.6$ ML, respectively. Thus obtained partial coverage on the rest atoms cannot be estimated with STM, and the present SDR-TDS method is the only available means to evaluate it. The partial coverages of Br are plotted against the total coverage in Fig. 4(a). The result of Cl adsorption is shown in Fig. 4(b). Open circles represent the partial coverage of the adatoms, whereas closed circles represent the partial coverage of the rest atoms. Error bars correspond to the sum of the errors of densities of saturated dangling bonds and broken back bonds shown in Fig. 3. The partial coverage on the rest atoms (closed circles) for Br adsorption is almost 0 below 0.3 ML and then increases with a slope of about 0.6. On the other hand, the slope of the partial coverage on the rest atoms for Cl adsorption is about 1/3 below 0.3 ML and slightly decreases above 0.3 ML, then increases to about 0.7 above 0.6 ML. Meanwhile, the partial coverage on the adatoms (open circles) for Br adsorption increases with a slope of about 1 below 0.3 ML, then the slope decreases to about 0.4. On the other hand, the slope for Cl adsorption is about 2/3 below 0.3 ML and increases to about 1 above 0.3 ML, then decreases to 0.3 above 0.6 ML. The developments of the partial coverages for Br and Cl adsorption are similar above 0.6 ML and the chemical trend can be clearly seen below 0.6 ML. The slopes for the adatoms and the rest atoms change around 0.3 ML in a opposite way for Br and Cl adsorption. Consequently, we concentrate on the adsorption process below 0.6 ML.

The experimental results shown in Figs. 3 and 4 establish the adsorption site preference in the adsorption process. For Br adsorption, the slope of the partial coverage on the adatoms at the first stage is almost 1.0 and that on the rest atoms is nearly 0, which means that all adsorbed Br atoms sit on the adatoms, and none on the rest atoms. On the other hand, the slope of the partial coverage on the adatoms for Cl adsorption is almost 2/3 and that on the rest atoms is nearly 1/3. This means that Cl atoms are adsorbed on both the adatoms and the rest atoms with equal probability because there are 12 dangling bonds at the adatoms and six native dangling bonds at the rest atoms in a clean 7×7 unit cell. As for the adsorption on the rest atoms, both interaction between halogen adsorbates and interaction between halogen atoms and the rest atoms should be taken into account at high coverage, however, only the latter is effective at low coverage. Since no Br atom sits on the rest atoms even at very low coverage, there must be a potential barrier for the Br atom to be adsorbed on the rest atoms. In other words, there is repulsive interaction between Br atoms and the Si rest atoms. On the contrary, Br adsorption on the adatoms is considered to be barrierless because the sticking probability on the dangling bonds for Br adsorption is higher than that for Cl adsorption[20] whose process was proved to be barrierless.[22]

At 0.1 ML in Br adsorption, about 5 adatoms per unit cell or 40% of the adatoms have adsorbed Br, while 60% of the adatoms have the dangling bonds. Nevertheless, the breaking of back bonds begins. An electron-stimulated ion desorption (ESD) study[30] reported that the desorption of $SiBr_2^+$ ions, suggesting polybromide formation, was apparent even at coverage as low as 0.1 ML for Br-covered Si(111), though no ion containing Si was detected from Cl-covered Si(111) at such low coverage. This result agrees well with ours at around 0.1 ML. There are two possibilities for the breaking of back bonds at such an early stage. In case I, the SiBr species at the adatoms hinders other SiBr species at the adatoms, and one $SiBr_2$ species is formed with a barrier lower than that to form an adjacent pair of SiBr species. A stronger repulsive interaction between Br adsorbates plays an essential role. In this case, a patterning in which Br atoms are adsorbed on every other adatom is expected. In case II, adsorption to the center adatoms are different from that to the corner adatoms, as suggested for the adatom with low electron density (center adatom) to be favored.[18] Since the interaction in the process of adsorption to the site of low electron density is effectively attractive, the barrier for the process is expected to be low. If one $SiBr_2$ species at the center adatoms is energetically preferred to the configuration with one SiBr species on the center adatom and the other SiBr species on the corner adatom, the breaking of back bonds begins after six center adatoms in the 7×7 unit cell (0.12 ML) are adsorbed. Interaction between Br adsorbate and the Si adatom plays an essential role. In this case, a patterning decorated with adsorbates on the center adatoms is expected. In both cases, underlying interactions suggest patternings of adsorbates on the Si(111) surface, although the patterning is different depending on the underlying interaction. On the other hand, the onset of back bond breaking in Cl adsorption is at 0.3 ML, that is, about 15 atoms per unit cell. Back bond breaking begins only after about 80% of dangling bonds at the adatoms and the rest atoms have adsorbed Cl. We can see little trace of interaction between Cl adsorbates or interaction between Cl adsorbate and the Si adatom.

The adsorption behavior above the onset of back bond breaking is quite different from that below the onset. In the range of $0.1<\theta<0.3$ ML in Br adsorption, the rest atoms remain intact [Fig. 4(a)] and the slopes of the densities of saturated dangling bonds and broken back bonds are nearly equal [Fig. 3(a)]. This means that about a half of impinging Br atoms are adsorbed on the dangling bonds of the adatoms and the other half breaks the adatom back bonds. In other words, 50% form monobromide and 50% form dibromide at the adatoms, but none is on the rest atoms.

In the range of $0.3<\theta<0.6$ ML in Br adsorption, about 40% of impinging Br atoms are adsorbed on the adatoms and about 60% are adsorbed on the native or emerging dangling bonds at the rest atoms [Fig. 4(a)]. On the other hand, in the range of $0.3<\theta<0.6$ ML in Cl adsorption, almost all the impinging Cl atoms break the adatom back bonds and are adsorbed on the adatoms [Fig. 3(b)]. In other words, newly adsorbed Cl atoms preferentially form dichlorides at the expense of the Cl atoms on the rest atoms. It seems as if a repulsive interaction between Cl adsorbates was strong in this range. Therefore the repulsive interaction is not simply determined by the geometric size of the atom (0.115 nm for Br and 0.100 nm for Cl),[31] but it is determined by the total

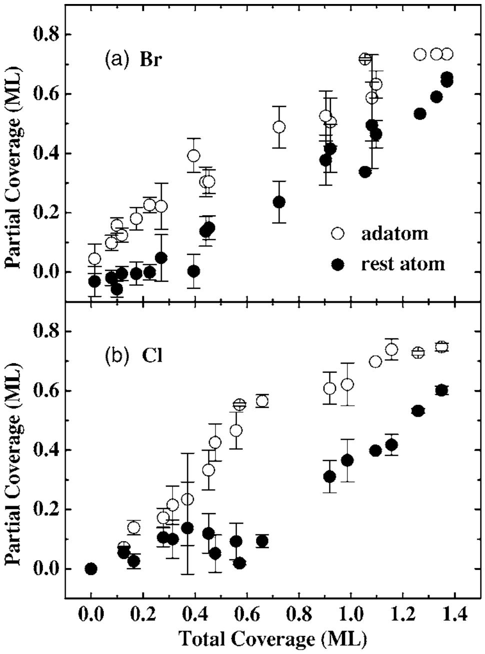

FIG. 4. The partial coverage on the adatoms, $a+b$ (open circles) and the partial coverage on the rest atoms, $\theta-(a+b)$ (closed circles) vs total coverage. Part (a) is for Br and (b) for Cl.

energy. The stronger repulsive interaction is a result of increase of the total energy due to distortion energy.

This study provides direct evidence for adsorption site preference and suggests a pattern formation on a Si(111) surface. As for the underlying interaction, repulsive interaction between adsorbates (case I) is reasonable, but interaction between Br adasorbate and the Si adatom (case II) is also possible. It is natural to accept case I because there are many evidences for this kind of interaction on a Si(001) surface.[2–13] Repulsive interaction qualitatively explains every result. However, the distance between Si adatoms on Si(111) is about 0.7 to 0.8 nm and much longer than the distance between dimers on Si(001), so that it is not quite sure that the repulsive interaction is effective to the Br adsorbates on the adatoms. In the previous paper on Br adsorption on Si(111),[20] we interpreted a higher sticking probability on adatom dangling bonds and a lower desorption energy in terms of a stronger repulsive interaction. Although the lower desorption energy was interpreted based on the analogy between the structure of the step edge on Si(111) and the dimer structure on Si(001), this analogy does not hold in the adsorption on the DAS structure. If adsorption on the rest atoms is blocked by a potential barrier, repulsive interaction between Br adsorbates is not necessary to explain the higher sticking probability on dangling bonds of the adatoms. In case II, adsorption preference to the adatom with low electron density[18] can also explain every experimental result. The rest atoms have higher electron density, and hardly adsorb halogen atoms. Back bond breaking by Br atoms occurs at lower coverage because back bonds of the Br-adsorbed Si adatom is more weakened than that of Cl-adsorbed Si adatom and $SiBr_2$ can be formed more easily than $SiCl_2$, as shown in Si(100).[10]

Anyhow, two kinds of studies are required to elucidate the underlying interaction and its chemical trend. One is STM study at the initial stage of adsorption using an electrochemical cell producing more atoms than molecules in order to investigate adsorption preference under the same condition as the present study. The other is total-energy calculation including potential barriers along several paths, such as that reported in Ref. 32.

IV. SUMMARY

The site preference of Br atoms in the adsorption process on Si(111)-7×7 at room temperature has been quantitatively studied. Partial coverages on the adatoms and the rest atoms were determined by means of SDR and TDS. The partial coverage on the rest atoms, which cannot be estimated by other techniques, even STM, reveals the adsorption site preference of bromine atoms. At the initial stage, Br atoms are adsorbed selectively on dangling bonds of the Si adatoms, but not on those at the rest atoms, and, at the later stage, dibromide species are formed on adatoms before monobromides reach 40% of the adatoms. On the other hand, Cl atoms are adsorbed randomly on the dangling bonds at both the adatoms and the rest atoms. The chemical trend of the observed site preference of halogen atoms is well interpreted in terms of repulsive interaction between halogen adsorbates or interaction between halogen adsorbate and the Si adatom. This study provides direct evidence of the adsorption site preference and suggests pattern formations of Br adsorbates on Si(111).

The information obtained in this study will be useful to understand the fundamental processes of halogen-etching of the Si(111) surface and will be applied to optimize the etching conditions. The patternings suggested in this study could be utilized to achieve site-selective etching and could be applied as a template to immobilize large molecules, such as biomolecules.

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*Electronic address: mtanaka@ynu.ac.jp
†Present address: Tokyo Seimitsu CO., LTD., 7-1, Shimorenjaku 9-chome, Mitaka-shi, Tokyo 181-8515, Japan.

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