IOPscience iopscience.iop.org

Home Search Collections Journals About Contact us My IOPscience

# Characterization of initial halogen adsorption on Si(111) surface by scanning tunnelling microscopy: correlation with optical measurements

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2006 J. Phys.: Condens. Matter 18 5895

(http://iopscience.iop.org/0953-8984/18/26/009)

View the table of contents for this issue, or go to the journal homepage for more

Download details:
IP Address: 129.252.86.83
The article was downloaded on 28/05/2010 at 11:58

Please note that terms and conditions apply.

J. Phys.: Condens. Matter **18** (2006) 5895–5903 doi:10.1088/0953-8984/18/26/009

# Characterization of initial halogen adsorption on Si(111) surface by scanning tunnelling microscopy: correlation with optical measurements

**Y Owa, K Shudo, M Koma, T Iida, S Ohno and M Tanaka**

Faculty of Engineering, Yokohama National University, Tokiwadai 79-5, Hodogaya-ku Yokohama, 240-8501, Japan

Received 31 January 2006, in final form 12 May 2006
Published 16 June 2006
Online at stacks.iop.org/JPhysCM/18/5895

**Abstract**
Initial adsorption processes of halogen atoms on a Si(111)-(7 × 7) surface were studied by means of scanning tunnelling microscopy (STM). The adsorption sites of halogen atoms were clarified directly with STM, and the results were compared with the partial coverage at each site, estimated previously from surface differential reflectance and thermal desorption spectroscopic analyses. The microscopic geometry of the atomic structure showed a good correspondence with the optical measurements, especially in terms of the density of the reacted sites. Bromine atoms were predominantly adsorbed near already adsorbed bromine, while chlorine atoms were almost randomly adsorbed. Polybromide formation occurred at coverage levels above 0.1 ML. Bromine atoms break the back-bonds of Si adatoms at lower levels of coverage than do chlorine atoms. The reason for the difference in adsorption behaviour between chlorine and bromine is discussed.

## 1. Introduction

Precise control of surface structures on a silicon wafer at the atomic level is critical for producing highly integrated circuits on a nanometre scale with sufficient reliability, and many researchers have investigated atomic processes on silicon surfaces. Halogen etching is widely used to generate nanoscale patterning with the aid of a resist layer. However, it is also possible, by controlling the preferential adsorption/desorption of the halogen, to produce nanostructures on a silicon surface without a resist layer [1]. Ogino *et al* reported patterning at the submicron scale without using photo-resist [2, 3]. Therefore, self-organization of silicon or silicon halide may provide a means to achieve nanoscale patterning. Such an approach would require a detailed understanding of the bond formation/deformation of halogen atoms on silicon surfaces during adsorption/desorption. The structure of the Si surface in the etching process was examined in detail by Weaver and his co-workers [4], and Sakurai and Nakayama theoretically calculated the energies of the structures that might be generated in order to analyse the activation path [5, 6]. Wijis and Selloni calculated the energy changes associated

 © 2006 IOP Publishing Ltd Printed in the UK 

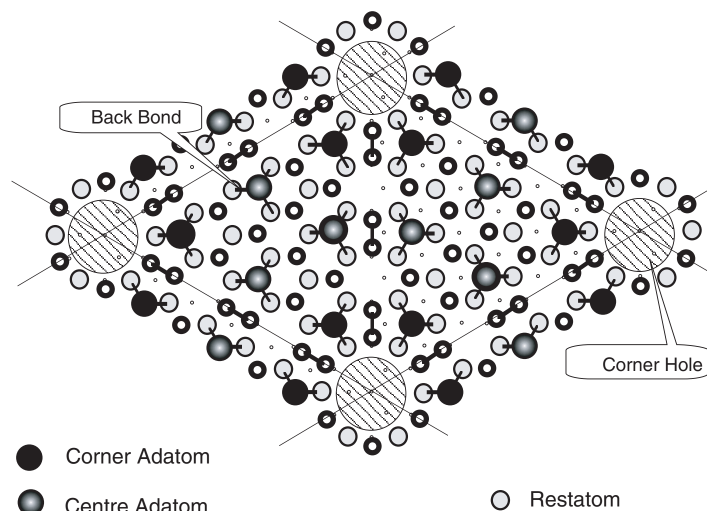


**Figure 1.** Schematic model of Si(111)-(7×7) DAS structure. Corner adatoms, which are adjacent to the corner holes (hatched), are shown as filled circles, while the other adatoms, called centre adatoms, are shown as gradated circles.

with halogen adsorption on Si(001) to evaluate bond formation [7]. To analyse the process, especially the energy, precise estimation of halogen coverage is required and an understanding of the geometric configuration is essential for identifying the reaction path. Among silicon surfaces, the (111) surface is the best studied because of the variety of reaction paths arising from its complex structure, i.e., the well known 7×7 surface reconstructing to dimer–adatom–stacking-fault (DAS) structure (figure 1) [8]. Here, we describe atomic-scale patterning on a Si(111) surface at very low coverage of halogen adsorbates, observed with scanning tunnelling microscopy (STM).

When chlorine atoms impact on the Si(111)-(7×7) surface, they react first with the Si-adatom (the Si atoms in the topmost layer) dangling bonds to form monochloride at low coverage, while higher coverage leads to the formation of dichloride and trichloride [9]. Cao *et al* showed that deformation of the bonds near the Si adatom is associated with polychloride formation [10, 11], and Boland *et al* confirmed that it was possible to distinguish the various types of chlorides from the displacements in STM images [12]. We show here that bromine adsorption can be similarly interpreted in terms of deformation in STM images.

Surface differential reflectance (SDR) is a powerful optical tool for evaluating the density of adsorbates in real time, even during high-pressure gas exposure. This method gives quantitative information about the averaged densities of various adsorbates at different reaction sites. In our previous SDR studies, we found that the distribution of adsorption structures is different between chlorine and bromine at low coverage [13, 14]. However, SDR cannot identify the structures involved at the atomic level. In this report, we employed STM to directly identify the adsorption sites of chlorine and bromine on a Si (111)-(7×7) surface.

## 2. Experimental procedure

The experiments were performed in an ultrahigh vacuum chamber with a base pressure of $1 \times 10^{-8}$ Pa. The Si(111) sample (B-doped, n-type, 10 Ω cm) was prepared in the chamber by repeated cycles of annealing to 1150 °C to obtain a well-ordered Si(111)-(7×7) surface. The

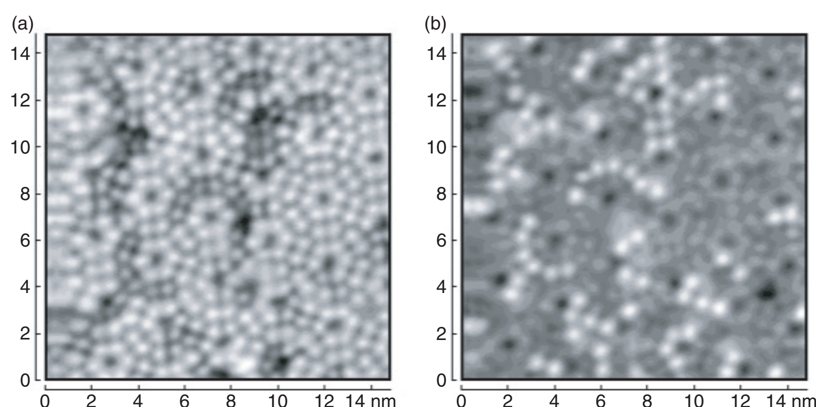


**Figure 2.** STM topograph of Si(111)-(7×7) exposed to bromine gas. The size of the area is 15×15 $nm^2$. The DAS structure can be recognized. The tunnelling current was 0.1 nA. Each spherical dot corresponds to one adatom, as illustrated in figure 1. (a) The sample bias was +1 V. The dark dots are bromine adsorbates, while the non-reacted sites are bright. (b) The sample bias was +3 V. Bromine-adsorbed sites are brighter than the non-reacted sites.

halogen gases were generated from AgCl and AgBr electrochemical cells doped with CdCl and CdBr, respectively [15]. The gases were applied to the clean Si(111)-(7×7) surface at room temperature. The cells were maintained at ∼400 K. The halogen flux was estimated with a quadrupole mass spectrometer and from the output of the ionization gauge. The coverage was controlled by adjusting the electric current through the silver halide cells. The distribution of halogen atoms on the adatom dangling bonds (ADDBs) was directly measured from the STM images.

## 3. Results and discussion

In STM images of a Si(111)-7×7 surface, spherical spots appear at the positions of ADDBs in the DAS structure (figure 1). Figure 2(a) shows that bromine adsorbed at ADDBs is imaged as darker spots than non-reacted ADDBs at the sample bias of +1 V. In contrast, figure 2(b) shows that these bromine adsorbates appear as brighter spots at the sample bias of +3 V. The appearance of reacted and unreacted ADDBs in relation to bias voltage is similar to that in the case of chlorine [12]. Boland and Villarrubia have reported that Si–Cl bond formation reduced the density of states near the Fermi energy and darkened the STM image at chlorine adsorption ADDBs on the silicon adatoms at the sample bias of 1 V [12]. Formation of antibonding states by the overlap between Si ADDBs and Br 4p orbitals leads to the bright appearance of the bromine adsorption ADDBs at the sample bias of 3 V [16, 17]. The coverage of halogen atoms was estimated from the average number per unit cell in the STM images; an atomic monolayer (ML) is defined as corresponding to the adsorption of 49 halogen atoms in one unit cell.

### *3.1. Initial adsorption (below 0.03 ML)*

ADDBs of halogen adsorption on Si(111)-(7×7) were examined at coverage below 0.03 ML. Figure 3 summarizes the average numbers of halogen atoms adsorbed at specific ADDBs per unit cell, subdivided into those with (1) no adjacent halogen atoms, (2) one adjacent halogen atom and (3) two or more halogen atoms. Each bar was obtained from counts of several images containing approximately a hundred 7×7 unit cells. The counts at centre adatoms are larger than those at corner adatoms for both halogens. Chlorine tended to be adsorbed more on the

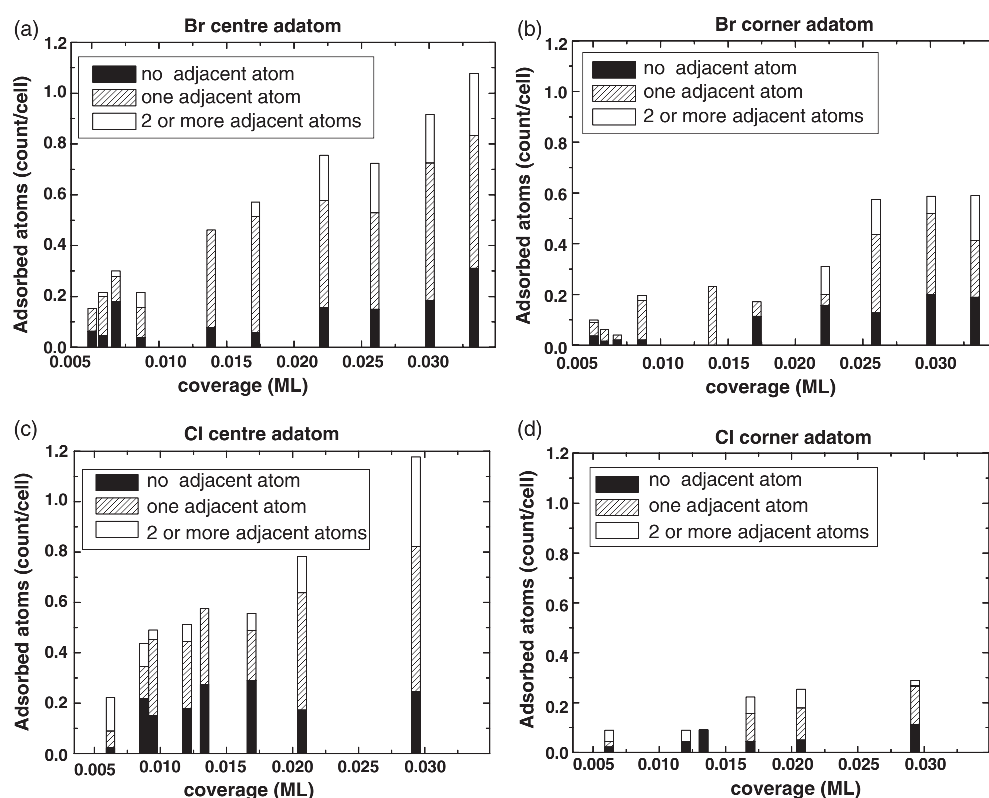


**Figure 3.** Adsorption site preference as a function of coverage. The counts per unit cell represent Br or Cl adsorption recognized from the STM images. Each count (bar) is subdivided to indicate adsorption at a site with no adjacent adsorbed atom, one adjacent adsorbed atom, or two or more adjacent adsorbed atoms. The fluctuation in the counts suggests inhomogeneity of the surface. Each bar is split to show isolated, single adjacent, and multiple adjacent adsorption. (a) Bromine adsorption at centre adatom, (b) bromine adsorption at corner adatom, (c) chlorine adsorption at corner adatom, and (d) chlorine adsorption at corner adatom.

centre adatoms, as compared with bromine, and chlorine atoms adsorbed at corner adatoms were rarely found below the coverage of 0.015 ML. It should be noted that especially at the centre adatoms, the proportion with no adjacent adsorbed atom (black bar) was larger in the case of chlorine (c) than in that of bromine (a). Adsorbed bromine atoms were rarely isolated, while the number of chlorine atoms with adjacent adsorbed atoms is similar to that without such atoms, indicating that bromine atoms showed a greater tendency to be adsorbed adjacent to the already adsorbed ADDBs. The relation was not so clear for the corner adatoms, because the fluctuation was relatively large compared to the total number of the adsorbed ADDBs.

The halogen gases emitted thermally from the cells have an incident kinetic energy at the surface of $\sim$0.034 eV, which is much smaller than the Si–Cl and Si–Br bonding energies [10]. Island formation takes place when chlorine gas is applied at the slightly higher translation energy of 0.05–0.11 eV [18], suggesting migration on the surface at the $\sim$10 nm scale. This can be interpreted as indicating that physisorbed chlorine in the metastable state can migrate on the surface before forming stable chloride at the adatoms. A precursor state has been suggested to be involved when the incident energy is less than 0.15 eV [19]. Our findings are consistent with a metastable precursor state migrating on the surface and tending to nucleate, since the

chlorine may be adsorbed at ADDBs after metastable migration where the adsorption barrier (0.05 eV) [19] is as low as the incident energy. This idea should also be applicable to bromine.

It appears to be the migration process that results in the different tendencies for adjacent adsorption between the two elements. If the migrating species is molecular, the tendency to be adsorbed at sites adjacent to existing halogen-adsorbed ADDBs must be due to migration, because direct chemisorption, e.g., at a very high translational energy such as 0.44 eV, did not result in segregation [18]. Dissociative adsorption of a chlorine molecule may occur via two mechanisms [20]: (i) one atom at an ADDB and the counterpart at the adjacent dangling bond of the rest-atom; (ii) the two atoms dissociated from the molecule are adsorbed at adjacent two ADDBs. Since the rest-atom is invisible with STM, model (i) cannot be directly visualized [9]. However, as bromine cannot be adsorbed at the rest-atom due to its large size and/or strong repulsive interaction [14], the two bromine atoms may be dissociatively adsorbed at two adjacent ADDBs as in model (ii). Thus, it is possible to explain the features of bromine adsorption in terms of the 'molecule on DAS' structure.

Migration on the surface requires kinetic energy until adsorption occurs at the preferred sites, since exposure to higher energy chlorine gas results in larger growth of islands (for energy up to 0.11 eV) [18]. We used electrochemical cells which generate molecular halogen gases containing some atomic gases, and the atomic component, which would be more active, may have a tendency to be adsorbed directly, or to have a shorter migration path. This may increase the proportion of isolated adsorption. Next, the bonding energy of Si–Cl may be higher than that of Si–Br, i.e., the interaction of chorine with the surface may be greater than that of bromine. Thus, chlorine atoms may have a smaller diffusion length than bromine atoms, which would therefore have a greater opportunity to reach electrically preferred ADDBs, i.e., sites adjacent to existing halogen-adsorbed ADDBs. The dissipation of the kinetic energy during the migration must be taken into account in considering the difference in the tendency for adjacent adsorption.

No matter whether the migration occurs in the form of molecular or atomic species, the adsorption of halogen at ADDBs is expected to cause charge transfer to the adjacent sites, i.e., the neighbours of the reacted ADDBs must be positively charged [10]. This induces lowering of the adsorption barrier near existing halogen-adsorbed ADDBs. Although quantitative analysis of barriers against migration, bond-formation, or dissociation in the adsorption process is difficult with STM, the results in figure 3 indicate that the barrier(s) in the case of bromine is different from that in the case of chlorine. Once chlorine atoms are chemisorbed on the surface, they do not migrate unless a kinetic energy of more than 0.86 eV is supplied [5].

Centre adatoms had higher reactivity than the corner adatoms, especially for chlorine. The reactivity ratio (centre:corner) can be estimated from the data in figure 3 to be in the range of about 2.5 to 3:1 for chlorine and 2:1 for bromine. This is consistent with the statistics of a concerted reaction mechanism [20], where the reactivity is associated with the rest-atoms. Recently, Tanaka *et al* have shown that at the initial stage (below 0.1 ML) chlorine atoms are adsorbed on the dangling bonds at both the adatom and the rest-atom, while bromine atoms are adsorbed at the former only [14]. The site preference may be related to the ability to interact with the rest-atom and the adatom: chlorine may interact strongly with the dangling bond at both the adatom and the rest-atom, and lose energy quickly, whereas weakly interacting bromine is too large to reach the rest-atom.

### *3.2. Polybromide formation (over 0.1 ML)*

The image of a bromine-adsorbed surface at the coverage of approximately 0.1 ML, shown in figure 4, illustrates the polybromide formation process. We regarded adsorption at adatoms displaced from the primary DAS position (shown as 'adatoms' in figure 1) as corresponding

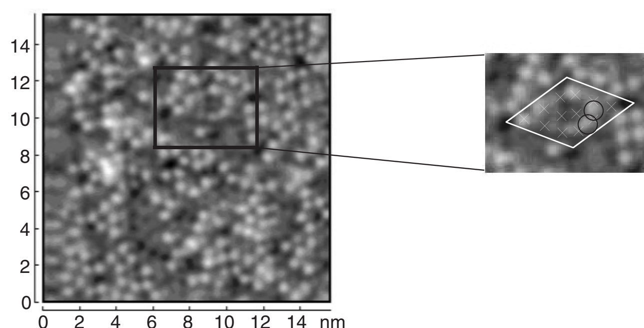


**Figure 4.** STM topograph of Br/Si(111) (sample bias = +3 V, tunnelling current = 0.1 nA). The scan size of the main panel is 15×15 $nm^2$. A part of the surface is zoomed into another image, in which the positions of the adatoms are marked with crosses in a 7×7 unit cell indicated with white lines. Polybromides are circled.

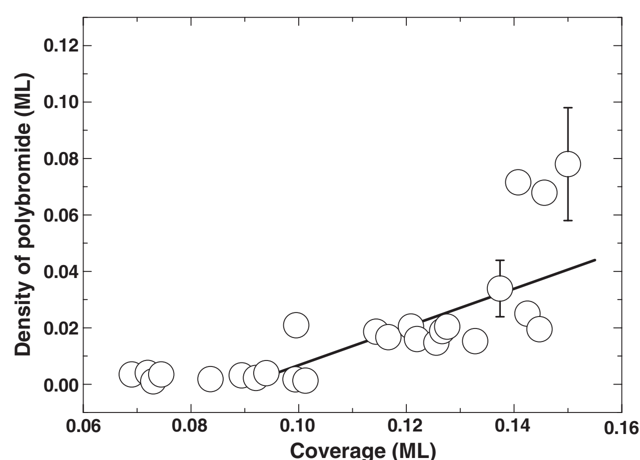


**Figure 5.** Plot of polybromide formation, determined from the count of reacted sites displaced from the primary position on Si(111)-(7×7), against coverage. Polybromide formation starts at about 0.10 ML. The slope (grey line in the figure) is 0.6 ± 0.2, and represents the probability of polybromide formation for a newly adsorbed bromine.

to the formation of polybromides. Although both dibromide and tribromide may be formed at high coverage [9], they cannot be distinguished in these topographic images. The number of polybromides can be estimated from the number of protrusions that are shifted from the original position of the adatom sites [12]. The estimated coverage of polybromide is depicted in figure 5. The number of ADDBs identified as polybromide fluctuated by ∼±30% among images, and it varied by about ±20% depending on the cut-off wavelength of the FFT filter. The formation of polybromide, which involves breaking the back-bonds beneath bromine adsorbed on the adatom, begins at 0.1 ML. During the polybromide formation, the slope of the plot is about 0.6 ± 0.2. This means that the probability of back-bond breaking to form polybromide is approximately 60% at adsorbed ADDBs.

In order to understand the adsorption process, we compared the statistical results in figure 5 with the results of quantitative analysis by means of SDR in figure 6, replotted from our previous report [14]. There are two components in the spectra, whose intensities correspond to the density of the halogen-terminated ADDBs (circles), and to the density of the adatom

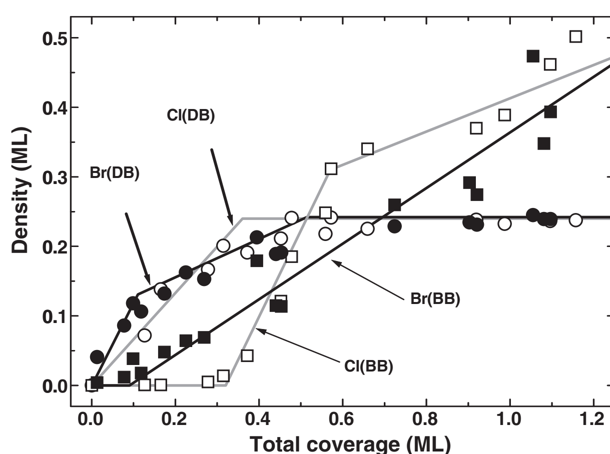


**Figure 6.** The densities of missing dangling bonds (DBs) and the broken back-bonds (BBs) obtained from previously reported SDR spectra, for chlorine (grey line) and bromine (black line). The total coverage of halogen was determined by means of thermal desorption spectroscopy.

back-bonds (ADBBs) (squares) broken to form polyhalide [21, 22]. The total coverage of these bromides was calibrated with TDS [9]. They roughly represent the average density of monobromide and polybromide formed.

The data in figure 6 indicate that all the bromine atoms were adsorbed on the ADDBs below 0.1 ML, and the bromine atoms start to break the ADBBs to form polybromides above 0.1 ML. In the range of coverage after the ADBBs start to be broken, the slope of the plot is 0.4 in the case of bromine. This means that 40% of the bromine atoms break the ADBBs to produce dibromide or tribromide, while the rest is adsorbed on the uncovered dangling bonds at the adatoms (40%, known from the slope of the plot for DB) and the rest-atoms (remaining 20%). As the rest-atoms are not seen in STM images, approximately half of the bromines adsorbed on the adatoms broke the back-bond. This is in good agreement with the slope of the line in figure 5, considering that the coverage in figure 5 was estimated from the STM image.

On the other hand, in the case of chlorine the slope changes at 0.3 ML for both the dangling bonds and back-bonds, as shown in figure 6. All of the chlorine atoms were adsorbed either on the ADDBs or on the rest-atom dangling bonds with equal probability below 0.3 ML [9]. At coverage over 0.3 ML, the ADDBs are all saturated, and some of the chlorine atoms start to break the ADBBs to form polychlorides.

At coverage from 0.1 to 0.3 ML a bromine atom breaks the ADBBs, and is likely to terminate the broken counterpart to form polybromide. In contrast, adsorption of chlorine atoms does not break ADBBs, although it should be noted that dangling bond termination occurs at the rest-atom as well [9]. The chlorine can access the rest-atom between the chlorinated adatoms with a small barrier that is comparable to that of access to the adatom. When nearly all the dangling bonds are terminated by chlorine, the adatoms start to form polychlorides. The different thresholds for the polyhalide formation of chlorine and bromine can be discussed in terms of energy. The back-bond is weakened when the dangling bond of the adatom is already terminated. In the desorption processes from halogen-adsorbed Si(001) in a geometry with small distortion, the desorption energy of bromide was calculated to be lower than that of chloride [23]. Thus, bromine effectively weakens the back-bond, so that it becomes more favourable to form polybromide than for adsorption to occur at the dangling bond at the rest-atom.

The discrepancies at the beginning of polyhalide formation (at 0.1 and 0.3 ML for bromine and chlorine, respectively) appear to reflect an essential difference between the two halogen elements. Bromine does not access rest-atoms but prefers adatoms, forming polybromide. The barrier to access at the rest-atoms may originate from the larger atomic radius of bromine (0.115 nm for bromine, versus 0.100 nm for chlorine [24]). Deformation, induced by the repulsive interaction, would be much larger for bromine than for chlorine when the distance between atoms is of the order of 0.1 nm on the surface. In the case of chlorine, the deformation is small when monochloride is formed on a Si(111) surface [6]. However, the differences between Si–Cl and Si–Br have not been considered in detail. In the case of chlorine, the deformation has been examined theoretically for adsorption [11], and repulsive interaction also affects the energy of back-bond breaking through deformation [5].

The onset of back-bond breaking estimated with STM (figure 5) is consistent with the results of SDR. The slight discrepancy of the slope for back-bond breaking between STM and SDR can be chiefly attributed to the larger errors in the STM measurements, due to the inhomogeneity of coverage on the same surface estimated from a limited number of STM images. There is also difficulty in counting the reacted dangling bonds at increased coverages, because the atomic displacement upon back-bond breaking is not constant. Nevertheless, the densities obtained with STM coincide reasonably well with the SDR results. It is important to note that the optical response shows the averaged properties over the macroscopic area of the surface. On the other hand, the fluctuation of the statistical results from the STM images indicates that the distribution of the adsorbates varies greatly at the atomic scale.

We could not identify any correlation among the sites of polybromide formation. From a static viewpoint, homogenous pattern formation [7] or a specific distribution of sites of polychloride formation may arise through the strong repulsive interaction of bromines adsorbed on the surface, as seen in the case of monochloride formation (figure 3). However, the dynamic aspect of migration (including the energy dissipation) is also important in influencing the site selectivity. Besides the effects of higher levels of the coverage, the bonding configuration and the ionic charge can vary fractionally when several neighbouring silicon atoms are chlorinated, as suggested by calculation [11]. The present results indicate that the occurrence of large statistical fluctuations in halogen adsorption processes, caused by the dynamic features, will have to be taken into account in order to develop atomic scale fabrication.

## 4. Summary

The adsorption of chlorine and bromine on a silicon surface was examined by STM to elucidate the mechanisms involved at the atomic scale. Bromine atoms tended to be adsorbed near bromine-reacted ADDBs. On the other hand, chlorine atoms tended to be adsorbed independently on the surface. In the case of bromine, polybromide formation was observed with STM above 0.1 ML, at which coverage the ADBBs start to break. The corresponding value for chlorine was 0.3 ML. The back-bonds at the already reacted adatoms are broken at higher probability in the case of bromine than chlorine. The adsorption statistics obtained with STM were broadly consistent with our previous SDR data. The correlation of the adsorption sites with the bond breaking/formation, suggested by the optical findings, was confirmed at the atomic level.

## References

[1] Shudo K, Kirimura T, Kaneko N, Takahashi M, Tanaka Y, Ishikawa T and Tanaka M 2004 *Surf. Sci.* **566/568P1** 425–9

Shudo K, Koike Y, Owa Y, Koma M, Ohno S and Tanaka M 2006 Activity report *ALC'05: Proc. 5th Atomic Level Characterizations* Japan Society for the Promotion of Science (JSPS) at press

[2] Ogino T 1997 *Surf. Sci.* **386** 137
[3] Ogino T, Hibino H, Homma Y, Kobayashi Y, Prabhakaran K, Sumitomo K and Omi H 1999 *Acc. Chem. Res.* **32** 447
[4] Aldao C M and Weaver J H 2001 *Prog. Surf. Sci.* **68** 189
[5] Sakurai S and Nakayama T 2002 *J. Cryst. Growth* **237–239** 212
[6] Sakurai S and Nakayama T 2001 *Surf. Sci.* **493** 143
[7] de Wijis G A and Selloni A 2001 *Phys. Rev.* B **64** 041402
[8] Takanayagi K, Tanishiro Y, Takahashi M, Motoyoshi H and Yagi K 1985 *J. Vac. Sci. Technol.* A **3** 1502
[9] Shudo K, Washio H and Tanaka M 2003 *J. Chem. Phys.* **119** 13077
[10] Cao P and Smith P V 1995 *J. Phys.: Condens. Matter* **7** 7113
[11] Smith P V and Cao P 1995 *J. Phys.: Condens. Matter* **7** 7125
[12] Boland J J and Villarrubia J S 1990 *Science* **248** 838
[13] Tanaka M, Yamakawa E, Shirao T and Shudo K 2003 *Phys. Rev.* B **68** 165411
[14] Tanaka M, Shudo K and Numata M 2006 *Phys. Rev.* B **73** 115326
[15] Spencer N D, Goddard P J, Dacies P W, Kitson M and Lambert R M 1983 *J. Vac. Sci. Technol.* A **1** 1554
[16] Boland J J and Villarrubia J S 1990 *Phys. Rev.* B **41** 9865
[17] Pechman R J, Wang X-S and Weaver J H 1995 *Phys. Rev.* B **52** 11412
[18] Yan C, Jensen J A and Kummel A C 1994 *Phys. Rev. Lett.* **72** 4017
[19] Sullivan D J D, Flaum H C and Kummel A C 1993 *J. Phys. Chem.* **97** 12051
[20] Jensen J A, Yan C and Kummel A C 1996 *Phys. Rev. Lett.* **76** 1388
[21] Noguez C, Beitia C, Preyss W, Shkrebtii A I, Roy M, Borensztein Y and Del Sole R 1996 *Phys. Rev. Lett.* **76** 4923
[22] Tanaka M, Shirao T, Yamauchi D and Ota K 2001 *Appl. Surf. Sci.* **169** 212
[23] Aizawa H, Tsuneyuki S and Ogitsu T 1999 *Surf. Sci.* **438** 18
[24] Slater J C 1964 *J. Chem. Phys.* **39** 3199