

Atomic structural changes of a Br-chemisorbed Si(111)-7×7 surface under 10–150 eV electron impact

Kozo Mochiji and Masakazu Ichikawa

Joint Research Center for Atom Technology, Angstrom Technology Partnership (JRCAT-ATP), c/o National Institute for Advanced Interdisciplinary Research (NAIR), 1-1-4 Higashi, Tsukuba, Ibaraki 305-0046, Japan

(Received 24 November 1999)

Electron-stimulated desorption from Br-chemisorbed Si(111)-7×7 surfaces was investigated by scanning tunneling microscopy. Irradiating these surfaces with electrons field emitted from the tip of the scanning tunneling microscope induced various desorption behaviors depending on the initial Br coverage and electron energy. At low Br coverage, Br atoms desorb but no atomic changes occur on the Si surface. At saturation coverage, Si adatoms as well as Br atoms desorb to a large extent. The cross section of Br atom desorption first increases near 15 eV and then increases by orders of magnitude with electron energy up to 150 eV. The cross section of adatom desorption, in contrast, is much less dependent on the electron energy in this energy region. These desorption behaviors are discussed from the viewpoint of electronic excitation at the Br-chemisorbed Si(111) surface.

I. INTRODUCTION

Electron-stimulated desorption (ESD) of halogen-adsorbed semiconductor surfaces has received much attention from the viewpoint of industrial applications as well as fundamental interest. Studies of the ESD of halogen-adsorbed semiconductor surfaces have so far concentrated on the analysis of desorbed particles,^{1–4} and have provided information on the species of desorbed particles and the way in which the yield of the desorbed particles changes as a function of electron energy. The surface structural changes induced by electron irradiation, however, especially those on the atomic scale, have been little studied for these halogenated surfaces. Baba and Matsui demonstrated that atoms on a chlorine-adsorbed Si surface can be manipulated by a scanning tunneling microscope (STM).⁵ They showed that chlorine atoms can be removed by applying a high pulse bias to the STM tip. We also reported that Si adatoms were removed from a Br-adsorbed Si(111) surface by STM scanning.⁶ These atom removals might be mainly due to the field induced in the narrow gap between the tip and the sample. Such a field evaporation should be distinguished from the ESD process, where the desorption is induced by electronic transitions to excited states of the surface. If the mechanism of ESD is to be elucidated, the effect of electron irradiation on the atomic structure at the surface must be studied.

We earlier developed a technique for irradiating a sample surface with field emission (FE) electrons from a STM tip that is away from the sample,^{7,8} and this technique enables the STM tip to be used for making *in situ* observations of the FE-irradiated area on the surface. Because we can observe the same area on a sample before and after electron irradiation, we can evaluate the effects of the irradiation site by site. In the present study we investigated ESD from a Br-chemisorbed Si(111) surface by using this technique, and the desorption behavior we observed is quite different from the results obtained in a previous study of STM etching.⁶

II. EXPERIMENT

The current study was conducted using a STM (USM-501, Unisoku Ltd.) mounted in an ultrahigh-vacuum chamber with a base pressure of about 5×10^{-9} Pa. The sample was an *n*-type (0.01 Ω cm) Si(111) wafer outgassed for 8 h at 650 °C and flash heated to 1200 °C. The Si(111)-7×7 surface was exposed to Br₂ molecules at room temperature by dosing with Br₂ gas through a variable-leak valve. The Br₂ gas was the vapor from pure liquid Br₂ (99.9%, TRI Chemical Inc.) in a glass cylinder. The STM tips were fabricated from 0.3-mm-wide tungsten wire that was electrochemically etched in a 2.5N KOH solution. Prior to use, the tips were bombarded by an electron beam in vacuum in order to remove any oxide. In the previous study we found that brominated Si adatoms can be etched by tip scanning at sample biases higher than +3.0 V.⁶ The STM images shown here were therefore obtained under constant-current conditions in which the sample bias voltage was lower than +2.5 V. The tunneling current versus bias voltage characteristics (*I*-*V* curves) at various points on the sample surfaces were determined by using a conventional sample-and-hold technique.

The FE irradiations of sample surfaces were performed at room temperature in the following steps. After the tip was positioned on the place in the STM image to be irradiated, the feedback loop was inactivated in order to move the tip away from the surface. The tip-to-sample distance was changed between 1 and 130 nm. Then a voltage was applied to the sample in order to extract FE electrons from the tip and the extraction voltage was varied between 10 and 150 V. A FE current was detected during the irradiation. Under these conditions the value obtained by multiplying the FE current (nA) by the irradiation time (s) and dividing by the square of the tip-sample separation (nm) is regarded as the relative dose density of electrons with which the sample was irradiated. In the later discussion, the kinetic energy of incident electrons will be corrected for the contact potential difference between the tip and the sample.

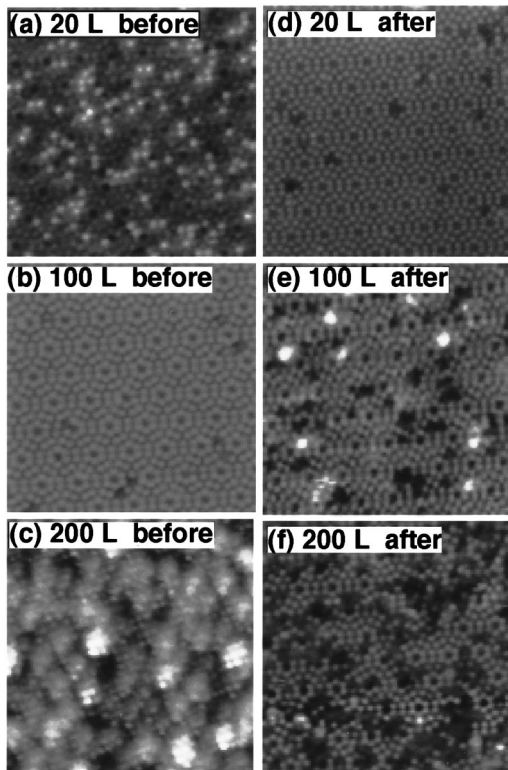


FIG. 1. STM images before and after FE irradiation of Si(111)-7 \times 7 surfaces dosed with 20–200 L of Br₂. Extraction voltage and FE current density were 50 eV and 10 nA s/nm². Sample biases for the observations were +2.5 V in (a), (b), and (c), and +1.0 V in (d), (e), and (f). The areas shown are 16 \times 16 nm².

III. RESULTS AND DISCUSSION

A. Effect of Br coverage

Figures 1(a), 1(b), and 1(c) show STM images before electron irradiation of Si(111)-7 \times 7 surfaces dosed with 20–200 L of Br₂. The images were obtained at a sample bias of +2.5 V. At sample biases around +1.0 V, the Br-bonded adatoms are darker than the surrounding unreacted adatoms because of the occupation of the dangling bonds, while at biases over +2.0 V most of them become brighter because of tunneling into the antibonding state of the Si-Br bond.^{9,10} Therefore the bright sites in these images represent Br-bonded adatoms. The density of these adatoms increased with the Br₂ exposure dose. At Br₂ doses up to 100 L the 7 \times 7 structure is retained and so most adatoms are singly brominated.¹¹ With further increase in Br₂ exposure up to 200 L, the periodicity of 7 \times 7 structure became a little blurry. This is because at doses much beyond the saturation level the Br₂ molecules react with the backbonds of the Br-bonded adatoms, forming multiply brominated silicons.¹²

The STM images of the above surfaces after irradiation with FE electrons extracted at 50 V are shown in Figs. 1(d), 1(e), and 1(f). These images were obtained at a sample bias of +1.0 V. There are dark sites at adatom positions, the number of which increases as the initial Br coverage increases. The brightness of these dark sites was not changed by changes in the applied bias, so they are thought to be vacancies of the adatoms that are produced by the electron irradiation. Some bright spots seen in Fig. 1(e) or 1(f) may

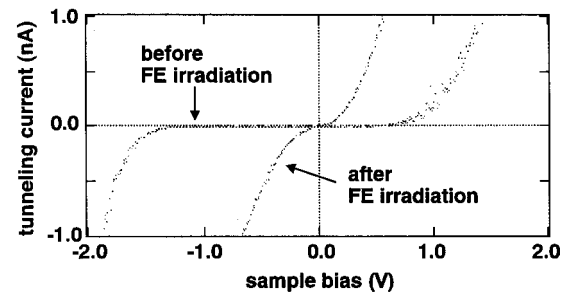


FIG. 2. Tunneling current versus sample bias voltage (I - V) curves obtained before and after FE irradiation of a Si(111)-7 \times 7 surface dosed with 200 L of Br₂. Extraction voltage and FE current density were 50 eV and 10 nA s/nm². The feedback loop was inactivated at a sample bias of +1.0 V and a tunneling current of 0.7 nA.

be isolated Si atoms that are removed from the adatom sites. The I - V curves obtained before and after FE irradiation of a surface dosed with 200 L of Br₂ are shown in Fig. 2. In the I - V curve obtained before irradiation there is a gap in the tunneling current at sample biases between -1.3 and +0.6 V. The gap is due to the saturation of dangling bonds of adatoms by Br bonding. In the I - V curve obtained after the FE irradiation there is no gap; the I - V curve resembles that of a clean surface. This result indicates that most of the adatoms remaining after the FE irradiation are Br-free.

Thus the electron irradiation induced various desorption behaviors depending on the initial Br coverage. At the low coverage resulting from a 20 L dose, Br atoms desorbed but adatoms hardly desorbed, so the density of adatom vacancies was nearly the same as that of the initial clean surface [Fig. 1(d)]. As Br coverage increased up to the saturation level, adatom desorption became notable even though the predominant desorption was that of Br atoms from the adatom layer [Figs. 1(e) and 1(f)]. As a result, the density of adatom vacancies produced by electron irradiation increased with initial Br₂ doses up to 200 L (Fig. 3). This is explained as follows: Adatoms are multiply brominated when the Br₂ dose is high and these multiply brominated adatoms (SiBr_{*x*},

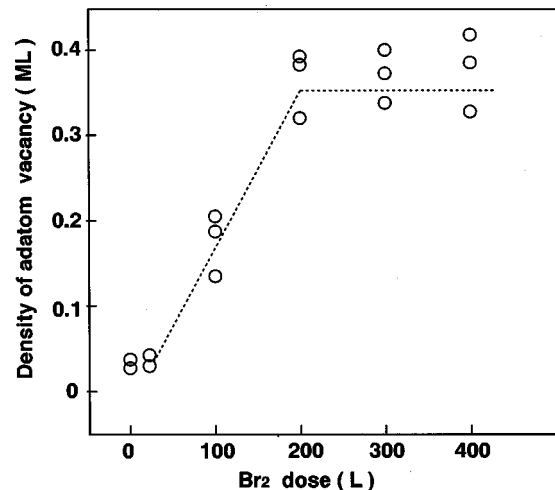


FIG. 3. Density of adatom vacancies as a function of initial Br₂ dose. Extraction voltage and FE current density were 50 eV and 10 nA s/nm².

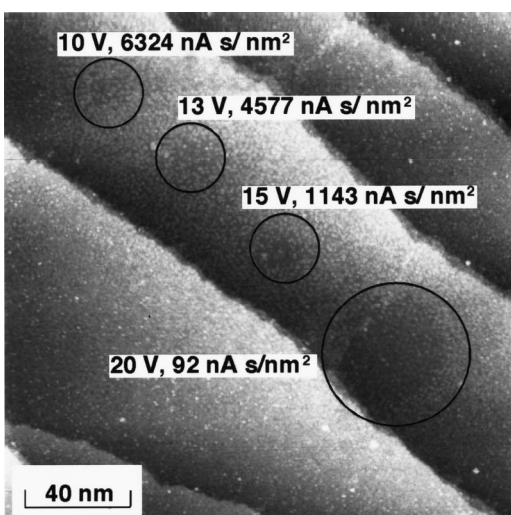


FIG. 4. STM image after FE irradiations of a Si(111)-7 \times 7 surface dosed with 400 L of Br₂. Extraction voltages of FE electrons were 10, 13, 15, and 20 V. The irradiation at each voltage was performed at the same distance between the tip and the sample (13 nm). The values indicated at each voltage are FE current density. The areas enclosed by circles were irradiated. Sample biases for the observation were +2.0 V.

$x=2$ or 3) desorb under electron irradiation more easily than singly brominated adatoms because of the reduced number of adatom backbonds. The density of adatom vacancies hardly increased at Br₂ doses beyond 200 L. This is probably because at room temperature the adatom bromination is almost saturated by doses near 200 L.

B. Effect of electron energy

Figure 4 shows the STM image of a fully Br₂-dosed surface after sequential irradiation by FE electrons at extraction voltages of 10–20 V. The irradiation at the voltages below 20 V changed the contrast in the STM image only slightly, in spite of very high electron dose densities. The area irradiated at 20 V, on the other hand, is markedly darker than unirradiated areas. Figure 5(a) shows a magnified image of the surface obtained after irradiation at 20 V. Over 60% of the adatoms are removed and the underlying rest layer is imaged. The remaining adatoms and the exposed rest atoms were Br-free as a result of the I - V measurement. The underlying rest layer seems to keep a 7 \times 7 periodicity among the partially remaining adatoms. This fact is not self-evident since it is not clearly understood how the surface reconstructs under the electron-stimulated desorption. Becker *et al.* reported that the hydrogen from a hydrogen-terminated Si(111)-1 \times 1 surface desorbs when the surface is irradiated with 2–10 eV electrons, converting the 1 \times 1 structure to the 2 \times 1 structure.⁸ We did not observe the desorption of Br atoms and adatoms at extraction voltages below 10 V, and, even at higher voltages, all the adatoms in a 7 \times 7 unit cell were not removed. The structural conversion produced by ESD may also depend on the size of the desorbed area as well as the excitation process.

On more careful inspection of the image shown in Fig. 5(a), several sets of four bright spots (some of them are enclosed by circles) smaller than an adatom exist, instead of

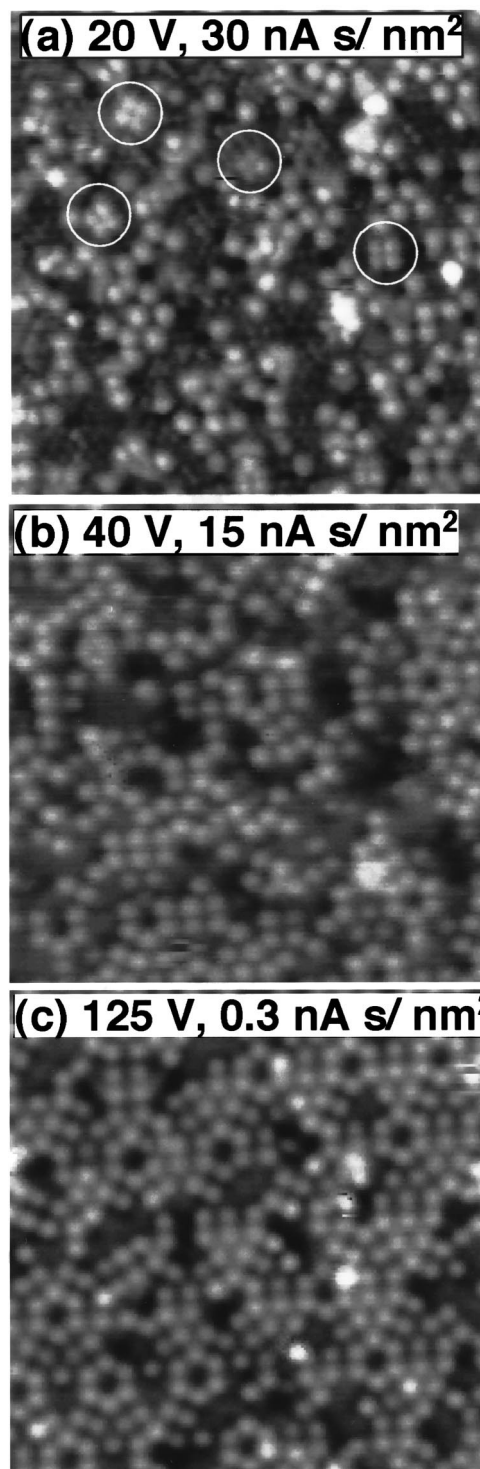


FIG. 5. STM images after FE irradiation of Si(111)-7 \times 7 surfaces dosed with 400 L of Br₂. Extraction voltages and FE current densities were (a) 20 V and 30 nA s/nm², (b) 40 V and 15 nA s/nm², and (c) 125 V and 0.3 nA s/nm². Sample bias for the observation was +1.5 V. The areas shown are 10 \times 10 nm². The areas enclosed by circles in (a) show four-Si-atom structures.

missing adatoms, around the dimer walls of the 7 \times 7 unit cells. The four bright spots are on top of the rest atoms. These features can be assigned to the four-Si-atom structures that were observed in the initial stage of Si deposition on Si(111)-7 \times 7 at room temperature.¹³ We propose the follow-

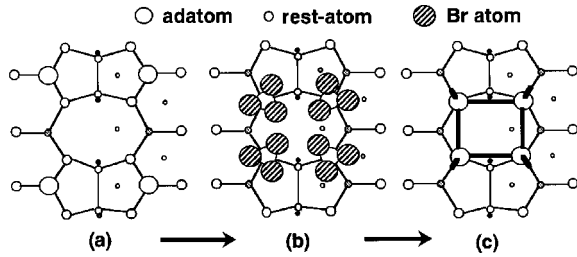


FIG. 6. Schematic representations of the top view around the dimer wall of a Si(111)-7 \times 7 unit cell: (a) before (clean surface) and (b) after Br₂ exposure, and (c) after FE irradiation. When an adatom is triply brominated as shown in (b), the position of the adatom is shifted to the top of the site on the rest atom by breaking two backbonds of the adatom.

ing mechanism shown in Fig. 6 for production of this structure: Some adatoms are triply brominated by Br₂ exposure up to oversaturation dosage. During the triple bromination, the position of the adatom is shifted to the top of the rest atom, which is bonded to the adatom, because four *sp*³ bonds of the Si-SiBr₃ structure are required to form an equilateral tetrahedron. After that, the Br atoms bonded to the Si atom preferentially desorb by FE irradiation and only the Si atoms remain. Each of these remaining Si atoms has three dangling bonds, and chemical bonds between the Si atoms are formed in order to reduce the surface energy.

As shown in Figs. 5(b) and 5(c), Br atoms were removed at much lower electron dose densities when the extraction voltage was increased from 20 to 40 or 125 V. The value of the electron dose density indicated in each image is the minimum value required to desorb most of the Br atoms in the 30 \times 30 nm² area at the corresponding extraction voltage (hereafter we call this electron dose density the critical dose density). The reciprocal of the critical dose density is shown in Fig. 7 as a function of the extraction voltage. For voltages up to 150 V, Br desorption was greatly enhanced by increases in extraction voltage; that is, with increases in electron energy.

The Br atoms are thought to be removed from the surface in two ways: by the breaking of Br-Si bonds and by the breaking of Si-Si backbonds. The removal rate for Br atoms is therefore given by

$$-dN_{\text{Br}}/dD_e = \sigma_{\text{Br}}N_{\text{Br}} + \sigma_{\text{Si}}\alpha N_{\text{Si}}, \quad (1)$$

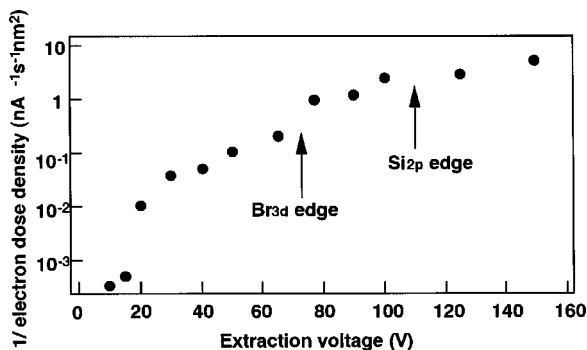


FIG. 7. Relation between extraction voltage and reciprocal of the critical dose density of FE electrons required for Br atom desorption. The initial Br₂ dose was 400 L. The measured area was 30 \times 30 nm².

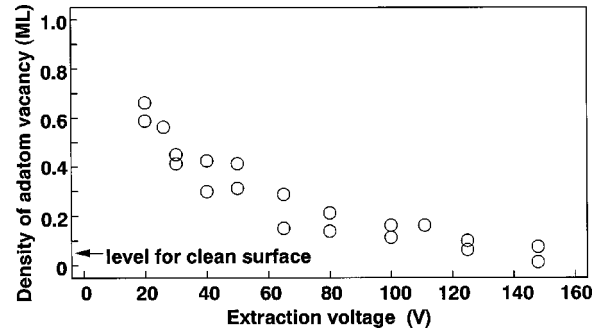


FIG. 8. Density of adatom vacancies produced by FE irradiation as a function of the extraction voltage. The initial Br₂ dose was 400 L, and the electron dose density at each extraction voltage was the critical dose density (see text).

where σ_{Br} and σ_{Si} are the cross sections for desorption of Br atoms and Si adatoms (SiBr_x), and N_{Br} and N_{Si} are the coverages of Br atoms and Si adatoms on the surface at the electron dose density D_e . The multiplicities of the bromination are neglected here for simplicity. The coefficient α is the coverage of Br atoms on the adatoms, and αN_{Si} can be replaced by N_{Br} . By integrating Eq. (1) we obtain

$$N_{\text{Br}} = N_{\text{Br}}^0 \exp[-(\sigma_{\text{Br}} + \sigma_{\text{Si}})D_e], \quad (2)$$

where N_{Br}^0 is N_{Br} at $D_e = 0$. When $N_{\text{Br}}/N_{\text{Br}}^0$ is given, the reciprocal of D_e provides the total cross section ($\sigma_{\text{Br}} + \sigma_{\text{Si}}$). From the result shown in Fig. 7, therefore, it is found that the total cross section increased by orders of magnitude as the extraction voltage increased up to 150 V. The second term in Eq. (1) corresponds to the removal rate for adatoms; that is,

$$-dN_{\text{Si}}/dD_e = \sigma_{\text{Si}}\alpha N_{\text{Si}} = \sigma_{\text{Si}}N_{\text{Br}}. \quad (3)$$

Substituting the right-hand side of Eq. (2) for N_{Br} and integrating the expression, we have

$$N_{\text{Si}} = N_{\text{Si}}^0 - N_{\text{Br}}^0 [\sigma_{\text{Si}}/(\sigma_{\text{Br}} + \sigma_{\text{Si}})] \{1 - \exp[-(\sigma_{\text{Br}} + \sigma_{\text{Si}})D_e]\} \quad (4)$$

where N_{Si}^0 is N_{Si} at $D_e = 0$. Since N_{Si}^0 is nearly equal to N_{Br}^0 at saturation coverage,

$$N_{\text{Si}} = N_{\text{Si}}^0 (1 - [\sigma_{\text{Si}}/(\sigma_{\text{Br}} + \sigma_{\text{Si}})] \{1 - \exp[-(\sigma_{\text{Br}} + \sigma_{\text{Si}})D_e]\}). \quad (5)$$

For $D_e \rightarrow \infty$,

$$(N_{\text{Si}}^0 - N_{\text{Si}})/N_{\text{Si}}^0 = \sigma_{\text{Si}}/(\sigma_{\text{Br}} + \sigma_{\text{Si}}). \quad (6)$$

This equation suggests that, at sufficiently high electron dose, the density of adatom vacancies approaches the ratio of the cross section of adatom desorption to the total cross section. As shown in Fig. 5, more adatoms remained as the extraction voltage increased from 20 to 40 or 125 V. The density of adatom vacancies is shown in Fig. 8 as a function of the extraction voltage. The electron dose density used at each voltage was the critical dose density. The density of adatom vacancies was hardly changed by irradiation with electron dose densities greater than the critical dose density. Therefore it should be noted that the desorption of Br-free adatoms is scarcely induced by electron irradiation. The den-

sity of adatom vacancies decreased with the extraction voltage and approached the level for the initial clean surface. This suggests that σ_{Br} in Eq. (6) increases more rapidly with the extraction voltage than does σ_{Si} . Therefore the dependence of the total cross section on the electron energy, shown in Fig. 7, actually represents the dependence of σ_{Br} at the higher electron energies.

As shown in Figs. 4 and 7, Br atom desorption became large at an extraction voltage near 20 V. For the exact determination of threshold electron energy for Br desorption, the electron energy should be corrected for the contact potential difference of the emitting and receiving surfaces. If we assume that most electrons are emitted at the Fermi level of the tip surface¹⁴ and that the work function of a Br-chemisorbed Si(111) surface is similar to that for a clean Si surface, 4.8 eV,¹⁵ the corrected threshold energy is about 15 eV. Neither experimental nor calculated data on the energy level of the valence electrons of a Br-chemisorbed Si(111) surface have been reported. It has, however, been shown both experimentally and theoretically that the ionization energies for the valence levels of the SiBr₄ molecule are close to those of the SiCl₄ molecule and that the energy difference between the two molecules is at most about 1 eV.^{16,17} At a first approximation, therefore, the energy levels of the valence electrons of the Br-chemisorbed Si(111) surface can be presumed to be close to those of the valence electrons of the Cl-chemisorbed Si(111) surface. The bonding (σ) and antibonding (σ^*) levels of the Si-Cl bond are respectively 12–13 and 3–4 eV below the vacuum level.^{18–20} Therefore, the excitation of a σ electron to the antibonding level requires 8–10 eV, which is a little far from the above threshold energy. The threshold energy at 15 eV is close to the energy needed to excite a σ electron to the vacuum level. Such an excitation leads to ion desorption and otherwise to neutral atom desorption through

the crossing to some neutral excited states.²¹ The energies for the ionization edge of Br 3*d* (~75 eV) and Si 2*p* (~110 eV) electrons are in the energy region studied here. The increase in the cross section of Br atom desorption (σ_{Br}) at high electron energies is mainly due to the excitations of these core electrons, although a resonant enhancement in the cross section near the ionization edges is not clearly observed in Fig. 7. Analyses of the desorbed species and their yield spectra will elucidate the desorption mechanism in more detail.

IV. CONCLUSION

A Br-chemisorbed Si(111) surface undergoes atomic-structural changes when electron-stimulated desorption occurs, and the desorption behavior depends on the initial Br coverage and electron energy. When the initial coverage is low, Br atoms desorb but Si adatoms hardly desorb. When the initial Br coverage is increased up to the saturation level, the adatom desorption increases greatly because the number of multiply brominated adatoms increases. The cross section of Br atom desorption first increases at an electron energy of 15 eV and then increases rapidly with the electron energy up to 150 eV. The threshold energy could correspond to ionization of the bonding electrons of the Si-Br bond. The cross section of the desorption of brominated adatoms, in contrast, depends little on the electron energy. *In situ* STM observation of a surface irradiated by field-emitted electrons from a STM tip will be essential for atomic-structural studies of ESD.

ACKNOWLEDGMENTS

This work, partly supported by NEDO, was performed at JRCAT under the joint research agreement between NAIR and ATP.

-
- ¹S. M. Mokler, P. R. Watson, L. Ungier, and J. R. Arthur, *J. Vac. Sci. Technol. B* **8**, 1109 (1990).
- ²D. Troost, H. J. Clemens, L. Koenders, and W. Monch, *Surf. Sci.* **286**, 97 (1993).
- ³D. Sterratt, Q. Guo, and E. M. Williams, *Nucl. Instrum. Methods Phys. Res. B* **101**, 84 (1995).
- ⁴Q. Guo, D. Sterratt, and E. M. Williams, *J. Electron Spectrosc. Relat. Phenom.* **72**, 31 (1995).
- ⁵M. Baba and S. Matsui, *Appl. Phys. Lett.* **65**, 1927 (1994).
- ⁶K. Mochiji and M. Ichikawa, *Jpn. J. Appl. Phys., Part 2* **38**, L1 (1999).
- ⁷M. Shibata, Y. Nitta, K. Fujita, and M. Ichikawa, *Appl. Phys. Lett.* **73**, 2179 (1998).
- ⁸R. S. Becker, G. S. Higashi, Y. J. Chabal, and A. J. Becker, *Phys. Rev. Lett.* **65**, 1917 (1990).
- ⁹R. J. Pechman, X.-S. Wang, and J. H. Weaver, *Phys. Rev. B* **52**, 11 412 (1995).
- ¹⁰K. Mochiji and M. Ichikawa, *J. Appl. Phys.* **86**, 841 (1999).
- ¹¹J. A. Golovchenko, J. R. Patel, D. R. Kaplan, P. L. Cowan, and M. J. Bedzyk, *Phys. Rev. Lett.* **49**, 560 (1982).
- ¹²R. B. Jackman, R. J. Price, and J. S. Foord, *Appl. Surf. Sci.* **36**, 296 (1989).
- ¹³H. Tanaka, T. Yokoyama, and I. Sumita, *Jpn. J. Appl. Phys., Part 1* **33**, 3696 (1994).
- ¹⁴Vu. Thien Binh, N. Garcia, and S. T. Purcell, *Adv. Imaging Electron Phys.* **95**, 63 (1996).
- ¹⁵M. J. Bozack, M. J. Dresser, W. J. Choyke, P. A. Taylor, and J. T. Yates, Jr., *Surf. Sci.* **184**, L332 (1987).
- ¹⁶B. D. El-Issa and A. Hinchliffe, *J. Chem. Soc., Faraday Trans. 2* **76**, 1375 (1980).
- ¹⁷J. C. Green, M. L. H. Green, P. J. Joachim, A. F. Orchard, and D. W. Turner, *Philos. Trans. R. Soc. London, Ser. A* **268**, 111 (1970).
- ¹⁸M. Schluter and M. L. Cohen, *Phys. Rev. B* **17**, 716 (1978).
- ¹⁹N. Aoto, E. Ikawa, and Y. Kurogi, *Surf. Sci.* **199**, 408 (1988).
- ²⁰R. D. Schnell, D. Rieger, A. Bogen, F. J. Himpsel, K. Wandelt, and W. Steinman, *Phys. Rev. B* **32**, 8057 (1985).
- ²¹R. D. Ramsier and J. T. Yates, Jr., in *Dynamics of Gas-Surface Interactions*, edited by C. T. Rettner and M. N. R. Ashfold (The Royal Society of Chemistry, Cambridge, 1991), p. 257.