Electron-stimulated ion desorption from bromine-chemisorbed Si(111) surfaces

Kozo Mochiji and Masakazu Ichikawa
Joint Research Center for Atom Technology, Angstrom Technology Partnership (JRCAT-ATP), National Institute for Advanced Interdisciplinary Research (NAIR), 1-1-4 Higashi, Tsukuba, Ibaragi 305-0046, Japan
(Received 17 August 2000; published 27 February 2001)

Electron-stimulated ion desorption from bromine-chemisorbed Si(111) surfaces was studied, using electrons in the energy range of 0.1–2 keV. Ion desorption behavior is classified into three regimes in terms of the initial bromine coverage. Only small yields of Br^+ ions are observed at low coverages, of the order of 0.01 monolayer (ML). In addition to an increased yield of Br^+ ions, $SiBr^+$ and $SiBr_2{}^+$ also appear at medium coverages of the order of 0.1 ML. The yield of all ion species is dramatically decreased at high coverages, of over 1 ML. The yield of the three kinds of desorption ions reaches its maximum at electron energies of around 0.2–0.3 keV, which suggests the effectiveness of exciting the Br *M* or Si *L* shells in the desorption process. The distribution of the kinetic energies of the Br^+ ions about 3 eV is interpreted as indicating a screened Auger-stimulated desorption model. In contrast, the desorption of the $SiBr_2{}^+$ cannot easily be explained by the model. The structural strain introduced by interatomic repulsion between neighboring bromine atoms may affect the localization of the holes in the back bonds and thus facilitate the desorption of the ions.

DOI: 10.1103/PhysRevB.63.115407 PACS number(s): 68.43.Mn, 68.35.Bs, 79.20.Kz, 81.65.Cf

I. INTRODUCTION

The irradiation of a surface by electrons or photons can induce the desorption of ions from the surface [desorption induced by electronic transitions (DIET)]. Analysis of electron-stimulated ion desorption (ESID) or photon-stimulated ion desorption (PSID) can provide information concerning the nature of chemical bonds at surfaces in both their ground and exited states, and on the conversion of electronic potential energy into nuclear motion.[1,2] At core-level excitation, an Auger-stimulated desorption model for the desorption of ions from covalent systems at surfaces has been proposed.[3] In this model, the lifetime of the multiple-hole states produced by Auger relaxation determines the probability of desorption. Accordingly, the predicted behavior in terms of desorption is strongly correlated with the electronic states of chemical bonds in which the multiple holes are produced.[4,5]

ESID and PSID from halogen-chemisorbed semiconductor surfaces are gaining considerable interest. This is mainly because these desorptions are regarded as an elemental process of etching. A number of reports on ESID and PSID from fluorine- or chlorine-chemisorbed Si surfaces have been published.[6–9] Only the halogen ions (F^+ or Cl^+) were desorbed from either type of surface, and no ions that contained Si were desorbed. We have previously reported on the atomic-structural changes of bromine (Br)-chemisorbed Si(111) surface by electron irradiation.[10,11] With electron energies in the 15–150-eV range, a number of Si adatoms were removed from the surface along with Br atoms. We have now extended our research to the study of ESID from bromine-chemisorbed Si(111) surfaces. We have found that the way in which ions are desorbed depends on the initial Br coverage on the surface. For instance, $SiBr_2{}^+$ ions are prominent among the desorbed species when the initial coverage is of order of 0.1 ML. In this paper, we characterize desorption behavior as a function of the initial Br coverage and the incident electron energy. In addition, we discuss the desorption mechanism in terms of Auger-stimulated desorption.

II. EXPERIMENT

The present study was carried out in a UHV system equipped with a time-of-flight (TOF) apparatus for ESID measurements (Fig. 1). A pulsed electron beam (pulse width 0.2 μs, frequency 500 Hz) emitted from an electron gun (LEG32, VG Microtech) was used to irradiate the sample. The current density of the electron beam incident upon the sample was of the order of 1 mA/cm^2. The rise in temperature within the sample that was induced by the electron beam was thus considered to be negligible. The incident angle of the electron beam was 45° from normal to the surface. A 360-mm-long ion drift tube was used. Ions passed through the drift tube to be detected by a microchannel plate (MCP) which faced to the surface. A negative potential, relative to that of the sample, was applied to a grid that was placed between the sample and the drift tube, so that desorbed ions

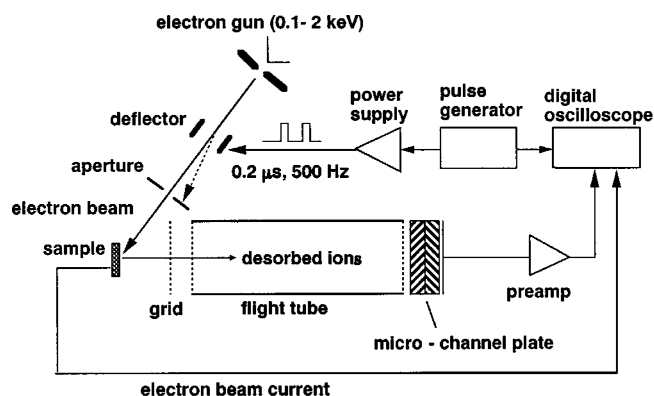

FIG. 1. Experimental setup for time-of-flight spectroscopy of desorbed ions.

 ©2001 The American Physical Society

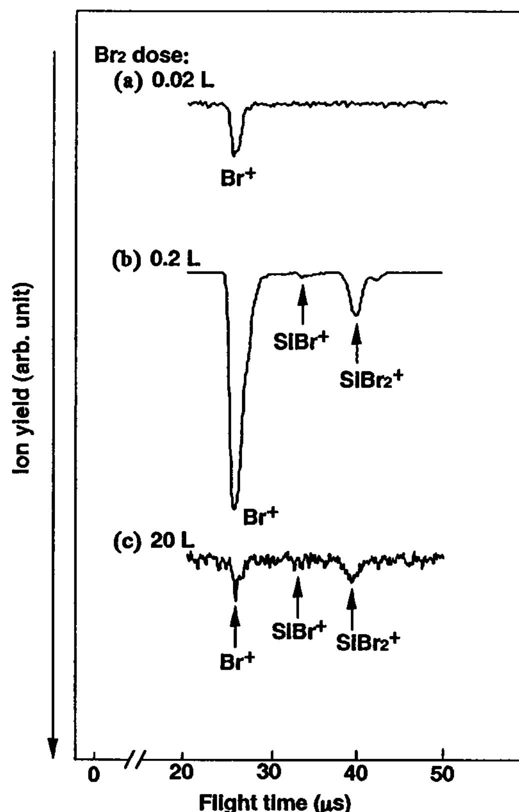

FIG. 2. Time-of-flight spectra of ESID from a Si(111) surface dosed with (a) 0.02 L, (b) 0.2 L, and (c) 20 L of Br_2. The energy of the incident electrons is 1 keV.

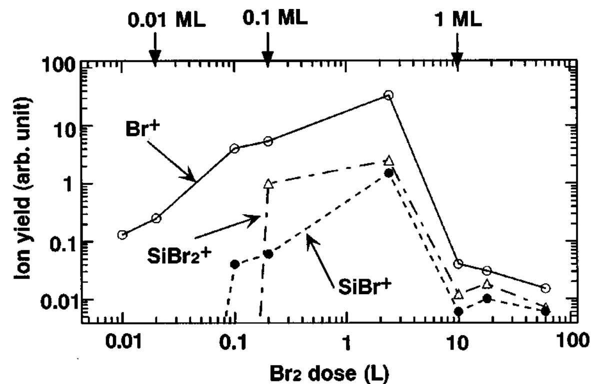

FIG. 3. Changes in the yield of ions desorbed from a Si(111) surface as a function of Br_2 dosage. The energy of the incident electrons is 1 keV. Br coverage by the STM analysis is shown.

would be more efficiently extracted from the sample. The sample, the grid, and the drift tube were typically biased at +10, −30, and −50 V, respectively. To measure the initial kinetic energy of the desorbed ions, however, the sample bias was turned off and the other two biases were minimized to as low a level as possible. The time-of-flight spectra were then converted to curves that showed the initial kinetic energy distribution by using a homemade program. TOF spectra were obtained by processing the detected ion signals through a digital oscilloscope (Waverunner LT322, Iwatsu-Lecroy). The yield for ion desorption was defined here as the value obtained by dividing the detected ion signal by the electron-beam current.

Samples were *n*-type (0.01-Ω cm) Si(111) wafers, outgassed for 8 h at 650 °C and then flash-heated to 1200 °C. The Si(111)-7×7 surface was exposed to Br_2 molecules at room temperature by introducing Br_2 gas through a stainless-steel pipe (length 400 mm, inner width 1.5 mm) attached to a variable leak valve. The distance between the end of the pipe and the sample was about 3 mm. Br_2 pressure at the sample surface was not measured but was roughly estimated to be 100 times higher than the value detected by the ion gauge mounted on the exposure chamber. The Br_2 gas was vapor from pure liquid Br_2 in a glass cylinder (99.9%, TRI Chemical, Inc.). The initial coverage of the sample surfaces by Br atoms was measured by using a scanning tunneling microscope (STM, USM-501, Unisoku Ltd.).

III. EXPERIMENTAL RESULTS

Figure 2 shows the TOF spectra for ions desorbed from a Si(111)-7×7 surface that has been dosed with 0.02, 0.2, and 20 langmuir (1 langmuir = 1 L = 10^{-6} Torr sec) of Br_2. The electron energy was 1.0 keV. The desorption of Br^+, $SiBr^+$, and ${SiBr_2}^+$ ions was observed. The yields and yield ratios of the three species varied dramatically according to the dosage of Br_2. This is summarized in Fig. 3. The Br coverage on the surface as measured by STM is also shown here. Desorption behavior can be classified into three regimes according to the initial degree of Br coverage. At low coverages of the order of 0.01 ML, the only ion species observed was Br^+. The yield of Br^+ ions increased in proportion to the coverage, and $SiBr^+$ and ${SiBr_2}^+$ ions were observed at medium coverages of the order of 0.1 ML. The yields of all three kinds of ions were dramatically decreased at high coverages of more than 1 ML. The appearance of the ${SiBr_2}^+$ suggests that a number of doubly brominated silicons are present as well as singly brominated silicons at medium coverage. Br_2 molecules dissociate at adatom sites, and one of the individual Br atoms will bond to the dangling bond of the adatom. On this occasion, the other Br atom may have a chance to break the back bond of the adatom and form the doubly brominated adatom.

The yields of Br^+, $SiBr^+$, and ${SiBr_2}^+$ ions were affected by the energy of the incident electrons, as shown in Fig. 4. The dependence of the Br^+ yield on the energy at low coverage and medium Br coverage resemble each other [Figs. 4(a) and 4(b)]. This suggests that the same excitation process leads to the desorption of Br^+ in regions with either degree of coverage. The yield of Br^+ increased rapidly as the energy increased to 0.2–0.3 keV. From that point, the yield gradually decreased as the energy increased. The threshold energies for the ionization of the core levels of Si and Br atoms are shown in Fig. 4(a). The enhanced yield of Br^+ for irradiation at 0.2–0.3 keV could be caused by the excitation or ionization of Si $2p$, Si $2s$, Br $3p$, or Br $3s$ levels. The dependence of the yield of $SiBr^+$ and ${SiBr_2}^+$ on electron energies at medium coverages is a little different from that for Br^+, especially at energies in the 0.1–0.2 keV. The effectiveness with which the relevant core holes induce the

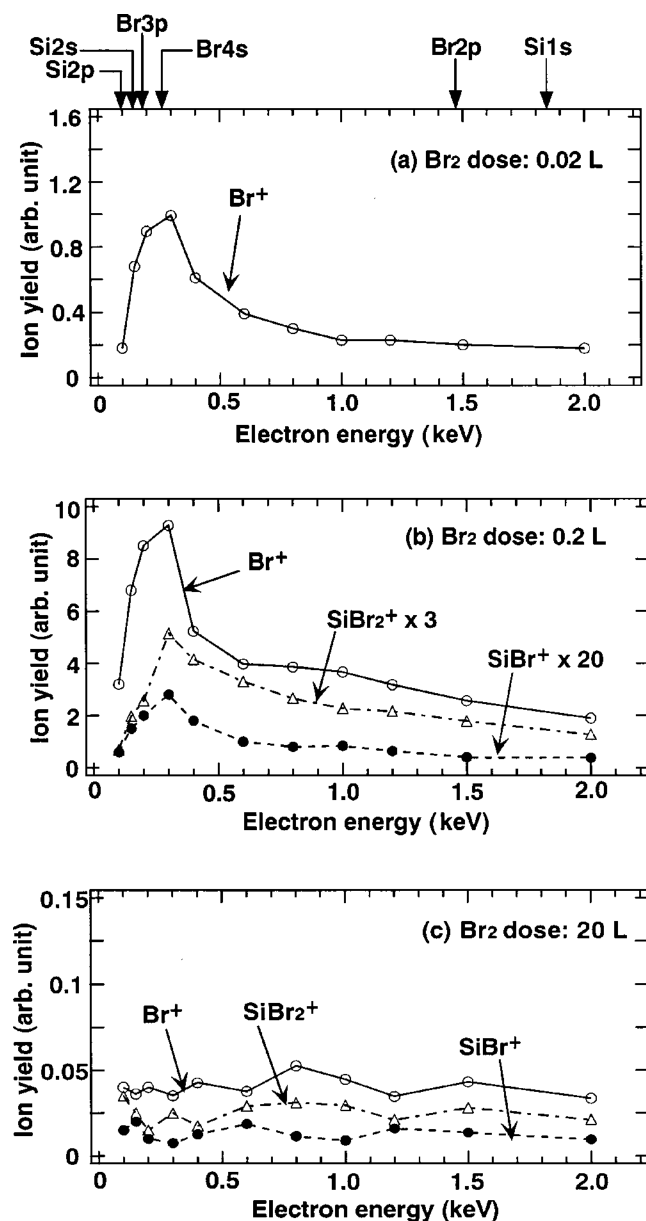

FIG. 4. The yields of ions desorbed from a Si(111) surface dosed with (a) 0.02 I, (b) 0.2 L, and (c) 20 L of Br_2, as a function of the energy of the electrons.

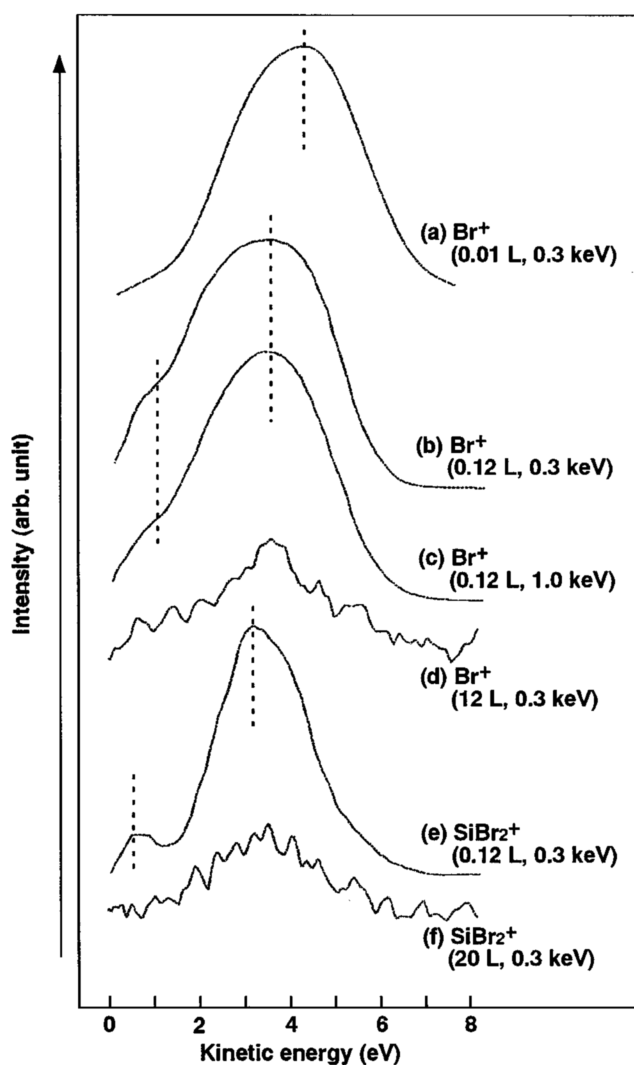

FIG. 5. The distribution curves for the initial kinetic energies of Br^+ and $SiBr_2{}^+$ ions desorbed from a Si(111) surface. The Br_2 dosage and energy of incident electrons are (a) 0.01 L, 0.3 keV, (b) 0.12 L, 0.3 keV, (c) 0.12 L, 1.0 keV, (d) 12 L, 0.3 keV, (e) 0.12 L, 0.3 keV, and 20 L, 0.3 keV.

desorption of $SiBr^+$ or $SiBr_2{}^+$ may be different from the equivalent phenomena in the desorption of Br^+. At high coverage by exposure at 20 L, the dependence of the yield of desorbed ions on electron energies was barely observable as shown in Fig. 4(c).

Figure 5 shows the distribution of kinetic energies among the desorbed Br^+ and $SiBr_2{}^+$ ions. This distribution also varied with the Br coverage. The peak energy for desorbed Br^+ at low coverage produced by exposure at 0.01 L is about 4 eV [Fig. 5(a)]. At medium coverage by exposure at 0.12 L, the main peak is shifted a little towards lower energies and a second smaller peak appears at about 1 eV [Fig. 5(b)]. At higher coverage by exposure at 12 L, the distribution curve is remarkably broad, although it looks noisy due to the limited number of ions contributing signals [Fig. 5(d)]. In contrast, the primary-electron energy has little effect on the distribution of kinetic energies. As shown in Figs. 5(b) and 5(c), when the electron energy decreased from 1.0 to 0.3 keV, the distribution curve spreads out a little towards lower energies but the position of the peak position does not change. As for the kinetic energy of the $SiBr_2{}^+$, the distribution curve is affected by the coverage in a similar way to the Br^+. At medium coverage, the smaller peak is clearly separated from the main peak [Fig. 5(e)]. Isotopic forms of bromine and silicon will be present but the difference in flight times of desorbed ions with isotopically different atoms is too small to be resolved in the present experiment. Accordingly, the multipeak distribution we have observed must be attributed to differences in the desorption processes for ions of the same species.

IV. DISCUSSION

Boo *et al.* have studied the photoionization of the silicon tetrabromide ($SiBr_2$) molecule in the photon-energy range of

30–130 eV.[12] They observed doubly charged ions like Br^{2+} and SiB_2^{2+} as well as singly charged ions. The presence of the doubly charged ions implies that an Auger relaxation process of core holes in the Si $2p$ level can lead to a three-hole state in the valence level. Higher excitation energies up to 300 eV, as we have used in our study, can produce core holes in deeper levels such as Si $2s$, Br $3p$, or Br $4s$ and generate a four-hole or morehole state in the valence level by a cascadelike Auger relaxation or shake-off processes. On the other hand, the ion desorption is not sufficiently high at much higher electron energies to ionize Br $2p$ or Si $1s$ level. This is probably due to the limited cross section of ionization at such levels.

We thus suppose that a two-hole state is produced in the Si-Br bond of the singly or doubly brominated Si adatom. According to the Auger-stimulated desorption model,[3,4] if the repulsion energy between the two holes is greater than the bandwidth of the covalent bond ($U_h > \Delta E$), the holes will be localized on the sites at which they are created for times much longer than the order of the inverse of the bandwidth ($1/\Delta E$). Such an extended lifetime of holes is conductive to the ion desorption. Rye and Houston experimentally examined the repulsion energy between holes produced as pairs in silicon halides and hydrides, by analyzing the line shape of their Auger-electron spectra.[13] As a result, they found that the repulsion energy between two holes produced in molecules in a given symmetrical configuration is proportional to the inverse of the effective distance between the two holes ($1/r_e$). By using this relation and taking the length of the Si-Br bond (0.22 nm) as the effective hole-hole distance, 11.3 eV is obtained as the repulsion energy (U_h) between holes of a pair produced in the Si-Br bond. As for the bandwidth of the Si-Br bond, no experimental or calculated data on the valence states of a Br-chemisorbed Si(111) surface have been reported. It has, however, been reported that the valence states of the $SiBr_4$ molecule are very close to those of the $SiCl_4$ molecule.[14,15] At a first approximation, therefore, we can presume that the valence states of a Br-chemisorbed Si(111) surface are close to those of a Cl-chemisorbed Si(111) surface. The calculations of Schluter and co-workers predict a bandwidth of about 2 eV for the σ bonding orbital of the Si-Cl bond.[16,17] Thus the relationship between U_h and ΔE for the Si-Br bond, $U_h > \Delta E$ ($11.3\,\mathrm{eV} > 2\,\mathrm{eV}$), absolutely supports the desorption of Br^+ from the Si-Br bond.

As shown in Fig. 5, the kinetic energy of the Br^+ is distributed around 3–4 eV, which is low when compared with the repulsion energy between the two holes. This is possibly due to the screening of the Si^+, including a mirror-image effect while the Br^+ is moving away from the surface, and so only a fraction of the potential energy is converted into kinetic energy carried by the desorbed Br^+ ion. The main peak in the kinetic energy distribution of Br^+ shifts slightly towards lower energies at medium coverage, as compared to low coverage. This may be caused by the increased screening effect because of the increased number of neighboring Br atoms, which will be negatively charged because of their high electronegativity.

A number of studies on electron-stimulated desorption ion angular distribution (ESDIAD) have shown that desorbed ions are emitted in the direction that corresponds to the bond axis at the surface.[18] For example, Bozack *et al.* studied the ESDIAD of F^+ from a Si(100)-2×1 surface.[6] Their result showed that the F^+ emission angle, 36° from normal to the surface, corresponds closely to the direction of the Si-F bond at the surface. Accordingly, the emission of Br^+ from singly brominated adatoms would be expected to be in the direction normal to the surface. This is not the case for desorption from doubly brominated adatoms, because such a Si-Br bond in the doubly brominated adatom is tilted at about 55° from the normal to the surface. Assuming that Br^+ is emitted in the direction of the bond axis, the flight time of Br^+ from the two kinds of bromides is different, and this should appear as a difference in the distribution of kinetic energies. Therefore, the main peak can be attributed to the Br^+ ions from the singly brominated adatoms and the small peak to the Br^+ ions from the doubly brominated adatoms.

The desorption process of $SiBr_2^+$ from doubly brominated adatoms can be classified into two types: one is a direct process where a two-hole state is produced in each back bond. The other is an indirect process where the two-hole state is produced only in one of the two back bonds. If the repulsion energy between the two holes can then overcome the binding energy of the other back bond, $SiBr_2^+$ is desorbed. For desorption of either type, two holes must be localized in the back bond. By an analysis similar to that of the two-hole state in the Si-Br bond, the repulsion energy between the two holes in the back bond is calculated as 10.5 eV by taking the length of the Si-Si bond (0.24 nm) as the effective hole-hole distance. If the electronic states of the back bonds are tightly coupled with those of the bonds in the bulk silicon, the bandwidth may spread by up to about 12 eV.[17] As a result, we obtain the relationship $U_h < \Delta E$ ($10.5\ \mathrm{eV} < 12\ \mathrm{eV}$), which suggests that the holes are delocalized in times that are short compared with those required for desorption. This is contrary to the experimental result of the present study. So far, the desorption of Si-compound ions from a F- or Cl-chemisorbed Si surfaces has not been observed,[18] and this is consistent with the above scenario. Aizawa, Tsuneyuki, and Ogitsu recently calculated the thermal desorption energy of halogen-chemisorbed Si(100) surfaces.[19] Their results show that the thermal desorption of $SiBr_2$ is promoted more than the thermal desorption of $SiCl_2$ because of the structural strain caused by repulsive interactions between neighboring Br atoms. This is also the case for a Br-chemisorbed Si(111) surface: for example, the internuclear distance between Br atoms at the doubly brominated adatoms and Br atoms bonded to the nearest rest atoms is estimated to be as narrow as ~0.15 nm. As a result, interatomic repulsion between these Br atoms would push the doubly brominated adatom upward, and thus elongate the back-bond length. Such a structural strain may relieve the electronic coupling between the back-bond state and the bulk states, and this should facilitate the localization of holes produced in the back bonds. In addition, the structural disorder at step or defect sites like Si-atom vacancies would also pay a role in the localization of the holes.

We now return to the difference between the direct and

indirect processes of the desorption of $SiBr_2^+$. For the indirect process, the repulsive energy operating on the adatom is one-half of that for the direct process, and some part of the repulsive energy should be expended in the breaking the back bond. Therefore, the difference between the the kinetic energies of $SiBr_2^+$ produced by the two process is

$$\Delta U = U_{\mathrm{dir}} - U_{\mathrm{in}} = \tfrac{1}{2} U_{\mathrm{dir}} + E_{\mathrm{Si\text{-}Si}}, \quad (1)$$

where U_{dir}, U_{in}, $E_{\mathrm{Si\text{-}Si}}$ represent the kinetic energies of the direct and indirect processes and the back-bond energy of the doubly brominated adatom, respectively. The calculation by Aizawa, Tsuineyuki, and Ogitsu showed that $E_{\mathrm{Si\text{-}Si}}$ is reduced to about 1.1 eV by interaction between the neighboring Br atoms and by the electronegativity of Br atom.[19] As shown in Fig. 5(e), the kinetic energy distribution curve of $SiBr_2^+$ at medium coverage has a main peak and a subpeak at about 3 and 0.5 eV, respectively. Assuming that the main peak is due to the direct process and the subpeak is due to the indirect process, the difference between their kinetic energies is almost consistent with the value obtained from Eq. (1).

As Br coverage increases, the average distance between adsorbed Br atoms decreases. This can lead to the overlapping of electrons within the adsorbing layer and reduced lifetimes for holes. As shown in Figs. 2 and 3, the yield of Br^+ is dramatically reduced at Br coverages of more than 1 ML, which support this scenario. However, the dependence of the reduced ion yield on electron energy at high coverage is barely visible in Fig. 4(c). Furthermore, the yield ratios of $SiBr^+$ or $SiBr_2^+$ to Br^+ at high coverage are larger than those at medium coverage. This suggests that a different desorption process is involved for high coverage. Irradiation by the primary electron beam produces a number of secondary electrons within the surface layer. There may be a peak near 10–20 eV in the intensity of the spectrum for secondary electrons emitted from the surface, regardless of the primary electron energy. These secondary electrons can ionize the electrons of the bonding orbitals of the Si-Br bonds and the back bonds and so break these bonds. In the previous study, we found that Br atoms and the adatoms are removed from the Br-chemisorbed Si(111) surface at an electron energy of 15 eV.[11] The yield of the desorbed ions induced by the secondary electrons is therefore less dependent on the primary electron energy. Rather, it reflects the populations of the chemical species (SiBr and $SiBr_2$) at the surface.

V. CONCLUSION

Irradiating Br-chemisorbed Si(111) surfaces with 0.1–2-keV electrons induces various ion desorptions depending on the initial Br coverage and electron energy. The yield of the desorbed ions reaches its maximum at electron energies in the 0.2–0.3-keV range, corresponding to the ionization of core levels in the Si and Br atoms. At low Br coverages of the order of 0.01 ML, the desorption of Br^+ ions is the only process observed. When the coverage is increased to be of the order of 0.1 ML, $SiBr^+$ and $SiBr_2^+$ are also desorbed, and this indicates the formation of doubly brominated adatoms even at coverages far below 1 ML. Yields of all ion species are decreased at coverages of more than 1 ML, because of electronic interaction between the adsorbates. Br^+ is desorbed from doubly brominated adatoms and singly brominated adatoms in a similar way through the Auger-stimulated desorption process, although the difference in the direction of the Si-Br bond in the two kinds of bromides causes a difference in the flight times of ions desorbed by each process. The desorption of $SiBr_2^+$ cannot easily be explained by the Auger-stimulated desorption model. Interatomic repulsion between neighboring Br atoms induces the structural strain in the back bonds, and this can promote the localization of the holes produced at the back bonds.

ACKNOWLEDGMENTS

The authors wish to thank to Dr. Hideaki Aizawa of the National Institute for Metals and Dr. Yoshiyuki Miyamoto of the NEC Corporation for helpful discussions. This work was performed under the management of a technological research association, the Angstrom Technology Partnership (ATP) at the Joint Research Center for Atom Technology (JRCAT), supported by the New Energy and Industrial Technology Development Organization (NEDO).

[1] M. L. Knotek, Phys. Today **37(9)**, 24 (1984).

[2] *Desorption Induced by Electronic Transitions, DIET-III*, edited by R. H. Stulen and M. L. Knotek (Springer, Berlin, 1988); *Desorption Induced by Electronic Transitions, DIET-IV*, edited by G. Betz and P. Varga (Springer, Berlin, 1990); *Desorption Induced by Electronic Transition, DIET-V*, edited by A. R. Burns, E. B. Stechel, and D. R. Jennison (Springer, Berlin, 1993).

[3] D. E. Ramaker, C. T. White, and J. S. Murday, J. Vac. Sci. Technol. **18**, 748 (1981).

[4] D. E. Ramaker, J. Vac. Sci. Technol. A **1**, 1137 (1983).

[5] M. Cini, Phys. Rev. B **32**, 1945 (1985).

[6] M. J. Bozack, M. J. Dresser, W. J. Choyke, P. A. Taylor, and J. T. Yates, Jr., Surf. Sci. Lett. **184**, L332 (1987).

[7] J. A. Yamorff, S. A. Joyce, C. W. Lo, and J. Song, in *Desorption Induced by Electronic Transitions, DIET-IV* (Springer, Berlin, 1990), p. 65.

[8] Q. Guo, D. Sterratt, and E. M. Williams, J. Electron Spectrosc. Relat. Phenom. **72**, 31 (1995).

[9] D. Sterratt, Q. Guo, and E. M. Williams, Nucl. Instrum. Methods Phys. Res. B **101**, 84 (1995).

[10] K. Mochiji and M. Ichikawa, Jpn. J. Appl. Phys., Part 2 **38**, L1391 (1999).

[11] K. Mochiji and M. Ichikawa, Phys. Rev. B **62**, 2029 (2000).

[12] B. H. Boo, Z. Liu, S. Y. Lee, and I. Koyano, J. Phys. Chem. A **102**, 8261 (1998).

[13] R. R. Rye and J. E. Houston, J. Chem. Phys. **78**, 4321 (1983).

[14] B. D. El-Issa and A. Hinchliffe, J. Chem. Soc., Faraday Trans. 2 **76**, 1375 (1980).

[15] J. 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).

[16] M. Schluter and M. L. Cohen, Phys. Rev. B **17**, 716 (1978).

[17] G. B. Bacheler and M. Schluter, Phys. Rev. B **28**, 2302 (1983).

[18] S. L. Bennett, C. L. Greenwood, and E. M. Williams, in *Desorption Induced by Electronic Transitions, DIET-V* (Springer, Berlin, 1993), p. 259.

[19] H. Aizawa, S. Tsuneyuki, and T. Ogitsu, Surf. Sci. **438**, 18 (1999).