Reconstruction of Br-chemisorbed Si(111) surfaces under electron-stimulated desorption

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We present atomic structural changes of the rest-atom layer under the electron-stimulated desorption of bromine-chemisorbed Si(111) surfaces. We used a scanning tunneling microscope as an electron-beam source, as well as for structural analysis. By the desorption of bromine atoms and adatoms, underlying rest atoms were imaged in a 7×7 structure along with corner holes and dimer walls. These rest atoms are adsorbate-free. The structure was uniquely observed by electron-stimulated desorption. Furthermore, we removed many adatoms by thermal etching in Br_2 gas in order to observe the rest-atom layer more clearly. By etching at 400 °C, the rest atoms were imaged in the 7×7 structure and are terminated with Br atoms. After the desorption of the Br atoms by electron irradiation, the rest atoms maintained the 7×7 structure, similar to the case in which adatoms are removed by electron irradiation. In contrast, etching at 450 °C produced a wide area of Br-terminated 1×1 structure such as that of a bulk, quenching the corner holes and dimer walls. Electron irradiation changed this surface into a 2×1 structure through Br desorption. We discussed the above results from the viewpoint of reconstruction behavior of the local structure produced by the electron-stimulated desorption.

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Electron-stimulated desorption (ESD) has been intensively studied through the analysis of desorbed particles.[1–3] However, little study has been done on atomic structural changes that occur under desorption. Earlier, we developed a technique for irradiating a sample surface with field-emission (FE) electrons from a scanning tunneling microscope (STM) tip that is distantly removed from the sample.[4] This technique enables us to observe the atomic structures of an FE-irradiated area by using the STM tip. Using this technique, we have studied electron-stimulated desorption of bromine-chemisorbed Si(111) surfaces. We previously reported the desorption behavior of Br atoms and adatoms that depends on the initial Br coverage and electron energy.[5,6] In this paper, we report on atomic structural changes of the underlying rest-atom layer by the desorption of adatoms. The rest atoms clearly appeared after the ESD of Br atoms and adatoms from a Br-chemisorbed Si(111)-7×7 surface. The array of the rest atoms shows a 7×7 structure outlined by dimer walls. These rest atoms are found to be free from any adsorbates including Br atoms. As far as we know, this is the first observation of a clean rest-atom layer in a 7×7 structure, and this structure is not self-evident. It is well known that chlorine- or Br-chemisorbed rest atoms are arranged in a 7×7 structure.[7–10] However, no one knows the manner in which the resultant Si surface undergoes a structural change if the Cl or Br atoms are removed at room temperature. We further report on the structural changes that occur under the ESD of Br atoms from a Br-chemisorbed rest-atom layer prepared by thermal etching of adatoms from Si(111)-7×7 surfaces in Br_2 gas.

The current study was conducted using an STM (USM-501, Unisoku Limited) 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 flashed to 1200 °C. In order to observe the rest-atom layer, the adatom layer of the Si(111)-7×7 surface was removed by both ESD and thermal etching. In the ESD experiments, the Si(111)-7×7 surface was exposed to Br_2 at room temperature by dosing Br_2 gas through a variable leak valve. The Br_2 gas was the vapor from pure liquid Br_2 (99.9%, TRI Chemical Incorporated) in a glass cylinder. The FE irradiations over the sample surface were performed at room temperature in the following way. After positioning the tip on the place in an STM image to be irradiated, the feedback loop was inactivated to move the tip away from the surface. The tip-to-sample distance was varied between 1 and 130 nm by applying a driving voltage to a *Z*-piezo device. Then a voltage was applied to the sample to extract FE electrons and the extraction voltage was varied between 10 and 150 V. An FE current was detected during the irradiation. Under these conditions for FE, the value of the FE current (in nA) multiplied by the irradiation time (seconds) over the square of the tip-sample separation (nm^2) is regarded as the relative dose density of electrons irradiated on the sample. The kinetic energy of the FE electrons 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 surface[11] and that the work function of a Br-chemisorbed Si(111) surface is similar to that for a clean Si surface, i.e., about 5 eV,[12] the kinetic energy E_k is approximately given by $E_k=E_x-5\,(\mathrm{eV})$, where E_x is the extraction voltage applied to the sample (V). As reported before,[5,6] the ESD behavior depends on the initial Br coverage and electron energy. When the initial coverage is low, Br atoms desorb but Si adatoms hardly desorb at all. When the initial coverage is increased up to the saturation level (Br_2 dosage >100 L), the adatom desorption increases greatly because the number of multiple brominated adatoms increases. The cross section of Br-atom desorption increases more rapidly with electron energy of 20–150 eV than that of adatom desorption. This fact indicates that the irradiation of the FE electrons with low energy is preferable

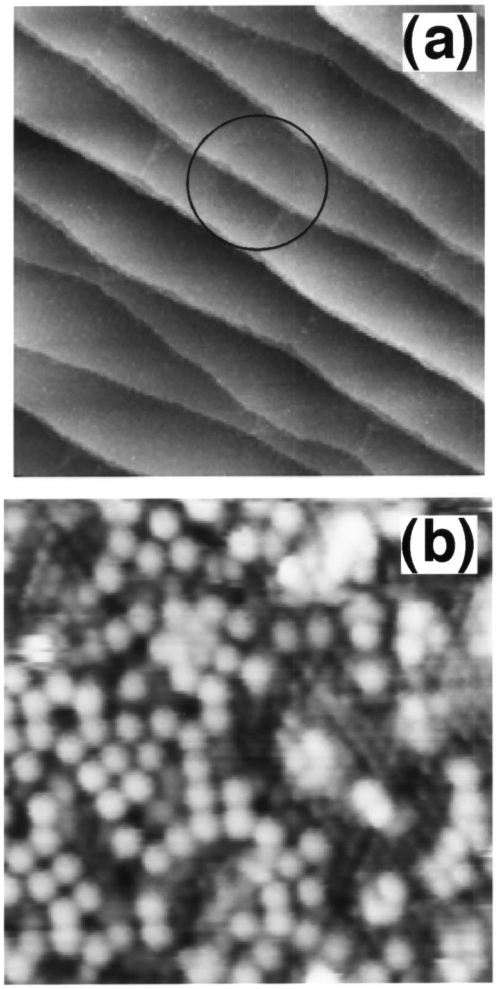

FIG. 1. (a) STM image after FE irradiation of a Si(111)-7×7 surface dosed with 400 L of Br_2. The energy and the dose density of electrons were 30 eV and 0.1 nA s/nm^2, respectively. The image was taken at a sample bias of +2.0 V and a tunneling current of 0.9 nA. (b) Magnified image of the irradiated area in (a). The image was taken at a sample bias of +1.0 V and a tunneling current of 0.8 nA. The areas shown are (a) 170×170 and (b) 9.5×9.5 nm.

for removing many adatoms. In this study, therefore, the irradiations of FE electrons were carried out at the energy of 30 eV.

For the thermal etching of the adatom layer, the Si(111)-7×7 surface was exposed to Br_2 gas at 400 °C–450 °C. Most adatoms were selectively etched and Br-terminated rest atoms appeared. Next, the Br-terminated surface was irradiated with FE electrons at room temperature.

Tunneling current-bias voltage characteristics (*I-V* curves) over sample surfaces were measured by using a conventional sample-and-hold technique. The feedback loop was inactivated at a given position of the STM image and *I-V* curves for fixed separations were obtained by measuring the variation of the tunneling current as a function of bias voltage at a constant tip-sample separation.

Figure 1(a) shows an STM image of a Si(111) surface dosed with 400 L of Br_2 after FE irradiation at an extraction voltage of 30 V. The irradiated area (enclosed by a circle)

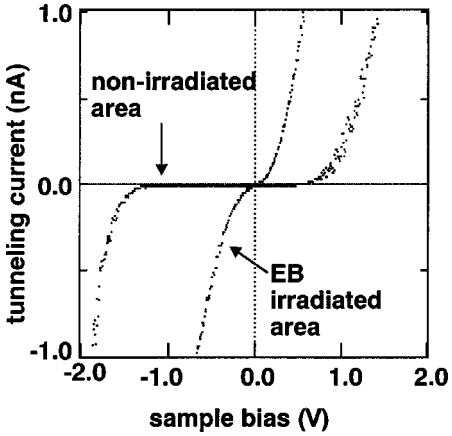

FIG. 2. Tunneling current-sample bias (*I-V*) curves measured over nonirradiated and FE-irradiated areas of the sample surface shown in Fig. 1(a). The feedback loop was inactivated at a sample bias of +1.0 V and a tunneling current of 0.7 nA.

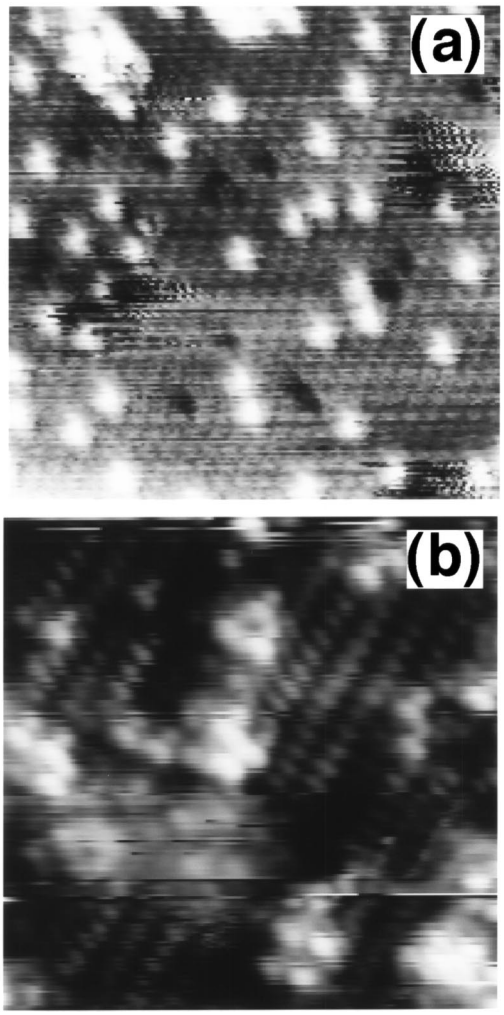

FIG. 3. STM images (a) before and (b) after Fe irradiation (50 eV) to Si(111)-7×7 surfaces dosed with 100 L of Br_2 at 450 °C. (a) was taken at a sample bias of +2.0 V and a tunneling current of 0.8 nA. (b) was taken at a sample bias of +1.0 V and a tunneling current of 0.8 nA. The areas shown are 7.8×7.8 nm.

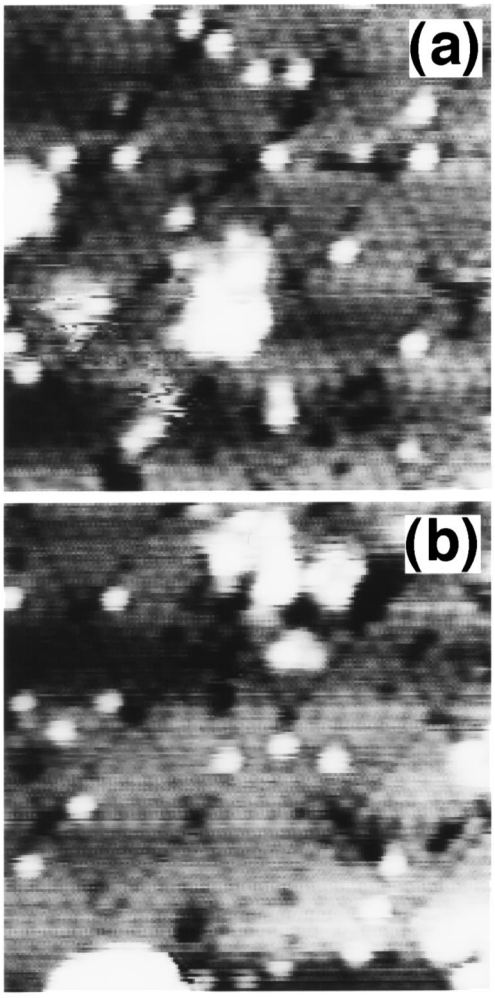

FIG. 4. STM images (a) before and (b) after FE irradiation (50 eV) to Si(111)-7×7 surfaces dosed with 50 L of Br_2 at 400 °C. (a) was taken at a sample bias of +2.0 V and a tunneling current of 0.8 nA. (b) was taken at a sample bias of +1.0 V and a tunneling current of 0.8 nA. The areas shown are 7.8×7.8 nm.

appears to be slightly darker than the nonirradiated area. The magnified image of this irradiated area is shown in Fig. 1(b). A number of the adatoms are removed and the underlying rest-atom layer is imaged. The tunneling current-bias voltage (*I-V*) curve measured over this FE-irradiated area is compared with that of the nonirradiated area in Fig. 2. In the *I-V* curve of the nonirradiated area, a gap in the tunneling current appears at the 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 of the FE-irradiated area, the gap is lost and the *I-V* curve resembles that of a clean surface. This result indicates that the remaining adatoms and exposed rest atoms were almost completely Br-free. The difference in the *I-V* curves between the rest atoms and the remaining adatoms was hardly observed. The two *I-V* curves should be different because the density of states for the two kinds of Si atoms are different. However, the spatial resolution in the present STM was not enough to measure the *I-V* curves with atomic specificity. A more careful inspection of Fig. 1(b)

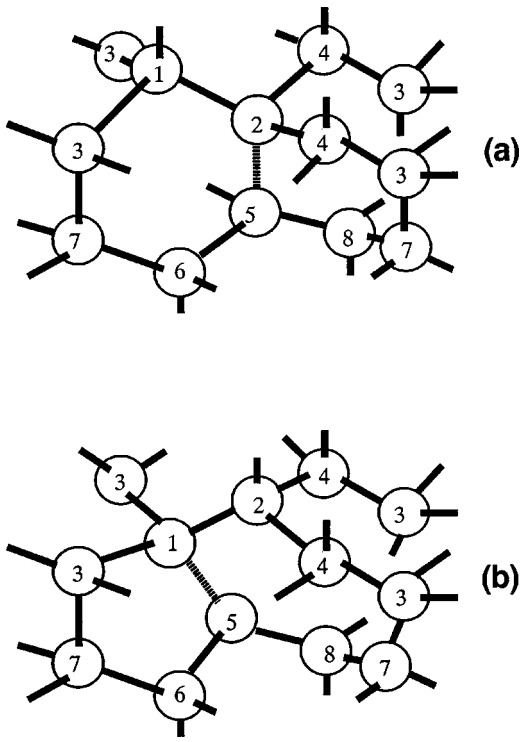

FIG. 5. Three-dimensional illustration of (a) the ideal Si(111) surface and (b) the Si(111)-2×1 π-bonded chain reconstruction.

reveals that corner holes and dimer domain boundaries are maintained and the rest atoms are apparently arranged in a 7×7 structure rather than a 2×1 structure. This is unusual because the Si(111) surface reconstructs to form a metastable 2×1 structure at room temperature.

To clarify the reason for this phenomenon, we investigated the structural changes of a Br-terminated rest-atom layer under ESD. Figure 3(a) shows an STM image of the Si(111) surface dosed with 100 L of Br_2 at 450 °C. From the figure, it can be seen that most adatoms are etched away and that the underlying rest-atom layer is clearly exposed. The results of *I-V* measurements show that the rest atoms are terminated with the presence of Br atoms. Hardly any corner holes or dimer walls are observed in this rest-atom layer, and a bulklike 1×1 structure is frequently produced. Thermal reaction with Br_2 may quench the dimer walls and corner holes. The FE irradiation desorbed Br atoms from the surface whose structure changed from a 1×1 to a 2×1 structure, as shown in Fig. 3(b). This is explained as follows: Before desorption of Br atoms, dangling bonds of the Si(111)-1×1 surface are terminated with Br atoms and the 1×1 structure is energetically stabilized. When the critical density of the Br atoms are desorbed, the resultant Si(111) surface lowers its free energy through a spontaneous transition to the 2×1 structure. Becker *et al.* produced a hydrogen-terminated Si(111)-1×1 structure by a modified hydrofluoric-acid solution wet chemical method.[13] They reported that electron bombardment to the surface desorbs the hydrogen, converting the 1×1 structure to a 2×1 structure. Their results correspond to our present results.

Figure 4(a) shows an STM image of a Si(111) surface

dosed with 50 L of Br_2 at 400 °C. Removing most adatoms clearly images the rest-atom layer, and the rest atoms are found to be terminated with Br atoms as can be seen from the results of *I-V* measurements. In this case, 7×7 structure corner holes and dimer walls exist, probably due to the controlled thermal reaction with Br_2. By irradiation of FE electrons, the Br atoms were desorbed but the array of the rest atoms was retained in the 7×7 structure as shown in Fig. 4(b). This result is similar to the case in which the adatom layer was removed by ESD as shown in Fig. 1(b).

The experimental results obtained in this study lead to the conclusion that the rest-atom layer of a 7×7 structure is not reconstructed to a 2×1 structure, while that of a 1×1 structure is reconstructed to a 2×1 structure. If all the Br atoms were desorbed away from the rest atoms in the 7×7 structure, the resultant surface would contain 21 dangling bonds in a half unit cell, which could increase the surface free energy by a considerable amount. Nevertheless, the reconstruction to the 2×1 structure does not occur at all. In the π-bonded chain model shown schematically in Fig. 5(a),[14] half of the bonds linking second-layer atoms to third-layer atoms are broken [such as the bonds between the atoms labeled ''2'' and ''5'' in Fig. 5(a)], allowing the second-layer atoms [such as the atoms labeled ''2'' in Fig. 5(a)] to rise to the surface to form π-bonded chains [such as the atoms labeled ''2'' and ''4'' in Fig. 5(b)]. Consequently, half of the surface atoms are lowered and shifted parallel to the surface, rebonding with the broken bonds of the third-layer atoms [such as the bond formed between atoms ''1'' and ''5'' in Fig. 5(b)]. The driving force for this reconstruction is rehybridization of the dangling bonds on the ideal surface to form π bonds, thereby saturating the surface valences. When the ideal surface spreads in a relatively wide area, such reconstruction can occur coherently in the area. On the other hand, the rest-atom layer exposed by the removal of adatoms can be regarded as a local 1×1 structure outlined by dimer walls. Most of the rest atoms are bound to dimer atoms [such as the atoms labeled ''3'' in Figs. 5(a) and 5(b)]. Therefore, the transformation of the rest atoms to the π-bonded chains is pinned by these dimer atoms. As a result, the 7×7 rest-atom structure may be maintained.

In summary, we have examined the atomic structural changes of Br-chemisorbed Si(111) surfaces under ESD by using the FE electrons from an STM tip. The desorption of Br atoms from the Br-chemisorbed 1×1 surface changes the surface into a 2×1 structure. On the other hand, by the desorption of adatoms or Br atoms from the Br-chemisorbed 7×7 surfaces, the surface structure is maintained in a 7×7 structure. The transformation of the rest atoms to the 2×1 structure is pinned by the bonds with the dimer atoms. So far, to our best knowledge no bare rest atoms arranged in a 7×7 structure have ever been observed. Such a structure is uniquely obtained by the removal of halogen atoms at room temperature under ESD and the structure is observed first by an *in situ* STM technique connected with FE-electron bombardment.

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[1] S. Mokler, P. R. Watson, L. Ungier, and J. R. Arthur, J. Vac. Sci. Technol. B **8**, 1109 (1990).
[2] D. Troost, H. J. Clemens, L. Koenders, and W. Monch, Surf. Sci. **286**, 97 (1993).
[3] Q. Guo, D. Sterratt, and E. M. Williams, J. Electron Spectrosc. Relat. Phenom. **72**, 31 (1995).
[4] M. Shibata, Y. Nitta, K. Fujita, and M. Ichikawa, Appl. Phys. Lett. **73**, 2179 (1998).
[5] K. Mochiji and M. Ichikawa, Phys. Rev. B **62**, 2029 (2000).
[6] K. Mochiji and M. Ichikawa, Phys. Rev. B **63**, 115407 (2001).
[7] J. S. Villarrubia and J. J. Boland, Phys. Rev. Lett. **63**, 306 (1989).
[8] M. Chander, Y. Z. Li, J. C. Patrin, and J. H. Weaver, Phys. Rev. B **47**, 13 035 (1993).
[9] R. J. Pechman, X. S. Wang, and J. H. Weaver, Phys. Rev. B **52**, 11 412 (1995).
[10] J. J. Boland and J. H. Weaver, Phys. Today **51**(1), 34 (1998).
[11] Vu. Thien Binh, N. Garcia, and S. T. Purcell, AIChE J. **95**, 63 (1996).
[12] M. J. Bozack, M. J. Dresser, W. J. Choyke, P. A. Taylor, and J. T. Yates, Jr., Surf. Sci. **184**, L332 (1987).
[13] R. S. Becker, G. S. Higashi, Y. J. Chabal, and A. J. Becker, Phys. Rev. Lett. **65**, 1917 (1990).
[14] J. A. Kubby and J. J. Boland, Surf. Sci. Rep. **26**, 130 (1996).