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STM study of Si(111)$\sqrt{3} \times \sqrt{3}$-R30°-B surface structure formed by HBO_2 irradiation

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Abstract

With irradiation of HBO_2 molecules onto the Si(111)-7 × 7 surface at ~750°C, the $\sqrt{3} \times \sqrt{3}$ structure, where B atoms occupy the T_4 sites, was formed as predicted from previous electron diffraction measurements. In the initial stage, HBO_2 molecules were found to react with the unfolded half-units of the Si(111)-7 × 7 surface. When the $\sqrt{3} \times \sqrt{3}$ structure was heated at ~900°C for 5 s, another $\sqrt{3} \times \sqrt{3}$ structure was formed. Upon comparison between the two structures, the high-temperature phase was attributed to the structure where B atoms occupy the S_5 sites.

Adsorption of foreign atoms on Si surface has attracted the great interest of many researchers. In particular, the behavior of boron (B) atoms on the Si(111) surface has been the subject of intense studies within the last several years because of its high potential as a candidate for the surfactant process to control crystal growth [1–8]. Generally, surface B atoms are introduced by using the surface segregation process of highly doped B atoms in the bulk crystal. In such a case, the $\sqrt{3} \times \sqrt{3}$ reconstructed structure is formed and a structural model where surface B atoms occupy the threefold sites underneath the Si adatoms (S_5 sites) was proposed. On the other hand, recently HBO_2 irradiation was reported to form another $\sqrt{3} \times \sqrt{3}$ structure on Si(111) surface [9,10], based on the following observations: (1) Si(111)$\sqrt{3} \times \sqrt{3}$-R30°-B electron diffraction pattern is completed at 1/3 monolayer (ML) even at the low sample temperature of ~700°C; (2) B coverage is saturated at 1 ML, and no additional B atoms can be deposited on the surface. Because the substrate temperature during HBO_2 irradiation was lower than the B diffusion temperature in this case, adsorbed B atoms are assumed to exist on the topmost layer (T_4 sites). In such a case, surface dangling bonds of Si adatoms will be terminated, which is a very impor-

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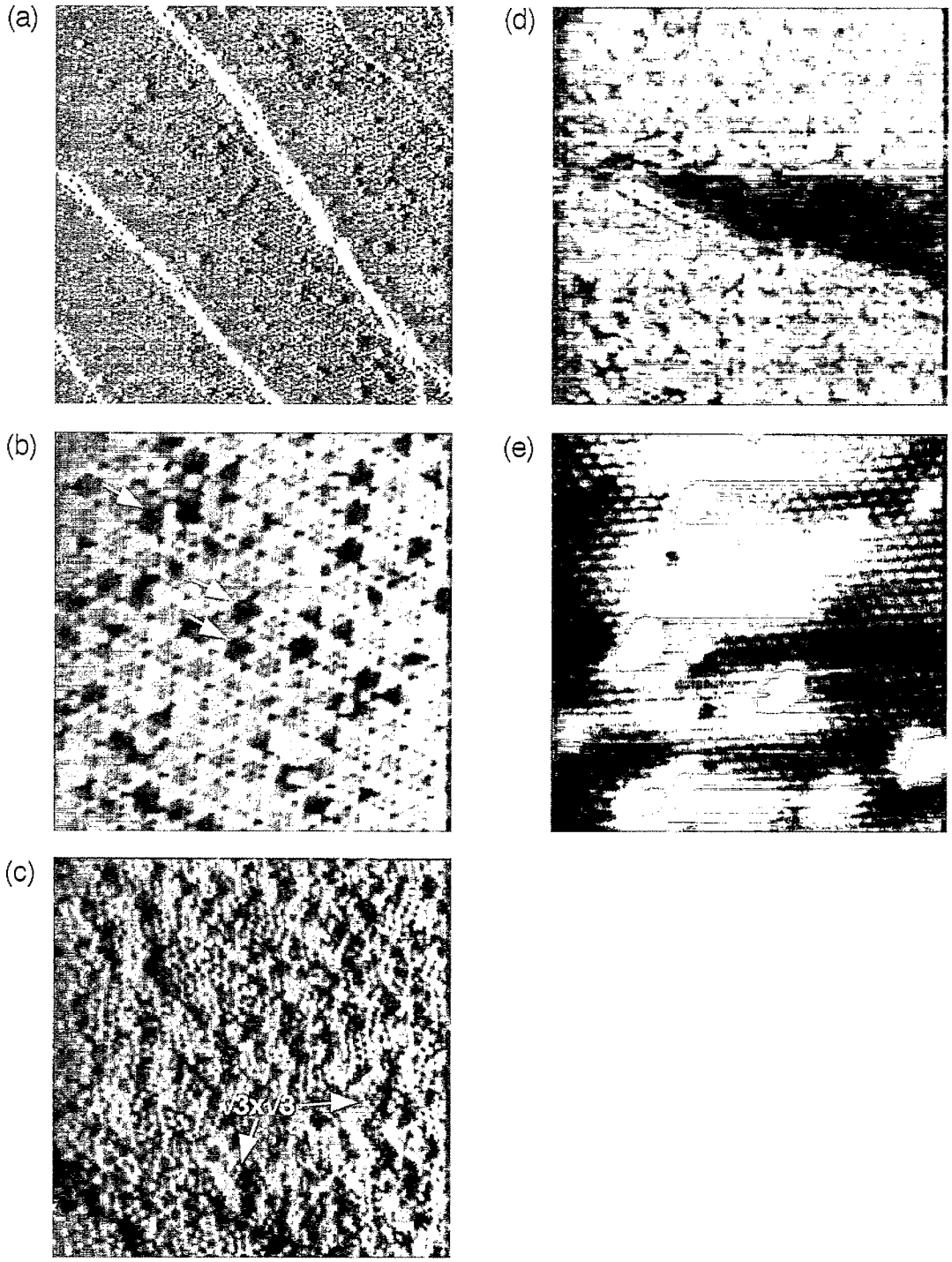
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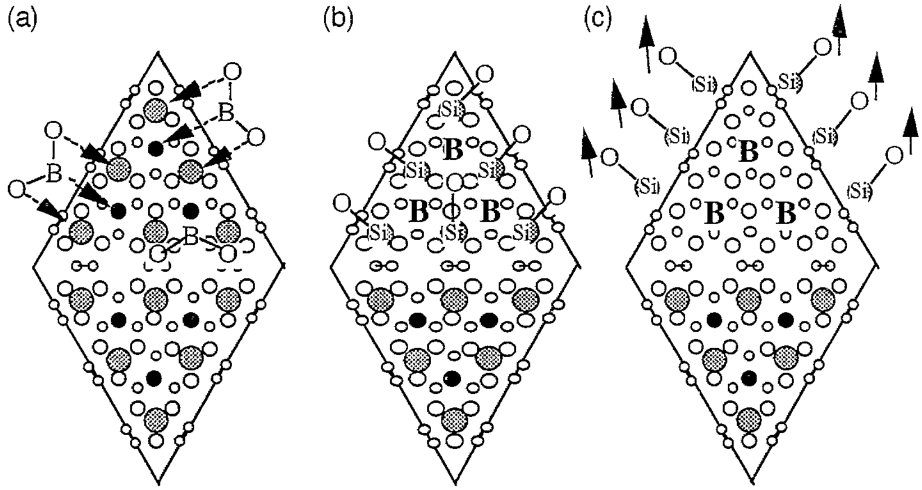

Fig. 2. A schematic model for the HBO_2 reaction with the Si(111)-7 × 7 surface.

tant characteristic for controlling the surface/interface electronic states.

In this paper, we present the results of scanning tunneling microscopy (STM) observations of the Si(111)$\sqrt{3} \times \sqrt{3}$-R30°-B surface structural formation by HBO_2 irradiation.

Arsenic-doped n-type Si(111) substrates were chemically cleaned and transferred into an ultrahigh vacuum (UHV) chamber. Samples were degassed for one day at ~ 500°C and subjected to flash heating (~ 1100°C). After confirmation of the clean 7 × 7 structure, sample temperature was kept at 650–750°C, and HBO_2 was irradiated on these surfaces. HBO_2 cell temperature during irradiation was ~ 800°C and irradiation time was varied from 30 s. Samples were cooled to room temperature after treatments, and observed by STM. All STM observation was performed at room temperature using an electrochemically etched W tip. The base pressure was ~ 1×10^{-10} Torr and the pressure during HBO_2 irradiation was ~ 2×10^{-8} Torr.

Fig. 1 shows the STM images obtained after HBO_2 irradiation with the Si substrate temperature T_{sub} of (a) ~ 650°C, and (b) to (e) ~ 750°C. When T_{sub} was ~ 650°C, island structures were formed as shown in Fig. 1(a). Since Si–O molecules remain on the surface at ~ 650°C, surface oxidation may occur and result in the observed island structure. In the case that T_{sub} was ~ 750°C, however, B-induced $\sqrt{3} \times \sqrt{3}$ structure was formed (Fig. 1(b)–(e)). These results are in good agreement with the results obtained previously by electron diffraction measurements [10].

Fig. 1(b)–(e) show the STM images obtained for the surface formed by HBO_2 irradiation of (b) 2 min, (c) 5 min, (d) 6 min and (e) 10 min, respectively. The substrate temperature was kept at ~ 750°C for (b) to (e). In the initial stage, Si(111)-7 × 7 structure still remained, but some unfolded half-units of the 7 × 7 structure became dark as shown in Fig. 1(b), which indicates that HBO_2 molecules react preferentially with the unfolded half-unit initially. This preference is supposed to be caused by the negative charge remaining on the BO_2 ions after dissociation

Fig. 1. STM images of Si(111) surface after HBO_2 irradiation. Irradiation time, tip vias voltage V_t, tunneling current I_t and size of scanning area are (a) 2 min, 1.8 V, 1.0 nA, 184 nm × 184 nm, (b) 2 min, 2.0 V, 0.4 nA, 33.5 nm × 33.5 nm, (c) 5 min, 2.0 V, 0.32 nA, 33.3 nm × 33.3 nm, (d) 6 min, 3.0 V, 0.33 nA, 33.5 nm × 33.5 nm, (e) saturated, −2.09 V, 0.43 nA, 16.3 nm × 16.3 nm, respectively. Sample temperature during HBO_2 irradiation was kept at ~ 650°C for (a), and ~ 750°C for (b) to (e).

of HBO_2 molecules, similarly to the case of $AlCl_3$ molecular adsorption on Si(111)-7 × 7 surface. When HBO_2 irradiation was continued, the 7 × 7 structure was broken down into the disordered structure in a large area. In addition, B-induced $\sqrt{3} \times \sqrt{3}$ structure was partially created in the disordered region (Fig. 1(c)). With further HBO_2 irradiation, $\sqrt{3} \times \sqrt{3}$ structure was observed to be grown over a wide area (Fig. 1(d)), and finally formed a complete $\sqrt{3} \times \sqrt{3}$ structure as shown in Fig. 1(e).

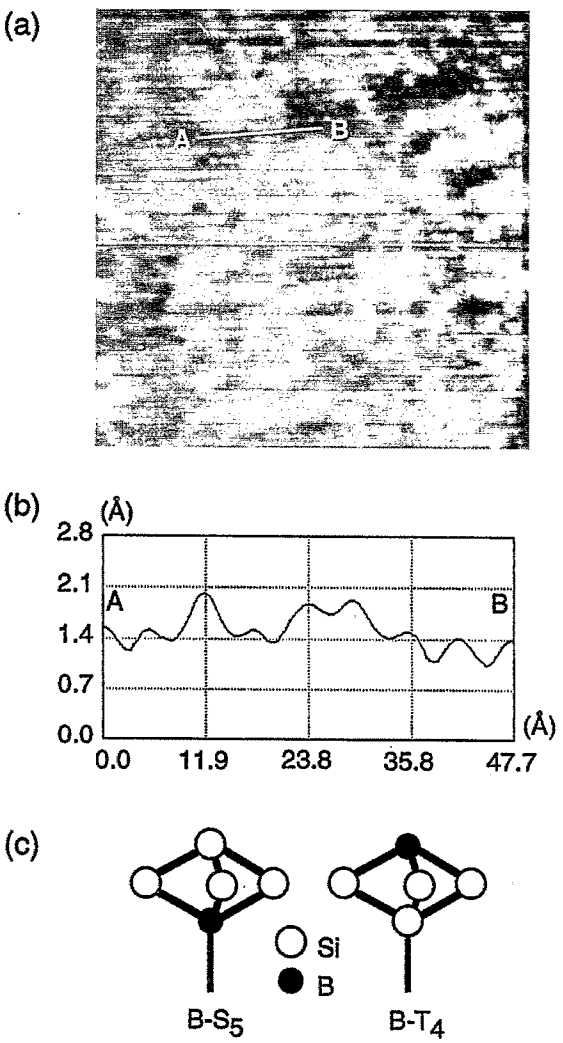

Fig. 3. (a) STM image obtained after heating the sample of $\sqrt{3} \times \sqrt{3}$ structure with T_4-site B atoms (Fig. 2(e)) at ~ 900°C for 5 s ($V_t = 1.38$ V, $I_t = 0.50$ nA, 17.2 nm × 17.2 nm). (b) Cross section along A–B line in Fig. 3(a). (c) $\sqrt{3} \times \sqrt{3}$ structural models which have S_5-site (left) and T_4-site (right) B atoms, respectively.

Fig. 2 shows a schematic model of the HBO_2 reaction process on the Si(111)-7 × 7 surface. In the regular 7 × 7 unit cell, charge transfer occurs from adatoms to rest atoms [11,12]. Therefore, rest atoms act as electron donors and adatoms do as electron acceptors in the chemical reaction process on the Si(111)-7 × 7 surface. In fact, in the case of $AlCl_3$ reaction with the Si(111)-7 × 7 surface [13], aluminum atoms react with rest atoms and chlorine atoms react with adatoms according to the difference in the electronegativity between Al and Cl atoms. Therefore, in the case of HBO_2 molecules, oxygen and B atoms are expected to react with adatoms and rest atoms, respectively (Fig. 2(a)). Thus the O–B bond becomes broken, and B atoms remain on Si rest atoms while O atoms remain on the Si adatoms (Fig. 2(b)). Because the Si substrate temperature during HBO_2 irradiation is kept at ~ 750°C, O atoms react with Si adatoms and will be evaporated as SiO molecules (Fig. 2(c)), the structure of which can be seen in Fig. 1(b) as indicated by arrows. When adatoms on the faulted halves are removed with further HBO_2 irradiation, B atoms occupy the T_4 sites and form the $\sqrt{3} \times \sqrt{3}$ structure. The number of O atoms is twice that of B atoms, and eight Si adatoms are evaporated as SiO molecules until one $\sqrt{3} \times \sqrt{3}$ unit cell is formed. According to this mechanism, before the complete $\sqrt{3} \times \sqrt{3}$ structural formation, a wide Si disordered area must be created, which agrees with our STM observation (Fig. 1(c)). The B atoms occupy the T_4 adatom sites on the basis of our model.

According to the photoemission study, T_4-site B atoms on the $\sqrt{3} \times \sqrt{3}$ structure diffuse inward with annealing at ~ 900°C, and form the other $\sqrt{3} \times \sqrt{3}$ structure where B atoms occupy the S_5-sites [14]. Fig. 3(a) shows the structural change observed in the $\sqrt{3} \times \sqrt{3}$ structure with annealing at ~ 900°C for 5 s. There exist two kinds $\sqrt{3} \times \sqrt{3}$ structures with different brightness as shown in Fig. 3(a). A cross section over the two $\sqrt{3} \times \sqrt{3}$ structures is shown in Fig. 3(b). The height difference between the two phases is about 0.04 nm, which is close to the value previously observed for the Si adatoms with and without S_5-site B atoms [2]. The high temperature

$\sqrt{3} \times \sqrt{3}$ phase formed by annealing is considered to be the $\sqrt{3} \times \sqrt{3}$ structure with S_5-site B atoms.

Conclusively, when HBO_2 molecules were irradiated onto the Si(111)-7 × 7 surface at ~650°C, island structures were formed. On the other hand, when the sample temperature was kept at ~750°C during the HBO_2 irradiation, $\sqrt{3} \times \sqrt{3}$ structure with T_4-site B atoms was formed. HBO_2 molecules were found to react with the unfolded half-units of Si(111)-7 × 7 initially. With the heat treatment of the $\sqrt{3} \times \sqrt{3}$ structure with T_4-site B atoms up to 900°C, B atoms diffused toward inside, and the $\sqrt{3} \times \sqrt{3}$ structure with S_5-site B atoms was formed.

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