Intermediate structures appearing in the phase transition of Si(111)-7×7 to $(\sqrt{3}\times\sqrt{3})R30°$ induced by HBO_2 molecular irradiation

K. Miyake,[a] T. Kaikoh, and K. Hata
Institute of Materials Science, Center for TARA, CREST, Japan Science and Technology Corporation (JST), University of Tsukuba, Tsukuba 305-8573, Japan

R. Morita and M. Yamashita
Department of Applied Physics, CREST, Japan Science and Technology Corporation (JST), Hokkaido University, Sapporo 060-8628, Japan

H. Shigekawa[b]
Institute of Materials Science, Center for TARA, CREST, Japan Science and Technology Corporation (JST), University of Tsukuba, Tsukuba 305-8573, Japan, and Department of Chemistry and Biotechnology, Graduate School of Engineering, The University of Tokyo, Hongo, Tokyo 113-8656, Japan

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We have investigated the breakdown process of the 7×7 structure during its transition to the $(\sqrt{3}\times\sqrt{3})R30°$ phase induced by HBO_2 irradiation. The 7×7 structure was destroyed over the wide area before the nucleation of the $(\sqrt{3}\times\sqrt{3})R30°$ phase. Even when the $(\sqrt{3}\times\sqrt{3})R30°$ structure nucleated in the disordered area, disordered structure existed between the domains of the 7×7 and $(\sqrt{3}\times\sqrt{3})R30°$ structural phases. The observed results are completely different from the $(\sqrt{3}\times\sqrt{3})R30°$ formation processes induced by other group III atoms, where $(\sqrt{3}\times\sqrt{3})R30°$ phases are formed as adjacent to the 7×7 structural domains. The surface B atom concentration in the 7×7, disordered, and $(\sqrt{3}\times\sqrt{3})R30°$ regions were estimated to be about one, three, and six per 7×7 unit cell. The disordered structure remained on the surface even after annealing the sample at 750 and 900 °C. And the B concentration in the disordered region did not change. These results indicate that the disordered structure is an intrinsic nature of the B-induced reconstruction, and suggest the existence of the relationship between the B atom concentration and the stability of the 7×7 structure. [S0734-2101(99)10204-5]

I. INTRODUCTION

Structure of the dimer-adatom-stacking fault (DAS)[1] is most widely accepted as the best model for the Si(111)-7×7 reconstructed surface because it has been compatible with the theoretical[2,3] and experimental[4,5] results. However, most of these studies were performed in the static form, and study on the dynamic process of the 7×7 structure has not yet been clarified. Therefore, study of the dynamics of phase transitions between the 7×7 and the other structures is still attracting considerable attention, and is important in order to understand the mechanism for the formation and stabilizing processes of the DAS structure.

It is well known that the 7×7 structure changes into $(\sqrt{3}\times\sqrt{3})R30°$ structures by deposition of the group III atoms onto the surface. In general, there coexist osculating large domains of the 7×7 and $(\sqrt{3}\times\sqrt{3})R30°$ structures on the surface, and the $(\sqrt{3}\times\sqrt{3})R30°$ structural domains are formed by being connected to the 7×7 domains during the phase transitions.[6–8] In the case of B atom, however, the $(\sqrt{3}\times\sqrt{3})R30°$ domains are never adjacent to the 7×7 domains and there always exists disordered structural region between the 7×7 and $(\sqrt{3}\times\sqrt{3})R30°$ domains. Therefore, it is interesting and important to study the B-induced transition process for the understanding of the stability of the 7×7 structure.

According to the previous reports,[9,10] 7×7 structure remained on the surface even when 1–2 B atoms were included in a 7×7 unit cell, but was destroyed with the concentration of several B atoms.[10] It is intriguing to clarify that how many B atoms break the 7×7 structure. However, the B-induced reconstruction was introduced by annealing a heavily B-doped Si(111) substrate to segregate the dopant to the surface.[9,10] Therefore, in this case, B atoms, originally included in the bulk, are considered to suppress the formation of the 7×7 structure instead of the breaking process described above. Furthermore, the surface B concentration is difficult to be controlled by this conventional heat treatment. In addition, since a similar disordered structure was observed on the quenched Si(111) surface,[11–13] the effect must be discriminated.

Recently, the B-induced $(\sqrt{3}\times\sqrt{3})R30°$ structure was found to be formed by the deposition of B compounds ($B_{10}H_{14}$ B_2O_3, and HBO_2).[14–21] In this case, control of the surface B concentration is easier compared to the conventional high-temperature annealing processes.

In this article, we analyzed in detail the breakdown process of the 7×7 structure and the disordered structure formed during the phase transition from the 7×7 to $(\sqrt{3}\times\sqrt{3})R30°$ structure induced by HBO_2 molecular deposition.

[a]Electronic mail: miyake@ims.tsukuba.ac.jp
[b]Electronic mail: hidemi@ims.tsukuba.ac.jp; world wide web: http://dora.ims.tsukuba.ac.jp

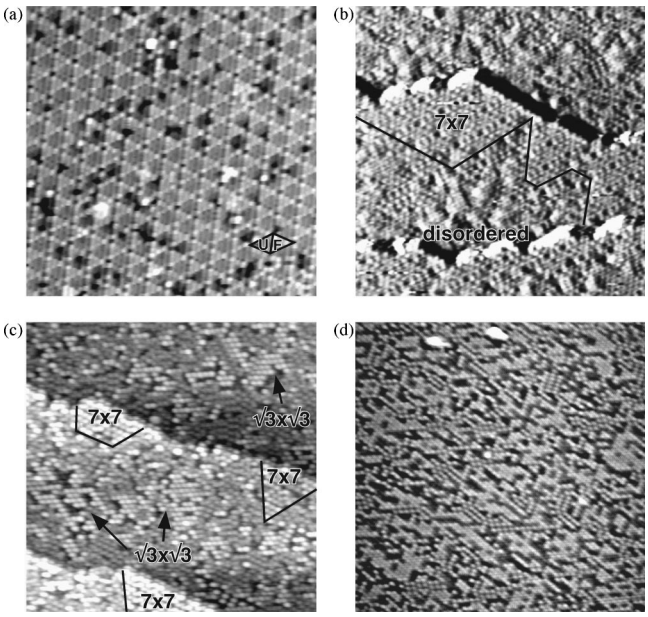

FIG. 1. STM images of the surfaces formed by (a) 3, (b) 5, (c) 6, and (d) 15 min of HBO_2 irradiation. Tip bias voltage V_s, tunneling current I_t, and scan size are (a) −2.0 V, 0.4 nA, 35 nm×35 nm, (b) 2.6 V, 0.4 nA, 35 nm×35 nm, (c) −3.0 V, 0.33 nA, 35 nm×35 nm, and (d) 1.0 V, 1.0 nA, 35 nm×35 nm, respectively.

II. EXPERIMENTS

Phosphorus-doped *n*-type Si(111) (ρ=1 Ω cm) substrates were used in this study. The samples were chemically cleaned by acetone before being loaded into the ultrahigh vacuum (UHV) chamber. The samples were outgassed at ~500 °C for 12 h. Subsequently, the samples were flashed at about 1150 °C in order to form the 7×7 structure. After confirming the formation of the clean 7×7 structure by scanning tunneling microscopy (STM), HBO_2 molecules were irradiated onto the surface. HBO_2 was irradiated from BN cell heated by a W wire coil. All irradiations were performed with the substrate temperature being kept at ~750 °C in order to prevent oxygen incorporation. The HBO_2 cell temperature during irradiation was kept at ~800 °C. All STM observations were performed at room temperature using an electrochemically etched W tip. The base pressure was $\sim 1 \times 10^{-10}$ Torr and the pressure during HBO_2 irradiation was less than 2×10^{-8} Torr. When it was impossible to observe the same area, for example due to additional irradiation or annealing at high temperature, the observed structures were checked over a wide area for each condition.

III. RESULTS AND DISCUSSION

A. Destruction of the 7×7 structure by HBO_2 irradiation

Figures 1(a)–1(d) show STM images of the surfaces formed by (a) 3, (b) 5, (c) 6, and (d) 15 min of HBO_2 irradiation. In the initial stage, 7×7 reconstruction remained on the surface as shown in Fig. 1(a). However, some adatoms became dark. Since these dark adatoms were observed after HBO_2 irradiation, they are considered to be resulted from the reaction with HBO_2 molecules. In addition, they were observed preferably in the unfaulted half units, similarly as the previous results.[11,20,21]

With increase in the HBO_2 irradiation time, the disordered structure appeared on the surface through the destruction of the 7×7 structure. However, the 7×7 structure still remained on the surface at this stage, and the $(\sqrt{3}\times\sqrt{3})R30°$ structure was not formed [Fig. 1(b)]. With further irradiation, the 7×7 structure disappeared except around the step edge here, and the disordered structure expanded over the surface [Fig. 1(b)–1(c)]. Recently, 7×7 domain was confirmed to have temperature dependent critical size for the stable existence on the surface.[22] Since B atoms induce strain on the surface here, similar critical size must exist. The observance of the small 7×7 domains at the step edges in Fig. 1(c) may be due to the fact that 7×7 structure is stable at step edges. In fact, a larger 7×7 domain with the size of 12 nm×12 nm size was observed in a different terrace.

In addition, the $(\sqrt{3}\times\sqrt{3})R30°$ structure nucleated in the disordered structure at this stage, but the $(\sqrt{3}\times\sqrt{3})R30°$ structural area was not adjacent to the 7×7 structural domains. There always existed the disordered structure between the 7×7 and $(\sqrt{3}\times\sqrt{3})R30°$ domains. Finally, 7×7 structural area disappeared and the surface was covered with the small domains of the $(\sqrt{3}\times\sqrt{3})R30°$ structure [Fig. 1(d)]. The $(\sqrt{3}\times\sqrt{3})R30°$ structural domain is grown and a large domain of a single phase of a $(\sqrt{3}\times\sqrt{3})R30°$ structure formed on the surface after further irradiation.[20] This formation process is quite different from the process induced by the other group III atoms. In the next section, we consider and discuss the breakdown process of the 7×7 structure in detail.

B. Selective reaction in the initial stage

When atoms or molecules are adsorbed on the Si(11)-7×7 surface, most of them generally react with the faulted half units of the 7×7 structure in the initial stage.[23] However, B atoms react preferentially with the unfaulted half units of the 7×7 structure as shown in Fig. 1(a).[11,20,21] It is well known that the unfaulted half units of the Si(111)-DAS structure are observed darker compared to the faulted half units at negative sample bias voltages by STM. This means that the unfaulted half unit of the 7×7 structure is more positive than the faulted half unit. In addition, with comparison of the center and corner adatoms in each half unit cell, the amount of charge transfer from them to the rest atoms is larger for the center adatoms than the corner adatoms.[24,25] From these facts, center adatoms in unfaulted half units are most positive among the adatoms in a 7×7 DAS unit. In consideration of this surface charge distribution with the fact that HBO_2 molecules react preferentially with the center adatoms in the unfaulted half units, negatively charged molecules are considered to be included in the molecules deposited onto the surface.

In order to clarify the reaction process on the surface, we measured the temperature dependence of the mass spectra of the molecules from the HBO_2 source. Figure 2 shows the change of the mass signals with the HBO_2 cell temperature.

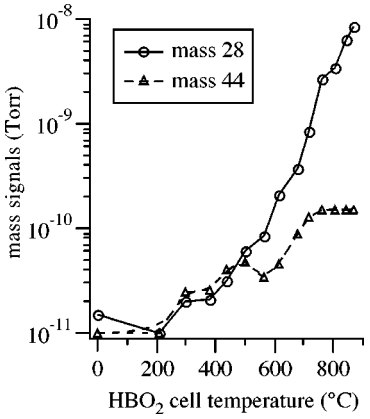

FIG. 2. Temperature dependence of mass signal from HBO_2 source.

Two dominant peaks related to HBO_2 molecule were observed; mass 28 and 44 signals corresponding to HBO and HBO_2 molecules, respectively. Both components increase with temperature, however, mass 28 peak becomes larger from around 600 °C. For the HBO_2 cell temperature of the experimental condition, ~800 °C, mass 28 is two orders larger than the other. This result indicates that the molecular flax onto the surface mostly consists of HBO molecules. Since a HBO_2 molecule has the structure of H–O–B=O, HBO molecules is considered to be produced as the oxygen molecules of the right end being removed (H–O–B). Therefore, HBO molecules are expected to become negatively charged, and they may react with the positively charged adatoms; center adatoms in the unfaulted half units, which is consistent with the STM results obtained.

C. Structures of the intermediate phases

In this section, we analyze the disordered structures observed during the phase transition from 7×7 to $(\sqrt{3}\times\sqrt{3})R30°$ structure [Figs. 1(a)–1(d)], and its relation to the 7×7 structure in detail. The disordered structure existing between the 7×7 and $(\sqrt{3}\times\sqrt{3})R30°$ appears only for the B/Si surface, but not for the surface formed by the other group III atoms as described above. Why does only a B atom induce the disordered structure?

According to the previous reports on the B-induced reconstruction formed by annealing a heavily B-doped Si(111) substrate,[9,10] 7×7 structure remained on the surface even when 1–2 B atoms were included in a 7×7 unit cell, but was destroyed at the B concentration of several atoms per the cell. Figure 3 shows a magnified STM image of the boundary between 7×7 structure and the disordered structure. According to the previous reports,[14,26] the bright and dark protrusions in the positive sample bias (empty state image) correspond to the Si and B related adatoms, respectively. We counted the concentrations of the B related adatoms in the 7×7, disordered and $(\sqrt{3}\times\sqrt{3})R30°$ structures. The average concentrations were about one, three, and six per 7×7 unit cell for the 7×7, disordered and $(\sqrt{3}\times\sqrt{3})R30°$ structural regions, respectively. This is quite consistent with the previous

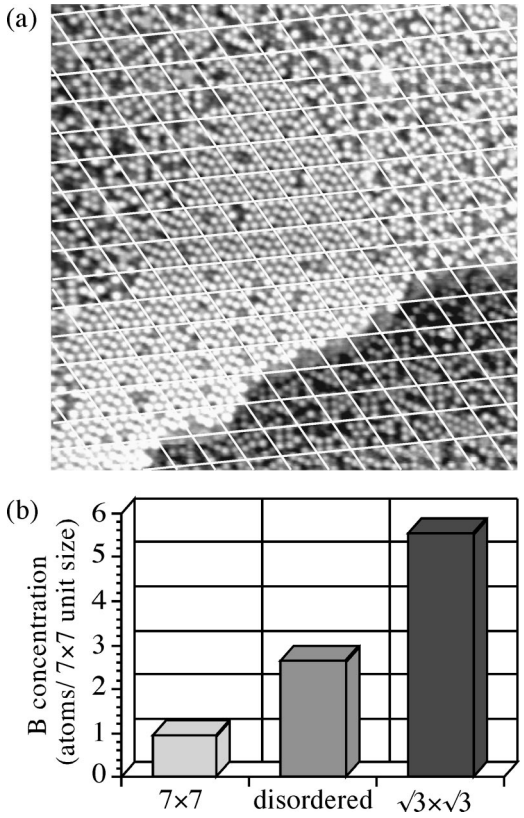

FIG. 3. (a) Magnified STM image of the boundary between 7×7 and the disordered structures (V_s=2.1V, I_t=0.45 nA, 35 nm×35 nm). (b) The surface B atom concentration (atoms per 7×7 unit cell size) in the 7×7, disordered, and $(\sqrt{3}\times\sqrt{3})R30°$ regions.

results that the 7×7 reconstruction was destroyed by the existence of the several B atom concentration per 7×7 unit cell.[10]

In a previous paper,[21] we showed those adatoms surrounding the firstly reacted adatom have higher reaction probability for the following HBO_2 molecules compared to the normal adatoms. Therefore, B atoms have a tendency to concentrate from the beginning of the reaction. Then when the number of concentrated B atoms reaches to the value of three atoms per 7×7 unit cell, the 7×7 structure is considered to break. However, the 7×7 structure still remains in the region with low B concentration. Consequently, there exist the 7×7 and the disordered structure on the surface.

In the case of the $(\sqrt{3}\times\sqrt{3})R30°$ structural formation by annealing heavily B-doped Si(111) substrate, B atoms are included in the bulk from the beginning and are considered to suppress the formation of the 7×7 structure. On the other hand, when the B atoms are deposited on the 7×7 surface, they are considered to break the 7×7 structure at the critical B concentration on the surface. In any case, existence of almost three B atoms is enough to make the 7×7 structure unstable.

The 7×7 structure is stabilized by the energy balance between the reduction of the dangling bonds and introduction of the unfavorable strains concerning the dimer wall and the local 2×2 reconstruction. In the case of the 7×7 structure,

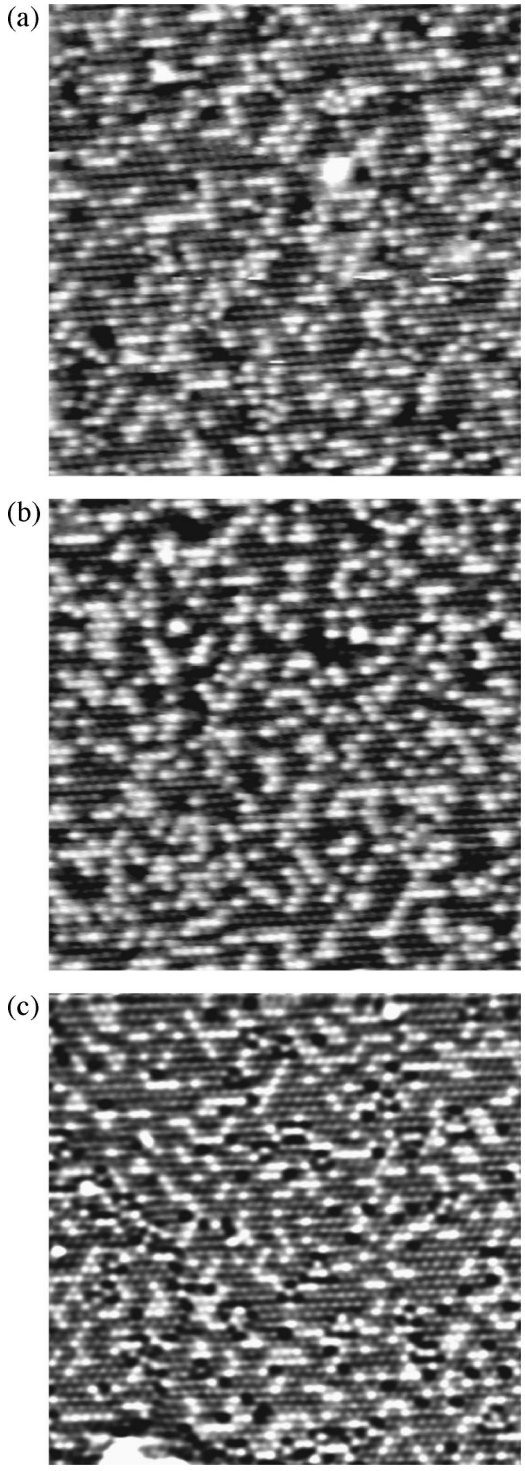

FIG. 4. STM images of (a) the surface formed by 25 min of HBO_2 irradiation ($V_s=2.0$ V, $I_t=0.8$ nA, 30 nm×30 nm), (b) the surface after annealing (a) at 750 °C for 5 min ($V_s=2.0$ V, $I_t=0.87$ nA, 30 nm×30 nm), and (c) the surface after annealing (b) at 900 °C for 8 s ($V_s=2.0$ V, $I_t=1.0$ nA, 30 nm×30 nm).

introduced strains are tensile strain.[27] When the surface is alloyed with Ge or Sn, compressive strain is introduced, which reduces the unfavorable strain in the surface and is considered to stabilize the 7×7 DAS structure.[28–30] In the case of B atoms, however, the ideal B–Si bond length, as

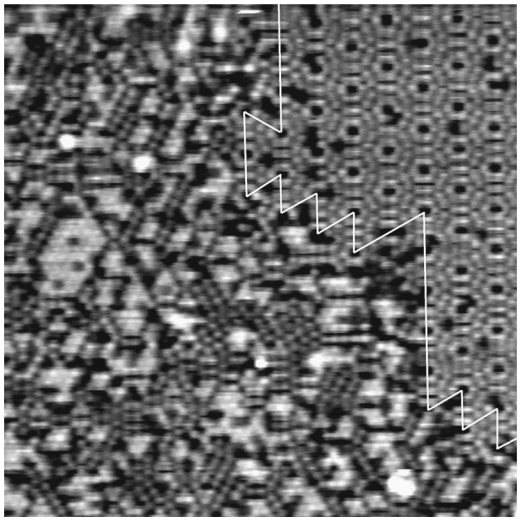

FIG. 5. STM image of the surface after annealing the sample of Fig. 1(b) at 750 °C for 5 min ($V_s=2.5$ V, $I_t=0.3$ nA, 35 nm×35 nm).

derived from covalent radii, is significantly less than the ideal Si–Si bond length.[31] Therefore, the shorter B–Si bond length increases the tensile stress in the surface layers, resulting in the decrease of the relative stability of the 7×7 DAS structure. Then the 2×2 and/or $c(2\times4)$ adatom arrangement without dimer wall is considered to become more stable than the 7×7 DAS structure at the critical surface B concentration.

On the other hand, about 16 B atoms per 7×7 unit are necessary to form the $(\sqrt{3}\times\sqrt{3})R30°$ structure completely. Even in the actual, about six B atoms seem to be necessary to start the transition as shown in Fig. 3. This value is still larger than the observed critical B concentration (about three B atoms per 7×7 unit cell). Therefore, destruction of the 7×7 structure does not result in the $(\sqrt{3}\times\sqrt{3})R30°$ structure, but changes into the other structures, such as 2×2 or $c(2\times4)$ first.

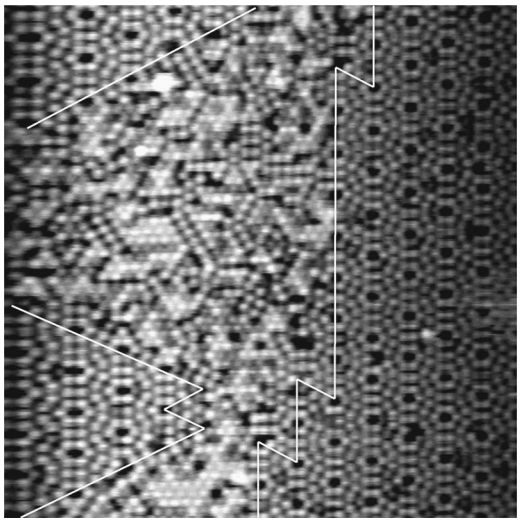

FIG. 6. STM image of the surface after annealing the sample of Fig. 5 at 900 °C for 2 s ($V_s=3.0$ V, $I_t=0.33$ nA, 35 nm×35 nm).

The disordered structure almost covers the surface instead of the formation of the $(\sqrt{3}\times\sqrt{3})R30°$, which is completely different from the $(\sqrt{3}\times\sqrt{3})R30°$ structures formed by other III atoms. In the other cases, small $(\sqrt{3}\times\sqrt{3})R30°$ structural domains are formed adjacent to the 7×7 structural domains.

In order to clarify the relation between B atoms and the intermediate structures, we analyzed the disordered structures more in detail.

D. Structure of the annealed surface after HBO_2 irradiation

First, we annealed the completed $(\sqrt{3}\times\sqrt{3})R30°$ structure in order to check the surface B concentration before and after annealing. Figure 4 shows the STM images of (a) the surface formed by 25 min of HBO_2 irradiation, (b) the surface after annealing the sample (a) at 750 °C for 5 min, and (c) the surface after annealing the sample (b) at 900 °C for 2 s.

As shown in Fig. 4(a), the surface was covered with the completed $(\sqrt{3}\times\sqrt{3})R30°$ structure. There exist bright and dark adatoms on the surface. These adatoms correspond to the Si and B related adatoms, respectively.[20] The surface structure obtained after annealing the sample (a) at 750 °C [Fig. 4(b)] is quite similar to that of (a), and there is little change of the ratio of the two kinds of adatoms. The surface B concentration did not change with annealing at 750 °C. This fact indicates that it is proper to keep the substrate temperature at 750 °C during HBO_2 irradiation in order to prevent oxygen incorporation.

On the other hand, some defects are introduced after annealing the sample at 900 °C as shown in Fig. 4(c). According to the x-ray photoelectron spectroscopy (XPS) measurement,[15] the deposited B atoms remained on the surface after annealing at about 700 °C, but begun to diffuse into the bulk at annealing temperature of 900 °C. Since the concentration of B atoms is higher at the surface in this case, B atoms will not come back to the surface once they move into the bulk. Our STM results look consistent with the XPS result.

On the basis of the obtained results, let us analyze the surface after annealing the sample in the intermediate stage of the breakdown process. Figure 5 shows the STM image of the surface after annealing the sample of Fig. 1(b) at 750 °C for 5 min. It clearly shows that there exists similar disordered structure on the surface even after annealing at 750 °C. As we have checked above [Fig. 4(b)], B atoms still remained on the surface. In addition, the surface structure did not change before and after annealing at 750 °C, and the surface B concentration at the disordered structure is about three atoms per 7×7 unit, which is equivalent to that before annealing. We did not observe $(\sqrt{3}\times\sqrt{3})R30°$ structural domains formed adjacently with the 7×7 structural domains like the case of other group III atoms.

Next, the sample was heated up to 900 °C, where the B atoms are considered to diffuse into the bulk. Figure 6 shows an STM image after annealing the sample shown in Fig. 5 at 900 °C for 2 s. The disordered structure still remains on the surface, even the size of the areas is smaller than that of Fig. 5. This change must be due to the diffusion of B atoms into the bulk, however, there still existed about three B atoms per 7×7 unit at the disordered structure, i.e., there is not change in the B concentration at the disordered structure even after annealing at 900 °C. The observed phenomena must be related to the balance among the diffusion of B and Si atoms, formation of the 7×7 phase, and stability of the disordered structures.

The obtained results strongly suggest that the disordered structure observed here is an intrinsic nature of the B-induced reconstruction, differing from the disordered structure formed by quenching. Tensile stress induced by B atoms may play an important role in the mechanism. On the other hand, existence of almost three B atoms is enough to destroy the 7×7 structure, but about six B atoms are necessary to form the $(\sqrt{3}\times\sqrt{3})R30°$ structural domains on the surface. This fact may suppress the formation of the $(\sqrt{3}\times\sqrt{3})R30°$ structure in adjacent to the 7×7 structure.

In order to clarify the nature of the B/Si surface, it is necessary to analyze the phase transition induced by other group III atoms from the view points discussed in this article.

IV. CONCLUSION

We analyzed the breakdown process of the Si(111)-7×7 DAS structure induced by HBO_2 irradiation. HBO molecule was a dominant species in the B source flax. Because HBO was negatively charged, molecules preferentially reacted with the center adatoms in the unfaulted half-units. With further irradiation, the disordered area appeared on the surface before starting the nucleation of $(\sqrt{3}\times\sqrt{3})R30°$. The average surface B concentrations in the 7×7, disordered, and $(\sqrt{3}\times\sqrt{3})R30°$ regions were about one, three, and six atoms per 7×7 unit cell, respectively. The disordered structure remained even after annealing at 750 and 900 °C and the surface B concentration in the disordered region did not change. These results suggest that the disordered structure observed here is induced by a stable intrinsic nature of the B/Si(111) structure, and the critical value of the B concentration to destroy the 7×7 structure is about three per 7×7 unit cell.

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