

Site preferences of oxygen and boron atoms during dissociative reaction of HBO₂ molecules onto the Si(111)-7×7 surface

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Using scanning tunneling microscopy (STM), we succeeded in observing the initial process of the HBO molecule on the Si(111)-7×7 surface for the first time. Since HBO₂ molecules are commonly used as the B source in the molecular beam epitaxy system, and the dominant flux from the HBO₂ source in the ordinary condition is the form of HBO, analysis of the HBO reaction process is highly important. When the substrate temperature was kept at room temperature during the molecular irradiation, the adsorbed HBO molecules remained on the surface without dissociation. With the substrate temperature being increased, the dissociation process was activated, and the oxygen- and boron-related adatoms were produced at the corner and center adatom sites in the 7×7 units, respectively. The site dependence was well determined by the bias voltage dependent STM. The selective reaction site of oxygen atoms was comprehensively explained by their electronegativity and charge distribution in the Si(111)-7×7 surface adatoms. On the other hand, regarding the selectivity for the boron atoms, introduction of the surface strain effect was found to be essential.

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I. INTRODUCTION

Boron (B) atom shows characteristic properties on Si(111)-7×7 surface differing from other group III atoms (Al, Ga, In). Despite group III atoms (Al, Ga, In) occupying the *T*₄ adatom site on the Si(111) surface, the B atom occupies the *S*₅ site in the second layer directly underneath the Si *T*₄ adatom.¹⁻³ In addition, B atoms are stable with respect to the deposition of Si overlayers and the two-dimensional B layer at the Si/Si(111) interface is electrically active. Therefore, boron is thought to be one of the most promising candidates for the atomic layer doped (δ -doped) structure. Consequently, it is very important to clarify how B atoms behave on the Si(111) surface in order to control the structure and property of atomic layer doped structure.

The B-induced reconstruction was conventionally introduced by annealing a heavily B-doped Si(111) substrate to segregate the dopant to the surface.²⁻⁹ However, this conventional heat treatment makes it difficult to control the surface B concentration. Recently, it was found that the B induced ($\sqrt{3}\times\sqrt{3}$)R30° structure was also formed by the deposition of B compounds (B₁₀H₁₄, B₂O₃, and HBO₂).^{1,10-14} In this case, control of the surface B concentration is easier compared to the conventional method. Especially, HBO₂ molecules commonly used as a B source in the molecular beam

epitaxy (MBE) system showed the possibility of forming the atomic layer doped structure.¹²⁻¹⁴

Therefore, the introduction process of the B atoms on Si(111)-7×7 surface by the molecular irradiation, especially using HBO₂ source, is most important, and has been studied extensively, for example, by scanning tunneling microscopy (STM).¹⁵⁻¹⁸ However, its phase transition mechanism is still unclear. The 7×7 structure is destroyed over the wide area before the nucleation of the ($\sqrt{3}\times\sqrt{3}$)R30° phase in the case of B induced reconstruction process.¹⁸ 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 phase. Subsequently, a ($\sqrt{3}\times\sqrt{3}$)R30° structure consisting of mixed Si and B atoms was formed and B atoms formed a network and induced phase ordering between domains.¹⁷ These phenomena 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.

In order to understand the characteristic phase transition processes, it is necessary to clarify the molecular reaction process of HBO₂ molecules on Si(111)-7×7 surface. Recently, HBO₂ molecules were found to preferentially react with unfaulted halves of the 7×7 unit in spite of the fact that almost all atoms and molecules react with faulted half units.^{15,16} The selectivity of the chemical reaction process

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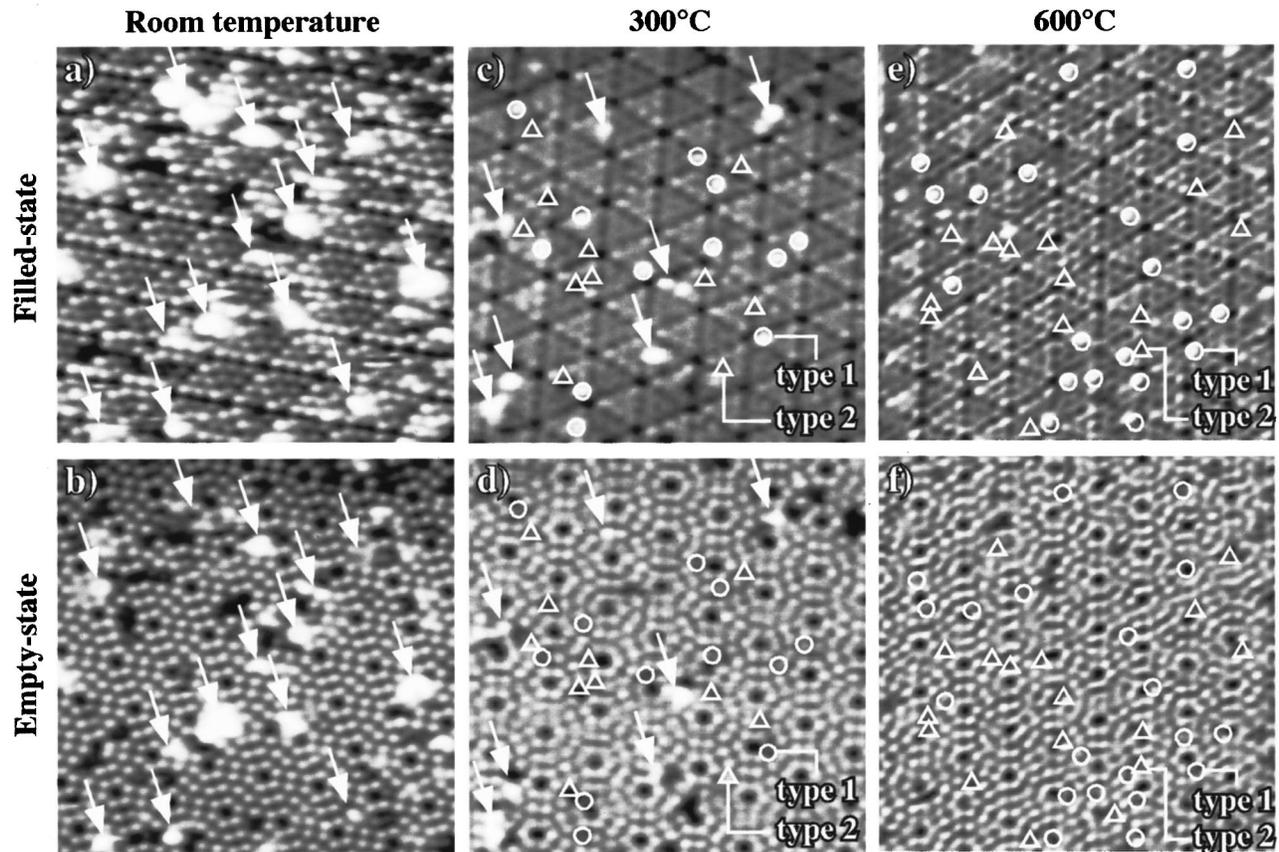


FIG. 1. STM images obtained after molecular irradiation at substrate temperatures of RT [(a) and (b)], 300 °C [(c) and (d)] and 600 °C [(e) and (f)]. Figures (a), (c), (e), and (b), (d), (f) are the filled [tip bias (V_t)=2.0 V and tunneling current (I_t)=0.3 nA] and empty-state (V_t =-2.0 V and I_t =0.3 nA) images, respectively. Arrows, open circles, and open triangles indicate bright protrusions, type 1 and type 2 adatoms, respectively.

was attributed to the charge distribution of the molecule. However, detail reaction process still remains unsolved.

In this article, we present our recent result on the dissociative reaction process of HBO₂ molecules on Si(111)-7×7 surface studied by STM.

II. EXPERIMENT

Phosphorus-doped *n*-type Si(111) (ρ =0.375–0.625 Ω cm) substrates were used in this study. The samples were chemically cleaned by acetone before being loaded into the ultra-high vacuum (UHV) chamber. After being outgassed at \sim 500 °C for 12 h, 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 STM, molecules were irradiated on the surface by heating the HBO₂ cell at \sim 800 °C. With this condition, the HBO molecule was confirmed to be the dominant species in the flux from the B source as reported previously.¹⁸ Irradiation time was fixed at 3 min. The substrate temperature during the treatment was varied from room temperature (RT) to 600 °C. All STM observations were performed at RT using an electrochemically etched tungsten tip. The base pressure was \sim 1×10⁻¹⁰ Torr and the pressure during the molecular adsorption process was less than 2×10⁻⁸ Torr.

III. RESULTS AND DISCUSSION

Figure 1 shows STM images obtained after molecular irradiation at substrate temperatures of RT [(a) and (b)], 300 °C [(c) and (d)] and 600 °C [(e) and (f)]. Figures 1(a), 1(c), 1(e), and 1(b), 1(d), 1(f) are the filled- [tip bias (V_t)=2.0 V and tunneling current (I_t)=0.3 nA] and empty-state (V_t =-2.0 V and I_t =0.3 nA) images, respectively. When the substrate temperature during the molecular irradiation was kept at RT, bright protrusions indicated by arrows in Figs. 1(a) and 1(b) were observed at both bias polarities. On the other hand, when the substrate temperature was kept at 300 °C, two characteristic-type adatoms that differ from normal 7×7 adatoms were observed on the surface in addition to the bright protrusions. One is the adatoms, which were bright in filled-state images but were slightly dark in empty-state images [type 1 adatoms; open circles in Figs. 1(c) and 1(d)]. The other is the adatoms, which were darker than normal 7×7 adatoms in both filled- and empty-state images [type 2 adatoms; open triangles in Figs. 1(c) and 1(d)]. Magnified images of the type 1 and type 2 adatoms are shown in Fig. 2. When the substrate temperature during molecular irradiation was kept at 600 °C, the bright protrusions observed in Figs. 1(a)–1(d) did not appear, and only type 1 and type 2 adatoms were observed on the surface.

Since the bright protrusions were observed at only lower

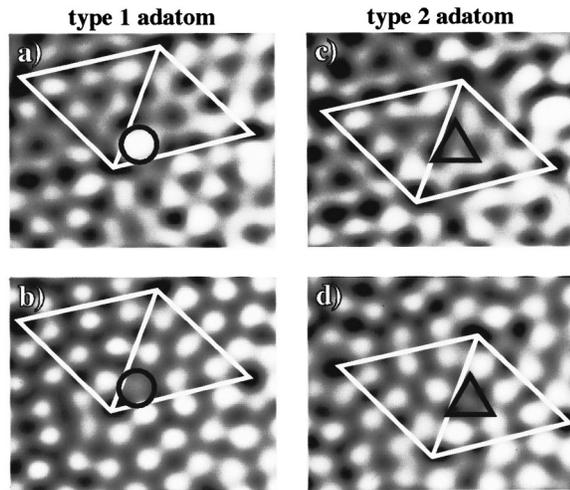


FIG. 2. Magnified images of the type 1 and type 2 adatoms. Figures (a), (c), and (b), (d) are the filled- ($V_t=2.0$ V and $I_t=0.3$ nA) and empty-state ($V_t=-2.0$ V and $I_t=0.3$ nA) images, respectively. Open circles and open triangles indicate type 1 and type 2 adatoms, respectively.

temperatures, they are considered to be the nondissociated HBO molecules. On the other hand, according to the previous reports about the oxygen molecule adsorption on Si(111) surface, bright adatoms were observed on the surface at negative sample bias voltage (filled-state image) after oxygen adsorption.¹⁹ And it is well known that boron-related adatoms are observed darker than normal Si adatoms in both bias polarities. Therefore, in consideration of the bias dependence of STM images in Fig. 1, and the fact that the ratio of the type 1 and type 2 adatoms increased with the substrate temperature, the type 1 and type 2 adatoms are considered to correspond to the dissociated oxygen- and boron-related adatoms, respectively.

In order to confirm this reaction process, the sample formed by molecular irradiation at 300 °C was annealed at 600 °C for 1 min. There existed the bright protrusions, type 1 and type 2 adatoms on the surface before annealing as shown in Figs. 1(c) and 1(d). After annealing at 600 °C, however, the bright protrusions disappeared and only type 1 and type 2 adatoms were observed on the surface. Namely, the HBO molecules were dissociated, and oxygen- and boron-related adatoms were produced during the annealing process at 600 °C. These results strongly support our assignment about the oxygen- and boron-related adatoms on the basis of the bias dependence of STM images. Since the numbers of the increased oxygen- and boron-related adatoms were comparable with the number of the original HBO molecules, desorption of the HBO molecules during annealing process was negligible. In addition, taking these results into consideration with the fact that H atoms are desorbed at 600 °C, the effect of the H atoms on the observed structures is also neglected.

Next, we consider the reaction process of HBO molecules on Si(111) surface. As shown in Figs. 1(a) and 1(b), the bright protrusions were often observed at the adatom site. At lower temperatures, HBO molecules remain on the surface without dissociation. Since the electronegativity of the oxygen atom is larger than that of boron atom, HBO molecules

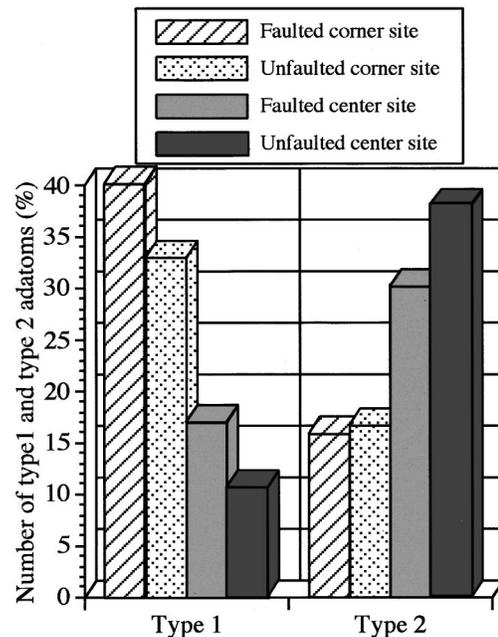


FIG. 3. Site distribution of oxygen- and boron-related adatoms in the 7×7 unit cells obtained by counting their STM images.

are supposed to be polarized, i.e., oxygen and boron atoms are expected to be charged as $-\delta$ and $+\delta$, respectively. On the other hand, it is well known that the dimer-adatom-stacking fault (DAS) structure has a characteristic electronic property; charge transfer from the top-layer adatoms to the rest atoms in the underlayer.^{20,21} Consequently, the rest atom and adatom may play as an electron donor and acceptor, respectively. Taking the difference in the electronegativity between the oxygen and boron atoms into consideration, the oxygen atoms in the molecules are expected to bond directly to a Si adatom.

When the substrate temperature was higher, the dissociation process was activated. And oxygen and boron atoms showed a tendency to occupy their preferential sites. Figure 3 shows the site distribution of oxygen- and boron-related adatoms in the 7×7 unit cells obtained by counting their STM images. With regard to the oxygen-related adatoms, the site preference ratios were about 1.3:1 for the faulted half to the unfaulted half, and 2.7:1 for the corner to the center adatoms. According to the previous reports on the O_2 molecular adsorption onto the Si(111)- 7×7 surface, the values were 4:1 and 2:1, respectively.¹⁹ Therefore, the observed difference in the occupation between faulted and unfaulted sites looks small compared to the previous case; however, the uncertainty was a few percent, and the site preference existed all over the surface. Then, we concluded that the oxygen adatoms preferentially occupy faulted corner sites. The difference between our results and previous results probably comes from the processes used in the two experiments; oxygen molecule adsorption and HBO₂ molecule irradiation. On the other hand, the boron-related adatoms were observed at the unfaulted center sites. In order to explain these site preferences, the difference in the electronegativity regarding the oxygen, boron, and Si atoms is considered.

Since the electronegativity of oxygen is larger than that of silicon, oxygen atoms play as an electron acceptor to Si atoms and are considered to react with the Si adatoms with higher electron density. On the other hand, it is well known that the faulted half units of the Si(111)-DAS structure are observed brighter compared to the unfaulted half units in STM images at negative sample bias voltages. This means that the faulted half units in the 7×7 structure are more negatively charged compared to the unfaulted half units. In addition, regarding the center and corner adatoms in each half unit cell, the amount of charge transfer from them to the rest atoms is smaller for the corner adatoms than the center adatoms.^{20,21} In consideration of this surface charge distribution together with the difference in the electronegativity between oxygen and silicon, it is probable that the oxygen atoms preferentially occupy the corner adatom sites in the faulted half units.

On the other hand, the electronegativity of boron is almost the same as that of silicon. Therefore, it is difficult to explain the site preference of the boron-related adatoms by only the difference in the electronegativity. One possible mechanism is to consider the effect of the surface strain at the adatom sites. From the 7×7 DAS model, the dimer wall and the local 2×2 reconstruction introduce the tensile strain. Since the center and corner adatoms are surrounded by one and two dimers, respectively, the strain energy of the corner adatoms is larger than that of the center adatoms. On the other hand, the ideal B–Si bond length, as derived from covalent radii, is significantly less than the ideal Si–Si bond length.²² Therefore, when Si atoms are replaced by B atoms, the shorter B–Si bond length increases the tensile strain in the surface layers. Consequently, boron atoms are considered to occupy the center adatom sites.

As has been discussed here, surface strain is considered to play an important role in the B introduction process. Such phenomena have been observed in the case of B induced Si(111) surface reconstruction as mentioned in the introduction of this article.^{17,18} For example, the 7×7 structure is destroyed over the wide area before the nucleation of the $(\sqrt{3}\times\sqrt{3})R30^\circ$ phase.¹⁸ Boron induced strain must be necessary to explain the mechanism. Compared to the previous result,¹⁵ less difference of the B reaction site between FH and UH shown in Fig. 3 is explained by the less mobility of the molecules/atoms in this case due to the lower substrate temperatures used for the experiment.

According to the previous x-ray photoelectron spectroscopy (XPS)¹⁰ and STM¹ experiments, B atoms remain on the surface up to $\sim 700^\circ\text{C}$ occupying the T_4 adatom site, but diffuse into the bulk side at $\sim 900^\circ\text{C}$ and occupy the S_5 substitutional site. In fact, when the $(\sqrt{3}\times\sqrt{3})R30^\circ$ surface formed by HBO₂ irradiation at 750°C was flashed at 900°C , two kinds of $(\sqrt{3}\times\sqrt{3})R30^\circ$ structures with different brightness were observed by STM. In the case of this article, the substrate temperature during HBO₂ irradiation was kept at 300 and 600°C . Therefore, B atoms are considered to remain on the surface adatom sites. However, in order to determine the precise position of boron atoms, further study

such as scanning tunneling spectroscopy (STS) measurement, together with the theoretical calculation, is necessary for each adatom site.

IV. CONCLUSION

We succeeded in observing the initial reaction process of the HBO molecule on the Si(111)- 7×7 surface for the first time. When the substrate temperature during molecular irradiation was kept at RT, the adsorbed HBO molecules remained on the surface without dissociation. On the other hand, when the substrate temperature was kept at 600°C , HBO molecules were dissociated, and the oxygen- and boron-related adatoms were produced at the corner and center adatom sites in the 7×7 units, respectively. Intermediate transition process was observed at 300°C . The site preference of oxygen-related adatoms was explained by the difference in the electronegativity well. Regarding the selectivity for the boron-related sites, importance of the surface strain effect was pointed out.

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