

# Selective chemical reaction of HBO<sub>2</sub> molecules on the Si(111)-7 × 7 surface studied by scanning tunneling microscopy

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## Abstract

In the chemical reaction of HBO<sub>2</sub> molecules with Si(111)-7 × 7 surface, change in the charge density on the adatoms of the 7 × 7 units during the process was found to play an exceedingly important role. The molecules preferentially reacted with the center adatoms in the unfaulted half units first. In the filled state STM images, the center adatoms surrounding the reacted center adatoms became dark compared to those in the normal 7 × 7 units, which indicates existence of some charge transfer caused by the reacted center adatoms. Since HBO<sub>2</sub> molecules tend to react with the adatoms in less charge density, such charge redistribution is supposed to increase the chemical reactivity of the modified center adatoms. In fact, center adatoms in the faulted half units, which were adjacent to the firstly reacted center adatoms, reacted subsequently with the HBO<sub>2</sub> molecules. According to this process, chain structures were formed by the reacted center adatoms, which may be related to the B network structure previously observed. © 1998 Elsevier Science B.V. All rights reserved.

**Keywords:** Adatoms; STM images; HBO<sub>2</sub> molecules; Charge redistribution; Center adatoms

## 1. Introduction

Group III atoms are known to form  $\sqrt{3} \times \sqrt{3}$  structures on the Si(111) surface. In the case of the B induced  $\sqrt{3} \times \sqrt{3}$  structure, the most stable site for B atoms is the S5 site instead of the T4 site [1–5], differing from the structure formed by the other group III atoms (Al, Ga, and In) [6,7]. In addition, according to the recent results of scanning tunneling microscopy (STM) on the B/Si(111)- $\sqrt{3} \times \sqrt{3}$  structural formation process induced by HBO<sub>2</sub> irra-

diation [8–10], B atoms showed other characteristic properties; B atoms reacted preferentially with the center adatoms in the unfaulted half units of the Si(111)-7 × 7 DAS structure. And after complete destruction of the 7 × 7 structure, B atoms interacted with each other to form a self-ordered network in the formation process of the  $\sqrt{3} \times \sqrt{3}$  structure [10]. The observed results are completely different from what observed in the  $\sqrt{3} \times \sqrt{3}$  structural formation processes induced by other group III atoms; for example, when metals such as Al atoms are deposited on a Si(111)-7 × 7 surface, 7 × 7 structural domains coexist with the  $\sqrt{3} \times \sqrt{3}$  structural domains until the end of the complete formation of the  $\sqrt{3} \times \sqrt{3}$  structure [11]. Therefore, from both funda-

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mental and practical standpoints of view, it is exceedingly interesting and important to study the detailed mechanism of the  $\sqrt{3} \times \sqrt{3}$  structural formation process induced by the HBO<sub>2</sub> molecular irradiation.

In this paper, we present our recent results of the STM study performed on the initial stage of the  $\sqrt{3} \times \sqrt{3}$  formation process induced by HBO<sub>2</sub> irradiation.

## 2. Experimental

Phosphorus-doped n-type Si(111) ( $\rho = 0.375 \sim 0.625 \Omega \text{ cm}$ ) substrates were used in this study. After chemical cleaning, samples were degassed at  $\sim 500^\circ\text{C}$  and subjected to flash heating in ultrahigh vacuum (UHV) condition. After confirming the formation of clean  $7 \times 7$  structure, HBO<sub>2</sub> molecules were irradiated on this surface with the substrate temperature being kept at  $\sim 750^\circ\text{C}$ . HBO<sub>2</sub> cell temperature during irradiation was kept at  $\sim 800^\circ\text{C}$ . STM observation was performed at room temperature using electrochemically etched tungsten tip. The base pressure was  $\sim 1 \times 10^{-10}$  Torr and the pressure during HBO<sub>2</sub> irradiation was less than  $2 \times 10^{-8}$  Torr.

## 3. Results and discussions

Fig. 1 shows an STM image of the Si(111)- $7 \times 7$  surface obtained after the HBO<sub>2</sub> irradiation of 3 min. As is shown in Fig. 1, some adatoms in the  $7 \times 7$  units have become dark during the HBO<sub>2</sub> irradiation, so that these darker adatoms are attributed to the reacted sites with the HBO<sub>2</sub> molecules. In addition to the preferential reaction of the HBO<sub>2</sub> molecules with the center adatoms in the unfaulted half units [9], the reacted adatoms seem to form chains rather than the randomly scattered structure, indicating the existence of some interaction between B atoms adsorbed on the surface. In the chemical reaction mechanism of the HBO<sub>2</sub> molecules with the  $7 \times 7$  surface, these characteristic properties must be explained comprehensively.

A reaction mechanism of HBO<sub>2</sub> molecules with Si has been proposed by Lin et al. [12]. According to

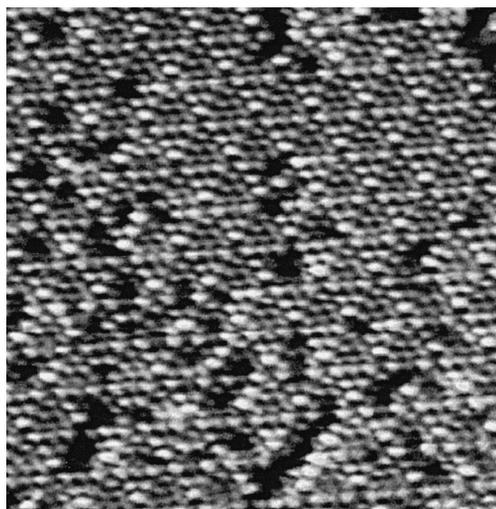
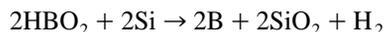


Fig. 1. STM image obtained after HBO<sub>2</sub> irradiation of 3 min (sample bias;  $V_s = -1.0$  V, and tunneling current;  $I_t = 1.0$  nA).

the model, HBO<sub>2</sub> molecules react with Si surface with a two-step process mechanism as follows: First, Si surface is oxidized by the oxygen atoms of the HBO<sub>2</sub> molecules as



or



When the substrate temperature is high enough, the silicon oxide (SiO<sub>2</sub>) formed in the first step is removed from the surface in the second step as

$$\text{SiO}_2 + \text{Si} \rightarrow 2\text{SiO}.$$

In such a case, surface temperature is high enough to evaporate H<sub>2</sub> and H<sub>2</sub>O molecules too, so that their influence on the process is trivial. In our experiment, the substrate temperature was kept about  $750^\circ\text{C}$  during HBO<sub>2</sub> irradiation, which satisfies the condition described here.

On the basis of the chemical reaction model proposed by Lin et al., Si surface is oxidized by the oxygen (O) atoms of the HBO<sub>2</sub> molecules first. Since it is well known that O atoms occupy the back bond of adatoms as an intermediate state at the initial stage of Si(111)- $7 \times 7$  oxidation [13], Si atoms in the second layer are considered to desorb from the surface during the second step. However, since an underlayer Si atom has four covalent bonds, while an

adatom has three covalent and one dangling bonds, adatoms are more easily desorbed compared to the underlayer Si atoms. In fact, defects formed after  $\text{HBO}_2$  irradiation have a structure similar to that of the adatom vacancy, as shown in Fig. 1.

The observed structure seems to be explained well by the chemical reaction model proposed by Lin et al. [12]. However, there are some observed critical differences between the model and our experimental results. Fig. 2 shows a relation in the number of the reacted adatoms in the  $7 \times 7$  units after 3 min  $\text{HBO}_2$  irradiation; horizontal axis indicates the number of the reacted adatoms in a  $7 \times 7$  half unit, and the vertical axis does the relative ratio among the numbers of the  $7 \times 7$  half units with the reacted adatoms from 0 to 6. From the model proposed by Lin et al., two Si adatoms must be desorbed from the surface in the reaction of each  $\text{HBO}_2$  molecule; however, according to the STM images, there are a lot of  $7 \times 7$  half units in which odd number adatoms are reacted and removed, as shown in Fig. 2. Therefore, some new mechanism must be introduced in our case.

One possible mechanism for the comprehensive explanation of the observed results is to take into

account the more detailed reaction processes. If the fragments such as HBO or BO molecules produced by the decomposition of  $\text{HBO}_2$  molecules may play an essential role in the reaction process, one  $\text{HBO}_2$  molecule remains one adatom vacancy. As shown in the previous reports [8,9],  $\text{HBO}_2$  molecules react preferentially with the unfaulted half units of  $7 \times 7$  DAS structure, in spite of the fact that, in general, atoms and/or molecules react preferentially with the faulted half units. If the characteristic preference observed in the  $\text{HBO}_2/\text{Si}$  chemical reaction process is caused by the negative charge remaining on ions, e.g., HBO or BO, the anions prefer to react with positively charged adatoms, i.e., center adatoms in the unfaulted half units.

In order to understand the reaction mechanism more in detail, we performed a Monte Carlo simulation to analyze the experimental results shown in Fig. 2, in which (1) one Si adatom was assumed to be removed in the reaction process of one  $\text{HBO}_2$  molecule, and (2) all Si adatoms were assumed to have the same reaction probability with the  $\text{HBO}_2$  molecules during all through the process. The ratio of ( $\text{HBO}_2$  molecules)/( $7 \times 7$  half units) was chosen as close to the experimentally obtained value,  $1/2$ . The distribution obtained by the simulation is shown in Fig. 2, which seems to be in good agreement with the experimental result. However, there exist a slight difference between the theoretical and experimental results. For the  $7 \times 7$  half units in which the number of reacted adatoms is less than 2, calculated values are close to or larger than the measured values. On the other hand, when the number of the reacted adatoms in a half unit is more than 3, measured values are larger than those of the calculated ones. The obtained results indicate the characteristic that the half units in which some adatoms have been reacted already with  $\text{HBO}_2$  molecules have higher reaction probability for the following  $\text{HBO}_2$  molecules, compared to the half units which have not reacted; our assumption (2) described above looks wrong.

Lin et al. based on the experimental results obtained for the B-doping process caused by the coadsorption of  $\text{HBO}_2$  molecules with Si MBE growth, and, as can be seen in the chemical reaction equations, reaction sites are not considered at all. However, since  $\text{HBO}_2$  molecules were irradiated onto the

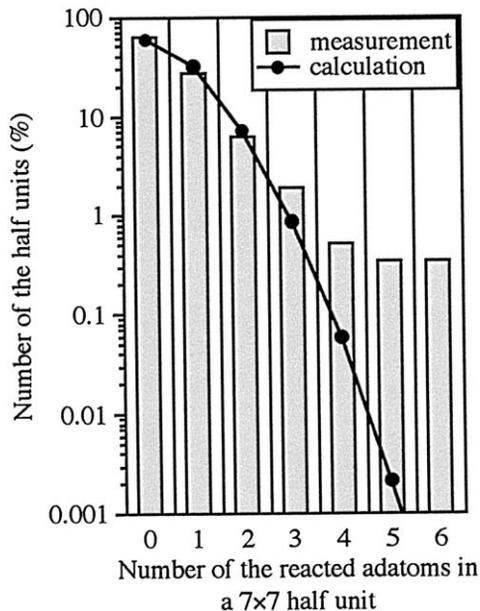


Fig. 2. Number of  $7 \times 7$  half units in which one to six adatoms are reacted with  $\text{HBO}_2$  molecules. Result of a Monte Carlo simulation is shown together.

well ordered Si(111)- $7 \times 7$  surface in our case, the reaction sites on an atomic scale must play an important role in our case; the reaction process must be strongly affected by the change in the surface atomic structures caused by the reaction process itself. Let us see the detailed reaction processes next.

Fig. 3a shows the number of the half units, in which only one isolated Si adatom is reacted as shown in Fig. 3b and c. The reacted adatoms in the

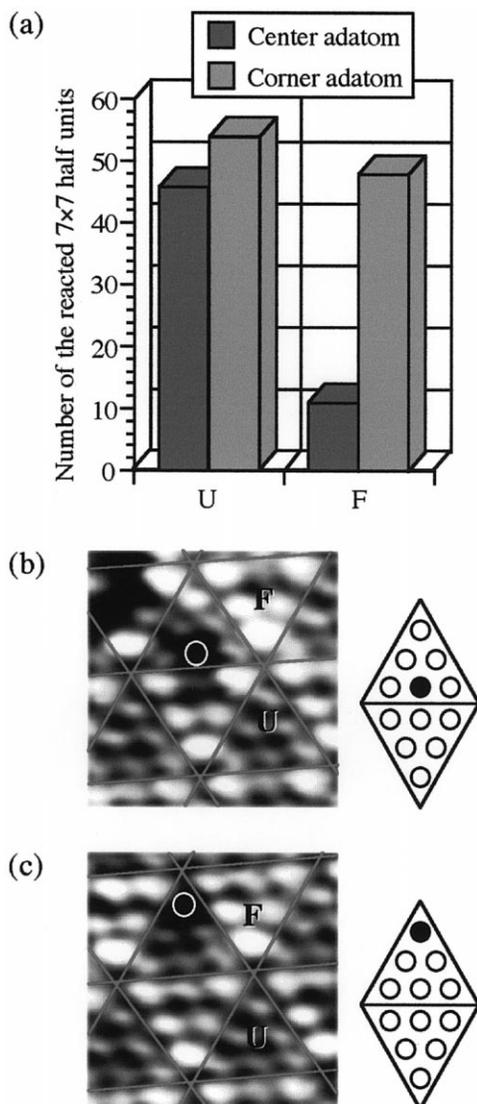


Fig. 3. (a) Number of  $7 \times 7$  half units in which isolated center or corner adatom is reacted with  $\text{HBO}_2$  molecule as shown in (b) and (c).

units are indicated by solid circles in the schematics in Fig. 3b and c, and U and F indicate unfaulted and faulted half units, respectively. According to the results shown in Fig. 3a, center adatoms, especially in the faulted half units, seem to be less reactive with  $\text{HBO}_2$  molecules compared to the corner adatoms. However, as we showed in our previous paper [9], the center adatoms were more reactive than the corner adatoms. These results suggest the existence of some more detailed processes in the reaction mechanism as expected. The observed phenomena may be due to the effect of the first reaction onto the subsequent reaction processes.

Fig. 4a shows the number of the half units in which adatoms are reacted in the fashion of pairing as shown in Fig. 4b to d. As is shown in Fig. 4a, in the pairing form, most part is the center adatoms which react with each other crossing the boundary between the faulted and unfaulted half units; all the reacted center adatoms in faulted half units are adjacent to the reacted center adatoms in unfaulted half units. In fact, the observed F–F pair shown in Fig. 4d had a structure consisting of two U–F units; U–F–U in Fig. 4d. On the other hand, the number of the half units with one reacted center adatom is not so large as shown in Fig. 3a, in spite of the preferential reaction of them in the first stage. These results support the mechanism that  $\text{HBO}_2$  molecules preferentially react with the center adatoms in the unfaulted half units first, then the subsequent  $\text{HBO}_2$  molecules tend to react with the center adatoms adjacent to the firstly reacted center adatoms.

The mechanism described above was discussed concentrating on the change in the electronic structure during the reaction, next. As is well known, the DAS structure has a characteristic electronic property; charge transfer from the top-layer adatoms to the rest atoms in the under-layer [14]. Since the amount of charge transfer from adatoms to rest atoms depends on the number of rest atoms which surround the adatoms, structures of the underlayers can be discussed by considering the redistribution of charge density on adatoms in STM images at negative bias voltages [15,16]. In the case of our experiment, desorption of adatoms increases the number of dangling bonds, which lower the charge density on the surrounding adatoms. Such charge redistribution is expected to result in the increase in the reactivity

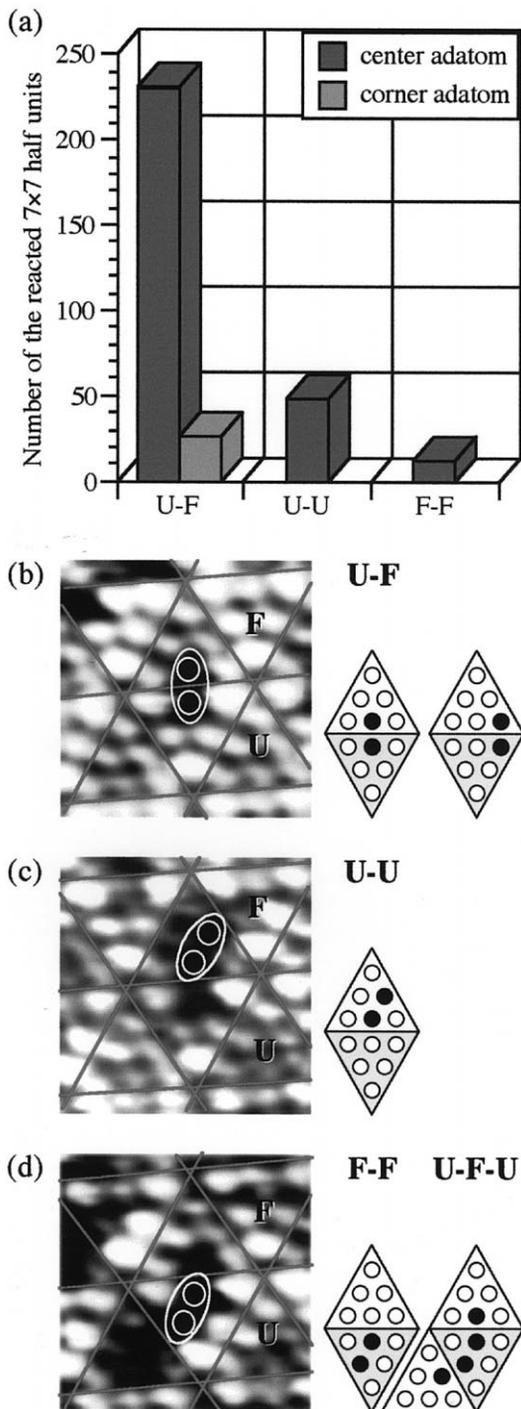


Fig. 4. (a) Number of half units in which adatoms are reacted in the fashion of pairing forms as shown in (b) to (d).

of the center adatoms surrounding the reacted center adatoms. Experimentally, in the STM images obtained at negative bias voltages, center adatoms adjacent to the reacted center adatom were observed to be darker compared to those in the normal  $7 \times 7$  structure, which agrees well with the proposed mechanism. In any case, the reaction process described here tends to form chains of the reacted sites instead of the randomly reacted one, which may be related to the network formation process observed previously [10].

From the analysis of the site-dependent adsorption mechanism, initial stage of the  $\text{HBO}_2/\text{Si}(111)-7 \times 7$  surface chemical reaction process was explained comprehensively. In order to clarify the reaction mechanism on an atomic scale more in detail, further study, such as determination of the surface structure including B atoms, must be performed.

#### 4. Conclusions

We have investigated in detail the reaction process of  $\text{HBO}_2$  molecules with the  $\text{Si}(111)-7 \times 7$  surface by using STM.  $\text{HBO}_2$  molecules first reacted preferentially with the center adatoms in the unfaulted half units. Charge redistribution on adatoms in the  $7 \times 7$  units was caused by the first reaction of the center adatoms, which resulted in the modification of the reaction probability of the adatoms, and made the center adatoms surrounding the firstly reacted center adatom more reactive for the following  $\text{HBO}_2$  molecules. As a result of the observed processes, a chain network consisting of the reacted sites was formed on the surface.

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