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Self-organized network structure appearing in the B/Si(111)-($\sqrt{3} \times \sqrt{3}$)R30° phase formation process studied by scanning tunneling microscopy

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Abstract. In the initial stage of the Si(111)-($\sqrt{3} \times \sqrt{3}$)R30° structural formation by HBO_2 molecular irradiation onto a Si(111)-7 × 7 surface at ∼ 750 °C, B atoms interacted with each other to form chains from the beginning, and a ($\sqrt{3} \times \sqrt{3}$)R30° structure consisting of Si and B atoms was formed. The observed result is completely different from the ($\sqrt{3} \times \sqrt{3}$)R30° structural processes induced by other group III atoms; in general, when metals such as Al are deposited on a Si(111)-7 × 7 surface, large 7 × 7 and ($\sqrt{3} \times \sqrt{3}$)R30° structure domains exist separately. With an increase in the amount of the B component to about half the number of adatoms, B atoms formed a network with the same ($\sqrt{3} \times \sqrt{3}$)R30° phase, resulting in the formation of an ordered ($\sqrt{3} \times \sqrt{3}$)R30° structure. Off-phase disordered areas remaining on the surface were limited to the areas occupied by Si atoms. The obtained results indicate that the interaction caused by B atoms plays an essential role in the formation process of the ordered ($\sqrt{3} \times \sqrt{3}$)R30° structure of this surface.

With the recent development of scanning tunneling microscopy (STM) [1] and its application to the atom manipulation [2–4], nanometer-scale fabrication of semiconductor surfaces has been attracting considerable attention these years. For example, selective adsorption of Ga atoms onto the hydrogen-missing dangling bonds in the hydrogen-terminated Si(100) surface was demonstrated by controlling the structure of hydrogen-missing defects using STM tip [5]. Since characteristics of semiconductor surfaces are drastically changed by adsorption of foreign atoms, modification of semiconductor surfaces terminated by adsorbates has very high potential over the field of nano-scale fabrication. However, in general, the area modified by the manipulation using STM tip is very limited spatially.

Recently, selective desorption of Ga atoms and formation of self-ordered Si(111)-7 × 7 structure near the step edge was induced by STM tip on the Si(111)-($\sqrt{3} \times \sqrt{3}$)R30°–Ga surface [6]. In this case, Si(111)-7 × 7 structural domain with width 7.0 nm and length more than 140 nm was formed on the surface, which indicates the importance of self-ordering processes in this field, as has been recognized in the structural control of organic materials. Thus, in order to realize the nano-scale science on semiconductor surfaces, it is essential to understand and develop the self-organized structural formation process on semiconductor surfaces.

On the other hand, boron (B) is one of the major p-type dopants for Si crystal, and has been playing important roles in semiconductor technology. For example, since the B atom is less segregable compared to other group III atoms (Al, Ga and In), it has attracted considerable attention as a promising candidate for the formation of atomic-layer-doped (δ-doped) structure. Therefore it is very important to control the B/Si surface structures on an atomic scale. However, the B-induced reconstructed surface has generally been formed by annealing a heavily B-doped substrate [7–11]. Since the formation process requires a high treatment temperature of ∼ 1000 °C in order to segregate the dopant from the surface, it was very difficult to control the B/Si surface.

Recently, a new process to form the B/Si(111)-($\sqrt{3} \times \sqrt{3}$) R30° surface was found; 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, HBO_2) [12–17]. In general, the process temperatures is lower than the diffusion temperature of B atoms. B atoms occupy the T_4 sites on the surfaces formed by the molecular deposition, and change their sites from T_4 to S_5 by annealing of the surface. Therefore, the ($\sqrt{3} \times \sqrt{3}$)R30° structure formed by molecular deposition may be controllable in the sense of self-ordering. Especially, in the case of the ($\sqrt{3} \times \sqrt{3}$)R30° structure formed by HBO_2 molecular deposition, since B atoms selectively react with the Si(111)-7 × 7 center adatoms [18], formation of characteristic structures is highly expected on this surface.

In this work, we present the results of STM observation of the formation process of the ordered Si(111)-($\sqrt{3} \times \sqrt{3}$)R30° structure formed by HBO_2 irradiation in detail; a self-

organized network formation process was found on this surface for the first time.

Phosphorus-doped n-type Si(111) ($\varrho = 1.5\,\Omega\,\mathrm{cm}$) substrates were chemically cleaned and degassed at $\sim 500\,°\mathrm{C}$ before being subjected to flash heating in order to form the 7×7 structure. After it was confirmed that a clean 7×7 structure had been obtained, HBO_2 molecules were irradiated onto the surface with the substrate temperature kept at $\sim 750\,°\mathrm{C}$. The HBO_2 cell temperature during irradiation was kept at $\sim 800\,°\mathrm{C}$. 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.

Figures 1a–d show STM images of surfaces formed by (a) 3 min, (b) 15 min, (c) 20 min, and (d) 50 min of HBO_2 irradiation. Since additional irradiation at $\sim 750\,°\mathrm{C}$ was carried out before each measurement, it was impossible to observe the same area. However, the observed structures were checked over a wide area for each condition. In the initial stage shown in Fig. 1a, the Si(111)-7×7 structure still remained, but some unfaulted half-units of the 7×7 structure became dark, which indicates that HBO_2 molecules initially react preferentially with the unfaulted half-units, as previously observed [18, 19]. A magnification of a portion of Fig. 1a and a schematic of this structure are shown in Figs. 2a, b, respectively. U and F indicate unfaulted and faulted halves, and reacted adatoms are represented by closed circles. In addition to this characteristic, the reacted adatoms seem to form chains rather than being randomly scattered, as shown in Fig. 2, which suggests that there exists some interaction with B atoms adsorbed on the surface.

With further irradiation, the disordered area increased in size. After the 7×7 structure was completely broken, the surface was covered with $(\sqrt{3} \times \sqrt{3})R30°$ domains consisting of atoms exhibiting two different degrees of brightness (Fig. 1b). According to the photoemission study by Cao et al. [13], B atoms, which occupy the T_4 site first, diffuse inwards upon heating at $\sim 900\,°\mathrm{C}$, to occupy S_5 sites. In this case, since the substrate temperature during HBO_2 irradiation was lower than the B diffusion temperature, B atoms are considered to adsorb on the surface. Since the ratio of dark to bright atoms increased with further B deposition (Figs. 1c, d), the bright and dark atoms were inferred to be Si and B atoms, respectively.

In the stage of Fig. 1b, islands of B atoms, in a chain form, remain isolated and the surface consists of a number of $(\sqrt{3} \times \sqrt{3})R30°$ structural domains; the phase of the domains is not ordered to be single. A magnified image and its schematic of the structure, indicated by a rectangle in Fig. 1b, is shown in Fig. 3. Open and solid circles indicate Si and B atoms, respectively, and boundaries of $(\sqrt{3} \times \sqrt{3})R30°$ domains with mismatched phase to each other are indicated by solid lines. The domains with three different phases are represented by white, light gray and dark gray areas in Fig. 3.

With an increase in the B amount of the component to about half the number of adatoms, B atoms were found to

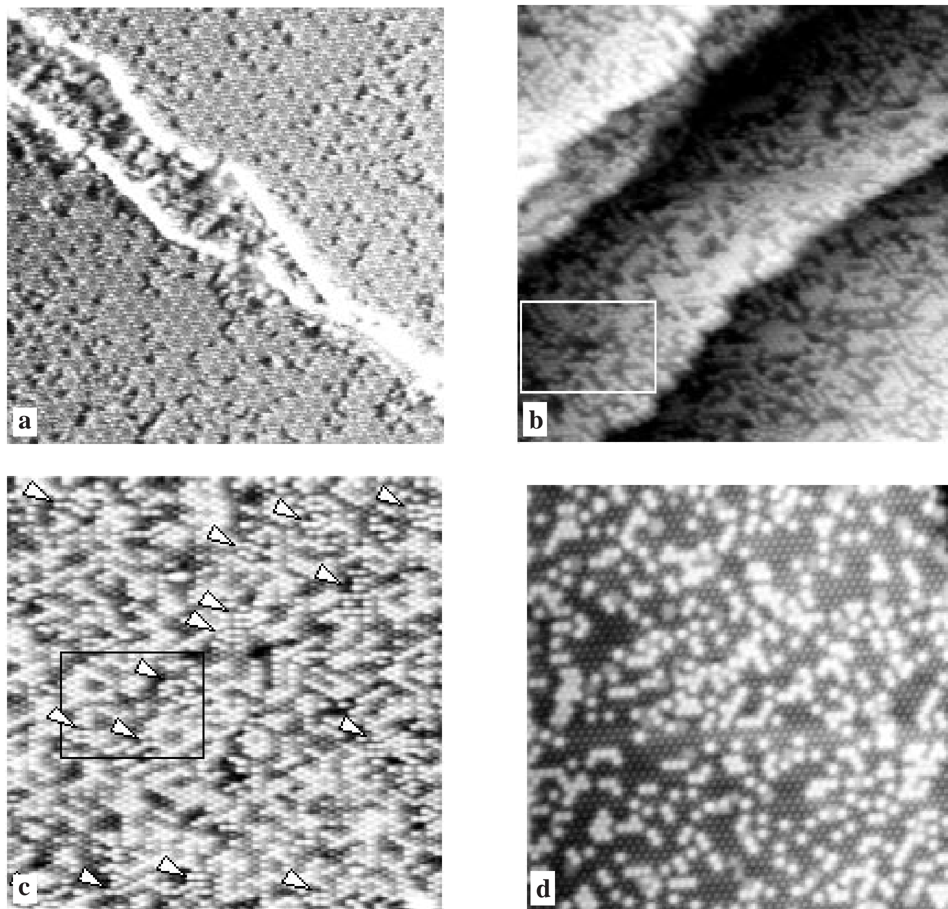

Fig. 1a–d. STM images of Si(111) surface after HBO_2 irradiation at 750 °C. Irradiation time, tip bias voltage V_t, tunneling current I_t and scan size are, respectively, **a** 3 min, 1.0 V, 1.0 nA, 70 nm×70 nm, **b** 15 min, –1.0 V, 1.0 nA, 35 nm×35 nm, **c** 20 min, –1.0 V, 0.5 nA, 35 nm×35 nm, and **d** 50 min, –1.5 V, 0.98 nA, 35 nm×35 nm

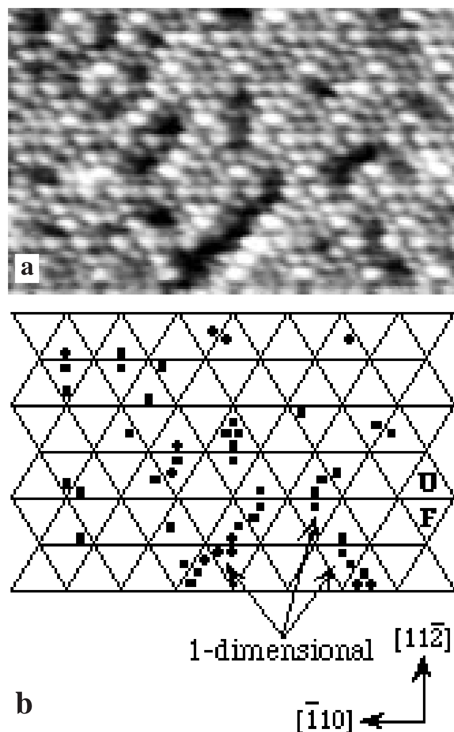

Fig. 2. a Magnified image of Fig. 1a, and b its schematic structure. In **b**, *triangles* indicate half-unit cells of 7×7 structure, and reacted adatoms are represented by *closed circles*

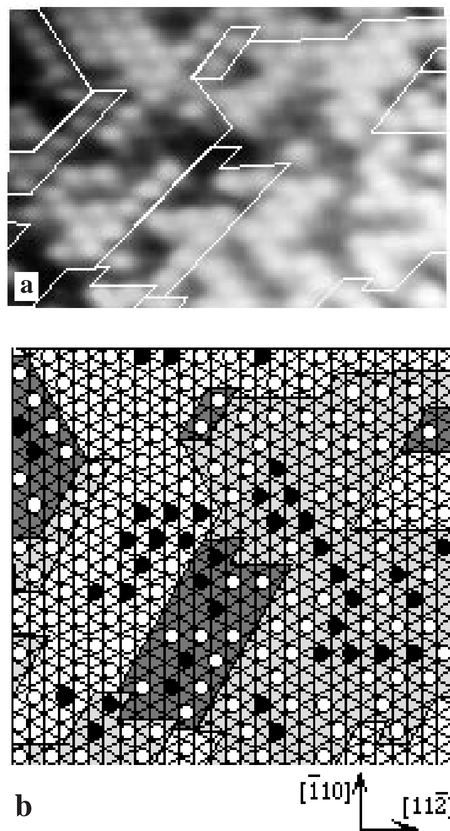

Fig. 3. a Magnified image of Fig. 1b, and b its schematic structure. In **b**, boundaries of $(\sqrt{3} \times \sqrt{3})$R30° domains with different phases are indicated by *solid lines*, and the domains with three different phases are represented by white, light gray, and dark gray areas. *Open and solid circles* indicate Si and B atoms, respectively

form a network with the same $(\sqrt{3} \times \sqrt{3})$R30° phase, resulting in the formation of a large domain of a single phase of a $(\sqrt{3} \times \sqrt{3})$R30° structure on the surface. In Fig. 1c, $(\sqrt{3} \times \sqrt{3})$R30° phase formed by B atoms, darker atoms in the figure, has the same phase all over the surface in the figure. Small off-phase $(\sqrt{3} \times \sqrt{3})$R30° domains remained only in the areas occupied by Si atoms, as indicated by arrows in Fig. 1c. A magnified image and its schematic of the structure indicated by a rectangle in Fig. 1c is shown in Fig. 4. Areas of off-phase Si atoms are enclosed by solid lines. The network of B atoms shown in Fig. 1c and Fig. 4 form branches in three-fold symmetric directions, as indicated by arrows in Fig. 4. The remaining Si adatoms were replaced by B atoms with further deposition of HBO_2 molecules, and a completely ordered $(\sqrt{3} \times \sqrt{3})$R30° surface was formed in the stage shown in Fig. 1d, where small Si domains of 1–2 atomic widths are isolated from each other by the B network.

The formation process observed here is completely different from that of the $(\sqrt{3} \times \sqrt{3})$R30° structures induced by other group III atoms. For example, when Al atoms are deposited on a Si(111)-7×7 surface, large 7×7 and $(\sqrt{3} \times \sqrt{3})$R30° domains coexist and their domain boundaries are stabilized by Al(Si) atoms [20]. On the other hand, in the case of the B-induced $(\sqrt{3} \times \sqrt{3})$R30° surface formed by HBO_2 irradiation, B atoms seemed to interact with each other in a one-dimensional manner from the beginning, and a $(\sqrt{3} \times \sqrt{3})$R30° structure consisting of mixed Si and B atoms was formed. Boron atoms formed a network and induced phase ordering between domains (Fig. 1a–c). The obtained

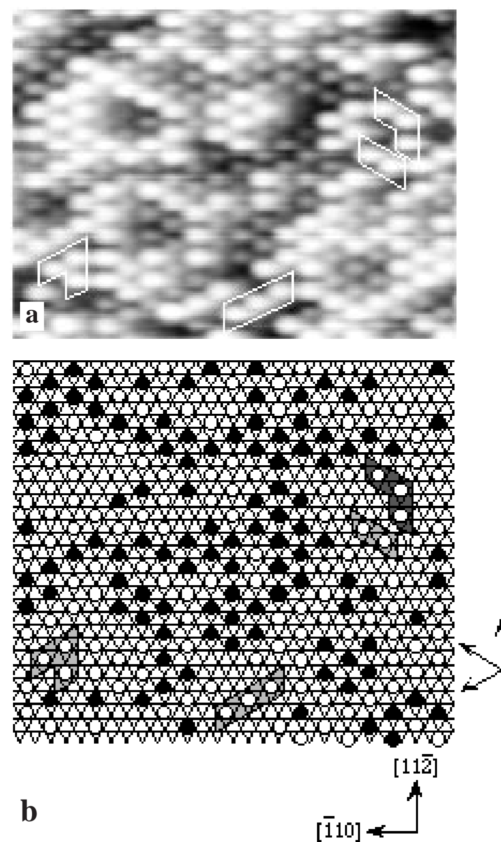

Fig. 4. a Magnified image of Fig. 1c, and b its schematic structure. In **b**, areas of off-phase Si atoms are enclosed by *solid lines*. *Open and solid circles* correspond to Si and B atoms, respectively

results indicate that the balance between Si−Si, Si−B and B−B adatom interactions plays an essential role in the formation of the self-organized $(\sqrt{3} \times \sqrt{3})$R30° structure.

Further experiment and theoretical study is necessary for a more detailed understanding of the mechanism of the self-ordering process described in this manuscript.

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