

Atomic structures of boron-induced protrusion features on Si(100) surfaces

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It is known that ultrahigh doping can be realized for boron on Si(100) substrates, while boron-induced features on a heavily boron-doped Si(100) surface cannot form any periodic structure. Here, we demonstrate that boron-induced features actually result from the adsorption of boron-silicon addimers, owing to the underneath substitutional boron atoms at the second layer. Furthermore, more closely arranged boron atoms at the second layer make the energy of the (2×1) surface lower, and the whole second layer can be completely occupied by boron atoms while the surface is still (2×1) reconstructed.

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I. INTRODUCTION

Boron (B) is a widely used *p*-type dopant in silicon-based semiconductor technology, and its particular properties in the silicon crystal have been interesting for up-to-date silicon devices.¹⁻³ Ultrahigh doping can be realized for B on Si(100) substrates with a volume concentration of up to 25%.^{4,5} The understanding of the related atomic process involves the B effects on silicon surfaces, since the B doping in silicon is inevitably related to the B segregation and B-induced atomic structures on silicon surfaces.⁶ It has been found from scanning tunneling microscope (STM) observations that the segregated B atoms from silicon can induce a $(\sqrt{3} \times \sqrt{3})$ structure on the (111) surface.⁷ Such a B-Si alloy surface becomes so stable that a silicon epitaxy can be changed, giving rise to stacking faults in a grown film.⁸ On a Si(100) surface, however, all the published STM observations have demonstrated a common fact that the segregated B atoms from a heavily B-doped sample cannot accumulate enough so as to change the original (2×1) reconstruction, regardless of how high the annealing temperature and how long the annealing time.⁹⁻¹² This experimental fact doubts a conclusion from some Auger measurements and STM investigations that a Si(100) surface can reconstruct into *c*- (4×4) with B atoms of 0.5 monolayer.¹³ This divergence has lasted for more than ten years, and the atomic structures of B-doped Si(100) surfaces have been an intriguing problem. Because Si(100) is usually used as substrates for device manufacture, it is undoubtedly important to find out the B doping capacity of a Si(100) surface and related surface structures.

The first report of Si(100):B surfaces was on several *c*- (4×4) reconstructions that occur during chemical vapor deposition of B from diborane (B_2H_6) or decaborane ($B_{10}H_{14}$) gas on Si(100) surfaces at temperature of 542 °C.¹³ Such periodic structures were considered as effects of 0.5 monolayer B atoms on Si(100) surfaces and intensively modeled.¹⁴⁻¹⁶ Actually, the *c*- (4×4) reconstructions are only metastable below 600 °C and they will all disappear at higher temperatures. Furthermore, all the *c*- (4×4) reconstructions that have ever been found on Si(100) surfaces result in a common atomic structure, but there may be different

mechanisms of its formation.¹⁷⁻¹⁹ Particularly, in the case of boron hydrides used, the hydrogen can also play an important role in the *c*- (4×4) formation.^{20,21} Moreover, it is already well known in the literatures that clean Si(100):B surfaces can be prepared by annealing heavily B-doped silicon substrates in an ultrahigh vacuum. In this case, the segregated B atoms on a Si(100) surface just induce randomly distributed protrusions, most of which are paired, some single and some tripled or several assembled, but all never aggregate a patch of periodic structure.⁹⁻¹² Such behaviors of protrusions have been confusing in understanding the Si(100):B surfaces, and so far, there is no acceptable model for them. In this paper, we will reveal the atomic structures of the B-induced protrusion features and will further discuss the B doping capacity on Si(100) surfaces.

II. BORON-INDUCED PROTRUSION FEATURES

We first check Si(100):B surfaces that present the B-induced protrusions in experiment. Our samples were prepared by annealing heavily B-doped Si(100) samples ($\rho = 0.01 \Omega \text{ cm}$) in an ultrahigh vacuum, as had been done by Kulakov *et al.*,⁹ and they were observed by using an STM equipped in the vacuum system. Figure 1 shows one of our high-resolution STM images, where arrow I points to a single protrusion, arrow II to paired protrusions, and arrow III to tripled protrusions. In a block of tripled protrusions, the middle one is clearly bigger and higher than the other two on both its sides. In addition, a few percent of protrusions may also appear in a different size or brightness in STM images (not shown here). All the protrusions are located between two dimer rows, which can be recognized in the image with the aid of two connected circles that represent a dimer.²² Compared with dimers as marked, we can see that each protrusion makes four adjacent atoms invisible, which belong to four adjacent dimers, and the whole appearance is mirror symmetric with respect to the dimer orientation. It is interesting to note a striking phenomenon in our STM observations that the atom rows beside all the protrusions become bent as if they were attracted by the protrusions, which is indicated in the figure by connected dots. The

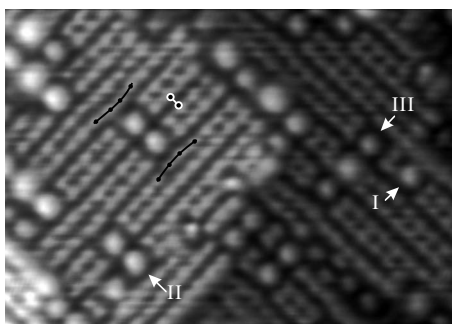


FIG. 1. An empty state STM image presents common features of B-induced protrusions and striking bending of atom rows beside all the protrusions. The image was acquired at a sample voltage of 2.0 V and a tunneling current of 0.2 nA. Arrow I points to a single protrusion, arrow II to paired protrusions, and arrow III to tripled protrusions. The bending of atom rows next to the protrusions is marked by connected dots. The two connected circles indicate the position of a dimer.

dotted atoms next to a protrusion can deviate from their original positions by as large as 0.8 Å. This surface strain phenomenon provides an evidence about B-Si interaction on a Si(100) surface and will be particularly considered in our modeling below.

In order to investigate the structural features of the protrusions, we performed *ab initio* calculations using the CASTEP computer program,²³ which employs the plane-wave pseudopotential method based on the density functional theory within the localized density approximation. For such calculations, one has to periodically arrange the protrusion blocks on a Si(100)-(2 × 1) surface and the distance between them should be large enough to prevent their interaction. In practice, we could construct a periodic block with a top area of 6 × 3 unit cells of the Si(100) surface and a thickness of ten atomic layers owing to our limited computation capacity. The positions of the atoms of the bottom four layers were fixed during the structural optimization. The plane-wave kinetic energy cutoff was 160 eV and the *k* points for the Brillouin-zone sampling were 1 × 2 × 1 using the Monkhorst-Pack scheme. The STM simulations were generated from the results of CASTEP calculations with the Tersoff-Hamann approach.²⁴

Before engaged in our modeling, we would like to have a look at two models that have ever been proposed for the paired protrusions, in order to present some clues for further consideration. One is the denuded silicon atom model⁹ and the other is the B-adsorption model.¹¹ Based on our *ab initio* calculations, the structures and the STM images of these two models were simulated. From the optimized atomic structures and their STM images shown in Fig. 2, we can see that in the denuded silicon atom model, a B atom located at the third layer can pull the surface atoms toward its side, while in the B-adsorption model, the adsorbed B clearly pushes the adjacent atoms away. However, both of them cannot correctly reproduce the typical features of protrusions as STM images display. Considering the surface strain induced by B, as indicated in Fig. 1, it seems necessary to have an adsorbed dimer that connects two neighboring dimer rows so as to

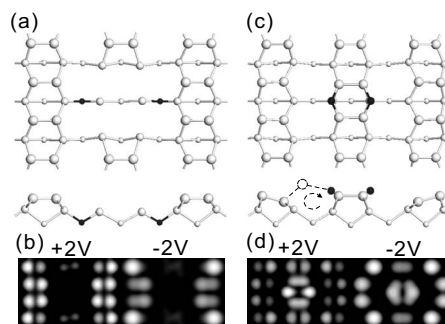


FIG. 2. Structures and STM simulations of two models that have ever been proposed. [(a) and (b)] Optimized structure (upper: top view; lower: side view) and its STM images simulated from the denuded silicon atom model. [(c) and (d)] Optimized structure (upper: top view; lower: side view) and its STM images simulated from the B-adsorption model. In side view of (c), an atom is supposed to be adsorbed as indicated by a dashed circle to form a closed ring.

form a closed ring, as indicated in Fig. 2(c), and such a ring would contain several B atoms to shrink in size, since a B-Si or B-B bond is shorter than a Si-Si one.⁷

Based on the calculated surface energies and the simulated STM images of symmetrically paired rings with various Si-B configurations, we were able to determine the atomic structure that reproduces the features of paired protrusions. As shown in Fig. 3, a ring mentioned above is related to an adsorbed dimer (A_1 and A_2), four surface atoms (B_1 , B_1' , B_2 , and B_2'), two subsurface atoms (C_1 and C_2), and one atom at the third layer (D_1). If an adsorbed dimer contains a B atom, this B atom will be invisible in the simulated STM images because a B atom just has three covalent electrons and these electrons are all combined into covalent bonds at deep energy levels. Thus, a protrusion may be reproduced with a B atom at the position marked by A_1 and with a Si atom at the position A_2 . Connected with an adsorbed dimer are four surface atoms. Because a block of B-induced protrusions has the mirror symmetry with respect to the orientation of the dimers, occupation of B atoms at these four sites must have the same symmetry. Therefore, these four sites might contain four, two, or zero B atoms. However, in all the cases of B atoms at these four sites, the simulated STM images of Si-B addimers do not accord with the experiments, and the surface energies are high. So the occupations of B atoms at these four sites are not favored. The last three sites at the second and the third layers are located along the symmetry axis and might be equally available for B atoms to occupy. Thus, the pos-

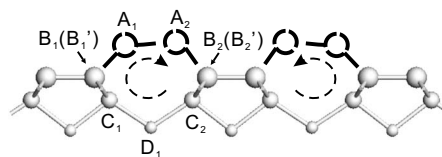


FIG. 3. The possible positions of B atoms in a ring. The surface energies of symmetrically paired rings are shown in Table I.

TABLE I. Surface energies (Ref. 25) of symmetrically paired rings with B atoms at different positions. The possible positions of B atoms in a ring are marked in Fig. 3.

Positions	Energy (eV)
(A ₁)	-0.56
(A ₁ ,C ₁)	-3.31
(A ₁ ,C ₂)	-3.06
(A ₁ ,D)	-2.87
(A ₁ ,C ₁ ,C ₂)	-4.35
(A ₁ ,C ₁ ,D)	-3.41
(A ₁ ,C ₂ ,D)	-3.32
(A ₁ ,C ₁ ,C ₂ ,D)	-3.24

sible sites for B atoms would be those marked by A₁, C₁, C₂, and D. The calculated surface energies for a block of paired rings with various Si-B configurations at these four sites are listed in Table I. Clearly, one B atom in an adsorbed dimer and two B atoms at the positions of the second layer (A₁, C₁, and C₂), forming symmetrically paired Si-B rings, lead to the minimum of surface energy of -4.35 eV.

Figure 4(a) shows the optimized atomic structure of paired rings with B atoms at positions A₁, C₁, and C₂. The observed surface strain is reproduced in our simulated STM images, as shown in Fig. 4(b), where small displacements of atoms are marked with connected dots. Meanwhile, it is determined that the protrusion features are actually contributed by the silicon atoms in the adsorbed dimers. Furthermore, the observed protrusions become weak with decrease of absolute sample voltage value, which is more pronounced for STM observations at positive sample voltages than at negative ones.⁹ We show such a phenomenon in Fig. 4(c), where the images in the upper row are from our experiments and those in the lower row from our simulations. Figure 4(d) shows the relative heights of protrusions with respect to their surrounding surface atoms, which were measured and simulated. On the whole, the simulated results agree well with the experimental observations.

There is still an artifact in the simulated STM images that the atoms surrounding the paired protrusions appear in different brightness. This problem could arise from the close arrangement of calculated blocks because the similar phenomena are often observed in experiments when two protrusion blocks are located close enough. We consider that there exists some interaction between the protrusion blocks because the surface energy calculated for a block of paired protrusions increases when the block size is decreased, as shown in Table II. This result suggests that the dense arrangement of protrusions is energetically unfavorable, which agrees with the experiments. Such an interaction may result from the surface strain, as shown in Fig. 1. The calculation of a sparse enough arrangement of the protrusion blocks would help identify the artifact, if we could have enough computer capacity. On the other hand, the dynamic effects of the dimers may also be a reason. Our simulation is based on the calculations at 0 K, while the Si dimers are usually in flip-flop motion induced by thermal activation at room

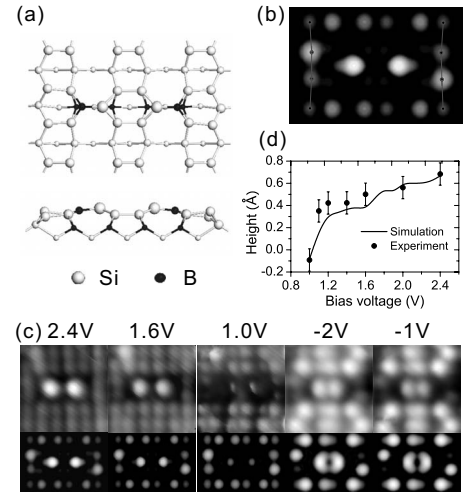


FIG. 4. Atomic structure of paired protrusions. (a) Optimized structure of symmetrically paired Si-B rings. Upper: top view; lower: side view. (b) A simulated STM image at sample voltage of 2 V. The connected dot marks indicate the displacements of the atoms toward the protrusions. (c) Appearance of protrusions changes with sample voltage. Upper row: experimental results; lower row: simulated results. (d) Relative heights of protrusions with respect to the average height of the surrounding surface atoms.

temperature²⁶ or by the probe effect of STM,²⁷ which would lead the atoms to appear in the same height during STM observations.

According to our calculations, the symmetrically paired rings with three B atoms in each one result in the most stable block of paired protrusions with an energy of -4.35 eV.²⁵ If any of the three B atoms is replaced by a Si atom, the block energy will increase. Figures 5(a), 4(b), and 4(c) show the optimized structures IIa, IIb, and IIc, and their simulated STM images are shown in Figs. 5(d), 4(f), and 4(g), respectively. For the structure IIa, the block energy will increase by 0.13 eV and the STM image will exhibit two resolvable parts in the filled state, but they are hardly resolved in the empty state and seemingly appear as a big one [Fig. 5(d)]. In the case of structure IIb, the block energy will increase by 0.47 eV, the surface protrusion will become much pronounced in the empty state image, and its appearance will not change with the sample voltage [Fig. 5(f)]. If it is structure IIc, the block energy will increase by 0.60 eV, but the influence on the surface protrusion is weak [Fig. 5(h)]. Considering a protrusion as a basic unit, the Si-B rings with different number of B atoms lead to protrusions with different brightness and size, as observed in STM images.^{9,12} For instance, the middle one of tripled protrusions, shown in Fig. 5(e), may result from a substitutional Si addimer for the Si-B one and some brighter protrusions, shown in Fig. 5(g), may have a structure of IIb.

TABLE II. Surface energies (Ref. 25) of paired protrusions arranged in different periods.

Period	(4 × 2)	(6 × 2)	(6 × 3)
Energy (eV)	-2.35	-3.29	-4.35

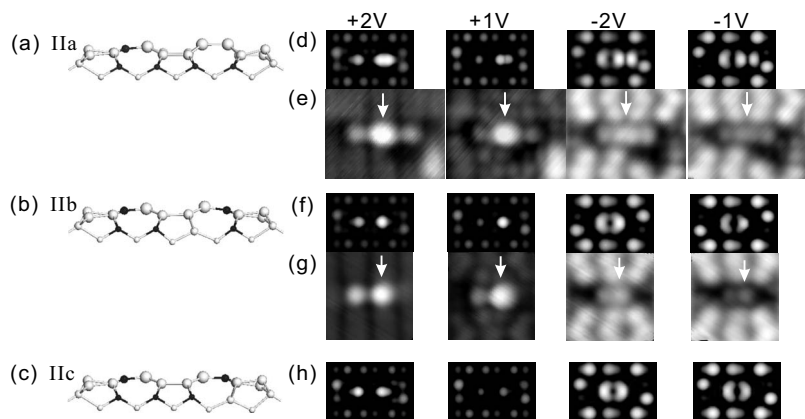


FIG. 5. Shortage of one B atom in a Si-B ring gives rise to metastable protrusions. [(a)–(c)] Optimized structures of paired Si-B rings with three B atoms in the left and with two in the right. [(d), (f), and (h)] Simulated STM images from structures IIa, IIb, and IIc, respectively. [(e) and (g)] The experimental results of the protrusions with different appearances which may correspond to structures IIa and IIb, respectively.

III. BORON DOPING CAPACITY

As demonstrated above, a block of paired protrusions results from two symmetrically paired rings, each of which contains one B atom in the addimer and two B atoms at the positions of the second layer. According to the simulated STM images shown in Fig. 4 and the calculated surface energies shown in Table I, we can see that the Si-B addimers display the main STM features of the paired protrusions while the B atoms at the second layer are indispensable for stabilizing the structures. From the viewpoint of surface energy, the Si-B addimers could not survive if there were no B atoms underneath at the second layer, but the protrusion density was limited because of their strong interaction, although the B density at the second layer could be high. After removing the Si-B addimers in the structural optimization, we found that more closely arranged B atoms at the second layer make the energy of the (2×1) surface lower, and when the whole second layer is occupied by B atoms,

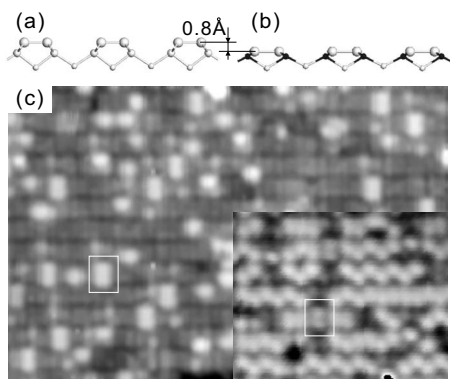


FIG. 6. Si(100)- (2×1) surfaces resulting from B atoms occupying the whole second layer. (a) Structure of the clean (2×1) surface; (b) structure of the (2×1) surface with a complete second layer of B atoms. (c) A filled state STM image presenting the surface with B at the second layer, which was acquired at a sample voltage of -1.6 V and a tunneling current of 0.3 nA. As a comparison, the inset shows a filled state STM image of the surface with low B coverage, which was acquired at a sample voltage of -2.0 V and a tunneling current of 0.2 nA. A block of paired protrusions is marked by a frame on both figure and inset.

the surface energy decreases by a value of 30.1 meV/ \AA^2 with respect to the clean Si(100)- (2×1) surface. Figures 6(a) and 6(b) show the side views of optimized Si(100)- (2×1) surfaces without any B atom and with pure B atoms at the second layer, respectively. Because of the short Si-B bonds, the surface atoms are lowered by 0.8 Å, as indicated in Figs. 6(a) and 6(b). We prepared such surfaces by annealing samples at 1200 °C, which had been implanted by a B dose of 10^{16} atoms/ cm^2 at energy of 60 keV. Figure 6(c) shows a filled state STM image of such surfaces, in which there are also protrusions randomly dispersed on the (2×1) -reconstructed surface. However, compared to the Si(100)- (2×1) surfaces with low B coverage, as shown in the inset of Fig. 6(c), the dimers of the (2×1) surface become much lower than the protrusions by about 1.0 Å and single protrusions become more than paired ones. According to our simulations, these protrusions have the same structures as demonstrated above, but the second layer underneath the (2×1) surface should be completely doped with B.

IV. SUMMARY

In summary, the STM observed protrusions and related surface strain result from the Si-B rings that may have B atoms in the addimers and at the subsurface layer. The protrusions cannot accumulate to form a patch of any periodic structure owing to the strong interaction between the structural modules. The subsurface layer can be completely doped with B, while the (2×1) reconstruction of the surface basically remains, which is very important for understanding ultrahigh doping of B on Si(100) surfaces.

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