

Adsorption of Boron on Si(111): Its Effect on Surface Electronic States and Reconstruction

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Adsorption of B induces a $(\sqrt{3}\times\sqrt{3})R30^\circ$ reconstruction on Si(111). By combining scanning-tunneling-microscope topographs and spectra with first-principles calculations we are able to follow the different stages of B incorporation in the Si surface and the corresponding changes to the surface electronic states. We find that the thermodynamically stable configuration consists of a B substitutional atom directly below a Si adatom at a T_4 site. The stability of this configuration is due to the relief of subsurface strain by the short B-Si bonds and the passivation of the surface obtained through charge transfer from the Si adatom to the substitutional B.

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In recent years it has become feasible to alter the electronic and structural characteristics of semiconductor surfaces by controlled adsorption of foreign atoms. The adsorbed atoms can change the character of surface electronic states and form new ordered phases with properties that differ qualitatively from those of the clean surface. This effect has been observed, for instance, by deposition of column-III (Al, Ga, In)¹⁻³ and column-V (As)⁴ atoms on the Si(111) surface. The systems mentioned above consist of adsorbate atoms with covalent radii larger than that of the substrate atoms. A more interesting situation may arise by depositing adsorbate atoms with covalent radius smaller than that of the substrate atoms. In this case, incorporation of adsorbate atoms at surface sites might be inhibited due to strain, and their propagation to deeper layers could become thermodynamically favorable. Incorporation of these foreign atoms at near-surface layers can possibly affect the structure and electronic properties of the surface through lattice strain and charge-transfer interaction. We have observed precisely such novel effects by depositing B on the Si(111) surface.

Here we use scanning tunneling microscopy (STM) and spectroscopy (STS) to study the adsorption sites and electronic states of the structures formed by B deposition on Si(111). We also use first-principles total-energy calculations to establish the relative stability of the possible adsorption configurations, and to help assign their electronic spectra. We find that B, depending on the deposition conditions and subsequent annealing, can occupy several different sites. The lowest-energy structure is found to involve a new configuration in which B resides in a subsurface fivefold-coordinated site directly below a Si adatom at a T_4 position. This subsurface B layer stabilizes a $(\sqrt{3}\times\sqrt{3})R30^\circ$ Si reconstruction (in the following referred to as $\sqrt{3}$ reconstruction) and strongly modifies the electronic properties of the surface. To our knowledge, this is a unique situation where atoms originally deposited on top of a surface are found embedded underneath two layers of the host material, in a thermodynamically stable configuration.

Boron deposition on clean Si(111)(7×7) was accomplished by exposing the sample to decaborane $B_{10}H_{14}$ (DB) at room temperature and followed by annealing to temperatures above that of hydrogen desorption ($> 500^\circ\text{C}$). The scanning tunneling microscope used in this study and the setup for obtaining scanning tunneling spectra have been described in detail in earlier work.⁵ The Si(111) surface preparation procedure is the same as that used in Ref. 5. First-principles electronic structure calculations were performed using pseudopotential local-density-functional theory^{6,7} with a plane-wave basis and a slab configuration. The slabs consist of five double layers in the (111) direction and are separated by a vacuum region equivalent to three bond lengths prior to the addition of adatoms. The calculations were carried out using a large plane-wave basis with kinetic energy up to 12 Ry and four sampling points in the irreducible part of the surface Brillouin zone. Full atomic relaxation is included by minimization of Hellmann-Feynman forces. Energy difference between the various configurations investigated are converged to within 0.2 eV per $\sqrt{3}$ unit cell.

The deposition of B on Si(111) is known to produce a $\sqrt{3}$ reflection high-energy electron-diffraction (RHEED) pattern.⁸ The observation of this pattern is not surprising, given the fact that B is a trivalent element and such atoms tend to saturate the Si surface dangling adatom in each unit cell.¹⁻³ However, unlike other group-III atoms investigated so far, B may render the usual T_4 adatom geometry unstable. This is because the bonds of B to its three Si neighbors should be much shorter than other group-III adatom-substrate bonds, which would induce considerable tensile stress. Moreover, the short B-Si bonds would place the B atoms very close to the second-layer Si atom situated below the T_4 site, leading to strong overlap repulsion. Besides the T_4 site there exist two other high-symmetry sites where the B atom might be incorporated. One is the surface threefold hollow site (H_3), and the other is a substitutional site in the second layer directly below the T_4 position. We shall denote the substitutional site by B- S_5 , since in this case the B atom

has five Si neighbors. Simple electron counting indicates that a B adatom in H_3 or T_4 sites saturates the surface dangling bonds, whereas when B is substitutional, passivation of dangling bonds can be achieved by a Si adatom in a T_4 position directly above the B atom. Our total-energy calculations show that the lowest energy state is in fact the B- S_5 configuration with the B- T_4 configuration lying 1.0 eV per $\sqrt{3}$ unit cell higher in energy and the B- H_3 configuration lying 2.1 eV higher in energy. The reasons for the stability of the B- S_5 site can be deduced by considering the atomic relaxations of the following three structures: two configurations which involve B in T_4 and S_5 sites and one configuration without B, consisting of a simple Si- T_4 adatom. All structures are in $\sqrt{3}$ periodicity and their calculated relaxations are shown in Fig. 1. The simple Si- T_4 $\sqrt{3}$ adatom geometry is not the favored reconstruction of the clean Si(111) surface, despite the fact that it has a lower dangling-bond density than the observed 7×7 reconstruction. This implies that a large strain is associated with the Si- T_4 $\sqrt{3}$ structure which makes it unstable with respect to the 7×7 reconstruction on the clean Si surface. Interestingly, the Si- T_4 $\sqrt{3}$ geometry is observed to coexist with B-induced $\sqrt{3}$ islands on the B/Si(111) surface. From Fig. 1 we see that the subsurface distortions induced by the B- T_4 and the simple Si- T_4 configurations are very

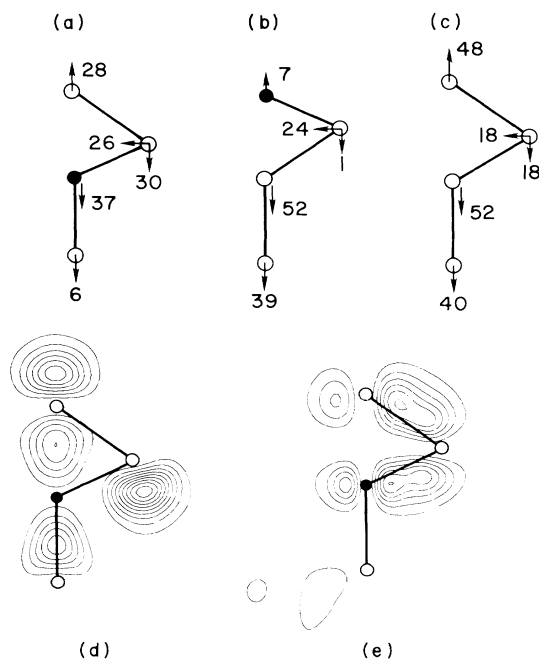


FIG. 1. Atomic relaxations of three $\sqrt{3}$ reconstructions: (a) B- S_5 (b) B- T_4 , and (c) Si- T_4 . The top three layers and the adatoms are shown on the (110) plane. Relaxations are given as displacements from ideal positions in 10^{-2} Å. Panels (d) and (e) show the charge density of the surface unoccupied and occupied bands, respectively, for the B- S_5 geometry.

similar, which suggests that the B- T_4 structure is also under large strain. Thus, from strain considerations alone, one would predict that the B- T_4 structure is not an optimal configuration. By contrast, the short B-Si bonds allow for an optimal relaxation of the two surface layers in the B- S_5 configuration thereby containing the stress induced to the substrate to the top two layers.

Another important consideration for the stability of the different structures is the distribution of electron density. In the B- T_4 configuration there is no charge transfer between Si and B, since the B atom is at the adatom position and participates in the formation of three covalent bonds. In the B- S_5 configuration, charge transfer occurs from the Si adatom to the substitutional B to satisfy the bond-charge requirements of the trivalent B atom which participates in the formation of four covalent bonds. Analogous charge transfer involving transfer of electrons from adatoms to rest atoms has been predicted to occur at the 7×7 surface⁹ and its occurrence has been confirmed by STM experiments.⁵ On the 7×7 surface, charge transfer involves sites separated by 4.7 Å, while in the B- S_5 site, charge transfer occurs over a distance of only 2.2 Å and thus is energetically more favorable. Very recently, a different structure involving B in a fourfold-coordinated substitutional site (B- S_4) was proposed to explain the $\sqrt{3}$ structure of B/Si(111).¹⁰ We have calculated the energy of this structure and found it to be also about 1 eV higher than that of B- S_5 .

While the B- S_5 configuration is predicted to be the lowest-energy configuration, its formation through B adsorption requires the breaking of Si-Si bonds so that B can occupy the substitutional site. The same is true for the B- S_4 structure. Thus, one would expect that the occupation of the T_4 site by B would be kinetically favored, while at equilibrium B should occupy the S_5 site. Using STM and STS we can directly probe the evolution of the geometry and electronic structure of the B/Si(111) system at the different deposition stages.

At low exposures [< 0.2 L (1 L = 10^{-6} Torrsec)] of DB and after a brief annealing to 600°C, an on-top adsorption of Si adatoms in the 7×7 unit cell is observed [Fig. 2(a), region A]. The corresponding dangling-bond surface states are eliminated, resulting in the darker appearance of the reacted adatoms. This behavior is completely analogous to what is observed in the reaction of the 7×7 surface with NH_3 molecules.⁵ Higher DB exposures or the presence of defects, which promote clustering of the DB molecules, lead to $\sqrt{3}$ domains which coexist with 7×7 areas [see Fig. 2(a), region B]. From topographs of such areas the registry of $\sqrt{3}$ sites on the Si(111) lattice can be determined. Thus, we find that indeed the $\sqrt{3}$ structure involves Si(111) T_4 sites. At yet higher exposures and longer annealing, the 7×7 reconstruction vanishes and the surface structure is predominantly $\sqrt{3}$ [Figs. 2(b) and 3(a)].

Two kinds of $\sqrt{3}$ regions, distinguished by different

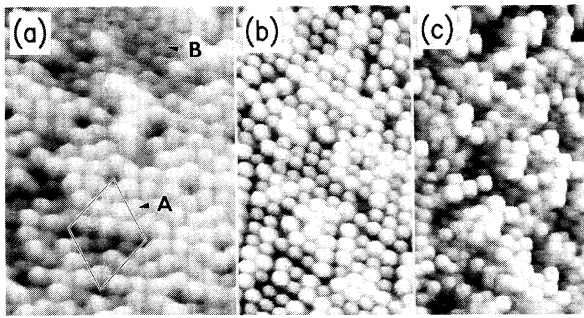


FIG. 2. (a) Topograph of the surface produced by exposing Si(111)7 \times 7 to 0.2 L DB at room temperature followed by a brief anneal to 600°C. Sample bias +2 V. (b) Si(111) exposed to 0.4 L DB and briefly annealed to 800°C. Sample bias +2 V. (c) As in (b) with sample bias -2 V.

brightness, are seen in the STM topographs. A combined analysis of experimental and theoretical results indicates that the bright $\sqrt{3}$ regions correspond to simple Si- T_4 adatoms and the dark regions correspond to B- T_4 adatoms. Tunneling spectra obtained over “bright” atoms are shown in Fig. 4(a). They show characteristic peaks for occupied and unoccupied states at -0.5 and +0.5 eV, respectively. This spectrum is nearly identical to that of Si adatoms on T_4 sites of the clean 7 \times 7 surface. The dark $\sqrt{3}$ regions on the other hand, are directly correlated with higher DB exposure and involve B as an adatom in a T_4 site. As can be seen in Fig. 1, the B atom in such a configuration is located 0.41 Å below a Si adatom in a T_4 site. Moreover, our calculations indicate that the unoccupied states associated with the B adatom have a more contracted electronic charge distribution than those associated with the Si adatom. As a result of the lower height and the more contracted charge distribution, the positive-bias image of the B-derived $\sqrt{3}$ structure appears darker than the image of the Si-derived $\sqrt{3}$ structure. In images of the occupied states, Si adatoms remain bright, while B adatom sites become very dark and hardly visible [Fig. 2(c)]. This behavior is also observed in the corresponding spectrum shown in Fig. 4(b). The dispersal of the B-derived $\sqrt{3}$ islands inhibits the formation of 7 \times 7 Si structures and stabilizes the $\sqrt{3}$ Si-adatom reconstruction, which on a clean surface is unstable.

Finally, samples exposed to large quantities of DB (> 1 L) and annealed to 1000°C show a $\sqrt{3}$ structure with essentially a single type of atomic site [Fig. 3(b)]. STM line scans along the long axis of the unit cell are symmetric, in disagreement with a B- S_4 model.¹⁰ Low-energy ion-scattering-spectroscopy studies¹¹ of this surface show the presence of Si atoms only in the top layer. This $\sqrt{3}$ structure can be imaged by tunneling to both occupied and unoccupied states. The tunneling spectrum of this structure [Fig. 4(c)] is very different from that

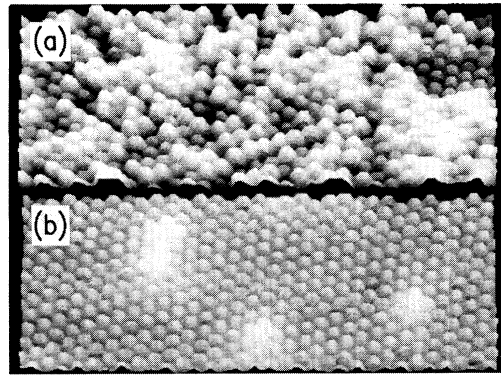


FIG. 3. Topographs of the surfaces produced by exposing Si(111)7 \times 7 to (a) 0.4 L DB and briefly annealing to 800°C. Sample bias +2 V. (b) 1 L DB and annealing to 1000°C. Sample bias +2 V.

observed over simple Si adatoms in the Si-derived $\sqrt{3}$ structure [Fig. 3(a)]. It shows the opening of a gap with a strong unoccupied band peaked at about 1.5 eV above E_F and an occupied band at about 1.8 eV below E_F . All spectral and structural characteristics of the uniform $\sqrt{3}$ domains are in agreement with the theoretical predictions for the thermodynamically favored B- S_5 configuration. As already mentioned, Si-to-B charge transfer leaves the Si dangling-bond state empty which appears as a strong unoccupied band in spectrum 4(c). From the charge-density plots of Fig. 1, it is seen that the unoccupied state [Fig. 1(d)] is clearly associated with the Si-adatom dangling bond, whereas the occupied state [Fig. 1(e)] is a surface resonance with strong Si-Si back-bond character.

These findings suggest that the properties of the B/Si(111) surface could be effectively used in surface

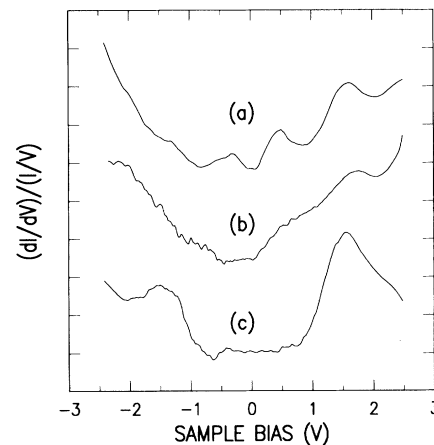


FIG. 4. Atom-resolved tunneling spectra obtained over (a) “bright”-atom sites in Fig. 3(a); (b) “dark”-atom sites in Fig. 3(a); (c) atoms of the stable $\sqrt{3}$ configuration shown in Fig. 3(b).

chemistry and microelectronic applications. As a result of the charge transfer described above, the surface Si layer has no partially occupied orbitals, and thus it is semiconducting. We also find that the chemical properties of the Si adatoms on this surface are drastically modified by the Si-to-B charge transfer. Of equal interest is the prospect of using the B/Si(111) surface to fabricate the long-sought δ -doped structures,¹² that is, structures in which all dopants are confined in very thin layers embedded in the host material. The uniformity of STM topographs and spectra of the $\sqrt{3}$ surfaces, such as the one shown in Fig. 3(b), indicates that the subsurface B layer is indeed homogeneous and stable. Since B is in a subsurface layer, deposition on top of the $\sqrt{3}$ surface may not affect the B layer. It should be possible under appropriate conditions to deposit additional Si layers with minimal smearing of the B distribution. This goal could be realized, e.g., through low-temperature molecular-beam epitaxy or, better yet, through low-temperature chemical vapor deposition of Si as employed by Meyerson *et al.*¹³

In conclusion, we have shown that the bonding site of B on Si(111) is determined by competing kinetic and thermodynamic factors. At low temperatures, B adsorbs as an adatom on a T_4 site, which is the stable configuration for other group-III elements as well. However, due to the small size of B, the T_4 adatom configuration is not the lowest-energy structure. With proper annealing, B occupies a subsurface substitutional site directly below a Si adatom. The stability of this novel site is traced to the relief of subsurface lattice strain, and the emptying of Si-adatom dangling-bond orbitals by charge-transfer

to the substitutional B atom.

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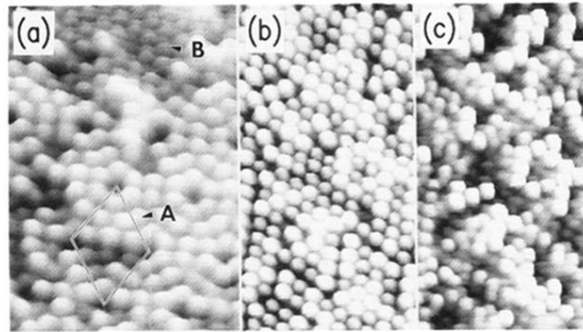


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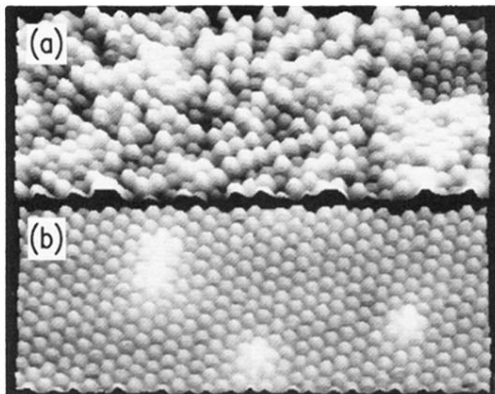


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