RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 41, NUMBER 2 15 JANUARY 1990-I

Electronic states due to surface doping: Si(111) $\sqrt{3}\times\sqrt{3}$ B

Efthimios Kaxiras, K. C. Pandey, F. J. Himpsel, and R. M. Tromp
IBM Research Division, Thomas J. Watson Research Center, Yorktown Heights, New York 10598

(Received 18 August 1989)

A $\sqrt{3}\times\sqrt{3}$ surface reconstruction is obtained on Si(111) when B diffuses from the bulk to the surface in heavily doped Si samples. First-principles total-energy calculations show that the lowest-energy atomic configuration for this reconstruction consists of a B atom at a subsurface substitutional site, directly underneath a Si adatom. Surface electronic states observed by photoemission and inverse photoemission experiments are analyzed through electronic structure calculations and shown to be related to the back-bond and the dangling-bond states of the Si adatom.

Deposition of foreign atoms on semiconductor surfaces can alter the reconstruction of a clean surface and sweep surface electronic states out of the fundamental band gap of the material. The changes in the structure and electronic states of the surface are the direct result of a topmost layer of foreign atoms which reside either in bulk-terminated sites [e.g., As/Si(111) (Ref. 1)] or in adatom sites [e.g., Ga/Si(111) (Ref. 2)]. In this paper we report on the properties of an unusual system where the foreign atom, which is B, resides *underneath* the surface layer. Electron diffraction studies[3] report that by diffusing B from the bulk toward the surface in heavily doped Si samples, a $\sqrt{3}\times\sqrt{3}$ reconstruction of Si(111) is obtained. Our total-energy minimization calculations show that, under equilibrium conditions, this reconstruction consists of B atoms at substitutional sites in the second Si layer. We shall report experimental observation by angle-resolved photoemission and inverse photoemission studies of the surface electronic states of this atomic reconstruction. We shall also provide a theoretical analysis of the character of surface states, based on first-principles calculations.

The samples were highly B-doped (5×10^{19} cm^{-3}) Si(111) wafers, which were cleaned by repeated heating cycles to 1050 °C. The 7×7 low-energy electron diffraction pattern started to transform into a $\sqrt{3}\times\sqrt{3}$ pattern after about 5 min of accumulated heating time. The latter pattern stabilized and sharpened after about 20 min heating time. The $\sqrt{3}\times\sqrt{3}$ structure is correlated to segregation of B near the surface region by the appearance of a B Auger peak. Apparently, the $\sqrt{3}\times\sqrt{3}$B structure lowers the surface energy of the 7×7 reconstruction, thereby providing the driving force for B segregation. It is possible that a small fraction of the surface remains B deficient (see also Refs. 4 and 5), leaving some weak Si dangling-bond states in the surface band gap. Such weak states may be responsible, e.g., for a shoulder below the adatom state in inverse photoemission experiments and a weak peak near the Fermi level in photoemission experiments. The position of the Fermi level above the valence-band maximum (VBM), as determined from Si $2p$ core-level measurements,[6] changed from 0.65 eV in the clean Si(111) 7×7 surface to 0.5 eV in the $\sqrt{3}\times\sqrt{3}$B structure. The inverse photoemission data were obtained with a spectrograph system with an energy resolution of 0.3 eV. Spectra taken at normal incidence with various initial energies showed that the B-induced state does not exhibit any dispersion perpendicular to the surface, as expected from a purely two-dimensional state. The spectra shown here were taken at an initial energy of 11 eV above the Fermi level. The photoemission data were taken at the HeI resonance line (21.1-eV photon energy).

Perhaps the most important aspect of the problem is to establish the atomic configuration responsible for the $\sqrt{3}\times\sqrt{3}$ reconstruction. To this end, we have performed total-energy calculations using pseudopotential local-density functional (LDF) theory with a plane-wave basis. We have considered the following high-symmetry configurations for the reconstruction: (i) A B atom at the T_4 adatom position, directly above a second-layer Si atom (called B-T_4 in Fig. 1). This is the position that other column III atoms assume when deposited on the Si surface. (ii) A B atom at the H_3 adatom position, in the center of an open hexagon defined by first- and second-layer Si atoms (called B-H_3 in Fig. 1). This is an alternative adatom position which is energetically unfavorable

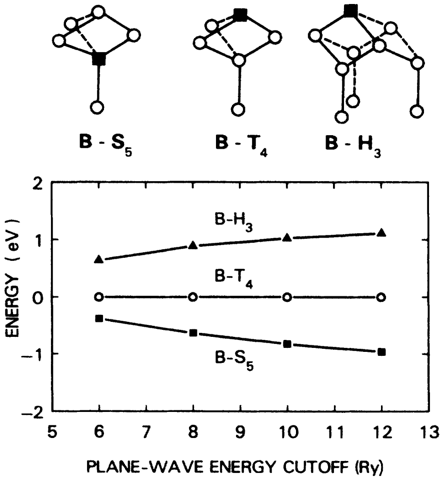

FIG. 1. The three possible positions of the B atom (square): B-S_5 is the substitutional position with a Si adatom directly above; B-T_4 is the adatom position above a second-layer Si atom; B-H_3 is the adatom position above an open hexagon of Si atoms. The total-energy differences between these configurations are given as a function of plane-wave energy cutoff.

for Si and for column III adatoms, but cannot be *a priori* excluded for B. (iii) A B atom at a second-layer substitutional site, directly underneath a Si-T_4 adatom. We shall denote this site by B-S_5, since in this configuration B has five Si neighbors (see Fig. 1). This site was independently proposed by Headrick *et al.*,[7] Bedrosian *et al.*,[5] and Lyo, Kaxiras, and Avouris.[4]

The above configurations will give rise to an electronically passive surface: The number of available valence electrons is exactly equal to that needed to satisfy all the covalent bonds. In the B-T_4 and the B-H_3 configurations there is no charge transfer, since the B atom participates in the formation of three covalent bonds. In the B-S_5 configuration, one electron is transferred from the Si adatom, which forms three bonds, to the B atom directly below it, which participates in the formation of four bonds. The calculated relative energies of these three configurations are shown in Fig. 1, as a function of the highest kinetic energy of plane waves included in the basis set. The relative energy differences (which are well converged at the highest kinetic energy of 12 Ry) show that the B-S_5 configuration is the lowest-energy geometry. A fourth possible configuration of lower symmetry has been proposed for this reconstruction, on the basis of scanning-tunneling-microscope (STM) experiments.[8] This configuration consists of a Si-T_4 adatom and a fourfold bonded substitutional B atom which, however, is not directly below the Si adatom. The charge transfer required to satisfy the covalent bonds in this case takes place over a longer distance than in the B-S_5 configuration. This will result in higher Coulomb-energy cost. Indeed, we have calculated the energy of this configuration and found it to be 1.0 eV per $\sqrt{3}\times\sqrt{3}$ unit cell higher than the B-S_5 configuration.

Thus, our calculations show unambiguously that, among the structures considered, the B-S_5 configuration, consisting of a B atom at a substitutional site directly underneath a Si adatom, is the energetically preferred structure. Independent evidence which also favors the B-S_5 configuration is provided by STM spectroscopy experiments coupled with electronic structure calculations,[4,5] ion-scattering spectroscopy experiments,[9] and x-ray diffraction experiments.[7] In the following we shall assume that this is the thermodynamically stable configuration which gives rise to the $\sqrt{3}\times\sqrt{3}$ reconstruction after repeated annealing. We shall analyze the surface electronic states of the B-S_5 configuration and compare them to experimental observations.

Inverse photoemission experiments reveal the existence of a band-gap state which at the center Γ of the surface Brillouin zone (SBZ) lies 1.8 eV above the VBM (see Fig. 2). This state disperses downward along the ΓK and ΓM directions of the SBZ. The experimental position is 1.3 eV above the VBM at K and 1.5 eV at M (the reported experimental energies have an error bar of ±0.1 eV). Our first-principles calculations give a band-gap state which lies 0.5 eV below the experimental state, but has exactly the same dispersion toward the edges of the SBZ. This is a typical level of agreement between experiment and LDF calculations.[10] The difference in absolute energy is due to self-energy effects, which tend to move unoccupied states up relative to the VBM. This effect is not treated accurately by LDF theory.

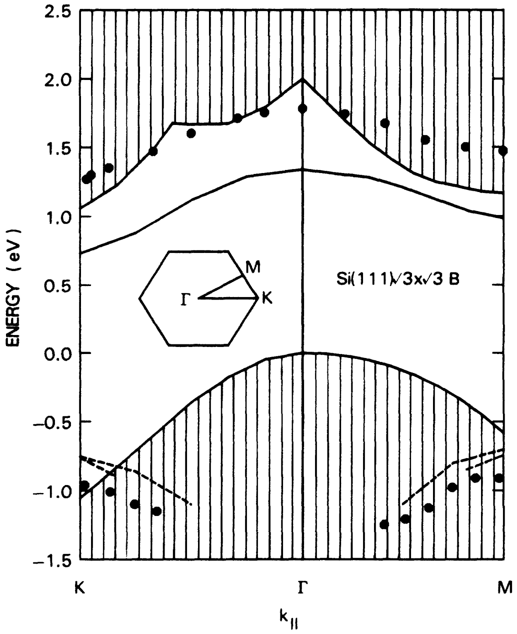

FIG. 2. Energy bands for the B-S_5 configuration of the Si(111)$\sqrt{3}\times\sqrt{3}$B reconstruction. Calculated surface states (full lines) and resonances (dashed lines) are compared to the results from photoemission and inverse photoemission experiments (dots). Projected bulk states are shaded. The surface Brillouin zone is shown as inset.

The unoccupied band-gap state, identified by inverse photoemission experiments, is due to an empty dangling-bond state associated with the Si adatom of the B-S_5 configuration. This is demonstrated in Fig. 3, where charge-density contours are shown for this band at the K (top part of Fig. 3) and Γ (middle part of Fig. 3) points of the SBZ. This state is compared to the prominent feature of the clean Si(111) 7×7 surface (bottom part of Fig. 3). The experimental signatures of the unoccupied band-gap state for the Si(111)$\sqrt{3}\times\sqrt{3}$-B surface and that for the Si(111) 7×7 clean surface are very similar. At present, it is not possible to perform first-principles calculations for the 7×7 reconstruction due to the very large unit cell. The most prominent electronic features of the 7×7 surface are believed to be associated with surface adatoms and rest atoms, which are locally arranged in a 2×2 configuration.[11] Thus, we have used a 2×2 unit cell which contains one adatom and one rest atom to examine the character of surface states which presumably resemble those of the 7×7 reconstruction. The unoccupied band-gap state of this 2×2 unit cell is associated with the dangling bond of the Si adatom, as indicated by the charge-density contours in the bottom part of Fig. 3. The distribution of charge in this state is very similar to that of the unoccupied state in the B-induced $\sqrt{3}\times\sqrt{3}$ reconstruction. The small changes in the two charge-density distributions are due to differences in electronegativity between Si and B and differences in the relaxation of their neighbors.

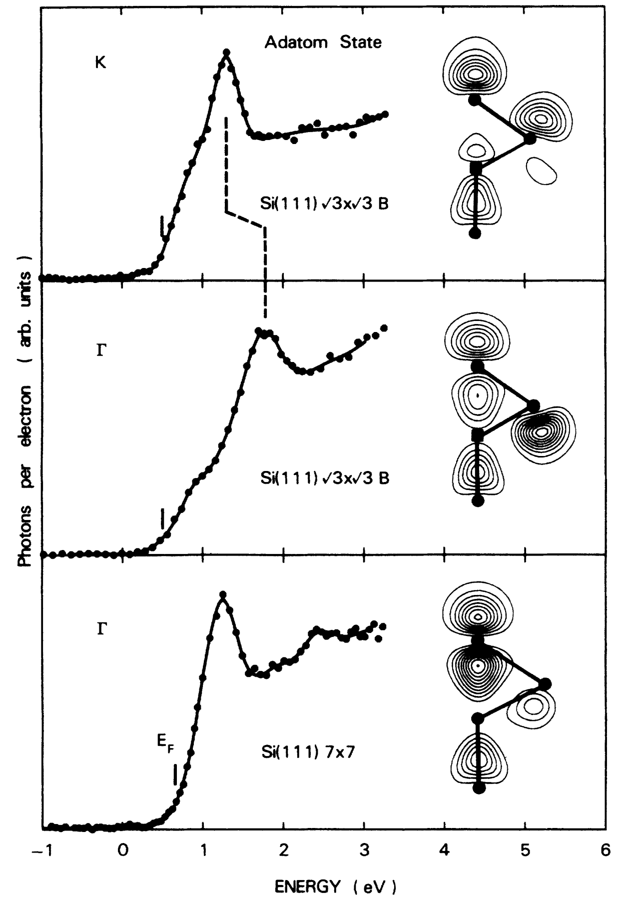

FIG. 3. Inverse photoemission spectra and calculated charge-density distribution of the unoccupied surface state of the Si(111)$\sqrt{3}\times\sqrt{3}$B reconstruction (top and middle parts for *K* and Γ, respectively). This state is compared to the adatom dangling-bond state of the clean Si(111) 7×7 reconstruction (experiment) and the corresponding Si(111) 2×2Si adatom state (theory) at the bottom part.

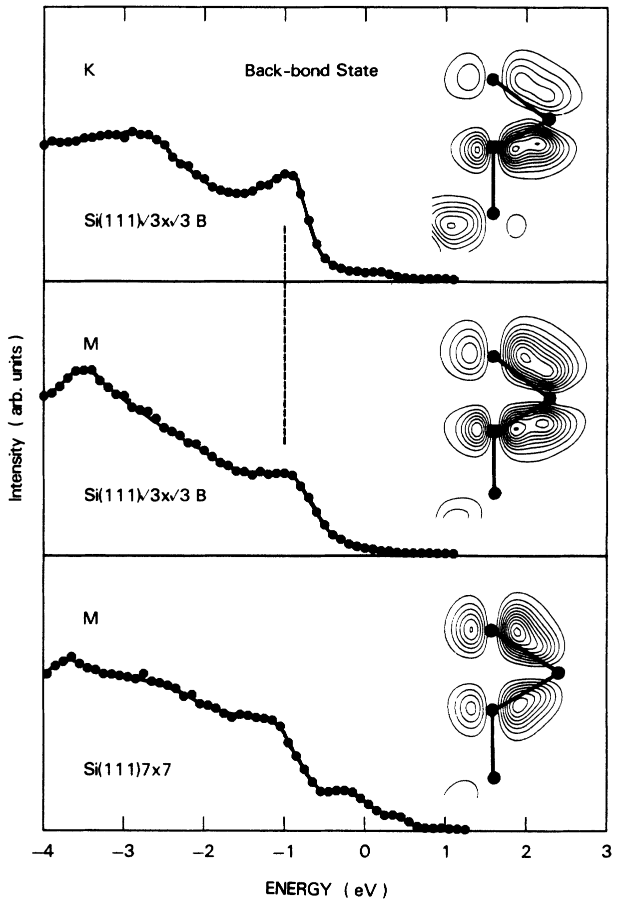

FIG. 4. Photoemission spectra and calculated charge-density distribution of the surface resonance state of the Si(111)$\sqrt{3}\times\sqrt{3}$B reconstruction (top and middle parts for *K* and *M* points, respectively). This state is compared to the adatom back-bond state of the clean Si(111) 7×7 reconstruction (experiment) and the corresponding Si(111)$\sqrt{3}\times\sqrt{3}$Si adatom state (theory) at the bottom part.

Photoemission experiments reveal that there exist occupied states with strong surface character near the boundaries of the SBZ which disperse downward as the magnitude of the *k* vector decreases (Fig. 2). Our calculations indicate the existence of surface-related states near the SBZ boundaries (shown as dashed lines in Fig. 2), which have approximately the correct dispersion but lie 0.2 eV higher in energy than experimental values (dots in Fig. 2).[12] The agreement between experiment and the LDF calculated bands for these occupied surface states is better than that obtained for the unoccupied gap state. Again, this is typical for LDF calculations.[10] The charge density of these states has a strong component at the back bonds of the Si adatom and small contributions from substrate bonds, indicating resonant character, as shown by the charge-density contour plots at the *K* and *M* points of the SBZ (Fig. 4, top and middle parts). For comparison, we include in Fig. 4 the photoemission spectrum of the clean Si(111) 7×7 surface, taken at the same angle of incidence as the *M* spectrum of the Si(111)$\sqrt{3}\times\sqrt{3}$B surface (Fig. 4, bottom part). The accompanying charge-density contour plot is from the *M* point of a clean Si(111)$\sqrt{3}\times\sqrt{3}$ surface, saturated with Si adatoms. This choice was dictated by the impossibility of performing first-principles calculations for the 7×7 reconstruction and the need for a consistent comparison of wave-function character. We expect that the essential features of the wave function associated with the Si adatom back bonds is not drastically affected by the periodicity, due to the localized nature of this state. Comparing the bottom and middle parts of Fig. 4, shows that the character of the back-bond wave function in the clean Si surface and the B-reconstructed Si surface is very similar at the *M* point of the SBZ. The wave-function character changes somewhat at the *K* point of the SBZ, but retains a significant component in the Si adatom back bond (top part, Fig. 4).

In summary, we have examined the B-induced $\sqrt{3}\times\sqrt{3}$ reconstruction of Si(111), for samples in which B was diffused to the surface from the bulk. Through first-principles total-energy calculations we identify the lowest-energy configuration among several candidates. This configuration consists of a B atom in a substitutional second-layer site, directly underneath a Si-T_4 adatom. The surface-related states of this atomic configuration were analyzed and compared to the results of angle-resolved photoemission and inverse photoemission studies. An unoccupied band-gap state observed in inverse photoemission experiments was shown to be related to the Si adatom dangling bond and found to be similar in character to the adatom dangling-bond state of the clean Si(111) 7×7 reconstruction. Surface resonance states related to the Si adatom back bonds were also identified near the boundaries of the surface Brillouin zone.

---

[1] R. S. Becker, B. S. Swartzentruber, J. S. Vickers, M. Hybertsen, and S. G. Louie, Phys. Rev. Lett. **60**, 116 (1988); R. I. G. Uhrberg, R. D. Bringans, M. A. Olmstead, R. Z. Bachrach, and J. E. Northrup, Phys. Rev. B **35**, 3945 (1987).

[2] J. M. Nicholls, B. Reihl, and J. E. Northrup, Phys. Rev. B **35**, 4137 (1987).

[3] H. Hirayama, T. Tatsumi, and N. Aizaki, Surf. Sci. **193**, L47 (1988); V. V. Korobtsov, V. G. Lifshits, and A. V. Zotov, *ibid.* **195**, 466 (1988).

[4] I.-W. Lyo, E. Kaxiras, and Ph. Avouris, Phys. Rev. Lett. **63**, 1261 (1989).

[5] P. Bedrosian, R. Meade, K. Martensen, D. M. Chen, J. A. Golovchenko, and D. Vanderbilt, Phys. Rev. Lett. **63**, 1257 (1989).

[6] A. B. McLean, L. J. Terminello, and F. J. Himpsel (unpublished).

[7] R. L. Headrick, I. K. Robinson, E. Vlieg, and L. C. Feldman, Phys. Rev. Lett. **63**, 1253 (1989).

[8] F. Thibaudau, Ph. Dumas, Ph. Mathiez, A. Humbert, D. Satti, and F. Salvan, Surf. Sci. **211-212**, 148 (1989).

[9] F. Boszo (unpublished).

[10] M. S. Hybertsen and S. G. Louie, Phys. Rev. Lett. **58**, 1551 (1987).

[11] R. Wolkow and Ph. Avouris, Phys. Rev. Lett. **60**, 1049 (1988); Ph. Avouris and R. Wolkow, Phys. Rev. B **39**, 5091 (1989).

[12] The resonance state at K is twofold degenerate, whereas at M there are two resonance states, approximately 0.1 eV apart (see Fig. 2). Only the highest-resonance states were followed to small k values in Fig. 2, since states that lie deeper in the valence band are more difficult to identify, both theoretically and experimentally, due to stronger overlap with substrate bonds.