Atomic structure of Si(111) $(\sqrt{3} \times \sqrt{3})R30°$-B by dynamical low-energy electron diffraction

H. Huang and S. Y. Tong
Department of Physics and Laboratory for Surface Studies,
University of Wisconsin-Milwaukee, Milwaukee, Wisconsin 53201

J. Quinn and F. Jona
Department of Materials Science, State University of New York, Stony Brook, New York 11794
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The geometric structure of Si(111) $(\sqrt{3} \times \sqrt{3})R30°$-B formed by annealing highly doped Si(111) samples was determined by low-energy electron diffraction. The optimal structure has the B atom occupying a substitutional B_5 site, different from adatom sites occupied by other group-III metals. Three-dimensional atomic coordinates and surface bond lengths have been determined. With B at the B_5 site, the compressive stress between Si and B atoms disappeared in the near-surface region. The difference between an all Si $\sqrt{3}$ reconstruction structure stabilized by B doping with another structure observed by Ag doping is discussed.

It has been known for some time that the adsorption of various metal atoms on the (111) surface of Si or Ge frequently induces a $(\sqrt{3} \times \sqrt{3})R30°$ superlattice.[1] Recent studies showed that for Al, Ga, and In on Si(111) and Pb on Ge(111), an ordered adatom structure is formed at $\frac{1}{3}$ monolayer (ML) coverage with the metal atoms occupying T_4 sites (threefold symmetrical sites over Si atoms in the second layer) above a (1×1) relaxed (but unreconstructed) semiconductor substrate.[2–10] In the case of Pb on Ge(111),[7–10] however, another $(\sqrt{3} \times \sqrt{3})R30°$ structure exists at a higher coverage. This new structure consists of a double layer of Pb adatoms: a lower $\frac{1}{3}$ ML of Pb atoms at H_3 sites (threefold symmetrical sites over Ge atoms in the fourth layer) and a higher 1 ML of Pb atoms at off-centered T_1 sites (atop sites over Ge atoms in the first layer). The situation for the $\sqrt{3}$ structures of Ag and Ta on Si(111) is quite different. Recent studies by dynamical low-energy electron diffraction showed that the Ag (or Ta) atoms are disordered.[11,12] The role of the metal atoms is to dope the Si surface, thus stabilizing a $\sqrt{3}$ reconstruction of the (111) surface consisting entirely of Si atoms.[11]

For the cases studied, the metal-semiconductor interface shows a variety of $\sqrt{3}$ reconstructions. However, the group-III elements Al, Ga, and In show a common trend of forming $\frac{1}{3}$-ML ordered adatoms at T_4 hollow sites. A qualitative explanation of this trend is that an adatom at a threefold hollow site satisfies three dangling bonds of the semiconductor surface. With $\frac{1}{3}$ ML of group-III adatoms, the resulting $\sqrt{3}$ structure has no unpaired bonds.[13] In this paper, we investigate the chemisorption site and reconstruction structure of a recently reported[14,15] Si(111) $(\sqrt{3} \times \sqrt{3})R30°$-B phase, to see if the above trend applies to the smallest group-III element. The structural analysis is carried out by dynamical low-energy electron diffraction (LEED).

To prepare the sample for *IV* spectra measurement, we started with Si(111) wafers that were highly B doped (0.0016–0.0025 Ω cm). These B-doped Si wafers were cleaned in the vacuum system (base pressure 10^{-10} Torr) with cycles of Ar-ion bombardments (5×10^{-5} Torr Ar, 375 eV, 2 μA) for 1 h and annealed at 1200 °C for 20–30 min. Four such cycles produced an excellent $\sqrt{3}$ LEED diffraction pattern. Auger spectra showed on Si and B peaks, with C and O close to the noise level. The data used in this work were obtained from surfaces with the following typical Auger-electron spectroscopy ratios (as measured with a LEED-optics retarding-field analyzer): B(179 eV)/Si(107 eV) = 0.85 to 0.90; C(272 eV)/Si(107 eV) = 0.09 to 0.1; O(510 eV)/Si(107 eV) = 0.04 to 0.05.

LEED intensity data were recorded several times, after similar and different preparation procedures. Argon-ion bombardments followed by anneals at 1000 °C for 20 min produced poor (7×7) LEED patterns, but anneals at 1200 °C or 1300 °C produced sharp $\sqrt{3}$ patterns. No change in the LEED *I-V* spectra of the $\sqrt{3}$ structure were detected depending on the annealing temperature. The intensity data were recorded with a TV-camera and microcomputer combination as described elsewhere.[16] Overall, 52 LEED spectra were recorded. These data were normalized to constant incident electron current and corrected for background; degenerate beams were averaged. For the analysis of the structure, eighteen beams (nine integral order, nine fractional order) at normal incidence were used.

The dynamical LEED calculations were performed using the real and reciprocal spaces symmetrized LEED code.[17] The atomic positions in five surface planes [the adatom plane, and two (1×1) double layers below] were varied. Deeper Si atoms were held at bulk positions. With the C_{3v} symmetry at normal incidence, the symmetrized LEED code selects per $\sqrt{3}$ cell one adatom and three substrate atoms (instead of six) in each of the two double layers below. The multiple-scattering calculations used six partial waves and a constant inner potential of 6 eV.

Surface models in which the B atom was placed as an adatom at H_3, T_1, and T_4 sites were tried, as well as a
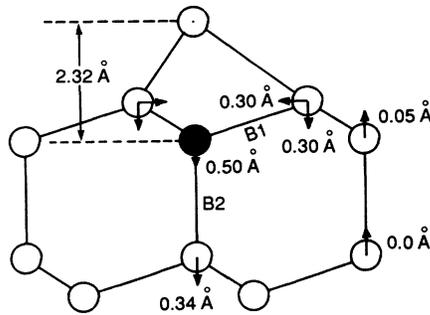
FIG. 1. The preferred Si(111) ($\sqrt{3} \times \sqrt{3}$)R30°-B structure, with B (filled circle) occupying the B_5 site. Arrows refer to atomic displacements from bulk sites. $B1 = 2.154$ Å, $B2 = 2.19$ Å. The experimental error bars are estimated to be 0.1 Å for the parameters perpendicular to the surface and 0.2 Å for the parameters parallel to the surface.

structure. The individual R factor for each beam is indicated.[18] The combined R factor for the ten beams shown in Figs. 2 and 3 is 0.211. The remaining eight beams [not shown except for the (21) beam depicted in Fig. 4] have a combined R factor of 0.289. Figure 4 shows the calculated spectra for the optimal B_5 and T_4 structures compared with experiment. There is a strong preference for the B_5 model.

The atomic displacements from the (1 × 1) bulk coordinates of the Si atoms in the optimal B_5 structure are indicated in Fig. 1. The major relaxations are for the B atom to relax 0.5 Å towards the bulk, its three Si neighbors above to relax radially inwards by 0.3 Å and down by 0.3 Å. The Si atom below the B atom in the third layer relaxes towards the bulk by 0.34 Å. With these relaxations, the Si—B bond $B1$ is 2.154 Å. Using a Si radius of 1.175 Å, the boron "radius" for this bond is 0.979 Å (compared to an atomic boron radius of 0.98 Å). The bond length $B2$ is 2.19 Å, yielding a boron radius of 1.015 Å for this bond. Finally, the distance between the Si adatom and the boron is 2.32 Å, indicating a much weaker bond. It is clear from these numbers that with the boron at the B_5 site, there is no compressive stress between the Si and B atoms in the near-surface region.

new B_5 structure, in which the B and Si atoms in the T_4 model were reversed (see Fig. 1). Optimizing the atomic coordinates in each model, we concluded that the B_5 structure gave the best agreement with the eighteen measured IV spectra. The optimized B_5 structure produced an R factor of 0.244.[18] The next best structure was the T_4 model (i.e., B adatom), but its R factor was worse by a significant 25% ($R = 0.305$). The H_3 and T_1 models were much worse and could be easily ruled out.

Figures 2 and 3 show the comparison of selected IV spectra between theory and experiment for the optimal B_5

Recent studies using total-energy calculations with STM,[19,20] x-ray scattering,[21] and photoemission–inverse-photoemission experiments[22] also preferred the B_5 configuration for the boron atoms. The electronic calculations indicated a charge transfer from the Si adatom to the boron atom below. The preference for the unorthodox site, which is a break from the trend established by other

FIG. 2. Comparison between theory and experiment for the optimal B_5 model, for integral-order beams.
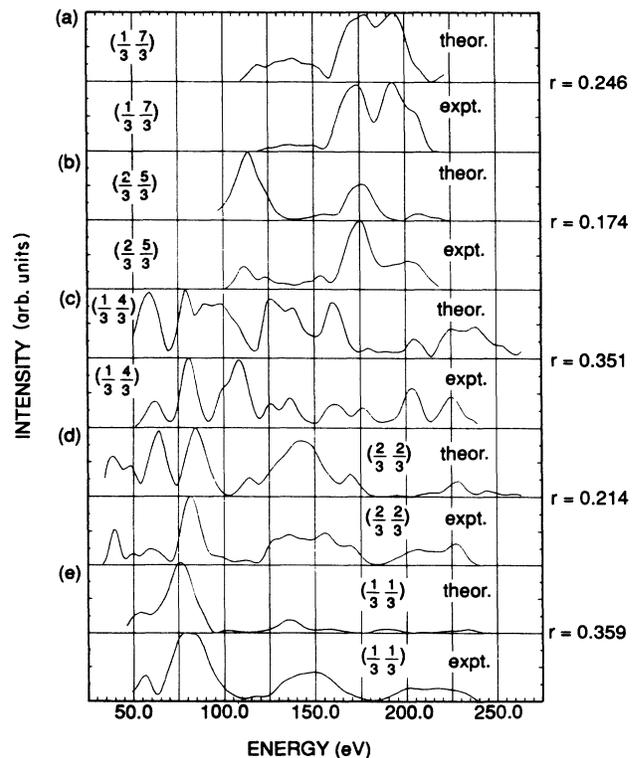
FIG. 3. Comparison between theory and experiment for the optimal B_5 model, for fractional-order beams.
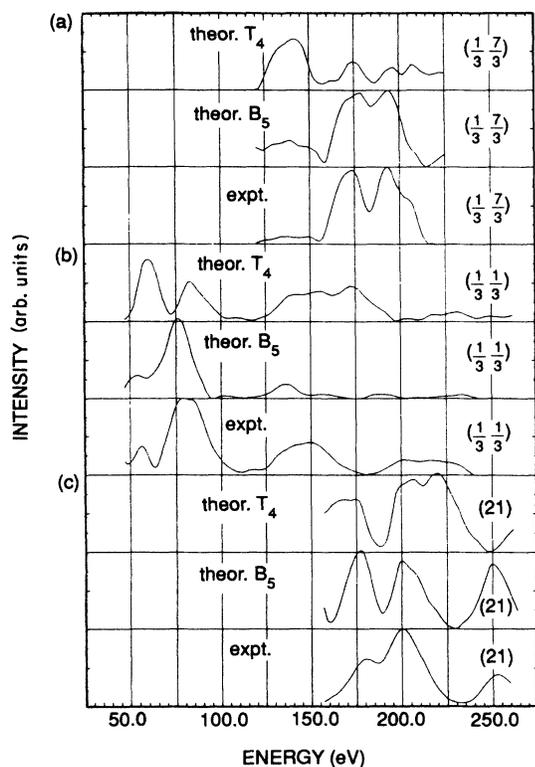
FIG. 4. Comparison between theory and experiment for two structural models: B_5 (boron substitutional) and T_4 (boron as an adatom).

group-III elements such as Al, Ga, and In, was explained by the smaller size of the boron atoms.[19,20]

Bedrossian et al.[19] suggested that a $(\sqrt{3}\times\sqrt{3})R30°$ structure composed of one Si adatom per $\sqrt{3}$ unit cell [on a (1×1) Si substrate] can be stabilized by boron doping in the near-surface layers. We followed the procedure described by these authors and deposited Si from a pure Si source onto the $\sqrt{3}$ structure to the point of obliterating the LEED pattern. Successive anneals of such a surface at 700, 750, 800, and 850°C for 10 min each time produced, in turn, high-background (1×1), diffuse $\sqrt{3}$, and mixtures of $\sqrt{3}$ with (7×7) structure. Anneals at 1000°C and higher always produced sharp root-3 patterns: The LEED IV spectra from these $\sqrt{3}$ patterns were found to be independent of the annealing temperature above 1000°C, and equal to those obtained with the preparation described above without Si deposition. We also measured IV curves from surfaces that were annealed at 1000°C for 20 s. These surfaces showed sometimes diffuse, sometimes sharp $\sqrt{3}$ spots, but the LEED IV curves were the same in all cases.

This observed invariance of the measured IV spectra suggests that the preparation procedure described above, involving deposition of Si over the B-$\sqrt{3}$ structure, failed

to produce the all-Si-$\sqrt{3}$ structure suggested by Bedrossian et al.[19] and by Lyo and co-workers[20] with sufficiently long-range order to be detected by LEED. According to Bedrossian et al.[19] with Si deposition, the all-Si-$\sqrt{3}$ structure is present over more than 20% of the surface (20% is the extent that the Si-$\sqrt{3}$ structure is present on surfaces prepared even without Si deposition).

This postulated Si-$\sqrt{3}$ structure, with Si adatoms in T_4 sites, is obviously different from that containing one vacancy per unit cell as determined by Fan et al.[11] on Si(111) surfaces doped with either Ag or Ta.[11,12] If confirmed, this postulated Si-$\sqrt{3}$ structure would therefore represent the second example of modification of a semiconductor surface structure by metal dopants. The difference between the $\sqrt{3}$ structure stabilized by Ag or Ta and that stabilized by B could be explained by the fact that Ag and Ta donate electrons to saturate the dangling bonds of the vacancy model,[11] while boron accepts electrons from the Si-Si $\sqrt{3}$ adatom configuration. The issue of Si structures stabilized by near-surface metallic dopants obviously requires further investigation.

In conclusion, we have carried out a quantitative LEED intensity analysis of a Si{111} $(\sqrt{3}\times\sqrt{3})$-B structure. We find that the B atoms replace Si atoms on a $\sqrt{3}$ array in the second layer of the substrate and are covered by Si adatoms in T_4 positions. The associated distortions of the substrate structure are indicated in Fig. 1. The all-Si-$\sqrt{3}$ structure postulated by scanning tunneling microscopy workers[19,20] could not be prepared with sufficiently long-range order to be detectable by LEED.

After completion of this work, the paper by Headrick et al.[21] appeared in print with the results of a structure determination of Si{111} $(\sqrt{3}\times\sqrt{3})$ B by synchrotron x-ray diffraction. To compare the results of Headrick et al. with ours we use the notation introduced by Headrick et al. [with Si(i) denoting Si atoms in the ith layer] and we list below for each structural parameter the value determined by Headrick et al. followed by ours in square brackets:

$$\Delta z_{Si(1)} = -0.17 \pm 20 \text{ Å } [-0.30 \pm 0.1 \text{ Å}],$$

$$\Delta r_{Si(1)} = -0.26 \pm 0.01 \text{ Å } [-0.30 \pm 0.2 \text{ Å}],$$

$$\Delta z_{Si(2)} < 0.06 \pm 0.20 \text{ Å } [+0.05 \pm 0.1 \text{ Å}],$$

$$\Delta r_{Si(4)} = -0.02 \pm 0.01 \text{ Å } [0 \pm 0.2 \text{ Å}],$$

$$\Delta z_{Si(4)} < 0.06 \pm 0.20 \text{ Å } [0 \pm 0.1 \text{ Å}].$$

The agreement is good within the quoted experimental errors, except for the Δz of B, which x rays cannot measure [0.5 Å], and the $\Delta z_{Si(3)}$ which the x-ray analysis did not consider [0.34 Å].

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