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Adatom registry on Si(111)-($\sqrt{3}\times\sqrt{3}$)R 30°-B

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We have used tunneling microscopy to determine the binding site of adatoms on Si(111)-($\sqrt{3}\times\sqrt{3}$)R 30° stabilized by surface boron doping. The adatoms are found to occupy the T_4 binding site, regardless of either the local dopant concentration or the presence or absence of a substitutional boron atom directly underneath individual adatoms.

The characteristics of semiconductor-metal interfaces have been studied intensively for some time.¹ In one set of related systems, early low-energy electron-diffraction (LEED) studies² established that the incorporation of various group-III elements on Si(111) below $\frac{1}{3}$ monolayer (ML) ($1\text{ ML}\equiv 7.8\times 10^{14}\text{ atoms/cm}^2$) transforms the surface from the 7×7 reconstruction, characteristic of clean, annealed Si(111), to a ($\sqrt{3}\times\sqrt{3}$)R 30° periodicity. Yet only recently has the complete determination of the associated real-space structures been possible. Following the establishment of the so-called " T_4 " binding site for silicon adatoms on clean Si(111)-(7×7),³ aluminum, gallium, and indium adatoms on Si(111) have also been found to occupy that T_4 binding site, wherein one adatom binds to three substrate silicon atoms, with the adatom directly above a silicon atom in the lower plane of the outermost double layer.⁴⁻⁹ Nevertheless, diversity still exists in the adsorption characteristics of the trivalent elements and is underscored by the dramatically different physical properties of the boron-rich and gallium-rich Si(111) surfaces.¹⁰

The present authors¹¹ and others¹²⁻¹⁵ have recently reported that surface boron doping of Si(111) departs from the pattern of adatom occupation by the impurity that is followed by the other group-III elements, in that the dopant boron atoms are separate and distinct from the adatoms. Therefore, the binding sites of both adatoms and dopants must be identified separately. In this Brief Report, we elaborate on our previous paper¹¹ by describing in detail our determination of the lateral adatom position on this system by scanning tunneling microscopy (STM), and we show how the symmetry of the tunneling images restricts the field of possible boron adsorption sites. The one that is actually realized must ultimately be determined independently of tunneling microscopy.

Figure 1(a) presents a tunneling image of Si(111)-($\sqrt{3}\times\sqrt{3}$)R 30°-B, prepared by annealing heavily-boron-doped Si(111) wafers ($\approx 10^{20}\text{ cm}^{-3}$) at 1000°C for 2 min in an ultrahigh-vacuum chamber with a base pressure of 10^{-10} Torr. The same procedure applied to more moderately doped wafers would yield the 7×7 reconstruction; the mechanism for the surface boron segregation that induces the ($\sqrt{3}\times\sqrt{3}$)R 30° surface lattice under the present conditions was discussed previously.¹⁶

We note the presence of two distinct types of adatoms, differing in their relative brightness in the image. We have previously associated the "darker" sites with the presence of boron, and the "brighter" sites with the absence of the dopant, and we have found that a ($\sqrt{3}\times\sqrt{3}$)R 30° structure could be stabilized with the surface boron concentration ranging locally from saturation at $\frac{1}{3}$ ML down to only 0.07 ML. The relative brightness of the two types of sites in the images was seen to follow from topographical and local electronic characteristics of this surface.^{11,13} The 6.7-Å spacing between the hexagonally close-packed adatoms in Fig. 1(a) is consistent with the ($\sqrt{3}\times\sqrt{3}$)R 30° periodicity of the LEED pattern, but a complete picture of the surface structure requires, in addition, a determination of the identity and binding geometry of the adatoms and subsurface substrate atoms.

An unreconstructed Si(111) substrate presents an adatom with two alternate, threefold binding sites known as the "filled" (T_4) and "hollow" (H_3) sites. The first places the adatom directly above an atom in the lower plane of the first substrate double layer, whereas the second does not. If all of the dangling bonds of an unreconstructed substrate are terminated in either fashion, the resulting close-packed, adatom-covered surface would display the ($\sqrt{3}\times\sqrt{3}$)R 30° periodicity. The two structures are inequivalent, but either one could give rise to a ($\sqrt{3}\times\sqrt{3}$)R 30° LEED pattern and to the tunneling image in Fig. 1(a). The T_4 binding site is believed to be favored, in general, for it accommodates a substrate relaxation under which the bond lengths and angles in the surface layer approach their bulk values.⁹

It has been recognized^{17,18} that the lateral adatom registry in a new structure can be deduced from STM images of an inhomogeneous surface that incorporates domains of both the undetermined structure and one of known binding configuration, such as the 7×7 reconstruction. In the present case, if interfaces between domains of ($\sqrt{3}\times\sqrt{3}$)R 30° and 7×7 are located, then the adatom positions in the former structure can be determined by comparison with a continuation, across the interface, of the registry of the latter domains. We have previously employed this procedure to establish T_4 occupation by gallium adatoms in Si(111)-

$(\sqrt{3} \times \sqrt{3})R 30^\circ$ -Ga, a simpler system within which the gallium is the adatom.^{5,6}

Figures 2(a) and 2(b) illustrate the application of this procedure to adatoms on Si(111)- $(\sqrt{3} \times \sqrt{3})R 30^\circ$ -B. The surface in this figure was prepared similarly to that in Fig. 1(a), but this time the sample was annealed for 2 min at 825°C rather than 1000°C. The lower temperature used here permitted the preservation of isolated regions of the 7×7 reconstruction, as evident from both Fig. 2(a) and the observed, simultaneous coincidence of two sets of LEED patterns corresponding to the two surface lattices present.

The corrugation trace in Fig. 2(b) presents the vertical tip displacement as a function of position along the line indicated in Fig. 2(a), which spans the interface between domains of the two periodicities. From this and other similar cuts, the adatom registry in the $(\sqrt{3} \times \sqrt{3})R 30^\circ$ domain is found to be consistent with that in the 7×7 region, establishing the T_4 configuration for the new structure. The dashed curve in Fig. 2(b) indicates how such a

FIG. 1. (a) $55 \times 55\text{-}\text{\AA}^2$ STM image of Si(111)- $(\sqrt{3} \times \sqrt{3})R 30^\circ$ -B, prepared by annealing heavily-B-doped Si(111), showing adatoms spaced $6.65\text{ \AA}$ apart. Tip bias -1.4 V , 1 nA . (b) Corrugation trace showing tip-sample separation vs lateral tip position along the line indicated in (a). The zero reference is arbitrary.

FIG. 2. (a) $110 \times 110\text{-}\text{\AA}^2$ STM image showing separate domains of the 7×7 and the $(\sqrt{3} \times \sqrt{3})R 30^\circ$ phases. Tip bias -1.3 V , 1 nA . (b) Corrugation trace acquired across the line indicated in (a), verifying consistency in the adatom binding site across the interface. Inconsistency across the interface would have resulted in the trace's taking the appearance of the dashed curve instead. The zero reference is arbitrary.

trace might have appeared if the $(\sqrt{3} \times \sqrt{3})R 30^\circ$ adatoms occupied the H_3 site, and the two cases are easily distinguished under STM.

Because of observed, nonuniform dopant distribution even within $(\sqrt{3} \times \sqrt{3})R 30^\circ$ regions of this particular surface, the consistency of the adatom binding site throughout $(\sqrt{3} \times \sqrt{3})R 30^\circ$ domains must still be verified. Near the 7×7 domain, where the supply of boron atoms is evidently reduced locally, the brighter, boron-free adatom sites in the $(\sqrt{3} \times \sqrt{3})R 30^\circ$ domains naturally dominate the landscape; the very presence of the 7×7 reconstruction, ordinarily found on the clean surface, indicates a local boron deficiency. Away from the interface, the "dark" sites can form the majority of adatoms, as in Fig. 1(a), yet the method of Fig. 2 can evidently be applied practically only to determine the registry of adatoms in the predominantly boron-free regions bordering an interface between structural phases.

If two distinct adatom binding sites, H_3 and T_4 , were both realized on the surface, depending on local boron concentration, then within $(\sqrt{3} \times \sqrt{3})R 30^\circ$ regions there should exist boundaries or atomic steps across which the adatom registry would change.⁴ We have searched ex-

FIG. 3. (a) STM image showing a boundary between the $(\sqrt{3}\times\sqrt{3})R30^\circ$ domains. (b) The region in (a), with a grid superimposed. The markers indicate the location of one type of binding site. The consistency of the adatom binding site across the boundary follows from the occurrence of each atom on a marker on both sides of the boundary. The arrows point to the boundary.

FIG. 4. (a) STM image showing a single atomic step in the $(\sqrt{3}\times\sqrt{3})R30^\circ$ surface. (b) The region in (a), with a grid superimposed. The markers indicate the locations of one type of binding site on one terrace. Thus, the adatoms on the upper terrace coincide with the markers, but those on the lower terrace must each fall on the centroid of a triangle of adjacent markers.

haustively for such defects under STM, but we have identified only registry-preserving boundaries (Fig. 3) and atomic steps (Fig. 4). In these figures, the grid markers superimposed on the tunneling images represent each available binding site of one type, either H_3 or T_4 , in one surface plane. The coincidence of adatoms and markers across the boundary between $(\sqrt{3}\times\sqrt{3})R30^\circ$ domains in Fig. 3 verifies the consistency of the binding site across that defect. If the registry is to be consistent across a single atomic step, then the adatoms on one terrace must appear to be out of registry with the continuation of a grid from the other terrace. This is indeed the case in Fig. 4, where the adatoms on the upper terrace coincide with markers, and those on the lower terrace do not.

While the exact location of the boron atom itself cannot be determined by STM alone, the possibilities can be restricted according to the symmetries of the LEED pattern and the STM images. An ideal $(\sqrt{3}\times\sqrt{3})R30^\circ$ termination would exhibit both the threefold rotational symmetry of the substrate and a mirror symmetry in the adatom layer and the first substrate double layer, about the short diagonal of its surface unit cell. The former is manifest in the LEED pattern and each of the STM images above, and Fig. 1(b) demonstrates that the latter symmetry is preserved in the tunneling image of the boron-rich surface for unit cells containing either “bright” or “dark” adatom sites. The corrugation trace displays the vertical tip displacement along the line indicated in Fig. 1(a), following the long diagonal of a surface unit cell. We observe that at all biases a saddle point falls directly between principal maxima that represent adatoms, so the trace within each unit cell is invariant under reflection about its midpoint. We do not observe manifestations of mirror-symmetry breaking, which was reported earlier¹⁹ and was apparently at variance with our Fig. 1.

To preserve both the rotational and mirror symmetries, the boron atom would lie along the vertical axis of threefold symmetry, passing through the adatom. Both the adatom and adsorbed boron would then share the same *lateral* position. The symmetry-imposed limit on the number of possible adsorption sites then greatly facilitates any further structural determination that might involve separate, computationally intensive analysis for each alternate structure under consideration. In this case, independent determinations of the vertical boron position by first-principles calculations^{11,13} and surface x-ray diffraction¹² needed to compare only two structures: that with boron in the T_4 adatom site and that with boron directly underneath that site. As described in those references, each measurement then favored the latter structure, where the adatom and dopant coincide laterally but not vertically. Thus, all adatoms in the STM images would be silicon. A “bright” site would have only silicon nearest neighbors; otherwise, the silicon adatom would sit above a substitutional boron atom. Stress relief was shown to play a crucial role in driving the novel structure of this boron-doped surface.

In summary, we have illustrated the determination of lateral adatom registry by STM for the boron-silicon system in which the adatom and dopant are separate and the

local dopant coverage is nonuniform. In addition, the tunneling images identify the lateral dopant position as coincident with the adatom.

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