Structure of Si(113) Determined by Scanning Tunneling Microscopy

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The Si(113) surface is very stable despite its high index but until now its atomic structure has been uncertain. Using a scanning tunneling microscope, we have obtained images of both empty and filled states which provide strong evidence for a particular structural model with a 3×2 unit cell. We explain our results in terms of a general rehybridization principle which accounts for the low surface energy and the spatial distribution of empty and filled states. Our images reveal a high density of domain boundaries which introduce energy states that pin the Fermi level and explain earlier reports of a 3×1 reconstruction.

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High-index Si surfaces tend to be unstable and to facet into lower-index planes upon annealing.[1,2] However, the Si(113) surface constitutes an interesting exception.[3,4] Gibson, McDonald, and Unterwald have annealed thin specimens of ⟨110⟩-oriented Si in vacuum and observed primarily facets of ⟨111⟩, ⟨100⟩, ⟨110⟩, and ⟨113⟩ orientation.[3] This indicates that the Si(113) surface has an energy that is comparable to that of the low-index surfaces, and implies that it has potential as a substrate for growth.[4] For epitaxial growth on III-V materials the {113} face has already shown crystal-growth properties that are superior to those of the low-index surfaces.[5] The structure of the Si(113) surface is important for two reasons. First, it may give clues to a general understanding of why certain faces of Si as well as other tetrahedrally bonded semiconductors are stable. Second, it is necessary step in understanding growth. Previous low-energy electron-diffraction (LEED) experiments suggest that the surface could have both 3×1 (Refs. 6 and 7) and 3×2 (Ref. 7) reconstructions, but the atomic arrangement is uncertain. In this Letter we report on the use of scanning tunneling microscopy (STM) to establish both the atomic and electronic structure of the Si(113) surface. This enables us to draw conclusions about the energetics that control the reconstruction not only of this surface but of Si and Ge surfaces in general.

The samples were cut from a 2×10^{18}-cm^{-3} Sb-doped single-crystal ingot and had a surface normal within 0.5° of the ⟨113⟩ direction. The surface was mechanically polished, followed by a Shiraki-type oxide etch-regrowth procedure. In UHV the sample was heated to 870 °C for 1 min to remove the surface oxide layer. This treatment generally resulted in surfaces with a 3×2 LEED pattern and atomically flat areas larger than 1000×1000 Å^2 as observed by STM.

Figure 1(a) shows an STM image recorded at a constant tunneling current I_t of 2 nA and a sample bias voltage V_s of -2 V corresponding to filled sample states. Figure 1(b) shows an image acquired with $I_t=2$ nA and $V_s=+2$ V corresponding to empty sample states. The star in both images marks equivalent locations. This registry was unequivocally established, over several samples, both by current imaging tunneling spectroscopy[8] (CITS) and by alignment of defect structures in images of the same area of the surface. The surface periodicity apparent in Fig. 1 corresponds to a 3×2 reconstruction.

The unreconstructed Si(113) surface consists of alter-

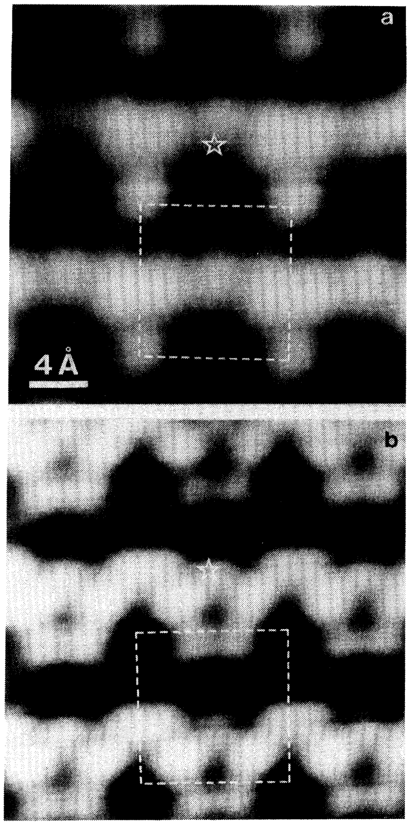

FIG. 1. STM images of the Si(113)3×2 surface recorded with $I_t=2$ nA and (a) $V_s=-2$ V and (b) $V_s=+2$ V. The stars indicate equivalent positions.

nating (111) and (001) terraces both of which are only a single atomic row wide in the [33$\bar{2}$] direction. The 1×1 unit cell has one atom representing the (111) terrace with one dangling bond (DB) and one atom representing the (001) terrace with two DBs. This arrangement leads to a number of possible models for the 3×2 reconstruction[9] based on rebonding at steps and dimer formation,[10] which are known from calculations to lower the surface energy.[11] Among the models suggested by Ranke[9] we find one that gives an excellent fit to our data. This reconstruction is shown in Fig. 2. It leads to a reduction of the number of DBs per 3×2 cell from 18 to 12. It has two dimers (atoms marked 2-3 and 6-7 in Fig. 2) and one rebonded step configuration (atom 1). The structure also contains three atoms (10–12) that are similar to the rest atoms of the Si(111)7×7 structure. All the features in our filled- and empty-state images are accounted for by DBs in this model. DBs 1–6 appear in the filled-state image whereas DBs 7–11 and 2 and 3 are seen in the empty-state image. The empty states on atoms 7–11 show up strongly, despite being associated with atoms situated ~2 Å lower than the outermost atoms of the surface. This means that the local density of empty states is concentrated only on certain atoms. However, for the filled states, the images resemble the topography of the surface. This means that we cannot tell whether the filled-state density is strongly localized on the topographically higher atoms or more evenly distributed over all atoms with DBs.

This spatial distribution of empty and filled states can be explained by a rehybridization of DB orbitals as follows. For an adjacent pair of atoms with DBs (such as atoms 6 and 7) buckling occurs.[12-14] One of the atoms of the pair (in this case 7) is depressed into a more sp^2-like configuration in order to maximize the orbital overlap with its bonding neighbors. The improvement of bonding is the driving force balancing the increased lattice strain. This tendency towards sp^2 for the depressed atom leaves the DB in a more p-like state which causes its energy to rise into the conduction band. Correspondingly, for the raised atom (6), the bond angle is decreased from the tetrahedral value, producing a more s-like DB; hence the DB energy is lowered into the valence band. Similar arguments can be applied to the group of atoms 1, 8, and 9, where 8 and 9 move towards a more sp^2-like configuration. Atoms 10 and 11 can also relax into the surface to become more sp^2 hybridized, producing empty, more p-like DB states. This observation of a spatial difference between filled and empty states, mainly associated with a buckling of the surface atoms, appears to be a more general phenomenon on tetrahedral semiconductor surfaces. The tilting of dimers on Si(100)-(2×1), for example,[12] is associated with a shift up in state energy for the lowered atom and vice versa for the raised atom. A similar effect is found on GaAs(110) (Ref. 14) and Si(111).[15] The Si(113) reconstruction is striking in that it has a very high density of atoms that can rehybridize towards sp^2 and thereby reduce the overall energy. We believe that the high stability of this surface is due to the energy reduction associated with the large number of sites having this rehybridization.

In the case of the tetramer made up from atoms 2–5, a further refinement of electronic structure becomes apparent by inspecting empty-state images as the voltage varies. The image in Fig. 3 shows that the empty states

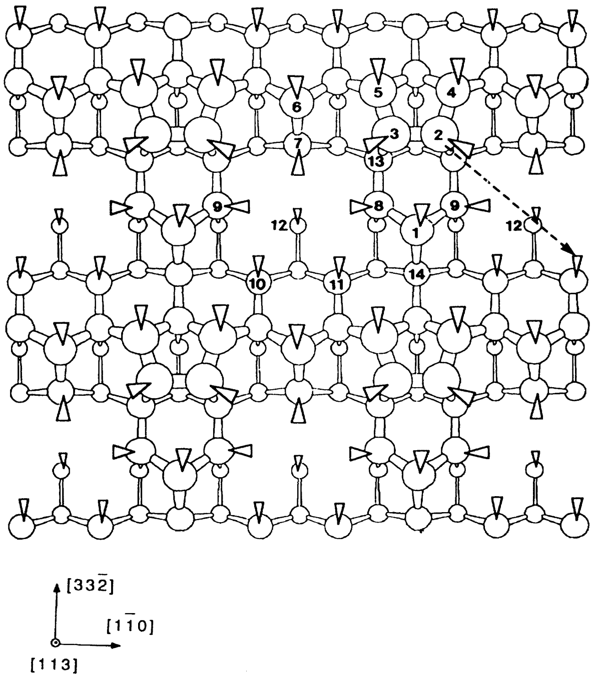

FIG. 2. Structural model of the 3×2 reconstruction.

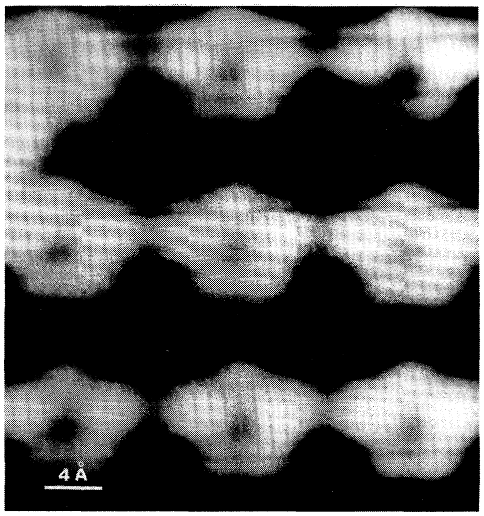

FIG. 3. STM image of the Si(113)3×2 surface obtained with $V_s=+1$ V and $I_t=0.5$ nA.

of the tetramer, which were seen in Fig. 1(b) at $V_s = 2$ V (atoms 2 and 3 are the highest topographically and thus most prominent), are no longer visible for $V_s = 1$ V. That is, these states have higher energy than the empty states of the DBs surrounding the central hole. This implies a stronger interaction between the DBs of the tetramer 2–5, most likely because of extended π bonding between the four adjacent DBs. This splits their states into components further apart in energy.

Figure 4 shows a large-area constant-current STM image recorded at 3 nA with a sample bias of -2.5 V. This image was obtained from a surface that had been annealed at 1100 °C for 1 min and then slowly cooled (approximately 0.15 °C/sec) to room temperature. Very similar images were obtained for higher cooling rates (≤ 20 °C/sec) and a range of annealing temperatures between 850 and 1100 °C. The image shows the same basic 3×2 reconstruction as seen in the previous high-resolution images. However, the 3×2 domains are relatively small, with an average diameter of 50–100 Å. The average domain size is smaller than the coherence length of the electron beam in LEED and should result in a broadening and decrease in intensity of the spots in the LEED pattern. However, for most of the domain boundaries the lateral phase shift between adjacent domains corresponds to a lattice vector of a 3×1 reconstructed surface. Hence the 3×1 spots of the LEED pattern will remain unperturbed by this type of disorder while the extra $\times2$ spots will suffer from destructive interference. This is consistent with our LEED patterns which typically showed extra $\times2$ spots that were both weaker and broader than those belonging to the 3×1 periodicity. During this investigation we never observed a pure 3×1 pattern from a clean sample. However, we suggest that the 3×1 pattern reported in previous literature[6,7] is due to a high density of phase boundaries of this type.

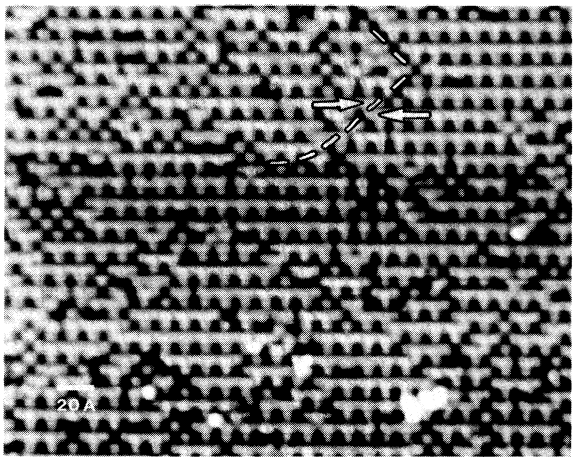

FIG. 4. STM image of the Si(113)3×2 surface obtained with $V_s = -2.5$ V and $I_t = 3$ nA. The dashed curve indicates a surface domain boundary.

A phase shift of the above type can be easily accomplished by moving the atoms labeled 2–5 and the atom joining 4 and 5 to the corresponding position above the atom labeled 12, as indicated by the dashed arrow in Fig. 2. This does not lead to any change in the number of DBs, nor does it lead to any major rearrangements of surrounding atoms. The resulting boundary is thus expected to alter the surface free energy by only a very small amount. This is in agreement with the high density of these boundaries and the fact that they do not anneal out even at quite slow cooling rates. All the atoms with DBs along the boundary still resemble those already present in the 3×2 unit cell. In fact, the only alterations that occur are of the type where a second nearest neighbor has been added or removed. For example, atom 13 resembles atom 10 but instead of all fourfold-coordinated neighbors it now has one neighbor with a DB. We suggest that these modifications reduce the rehybridization of some boundary DBs, and lead to a reduced shift in energy. The resulting domain-boundary states are shown in our tunneling spectra below.

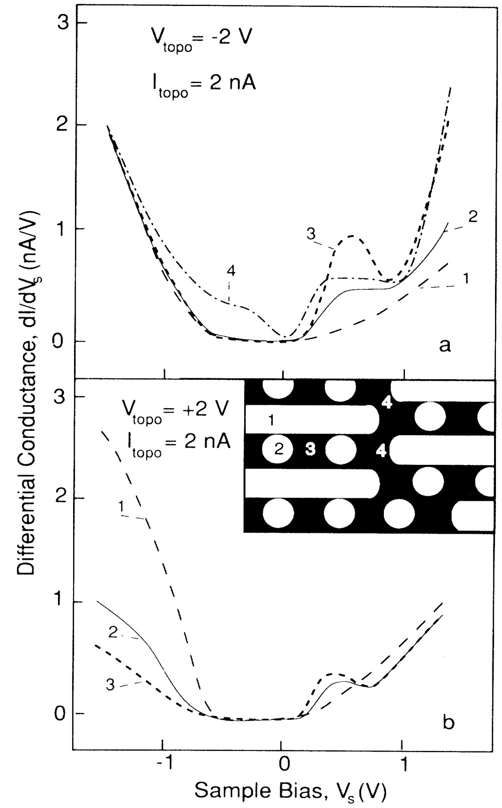

FIG. 5. Differential conductance dI_t/dV_s as a function of V_s. Inset in (b): A schematic drawing of a filled-state STM image. The spectra numbers 1–4 refer to the positions in the image.

In Fig. 5 we show differential tunneling conductance spectra for various sites in the 3×2 unit cell, obtained by CITS (Ref. 8) on both +2-V and −2-V topographic images. A marked onset in conductance corresponding to a state at +0.4 V is observed above all the DBs surrounding the edge of the hole (atoms 7–11). In positions corresponding to protrusions in the filled-state images, states at approximately −0.8 V are observed. A state at this energy has been observed using ultraviolet photoemission spectroscopy[7] and was associated with a 3×2 reconstruction on the basis of its observed k-space dispersion. Our STM data agree with this assignation. On nondefective 3×2 areas, no other energy states were observed closer to the Fermi level, which means that the surface band gap is approximately 1.2 eV. However, spectra obtained at phase boundaries (spectra 4 in Fig. 5) show the existence of states at the Fermi level. These energy levels arise from the perturbation of a DB at a domain boundary that is caused by a change in the bonds of a neighboring atom, as discussed above.

In summary, we have determined the structure for the relatively complex {113} surface of silicon. The deduced reconstruction emphasizes that, apart from reduction of the number of DBs, an important contribution to surface energy reduction is the rehybridization of the remaining DBs. A general trend for this rehybridization to produce dangling bonds with more pure s or p character is suggested on the basis of our results. In addition, we have observed domain boundaries which have very low energy and provide states at the Fermi level. The high density of these domain boundaries may explain previous reports of a 3×1 reconstruction for this surface.

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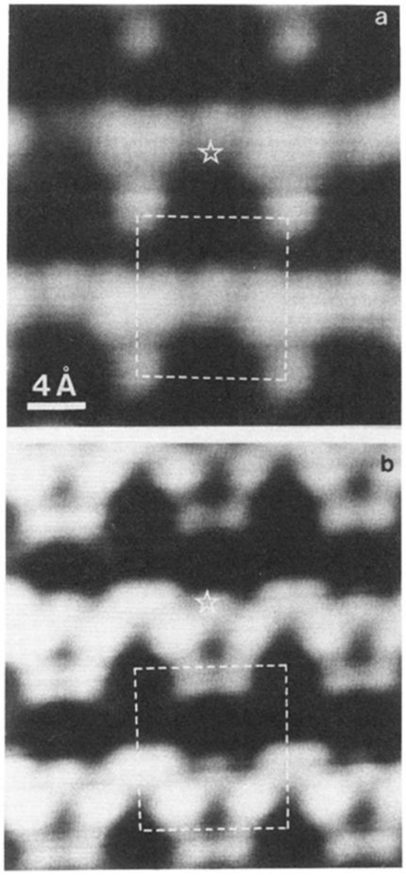
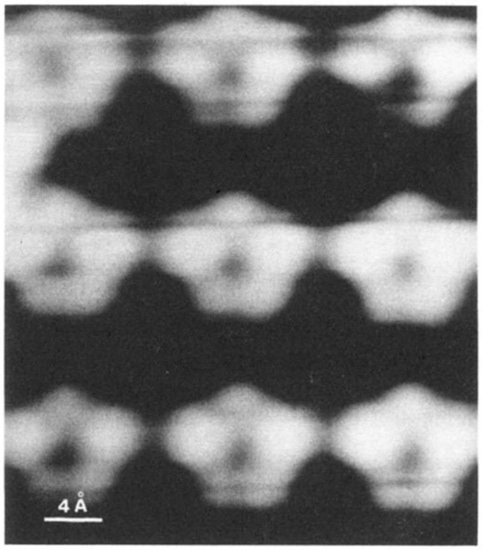


FIG. 1. STM images of the Si(113)3×2 surface recorded with $I_t = 2$ nA and (a) $V_s = -2$ V and (b) $V_s = +2$ V. The stars indicate equivalent positions.



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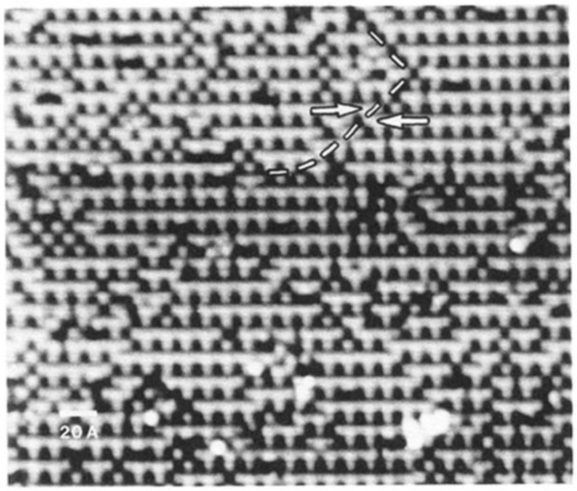

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