VOLUME 53, NUMBER 7 PHYSICAL REVIEW LETTERS 13 AUGUST 1984

Si(111)$\sqrt{3}\times\sqrt{3}$-Al: An Adatom-Induced Reconstruction

John E. Northrup
Xerox Palo Alto Research Center, Palo Alto, California 94304

(Received 29 May 1984)

First-principles pseudopotential total-energy and force calculations have been used to study the Si(111)$\sqrt{3}\times\sqrt{3}$-Al surface. A new adatom model of this reconstruction is proposed wherein each Al adatom sits in a threefold-symmetric site with three first-layer Si neighbors and one second-layer Si neighbor directly below. For this model, the calculated dispersion of the adatom-induced surface states is in good agreement with experiment. A theory for the observed momentum distribution of adatom-induced surface states is proposed.

PACS numbers: 68.20.+t, 73.20.Hb

Deposition of Al onto the Si(111) surface followed by thermal annealing produces many different ordered phases.[1-3] Lander and Morrison[1] discovered five separate phases, the simplest being the α-Si(111)$\sqrt{3}\times\sqrt{3}$-Al phase which was obtained with $\frac{1}{3}$ monolayer coverage and attributed to ordered adsorption of Al in the threefold hollow sites. Despite the apparent simplicity of this prototypical adatom-induced reconstruction, no conclusive structural determination has been obtained. In this paper, first-principles pseudopotential calculations of the surface atomic and electronic structure are reported. On the basis of these total-energy calculations, a new reconstruction which has a lower total energy than the threefold hollow-site model and is in good agreement with existing angle-resolved photoemission experiments[2] is proposed.

Lander and Morrison proposed that the α phase arose from the adsorption of $\frac{1}{3}$ monolayer of Al in the threefold hollow sites. In that model, denoted H_3, each Al is bonded to three surface atoms, eliminating the dangling bonds. An alternative model is one in which the Al is placed in the site above the second-layer Si atoms. In this position, the Al atoms each have four Si neighbors, three in the surface layer and one in the second layer directly below. The surface dangling bonds are eliminated in this model also. This structure is named the fourfold atop model (T_4). Illustrations of these two models are shown in Fig. 1. To decide between them, total-energy calculations have been performed.

The calculations were carried out by the momentum-space pseudopotential formalism[4,5] and employed norm-conserving pseudopotentials.[6] The local-density approximation was implemented with Ceperley and Alder's correlation energy functional as parametrized by Perdew and Zunger.[7] The Kohn-Sham equations[8] were solved in a plane-wave basis and were iterated to self-consistency for each geometry. Plane waves with kinetic energies up to 5 Ry were included in the basis set. A $\sqrt{3}\times\sqrt{3}$ supercell[9] containing eight layers of Si and ~ 14 a.u. of vacuum was used to model the surface. Inversion symmetry was imposed on the atomic positions. Forces calculated with the Hellmann-Feynman theorem were used to find the minimum-energy structure for each topology. This type of first-principles approach has been successful in calculating many of the ground-state bulk[10] and surface[11-13] properties of semiconductors.

Results of the total-energy calculations are shown in Fig. 2. The curves correspond to calculations where the energy is minimized with respect to the position of the Al adatom while keeping the substrate frozen. Also shown are the equilibrium energies for both models which have been determined by energy minimization with use of the Hellmann-Feynman forces. The effect of substrate relaxation is very large for the T_4 model and makes this structure more stable than the H_3 model by 0.3 eV/adatom. I propose therefore that the α-Si(111)$\sqrt{3}$-Al surface corresponds to the T_4 model.

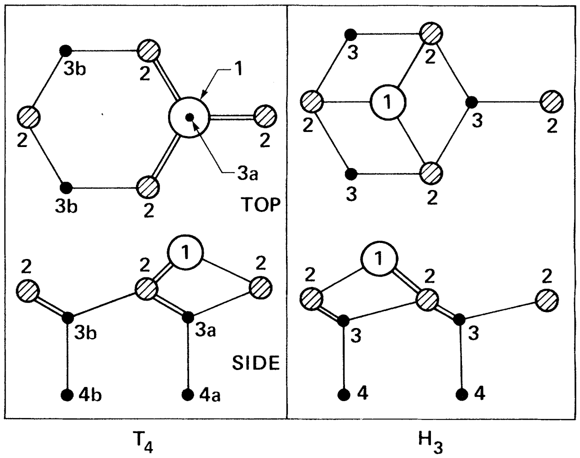

FIG. 1. Top and side schematic views of the T_4 and H_3 models. Atom No. 1 is the Al adatom.

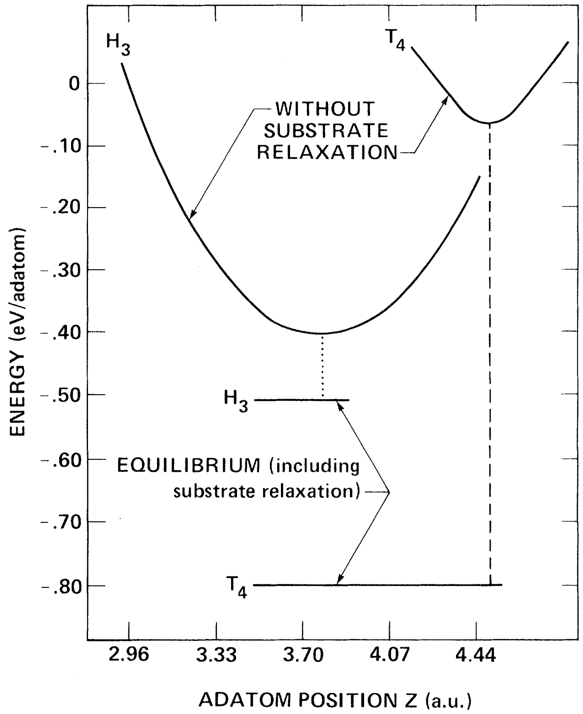

FIG. 2. Curves correspond to energy minimization with respect to adatom position z measured from the plane containing the second-layer atoms (type 3). Horizontal lines mark the energies of the completely relaxed geometries.

The calculated binding energy of an Al atom in the T_4 structure is 5.6 eV/adatom relative to the relaxed Si(111)1 × 1 surface plus a free Al atom. This indicates that α-Si(111)$\sqrt{3}$-Al is a very stable structure, in accordance with the fact that Si(100)-Al is unstable to the formation of Si(111)$\sqrt{3}$-Al etch pits.[1]

For H_3, the minimum energy corresponds to a bond length of 4.78 a.u. between the Al and three Si surface atoms. This is longer than the sum of the Pauling tetrahedral covalent radii for Al and Si (4.59 a.u.) because of the deviations from tetrahedral bond angles. For T_4, the distance is 4.72 a.u. from the Al to the Si surface atoms and is 4.63 from the Al to the second-layer Si atom (type 3a). The calculated deviations (δz) from the ideal positions for the T_4 model are (in atomic units) as follows: $\delta z_2 = -0.05$, $\delta z_{3a} = -0.63$, $\delta z_{3b} = 0.22$, $\delta z_{4a} = -0.33$, and $\delta z_{4b} = 0.18$. The type-2 atoms move laterally towards the axis containing the adatom by 0.23 a.u. The substrate relaxation is mainly a large downward movement of atoms 3a and 4a. These displacements are energetically favorable because they allow the Al adatom to move closer to the Si surface atoms by about 0.4 a.u. but still maintain an optimum distance ($\sim$4.6 a.u.) above the second-layer Si atom.

Hansson *et al.*[2] performed angle-resolved photoemission studies for the α phase, and found that the Al adatoms gave rise to two bands of surface states with a dispersion of 0.4 eV and centered 1.5 eV below the Fermi level. Electrons from these states are emitted at angles corresponding to wave vectors in the outer regions of the 1 × 1 Brillouin zone (BZ) (i.e., in the secondary $\sqrt{3} \times \sqrt{3}$ Brillouin zones). States with similar photoemission intensity patterns occur at an energy 1.8 eV below the Fermi level for the Si(111)7 × 7 surface.[14] If this similarity is not accidental, it is a consequence of the existence of (Al or Si) adatom-induced surface states in each case. As will be shown, the Al-induced surface states are derived from dangling-bond states on the free surface which have their wave vectors near the edges of the 1 × 1 Brillouin zone. These states couple to Al orbitals of p_x and p_y character in an energetically favorable way, and produce two states per adatom below the valence-band maximum (VBM). The dangling-bond surface states with wave vectors near the center of the 1 × 1 BZ cannot couple to these orbitals and they give rise to unoccupied states in the gap. Consequently, the character of the occupied Al-induced states is similar to that of the dangling-bond states at the *edges* of the 1 × 1 BZ, and so photoemission occurs at angles corresponding to initial-state wave vectors near the edges of the 1 × 1 BZ. An analogous argument applies for Si adatoms on Si(111). The calculated electronic structure for the H_3 model in the region of the valence-band maximum is shown in Fig. 3(a). Two surface-state bands of width 0.5 eV exist below the valence-band maximum. The character of these two bands is similar, and in terms of atomic orbitals corresponds to p_z orbitals on the Si surface atoms coupled to p_x and p_y orbitals on the Al atom.[15] An unoccupied band of surface states exists in the gap. The dispersion of the dangling-bond surface states on the relaxed Si(111)1 × 1 surface, folded back into the $\sqrt{3} \times \sqrt{3}$ BZ, is shown in Fig. 3(b). The three bands of surface states on the Al-covered surface are derived in a simple way from these dangling-bond states (DBS). The numbering of the bands in Fig. 3(b) indicates the region of the 1 × 1 BZ to which they correspond. The effect of adding an Al adatom is to lower the energy of the DBS in regions 2 and 3, and to raise the energy of the DBS in region 1. The states which are lowered are those states which couple favorably to a p_x or p_y orbital on the Al atom. Favorable coupling requires that the DBS amplitude changes sign from one sur-

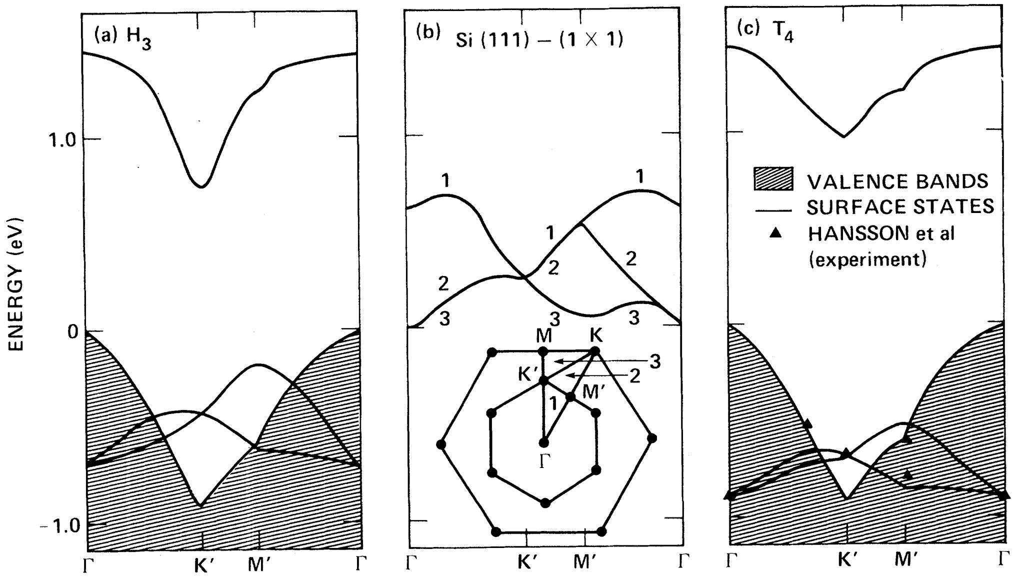

FIG. 3. (a) Dispersion of the three bands of surface states for the H_3 geometry. Energy is measured from the valence-band maximum. (b) Dispersion of dangling-bond states on a 1×1 relaxed surface folded back into the $\sqrt{3}\times\sqrt{3}$ BZ. (c) Dispersion of surface states in the T_4 model compared with experimentally determined peak positions. To compare experiment with theory, the Fermi level was assumed to be 0.8 eV above the VBM.

face atom to the next as shown in Fig. 4(a). Those DBS which have this property have their wave vector in the outer regions of the 1×1 BZ. However, zone-center DBS have wave functions with the same relative sign on neighboring surface atoms, and consequently their energy is raised by the coupling to the p orbital on the adatom.

The dispersion of the surface states for the T_4 model is shown in Fig. 3(c). The dispersion of these states is very similar to that for the H_3 structure, and has the same origin. One important difference is that the adatom-induced splitting of the dangling-bond band is larger for the T_4 geometry, causing the occupied surface states to occur at lower energy. The experimentally determined dispersion[2] is also shown in Fig. 3(c), and is in good agreement with theory. In particular, both experiment and theory show the existence of two occupied surface states with a total dispersion of about 0.4 eV and with an energy splitting between them at the M' point of 0.4 eV in theory and 0.25 eV experimentally. To compare experiment with theory, we have assumed that the Fermi level is 0.8 eV above the VBM. In reality, the Fermi level may be lower in energy, which would imply that the calculated surface states are slightly too high in energy.

In the angle-resolved photoemission experiments performed by Himpsel *et al.*[14] for Si(111)7×7, the maximum intensity of emission from the low-energy ($E_F - 1.8$ eV) surface state occurred for angles corresponding to initial-state wave vectors near the edges of the 1×1 BZ. The presence of adatoms on the 7×7 surface provides a natural explanation of this fact. Si adatoms produce surface states near this energy.[13] The character of these states is very similar to the Al-induced states, and so the preceding arguments concerning the momentum distribution of these states apply also to the Si adatom-induced states. An additional occupied surface state exists at higher energy ($E_F - 0.8$ eV) for Si(111)7×7 but not for α-Si(111)$\sqrt{3}$-Al. The ex-

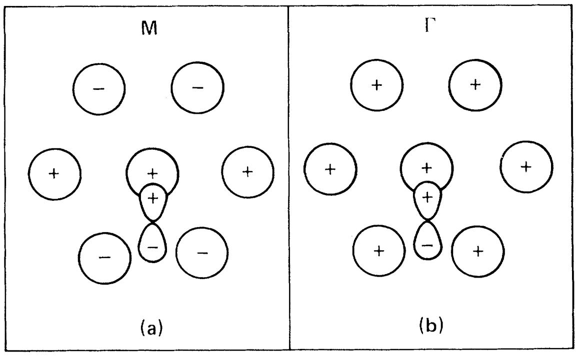

FIG. 4. (a) Coupling of a p_x orbital on an Al adatom to an M-point dangling-bond state is energetically favorable. (b) Coupling to a dangling-bond state at Γ puts an extra node in the wave function and is energetically unfavorable.

istence of this state for the 7×7 surface arises, presumably, from the dangling bonds on the free surface atoms[13] which are present in adatom models of the 7×7 reconstruction. The state is absent for the Al-covered surface because there are no free surface atoms for $\frac{1}{3}$-monolayer coverage. The relative energies of the upper and lower surface states calculated for a 2×2 adatom model for Si(111)[13] are consistent with photoemission experiments for the Si(111)7×7 surface.

Laser-annealed Si(111)1×1 and Ge(111)1×1 surfaces and the thermally annealed Si(111)7×7 and Ge(111)2×8 surfaces each exhibit two prominent surface states near the VBM with similar characteristic emission patterns.[14] Himpsel *et al.*[14] proposed that this similarity indicated a common local bonding geometry for all four surfaces. Disordered adatoms for the 1×1 surfaces, and ordered adatoms for the 7×7 and 2×8 surfaces, could explain these remarkable similarities. In this context it would be interesting to see if the structure of laser-annealed[3] Si(111)1×1-Al corresponds to disordered Al adatoms and, if so, to what extent surface-state photoemission from the disordered surface is different from that on the ordered surface.

I would like to thank Dr. D. J. Chadi, Dr. R. Z. Bachrach, and Dr. R. D. Bringans for discussions. This work is supported in part by the Office of Naval Research through Contract No. N00014-82-C-0244.

---

[1] J. J. Lander and J. Morrison, Surf. Sci. **2**, 553 (1964).

[2] G. V. Hansson, R. Z. Bachrach, R. S. Bauer, and P. Chiaradia, Phys. Rev. Lett. **46**, 1033 (1981).

[3] S. M. Bedair and H. P. Smith, Surf. Sci. **40**, 419 (1973).

[4] J. Ihm, A. Zunger, and M. L. Cohen, J. Phys. C **12**, 4409 (1979).

[5] M. T. Yin and M. L. Cohen, Phys. Rev. B **26**, 5668 (1982).

[6] D. R. Hamann, M. Schlüter, and C. Chiang, Phys. Rev. Lett. **43**, 1494 (1979).

[7] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[8] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1135 (1965).

[9] M. Schlüter, J. R. Chelikowsky, S. G. Louie, and M. L. Cohen, Phys. Rev. B **12**, 4200 (1975).

[10] M. L. Cohen, Phys. Scr. **T5**, (1982), and references therein.

[11] M. T. Yin and M. L. Cohen, Phys. Rev. B **24**, 2303 (1981).

[12] J. Ihm and J. D. Joannopoulos, Phys. Rev. Lett. **47**, 679 (1981).

[13] J. E. Northrup and M. L. Cohen, Phys. Rev. B **29**, 1966 (1984).

[14] F. J. Himpsel, D. E. Eastman, P. Heimann, B. Reihl, C. W. White, and D. M. Zehner, Phys. Rev. B **24**, 1120 (1981).

[15] The character of these states is very similar to the low-energy surface states calculated for a 2×2 Si adatom structure. This state was plotted in Ref. 13.