

First-principles study of steps on the Si(111):H surface

X.-P. Li, David Vanderbilt, and R. D. King-Smith*

Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08855-0849

(Received 18 February 1994)

The relaxations and vibrational properties of dihydride steps on the Si(111):H surface are studied from first principles. Besides the expected large relaxation of the SiH₂ unit on the step edge, long-range relaxations are found along a zigzag chain deep into the bulk. Three vibrational modes are found with frequencies 10.9, 22.5, and 56.0 cm⁻¹ higher than the Si-H stretching frequency on the terrace. A scissors mode is identified with frequency 262 cm⁻¹ higher than the Si-H wagging frequency. These frequency differences and mode assignments are in good agreement with experiment.

I. INTRODUCTION

The successful synthesis of nearly defect-free Si(111):H surfaces¹ has recently led to numerous studies of the unusual properties of this ideal semiconducting surface.²⁻⁴ It is an even richer subject for experiment and theory when steps are introduced by miscutting. By studying the Si-H stretching vibrations using polarized infrared absorption techniques, Jakob *et al.*⁵ showed that for proper preparation conditions, the steps are atomically straight, and the structure near the steps was also determined. Morin *et al.*^{6,7} measured the vibrational energy flow of the Si-H stretching modes and concluded that the steps act like sinks for the vibrational energy to transfer into the Si bulk. The distribution of the terrace sizes was determined by Jakob *et al.*⁸ by investigating the inhomogeneous broadening of the infrared spectra.

When the Si(111):H surface is miscut in the $\langle \bar{1}\bar{1}2 \rangle$ direction by 9°, atomically straight dihydride steps are obtained. The structure deduced for these steps⁵ is shown in Fig. 1. All the Si atoms remain fourfold coordinated. The dihydride unit, comprising H(1) and H(2) bonded to Si(1), is determined to lie within the (1 $\bar{1}$ 0) plane.⁵ Si(2) has four Si neighbors. All the dangling bonds are saturated, the distribution of terrace widths is centered at around six rows, the kink density is low, and the structure is remarkably stable.

We have theoretically studied the Si(111):H surface with dihydride steps, employing first-principles pseudopotentials within the framework of density functional theory and the local density approximation. This paper reports the detailed structural and vibrational properties of this surface from our calculations. Section II provides the computational details, including the information on the supercell, the initial atomic positions, and the pseudopotentials we used. Section III describes the relaxed structure, and Sec. IV gives the vibrational properties, focusing on the modes localized at the steps. Section V presents our conclusions.

II. COMPUTATIONAL DETAILS

The structure of the step is taken from Jakob *et al.*,⁵ and the step is assumed to be atomically straight from

$-\infty$ to $+\infty$ in the $\langle 1\bar{1}0 \rangle$ direction. This is a good approximation as the kink density is reported⁹ to be only a few percent. Therefore, in the $\langle 1\bar{1}0 \rangle$ direction, the periodicity is the same as that of the underlying lattice.

The experiments of Jakob *et al.*⁸ indicate that the terraces between two neighboring steps do not have exactly the same size. For surfaces miscut by 9°, the terrace sizes have a broad distribution peaked at six rows. To study

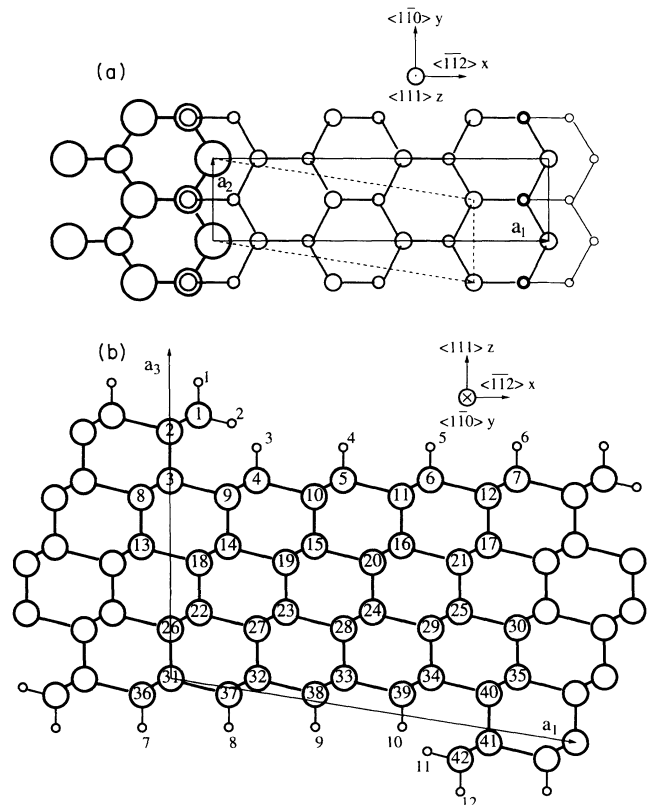


FIG. 1. Supercell used in the calculation. (a) Top view: H atoms are not shown, larger circles stand for higher positions (larger z coordinates). The dashed lines show the would-be supercell if n were 4. (b) Side view: larger circles are Si atoms and smaller circles are H atoms. All the numbered atoms are within the supercell.

the effects of this terrace size distribution from first principles is beyond our current capacity. We thus assume a constant terrace size, and argue that this assumption does not appreciably affect the relaxation and the dynamical properties that we are interested in as long as the terrace size is large enough. This argument is valid because the relaxation within the surface plane is well localized near the step, as we will see later. This assumption gives us periodicity in the surface direction perpendicular to the steps. Finally, we construct a slab geometry consisting of four double layers of Si (with appropriate number of H atoms to saturate all the dangling bonds) and a two-double-layer-thick vacuum. We thus arrive at a supercell structure that is periodic in all three dimensions.

The miscut angle θ and the number of rows on the terrace n are related by

$$\tan \theta = 2\sqrt{2}/(3n-1), \quad (1)$$

and the number of Si atoms and H atoms in the supercell are $2(4n+1)$ and $2(n+1)$, respectively. When $n=6$, $\theta=9.45^\circ$, which is the closest to the experimental condition, $\theta=9^\circ$. However, when n is even, the supercell symmetry is body-centered monoclinic, as shown in Fig. 1(a); this further complicates the calculations, especially the choice of k points. We thus compromise on the miscut angle, and choose $n=5$, that is, five rows on the terrace. The corresponding miscut angle is 11.42° , the total number of atoms in the supercell is 54, among them 12 are H atoms, and the symmetry is monoclinic (C_{2h}). The supercell is shown in Fig. 1. The directions $(\bar{1}\bar{1}2)$, $(1\bar{1}0)$, and (111) are chosen to be the x , y , and z axes, respectively. The lattice vectors are, in units of the lattice constant a of crystalline Si,

$$\begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix} = \begin{pmatrix} 7\sqrt{6}/6 & 0 & -\sqrt{3}/3 \\ 0 & \sqrt{2}/2 & 0 \\ 0 & 0 & 2\sqrt{3} \end{pmatrix}. \quad (2)$$

Two special k points, $(0, \frac{1}{8}, 0)$ and $(0, \frac{3}{8}, 0)$ in units of $2\pi/a_2$, are used, corresponding to a total of four k points in the whole first Brillouin zone. Use of a single k point in the a_1 and a_3 directions is adequate because the corresponding supercell dimensions are large.

To make the calculations tractable, we use first-principles ultrasoft pseudopotentials¹⁰ to represent the electron-nuclei interactions. The pseudopotential for hydrogen is generated in the neutral ground state; only the s channel is included, with one reference energy at the eigenvalue, and the cutoff radii for the valence wave function and for the local potential are 0.8 and 0.7 a.u., respectively. For Si, the pseudopotential includes s , p , and d channels. To make the d channel bound, a +1 charge state is used, and the occupation numbers are 1.0, 1.75, and 0.25 for the three channels, respectively. The cutoff radius is 1.7 a.u. for all the valence electronic wave functions and 1.2 a.u. for the local potential. Two reference energies are used for each channel, one at the eigenvalue and the other 0.5 – 1 Ry above the eigenvalue. The charge augmentation functions have cutoff radius 0.6 a.u. for hydrogen and 1.0 a.u. for silicon. Both the charge aug-

mentations and the pseudo wave functions are generated with optimum smoothness using a procedure similar to that of Rappe *et al.*¹¹ (When the reference energy is not an eigenvalue, so that the atomic wave function diverges at large radius, we have found the following *ad hoc* prescription to work quite well. We first replace the diverging tail by an arbitrarily chosen smooth tail which vanishes at large radius and which matches in value and first through third derivatives at the cutoff radius r_c . We then apply the Rappe-like procedure to optimize the smoothness inside r_c , and finally we reattach the correct tail outside r_c .) Wave functions are expanded in a plane-wave basis set with an energy cutoff of 20 Ry, which is very well converged for both Si and H. A conjugate gradient method¹² is used to diagonalize the Hamiltonian.

Using the above described pseudopotential and energy cutoff with ten special k points, the structural properties of diamond-structure bulk Si are calculated. The lattice constant, bulk modulus, and pressure derivative of the bulk modulus are found to be 3.578 Å, 0.97 Mbar, and 3.68, respectively, in good agreement with other pseudopotential calculations. The theoretical lattice constant is used in the step calculations.

III. RELAXATION

All the atoms are allowed to relax fully. The C_{2h} symmetry is automatically preserved, and the relaxation in the y direction is always zero because of mirror symmetry.

The Si-H bond lengths are shown in Table I. On a flat surface, this bond length is 1.506 Å, if all the other computational conditions are left unchanged. The bond lengths of the atoms H(4), H(5), and H(6) are almost unaffected by the steps, showing that the effect of the steps in the direction parallel to the surface is highly localized. The bond lengths of the three H atoms on the step change more, especially for H(2) and H(3). These two bonds are shortened by almost 0.01 Å. Raghavachari *et al.*¹³ argued that the relaxations are caused by the strong interaction between H(2) and H(3); our calculations clearly tend to confirm this picture.

On a flat surface, the bond lengths between the first- and second-layer Si atoms are 2.329 Å. As shown in Table II, they are only modestly modified by the existence of the step, except for the bond between Si(4) and Si(1) which has the largest relaxation of 0.023 Å. Further inside the bulk, the bond length variations are all small except along the zigzag chain of atoms Si(4), Si(10), Si(15), and Si(20). This relaxation pattern presumably has its origin in the interaction between H(2) and H(3), because this strong repulsion is approximately pointed at the di-

TABLE I. Calculated Si-H bond lengths. On a perfect surface without steps, the calculated Si-H bond length is 1.506 Å.

H atom	1	2	3	4	5	6
Bond length (Å)	1.502	1.497	1.498	1.505	1.506	1.508

TABLE II. Calculated Si-Si bond lengths. Primes denote atoms translated by a primitive lattice vector. The calculated bulk bond length is 2.329 Å.

Bond	Bond length (Å)	Bond	Bond length (Å)
1-2	2.319	2-3	2.337
3-8	2.336	3-9	2.330
4-9	2.323	4-10	2.306
5-10	2.320	5-11	2.315
6-11	2.320	6-12	2.317
7-12	2.320	7-2'	2.319
8-13	2.340	9-14	2.325
10-15	2.312	11-16	2.329
12-17	2.328	13-18	2.328
14-18	2.329	14-19	2.328
15-19	2.329	15-20	2.321
16-20	2.330	16-21	2.327
17-21	2.330	17-8'	2.330
20-24	2.319	21-25	2.327

rection of this chain. A less significant expansion along the zigzag chain of atoms Si(2), Si(3), Si(8), and Si(13) is also predicted. It appears to be caused by the combination of the upward force on H(2) and the compressive relaxation along the 4-10-15-20 Si chain. The fact that the large relaxations are along the zigzag chains is consistent with the work of Kane,¹⁴ which revealed the importance of the interactions along these chains.

The absolute relaxations of all the Si atoms are listed in Table III. Again, sizable relaxations are only observed along the two zigzag chains, apart from Si(1). The bond length between Si(1) and Si(2) stays the same as on a flat surface, and this large relaxation is due to a 3° rotation of the bond away from the step.

The four Si-H bonds corresponding to atoms H(1) through H(4) all rotate. The Si(1)-H(1) bond rotates away from the step [toward the left in Fig. 1(b)] by 3.5° relative to its ideal (vertical) orientation, or 0.5° relative to the Si(1)-Si(2) bond. The Si(1)-H(2) bond bends upward by 5.5° relative to its ideal orientation, or 2.5° relative to the Si(1)-Si(2) bond. The Si(4)-H(3) bond bends away from the step [toward the right in Fig. 1(b)] by 4.2°, and the Si(5)-H(4) bond bends toward the step [toward the left in Fig. 1(b)] by 0.9°, both relative to the vertical direction.

TABLE III. Absolute relaxations of Si atoms relative to the bulk.

Atom	Relaxation (Å)	Atom	Relaxation (Å)
1	0.15	2	0.04
3	0.04	4	0.12
5	0.04	6	0.01
7	0.01	8	0.02
9	0.01	10	0.07
11	0.01	12	0.01
13	0.01	14	0.01
15	0.05	16	0.01
17	0.02	18	0.01
19	0.01	20	0.03
21	0.01		

The relaxations are mainly caused by the strong repulsive interaction between atoms H(2) and H(3). In the ideal (unrelaxed) configuration, the distance between these two H atoms would be 1.39 Å. Since the open shells of both H atoms are saturated, this distance is too small, and the resulting repulsion gives rise to the relaxations described above. After the relaxation, the separation between these two H atoms becomes 1.78 Å.

This picture agrees qualitatively with the Hartree-Fock cluster calculations by Raghavachari, Jakob, and Chabal (RJC),¹³ but quantitatively, the agreement is poor. RJC reported a 20° rotation of the Si(1)-H(1) and Si(1)-H(2) bonds away from the step, although the displacement of Si(1) is 0.15 Å, the same as our result. Also, because of the limitation of their cluster size, RJC were not able to observe the long-range relaxation along the zigzag chains. The discrepancy regarding the Si-H bond rotations might arise from the fact that atom Si(10) is held fixed in the calculation of RJC, so that Si(4) and H(3) cannot relax sufficiently and H(2) has therefore to rotate more to compensate.

Hines *et al.*⁹ determined the Si(1)-H(1) bond rotation angle from angle-resolved Raman scattering, and found it to be $28 \pm 4^\circ$, which is considerably larger than our finding of 3.5° , and very close to RJC's results. Unfortunately the source of this discrepancy is unknown. One possible contributing factor may be that the interpretation of Ref. 9 was based on measurements of mode C_1 under the assumption that C_1 is completely localized on H(1). This assumption is a reasonably good approximation, but not in perfect accord with our theoretical findings (see next section). In any case, our results suggest that the interpretation of the Raman experiments might be reexamined with a view to determining whether alternative explanations consistent with a smaller rotation angle might be permissible.

IV. VIBRATIONS

Infrared absorption spectra taken by Jakob and Chabal⁵ on the stepped surface showed three sharp peaks at frequencies above the Si-H stretching frequency on a flat surface. Following the notation of Jakob and Chabal, we denote the Si-H stretching mode on a flat surface (at the Γ point) by A , and the three higher frequency modes on the stepped surface by C_1 , C_2 , and C_3 in the order of ascending frequencies. It is straightforward to study these modes in our first-principles calculation.

After the structure of the stepped surface is fully relaxed, we construct the dynamic matrix at the Γ point of the Brillouin zone by the frozen-phonon method. Since there are so many atoms in the supercell, it would be too time consuming to construct the full dynamic matrix. We therefore assume that the Si atoms are stationary, or equivalently that the mass of the Si atoms is infinite. This simplification introduces a known error of about -1%. Each of the H atoms is displaced in the $\langle \bar{1}\bar{1}2 \rangle$ (x) and $\langle 111 \rangle$ (z) directions by a small amount, and the forces on all the other atoms are calculated. The motion of the H atoms in the $\langle 1\bar{1}0 \rangle$ (y) direction need not be considered,

TABLE IV. Frequency differences compared with experiment and other calculations, in cm^{-1} . The “scissors mode” corresponds to atoms H(1) and H(2) attached to Si(1) moving against each other, and the “low-energy mode” corresponds to the same two H atoms moving in phase with each other (see text). “ $C_3 - C_2$ ” means the frequency of C_3 minus the frequency of C_2 , and “Scissors–Wagging” means the frequency of the “scissors mode” minus the frequency of the wagging mode on a flat surface.

	Previous theory ^a	Present theory	Expt.
$C_3 - C_2$	30	33.5	33.5 ^b
$C_2 - C_1$	16	11.6	7.5 ^b
$C_1 - A$		10.9	10.3 ^b
Scissors–Wagging		262	273 ^c
Low energy–Wagging		–158	

^aReference 13.

^bReference 5.

^cReference 16.

because a mirror symmetry prevents these modes from coupling to modes polarized in the x - z plane. The frozen-phonon displacements are taken to be only 5.4×10^{-3} Å, but the anharmonicity is still not negligible, especially in the bond-stretching direction. This anharmonicity is corrected by subtracting the anharmonic component of the potential established in our previous work.⁴ The errors caused by the approximations described here (fixed Si atoms and correction of anharmonicity by a potential derived on a flat surface) are all very small, and the total error in the vibrational frequencies is expected to be less than 2%. Moreover, we are mainly interested in frequency differences, in which case these errors tend to cancel further.

From our calculations, the high-energy modes C_1 , C_2 , and C_3 are mainly the Si-H stretching vibrations corresponding to H(1), H(3), and H(2), respectively. The coupling between these stretching vibrations is small, and some weight is also carried on H(4). C_1 has about 81% of its weight on H(1), 6% on H(3), and 12% on H(4); C_2 has about 11% on H(1), 12% on H(2), 62% on H(3), and 14% on H(4); C_3 has about 2% on H(1), 85% on H(2), and 12% on H(3). The small coupling between stretching vibrations is in qualitative agreement with experiment.¹⁵ Quantitatively, however, the coupling is larger than the estimate of 2% extracted from the interpretation of the experiment. The frequency differences among modes A , C_1 , C_2 , and C_3 are listed in Table IV, and the agreement with experiment is better than expected.

Each H atom has two wagging modes, of which we only calculate one. Fortunately the wagging modes we calculate are by far the more interesting ones. Rowe *et al.*¹⁶ observed a sharp peak at 910 cm^{-1} , 273 cm^{-1} higher than the frequency of the wagging mode on a flat surface, in their electron energy-loss experiment, and assigned it as the “scissors mode” corresponding to the two atoms H(1) and H(2) attached to Si(1) moving against each other. This mode also comes out of our calculation, and the frequency difference between it and the wagging mode on a flat surface is 262 cm^{-1} , in good agreement with the

experimental result. We further predict that one more wagging mode is localized near the step which is yet to be observed. It is a low-energy mode corresponding to the atoms H(1) and H(2) moving in phase with each other, with a frequency about 160 cm^{-1} lower than the wagging frequency on a flat surface.

V. CONCLUSIONS

We have studied the relaxation and dynamical properties of steps on the Si(111):H surface from first principles. A supercell of 42 Si atoms and 12 H atoms plus two double layers of vacuum is used, and the computational effort is sizable. The use of ultrasoft pseudopotentials is important for describing the hard H atoms.

As pointed out by Raghavachari, Jakob, and Chabal, the interesting relaxations can all be ascribed to the strong repulsive interaction between two H atoms at the step. The SiH₂ unit on the edge of the step and the H atom on the lower terrace near the step all rotate away from the step, and the relaxation of the Si atoms goes deep into the bulk along a zigzag chain.

Three high-frequency phonon modes are found to be localized at the step, with frequency differences in excellent agreement with experiment. A “scissors mode” is found, in good agreement with experiment, and another low-frequency wagging mode is predicted which is also localized at the step.

ACKNOWLEDGMENTS

The authors are grateful to Y. Chabal, M. Hines, and J. Rowe in AT&T Bell Labs for stimulating discussions and for informing us of their newest experimental results. This work is supported by NSF Grant No. DMR-91-15342, and the Cray YMP time was provided by the National Center for Supercomputing Applications.

- * Present address: Biosym Technologies, Inc., 9685 Scranton Road, San Diego, CA 92121.
- ¹ G. S. Higashi, Y. J. Chabal, G. W. Trucks, and K. Raghavachari, *Appl. Phys. Lett.* **56**, 656 (1990).
- ² P. Guyot-Sionnest, P. Dumas, Y. J. Chabal, and G. S. Higashi, *Phys. Rev. Lett.* **64**, 2156 (1990).
- ³ P. Guyot-Sionnest, *Phys. Rev. Lett.* **67**, 2323 (1991).
- ⁴ X.-P. Li and D. Vanderbilt, *Phys. Rev. Lett.* **69**, 2543 (1992).
- ⁵ P. Jakob and Y. J. Chabal, *J. Chem. Phys.* **95**, 2897 (1991).
- ⁶ M. Morin, P. Jakob, N. J. Levinos, Y. J. Chabal, and A. L. Harris, *J. Chem. Phys.* **96**, 6203 (1992).
- ⁷ K. Kuhnke, M. Morin, P. Jakob, N. J. Levinos, Y. J. Chabal, and A. L. Harris, *J. Chem. Phys.* **99**, 6114 (1993).
- ⁸ P. Jakob, Y. J. Chabal, K. Raghavachari, and S. B. Christman, *Phys. Rev. B* **47**, 6839 (1993).
- ⁹ M. A. Hines, Y. J. Chabal, T. D. Harris, and A. L. Harris, *Phys. Rev. Lett.* **71**, 2280 (1993).
- ¹⁰ D. Vanderbilt, *Phys. Rev. B* **41**, 7892 (1990).
- ¹¹ A. M. Rappe, K. M. Rabe, E. Kaxiras, and J. D. Joannopoulos, *Phys. Rev. B* **41**, 1227 (1990).
- ¹² D. R. King-Smith and David Vanderbilt, *Phys. Rev. B* **49**, 5828 (1994).
- ¹³ K. Raghavachari, P. Jakob, and Y. J. Chabal, *Chem. Phys. Lett.* **206**, 156 (1993).
- ¹⁴ E. O. Kane, *Phys. Rev. B* **31**, 5199 (1985); **31**, 7865 (1985).
- ¹⁵ M. A. Hines, T. D. Harris, A. L. Harris, and Y. J. Chabal, *J. Electron Spectrosc. Relat. Phenom.* **64/65**, 183 (1993).
- ¹⁶ J. Rowe *et al.* (unpublished).