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Theoretical determination of surface atomic geometry: Si(001)-(2 × 1)

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An energy-minimization scheme for the determination of the surface atomic geometry is presented. Hellmann-Feynman forces and total energies are calculated using an *ab initio* self-consistent pseudopotential approach. When applied to the Si(001)-(2 × 1) reconstructed surface, a buckled dimer geometry is found to have minimum total energy. The dimer bond length is shorter than the bulk bond length, suggesting multiple bond character. Comparisons with other structural models are discussed.

The determination of surface atomic geometry has been a major problem in surface science. We present here a theoretical approach to this problem based on an energy-minimization scheme using an *ab initio* self-consistent pseudopotential approach.[1] This *ab initio* approach has been demonstrated to yield accurate results for a variety of structural properties for both extended systems (e.g., phase transformation, static properties, and lattice vibrations for the Si crystal[1]) and localized systems (e.g., bond length and vibrational frequency for the Si_2 molecule[2]). The only input information needed in the energy-minimization scheme are the atomic numbers of the constituent elements and the two-dimensional spatial periodicities of the surface. By computing the Hellmann-Feynman forces[3] and the total energies, the minimum-energy atomic geometry is reached without any empirical fitting parameters.

The Si(001) surface is chosen as a prototype. This surface is one of the most studied of all solid surfaces. Low-energy electron diffraction (LEED),[4–9] photoemission,[10,11] chemisorption,[12–14] He diffraction,[15] He^+-ion scattering,[16] and theoretical studies[17–23] have all contributed significantly to our understanding of the reconstructed Si(001) surface, but there is still no conclusive determination of the atomic arrangement for this surface.

Using the atomic number of Si, the *ab initio* pseudopotential is constructed[24] to reproduce the all-electron atomic results of the valence energy levels, valence wave functions outside the core, and excitation energies. A supercell method[25] is used to create (artificial) periodicity perpendicular to the surface. The unit cell consists of eight atomic layers of Si and a vacuum region equivalent to five layers of Si. Inversion symmetry is imposed to facilitate the computation.

For a given atomic geometry, we solve Schrödinger's equation iteratively to self-consistency.[25] A plane-wave basis set is used for the wave-function expansion, and exchange and correlation are approximated by the Wigner interpolation formula.[26] The kinetic energy cutoff E_{pw} for the plane-wave basis set and the number of k points used in the Brillouin-zone summation are increased until the calculated lattice constant for Si bulk, the calculated bond length of the Si_2 molecule, and the Hellmann-Feynman forces are all convergent.[27] The total energy and Hellmann-Feynman forces on the atoms are calculated in the momentum space.[28] To find the most stable atomic arrangement, the atoms are further displaced using Hellmann-Feynman forces as a guide. The entire procedure is repeated until all the Hellmann-Feynman forces are sufficiently small[29]; that is, the total energy is minimized. The accuracy of the Hellmann-Feynman forces has been tested[30] in the bulk frozen-phonon calculation. The results for the calculated phonon frequencies are as accurate as those obtained by using the total energy approach.[1]

For the ideal Si(001)-(1 × 1) surface, the energy required for the surface formation is calculated to be 2.5 eV per surface atom, which is close to the value 2.3 eV per surface atom evaluated from direct counting of broken bonds. (The bond energy is 2.3 eV.[31]) We further relaxed the (1 × 1) surface by moving atoms in the direction $(\hat{z})$ perpendicular to the surface to minimize the total energy. The calculated atomic displacements Δz_i for the ith layer (counting from the surface) from unrelaxed positions are (in Å): $\Delta z_1 = -0.145$, $\Delta z_2 = -0.077$, $\Delta z_3 = -0.049$, and $\Delta z_4 = -0.018$. The energy gain from the relaxation is 0.03 eV per surface atom.

To examine the (2 × 1) reconstruction, we start with the simple dimer model[4,12] where only surface atoms are reconstructed to form a symmetric dimer with dimer bond length equal to the bulk bond length. The total energy of this geometry is lower than the (1 × 1) ideal structure by 1.5 eV per dimer. This is not a stable system since the Hellmann-Feynman forces acting on the atoms are still relatively large as shown in Fig. 1. While the forces on subsurface layers indicate that the directions of the

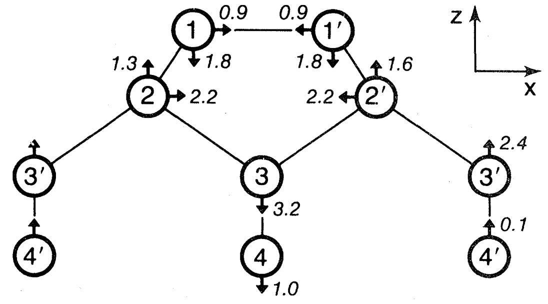


FIG. 1. Side view of the simple symmetric dimer model (Ref. 2 and 12) of Si(001)-(2 × 1). Atoms 1 and 1′ are in the surface layer, 2 and 2′ in the second, etc. The arrows and the corresponding numbers (in units of 10^{-2} Ry/a.u.) refer to the Hellmann-Feynman forces. The x components of the forces in the third and fourth layers are all smaller than 0.003 Ry/a.u. and not shown in this figure. The slight loss of reflection symmetry for the forces with respect to the perpendicular plane bisecting the graph arises from the artificial supercell geometry.

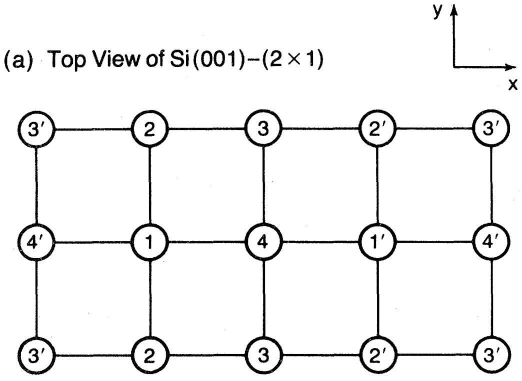
reconstruction are in general agreement with those proposed by Appelbaum and Hamann[21] using a Keating force-constant model,[32] the forces on the surface dimer suggest a dimer bond contraction rather than a bond elongation as proposed in Ref. 21.

To reach the minimum energy structure, we relax the atoms in the x and z directions (see Fig. 1). There are 16 degrees of freedom, and 18 possible atomic geometries are tried. A buckled dimer geometry is found to be the most stable structure. The energy is lower than the ideal (1 × 1) surface by 1.7 eV per dimer. The reconstruction parameters are shown in Fig. 2. This system is semiconducting in agreement with the photoemission results.[11]

The most important feature differing from previous dimer models[4,9,12,21,22] is that the dimer bond length (2.25 Å) is shorter than the bulk single-bond length (2.35 Å) and longer than the double-bond length [2.14 Å (Ref. 33)]. If we use the empirical equation by Pauling,[33] the bond order is calculated to be 1.4. This can be understood in simple chemical and physical terms. To satisfy the broken bonds of the surface atoms, the dimer is required to be doubly bonded. The directional forces acting on the dimer from the subsurface layers tend to pull the dimer apart. These two effects combine to give a bonding strength which is between the single and double bonds. The character of this multiple bond emerges naturally from our formalism in which valence electrons are allowed to propagate throughout the system self-consistently.

The back bond between atoms 1′ and 2′ (Fig. 2) is also strengthened but by a smaller amount. The bond length is 2.30 Å. The other back bond between atoms 1 and 2 has a negligible contraction of 0.01 Å compared to the bulk bond length. The remaining bond lengths in the system are within 2% of the bulk values.

(a) Top View of Si(001)-(2 × 1)



(b) Side View of Si(001)-(2 × 1) (Å)

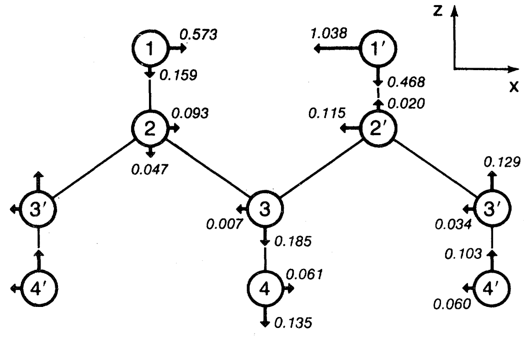


FIG. 2. Top and side view of Si(001). Atoms 1 and 1′ are in the surface layer, 2 and 2′ in the second, etc. The arrows and the corresponding numbers (in units of Å) refer to the atomic displacements from the ideal bulk positions. As described in the text, the displacements in the fourth layer have a large error (~0.05 Å) because of the artificial inversion symmetry used in the supercell geometry.

To give further support to our atomic geometry, we have calculated the equilibrium bulk and molecular (Si_2) bond lengths with the same E_{pw} as used in the surface calculation. The calculated bond lengths are 2.33 Å (experimental 2.35 Å) for Si bulk and 2.25 Å [experimental 2.246 Å (Ref. 34)] for Si_2. With both the extended (Si bulk) and the localized (Si_2) bonding character correctly described in the theory, our prediction for the atomic geometry on the Si(001)-(2 × 1) surface should be realistic. However, a few words of caution are in order. The artificially imposed inversion symmetry renders the atomic displacements in the innermost layers less reliable (error estimated to be ~0.05 Å). This effect diminishes for layers closer to the surface which are away from the inversion point. The displacements in the $\hat{y}$ direction are not considered in this calculation. We would expect to find a similar dimer bond contraction

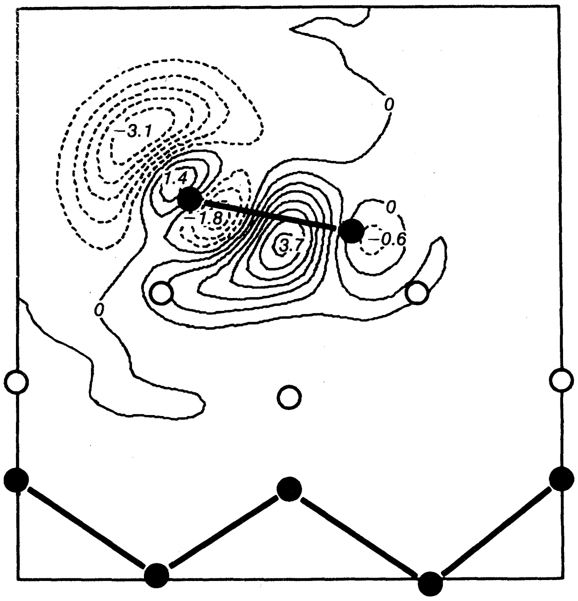


FIG. 3. Contour plot (in the xz plane indicated in Fig. 2) of the change in valence charge density (in units of $e/270$ a.u.^{3}) as the dimer bond is shortened from 2.35 Å [Chadi (Ref. 22)] to 2.25 Å for the buckled dimer models of Si(001)-(2 × 1). Dashed lines represent negative contours. The contour spacing is 0.5. The solid circles, the open circles, and the solid lines represent the atoms on the plane, the projections of the atoms not on the plane, and the schematic covalent bonds, respectively. See text for details.

even if these y displacements were included.

We also calculate the system with the atomic geometry of the buckled dimer model[22] proposed by Chadi and find that the energy is higher than our minimum energy geometry by 0.18 eV per dimer. Because of the geometry of the supercell (eight-layer slab with artificial inversion symmetry), the bonds between the central layers for Chadi's model are strained which accounts for part of this energy difference. To obtain a more meaningful comparison, we also calculate the total energy for the system which has the same subsurface atomic arrangement as proposed by Chadi, but the dimer bond is shortened to 2.25 Å (specifically, the surface atoms 1 and 1′ are displaced to give the same bond lengths between atoms: 1 − 1′, 1 − 2, and 1′ − 2′ as the corresponding ones in our minimum energy system). This system is more stable than that of Chadi's geometry by 0.10 eV per dimer. To illustrate the strenghtening of the dimer bond, Fig. 3 shows the electronic charge redistribution as the dimer bond is shortened. The electronic charge density is seen to move from the antibonding region near the up atom to the bonding region. This charge redistribution strengthens the dimer bond.

From this calculation and previous research, some physical aspects of the Si(001)-(2 × 1) surface become clear: (i) The ideal or relaxed (1 × 1) surface is unstable with respect to dimer formation which greatly stabilizes the system; (ii) a buckled dimer is more stable than the symmetric dimer because of a Peierls type of distortion; and (iii) the dimer bond is contracted from the bulk bond and exhibits a multiple bonding character.

The surface contraction of Si(001)-(1 × 1)2H has recently been measured to be 0.08 ± 0.03 Å by ion channeling and blocking experiments.[35] Because the major effect of H adsorption is to satisfy the dangling surface states, its influence on the surface contraction should be small. In our study on the relaxation of the Si(001)-(1 × 1) surface, the surface contraction is calculated to be 0.07 Å $(|\Delta z_1 - \Delta z_2|)$. Both the experiment and the theory lead independently to the same result (within error range).

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