Structural, Electronic, and Vibrational Properties of Si(111)-2×1 from *Ab Initio* Molecular Dynamics

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We present the results of an *ab initio* molecular-dynamics study of the Si(111) surface at low temperatures. Our findings for the equilibrium structure confirm the Pandey (2×1) chain model and are in very good agreement with both LEED and medium-energy ion-scattering data, showing in particular a large buckling of the surface chains. We describe the dynamical path followed during the reconstruction from the ideal bulk-terminated surface, which is found to be unstable. The phonon spectrum, which is calculated *ab initio* for the first time, shows well-defined surface modes at frequencies close to the measured values.

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One of the central issues of semiconductor surface physics is the reconstruction that the surface layers often undergo with respect to the bulk structure. In particular, key questions are the details of the resulting structure, its formation process, and the induced changes on the electronic and vibrational properties. The Si(111)-2×1 surface, which appears on cleaved surfaces at low temperature, although apparently simple, has several intriguing and not completely understood features in spite of almost twenty years of experimental and theoretical effort.[1] The basic key to understand the properties of this surface[2-4] was provided about ten years ago by Pandey's proposal for a structural model known as the π-bonded chain model.[5] However, in spite of the success of the model and of its subsequent refinements,[6,7] several issues remain open. In fact, a substantial buckling of the topmost layer chains ($b = 0.34$–0.4 Å) is essential for a quantitative interpretation of the low-energy electron-diffraction[8-10] (LEED) and medium-energy ion-scattering[11] (MEIS) data. This is at variance with Pandey's original suggestion[5] of $b = 0$ and Northrup and Cohen's (NC) value of $b = 0.1$ Å.[6] The energetics of the chain formation was also calculated by NC.[6] The calculations, however, were based on an educated guess for the reconstruction path, which in particular chooses the "buckled" (1×1) model as the starting configuration, rather than the (1×1) bulk-terminated geometry. The experimentally determined surface vibrational properties of Si(111)-2×1 exhibit a number of interesting features among which emerge a dispersionless mode at low energies[12] (∼10 meV) and a strongly dipole-active mode detected in the optic region (∼56 meV).[13] Different experiments,[14,15] however, suggest conflicting interpretations of the nature of the latter mode, which the available semiempirical calculations[16,17] are not able to solve. In fact, one approach, based on an empirical tight-binding model,[16] assigns the mode to a longitudinal-optical vibration of the topmost chains, while the other,[17] using a bond-charge model, ascribes it to a subsurface vibration polarized perpendicularly to the chains.

Such a state of affairs calls for an *ab initio* (i.e., nonparametrized and unbiased) approach, which is able to give an accurate description of static as well as dynamical properties of Si(111)-2×1. This is provided by the unified local-density-functional molecular-dynamics (MD) scheme[18] which in particular has been tested successfully for silicon in a variety of aggregation states.[19]

In this Letter, we present the first full application of the *ab initio* MD method to study a surface. In fact, while previous pioneering applications[20] of the method to surface studies where limited to geometry optimization from educated guesses, here we obtain without assumption the following main results: (i) The ideal (1×1) surface is unstable. It spontaneously evolves towards a Pandey-like 2×1 reconstructed surface and the transformation path is determined. (ii) The structural and electronic properties of the reconstructed surface are in much better agreement with experiments than are previous theories, showing in particular a substantial buckling of the surface chains. (iii) The main characteristics of the surface vibrational spectrum are satisfactorily reproduced and our assignment of the dipole-active mode supports the conclusion drawn in Ref. 16.

The details of the calculations not specified here are like those in Ref. 19. The geometry chosen is that of a periodically repeated slab of 64 Si atoms (8 atoms/layer), with one surface terminated by 8 H atoms, plus a vacuum region ∼9 Å wide. This leads to a ($\sqrt{3}$×4) surface supercell. For Si we have used norm-conserving pseudopotentials[21] with only s nonlocality, and only Bloch functions at the Γ point of this ($\sqrt{3}$×4) supercell were included. This corresponds to taking the following three **k** points of the (2×1) surface Brillouin zone (SBZ) into account: $\bar{\Gamma}$, $0.5\bar{\Gamma}\bar{J}$, $\bar{J}$. The energy cutoff for the plane-wave (PW) expansion was chosen at 8 Ry (corresponding to about 6000 PW's). In the MD runs performed at constant energy and fixed volume, a time step of 1.9×10^{-4} ps and a mass parameter for the electronic degrees of freedom of 400 a.u. were used. Six layers of Si atoms were allowed to move in all the calculations.[22]

We made an extensive search of the optimal surface geometry for the slab by means of a series of different calculations. Note that, due to periodic boundary conditions and to our choice of a $(\sqrt{3}\times 4)$ surface supercell, the search is restricted to surface patterns commensurate with the $(\sqrt{3}\times 4)$ surface supercell periodicity. Thus we exclude from the outset other and possibly more stable reconstructions such as the 7×7. Another restriction is of course that we keep the number of atoms constant. Otherwise our search is totally unbiased and no additional assumption is made. In a typical calculation we started from a surface with small random displacements of the atoms from the ideal positions. The spread of the displacements is similar to that induced by thermal motion at ~ 50 K. We then let the system evolve spontaneously under the action of the interionic forces. A spontaneous increase of the ionic temperature up to 300–400 K is observed. Since the total energy is conserved, this increase is due to a gain in ionic potential energy. The surface is then slowly cooled down to 0 K by rescaling the ionic velocities. The entire duration of a run is typically 4000–5000 time steps. Typical structures which characterize the reconstruction process are illustrated in Fig. 1. Characteristic features are the tendency of the atoms to approximately preserve the bond length, and the bond-switching process between 1(b) and 1(c), which leads to the formation of the fivefold and sevenfold rings. The ensuing intermediate structure [1(c), chain "high"] is already chainlike, but the direction of the tilt angle of the topmost chains relative to the substrate is reversed. In the final phase 1(d), however, which corresponds to the lowest energy, the sign of the tilt is changed in agreement with experiment. Calculations with different initial random displacements and with different annealing schedules were performed. We invariably obtained the 1(d) structure, however small the initial displacement amplitude. When we performed steepest-descent calculations, we found instead that the final state was influenced by the starting configuration. In particular, when we started with a randomly displaced ideal surface, we ended with the chain "high" arrangement which is a shallow local minimum only 5 meV/(surface atom) higher in energy than the 1(d) structure. Such a tiny energy difference is smaller than the accuracy of the calculation. In contrast, when starting from the original Pandey coordinates the correct result was readily obtained. We have checked that steepest descent applied directly to the ideal surface would end up in a saddle point about 0.3 eV/(surface atom) higher than the 1(d) modification. (This saddle-point configuration corresponds in particular to a strong reduction of the highest two layers distance, i.e., to about 1.15 a.u.) This set of results unambiguously shows that the ideal surface is not a stable local minimum and that at least two relevant minima exist with the 2×1 periodicity and a chainlike structure. We have also verified the instability of the ideal (relaxed) surface with an independent *ab initio* calculation of the dynamical matrix[23] which shows the occurrence of a soft phonon mode at the zone edge (point M) of the 1×1 structure. The displacement pattern of the atoms in this mode is approximately equal to that of the initial stages of the transformation observed dynamically.

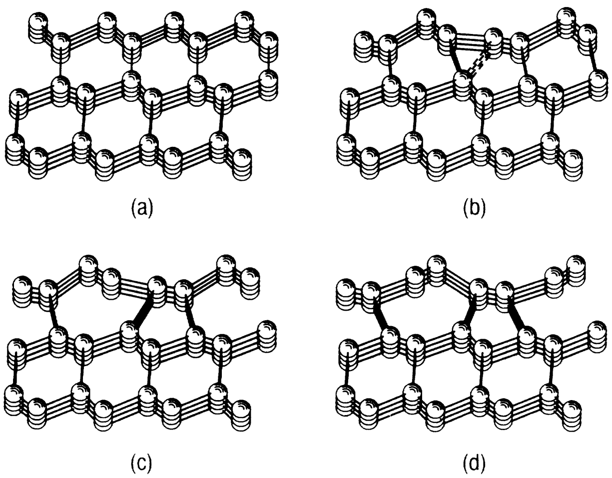

FIG. 1. Atomic structures, in the (110) plane, corresponding to selected instants in the reconstruction path: (a) ideal (initial), (b) one intermediate, (c) chain "high," and (d) chain "low" (final).

In agreement with NC calculations and with experiment, we find that the bonds along the topmost chains are slightly contracted with respect to bulk values (~ 2.2 Å). However, we find a substantial buckling of these chains ($b \sim 0.49$ Å), which is in better agreement with experiment. We also find that this buckling is accompanied by a net charge transfer from the "down" to the "up" atoms of the surface chains, with respect to the case $b=0$. This charge transfer is likely to have a stabilizing effect, which could possibly explain the large value of b observed. In Table I, we give the values obtained for the buckling of the first six layers for our geometry and compare them with the results of the refinement of LEED data[9] and with NC predictions.[6,24] The final details of our results could still depend on the number N_k of k points sampled. In order to check the stability of our results relative to the sampling of the SBZ we have

TABLE I. Buckling of different layers (in Å).

Layer	This work	LEED (Ref. 9)	NC (Ref. 6)
1	0.49	0.38 ± 0.8	0.10
2	0.04	0.07	0.05
3	0.02	0.07	0.08
4	0.27	0.20	0.30
5	0.16	0.13	0.20
6	0.01	0.03	···

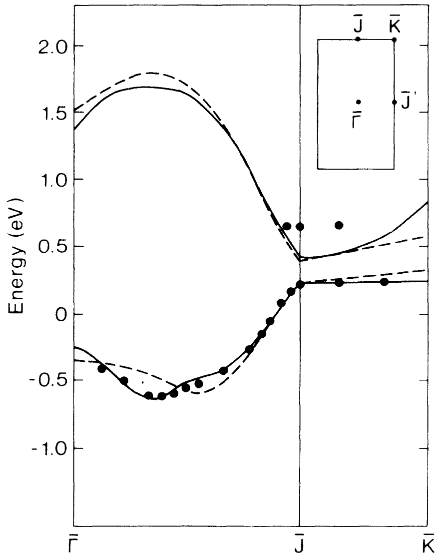

FIG. 2. Dispersion of surface-state energies. Circles: from experiment (Ref. 25); dashed line: from Ref. 6; and solid line: this work.

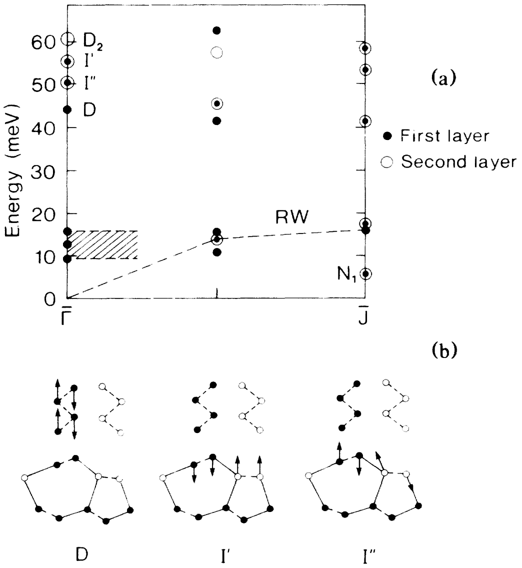

FIG. 3. (a) Calculated phonon dispersion along the $\bar{\Gamma}$-$\bar{J}$ direction and (b) displacement pattern of a few selected modes. The symbols indicate where the modes are mainly localized.

made total-energy calculations at fixed ionic positions for several structures (ideal, original Pandey model, NC geometry, and ours) and for increasingly finer meshes of uniformly distributed k points, i.e., with $N_k = 3$, 8, and 15 in the irreducible segment. The structural energy differences converge already for $N_k = 8$. On passing from $N_k = 3$ to $N_k = 8$, they decrease only by 0.03–0.04 eV/atom. In particular, the results confirm that our optimized chain structure is lower in energy than that of NC (by 0.04 eV/atom).

The variation in the structure that we find with respect to NC predictions does not affect the energy dispersion of the occupied states very much. Indeed, as shown in Fig. 2, the dispersion of the band of the surface states along the Γ-$\bar{J}$ direction turns out to be in excellent agreement with the most recent photoemission data.[25]

Finally, we have studied the vibrational properties of Si(111)-2×1 from the calculation of the ionic trajectories generated in an equilibrium MD run at ~120 K, which was followed for ~2 ps. By analyzing the velocity-velocity correlation function with a particularly efficient and accurate signal processing method,[26] we have obtained the phonon density of states and the k-resolved phonon spectral density. Also, for a few selected modes we have obtained an approximation for the eigenvectors through the correlation functions $\langle v_Q(t) \times v_Q(0)\rangle$, where $v_Q = \sum_i \mathbf{v}_i \cdot \mathbf{Q}_i$ is the projection of the ion velocities onto a guessed displacement field $\{\mathbf{Q}_i\}$. Some details have been reported elsewhere.[27]

An analysis of the local phonon density of states shows that the behavior of the third and fourth layers is already almost "bulklike" and that surface effects are confined to the top two layers. In Fig. 3(a) we show the calculated phonon energies at $\bar{\Gamma}$, $0.5\bar{\Gamma}\bar{J}$, and $\bar{J}$ and indicate with a symbol the layer(s) in which each mode is mostly localized.

In the acoustic region of the spectrum we find (i) the Rayleigh wave which is slightly higher than that observed,[12] (ii) several modes at $\bar{\Gamma}$ and $0.5\bar{\Gamma}\bar{J}$ grouping around 10 meV, in agreement with He-scattering experiments,[12] and (iii) a mode at $\bar{J}$ at about 5 meV which corresponds to a modulation of the buckling of the surface chains. This mode, although much too low in energy, resembles the N_1 mode of Ref. 16.

In the optic region at $\bar{\Gamma}$ the most relevant surface features are two longitudinal-optical vibrations along the first (D) and second (D_2) layer chains at ~44 and ~60 meV, respectively, and two subsurface yz-polarized modes at ~55 meV (I') and ~50 meV (I'') [see Fig. 3(b)].

In order to compare our findings with electron-energy-loss spectroscopy (EELS) results, we have calculated the longitudinal effective charges Z_L^* which determine the macroscopic polarization associated with each of the above modes.[28] The calculations were performed with the direct method introduced by Martin and Kunc.[28] In a few cases, we have repeated some computations with the linear-response approach[23,29] and checked for convergence relative to SBZ sampling. The two methods gave the same results within numerical accuracy. As a figure of merit we quote that we satisfy the acoustic sum rule $\sum_i (Z_L)^*_{\alpha\beta,i} = 0$ within ~(20–30)% of a typical Z_L^* value.

Our results indicate that the D mode has by far the largest polarization, thus supporting the empirical tight-binding calculations and the assignment based on recent

EELS. Instead, the I' mode, which corresponds to the prediction of the bond-charge model,[17] has a comparably small dipole moment.

The overall comparison of our results with the experiments is quite good except for the 5-meV mode at $\bar{J}$, which is not observed experimentally, and for the low frequency of the D mode (44 meV). This is due to our restricted sampling of the SBZ, which overweighs the coupling of these modes to the states at the zone edge. We have tested this point by performing more conventional dynamical matrix calculations using the approach of Ref. 23 which allows the inclusion of a much larger set of k points.[30] While most of the modes are unaffected, the D-mode frequency now becomes ~ 57 meV, very close to the experimental value of ~ 56 meV, and the frequency of the N_1 mode is shifted to 12 meV. Hence, the latter mode can now be assigned to the dispersionless branch observed experimentally at around 10 meV. These more refined calculations also show a strong anisotropic dipolar activity at ~ 57 meV, and a small isotropic contribution from the I' and I'' modes.

In conclusion, we have presented a new *ab initio* study of the structural, electronic, and vibrational properties of Si(111)-2×1, which gives a picture consistent with various experimental data. In particular, we confirm the Pandey-like chain structure. We find the existence of an additional relevant local minimum of the potential-energy surface, with "reverse" tilting of the topmost chains and separated from the lowest-energy isomer by a small barrier. The coexistence of these two structures may result in domains, which could be detected by either LEED with high coherence length or scanning-tunneling-microscopy imaging with large scan. Our study shows that *ab initio* molecular-dynamics studies of surface reconstructions are feasible and that much more complicated problems can soon be tackled in this area of physics.

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