Ab Initio Molecular-Dynamics Study of Defects on the Reconstructed Si(001) Surface

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We present a new defect model for the reconstructed Si(001) surface. *Ab initio* molecular-dynamics simulations at finite temperature show the existence of interstitial dimers which are recessed from the surface. These dimers and adjacent on-surface dimers are both symmetric. The possibility that missing dimer vacancies observed by scanning tunneling microscopy contain these new surface defects is pointed out.

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Due in part to their great technological importance in the semiconductor microfabrication of devices, and in part to the geometrical beauty of various patterns in atomic structures, semiconductor surfaces have been a subject of continued interest for the last three decades.[1,2] The Si(001) surface has been one of the most intensively studied of all semiconductor surfaces, but there has been no definite conclusion regarding its detailed atomic structure. Early diffraction studies showed that the surface has 2×1 symmetry.[1] The majority of later experimental studies[3-10] have also supported a 2×1 structure, although some of them have also reported higher-order $c(4\times2)$, $p(2\times2)$, and $c(2\times2)$ symmetry.[6-9] Models[11] which have been proposed to explain these experimental results can be grouped into three types, namely, dimer, vacancy, and conjugated-chain models. Of these, the dimer model seems to be the most probable. In this model the 2×1 symmetric structure is explained by dimer reconstruction of the surface atoms: Pairs of atoms on the ideal bulk sites on the surface, and which have two dangling bonds per atom, move towards each other to form bonds or dimers in order to reduce the total energy.[12]

Total-energy minimization calculations based on the dimer model have been performed to determine the ground-state geometry of the reconstructed Si(001) surface. Chadi,[13,14] Ihm, Cohen, and Chadi,[15] and Yin and Cohen[16] showed the asymmetric dimer, in which one atom buckles away from the surface while the other buckles in from the surface, to be energetically more favorable than the symmetric dimer. Almost all observed higher-order symmetric patterns on the surface can be successfully classified in terms of the different arrangements and/or orientations of the unit asymmetric dimer.[17] Furthermore, this model, which gives partially ionic bonds between surface atoms, successfully accounts for both the diffraction and photoemission data. However, some slightly modified models have also been proposed.[3-7,18]

Recent images of scanning tunneling microscopy[19] (STM) by Hamers and co-workers show the room-temperature surface to consist of areas with varying symmetry. Both symmetric and asymmetric dimers are observed. Symmetric dimers give 2×1 periodicity, whereas asymmetric dimers yield also $c(4\times2)$ and $p(2\times2)$ symmetric areas. The surface also contains a high density of defects, generally interpreted as dimer vacancies, which are randomly distributed over the surface. These defects often form small clusters, and the surface dimers near such clusters are asymmetric. These defects also appear occasionally in the symmetric dimer rows as individual dimer vacancies. This is similar to the missing dimer models proposed by Pandey.[20] Hamers and co-workers interpreted their observations as follows: (1) Many of the dimers which appear to be symmetric by STM may be actually rapidly flipping between the two buckling directions; (2) the presence of defects may prohibit the time-dependent flipping of dimers, leading to the static asymmetric dimers. It is appropriate therefore that the dynamics of dimers and of surface defects be investigated theoretically, in order to gain some insight into surface reconstruction.

Molecular dynamics is a powerful method for studying both structural and dynamical properties without requiring accurate initial geometrical information. Molecular-dynamics simulations of the Si(001) surface,[21,22] using empirical Stillinger-Weber potentials suggest that the surface consists of many areas of symmetric dimers, in which approximately 20%–30% of atoms are nondimerized. This ratio of defectiveness is consistent with the results of the STM.[19] However, the same STM experiments do not confirm the presence of nondimerized atoms, but rather what are apparently dimer vacancies. This indicates that empirical interatomic potentials cannot model the subtleties of atomic interaction on the Si(001) surfaces, and that the electronic structure should be explicitly calculated using quantum mechanics. *Ab initio* molecular dynamics using dynamical simulated annealing, first proposed by Car and Parrinello,[23] is suited to this approach. Thus the aim of our study is to clarify the defect structure and dynamical properties of dimers on the Si(001) surface by using *ab initio* molecular dynamics. In this Letter we report a new type of defect which may have been interpreted as a "dimer vacancy" in STM topography studies, which is quite different from the "dimer vacancy model" proposed by Pandey. A detailed analysis of dynamical properties will be discussed in a following paper.

In the original Car and Parrinello scheme, the calculation of electronic states in the framework of density-functional theory and time integration of Newton's equations of motion of the atomic coordinates are ingeniously combined through the Lagrangian formalism, thereby realizing a faster calculation than the conventional *ab initio* molecular-dynamics scheme. From the Lagrangian, one can derive the second-order differential equations of motion for both atomic coordinates and electronic wave functions. Our scheme is significantly different from their original scheme. In particular, in order to increase efficiency, we use the first-order equations for dynamical simulated annealing of the electronic wave functions.[24,25] The equation of motion is

$$\zeta \partial |m,t\rangle/\partial t = -(H-\varepsilon_m)|m,t\rangle , \qquad (1)$$

where H is the total Hamiltonian of the system, ζ is the convergence factor, $|m,t\rangle$ is an eigenvector of state m at time t, and $\varepsilon_m = \langle m,t|H|m,t\rangle$. The diagonal part of Eq. (1) is integrated analytically in a similar manner to that adopted by Payne, Joannopoulos, Allan, Teter, and Vanderbilt[26] in solving the electronic wave functions in the original Car and Parrinello formalism. Integration of (1) yields

$$\langle k|m,t+\Delta t\rangle = \exp(-\lambda_k^m \Delta t)\langle k|m,t\rangle - \{[1-\exp(-\lambda_k^m\Delta t)]/\lambda_k^m \zeta\}\sum_{k'}\langle k|H'|k'\rangle\langle k'|m,t\rangle , \qquad (2)$$

where Δt is a time step, and H' is the nondiagonal part of H, with its diagonal D giving $\lambda_k^m = (\langle k|D|k\rangle - \varepsilon_m)/\zeta$, in terms of a plane wave $|k\rangle$ and $|m,t\rangle = \sum_k |k\rangle\langle k|m,t\rangle$. Then, orthogonality is maintained by employing the Gram-Schmidt scheme. In each time step, self-consistency is checked. Only in the case of nonacceptable numerical error are additional calculations for the electronic state performed to ensure accurate Hellmann-Feynman forces. In this manner, the stability of the calculation is ensured, and the convergence time is 20 times faster than that of the original Car and Parrinello formalism, at least in the early stages of simulation.

In our simulation, the surface was modeled by a six-layer slab. Each layer contained four atoms, and the vacuum region was 6.5 Å deep. Periodic boundary conditions were applied to all directions. The atoms in the two lowest layers were fixed in their bulk positions, while those in the upper four layers were allowed to move freely. We used the local-density potential of Ceperley and Alder[27] parametrized by Perdew and Zunger[28] to compute the total energy. In the dynamical simulations, the local pseudopotential of Ihm and Cohen[29] was employed, the energy cutoff was 6 Ry (1750 plane waves), and the charge density was calculated by Γ-point sampling. (For the precise static total-energy calculations, which were performed to confirm our new defect structure, the norm-conserving pseudopotentials[30] including s, p, and d nonlocality, a 10-Ry energy cutoff, and four-k-point sampling were used.) Here dangling bonds of the bottom surface layer were saturated by hydrogen atoms.

The integration of equations of motion for atomic coordinates was performed by the leap-frog algorithm with a time step of 0.5 fs. Simulation runs, which comprised 3000 steps (1.5 ps), were initialized with atoms at ideal lattice sites. The initial temperature was 300 K, and the velocity distributions were varied in each of several runs. The excess energy, which stems from relaxation, and the formation of surface atom dimers, was removed by rescaling the velocities every step for the first 200 steps, and thereafter more gradually, with total energy being conserved after 800 steps. The averaged atomic positions were obtained from the next 2000 steps which had an equilibrium time-averaged temperature of approximately 200 K in each simulation. All the simula-

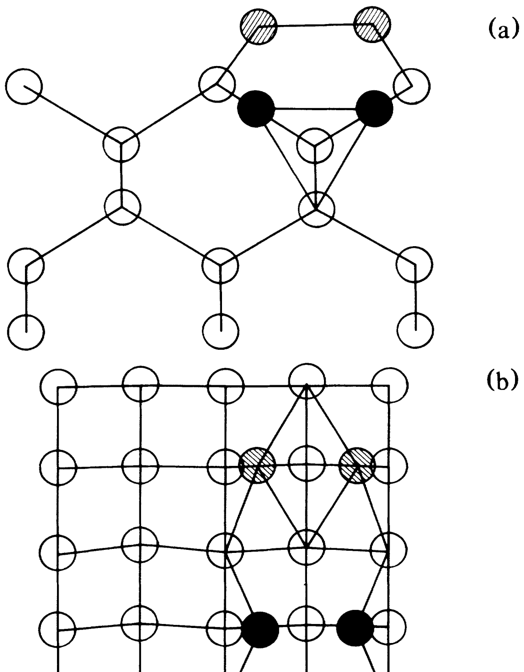

FIG. 1. (a) Side view of the interstitial dimer geometry of Si(001) surface. (b) Top view of the interstitial dimer model. Solid circles, shaded circles, and open circles stand for Si atoms at the positions of the interstitial dimer, the dimer on the surface, and the relaxed inner layers, respectively.

tions were performed on the supercomputers HITAC S-810 and S-820.

The formation of two (110) dimers in the free Si(001) surface was observed in every simulation run. In most simulations, 2×1 structures, which stem from asymmetric dimers, were obtained. However, a new defect dimer structure (Fig. 1) was found in some of the simulations. This structure was formed during the first 1000 steps and persisted to the end of the simulations. The most characteristic difference from previous dimer models[1-20,31,32] is that one dimer is recessed from the surface and is located at the interstitial position. Therefore, we will refer to this dimer as the interstitial dimer. The total energy of the interstitial dimer configuration (Fig. 1, interstitial dimer plus an on-surface symmetric dimer) is 2.05 eV/dimer less than that of the ideal surface. This value is obtained by dividing the total-energy difference between the two configurations by the number of dimers. As is clear from Fig. 1, the interstitial dimer is symmetric (the amplitude of dynamical buckling is less than 0.03 Å). Furthermore, the dimer on the surface is also neither buckled nor twisted. The interstitial dimer seems to prohibit buckling of an adjacent dimer on the surface. The average bond length of the interstitial dimer over a time interval of 1.0 ps (from 0.5 to 1.5 ps) is 2.33 Å, and that of the on-surface dimer is 2.24 Å (see Table I). These two values are close to the corresponding values of other dimer models. The bond length of the on-surface dimer accompanied by the interstitial dimer is much closer to that of the model of Pandey[20] and of Yin and Cohen.[16] Since this value is close to that of the Si_2 molecule, bonding of the dimer on the surface may have a localized character. On the other hand, the value of the bond length of the interstitial dimer is closer to that of the bulk length. Thus it has an extended character.

We performed precise static calculations, in order to get better estimates for the stability of the defect structure. The total energy is at most 0.37 eV/dimer higher than the energy of symmetric dimer models also found by us. This value is for the interstitial dimer at a concentration of 0.5 defects/(lattice unit)^2. The energy of the "isolated" interstitial dimer is expected to be lower, since relaxation of the surface up to some distance from the defect would occur. Dynamical screening arising from the vibration of dimers perpendicular to the surface should also lower the energy. Neither effect could be considered here. Therefore it is highly probable that the interstitial dimer, a new type of surface defect, exists at finite temperatures well below the melting point. Note that our total-energy calculations predict the energy difference (in the 2×1 structure) between the symmetric and asymmetric dimers to be small (the former are 0.01 eV/dimer lower than the latter).

As we stated earlier, in the STM images obtained by Hamers and co-workers,[19] there are what appear to be dimer vacancies in the symmetric dimer rows. Since the topograph obtained by STM is a reflection of the geometry of the top surface layer, the interstitial dimer would give the same image as a missing dimer or a dimer vacancy. Therefore, it is possible that at least some of the defects observed by Hamers and co-workers, previously thought to consist solely of dimer vacancies, are in fact interstitial dimers. If the lower layers could be seen with use of a high-resolution STM, the distinction between the interstitial dimer proposed here and the dimer vacancy would be made. However, no such study has been reported in the literature.

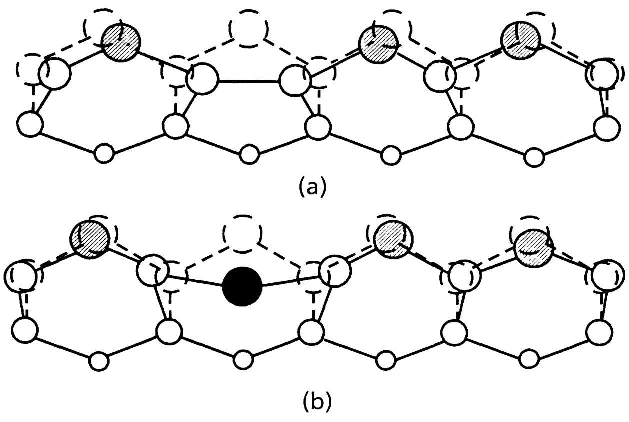

FIG. 2. Side views of (a) the missing dimer model proposed by Pandey (Ref. 20) and (b) the interstitial dimer model. Solid circles, shaded circles, open circles, and broken open circles stand for Si atoms at the positions of the interstitial dimer, the (normal) dimer on the surface, the relaxed inner layers, and the ideal bulk structure, respectively.

Finally, we consider the relationship of the interstitial dimer model to the missing dimer or the dimer vacancy model proposed by Pandey (see Fig. 2). From the static total-energy calculation,[20] Pandey proposed that a surface consisting of symmetric dimers, with dimer vacancies, could be energetically more favorable than one composed of asymmetric dimers, without dimer vacancies. In Pandey's model, the dimer vacancies play a twofold role in lowering the surface energy. First, they allow the formation of a dimer in the second layer, thereby reducing the number of net dangling bonds by two. Second, they increase the planarity of the surface, leading to an increase in the degree of π bonding. Thus, the distance in the [110] direction between the two dimers next to the dimer vacancy decreases. Meanwhile, for the interstitial dimer model, the distance of the two on-surface dimers next to the interstitial dimer will increase as illustrated in Fig. 2, because the displacements of the second-layer atoms bonded to the interstitial dimer are expansive (see Table I). Recent calculations[33] show that a dimer vacancy may be created at a cost of 0.28 eV/defect; this value indicates that dimer vacancies are more easily detected than interstitial dimers. However, the thermal energy associated with the annealing process for silicon (higher than 0.1 eV) is sufficient to overcome the kinetic-energy barrier to formation of the interstitial

TABLE I. Atomic coordinates (in units of Å) of the top three layers for the interstitial dimer geometry. Atoms 1–4 are the fourth layer; atoms 5–8 are the third layer; atoms 9–12 are the second layer; atoms 13–16 are the surface layer.

No.	[100]	[010]	[001]	No.	[100]	[010]	[001]
1	2.037	1.910	2.475	9	0.185	0.016	5.010
2	5.826	1.910	2.544	10	3.678	0.037	5.100
3	2.053	5.752	2.544	11	0.180	3.858	4.989
4	5.773	5.752	2.586	12	3.720	3.852	5.190
5	0.116	1.921	3.777	13	1.910	0.783	6.349
6	3.847	1.958	3.867	14	5.773	0.757	4.576
7	0.064	5.779	3.761	15	1.894	3.027	6.301
8	3.921	5.763	3.912	16	5.784	3.085	4.603

dimer (which we expect to be slightly greater than the formation energy). Direct comparison of these defects would be interesting, but lies beyond the scope of this work because of differences in simulation conditions (e.g., number of particles) necessitated by considerations of prohibitive computational expense.

In summary, we have applied *ab initio* molecular dynamics employing first-order equations of motion for the electronic wave functions, to the study of the 2×1 structure on Si(100) surface. Our calculations predict the existence of an interstitial dimer, which is symmetric and recessed from the surface. We proposed that some of the defects which have been assigned to dimer vacancies are actually interstitial dimers, a previously unreported type of surface defect. We believe that the proposed model should also be applicable to Ge(001).

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