SURFACE SCIENCE LETTERS

SUBPICOSECOND INTERCONVERSION OF BUCKLED AND SYMMETRIC DIMERS ON Si(100)

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Finite temperature molecular dynamics simulations provide the first theoretical evidence for subpicosecond dynamical behavior on a defect-free Si(100) surface; the instantaneous distribution of buckled and symmetric dimers is found to be ~ 2 : 3; buckled dimers *rapidly interconvert* with symmetric dimers, with the buckling direction alternating along a row; only symmetric dimers are observed on a time average; and we find that collective motion of ≥ 5 Si layers is involved in the reconstruction. Thus, the observed surface structure should depend on experimental time scales.

Despite numerous experimental [1–6] and theoretical [1,7–14] studies designed to elucidate the structure of the reconstructed Si(100) surface, the definitive configuration of the surface and near-surface atoms remains controversial. Low-energy-electron-diffraction (LEED) [1,2], He diffraction [3], ion scattering (ISS) [1,4], photoemission (PES) [1,5], and scanning tunnelling microscopy (STM) [1,6] have all led to the conclusion that the surface is composed of dimers in p(2 × 1), p(2 × 2), and/or c(4 × 2) domains. These have been interpreted in terms of dimers that are symmetric, buckled, and/or laterally-twisted.

Theoretical predictions have been as controversial as the experiments. Quantum mechanical calculations have been unable to resolve this structural issue, since some theories favor symmetric dimers [1,7,8], while others predict buckled dimers to be the global minimum energy structure [9,10]. Energy minimization calculations using molecular dynamics (MD) techniques yielded p(2 × 1) rows of symmetric dimers at $T = 0$ K [11,12]. Finite temperature MD simulations have also reported symmetric dimers, for a time-averaged structure [13].

The purpose of this Letter is to emphasize that previous studies of Si(100) reconstruction have mostly focussed on extracting one *static* structure to explain all of the experimental observations. We present the first theoretical evidence for an alternative, dynamical structure. The major conclusion is that a static picture is insufficient; our calculations indicate that a dynamic picture of the surface is more complete, in which buckled and symmetric dimers rapidly interconvert on a subpicosecond time scale [14].

The present report examines both the short-time dynamical behavior of the Si(100) surface during reconstruction and the final equilibrium structure. We have carried out microcanonical MD simulations of this process at three initial temperatures ($T_{init} = 100$ K, 298 K, and 500 K) starting from the bulk-terminated crystal. The interactions were modeled using the two- and three-body potential of Stillinger and Weber [15]. The classical equations of motion were integrated using the velocity Verlet algorithm, with a time step of 0.23 fs. The atoms were given random initial velocities chosen from a Gaussian distribution corresponding to the desired T_{init}. The surface was modeled by a two-dimensionally infinite slab containing either five or nine atomic layers. Each layer contained 72 atoms and was subject to periodic boundary conditions within the surface plane. In each calculation, the bottom layer was held fixed at the bulk positions. All of the simulations were run for a

total time of 10.35 ps, with the last 1.15 ps used to gather information about the equilibrium configuration of the system.

The surface layer configurations of the 9-layer slab after 9.2 ps for the three T_{init}'s are shown in fig. 1. The number of dimers formed along a particular row is strongly temperature dependent. The disorder increases with initial temperature, with up to seven dimers in a row for $T_{init} = 100$ K, no more than six for $T_{init} = 298$ K, and only four for $T_{init} = 500$ K. Defects in the form of isolated atoms were observed at all temperatures, in ~ 15% concentration. Over a very long simulation (~ 1
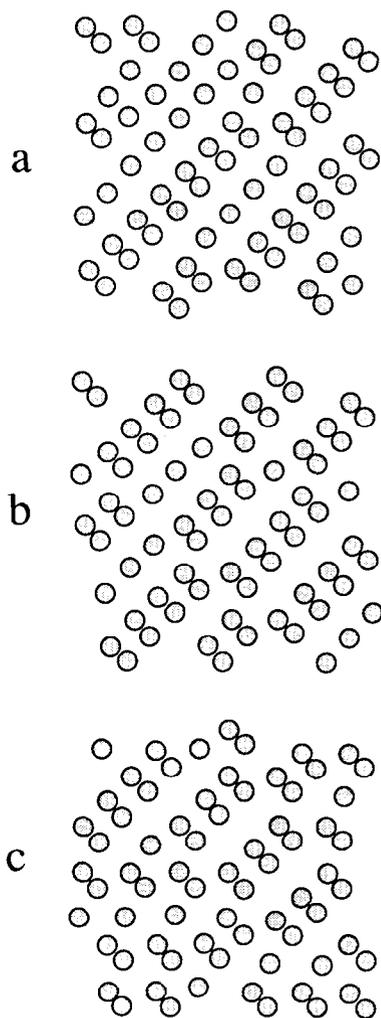

a

b

c

Fig. 1. Surface structures for the 9-layer slab at initial temperatures of: (a) 100 K, (b) 298 K, and (c) 500 K after 9.2 ps.

s), additional rearrangement eliminating isolated atoms undoubtedly would occur. Since such a simulation is currently impractical, a single run was performed where the surface atoms initially were displaced into a perfect p(2 × 1) pattern. The presence or lack of isolated atoms did not greatly affect the dynamic or static behaviour of the dimers [16].

Our structures differ somewhat from the STM images [1,6], in which longer range order is evident. Our correlation length is, of course, artificially limited by the size of our unit cell (32.562 Å on each side). However, the ordering observed by STM is undoubtedly due to the sample preparation process: the crystal was annealed to 1325 K and then slowly cooled down to room temperature. This procedure establishes long range order and obtains a global minimum energy structure. In order to realize such a structure, studies are underway where the crystal is heated to ~ 1325 K and then gradually quenched to room temperature [16].

Structural regularity depends on the thickness of the slab. Since these are constant energy simulations and the reconstruction event is extremely exothermic (~ 2 eV/dimer [3b]), the crystal heats up upon reconstruction. The crystal temperatures after 9.2 ps (T_{final}) for the 9-layer (5-layer) slab are 347 K (180 K), 480 K (880 K), 565 K (927 K) for $T_{init} = 100$ K, 298 K, and 500 K, respectively (where T_{final}'s for the 5-layer slab are shown in parentheses). Since the 5-layer slab has fewer degrees of freedom than the 9-layer slab, it generally heats up more, leading to more disorder. The 100 K 5-layer crystal did not heat up as much as the 100 K 9-layer crystal, because little reconstruction had occurred after 9.2 ps–only six dimers had formed! Although not shown, the surface layers obtained upon reconstruction of the 5-layer slab do not possess p(2 × 1) domains as large as those shown for the 9-layer slabs. Relaxation of the near-surface layers decays slowly into the crystal, with significant displacements until about the seventh layer, in agreement with various LEED analyses [1] and with the energy minimization calculations of Abraham and Batra [11].

The average dimer bond length of 2.42 Å is reasonable. For example, ISS [1] and LEED [1]

analyses indicate bond lengths of 2.36 and 2.47 Å, respectively. We observed no y-twist of the dimers, in agreement with energy minimization calculations [11]. The average lowering of the potential energy per dimer in the 9-layer slab was 0.91 (0.84), 0.86 (0.66), and 0.76 (0.55) eV/dimer for T_{init} = 100, 298, and 500 K, respectively (where the values in parentheses again are for the 5-layer slab). Earlier energy minimization simulations [11,12] predicted that the energy lowering should be about 1.6 eV/dimer. At finite temperatures, the dimers are hot and consequently the potential energy lowering is smaller.

Fig. 2 contrasts the time evolution of the potential energy for the 5-layer slab (fig. 2a) and the 9-layer slab (fig. 2b). The 5-layer slab exhibits induction periods of ~ 2.5 ps at 100 K and ~ 100 fs at 298 K. None of the 9-layer slab calculations exhibited induction periods and reconstruction was faster (~ 4–5 ps for $T \geq 298$ K and ~ 11 ps for $T = 100$ K) than for the 5-layer slab (~ 7 ps for $T \geq 298$ K and ~ 18 ps for $T = 100$ K). We have

calculated an upper bound for the reconstruction activation barrier of 0.03 eV (~ $k_b T$ for $T = 300$ K), by calculating the change in potential energy when two atoms are allowed to dimerize in the presence of a rigid background. Thus the induction period is not due to a large barrier and, since the fifth layer of the 5-layer slab was held fixed in the simulations, this strongly suggests that *collective motion of at least five atomic layers is involved in the reconstruction*. This is consistent with the findings of Lampinen et al. [3], who found that if the fourth layer was held rigid, no reconstruction occurred at all!

In the 5-layer slab 100 K simulation, first a single dimer forms, followed by dimers forming adjacent to it, leading to a p(2 × 1) row. The formation of each dimer can be correlated with discrete steps in the plot of potential energy versus time (fig. 2a). In the higher temperature cases, several dimers form initially, then they induce their neighbors to dimerize, continuing until two dimerizing rows meet and break the dimer chain.
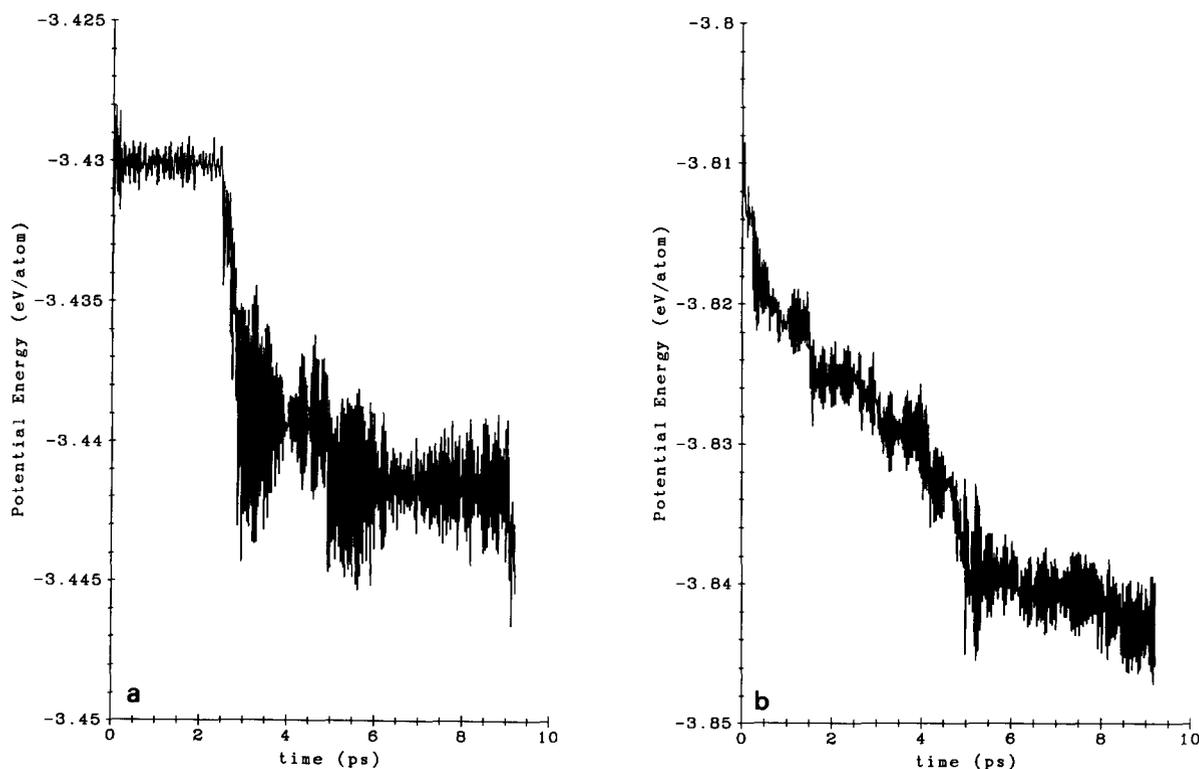

Fig. 2. Potential energy (eV/atom) versus time (ps) at T_{init} = 100 K for the (a) 5-layer and (b) 9-layer slabs.

This process is also responsible for the formation of isolated atoms, when each of an atom's neighbors dimerize away from it. At higher T_{init}, the energy falls off smoothly since multiple dimers form simultaneously. We also observed that the vibrationally hot dimers sometimes break apart and reform until the excess energy is carried down into the crystal.

In all cases, the rows consisted of symmetric dimers over a time average. However, we observed dimers with large vibrational amplitudes (instantaneously "buckled") and with small vibrational amplitudes (instantaneously "symmetric"), with the fraction of buckled dimers increasing from 30% to 44% with increasing crystal temperature. Furthermore, the ratio of buckled to symmetric dimers was found to be $\sim 1:1$ with a perfectly dimerized surface. The buckled dimers were tilted by up to $5°$ for $T_{init} = 100$ K and by up to $10°$ in both higher temperature cases. LEED *I–V* analyses have also extracted a buckling angle of $\sim 10°$ [17]. We also observe the dimer tilt direction to alternate along a row of dimers, in agreement with the STM images [1,6]. This alternating see-saw orientation of the dimers minimizes strain on the second layer atoms by stretching one bond to each second layer neighbor and compressing the other. If the dimers are tilted in the same direction, then each second layer atom has either both bonds to its neighboring dimer atoms stretched or both bonds compressed, leading to higher strain.

Although at any instant the rows of dimers appear alternately buckled, the time evolution of the relative atomic positions in each dimer reveals that the dimers *oscillate up and down in a concerted fashion* among these rows. Fig. 3 shows the motion of a pair of neighboring dimers on the 5-layer slab (after 9.2 ps) when $T_{final} = 180$ K. We have plotted $\Delta z = z_{left} - z_{right}$, where z is the absolute position normal to the surface of either the "left" or "right" atom in the dimer. At early times, Δz is of opposite sign for the two dimers, indicating they are buckled in opposite directions. Later on, they are in phase for ~ 0.3 ps before resuming the correlated motions of alternating dynamic buckling. Notice also that one dimer (solid line) begins as symmetric ($|\Delta z| \leq 0.1$ Å), quickly becomes
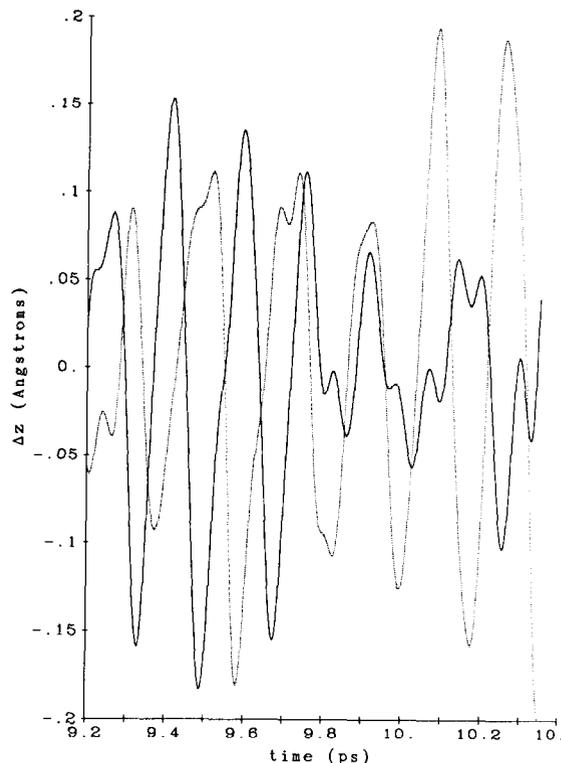

Fig. 3. Δz (Å) versus time (ps) for a neighboring pair of dimers.

buckled, then becomes essentially symmetric again, while the other dimer (dotted line) is buckled most of the time. Neighboring dimers in the perfect $p(2 \times 1)$ structure were found to exhibit even stronger correlation [16].

The buckled dimers become symmetric ($\Delta z = 0$) every 50 fs or so and they oscillate with a period of ~ 200 fs, corresponding to a surface phonon frequency of ~ 20.7 meV. This period varies, however, giving rise to a range of phonon frequencies. Calculation of the phonon density of states at finite temperature are in progress [16]. Surface phonon dispersion calculations [18] for Si(100) indicate an optical phonon mode ranging in energy from ~ 21 to 5 meV, in good agreement with our results. Inelastic He scattering experiments indicate that the surface phonon modes may be in the range of 10–15 meV [19], somewhat lower than our findings. However, it is unclear whether such a short range buckling mode would be detected by this method. At the higher temperatures,

the oscillations sometimes become more rapid and chaotic, with larger buckling amplitudes ($\Delta z_{max} \approx$ 0.7 Å). Still, these dimers appear symmetric on a time average. A previous theoretical study by Ihm et al. similarly found a critical temperature of 250 K above which the dimers are buckled randomly [20].

Our results suggest that *observed surface structures will depend on the time scale of the experiment*. For example, since LEED and PES events occur on a subfemtosecond time scale, those observations should probe a frozen surface where nearly half of the dimers are buckled and the rest are symmetric. Consistent with this suggestion, LEED patterns indicate both p(2 × 1) (symmetric dimers) and p(2 × 2)/c(4 × 2) symmetries (buckled dimers of different phase) and recent PES measurements [5] can be interpreted in terms of both symmetric dimers and nonpolar buckled dimers. By contrast, the STM sees a time-averaged image of symmetric dimers in defect-free regions, since the tip hovers over a dimer for ~ 0.1 s.

In sum, we have provided strong theoretical evidence that the defect-free, reconstructed Si(100) surface consists of neither solely symmetric nor only buckled dimers, but rather a rapidly interconverting mixture of the two. STM images suggest that permanently buckled dimers may exist near surface defects. We are currently exploring the equilibrium reconstructed Si(100) surface in the presence of such defects to search for buckled dimers that survive over long times.

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