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Theory of vacancy-stabilized ($\sqrt{3} \times \sqrt{3}$) displacive reconstruction of the clean Si(111) surface

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We show that a ($\sqrt{3} \times \sqrt{3}$) buckling distortion with one raised and two lowered surface atoms per unit cell lowers by as much as 0.18 eV/(surface atom) the energy of the clean, unreconstructed Si(111) surface. On the defect-free surface this state is not a true energy minimum, and is unstable against conversion into the lower energy (2×1) π-bonded chain reconstruction. A low concentration of added surface vacancies, however, is found to yield a buckled ($\sqrt{3} \times \sqrt{3}$) state which is a stable local minimum. Predictions are made for possible scanning-tunneling-microscopy observation of this displacive reconstruction.

The various reconstruction structures of the Si(111) surface have been the subject of intense theoretical and experimental research in the past 20 years.[1] It has been established that this surface has a stable (7×7) reconstruction, which is obtained by annealing, and a metastable (2×1) π-bonded chain structure,[2] which occurs upon cleavage at temperatures below $\sim$ 200 °C. Other reconstructions are known to occur in presence of adsorbates, and among them, the ($\sqrt{3} \times \sqrt{3}$) reconstruction is very common. Recently, however, a ($\sqrt{3} \times \sqrt{3}$) pattern has been reported for the *clean* Si(111) surface, after damaging and partially annealing the surface.[3] A vacancy model with one surface vacancy per $\sqrt{3} \times \sqrt{3}$ unit cell was suggested to explain this finding,[3] but later calculations indicated that such a vacancy pattern is highly unlikely on energetic grounds.[4,5] Alternatively, earlier calculations suggest that a $\sqrt{3}$ pattern of Si adatoms might be energetically favorable.[6] However, it has been subsequently shown that a (2 × 2) adatom structure is lower in energy than the $\sqrt{3}$ pattern,[7] hence removing the reason for Si adatoms to retain such a periodicity. Discarding these models for the $\sqrt{3}$ reconstruction, the question of the nature of this structure is fully open. This has led to recent suggestions that the observed $\sqrt{3}$ reconstruction might be impurity-stabilized,[8] and thus not a true feature of the clean Si(111).

In this paper we show that a state of local energy minimum exists for the clean Si(111) surface, where surface atoms have undergone a large periodic buckling of about 0.9 Å in a precisely $\sqrt{3}$ pattern. Although globally metastable (in the same sense in which the π-bonded chain is metastable), this state can subsist up to and above room temperature, and seems a plausible candidate for explaining the mysterious $\sqrt{3}$ reconstruction observed experimentally.[3] In particular, we find that a small but finite concentration of surface vacancies is the essential ingredient that prevents this $\sqrt{3}$ distortion from becoming unstable and spontaneously decaying into the (lower-energy) (2 × 1) π-bonded chain reconstruction.

Our calculations have been performed within the *ab initio* molecular-dynamics (MD) scheme,[9] recently used for several surface problems.[10,11] We use a repeated-slab geometry, where each slab has six Si layers, with 12 atoms per layer and a ($2\sqrt{3} \times 3$) surface cell. The cell length is $(3/\sqrt{2})a_0$=11.5 Å along the $[\bar{1}10]$ (hereafter x) direction, and $\sqrt{6}a_0$=13.3 Å along the $[11\bar{2}]$ (y) direction, where a_0=5.43 Å is the experimental lattice constant for Si. Other details are as in Refs. 10 and 11. We start with a clean, defect-free, Si(111)1 × 1 surface. When allowed to fully relax, this surface converts spontaneously into a (2 × 1) π-bonded chain structure[10,12] [note that, due to periodic-boundary conditions and to our choice of a ($2\sqrt{3} \times 3$) surface supercell, other possibly more stable reconstructions, such as the (7×7), are not allowed]. In the attempt to understand whether a surface defect could affect the (1×1) → (2×1) transformation, we created a vacancy on Si(111)1 × 1, and found, after full relaxation, that (i) spontaneous conversion into (2×1) no longer takes place; (ii) single-vacancy formation is exothermic—the energy release in going from the ideal unrelaxed surface to the system consisting of the relaxed vacancy plus a Si atom in the bulk phase is ΔE=1.4(4) eV per ($2\sqrt{3} \times 3$) unit cell; (iii) *the vacancy surrounds itself with the* $\sqrt{3}$ *buckling pattern shown in Fig. 1.* In this structure, the

second-nearest surface neighbors of the vacancy (at distance $\sqrt{3}a_0/\sqrt{2}$ from the vacancy site) are raised by 0.40 Å ("up" atoms), while all other first-layer atoms sink on the average by 0.47 Å ("down" atoms), with an average vertical distance to the second layer which is reduced from 0.78 Å to only 0.24 Å. Other features apparent from Fig. 1 are the lateral relaxations of the second-layer atoms towards either the vacancy (0.24 Å) or the raised surface atoms (0.17 Å on average). The average bond length between top- and second-layer atoms is 2.32 Å (bulk value is 2.35 Å), while that between second- and third-layer atoms is 2.34 Å for the vacancy nearest neighbors, and 2.44 Å for the others. Near the vacancy, the vertical compression of the top bilayer (apart from the raised atoms) and the lateral displacements of the second-layer atoms are qualitatively similar to those suggested by the low-energy electron diffraction work.[3]

An important point is that we find that this local buckling $\sqrt{3}$ distortion gives rise to an energy lowering as large as 1.9(5) eV per $(2\sqrt{3}\times 3)$ surface cell with respect to the unrelaxed vacancy. This suggests that *a $\sqrt{3}$ buckling distortion could represent a spontaneous tendency of the surface, even in the absence of defects.* Pursuing this idea, we eliminated the vacancy, and raised one surface atom out of every three (all other atoms, except the raised ones, being free to readjust their positions) in a $\sqrt{3}$ pattern on the defect-free surface. We indeed found a minimum when these atoms were raised by ~0.37 Å above the surface plane of the unrelaxed (1×1) structure. The $\sqrt{3}$-pattern energy minimum remains after a full steepest-descent relaxation, including the raised atoms, is allowed. This structure is similar to that induced by the vacancy: the surface buckling between up and down atoms is 0.82 Å, the top-bilayer vertical spacing (except for the raised atoms) is compressed to 0.26 Å while that between second and third layer is stretched to 2.42 Å. This "oscillatory" relaxation of the surface and subsurface atoms is similar in character to that occurring on the (1×1) structure.[12] This $\sqrt{3}$ structure falls ~0.18 eV/(surface atom) *below* the unrelaxed (1×1) surface (see Table I). If, instead, the raised atoms are fully removed, thus creating a $\sqrt{3}$ lattice of vacancies, the energy rises 0.07 eV/(surface atom) *above* that of the (1×1) surface (see again Table I), in qualitative agreement with previous calculations.[4] Hence, the defect-free $\sqrt{3}$-pattern buckled state seems at first an additional metastable state of the clean surface. The energy lowering of this structure is apparently associated with opposite dangling-bond-dehybridization tendencies ($sp^3 \rightarrow s$ and $sp^3 \rightarrow p_z$) of the up and down atoms, respectively. This implies some electronic charge transfer from down to up atoms, and a reduction of the density of states near the Fermi level, as shown in Fig. 2.

However, as shown in Table I, the (2×1) π-bonded chain state (studied previously with the same approach[10,11]) is far lower in energy, −0.45 eV against −0.18 eV per (1×1) unit cell. It is therefore important to ask whether there is an energy barrier between the two, i.e., whether the $\sqrt{3}$ buckled state is a true local minimum or instead only a (barrierless) saddle point. For this reason, we performed a number of microcanonical MD runs at various temperatures between T=50 and T=200 K. We found that after a few hundred time steps the temperature began to rise, the potential energy began to decrease, and the atomic positions in the slab indicated a structural transformation typical of the transition from the (1×1) to the $(2\times 1)\pi$-bonded chain geom-

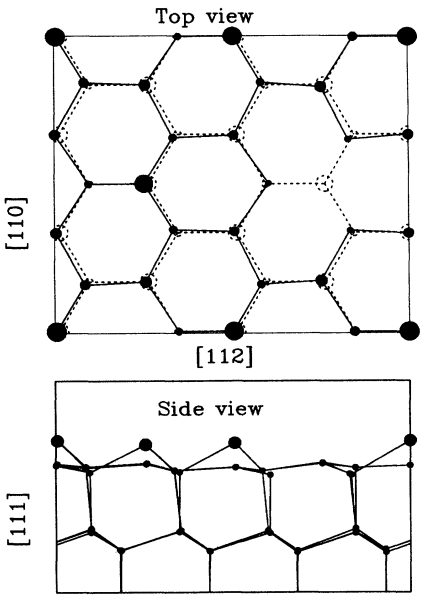

FIG. 1. Views of the (111) surface with a vacancy. Dots and lines represent atoms and bonds. Upper panel: top view of the two topmost layers. The size of the dots is proportional to the distance of atoms away from the surface. Dashed lines and empty dots show the perfect (1×1) surface prior to relaxation. Solid lines and solid dots show the fully relaxed vacancy structure, characterized by the $\sqrt{3}$ pattern of raised atoms around the vacancy site. Lower panel: side view of the relaxed structure.

TABLE I. Total energies of various surface structures referred to the energy of the ideal, unrelaxed surface. Values are given in eV/$(2\sqrt{3}\times 3)$ unit cell. In the presence of vacancies, the energy in the bulk phase of the missing atoms ($E_{\text{bulk}} = -3.909$ a.u. per atom, as calculated using a "slab-like" bulk supercell of 72 atoms) is added.

Surface structure	E [eV/$(2\sqrt{3}\times 3)$ cell]
$(\sqrt{3}\times\sqrt{3})$ lattice of vacancies	+0.8(5)
Ideal (1×1)	00.00
Relaxed (1×1)	−0.9(6)
Vacancy-induced $(\sqrt{3}\times\sqrt{3})$ buckled	−1.4(4)
Defect-free $(\sqrt{3}\times\sqrt{3})$ buckled	−2.1(3)
$(2\times 1)\pi$-bonded chain plus vacancy[a]	−3.6(0)
$(2\times 1)\pi$-bonded chain[a]	−5.4(0)

[a]Reference 11.

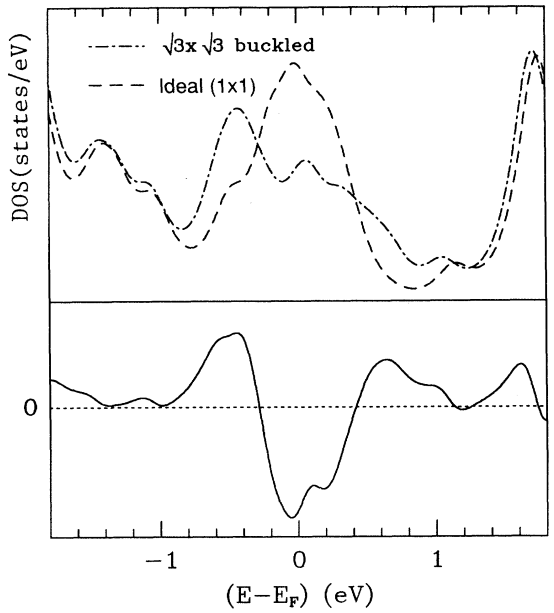

FIG. 2. Calculated surface density of states close to the Fermi energy E_F. Upper panel: (a) Ideal (1×1) surface (dashed line); (b) defect-free $\sqrt{3}$ buckled surface (dash-dotted line). Lower panel: difference between (b) and (a). Note the depletion near E_F, which helps to lower the energy of the $\sqrt{3}$ structure.

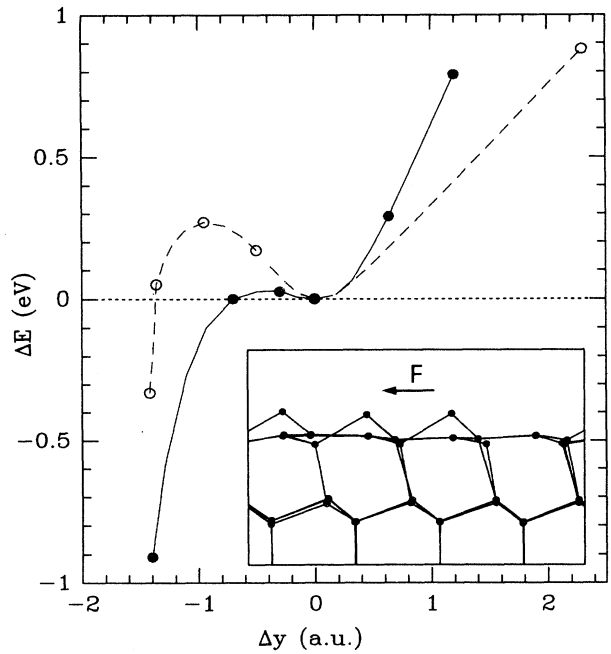

FIG. 3. Total-energy variations (with respect to equilibrium) as a function of the surface atoms average displacement caused by a constant external force $F = 7\times10^{-3}$ a.u. along $\pm y$ ($y \equiv [11\bar{2}]$) applied to the first two atomic layers. Solid dots, defect-free $\sqrt{3}$ buckled surface; empty dots, vacancy-induced $\sqrt{3}$ structure (see Fig. 1). Lines are only guides to the eye. The inset shows a side view of the $\sqrt{3}$ vacancy-induced structure during the relaxation in the presence of the force F along $-y$.

etry, i.e., an initial almost rigid shift of the atoms of the first two layers in the $[\bar{1}\bar{1}2]$ $(-y)$ direction, followed by the formation near the surface of some fivefold and sevenfold atomic rings characteristic of the $(2\times1)\pi$-bonded chain geometry.[10] Hence these thermal runs suggest an instability, or at best a very low energy barrier, of the defect-free $\sqrt{3}$ buckled state. In order to characterize this barrier (or the lack of it) further, we also studied the $T=0$ relaxation of the optimized $\sqrt{3}$ buckled structure when a constant external force F directed along $\pm y$ was applied to the atoms of the surface and subsurface layers [note that when F is along $-y$, the surface layers are forced to undergo distortions similar to those which initiate the transformation into the (2 × 1) chain structure]. As shown in Fig. 3, the results of these calculations confirm that the defect-free $\sqrt{3}$ buckled structure is essentially a barrierless saddle-point state and will spontaneously distort, eventually transforming into a (2 × 1) chainlike structure.

Vice versa, a clear energy barrier of height $\Delta E=0.26$ eV (see Fig. 3) is obtained by applying the same force to the defective structure (with vacancy) of Fig. 1. The final

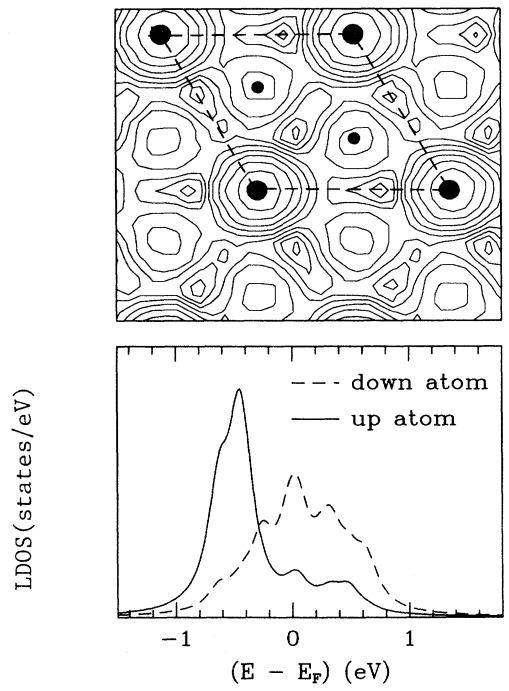

FIG. 4. Upper panel: Topographic map $\rho(\mathbf{r}, E_F)$=const of the defect-free $\sqrt{3}$ buckled surface at an average distance $z \sim 2.3$ Å above the surface. States in an energy window of 0.2 eV around E_F are considered. Maxima occur at the up and down atoms (big and small dots, respectively), while the minimum is in the middle between the two down atoms. The corrugation between up and down atoms is ~0.8 Å, close to the geometric buckling corrugation. The maximum corrugation is ~1.5 Å. The dashed line shows the $\sqrt{3}$ surface unit cell. Lower panel: Local DOS on the up and down atom of the $\sqrt{3}$ buckled surface, respectively.

state past the barrier is again a π-bonded chainlike state (with a vacancy). The vacancy-induced barrier is possibly related to the shortening of the second-to-third layer bonds of the vacancy nearest-neighbors. Unlike the relaxed bonds of the defect-free surface, which are stretched with respect to their bulk value, these bonds are here short and stiff and tend to resist the stretching-bending deformation necessary for the $(1 \times 1) \rightarrow (2 \times 1)$ conversion. Further proof of the local stability of the vacancy-induced $\sqrt{3}$ structure of Fig. 1 was provided by a rather long ($\sim$0.8 ps, corresponding to 4200 time steps) thermal MD run where T was gradually raised (by rescaling the ionic velocities) from 200 to 1000 K. The structure was found to be stable till roughly 500 K. It began to disorder at the higher temperatures with temporary formation of fivefold and sevenfold atomic rings typical of the (2×1) chain structure. In conclusion, the presence of only a few surface vacancies make the $\sqrt{3}$ buckled structure locally *stable*, by causing an energy barrier which *prevents* this state from decaying into the (2×1) chain structure.

The above results suggest the following picture. After damaging, surface vacancies may be present, and, if their concentration is large enough, they can stabilize the $\sqrt{3}$ buckled structure up to room temperature or above. At the same time, wrongly phased surface vacancies (three distinct equivalent sites are possible) may destructively interfere, thus yielding a relatively poor $\sqrt{3}$-pattern long-range order, as is observed experimentally.[3] As annealing progressively reduces the vacancy concentration, the surface may reach a critical point where the barrier may be overcome even at room temperature, and spontaneous conversion into the π-bonded (2×1) or possibly into the more stable (7×7) structure will eventually take place. The critical vacancy concentration for loss of stability at room temperature has not been pursued carefully, but can be crudely estimated to be of the order of 5%, since in our simulation (where the vacancy concentration is 8%) wild fluctuations in the atomic positions do not appear before $\sim$500 K.

Based on this *ab initio* study, we are able to make some predictions which should allow a test of this picture. The simplest is probably by scanning tunneling microscopy (STM) and spectroscopy (STS). In Fig. 4 we thus show a topographic map $\rho(\mathbf{r}, E_F)$=const of the $\sqrt{3}$ buckled surface (here taken without vacancies). The local density of states (LDOS) at the Fermi energy $\rho(\mathbf{r}, E = E_F)$ corresponds, in the simplest approximation, to the low-voltage STM topograph.[13] The predicted buckling amplitude at distance $z \sim 2.3$ Å above the surface is $\sim$0.8 Å, and should be readily observed. The peak shift of $\sim$0.7 eV in the LDOS on the up and down atoms (lower panel of Fig. 4) should correspondingly be measurable by STS. Finally, the presence of surface vacancies, even if few in number, should be easily detectable.

In summary, an *ab initio* study of the clean Si(111) surface has revealed a buckled $(\sqrt{3} \times \sqrt{3})$ reconstructed state, which is a local energy minimum, and may be capable of explaining recent observations. Surface vacancies have a crucial role in stabilizing this structure, but the required concentration is much smaller than the 33% required by the recently suggested $\sqrt{3}$-pattern vacancy structure.[3]

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[12] When, instead, the ideal surface is constrained to maintain the (1×1) symmetry during the relaxation, a saddle-point configuration is reached, where the distance between the two top layers is reduced from 0.78 to $\sim$0.61 Å, while that between the second and third layer is stretched from 2.35 to 2.40 Å. We refer in Table I to this saddle-point configuration as relaxed (1×1), whose energy is $\sim$0.08 eV/(surface atom) below the ideal (1×1) surface. This value is smaller than that, $\sim$0.17 eV/(surface atom), often reported in the literature (see, e.g., Ref. 6). The higher plane-wave energy cutoff used in this work accounts for most of this discrepancy.
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