Atomic Structure of Clean Si(113) Surfaces: Theory and Experiment

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High-index surfaces of Si are of potential technological interest but they tend to facet into low-index planes. The only known exception is Si(113) with a surface energy about as small as Si(001); however, its atomic structure remained unresolved. On the basis of scanning tunneling microscopy measurements and *ab initio* theory we present a new atomic model of Si(113) employing a novel idea of a subsurface self-interstitial. The calculated surface energy of Si(113) (3×2) is close to the value for Si(001)-$p(2 \times 2)$. The new model explains experimentally observed transitions between the 3×1 and 3×2 phases.

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Recently, a lot of effort has been devoted to improve epitaxial growth of such materials as Ge or GaAs on silicon. Although one can hardly understand initial stages of epitaxial growth without knowing the atomic structure of the substrate, there is at least one silicon surface which is of potential interest for epitaxy [1] but which has an unknown microscopic structure [2]. This surface, Si(113), is also an interesting example that a high-index plane can be thermally stable [3,4]. Most experimental studies find that Si(113) reconstructs in a 3×2 manner but some find a 3×1 pattern (see Ref. [2] for references). Though two scanning tunneling microscopy (STM) surveys [5,6] exist, the structure models proposed are questionable. First, the surface energy of Si(113) was calculated [7] to be much higher than was measured [4]. Second, substantial *ad hoc* corrections to the energy optimized atomic positions were needed to reproduce the measured STM images [8]. Here we show that a very different atomic structure produces similar STM images; thus, careful energy minimization turns out to be essential for an unambiguous interpretation of STM. The surface energy of a solid depends on the nature of the bonding at the surface, so too high calculated value of surface energy may imply that a wrong type of atomic reconstruction was assumed. The aim of our work is to dispel these and other doubts [9–11] by a combined experimental and theoretical study. We infer a realistic microscopic model for the 3×2 reconstruction which can explain the experimental data. The model shows a novel feature, a near-surface self-interstitial which stabilizes the 3×2 phase of Si(113). Such interstitials may act as stabilizing factors for steps, facets, or surfaces which are under tensile stress.

The experiments were carried out by means of a STM setup from OMICRON. We used undoped Si(113) samples (oriented to within 0.5°) of specific resistance exceeding 5000 Ω cm. The samples were flashed for nearly 10 sec at 1250 °C and cooled down quickly to 900 °C. After that the temperature was decreased slowly, from 900 to 700 °C at 1 K/sec and from 700 °C to 350 °C at 0.08 K/sec. The pressure did not exceed 5×10^{-10} mbar at 1250 °C; the base pressure was 5×10^{-11} mbar. This procedure results in clean and well-ordered Si(113)-(3×2) surfaces. The STM images (see below) agree with the study of Knall *et al.* [5] which was used by Wilson *et al.* [8] for the analysis of the atomic structure at Si(113).

To compute surface energies we performed self-consistent *ab initio* density functional theory calculations employing the local density approximation (LDA) with Perdew-Zunger parametrization [12,13], state-of-art pseudopotentials [14–16], and a Car-Parrinello-like technique [17,18]. We used slabs of 5 double layers of Si atoms. All Si atoms within the topmost 3 double layers on one side of the slab were relaxed and the remaining 2 double layers of Si atoms were frozen at their bulk sites. The truncated bulk side was passivated with hydrogen atoms; the distance between the outmost H plane and the outmost Si plane on the neighboring slab was 12 bohrs. The plane wave basis set was defined by the cutoff energy of 8 Ry and the electron density was calculated from a set of 4 special $\mathbf{k}_{\parallel}$ points in the irreducible part of the surface Brillouin zone for the 3×2 elementary cell. To simulate STM images we applied the result of Tersoff and Hamann [19] that, within the approximation of s-wave tip and low voltage V, the STM tip follows a surface $z(\mathbf{r})$ of constant density of states ρ_{eff}, where the density of states $\rho_{\text{eff}}(\mathbf{R})$ is built from states between the Fermi level E_F and $E_F + eV$, and $\mathbf{R}$ is the position of the apex atom of the tip.

To make our calculations feasible, we used relatively thin slabs, hydrogenized on one side. It was therefore not straightforward to obtain the absolute values of surface energy γ from the total energy of a given slab. We determined γ for each surface reconstruction as follows. First, we built slabs which were bulk truncated on both sides and we determined the surface energy γ_0 of the clean, truncated bulk surface. Next, we calculated surface energy differences $\Delta\gamma$ with respect to a reference slab which was bulk truncated on one side and terminated with hydrogen on the other side. Finally, doing calculations

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for hydrogen terminated slabs of different thickness we verified that the presence of hydrogen atoms on the back side of the slab had no significant effect on surface energy differences. Hence, knowing γ_0 and $\Delta\gamma$, we can obtain the surface energy γ simply as $\gamma_0 + \Delta\gamma$.

Additional tests were carried out to monitor the convergence of surface energies and simulated STM images with respect to slab thickness, separation between slabs, basis set, and Brillouin zone integration. We estimate an accuracy better than 1 meV/Å^2 for the calculated surface energy differences between relaxed structures. The absolute values of surface energies are overestimated by about 5–10 meV/Å^2 due to the neglect of atomic relaxation for deeper subsurface layers. We verified that the effect of this neglect is roughly the same for Si(113) and Si(001) and that it largely cancels out for the calculated surface energy differences between relaxed structures.

The bulk truncated Si(113) surface is shown in Fig. 1(a). It is metallic and has surface energy $\gamma_0 = 147$ meV/Å^2. This value is significantly lower than 177 meV/Å^2 obtained by Bird *et al.* [7]; we suspect that the main source of this disagreement is the very crude **k**-point sampling (Γ only) used in Ref. [7]. Surface energy differences are less affected than their absolute values [20].

Surfaces reconstruct to minimize surface energy. Conventionally, one views this process as driven by rebonding of dangling bonds and limited by the consecutive changes in bond lengths and angles which destabilize the surface by inducing local strain fields. A classic example of how nicely this simple idea works in practice is the case of 2 × 1 dimerization at Si(001). Applying these concepts and guided by experimental data available at that time, Ranke [21] proposed in 1989 four structure models for Si(113). Two of them are important for our discussion: the 3 × 1 dimerized model [Fig. 1(b)] with few dangling bonds and the 3 × 2 "surface void" structure [Fig. 1(c)] with more dangling bonds but presumably lower strain. Subsequent STM measurements [5] seemed to favor the 3 × 2 model [Fig. 1(c)]; however, Wilson *et al.* [8] have recently shown that when the topology of Fig. 1(c) is assumed, the experimental STM images can be reproduced only when several surface atoms are moved by as much as 0.5 Å away from the positions optimized by a tight-binding scheme. Apart from that, LEED studies demonstrated that adsorbates [9,10] and temperature [11] can induce transitions between the 3 × 2 phase and a 3 × 1 phase. To explain these transitions, Jacobi and Myler [10] have suggested that the 3 × 2 structure is in fact akin to the 3 × 1 model of Ranke: in the 3 × 2 phase each dimer built by the atoms labeled *C* in Fig. 1(b) is somehow distorted. The character of this hypothetical distortion remained, however, unclear.

Our *ab initio* investigation demonstrates that the relaxed 3 × 2 structure of Ranke [Fig. 1(c)] cannot account for the results of STM [compare Figs. 2(a) and 2(b)].

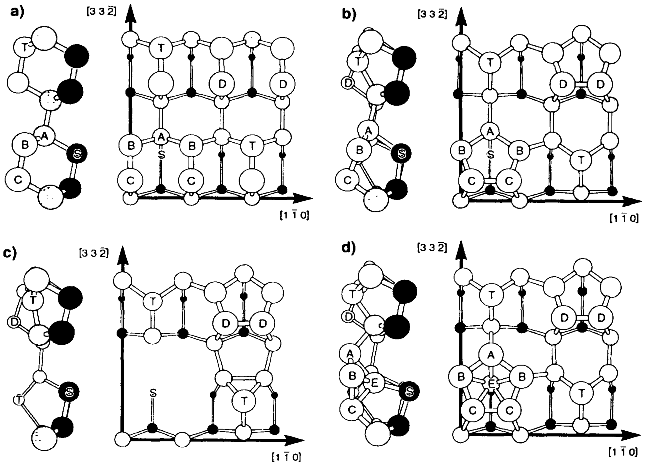
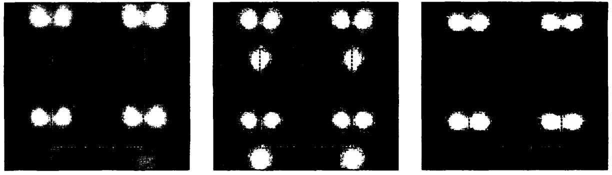
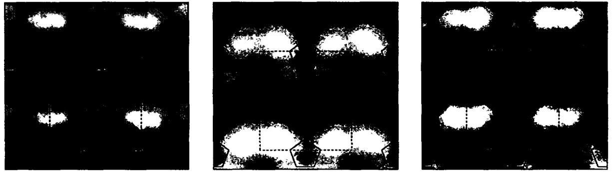


FIG. 1. Side and top views of different models of the Si(113) surface: (a) 1 × 1 truncated bulk, (b) 3 × 1 dimerized model of Ranke, (c) 3 × 2 "surface void" model of Ranke, and (d) 3 × 2 subsurface "interstitialcy." The gray scale represents the distance from the vacuum. 3 × 2 translation vectors are shown. The positions of all atoms displayed in (b), (c), and (d) have been energy optimized.

a) Computer simulations for the model of Ranke:



b) Measured STM images:



c) Computer simulations for the subsurface interstitialcy model:

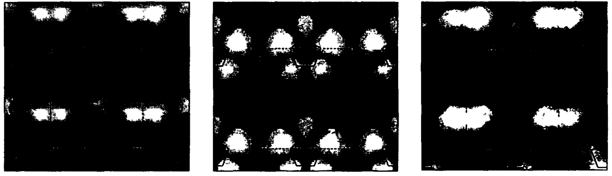


FIG. 2. STM images of the Si(113) surface and their calculated counterparts. The broken lines mark surface elementary cells. The left column shows occupied states (measured at −2.0 V, 2.0 nA), the middle and the right column show empty states (measured at 1.5 V, 1.0 nA and 3 V, 2 nA, correspondingly). The calculated pictures have been obtained within Tersoff-Hamann approximation for slabs separated by 18 bohrs of vacuum. (a) Energy integrated local density of states (LDOS) for the 3 × 2 Ranke model. The pentagon indicates the position of the void [Fig. 1(c)]. (b) STM images. Note the pentagonal structure, clearly visible around the sketched pentagon in the images of empty states: it is not reproduced by the model of Ranke. (c) LDOS for the 3 × 2 interstitialcy model. The pentagon indicates the position of atoms *A*-*B*-*C* [Fig. 1(d)]; the pentagonal structure is properly reproduced. Even though the calculated pictures show only the energy integrated LDOS, the overall agreement is very good.

Moreover, we calculated surface energies γ of Si(113) and Si(001) [22] (Table I). Assuming the relaxed 3×2 Ranke model, we obtained $\epsilon = (\gamma_{113} - \gamma_{001})/\gamma_{001} \simeq 0.17$, an order of magnitude bigger than the experimental value [4] $\epsilon \simeq 0.015$. Bird *et al.* suggested that though the surface energy of clean Si(113) may be high, in experiment it may be lowered due to contamination with carbon. Indeed, carbon contamination leads to the appearance of (113) facets at Si surfaces on the (111) to (001) azimuth [23]. This is, however, most probably a kinetic effect due to bunching of steps which get pinned at carbon-induced defects [23,24]. All these problems—incompatibility with phase transitions, incorrect STM images, and too high surface energy—taken together imply that the 3 × 2 "surface void" structure of Ranke is not a good model for Si(113). However, the relative surface energy difference ϵ calculated for the 3 × 1 model [Fig. 1(b)], $\epsilon \simeq 0.042$, is much closer to the experimental value. This indicates that the stable 3 × 2 topology can indeed be realized as a slight modification of the 3 × 1 model. However, the 3 × 1 structure is locally stable: though we perturbed the local arrangement of atoms labeled *A*, *B*, and *C* in Fig. 1(b) by an average displacement of about 0.2 Å, the resulting 3 × 2 structure relaxed to the initial 3 × 1 geometry. Some topological changes are therefore needed to stabilize the observed 3 × 2 phase.

At this point we introduce a new concept, which is based on theoretical results of Watkins *et al.* [25] who published in 1971 a study on the properties of self-interstitials in the diamond lattice. Using a linear combination of atomic orbital–molecular orbital cluster approach, Watkins *et al.* found that the total energy of a self-interstital is drastically (by several eV) lowered when the interstitial atom moves from a high-symmetry (tetrahedral or hexagonal) site into a ⟨001⟩-split or ⟨111⟩-split (bond centered) position. Near a surface, additional relaxation can provide a further reduction of energy. Moreover, a split interstitial introduces a large compressive stress which can relieve the local tensile stress around the atoms labeled *T* in Fig. 1(b). To test this idea, we considered the structure shown in Fig. 1(d), where an extra atom *E* ("interstitialcy") is inserted. The surface energy of this structure is *lower* than the surface energy of the 3 × 1 dimerized pattern (Table I). The calculated ratio $(\gamma_{113} - \gamma_{001})/\gamma_{001} \simeq 0.021$ is close to the experimental value [4] of 0.015. The local density of states changes such that the simulated STM pictures contain the essential features of the experimental images [compare Fig. 2(b) and Fig. 2(c)]. Particularly, the characteristic pentagonal group of spots due to empty states around the pentagon marked in Fig. 2(b) is now reproduced. The new structure can be viewed as a case of Jacobi and Myler's "3 × 2 distorted dimer", where the mobile element responsible for $3 \times 2 \rightleftharpoons 3 \times 1$ is the weakly bonded interstitialcy. We conclude that our model consistently describes the experimental findings about clean Si(113).

One may expect that a structure with two interstitialcies per a 3 × 2 cell (i.e., with 3 × 1 periodicity) has an even lower surface energy. The reason why this is not the case is quite interesting. The fundamental 3 × 1 reconstruction of Fig. 1(b) leads to a metallic surface. The 3 × 2 interstitialcy structure is semiconducting, with the energy gap of about 0.5 eV: the interstitialcy can be seen as a double donor which provides two electrons per 3 × 2 cell and fills up the metallic surface band. The electrons donated by the second interstitialcy go to states in the "conduction band." This costs extra energy and the net result is that the surface energy of the 3 × 1 interstitialcy structure is higher (Table I).

For completeness, we considered [26] also a number of other plausible models of Si(113). We found that only the 3 × 2 interstitialcy structure is more stable than the 3 × 1 dimerization. Surface energies of the other structures [26] cluster in the range between 105 and 120 meV/Å^2.

Finally, it is interesting to note that Si self-interstitials tend to aggregate on {113} in the bulk, forming strictly planar defects [27]. Also in this case the interstitial atoms line up along the ⟨110⟩ direction. The most pronounced difference is, however, that the subsurface interstitials are sixfold coordinated while the bulk interstitials are fourfold coordinated. We expect that during epitaxial growth the interstitial atoms segregate to the surface, where they can profit from the surface strain and retain their coordination number. Still, we cannot exclude that under certain conditions some interstitial atoms will remain on {113} plains and become seeds for planar {113} defects.

TABLE I. Calculated surface energies for various reconstructions at Si(113) and Si(001) [22] surfaces. The presence of the near-surface self-interstitial complicates the simple view of surface reconstruction as a balance between a tendency to minimize the density of dangling bonds and a tendency to minimize the surface strain: the self-interstitial is sixfold coordinated and it is not obvious how to assign "dangling bonds" in this case.

Structure	Dangling bonds /Å^2	Surface energy meV/Å^2
Si(113) Truncated bulk	0.125	147
Si(113)-(3 × 2) Ranke	0.084	111
Si(113)-(3 × 1) Ranke	0.070	99
Si(113)-(3 × 1) interstitial	···	99
Si(113)-(3 × 2) interstitial	···	97
Si(001)-*p*(2 × 2)	0.069	95

In summary, using a new concept of near-surface interstitialcy we have presented a novel model of the Si(113) surface [28]. The new model consistently describes experimental data. In particular, STM images and surface energy ratio $\gamma_{113}/\gamma_{001}$ are satisfactorily reproduced.

[1] J. Knall and J.B. Pethica, Surf. Sci. **265**, 156 (1992).

[2] J. Schreiner, K. Jacobi, and W. Selke, Phys. Rev. B **49**, 2706 (1994).

[3] J.M. Gibson, M.L. McDonald, and F.C. Unterwald, Phys. Rev. Lett. **55**, 1765 (1985).

[4] D.J. Eaglesham, A.E. White, L.C. Feldman, N. Moriya, and D.C. Jacobson, Phys. Rev. Lett. **70**, 1643 (1993).

[5] J. Knall, J.B. Pethica, J.D. Todd, and J.H. Wilson, Phys. Rev. Lett. **66**, 1733 (1991).

[6] M.J. Hadley, S.P. Tear, B. Röttger, and H. Neddermeyer, Surf. Sci. **280**, 258 (1993).

[7] D.M. Bird, L.J. Clarke, R.D. King-Smith, M.C. Payne, I. Stich, and A.P. Sutton, Phys. Rev. Lett. **69**, 3785 (1992).

[8] J.H. Wilson, D.A. McInnes, J. Knall, A.P. Sutton, and J.B. Pethica, Ultramicroscopy **42-44**, 801 (1992).

[9] U. Myler, P. Althianz, and K. Jacobi, Surf. Sci. **251/252**, 607 (1991).

[10] K. Jacobi and U. Myler, Surf. Sci. **284**, 223 (1993).

[11] Y.R. Xing, J.P. Zhang, J.A. Wu, C.Z. Liu, and C.H. Wang, Surf. Sci. Lett. **232**, L215 (1990).

[12] D.M. Ceperley and B.I. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[13] P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[14] G.B. Bachelet, D.R. Hamann, and M. Schlüter, Phys. Rev. B **26**, 4199 (1982).

[15] L. Kleinman and D.M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).

[16] X. Gonze, R. Stumpf, and M. Scheffler, Phys. Rev. B **44**, 8503 (1991).

[17] R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).

[18] R. Stumpf and M. Scheffler, Comput. Phys. Commun. (to be published).

[19] J. Tersoff and D.R. Hamann, Phys. Rev. B **31**, 805 (1985).

[20] When the surface is allowed to relax within the constraints of 1×1 periodicity, the surface energy is reduced to $\gamma = 126$ meV/Å^2. The relaxation energy $\Delta\gamma = 21$ meV/Å^2 is comparable to $\Delta\gamma = 19$ meV/Å^2 quoted in Ref. [7]. The reconstruction energy for the 3×2 Ranke [Fig. 1(c)] structure, $\Delta\gamma = 36$ meV/Å^2, is also reasonably close to $\Delta\gamma = 39$ meV/Å^2 obtained in Ref. [7].

[21] W. Ranke, Phys. Rev. B **41**, 5243 (1990).

[22] J. Dąbrowski, E. Pehlke, and M. Scheffler, Phys. Rev. B **49**, 4790 (1994),and J. Dąbrowski (unpublished).

[23] Y.-N. Yang and E.D. Willams, J. Vac. Sci. Technol. A **3**, 2481 (1990).

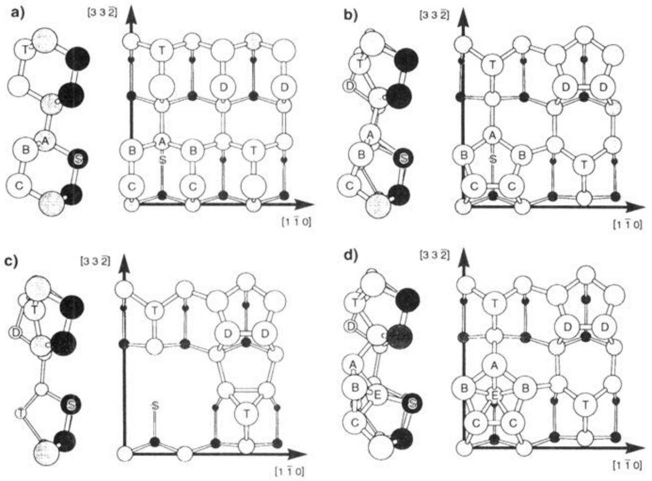
[24] M. Mundschau, E. Bauer, W. Telipes, and W. Święch, Surf. Sci. **223**, 413 (1989).

[25] G.D. Watkins, R.P. Messmer, C. Weigel, D. Peak, and J.W. Corbett, Phys. Rev. Lett. **27**, 1573 (1971).

[26] J. Dąbrowski and G. Wolff (to be published).

[27] M. Kohayama and S. Takeda, Phys. Rev. B **46**, 12 305 (1992), and references therein.

[28] A full list of coordinates is available from the first author. Contact: jarek@th1.ihp-ffo.de.



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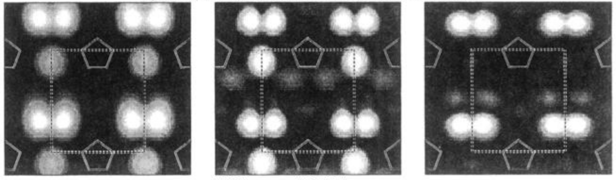
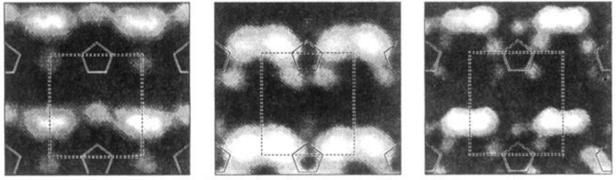
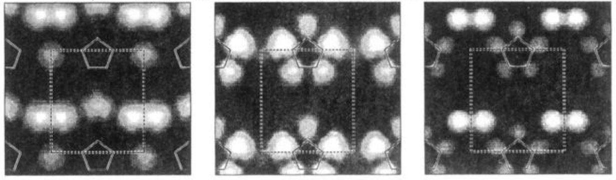


b) Measured STM images:



c) Computer simulations for the subsurface interstitialcy model:



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