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Model for the energetics of Si and Ge (111) surfaces

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The reconstructions observed on the annealed (111) surfaces of Si and Ge can be explained on the basis of a simple model of the surface energetics. The driving force for the Si 7×7 reconstruction is the formation of dimer-row domain walls, which order in a triangular pattern for topological reasons. Adatoms play an incidental role only. Chemical or strain-induced variations in the parameters of the model can lead to transitions between energetically competitive 7×7, 5×5, $c2\times8$, and other structures.

The longstanding puzzle concerning the structure of the Si(111)-7×7 surface reconstruction may have been solved, in the sense that several experiments[1-4] strongly support the "dimer adatom stacking-fault" (DAS) model of Takayanagi, Tanishiro, Takahashi, and Takahashi.[1] However, several critical questions remain. Why should such a complicated structure be the energetically stable surface configuration? Why are the annealed Si and Ge surfaces so different, when Si and Ge are so similar chemically? What are the important energies in the problem? In particular, what balance of energies favors the Si 7×7 over the analogous 5×5 or 9×9 structures?

To date, *ab initio* calculations of structural energies have not proven very decisive in answering such questions. Northrup[5] has calculated the energies of simple $\sqrt{3}\times\sqrt{3}$ and rectangular 2×2 arrays of adatoms on an otherwise ideal Si 1×1 surface, and finds that these structures are indeed favored over the simple 1×1. Because of the large unit cell of the DAS model, however, *ab initio* methods cannot be expected to yield reliable information on the energetics of the dimer rows and corner holes in the near future. On the other hand, some estimates of these latter energies can be extracted from more empirical approaches.[6,7] In addition, several workers[8,9] have shown that topological considerations have important consequences for the surface structure, especially for the ordering of domain walls.

Here, an attempt is made to develop a unified model based in part on all of the above considerations. In this model, the driving force for the 7×7 reconstruction is the formation of dimer-row domain walls, which have a net *negative* (i.e., exothermic) creation energy per unit length, and *not* the stress-relief mechanism often cited.[8] The model has as its ground state the observed 5×5 and 7×7 DAS structures in certain regions of parameter space, and a simple adatom phase elsewhere. The identification of the latter with the $c2\times8$ phase seen on Ge then leads to a unified and powerful picture of the ordering and energetics of the annealed Si and Ge (111) surfaces. For example, it provides a natural explanation for experiments which show a strain dependence of the surface reconstruction pattern,[10-13] e.g., the transformation of $c2\times8 \rightarrow 7\times7$ with compression of the Ge(111) surface.[10] (While the identification of the Ge $c2\times8$ as a simple adatom phase is highly controversial, I argue below that the weight of the experimental evidence supports it.) The adatoms play only an incidental role, in contrast with previous suggestions;[6] according to the present model, Si would *still* have a 7×7 dimer stacking-fault reconstruction even if the adatoms did not occur.

The DAS structure consists of triangular adatom-covered "islands," separated by domain walls (DW's) of type *W*, Fig. 1(a), ordered as in Fig. 1(b). Half of the triangular islands have a subsurface "stacking fault" (stacking sequence ...*ABCB* instead of ...*ABCA*). Let us first consider the unphysical case in which the adatom binding energy[14] is taken to be negative, so that adatoms do *not* occur. Let (i) p be the surface energy per 1×1 cell of the

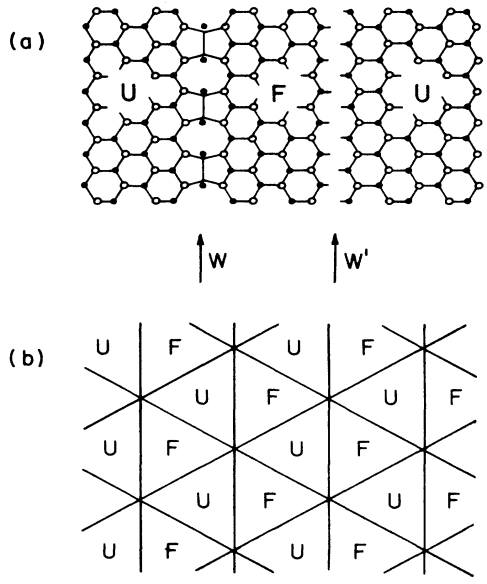

FIG. 1. (a) Two inequivalent domain walls *W* and *W'*, separating faulted (*F*) from unfaulted (*U*) island regions. Open circles represent surface atoms of the island regions, and filled circles forming an uninterrupted triangular array represent the undistorted positions of subsurface atoms. Possible adatoms are not shown. "Dimers" are bonds shared by two fivefold rings in wall *W*. (b) Ordering of domain walls of type *W* (solid lines) in the DAS model.

relaxed 1×1 surface (essentially the dangling-bond energy), (ii) d be the contribution per dimer to the surface energy, (iii) c be the contribution per corner hole to the surface energy, and (iv) Δf be the additional surface energy per 1×1 cell of a faulted region.[15] Now the relative DW creation energy may be written $\Delta w = \frac{3}{2}d - p$, because the formation of the DW shifts the surface atoms in the faulted region away by a third of a lattice vector [see Fig. 1(a)], so that the creation of $1\frac{1}{2}$ dimers is accompanied by the elimination of one dangling bond. Thus, if d is sufficiently small, then $\Delta w < 0$, and the DW has *negative* creation energy per unit length, i.e., DW formation is *exothermic*. Estimates indicate[6] $d \cong 0.5$ eV while $p \cong 1.5$ eV, so that $\Delta w < 0$ is indeed plausible. Here, dangling-bond removal by DW formation is taken to be the driving force for the 7×7 reconstruction.

If the introduction of DW's (dimers) is in fact the driving force, one might object that the lowest-energy structure ought to be a dense pattern of parallel DW's. However, a pattern of this kind formed from DW's of type W is *topologically impossible*.[8,9] As shown in Fig. 1(a), to return from a faulted region to an unfaulted one along a boundary parallel to W requires a *topologically inequivalent* DW of type W'. A reconstruction of W' involving dimers and five- and sevenfold rings has been proposed[9] as a basis for the Ge $c2\times8$ structure. However, it has twice as many dimers per unit length as W, and is estimated to have a much larger strain energy.[7,9] I propose instead that W' is so energetically unfavorable that it does not occur, and assume, following Becker and coworkers,[16,17] that the Ge (Ref. 16) and related fragmentary structure seen on Ge and laser-annealed Si (Refs. 16 and 17) are simple ordered adatom phases. In this case, the only allowed DW's are of type W, and these can occur in only three of the six possible orientations. That is, a (convex) unfaulted region bounded by W *must* be triangular with the vertical wall on the right, and conversely for a faulted region, as shown in Fig. 1(b). Since an energy cost will be associated with DW intersections, the only remotely favorable configuration made up of such triangles is the one shown in Fig. 1(b), which is the basis of the DAS model.

The tendency to DW formation may be offset by the costs of the associated corner holes and stacking faults. Consider a $(2n+1)\times(2n+1)$ dimer stacking-fault (DS) structure ordered as in Fig. 1(b). The island regions fill $2n(2n+1)$ 1×1 surface cells, the DW's fill $2n$, the corner hole fills one, and half the surface is faulted. Thus, the total energy per 1×1 surface region is

$$E_{\rm DS} = \frac{1}{2}\Delta f + \frac{2n(2n+1)p + 3nd + c}{(2n+1)^2}, \tag{1}$$

or, relative to the 1×1 phase,

$$\Delta E_{\rm DS} = \frac{1}{2}\Delta f + \frac{2n\Delta w + \Delta c}{(2n+1)^2}, \tag{2}$$

where $\Delta c = c - p$ is the relative corner-hole energy ($\Delta c > 0$). A (zero-temperature) "phase diagram" as a function of the dimensionless parameters $\tilde{f} = \Delta f / |\Delta w|$ and $\tilde{c} = \Delta c / |\Delta w|$ has been constructed in Fig. 2(a) by minimizing Eq. (2). If $\tilde{f} = \tilde{c} = 0$, the system adopts the densest possible arrangement of DW's, e.g., 3×3. But because the density of corner holes varies quadratically as the DW density, a positive $\tilde{c}$ favors a dilute DW structure, i.e., large n. This competition determines n. However, the energy cost per 1×1 cell due to the stacking fault is *independent* of DW density. Thus, $\tilde{f}$ imposes a kind of cutoff at large n; if the DW structure becomes too dilute, it becomes favorable to jump into a fault-free 1×1 phase and gain energy $\Delta f/2$. Estimates of the model parameters for Si, as derived from a combination of *ab initio* and empirical calculations, are given in Table I and are represented as the filled circle in Fig. 2(a). We find that even *without* adatoms, the Si(111) surface would be expected to adopt a 7×7 (or possibly 5×5) dimer stacking-fault reconstruction.

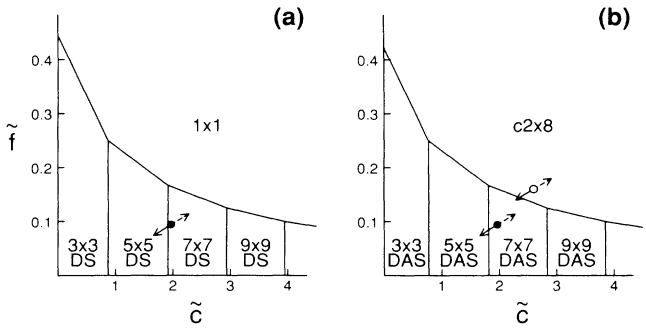

FIG. 2. (a) Ground-state structure as a function of dimensionless corner-hole energy $\tilde{c}$ and stacking-fault energy $\tilde{f}$ in the absence of adatoms. Filled circle shows estimated position of parameters for Si; solid (dashed) arrows show expected variation of the parameters with a 0.5% compression (expansion) of the surface lattice constant. (b) Same as (a), but after decoration by adatoms. A speculative position for the Ge parameters is indicated by the open circle.

Several experiments show that the surface-reconstruc-

TABLE I. Values of the parameters used in the model (see text), and their derivatives with respect to isotropic strain ε of the substrate in the surface plane (i.e., the area change is 2ε). All energies in eV.

	Parameter value	Strain derivative
p	1.45[a]	−1.0[a]
d	0.53[b]	10.2[b]
c	2.71[b]	8.4[b]
Δf	0.06[a]	1.0[a]
a	0.28[c]	. . .

[a]From *ab initio* local-density calculations of surface energy and stress (Ref. 18).

[b]The Keating calculations of Ref. 6 were repeated, and extended to obtain the strain derivatives of d and c. The values of d and c are in good agreement with Ref. 6, using the interpretation $c = E^{db} + E'_{\rm strain}$.

[c]Extracted from Ref. 5; see text. Note that a much larger value $a = 1.3$ eV, is used in Sec. VI of Ref. 6.

tion pattern is sensitive to surface strain. Strain can be applied either by epitaxial growth of a layer of material on a lattice-mismatched substrate,[10] or by alloying in the surface region.[11-13] In general, these experiments indicate a trend from $c2\times8 \rightarrow 7\times7$ DAS $\rightarrow 5\times5$ DAS with increasing compression of the surface layer. In order to model this effect, the derivatives of the model parameters with respect to strain have also been estimated; the details will be presented elsewhere.[18] It is found that Δw, Δf, and Δc are all reduced (Δw becomes more negative) with compressive strain, basically because all of these elements are under some intrinsic tensile stress. The expected shift due to a 0.5% compression (expansion) of the Si-surface lattice vector is indicated by the solid (dashed) arrow in Fig. 2(a). The trend is $1\times1 \rightarrow 7\times7$ DS $\rightarrow 5\times5$ DS with compression.

Up to now, adatoms have been absent; let us now consider the physical case of a positive adatom binding-energy[14] a. The decoration by adatoms then converts the 5×5 DS $\rightarrow 5\times5$ DAS, and the 7×7 DS $\rightarrow 7\times7$ DAS. The decoration of the islands of the DAS models is locally (hexagonal) 2×2; thus, we might expect the adatom decoration to convert the 1×1 region in Fig. 2(a) to a (hexagonal) 2×2 adatom phase. Actually, there are three very similar ordered adatom phases with the same adatom density, with periodicities 2×2, $c2\times4$, and $c2\times8$ with respect to the hexagonal axes, respectively.[19,20] (This notation follows Refs. 16, 17, 19, and 20; the 2×2 and $c2\times4$ structures here are sometimes referred to elsewhere as "$c2\times2$" and "2×2," or "hexagonal 2×2" and "rectangular 2×2," respectively.) The energies of these phases are expected to be very close,[19,20] and it is not possible to predict *a priori* which will be lowest. (The ordering on the DAS islands is likely to remain 2×2 in any case, because the triangular shape exactly accommodates the 2×2 structure.) It is assumed here that the $c2\times8$ phase is in fact lowest in energy, and that it is this phase which is observed on annealed Ge(111) surfaces. [Because less information is available, the model parameters have not been carefully estimated for Ge, but an open circle has been placed in the $c2\times8$ region of Fig. 2(b) for illustrative purposes.] It is argued that Fig. 2(b) is the fundamental phase diagram for the annealed Si and Ge (111) surfaces.

Note that the only effect of the adatom decoration on the phase boundaries is to shift them slightly to the left. This is derived as follows. The $(2n+1)\times(2n+1)$ DAS phase contains $n(n+1)$ adatoms, whereas the same area of a simple adatom phase of density $\frac{1}{4}$ would contain $n(n+1)+\frac{1}{4}$. The energy difference $a/4$ can simply be absorbed into a renormalized corner-hole energy $\Delta c' = \Delta c + a/4$. Then the relative energies of the phases are again given by Eq. (2), but with $\Delta c'$ replacing Δc. Northrup has calculated the energy of the $c2\times4$ adatom phase (top site) to be -0.07 eV per 1×1 cell relative to the relaxed 1×1 surface;[5] assuming as above that the adatom energy is insensitive to the precise periodicity, this yields an estimate $a=0.28$ eV. Then the shift in $\tilde{c}$ is $a/4|\Delta w|$ or ~ 0.1, which is the magnitude of the shift shown in going from Fig. 2(a) to 2(b). (If the $c2\times8$ adatom phase is significantly lower in energy than the 2×2 version, then $\tilde{f}$ will be renormalized in an analogous manner; the vertical shift of the phase boundaries due to this effect is estimated to be small.)

In summary, *on the assumption* that the Ge $c2\times8$ is a simple ordered adatom phase, a natural explanation for the observed phases of annealed Si and Ge (111) surfaces emerges. In this scenario, the "primary" event is the generation of dimer-row DW's in order to reduce dangling bonds. If the energy costs of corner holes and stacking faults are too great, this will not occur, and a simple adatom phase results. This is assumed to be the case for unstrained Ge (111). If the dimer-row DW's do occur, as on Si (111), topological considerations imply that they must order into the triangular pattern of the DAS 5×7, 7×7, etc., models. The "secondary" event is the decoration of the surface by adatoms. For DAS structures, the triangular shape of the islands ensures a 2×2 pattern there. For dimer-free surfaces such as Ge, the $c2\times8$ ordering of adatoms is assumed to be lowest in energy.

This scenario provides answers to the questions posed in the opening paragraph. The chemical similarity of Si and Ge is reconciled by supposing that Si and Ge lie nearby in parameter space, as shown in Fig. 2(b), but that they just happen to fall on opposite sides of a phase boundary. The physically important parameters are a negative domain-wall energy and positive faulting and corner-hole energies; the DAS periodicity is found to be determined by the relative magnitude of the domain-wall and corner-hole energies. Moreover, the strain dependence of the model parameters naturally predicts the trend $c2\times8 \rightarrow 7\times7$ DAS $\rightarrow 5\times5$ DAS with compression of the surface layer. This is so even though stress is *not* the driving force for the surface reconstruction.

Let us return, finally, to the controversial identification of the Ge $c2\times8$ surface as a simple adatom phase. The evidence *against* this identification comes primarily from Rutherford backscattering (RBS) experiments[21] showing large blocking peaks for off-normal incidence. This has been interpreted as an indication of the presence of stacking faults, as on Si 7×7. However, the following reservations can be raised. First, scanning tunneling microscope images show that the Ge $c2\times8$ surface tends to be significantly disordered;[16] the RBS data may include contributions from defects, steps, and islands of other phases. Second, impact-collision ion-scattering spectra[22] on Ge $c2\times8$ look quite different from those for Si, the Ge surface showing no strong focusing peaks. Third, the adatoms are assumed here to reside on the "top" sites; the RBS analysis was based on the "hollow" site geometry.[21] For these reasons, I do not believe the RBS data by themselves are compelling. There are several arguments in *favor* of the simple adatom model. First, the only remotely plausible model suggested to date for a faulted $c2\times8$ structure[9] has much larger bond strain energies than in the DAS model.[7,9] Second, recent experiments on the physisorption energies of noble gasses are consistent with the adatom model but not with the faulted model.[23] Third, a comparison of photoemission spectra from Si 7×7 and Ge $c2\times8$ (Ref. 24) indicates that the latter has equal densities of dangling bonds in the adatom and original surface ("rest-atom") layers.[25] This can only occur for simple adatom phases. Finally, perhaps the most obvi-

ous argument is the well-known fragility of the $c2\times8$ surface. The availability of several ordered adatom phases with equal densities and nearly equal energies would be expected to make a simple adatom surface very easy to disorder,[20] whereas the dimer-row domain walls of the DAS model involve a deeper reconstruction with stacking-fault formation and are, therefore, much more robust. This is in accord with the experience that it is harder to prepare well-ordered Ge surfaces, and that they disorder at lower temperatures than the Si 7×7.

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[14]The adatom binding energy is defined as the energy released when a single atom is taken from a bulk reservoir and placed in a relaxed adatom (top) configuration on a relaxed 1×1 surface.

[15]Precisely speaking, the parameters p, d, c, and Δf are to be *defined* by the large-n limit of Eq. (1). Related models have been proposed by Qian and Chadi (Ref. 6) who do not discuss the corner-hole energy, and by Northrup (Ref. 5) where the assumptions $\Delta f=\Delta c=0$ are implicit.

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