

Absence of Large Compressive Stress on Si(111)

David Vanderbilt

Lyman Laboratory of Physics, Harvard University, Cambridge, Massachusetts 02138

(Received 10 July 1987)

The surface-stress tensor is calculated from first principles for several Si(111)1×1, 2×1, and 2×2 surfaces. Contrary to widely held expectations, only a weak compressive stress is found for the unreconstructed 1×1 surface. Reconstructions involving π -bonded chains or adatoms are predicted to be under substantial *tensile* stress. The results indicate that relief of surface stress is *not* the driving force for the 7×7 reconstruction. The stress is shown to be useful in prediction of the effect of externally applied strain, which can drive changes in the surface reconstruction pattern.

PACS numbers: 68.35.Bs, 68.35.Md

A solid surface is characterized by an intrinsic two-dimensional surface-stress tensor, which is defined as

$$\sigma_{ij}^{\text{surf}} = A_0^{-1} \partial E / \partial \eta_{ij}, \quad (1)$$

where E is the surface energy per surface cell, η_{ij} is the surface-strain tensor, and A_0 is the equilibrium surface-cell area.¹ Unlike the surface tension on a liquid, the crystal surface stress can be either compressive or tensile, and need not be isotropic. In this paper, the first *ab initio* calculations of surface stress for semiconductors are reported.

The importance of the surface stress as a factor in surface reconstruction is beginning to be widely recognized. First, several authors have suggested that relief of surface stress may be the driving force for the 7×7 reconstruction of the Si(111) surface.²⁻⁴ A calculation by Pearson *et al.*,⁵ showing a large compressive stress at the Si(111)1×1 surface, has reinforced this interpretation.⁶ However, this calculation is based on a highly approximate empirical potential which is of questionable validity for Si.⁷ Moreover, alternative explanations for the 7×7 based on dangling-bond reduction⁸⁻¹⁰ and/or adatom formation^{9,10} are available. Second, several experiments on Si and Ge(111) surfaces show that transitions between different reconstructions can be induced by external strain, applied either directly by epitaxial growth of a layer of material on a lattice-mismatched substrate,¹¹⁻¹³ or effectively by alloying in the surface region.¹³⁻¹⁵ Finally, the surface stress can affect the populations of surface defects such as vacancies and interstitials.

Nielsen and Martin¹⁶ have demonstrated the feasibility of carrying out realistic *ab initio* calculations of stress within the local-density approximation (LDA) for bulk systems. Needs¹⁷ has recently applied this approach to calculate the stress on Al(111) and (100) surfaces. Here, stress tensors are calculated for unfaulted and faulted 1×1 and 2×2 adatom models, and for the 2×1 π -bonded chain structure,¹⁸ on Si(111). (The "faulted" structures have the surface stacking sequence . . . *aAbBa* instead of . . . *aAbBc*, as though a stacking fault were located at the surface.) The principal result is that the 1×1 and 2×2 adatom surfaces are *not* under strong

compressive stress, in contradiction to the central assumption of the stress-relief model for the Si 7×7 reconstruction. Adatoms are found to make a *tensile* contribution. The stress due to dimers in the 7×7 dimer adatom stacking-fault (DAS) model¹⁹ is estimated with use of a Keating model,¹⁰ and is also found to be tensile. The consequences for models of 7×7 formation are discussed below.

Total energies, forces, and stresses were calculated simultaneously within LDA with norm-conserving pseudopotentials²⁰ and Wigner exchange correlation.²¹ A slab thickness of five double layers plus 9.0 Å of vacuum and a plane-wave energy cutoff $E_{\text{cut}} = 8$ Ry were used for 1×1 and 2×1 reconstructions. To make the calculation of the 2×2 tractable, only four double layers (34 atoms/cell) plus 7.7 Å of vacuum (between adatoms) and $E_{\text{cut}} = 5$ Ry were used. (The relaxed 1×1 surfaces were also recalculated with this reduced convergence as a reference for the 2×2 calculations. The stresses were found to be too compressive by ≈ 1.0 eV/cell for both faulted and unfaulted 1×1 surfaces; most of this error is due to the 5-Ry cutoff.) The k -point sets were well converged, consisting of 7, 8, and 3 k points in the irreducible zone ($\frac{1}{12}$, $\frac{1}{4}$, and $\frac{1}{12}$ of the full zone) for 1×1, 2×1, and 2×2 cells, respectively. A 10- k -point set was used for reference bulk calculations.

On the assumption that there is no contribution to the stress from the deep-bulk portion of the slab (i.e., from beyond a surface penetration depth), the 2D surface-stress tensor σ^{surf} is related to the full 3D supercell stress tensor σ by

$$\sigma_{ij}^{\text{surf}} = \frac{1}{2} c \sigma_{ij}, \quad (2)$$

where c is the supercell lattice constant in the z direction, and i and j run over x and y . (As a check, the z components of σ ought to vanish.) The surface stress was obtained from Eq. (2) after several important precautions were taken. First, the slab calculations were carried out with the x - y lattice constants fixed at the appropriate equilibrium values predicted theoretically from a reference bulk calculation with the same energy cutoff.

Second, the forces were used to relax the atom positions thoroughly. Third, a correction was made to remove a fictitious tensile stress which arises from a "basis-set effect." This effect occurs because the stress is implicitly calculated with the number of plane waves held constant; convergence is much faster if the G -space cutoff is held constant instead.²² To account for this, a correction

$$(2N/3\Omega)(\partial E_{\text{tot}}/\partial \ln E_{\text{cut}})\delta_{ij} \quad (3)$$

is added to σ_{ij} . Here N is the number of atoms per supercell, Ω is the supercell volume, and E_{tot} is the bulk energy per atom. The derivative in parentheses is calculated once and for all by carrying out a series of bulk calculations (at fixed lattice constant) for twelve values of E_{cut} between 3 and 14 Ry, obtaining a polynomial least-squares fit to the curve of E_{tot} vs $\ln E_{\text{cut}}$, and evaluating the desired derivative at E_{cut} . (A related procedure has been used by Dacosta *et al.*²²) With this correction, the bulk stress is found to have converged well with $E_{\text{cut}}=8$ Ry (e.g., 90% of the improvement in going from $E_{\text{cut}}=5$ to 14 Ry has occurred by $E_{\text{cut}}=8$ Ry). With all of these precautions, the z components of the calculated stress tensor were indeed close to zero, typically an order of magnitude smaller than the x and y components.

The results of the calculations are given in Table I. The adatoms are placed in the "top" or T_4 site, i.e., just above second-layer atoms. The surface energies and geometries obtained are generally in good agreement with those of previous calculations,^{9,18,23,24} although the reduction of the surface energy due to adatoms is found to be somewhat larger than in Ref. 9. No previous calculations exist for the faulted 1×1 or 2×2 surfaces. The faulting energy for the 1×1 surface, 0.06 eV/cell, is about twice as large as that expected from a previous calculation of the bulk stacking-fault energy.²⁵ The surface layer is found to relax outward slightly on the faulted surfaces compared to the unfaulted ones; the height differences are ≈ 0.08 Å and ≈ 0.04 Å for 1×1 and 2×2 adatom surfaces, respectively.

The principal new results are the stresses given in

TABLE I. Calculated surface energy and stress for Si(111) surfaces.

Structure	E [eV/(1×1 cell)]	σ_{ii} [eV/(1×1 cell)]
1×1	1.45	-0.5
1×1 (faulted)	1.51	0.0
2×1 π chain	1.15	1.4 ^a 0.4 ^b
2×2 adatom	1.34	1.8
2×2 adatom (faulted)	1.36	2.2

^aParallel to surface chains.

^bPerpendicular to surface chains.

Table I. The 1×1 surface shows only a weak compressive stress of -0.5 eV per 1×1 cell, which should be compared with the much larger value -2.7 eV found in Ref. 5. (A negative stress is compressive.) Evidently the tendency of the surface bonds to contract (as a result of reduced coordination of the surface atom) is easily accommodated by the inward relaxation of the topmost atoms. The remaining compressive stress is caused by a small additional inward relaxation that can be traced to the metallic k -space filling of the dangling-bond surface state, and is therefore thought to be related to substrate-mediated dangling-bond interactions. Surface faulting is found to make a tensile contribution to the surface stress, so that the net stress on the faulted 1×1 surface is found to be zero within the accuracy of the calculation.

The 2×1 Pandey π -bonded chain structure is found to be under moderately strong tension along the chain, with a weaker tensile stress in the perpendicular direction. The tension along the chain may be understood as due in part to the π bonding; a compressive external strain along the chain increases the π bonding and therefore lowers the energy.

Finally, the 2×2 adatom structures are found to be under strong tensile stress. The accuracy here is less than for the 1×1 and 2×2 structures because of the smaller energy cutoff and thinner slab. However, the tests of reduced convergence for 1×1 surfaces suggest that if anything the magnitude of the tensile stress is probably underestimated. Thus, the sign and order of magnitude of the effect are predicted with confidence. The three atoms neighboring the adatom are found to move radially inward to minimize the surface energy, consistent with previous theory²⁴ and x-ray scattering experiments.²⁶ It is not surprising that this displacement results in a tensile stress in the surface plane.

In light of these results, it appears unlikely that the relief of compressive stress is the driving force for the 7×7 surface reconstruction. The island regions of the 7×7 DAS model, which are faulted or unfaulted 2×2 adatom structures, are found to be under *tension*. The dimer domain walls of the DAS model are able to relieve compression, but not tension, because they tend to pull in neighboring material, i.e., they are under tension themselves, as discussed next.

Because the DAS cell is too large for current first-principles calculations, an empirical potential model is used to estimate the stress contributed by the dimer domain walls and corner holes. The Keating calculations of Qian and Chadi¹⁰ on adatom-free dimer stacking-fault (DS) models have been repeated and extended to obtain the stresses; details are given elsewhere.²⁷ (The strain energy is calculated to be 0.54 eV per dimer, plus 1.26 eV of additional dimer strain for each corner hole, in agreement with Ref. 10.) Dimers are found to contribute a tensile stress of 5.1 eV each, and the additional tensile stress in the vicinity of the corner holes is 4.2 eV. The tension in the dimers is also evident in the relaxed

TABLE II. Estimated surface energy and stress for unreconstructed surface and for adatom-free analogs of DAS structures.

Structure	E [eV/(1×1 cell)]	σ_{ii} [eV/(1×1 cell)]
1×1	1.450	-0.50
5×5 DS	1.428	1.22
7×7 DS	1.427	0.83
9×9 DS	1.432	0.61

geometry, which shows an average expansion of $\approx 1.5\%$ of the surface islands of the 7×7 DS structure.²⁷ (A similar expansion is seen in x-ray experiments.²⁶) Since the intrinsic stress of a 1×1 surface is identically zero within the Keating potential, this expansion must come from the "pull" of the dimers.

As mentioned above, several experiments have shown that externally applied strain can drive changes in the surface reconstruction pattern. To see how such an effect can arise theoretically, recall that the surface energy depends on strain according to

$$E = E_0 + \sum_{ij} \sigma_{ij}^{\text{surf}} \eta_{ij} + O(\eta^2), \quad (4)$$

which follows from Eq. (1). For example, consider transitions between 1×1 and $(2n+1)\times(2n+1)$ DS adatom-free surfaces. The energies of the DS surfaces are estimated by combination of the empirical and first-principles results according to⁸

$$E_{\text{DS}} = E_{\text{DS}}^{\text{Keating}} + (4n^2 + 2n + 1)E_{\text{db}} + \frac{1}{2}(2n+1)^2 E_{\text{fault}}. \quad (5)$$

Here the dangling-bond energy E_{db} and faulting energy E_{fault} are taken as $E_{\text{db}} = E_{1\times 1}^{\text{LDA}}$ and $E_{\text{fault}} = E_{1\times 1}^{\text{LDA-F}} - E_{1\times 1}^{\text{LDA}}$, where $E_{1\times 1}^{\text{LDA-F}}$ and $E_{1\times 1}^{\text{LDA}}$ are the energies of faulted and unfaulted 1×1 surfaces given in Table I. The stresses are combined in the same fashion. Table II summarizes the results, and Fig. 1 shows a linearized plot of the corresponding surface energy as a function of externally applied isotropic strain, following Eq. (4). A 7×7 DS structure is predicted to be lowest in energy in the absence of strain, but compression or expansion on the order of $\approx 1\%$ is seen to be sufficient to drive transitions to 5×5 DS or 1×1 phases, respectively. The trend is $1\times 1 \rightarrow 7\times 7 \text{ DS} \rightarrow 5\times 5 \text{ DS}$ with compression primarily because compression relieves the tensile stress inherent in the dimers and therefore favors a higher density of dimers. The corresponding diagram for adatom-covered surfaces is more difficult to predict, but a similar trend is anticipated. Adatom decoration is expected to convert the 5×5 DS, 7×7 DS, and 1×1 phases to 5×5 DAS, 7×7 DAS, and $c2\times 8$ phases, respectively.⁸ The predicted trend is therefore $c2\times 8 \rightarrow 7\times 7 \text{ DAS} \rightarrow 5\times 5 \text{ DAS}$ with external compression, which appears to be con-

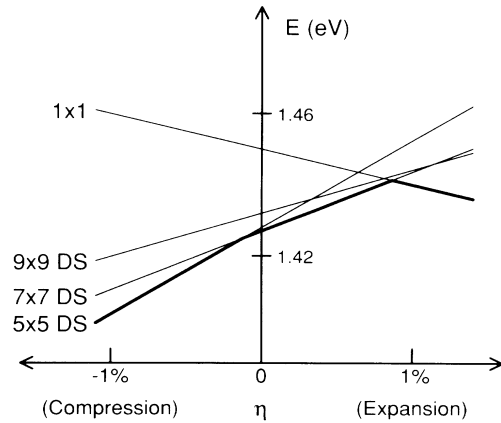


FIG. 1. Linearized surface formation energy per 1×1 cell as a function of isotropic external strain in the x - y plane for adatom-free surfaces in Table II.

sistent with most of the strain experiments.^{11,13-15}

According to the present view, then, the Si 7×7 DAS structure is *not* stabilized by a favorable elastic interaction between domain walls and compressed islands, as previously thought.^{3,4} Instead, it is stable because of dangling-bond reduction,⁸ in spite of unfavorable strain interactions between the domain walls and the islands, both of which are under tension. Externally applied compression¹¹ or alloying with Ge or Sn in the surface layer¹³⁻¹⁵ reduces this unfavorable interaction, increasing the relative stability of 7×7 and 5×5 DAS structures.^{8,27}

In summary, *ab initio* LDA calculations of semiconductor surface stress have been carried out for the first time. The relaxed 1×1 and 2×2 adatom surfaces of Si(111) are found to exhibit weak compressive and strong tensile stress, respectively. The island regions of the 7×7 DAS model are therefore expected to be under tension, which is inconsistent with the stress-relief model of 7×7 formation. Nevertheless, externally applied compressive strain does tend to relieve the intrinsic tension in the dimer domain walls; this provides a natural explanation for experiments which show that compression tends to stabilize 7×7 and 5×5 DAS structures.

This work has been supported by the Harvard Materials Research Laboratory under National Science Foundation Grant No. DMR-86-14003. Supercomputer time was made available through the National Allocations Committee of the John von Neumann Computer Center. In addition, I would like to thank R. M. Martin, I. K. Robinson, J. Tersoff, and M. B. Webb for stimulating discussions.

¹R. Shuttleworth, Proc. Phys. Soc. London, Sect. A **63**, 444

(1950).

- ²J. C. Phillips, Phys. Rev. Lett. **45**, 905 (1980).
- ³T. Ichikawa and S. Ino, Surf. Sci. **136**, 267 (1984).
- ⁴E. G. McRae, Surf. Sci. **147**, 663 (1984).
- ⁵E. Pearson, T. Takai, T. Halicioglu, and W. A. Tiller, J. Cryst. Growth **70**, 33 (1984).
- ⁶E. G. McRae, Surf. Sci. **163**, L766 (1985).
- ⁷The authors of Ref. 5 state that their potential, consisting of central two-body and Axilrod-Teller three-body terms, was chosen for "purely pragmatic reasons" and that there is "no direct theoretical justification for using these potentials."
- ⁸D. Vanderbilt, Phys. Rev. B (to be published).
- ⁹J. E. Northrup, in *Proceedings of the Eighteenth International Conference on the Physics of Semiconductors*, edited by O. Engström (World Scientific, Singapore, 1987), p. 61.
- ¹⁰G.-X. Qian and D. J. Chadi, J. Vac. Sci. Technol. **B 4**, 1079 (1986).
- ¹¹H.-J. Gossman *et al.*, Phys. Rev. Lett. **55**, 1106 (1985), and J. Vac. Technol. **A 3**, 1633 (1985).
- ¹²A. Ourmazd *et al.*, Phys. Rev. Lett. **57**, 1332 (1986).
- ¹³K. Nakagawa, P. M. J. Maree, and J. F. van der Veen, in *Proceedings of the Eighteenth International Conference on the Physics of Semiconductors*, edited by O. Engström (World Scientific, Singapore, 1987), p. 93.
- ¹⁴T. Ichikawa and S. Ino, Surf. Sci. **105**, 395 (1981), and **136**, 267 (1984).
- ¹⁵H.-J. Gossman and L. C. Feldman, Surf. Sci. **155**, 413 (1985).
- ¹⁶O. H. Nielsen and R. M. Martin, Phys. Rev. B **32**, 3792 (1985).
- ¹⁷R. J. Needs, Phys. Rev. Lett. **58**, 53 (1987).
- ¹⁸K. C. Pandey, Phys. Rev. Lett. **47**, 1913 (1981), and **49**, 223 (1982).
- ¹⁹K. Takayanagi, Y. Tanishiro, M. Takahashi, and S. Takahashi, J. Vac. Sci. Technol. **A 3**, 1502 (1985), and Surf. Sci. **164**, 367 (1985).
- ²⁰D. Vanderbilt, Phys. Rev. B **32**, 8412 (1985).
- ²¹E. P. Wigner, Phys. Rev. **36**, 1002 (1934).
- ²²P. G. Dacosta, O. H. Nielsen, and K. Kunc, J. Phys. C **19**, 3163 (1986).
- ²³J. E. Northrup and M. L. Cohen, J. Vac. Sci. Technol. **21**, 333 (1982).
- ²⁴J. E. Northrup, Phys. Rev. Lett. **57**, 154 (1986).
- ²⁵M. Y. Chou, M. L. Cohen, and S. G. Louie, Phys. Rev. B **32**, 7979 (1985).
- ²⁶I. K. Robinson, W. K. Waskiewicz, P. H. Fuoss, and L. J. Norton, unpublished.
- ²⁷D. Vanderbilt, in *Proceedings of the Second International Conference on the Structure of Surfaces*, Amsterdam, 1987 (to be published).