Origins of Stress on Elemental and Chemisorbed Semiconductor Surfaces

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First-principles calculations of stress and energy have been performed on 1×1 substitutional and $\sqrt{3}\times\sqrt{3}$ adatom-covered Si(111) and Ge(111) surfaces, using a variety of column-III, -IV, and -V adsorbates. Trends in surface stresses are understood in terms of three contributing factors: the relative atomic size of the adsorbate and substrate atoms, the chemical nature of the adsorbate species, and the bonding topology of the surface reconstruction.

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A number of interesting phenomena which apparently result from surface stress have recently been observed. For instance, it has been found that the application of an isotropic surface strain by growth on a lattice-mismatched substrate or by alloying can drive a transition from one surface reconstruction to another.[1,2] More recently, Men, Packard, and Webb[3] used a cantilevered bar to apply an anisotropic external strain to a Si(100) wafer, and found that this favored a reconstruction of one orientation over another. Moreover, Alerhand *et al.*[4] showed that even in the absence of an external strain, long-range elastic interactions will favor the formation of stress domains on any surface which reconstructs with degenerate phases of differing intrinsic stress. Finally, it appears that the presence of a strong stress may induce surface defects. On the 1×1 As:Si(111) and 1×1 As:Ge(111) surfaces, for example, Becker, Klitsner, and Vickers[5] report the presence of point and line defects which persist even after many annealing cycles, and suggest that these defects may serve to relieve surface stress.

Despite the mounting importance of the role of stress in understanding surface phenomena, there has been little work on the microscopic origins of this important quantity. In this paper, we report the results of a series of state-of-the-art calculations of surface stress on elemental and chemisorbed semiconductor surfaces. By examining the trends of the stress as function of the row and column of the adsorbate species, we have identified three principal sources of surface stress. First, there may be an atomic size mismatch between the adsorbate and substrate; although this is most often cited as the origin of surface stress, we find that it is frequently not the dominant effect. A more important origin of surface stress is the chemical nature of the adsorbate, which will effect the hybridization of the surface atoms. Finally, we find that an unusual bonding topology of a surface reconstruction will also induce a significant surface stress. Although we discuss the microscopic origins of stress on surfaces, we anticipate that these arguments will be quite general, and will also apply to stress at point and line defects and at interfaces.

In order to calculate surface energies and stress, we have performed *ab initio* pseudopotential calculations, using the local-density approximation. The Hamiltonian was solved self-consistently in a basis of plane waves up to 8 Ry with some tests performed up to 12 Ry. A dielectric matrix and Keating matrix were used to accelerate the convergence of the charge density and atomic forces, respectively.[6] The semi-infinite surface was treated as a slab with a thickness of five double layers, and these slabs were repeated with a spacing of three double layers of vacuum. The stress was calculated using the method of Nielsen and Martin,[7] and the surface stress

$$\sigma_{ij}^{\text{surf}} = \frac{1}{A}\frac{dE^{\text{surf}}}{d\epsilon_{ij}} \tag{1}$$

was deduced as in Ref. 8, in which the results for the elemental surfaces were presented. The basis set correction term[9] was calculated explicitly for Si and Ge, and deduced for B, Al, Ga, and As by requiring that the $\hat{\mathbf{z}}$ components of the stress vanish.

In our study of chemisorbed surfaces, we have considered two classes of surface reconstructions. We have studied the 1×1 substitutional surfaces, in which the top layer of substrate atoms is replaced by adsorbate atoms, and $\sqrt{3}\times\sqrt{3}$ and 2×2 adatom-covered surfaces, in which the chemisorbed species adsorb at the top (T_4) site,[10] above the second-layer atoms. Of all the surfaces we study, only three have been observed experimentally: In the 1-monolayer (ML) regime, arsenic exhibits a substitutional phase on both Si(111)[11] and Ge(111);[5] and in the $\frac{1}{3}$-ML regime, gallium adsorbs on Si(111) to form a $\sqrt{3}\times\sqrt{3}$ adatom-covered surface.[12] (Although a stable phase of Ga in the 1-ML regime has also been observed, scanning-tunneling-microscopy measurements suggest that this phase is not a simple substitutional one, but involves some discommensuration.[13]) Nevertheless, it is of great value to examine a variety of real and fictitious surfaces in order to observe trends and uncover the origins of surface stress. Because all surfaces studied have a C_{3v} symmetry, the surface stress must be isotropic. The stress, and some parameters describing the surface

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TABLE I. Stresses and bond angles of 1×1 substitutional surfaces on Si(111) and Ge(111). All stresses in eV/(1×1 cell). A bond angle of 120° (109.4°) corresponds to an sp^2 (sp^3) hybridization.

	B:Si(111)		
σ_{ii}	4.87		
θ	119.0°		
	Al:Si(111)	Si(111)	
σ_{ii}	−6.45	−0.54	
θ	117.9°	114.0°	
	Ga:Si(111)	Ge:Si(111)	As:Si(111)
σ_{ii}	−4.45	−1.12	2.27
θ	119.3°	111.5°	104.5°
		Ge(111)	As:Ge(111)
σ_{ii}		−0.73	2.64
θ		112.6°	104.7°

relaxation, are reported in Tables I and II.

The most obvious source of surface stress is an atomic size effect, corresponding to the intuitive notion that as the atomic size of the adsorbate increases, the compressive stress of the surface increases. For example, a comparison of the 1×1 Si(111) and 1×1 Ge:S(111) surfaces in Table I reveals a greater compressive (more negative) stress for the latter. This increased compressive stress is a result of the larger size of the Ge atom, which has a covalent radius 4% larger than that of Si.[14] Similarly, the large tensile stress of the 1×1 B:Si(111) (see Table I) is an extreme example of the atomic size effect. Since the boron occupies a position of threefold symmetry, only its $\hat{z}$ coordinate may relax. The B−Si bond length is shortest when these atoms are coplanar, corresponding to a bond length of 2.22 Å, and bond angles of 120°. The ideal B−Si bond length, as derived from covalent radii, is significantly less than 2.22 Å (see Fig. 1), which induces the tensile stress. [The decrease in stress between the 1×1 Al:Si(111) and the 1×1 Ga:Si(111) surfaces violates our expectation that stress will increase as the adsorbate moves down the column of the periodic table. However, gallium has a number of anomalous properties, e.g., its atomic size is the same as that of aluminum, because it is the first group-III element with a filled d shell.[15]]

The effects of changing the row of the substrate can also be understood in terms of the atomic size effect. The 1×1 As:Si(111) surface is under a tensile stress, for reasons to be discussed later. Adsorbing As on Ge(111) increases this tensile character, since Ge has a larger lattice constant than Si. Similar reasoning applies to stress on the 1×1 Ge:Si(111) and 1×1 Ge(111) surfaces.

Whereas atomic size effects were sufficient to understand the changes in surface stress as a function of the row of the adsorbate or substrate species, it does not explain the trends in the stress as the column of the adsorbate species is varied. Arsenic, for instance, is the same size as silicon, but 1×1 As:Si(111) is under a strong tensile stress, whereas 1×1 Si(111) is under mild compressive stress. In order to understand these trends, we must consider the *chemical* nature of the adsorbate species. For the group-III elements, such as Ga, the adsorbate contributes only three electrons to the bonds with its neighbors. In this case, the surface band is empty, and so the surface energy is lowered by sp^2 hybridizing the Ga atom. Note, from Table I, that the bond angles of the group-III adsorbates are all near 120°. Because increasing the bond angles necessarily decreases the bond lengths (see Fig. 2), the relaxed bond lengths of Ga and Al are less than the ideal bond lengths, and so the surface is under a compressive stress. Each arsenic adsorbate, on the other hand, has five electrons outside the core. Three of these participate in bonds to surface silicons, leaving two electrons in a lone pair. Because of Coulomb repulsion between the lone pair and bond charge,[16] the As atom prefers to hybridize with bond angles less than those of a perfect tetrahedron. With decreasing bond angles, the bond lengths increase, inducing a tensile stress. [The same hybridization preferences are responsible for the buckling observed on GaAs(110).] Finally, the group-IV elements have only one electron in the surface band. The hybridization is intermediate between sp^2 and sp^3, causing a weaker compressive stress.

TABLE II. Stresses and relaxation parameters (see Fig. 3) for $\sqrt{3}\times\sqrt{3}$ and 2×2 adatom-covered Si(111) surfaces. All adatoms are in the T_4 site. The bulk separation is $b=3.84$ Å.

Structure	σ_{ii} [eV/(1×1 cell)]	b (Å)	ϕ (deg)
$\sqrt{3}\times\sqrt{3}$ Ga:Si(111)	1.35	3.59	92.9
$\sqrt{3}\times\sqrt{3}$ Si:(111)	1.70	3.52	89.0
$\sqrt{3}\times\sqrt{3}$ As:Si(111)	2.34	3.32	81.8
2×2 Si(111)	1.66	3.65	95.2

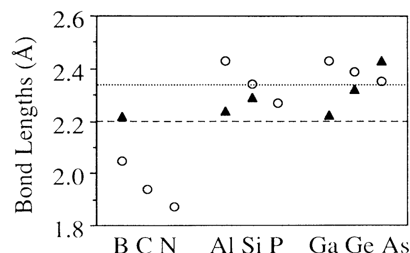

FIG. 1. Ideal bond lengths between silicon and chemisorbed species predicted from covalent radii (circles); and calculated on relaxed 1×1 Si(111) surfaces (triangles). Surfaces in which relaxed bond lengths are less (greater) than ideal bond lengths are under tension (compression). Dashed line is minimum bond lengths allowed on 1×1 surface; dotted line represents ideal Si−Si bond lengths.

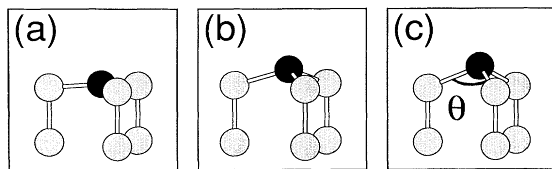

FIG. 2. Relaxed positions of three 1×1 Si(111) substitutional surfaces. The top layer (dark spheres) represent Ga, Ge, and As in (a), (b), and (c), respectively. From left to right, bond angles decrease and surface stresses increase.

Thus the surface stresses and relaxations for different adsorbates within a row of the periodic table may be understood in terms of the *chemical* nature of the chemisorbed species. Note that the surface relaxations *cannot* be understood in terms of a size effect alone, as the calculated bond lengths obey the *opposite* trend from that predicted by covalent radii (see Fig. 1).

In addition to size and chemical effects, surface stress may also result from any unusual bonding configurations present at a surface. For instance, we have found that the tensile stress associated with adatom-covered surfaces is a consequence of the relaxation mechanism of the adatom unit cell. For adatoms in the T_4 site, the driving force of the relaxation process is to relieve the bond angle stress between atoms 1, 2, and 5 (see Fig. 3), and to achieve a more natural separation between atoms 1 and 5. This driving force causes the nearest-neighbor surface atoms (2–4) to decrease their separation and introduces a tensile stress into the adatom cell. A number of other cases in which the bonding topology of a surface has a dominant influence on the surface stress have been discussed previously. These include the π-bonded chain structure[17] of cleaved Si(111), which displays a strong tensile stress primarily along the chain direction;[2] the dimer reconstruction on the Si(100) surface,[4] which causes a tensile stress parallel to the dimer and a compressive stress in the perpendicular direction; and the dimers and surface stacking faults which are present in the 7×7 Si(111) reconstruction, both of which introduce a tensile stress.[2]

In general, the observed surface stress may result from a combination of the factors discussed above. The chemisorbed adatom surfaces, for example, are all under tensile stress as a result of the bonding topology of the adatom cell. The degree of tensile stress, however, is modulated by the chemical nature of the adsorbate (see Table II). Like the 1×1 Ga:Si(111) surface, the $\sqrt{3}\times\sqrt{3}$ Ga:Si(111) surface has an empty dangling-bond band, and so the bond angles increase slightly compared to the $\sqrt{3}\times\sqrt{3}$ Si(111) surface. As before, the surface tensile stress decreases when Ga is adsorbed, and so the distance between the nearest-neighbor surface atoms (2–4) is increased. The $\sqrt{3}\times\sqrt{3}$ As:Si(111) surface also follows the same trend as the 1×1 As:Si(111) surface, with decreased bond angles and a more tensile surface stress.

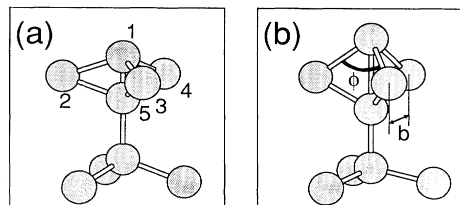

FIG. 3. Adatom structure for $\sqrt{3}\times\sqrt{3}$ Si(111). (a) Unrelaxed adatom cell in which all atoms, except adatom (atom 1), are in bulk positions. (b) Relaxed adatom cell.

Thus, as expected, the degree of tensile stress on the $\sqrt{3}\times\sqrt{3}$ adatom-covered surfaces increases as the adsorbate species is varied from group III to IV.

The stress of the 2×2 elemental adatom surface of Si may also be understood in simple terms. Of the four surface atoms in the 2×2 cell, the adatom bonds to three, which leaves one surface atom, the rest atom, with an unsaturated dangling bond. Because of charge transfer in the unit cell,[8] the rest atom has a lone pair and the adatom orbital is empty. Thus the rest atom and adatom are analogous to the As and Ga on the 1×1 As:Si(111) and $\sqrt{3}\times\sqrt{3}$ Ga:Si(111) surfaces, respectively. For this reason, we suggest that the 2×2 surface is similar to a composite of the 1×1 As:Si(111) and $\sqrt{3}\times\sqrt{3}$ Ga:Si(111) surfaces. In support of this interpretation, we note that the relaxation of the adatom cells are similar (see Table II), and the bond angles of the rest atom (99.8°) and the As atom (104.5°) are both less than the ideal tetrahedral value. The surface stress of the 2×2 adatom surface, 1.66 eV/(1×1 cell), is also close to the area-weighted average of the 1×1 As:Si(111) and $\sqrt{3}\times\sqrt{3}$ Ga:Si(111) surfaces which is 1.58 eV/(1×1 cell).

Finally, in addition to calculating surface stresses, we have also calculated surface energies for chemisorbed Si(111) surfaces (see Table III). (The surface energy represents the cost per unit area to create a surface from bulk Si and Ge atoms and free non-spin-polarized B, Al, Ga, and As atoms. Free-atom energies were calculated in a fictitious fcc cell with 8-Å separation.) We note that adatom-covered $\sqrt{3}\times\sqrt{3}$ As:Si(111) is unstable to decomposition into regions of 1×1 As:Si(111) and elemental Si(111), which prefers a 7×7 dimer-adatom

TABLE III. Energies of chemisorbed surfaces.

Structure	E [eV/(1×1 cell)]
1×1 Ga:Si(111)	−3.01
1×1 As:Si(111)	−5.34
$\sqrt{3}\times\sqrt{3}$ Ga:Si(111)	−0.35
$\sqrt{3}\times\sqrt{3}$ As:Si(111)	−0.86

stacking-fault (DAS) reconstruction.[18] The surface energy of 7×7 DAS Si(111) is estimated to be close in value to the energy of 2×2 Si(111),[19] which is 1.24 eV/(1×1 cell),[8] and so we calculate that the energy released on phase separation is $\Delta E = -0.09$ eV/(1×1 cell). Adatom-covered surfaces of Ga, on the other hand, do not prefer to phase separate [$\Delta E = +0.17$ eV/(1×1 cell)]. This is consistent with the experimental findings that adatom coverings of Ga on Si are often reported,[12] but arsenic prefers to adsorb in a substitutional manner.[11]

In summary, we have carried out first-principles calculations of surface stress for a variety of elemental and chemisorbed semiconductor surfaces. Moreover, we have argued that all the observed trends can be understood in terms of three dominant factors which contribute to the surface stress. These are the relative atomic sizes of the adsorbate species, the chemical nature of the adsorbate species, and bond topology of the reconstruction. We believe that these considerations are quite general, and may be used to predict qualitatively the stresses at other semiconductor surfaces.

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[1]H. J. Gossman, J. C. Bean, L. C. Feldman, D. G. McRae, and I. K. Robinson, Phys. Rev. Lett. **55**, 1106 (1985).

[2]D. Vanderbilt, Phys. Rev. Lett. **59**, 1456 (1987).

[3]F. K. Men, W. E. Packard, and M. B. Webb, Phys. Rev. Lett. **61**, 2469 (1988).

[4]O. L. Alerhand, D. Vanderbilt, R. D. Meade, and J. D. Joannopoulos, Phys. Rev. Lett. **61**, 1973 (1988).

[5]R. S. Becker, T. Klitsner, and J. S. Vickers, J. Microsc. Oxford **152**, 157 (1988).

[6]D. Vanderbilt and S. G. Louie, Phys. Rev. B **30**, 6118 (1984).

[7]O. H. Nielsen and R. M. Martin, Phys. Rev. B **32**, 3792 (1985).

[8]R. D. Meade and D. Vanderbilt, Phys. Rev. B **40**, 3905 (1989).

[9]R. D. Meade and D. Vanderbilt, in *Proceedings of the Materials Research Society,* edited by J. Tersoff, D. Vanderbilt, and V. Vitek (Materials Research Society, Pittsburgh, PA, 1989), p. 451.

[10]J. E. Northrup, Phys. Rev. Lett. **57**, 154 (1986).

[11]M. A. Olmstead, R. D. Bringans, R. I. G. Uhrberg, and R. Z. Bachrach, Phys. Rev. B **34**, 6041 (1986).

[12]J. Zegenhagen, J. R. Patel, P. Freedland, D. M. Chem, J. A. Golovchenko, P. Bedrossian, and J. E. Northrup, Phys. Rev. B **39**, 1298 (1989).

[13]D. M. Chen, J. A. Golovchenko, P. Bedrossian, and K. Mortensen, Phys. Rev. Lett. **61**, 2867 (1988).

[14]Because the electronegativities of these elements are close in value, we are free to use the covalent radii to estimate bond lengths without correcting for ionic effects.

[15]N. N. Greenwood and A. Ernshaw, *Chemistry of the Elements* (Pergamon, Oxford, 1984).

[16]Similar reasoning applies to the case of ammonia. See, for example, Karplus and Porter, *Atoms and Molecules* (Benjamin/Cummings, Menlo Park, CA, 1970).

[17]K. C. Pandey, Phys. Rev. Lett. **47**, 1913 (1981); **49**, 223 (1985).

[18]K. Takayanagi, Y. Tanishiro, M. Takahashi, and S. Takahashi, J. Vac. Sci. Technol. A **3**, 1502 (1985); Surf. Sci. **164**, 367 (1985).

[19]D. Vanderbilt, Phys. Rev. B **36**, 6209 (1987).