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Energy-Minimization Approach to the Atomic Geometry of Semiconductor Surfaces

D. J. Chadi
Xerox Palo Alto Research Center, Palo Alto, California 94304
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The (110) surface atomic geometries of GaAs and ZnSe and of 2×1 reconstructed (111) surface of Si are calculated by minimizing the total energy of the electron-ion system. The corresponding reductions in total energy between the relaxed and unrelaxed surfaces are calculated to be -0.51, -0.30, and -0.37 eV per surface atom, respectively. Subsurface relaxations are generally found to make a very small (≤ 0.02 eV) contribution to the reduction in total energy.

Recent analyses of low-energy electron-diffraction (LEED) intensities have shown that atomic rearrangements on semiconductor surfaces are pervasive and involve large atomic displacements[1]. Additional evidence for this has come from studies of surface electronic structure. The metallic or nonmetallic nature of the surface, the positions of surface states, and their dispersion and symmetry are strongly dependent on the surface atomic geometry. In this way from a comparison of theoretical and experimental surface spectra information on surface structure has been obtained.[2-7]

In this Letter a total-energy-minimization approach to semiconductor surface-structure determination is presented. The only input into the calculation are from bulk electronic and lattice-dynamical properties. The approach is based on a semiempirical model for the variation of the total energy ΔE_{tot} with changes in atomic coordinates. In the bulk, the elastic coefficients and phonons frequencies can be directly related to the variation in E_{tot} with atomic displacements; therefore, the accuracy of the model for ΔE_{tot} can be easily tested. An energy-minimization approach to structural properties of crystals[8-10] and surfaces[11-15] has also been utilized in several recent works.

The total energy E_{tot} of an electron-ion system can be expressed as

$$E_{\text{tot}} = E_{ee} + E_{ei} + E_{ii}, \tag{1}$$

where E_{ee}, E_{ei}, and E_{ii} denote the electron-electron, electron-ion, and ion-ion interaction energies, respectively. It is useful to introduce the "band-structure" energy defined as

$$E_{\text{bs}} = \sum_{\vec{k},n} E_n(\vec{k}), \tag{2}$$

where the sum of single-particle energies is taken over occupied states, with wave vector $\vec{k}$ and band index n. In terms of E_{bs} and making use of the fact that $E_{\text{bs}} = E_{ei} + 2E_{ee}$, Eq. (1) can be expressed as

$$E_{\text{tot}} = E_{\text{bs}} + U, \tag{3}$$

where $U = E_{ii} - E_{ee}$. The advantage of Eq. (3) over Eq. (1) is that for two ions that are separated by a distance much larger than the Thomas-Fermi screening length the combined ion-plus-screening-electron system is nearly neutral and U is close to zero. One would therefore expect that to a good approximation this term can be described by a short-range-force-constant model.

To calculate E_{bs} the Slater-Koster[16] tight-binding method was used. The tight-binding parameters were chosen to be identical to those used in our previous work[8] on structural properties of crystalline semiconductors. For the bulk the conditions imposed on E_{tot} were that at equilibrium it satisfy

$$\partial E_{\text{tot}}/\partial V = 0 \tag{4}$$

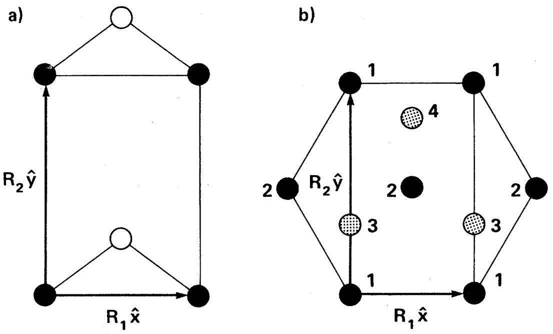
and

$$V\partial^2 E_{\text{tot}}/\partial V^2 = B, \tag{5}$$

where V denotes volume and B the bulk modulus. For a given dependence of the tight-binding param-

TABLE I. Force-constant parameters for Si, GaAs, and ZnSe.

	U_1	U_2
Si	−23.19	53.35
GaAs	−17.72	44.80
ZnSe	−14.15	36.69



(110) SURFACE

(111) SURFACE

FIG. 1. The two-dimensional unit cells for (110) and 2×1 reconstructed (111) surfaces are shown. The dotted spheres denote second-layer atoms. The numbers next to the atoms identify equivalent atoms. See Tables III and IV for atomic displacements from unrelaxed positions shown above.

eters on nearest-neighbor distance d, the above equations can be satisfied by taking

$$\Delta U = \sum_{i>j} (U_1\epsilon_{ij} + U_2\epsilon_{ij}^2), \qquad (6)$$

where ϵ_{ij} is the fractional change in the distance between two nearest-neighbor atoms denoted by i and j. For a d^{-2} dependence of the tight-binding parameters on d, the values of U_1 and U_2 that satisfy Eqs. (4) and (5) are given in Table I.

Without using any additional parameters the above model for E_{tot} also predicts the correct angular-restoring forces. The elastic coefficients $C_{11} - C_{12}$ and C_{44}, and the zone-boundary transverse-acoustic (TA) mode at X are all related to angular restoring forces.[8] The agreement between the calculated (from ΔE_{tot}) and experimental values of these quanitites shown in Table II is sufficiently close that no additional force-constant parameters were used. To test the accuracy of the parameters in predicting ΔE_{tot} for other situations we have also calculated the transverse-optic (TO) mode at Γ. This mode involves changes in both bond lengths and angles but none in volume. The calculated and experimental values of the TO frequencies for Si, GaAs, and ZnSe shown in Table II agree to within 4%. The model used in calculating ΔE_{tot} is therefore sufficiently accurate for considering general types of atomic motion.

Since bond lengths at the surface were not constrained to remain fixed in the calculations we have also tested the adequacy of the harmonic expansion in Eq. (6). For Si the coefficient U_3 of ϵ_{ij}^3 in Eq. (6), obtained from the results of Keating[17] and of Wendel and Martin[9] is found to be around −166 eV. This indicates that the fractional change in bond lengths has to be as large as 32% before the cubic term gives a contribution equal to that of the quadratic term. The cubic term results in corrections of about 0.002 Å in the displacements of surface atoms and was included only in the calculations for Si.

For all three surfaces considered here the electronic configuration is such that after relaxation all bands are either completely filled or empty. The electron-electron interaction energy at the surface is, therefore, similar to that in the bulk. To determine surface structure, all parameters were therefore assumed to be the same at the surface as in the bulk. To obtain E_{bs} the energies of all occupied states, whether bulk or surface derived, were summed. Calculations for eight- to twelve-layer-thick slabs show that ΔE_{bs} arising from surface relaxation is insensitive to the number of layers used.

TABLE II. The cubic lattice constant and bulk modulus B were fitted to the values shown above. The values of some bulk elastic coefficients and phonon frequencies calculated from E_{tot} are compared to experimental values (in parentheses).

	a (Å)	B (10^{11} erg/cm^3)	$C_{11} - C_{12}$ (10^{11} erg/cm^3)	C_{44} (10^{11} erg/cm^3)	TA(X) (10^{12} Hz)	TO(Γ) (10^{12} Hz)
Si	5.44	9.78	10.76 (10.18)	9.21 (7.96)	6.66 (4.49)	15.6 (15.6)
GaAs	5.65	7.48	6.43 (6.49)	6.35 (5.92)	3.12 (2.39)	8.46 (8.1)
ZnSe	5.65	5.95	3.34 (3.22)	3.50 (4.41)	2.38 (2.10)	6.28 (6.21)

TABLE III. Atomic displacements in *A* from unrelaxed positions for the (110) surfaces of GaAs and ZnSe. The superscripts *a* and *c* refer to anion and cation, respectively. The subscript 1 refers to the surface layer, 2 to the subsurface, etc. The normal to the surface is in the *z* direction. ΔE_{tot} is in eV per surface atom. θ is the bond rotation angle at the surface.

	θ	ΔE_{tot}	Δy_1^a	Δy_1^c	Δz_1^a	Δz_1^c	Δz_2^a	Δz_2^c	Δz_3^a	Δz_3^c
GaAs										
This work	27.3°	−0.51	0.19	0.35	0.19	−0.46	−0.06	0.07	0.02	−0.04
Ref. 16	26.4°	−0.39	⋯	⋯	0.20	−0.50	−0.05	0.05	0.025	−0.025
Ref. 17	34.8°	−0.42	0.34	0.60	0.20	−0.60	⋯	⋯	⋯	⋯
Ref. 18	27.1°	−0.46	0.32	0.48	0.10	−0.55	⋯	⋯	⋯	⋯
ZnSe (this work)	25.6°	−0.30	0.18	0.37	0.04	−0.55	−0.05	0.12	0.04	−0.04

The two-dimensional unit cell for the (110) surface of GaAs and ZnSe is shown in Fig. 1(a). The changes in atomic coordinates (for the first three surface layers) from unrelaxed, bulk-terminated positions calculated for[12] GaAs and ZnSe as well as several LEED-determined structures[18-20] for GaAs are shown in Table III. The angle θ formed by nearest-neighbor cation-anion bonds the surface with the bulk terminated plane and ΔE_{tot} (in eV per surface atom) are also given in Table III. For GaAs the value of −0.51 eV per surface atom for ΔE_{tot} is relatively close to the value of −0.65 eV obtained recently by Goddard *et al.* using cluster-type calculations.[15] The *absolute* values of the normal displacements of surface and subsurface atoms in GaAs are in good agreement with the LEED results of Ref. 18 (see Table III). The *relative* displacements of nearest-neighbor surface atoms are nearly identical to the LEED results of Ref. 20. For ZnSe, LEED studies[21] indicate a surface structure similar in many respects to that of GaAs but no definite structure for ZnSe has been determined yet. Our calculations show the main difference in the surface relaxations of GaAs and ZnSe to be in the normal displacements of the surface anions; the Se atoms do not move appreciably from their bulk-terminated positions as compared to As atoms. The bond-length variations are calculated to be between −2.9% to 1.7% in GaAs and −7% to 2.7% in ZnSe.

The energy lowering arising from subsurface relaxations was found to be very small (≤ 0.02 eV), typical of room-temperature bulk phonon frequencies. This suggests that low-temperature LEED measurements would be required if subsurface relaxations are to be accurately determined. It als indicates that the phonon contribution to E_{tot} would be needed in the calculations.

We have also applied our method to the (111) surface of Si. The 1×1 relaxed surface structure has been recently calculated by Ihm and Cohen[14] and by Redondo *et al.*[15] Their calculations indicate an inward relaxation of between 0.15 and 0.08 Å, respectively. LEED studies[22,23] indicate a contraction of between 0.12 and 0.16 Å. Our method which is not well suited for treating metallic surfaces indicates that the surface remains unrelaxed.

The two-dimensional unit cell for the 2×1 surface of Si is shown in Fig. 1(b). The basic features of the 2×1 reconstruction were first described by Haneman[24]: The reconstruction involves the raising and lowering of alternate rows of atoms; the transverse displacements of subsurface atoms are such as to keep the bond lengths nearly constant. Modified versions of the Haneman model have been used in calculations of sur-

TABLE IV. Atomic displacements in angstroms from unrelaxed positions for the 2×1 reconstructed (111) surface of Si. The superscripts refer to the type of atoms shown in Fig. 1(b). The subscript 1 refers to the surface layer, 2 to the subsurface.

ΔE_{tot}	Δy_1^1 (Δz_1^1)	Δy_1^2 (Δz_1^2)	Δy_2^3 (Δz_2^3)	Δy_2^4 (Δz_2^4)
≈ −0.36	0.06 (0.31)	0.0 (−0.44)	−0.13 (0.0)	0.09 (0.0)

face electronic spectra.[2-4] The main results of our calculation for the displacements of the first two surface layers as shown in Table IV give an inward (outward, i.e., away from bulk atoms) vertical relaxation of about 56% (45%) of the bulk interlayer spacing for type-1 (type-2) surface atoms in Fig. 1(b). These are much larger than the corresponding Haneman[24] values of 15% (23%), nevertheless the resulting bond-length variations are only between -1.7% and 3.4%. The uncertainties for the calculated normal displacements are about ± 0.04 Å. The calculated ΔE_{tot} of -0.36 eV includes a contribution of -0.02 eV from third-layer transverse distortions of ± 0.08 Å. The calculations show no reduction in E_{tot} arising from vertical displacements of second-layer atoms.

In summary, the surface atomic geometries of several semiconductors were calculated by using a total-energy-minimization approach. The method is efficient, and judging from the results for GaAs it should yield results consistent with LEED-determined structures. Application of the method to a number of other semiconductors is in progress.

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