Total energy minimization for diamond (111) surfaces: Support for an undimerized π-bonded chain reconstruction

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A self-consistent linear combination of atomic-orbitals (LCAO) approach to local density theory is used to calculate total energies for the 1×1 and various reconstructed 2×1 models of the diamond (111) surface. Among the many models suggested, only the Pandey π-bonded chain model has a lower energy than that of the 1×1 surface. A minimum-energy structure is obtained for this model after extensive consideration of relaxations. *No* dimerization of the surface chain is found to occur.

The (111) surfaces of the tetrahedral elements C, Si, and Ge are found to undergo a remarkable variety of surface reconstructions.[1] A possible common denominator is the apparent occurrence of a 2×1 reconstruction on all three surfaces; the similarity of the angle-resolved photoemission results[2–4] suggests that a common structure may be responsible. Pandey's proposed π-bonded chain model[5] has recently attracted much attention as a possible candidate for this structure.

The 2×1 reconstruction occurs upon cleavage in Si and Ge, but is only metastable. On diamond, the $2\times2/2\times1$ structure appears upon annealing at $\sim1000\,^{\circ}\mathrm{C}$,[6] and is presumably the thermodynamically stable structure. [Low-energy-electron diffraction cannot distinguish between a true 2×2 or disordered domains of 2×1 for this surface; the similarity of the angle-resolved ultraviolet photoemission[2] (ARUPS) to that of Si (Ref. 3) and Ge (Ref. 4) suggests the latter.] Comparison of ARUPS results[2] with the calculated energy dispersion of occupied surface states yields some indirect evidence for the Pandey π-bonded chain model,[5,7] possibly with some dimerization along the chain.[5] However, discrepancies in the location and dispersion of the surface state persist,[7] and the model remains controversial[8–10] with several alternative models suggested.

In this paper, we report direct energy minimization calculations for a variety of 2×1 reconstruction models of the C(111) surface. Because of the localized nature of the carbon wave functions, a first-principles linear combination of atomic-orbitals (LCAO) approach to local density theory (LDA) has been used to calculate total energies. The unrelaxed Pandey π-bonded chain model is found to have a lower energy than any other 2×1 model tested, about equal to that of the ideal 1×1 surface. Relaxation lowers the energy substantially, so that the relaxed Pandey model is ~0.3 eV lower in energy than the relaxed 1×1 surface. Dimerization of the Pandey chain model is always found to *increase* the energy of the system.

The method is a generalization of the first-principles LCAO approach of Chelikowsky and Louie[11] (CL) to cases (e.g., surfaces, defects, or heteropolar materials) for which charge transfer between inequivalent atoms must be treated self-consistently. The details will be presented elsewhere,[12] but we give a brief description here. In the CL approach, the potential is constructed as

$$V_0(\vec{r})=\sum_{\vec{R},\vec{\tau}} V_{\mathrm{eff}}(\vec{r}-\vec{R}-\vec{\tau}) \ , \tag{1}$$

where the effective potential V_{eff} is chosen once and for all for a given element by fitting $V_0(\vec{r})$ to $V_{\mathrm{LDA}}(\rho_{\mathrm{cry}})$, with ρ_{cry} being the crystal charge density for one reference bulk crystal structure. While the Kohn-Sham one-electron potential V_{LDA} is not strictly separable into atom-centered terms, the best fit V_0 nevertheless gives a good approximation to it. Next, the Schrödinger equation is solved for the wave functions and charge density, from which the variational LDA total energy $E_{\mathrm{tot}}(\rho,V_{\mathrm{ion}})$ is finally calculated. (E_{tot} depends only on the output charge density and the ionic pseudopotential V_{ion}, and *not* on V_0.) The fact that this procedure works well (e.g., the lattice constant and zone-center phonon frequencies of diamond are given to within 1%)[11] indicates that $V_0(\vec{r})$ produces an accurate ground-state charge density for bulk systems.

At a surface, however, charge transfer results in an electron population $Q_{\vec{\tau}}$ on site $\vec{\tau}$ which differs from the mean Q_0, and this inequivalence means Eq. (1) is no longer valid. [The charge density obtained by solving $V_0(\vec{r})$ would have errors mostly in the low Fourier components ($q<G_{\mathrm{min}}^{\mathrm{bulk}}$); these errors are serious because of Coulomb terms $\propto q^{-2}$ in E_{tot}.] To account for the inequivalence, we replace Eq. (1) by

$$V(\vec{r})=V_0(\vec{r})+\sum_{\vec{R},\vec{\tau}} c_{\vec{\tau}}\,g(\vec{r}-\vec{R}-\vec{\tau}) \ , \tag{2}$$

where the function g is a broad Gaussian, $\exp(-\alpha r^2)$, with $\alpha=0.12$ a.u.$^{-2}$ for carbon. The coefficients $c_{\vec{\tau}}$ are chosen by requiring that $V(\vec{r})$ have the same low Fourier components as $V_{\mathrm{LDA}}(\rho_{\mathrm{cry}})$, except that ρ_{cry} is replaced by

$$\rho'_{\mathrm{cry}}(\vec{r})=\sum_{\vec{R},\vec{\tau}} \frac{\vec{Q}_{\vec{\tau}}}{Q_0}\rho_{\mathrm{atom}}(\vec{r}-\vec{R}-\vec{\tau}) \ , \tag{3}$$

with ρ_{atom} the free atom charge density. The potential $V(\vec{r})$ is solved for the wave functions, whose LCAO coefficients give new values of $Q_{\vec{\tau}}$; these, in turn, are used to generate new $c_{\vec{\tau}}$'s, Eqs. (2) and (3), and the loop is iterated to self-consistency for $Q_{\vec{\tau}}$.

We have implemented the method on a slab geometry 10 atomic layers thick (20 atoms per cell for 2×1 models). As in the bulk calculations of CL,[11] three decay constants are used for each s- or p-type Gaussian orbital in the basis. A Hamann-Schluter-Chiang pseudopotential[13] is used in conjunction with Hedin-Lundquist exchange correlation.[14] Sets of 7, 8, and 16 k points in the irreducible zone were used for 1×1, mirror-symmetric 2×1, and other 2×1 models,

respectively. Iteration was continued until input and output Q_τ's differed by less than 0.01 electron.

The results are summarized in Table I. The energy per surface atom for the ideal 1×1 model is used as a zero of energy. Relaxing the first two surface bonds [Fig. 1(a)] lowers the energy by 0.37 eV. Four topologically distinct 2×1 models have been tested: the Haneman buckling model,[15] the Pandey π-bonded chain model,[5] the Chadi π-bonded molecule model,[16] and the Seiwatz single chain model.[17] Buckling of the ideal 1×1 surface is found to raise the energy. Of the other three models, the Pandey chain model[18] clearly has the lowest energy. The Chadi molecule model, in second place, has not been relaxed further because the calculated surface state dispersion[7] is clearly inconsistent with ARUPS data.[2] The Seiwatz chain model can be decisively ruled out on the basis of total energies alone.

The energy of the Pandey chain model was minimized by adjusting the four surfacemost bond lengths to give the "relaxed" structure of Fig. 1(b), lowering the energy to -0.47 eV. (Tilting of the surface chain was also tested and found unfavorable.) A surprising feature of this relaxed geometry is the 8% lengthening of the subsurface interlayer bond. The surface chain bond, on the other hand, is only contracted by 4%, a value roughly midway between that of graphite and diamond.

Dimerization of this relaxed chain geometry was tested carefully; in addition to the geometries of Table I, a small ($\pm1\%$) and large ($-18\%/+44\%$)[10] dimerization were tested. For small dimerization, the results were checked with k-point sets containing an extra 16 k points in the vicinity of the $\overline{JK}$ zone boundary, where a gap opens in the surface bands. In all cases, dimerization led to an increase in the total energy, contrary to previous speculations.[5,10]

Finally, the chain geometry was relaxed further using a Keating force-constant model[19] to direct the relaxation of the subsurface atoms in the middle of the slab while the four surfacemost bond lengths were held fixed. The LDA total energy of this final geometry is found to be -0.68 eV. This further relaxation relieves some of the bond angle strains on the third-layer atoms (e.g., from 85° and 134° to 93° and 123°, respectively). The dependence of the surface energy upon slab thickness has been tested within the Keating model, and has been found to be converged to within 0.02 eV.

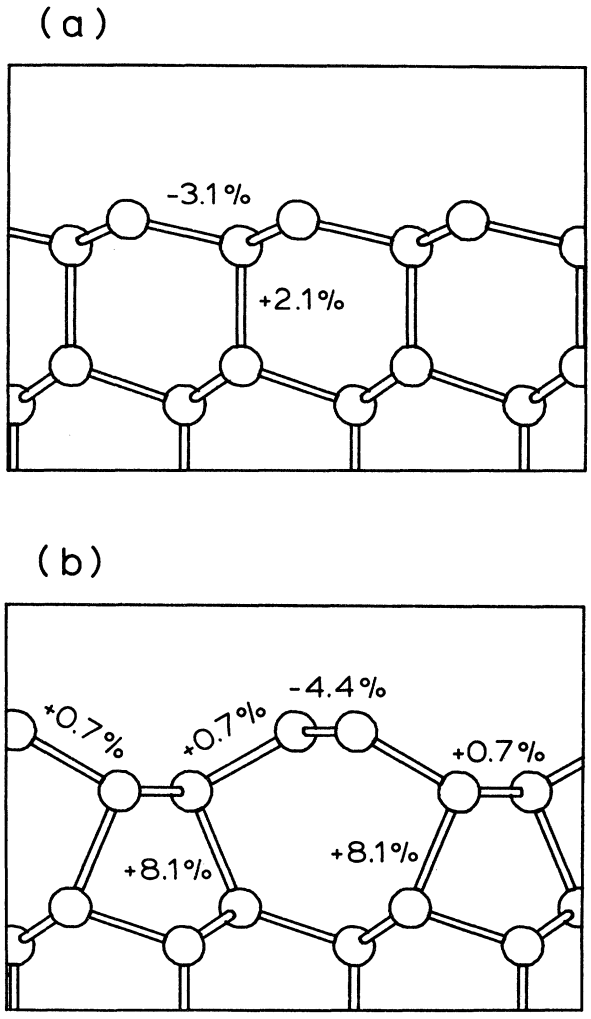

FIG. 1. Illustration of bond-length changes (with respect to bulk) which occur upon relaxation of (a) 1×1 and (b) 2×1 Pandey chain models.

TABLE I. Calculated total energies of C(111) 1×1 and 2×1 surface reconstruction models.

Surface model	Energy [eV/(surface atom)]
Ideal 1×1	0.00
Relaxed 1×1	−0.37
Buckled[a] ($\Delta z=\pm0.26$ Å)	0.35
Chadi π-bonded molecule[b]	0.28
Seiwatz single chain[c]	1.30
Ideal Pandey π-bonded chain[d]	−0.05
Relaxed Pandey π-bonded chain	−0.47
Same with $\pm2\%$ dimerization	−0.46
Same with $\pm4\%$ dimerization	−0.43
Same with $\pm6\%$ dimerization	−0.38
Fully relaxed Pandey chain	−0.68

[a]Reference 15. [c]Reference 17.
[b]Reference 16. [d]Reference 10.

It is interesting to compare these results with those of Northrup and Cohen[20] for Si, where the ideal and relaxed Pandey chain models have energies of -0.22 and -0.36 eV, respectively (compared with ideal 1×1). In diamond, the ideal Pandey model is less favorable, but relaxations are more important. We attribute this to the highly directional nature of the sp^3 bonds in carbon, which implies that bond angle variations are more costly. We may take K_θ/K_r from a Keating model[19] as a measure of relative bond angle stiffness; this ratio gives 0.23 and 0.11 for C and Si, respectively. Evidently, the large bond angle distortions in the third layer are more costly in C, and the relaxations which relieve bond angle strain are more important. This view is consistent with the 8% bond lengthening of the subsurface interlayer bond, which we attribute to bond weakening resulting from bond angle distortion.

Figure 2 shows the calculated surface band structure for the fully relaxed Pandey chain model. Experimental ARUPS data[2] are shown for comparison. The major

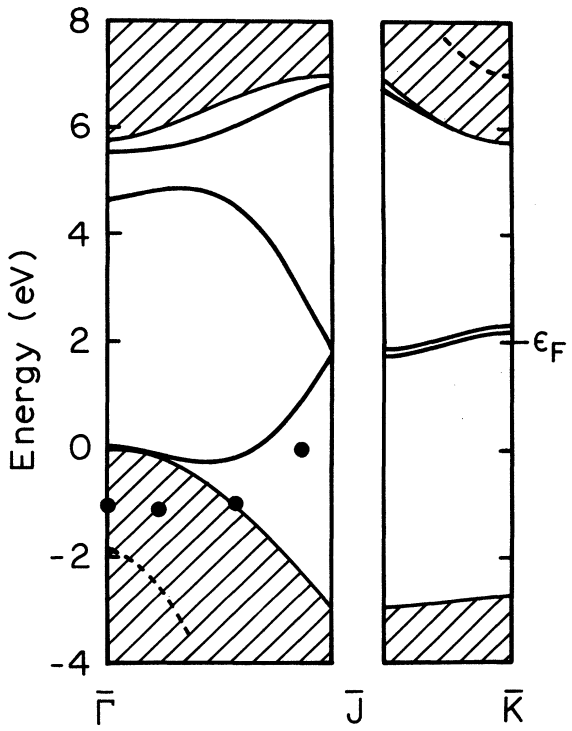

FIG. 2. Calculated surface bands (solid lines) and resonances (dashed lines) for the fully relaxed Pandey chain model. The bulk projected band structure (shaded) and the experimental ARUPS data of Ref. 2 (black dots) are shown for comparison.

features in the gap are the occupied and unoccupied surface bands associated with the surface chains.[21] The dispersion of the occupied band along $\bar{\Gamma}\bar{J}$ has been greatly reduced from that of Pandey,[5] who found a difference of $\gtrsim 3$ eV between $E(\bar{\Gamma})$ and $E(\bar{J})$. This was already reduced to ~ 2.3 eV in our previous calculation on the ideal structure,[7] and has now been reduced to ~ 1.7 eV due to relaxations (primarily the lengthening of the surface chain bonds by $\sim 4\%$ from their "ideal" graphitic values). The dispersion is thus in good agreement with experiment without the need for dimerization, thereby removing one of the major motivations for the dimerized model. The calculated band is too high by a rigid shift of ~ 1 eV, but this is also true (by ~ 0.3 and ~ 0.8 eV, respectively) for Si and Ge.[20] Moreover, according to density functional theory, the LDA total energies are expected to be more meaningful than the eigenvalues, which cannot be interpreted directly as electron removal energies.[20] While our surface in Fig. 2 would appear to be metallic, we note that antiferromagnetic ordering along the chain π manifold may open a gap,[22] so that no contradiction with recent electron-energy-loss experiments[9] is required.

In summary, we have calculated the total energy of several proposed 2×1 reconstruction models for the C(111) surface. The *undimerized* Pandey π-bonded chain model is found to have the lowest energy, ~ 0.3 eV lower than that of a relaxed 1×1 structure. The dispersion of the calculated surface band is found to be in good agreement with experiment, without the need for dimerization. The other models considered are shown to be implausible on the basis of total energy and surface state dispersion. We hope to have stimulated further experimental work in this area.

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[1]For a recent review, see D. Haneman, Adv. Phys. 31, 165 (1982).
[2]F. J. Himpsel, D. E. Eastman, P. Heimann, and J. F. van der Veen, Phys. Rev. B 24, 7270 (1981).
[3]F. Houzay, G. Guichar, R. Pinchaux, G. Jezequel, F. Solal, A. Barsky, P. Steiner, and Y. Petroff, Surf. Sci. 132, 40 (1983), and references therein.
[4]J. M. Nicholls, G. V. Hansson, R. I. G. Uhrberg, and S. A. Flodstrom, Phys. Rev. B 27, 2594 (1983).
[5]K. C. Pandey, Phys. Rev. Lett. 47, 1913 (1981); Phys. Rev. B 25, 4338 (1982).
[6]J. J. Lander and J. Morrison, Surf. Sci. 4, 241 (1966).
[7]D. Vanderbilt and S. G. Louie, J. Vac. Sci. Technol. B 1, 725 (1983).
[8]W. S. Yang and F. Jona, Phys. Rev. B 29, 899 (1984).
[9]S. V. Pepper, Surf. Sci. 12, 47 (1982).
[10]D. J. Chadi, in *Proceedings of the IXth International Vacuum Congress and Vth International Conference on Solid Surfaces,* edited by J. L. de Segovia (Imprenta Moderna, Madrid, Spain, 1983), pp. 80–88.
[11]J. R. Chelikowsky and S. G. Louie, Phys. Rev. B 29, 3470 (1984).
[12]D. Vanderbilt and S. G. Louie, J. Comput. Phys. (to be published).
[13]D. R. Hamann, M. Schluter, and C. Chiang, Phys. Rev. Lett. 43, 1494 (1979).
[14]L. Hedin and B. I. Lundquist, Phys. Rev. B 13, 4247 (1976).
[15]D. Haneman, Phys. Rev. 121, 1093 (1961).
[16]D. J. Chadi, Phys. Rev. B 26, 4762 (1982).
[17]R. Seiwatz, Surf. Sci. 2, 473 (1964).
[18]This unrelaxed Pandey model has all bulk bond lengths except for the graphite length for surface chain bonds.
[19]R. Tubino, L. Piseri, and G. Zerbi, J. Chem. Phys. 56, 1022 (1972).
[20]J. E. Northrup and M. L. Cohen, Phys. Rev. Lett. 49, 1349 (1982); Phys. Rev. B 27, 6553 (1983).
[21]We find a second unoccupied surface band in the neighborhood of the conduction-band edge; it is similar to the bulk conduction band in character, and weakly localized in the vicinity of the lengthened subsurface interlayer bond.
[22]M. Lannoo and G. Allan, Solid State Commun. 47, 153 (1983).