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Reconstruction of Semiconductor Surfaces: Buckling, Ionicity, and π-Bonded Chains

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Buckling distortions, widely thought to lower the total energy of semiconductor surfaces, are shown to actually raise the energy of Si(111)-2× 1. The π-bonded–chain reconstruction, in contrast, stabilizes the surface, even relative to recently proposed magnetic reconstructions. Calculations for GaAs(110) reveal that the large charge transfers associated with buckling can stabilize the surface of heteropolar semiconductors, by returning the ions of the bulk to neutral atoms at the surface. These conclusions are based on self-consistent pseudopotential calculations.

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The idea that buckling distortions energetically stabilize semiconductor surfaces has enjoyed great popularity since it was introduced in 1961 by Haneman.[1] Its popularity is due in part to its intuitive appeal and in part to estimates of the stabilization energy based on electronic-structure calculations.[2] The intuitive appeal of the buckling idea is easy to appreciate. The electrons in tetrahedral semiconductors reside in bond orbitals which project from each atom in the four tetrahedral directions. The diamond and zinc-blende crystal structures permit all the bond orbitals to be joined perfectly inside the semiconductor, but at the surface one or more of these bond orbitals is left "dangling" from each atom. On the unreconstructed (111) surface of such systems, e.g., one such dangling bond projects directly into the vacuum from each atom. Since there is one electron in each dangling bond, such a surface corresponds to a half-filled band and is therefore metallic, in conflict with experiment. It is very natural to think that such a system will spontaneously reduce its symmetry, so as to lower the energy of the states in the occupied half of the band, thereby energetically stabilizing the surface and, at the same time, introducing an energy gap between the occupied and unoccupied states, as is observed. This is the intuitive appeal of Jahn-Teller symmetry-breaking distortions in general and of the buckling idea, in particular.

According to the buckling idea, half of the surface atoms recede toward the bulk crystal; the remaining half move outward. A crucial aspect of buckling, fully appreciated by Haneman,[1] is that the rehybridization of the atomic orbitals caused by the change in geometry leads to substantial charge transfer from the receding atoms to the outwardly displaced atoms. Whereas non-self-consistent electronic-structure calculations[2] indicate that such charge transfer is possible for homopolar systems, such as Si, the present fully self-consistent calculations, by contrast, reveal that intra-atomic Coulomb-energy costs preclude such charge transfer for homopolar semiconductors. Heteropolar semiconductors, such as GaAs, are interestingly different in this regard, because the bulk semiconductor is comprised of ions and the charge transfer associated with buckling provides a means by which the ions can be converted to neutral atoms at the surface. The present self-consistent calculations indicate that, for the surfaces of homopolar semiconductors, such as Si(111), the recently proposed π-bonded-chain reconstruction[3] is much more effective in lowering the total energy of the surface. While the present study is confined to Si(111) and GaAs(110), I have studied the total-energy implications of a very large number of specific reconstruction models. The consistency of the results for all these models suggests that my important qualitative conclusions are quite general.

In the present analysis, I calculate the atomic-geometry dependence of the total energy using the "local-density" description of exchange and correlation, implemented with self-consistent pseudopotential theory. I approximate the semi-infinite semiconductor by a "slab" of infinite extent in two directions, and of finite extent in the third.[4] All aspects of the theoretical approach have been tested previously.[5,6] In particular, for both Si and GaAs, the calculated bulk properties[7] (the energy bands, lattice constant, cohesive energy, and bulk modulus) based on these potentials are all in good agreement with experiment and, for Si, almost identical to the results reported by Yin and Cohen.[8] The pseudopotentials used are nonlocal and norm conserving.[9] Several of the calculations were repeated using local pseudopotentials,[5,6] without significant effect. Wave functions were expanded in plane waves and total-energy calculations were carried out in reciprocal space.[10] I emphasize two technical points. First, all controllable approximations, the number of plane waves used to expand various quantities, e.g., were held fixed as the atomic geometry was varied. (For example, the reference calculation for the ideal Si 1× 1 surface was performed using a 2× 1 unit cell.) Second, a very high degree of self-consistency was required and achieved in all the calculations.[11] I estimate that the controllable errors in total-energy differences discussed below are smaller than 0.02 eV/(surface atom). Since I use the "supercell" technique to study the slab geometry, the above-mentioned bulk calculations[7] constitute a test of my implementation of the theory. In addition, however, further tests have been carried out by repeating the surface band calculations of previous workers[5,6] for the relaxed Si(111)-1× 1 and GaAs-(110) surfaces. Apart from small discrepancies due, I believe, to greater self-consistency here, the two sets of calculations agree well.

Consider now the quantitative results of the calculations. In Fig. 1 I compare the total-energy benefit to the (111) surface of Si resulting from two types of surface reconstruction, buckling and relaxation (the uniform displacement of *all* surface-layer atoms toward the bulk). The reconstruction model of Ref. 2 labeled "Chadi" in Fig. 1 is the particular combination of buckling and relaxation that minimizes the total energy calculated non-self-consistently. The total-energy difference between the dashed and dotted lines in Fig. 1 isolates the effect of self-consistency (~ 0.35 eV/atom) for this particular geometry. The aspect of Fig. 1 that I emphasize most strongly, however, is that buckling is seen to *raise* the total energy of the surface. This result is not restricted to the "Chadi" model; I obtained similar results for all of the buckling models in the literature.[1,2,5,12]

Figure 2 deals with the second purported virtue of buckling, the creation of a gap separating the occupied and unoccupied states. Shown in Fig. 2

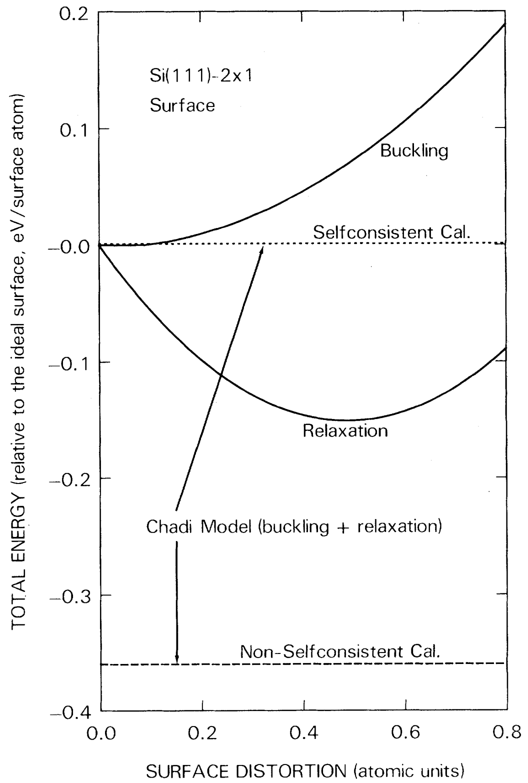

FIG. 1. Total-energy variation for buckling and relaxation distortions of the surface of a homopolar semiconductor. Note that the self-consistent result for the Chadi model (dotted line) is only coincidentally very close to zero.

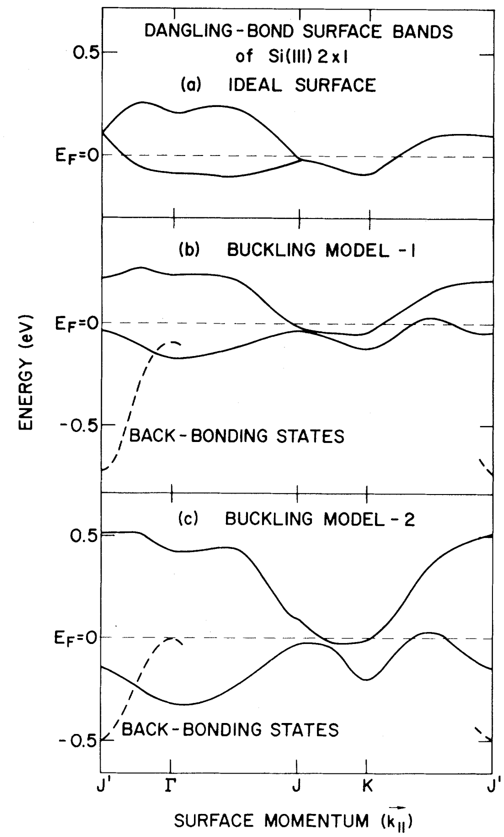

FIG. 2. Surface energy bands along the principal directions in the surface Brillouin zone.

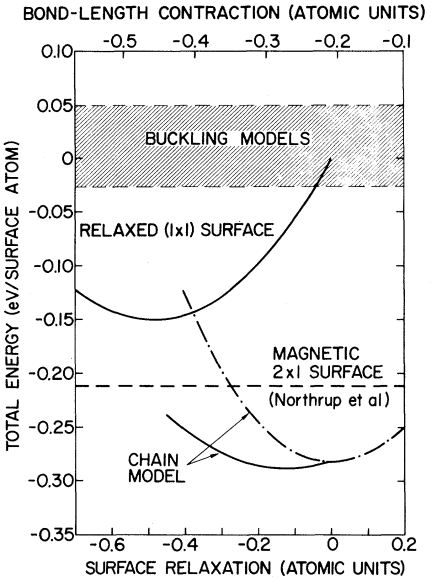

FIG. 3. Stabilization of Si(111)-2×1 surface by π-bonded–chain reconstruction.

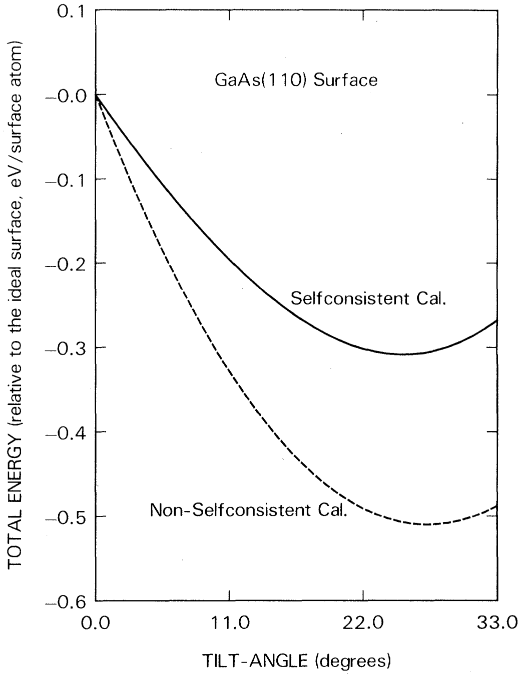

FIG. 4. Stabilization of the surface of a heteropolar semiconductor by buckling reconstruction.

is the dispersion (dependence of the orbital energy on momentum parallel to the surface) of the dangling-bond surface state. Three surface geometries are considered: (1) unreconstructed, (2) small buckling,[1] and (3) large buckling.[2] All previous calculations[5,13] find a gap proportional to the degree of buckling, in agreement with Haneman's analysis.[1] I find no gap, even for large amounts of buckling. Here, again, self-consistency is the distinguishing feature of the present analysis. The opening of the gap is resisted by the dependence of the self-consistent potential in the vicinity of each atom on the number of electrons in that region; as electrons are removed (by buckling, e.g.) the electrostatic potential in that region is lowered; the lowered potential attracts electrons to that region. Quantitatively, the dependence of the potential on atomic charge (the intra-atomic Coulomb integral) is large (~ 5 eV/unit charge). Consistently, the calculations on which Fig. 2 is based exhibit very little charge tranafer.

Consider now the alternative to buckling distortions offered by the π-bonded–chain model.[3] The significant virtue of this model is that the bond topology of the surface is changed so that the dangling-bond orbitals reside on nearest-neighbor atoms. In this configuration, the bond orbitals are close enough to interact significantly, causing a substantial reduction of the total energy. This total-energy reduction is compared in Fig. 3 to three other types of reconstruction; buckling,[1,2,5,12] relaxation, and magnetic.[14] In the magnetic reconstruction, the surface spontaneously reduces its symmetry by permitting electrons of different spin to congregate on different surface atoms. Figure 3 shows that the π-bonded–chain model reduces the surface energy more than all the other models presently available. Furthermore, Fig. 3 represents only an upper bound to the total energy for the chain model, but an approximate lower bound for the other types of reconstruction, because the positions of the subsurface atoms have been optimized only for the other models. [Only the total-energy dependences on intrachain bond length (dash-dotted line) and chain-bulk separation (solid line) are considered here.] Since the chain model involves a change in the bond topology at the surface, the effect of optimization of the positions of the subsurface atoms may be larger than for other types of reconstruction. With regard to the presence or absence of a gap in the excitation spectrum, I remind the reader that a principal motivation for the introduction of the chain model[3] is its consistench with spectroscopic data.[15] Note also that, in contrast to buckling, charge transfer is not required by reconstructions of the π-bonded–chain type.

Finally, Fig. 4 demonstrates that buckling *can* be effective for surfaces of heteropolar semiconductors. Shown in Fig. 4 is the total energy of GaAs(110) as a function of the degree of buckling. We see, in contrast to the homopolar system considered in Fig. 1, that both the present self-consistent and non-self-consistent[2] calculations show an energy reduction, although the non-self-consistent analysis again overestimates the energy benefit by a large amount.

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[2] D. J. Chadi, Phys. Rev. Lett. 41, 1062 (1978).

[3] K. C. Pandey, Phys. Rev. Lett. 47, 1913 (1981).

[4] For the Si(111)-2×1 surface, ten-layer slabs separated by vacuum, with the (111) unit cell dimension of 41.26 a.u., were used. For GaAs(110) nine-layer slabs with the (110) unit cell dimension of 47.4 a.u. were used. All plane waves with kinetic energy less than 3 Ry (approximately 325) were treated exactly and those with kinetic energy between 3 and 6 Ry (approximately 500) were treated by Löwdin's perturbation scheme. Perturbation corrections to wave functions were also calculated. The exchange-correlation potentials were evaluated in real space at about 14 000 uniformly spaced points in the unit cell. Self-consistent-field iterations were based on nine k points in the irreducible section of the Brillouin zone. At no stage in the present calculations were any cutoffs, either in potential or charge density, used.

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[7] K. C. Pandey, to be published.

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[11] Self-consistent-field iteration was continued until the mean square and maximum difference throughout the unit cell between the input and output potentials were less than 10^{-6} and 10^{-3} Ry. All Fourier components of the potential were allowed to vary throughout the calculation.

[12] R. Feder, W. Mönch, and P. P. Auer, J. Phys. C 12, L179 (1979).

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[14] J. E. Northrup, J. Ihm, and M. L. Cohen, Phys. Rev. Lett. 47, 1910 (1981). These authors have independently found results similar to ours for the buckling and relaxation models.

[15] Except for a smaller gap, the energy bands based on the present calculations are nearly the same as reported in Ref. 3.