[13] We have applied a small correction ($<10\%$) to Eq. (6) to allow for the heat flowing from the solid and liquid into the cell walls. This correction was determined by measuring the time constant τ_2.

[14] It is also true that $\langle t_{SL}\rangle$ must be ≤ 1. $\langle t_{SL}\rangle$ can be calculated from a relation like Eq. (4), and is smaller than $\langle t_{LS}\rangle$ by a factor of about 5. Thus, the condition $\langle t_{LS}\rangle \leq 1$ is a more severe limit than $\langle t_{SL}\rangle \leq 1$.

Spin Polarization and Atomic Geometry of the Si(111) Surface

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Based on pseudopotential local spin-density calculations, it is proposed that the minimum-energy Si(111) nonbuckled surface is stable against 2×1 buckling distortions. A 2×1 antiferromagnetic spin-density wave, localized on the surface, enhances the stability of this structure.

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Although Si(111) is the most studied surface in solid-state physics, questions regarding the structural and electronic properties persist. This surface has been studied experimentally and theoretically by a variety of techniques.[1] New angle-resolved photoelectron spectra for the 2×1 cleaved surface[2,3] and the 1×1 laser-annealed surface[4,5] point to the possible importance of correlation effects. It was proposed by Himpsel *et al.*[2] and Zehner *et al.*[4] that, because of the small dispersion of the surface bands (on both cleaved and laser-annealed surfaces), correlation effects might be important for a correct interpretation of the experimental results. Del Sole and Chadi[6] have advanced a model in which electron correlation effects are included and are crucial in determining the properties of the surface.

In the self-consistent pseudopotential calculations reported here, the local spin-density–functional formalism[7,8] is used so that the total energy may be minimized with respect to both the spin alignment and the atomic positions. The objective is to determine the surface structure by varying the atomic positions until the Hellman-Feynman (HF) force on each atom approaches zero; that is, a minimum in the total energy is found. A similar approach,[9] restricted to the local density approximation, has recently been used to predict the atomic geometry of Si(001).

We consider geometries which have translational symmetry that is at least 2×1. Within the 2×1 unit cell, the surface may be either buckled or nonbuckled, and the spin alignment may be either paramagnetic, antiferromagnetic, or ferromagnetic. The calculations are performed on slabs of silicon consisting of ten layers of atoms. Each slab is placed in a supercell. The ionic pseudopotential used in these calculations is generated with the method of Hamann, Schlüter, and Chiang.[10] This pseudopotential has been used to calculate accurately the ground-state properties of bulk silicon.[11]

For a given set of atomic positions, the electronic structure is calculated self-consistently in momentum space.[12] The number of plane waves included in the expansion of the wave function and the number of $\boldsymbol{k}$ points included in the Brillouin sum is increased until the HF force on each atom has converged; this enables us to obtain a convergent result for the atomic positions. With this convergence criterion, calculations of the bulk lattice constant and spin-polarized calculations of the Si_2 molecular bond length[13] give results which are within 1% of the experimental values. For Si_2, we obtain a ${}^3\Sigma_g{}^-$ ground state, in agreement with experiment. This demonstrates the ability of the local spin-density formalism, even when applied to the valence electrons only, to predict the correct ground-state properties.

For the spin-nonpolarized calculations, the Wigner interpolation formula[14] is used to approximate the effects of correlation. In the spin-polarized calculations, the exchange-correlation energy functional (ECEF) of Gunnarsson and Lundqvist[8] (GL) is employed. The ECEF's of von Barth and Hedin[7] and Ceperley and Alder[15,16] are tested, and their use instead of the GL ECEF led to only minor quantitative differences. For purposes of comparing the total energies of polarized and nonpolarized calculations, we employed the GL ECEF for the polarization-dependent part of the ECEF and the Wigner ECEF for the polarization-independent part. This enables us to avoid repeating the nonpolarized calculations with the GL ECEF. No qualitative feature of these calculations depends on the choice of the ECEF.

We first describe the results of calculations in which the atoms are constrained to move vertically, and 1 × 1 structural symmetry is maintained. Using the HF forces as a guide, we find the minimum-energy nonbuckled paramagnetic surface structure (geometry 2 in Fig. 1) by testing geometries with successively smaller forces and lower total energies. In this geometry, the distance between the top two layers contracts to 0.93 a.u. (compared to 1.48 a.u. in the bulk), and the subsurface atoms remain within 0.02 a.u. of their ideal positions. This nonbuckled paramagnetic surface is stable with respect to small 2 × 1 buckling distortions (including lateral displacements of the subsurface atoms). For each distortion tested, the total energy increased, and restoring forces developed on the displaced atoms.

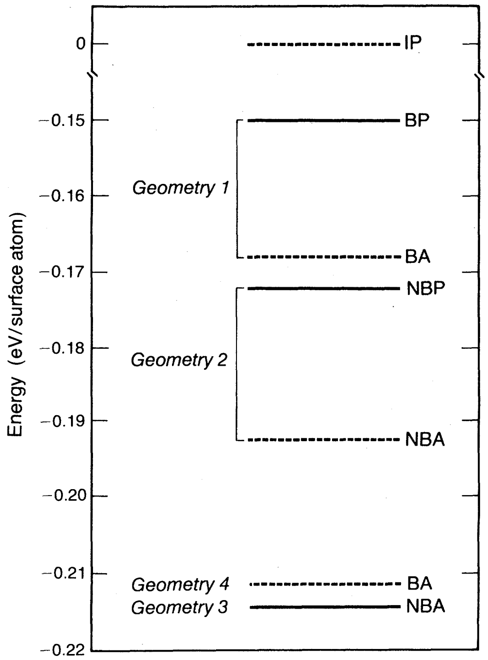


FIG. 1. Energy diagram. Energies are measured with respect to the ideal paramagnetic (IP) surface. BP denotes a buckled paramagnetic surface, BA denotes a buckled antiferromagnetic surface, NBP denotes a nonbuckled paramagnetic surface, and NBA denotes a nonbuckled antiferromagnetic surface. The energy levels indicated with dash lines correspond to structures with forces still acting on the atoms; those levels indicated with solid lines correspond to structures in which the forces are zero.

However, the total energy of this geometry is lowered (by 0.020 eV per surface atom) when the spin density is allowed to vary. The electrons in the dangling-bond surface states then become correlated in such a way that the spin-up electrons are mainly localized on one of the surface atoms (type 1) in each unit cell, and the spin-down electrons are localized on the other surface atoms (type 2). (For this nonbuckled geometry, the type-1 and type-2 atoms are structurally equivalent.) This spin ordering reduces the translational symmetry of the spin-dependent exchange-correlation potentials from 1 × 1 to 2 × 1, and this reduction in symmetry allows for the possibility of an exchange-correlation energy gap. The unoccupied dangling-bond surface states correspond to spin-up electrons localized on type-2 atoms and spin-down electrons localized on type-1 atoms. The energy gap separating the occupied and empty states arises from the increased Coulomb repulsion between electrons of the opposite spin relative to the Coulomb repulsion between electrons of the same spin.

Once the nonbuckled surface becomes an antiferromagnetic insulator, nonzero forces develop and so the total energy can be reduced as the atoms are moved closer to new equilibrium positions. In the minimum-energy nonbuckled anti-

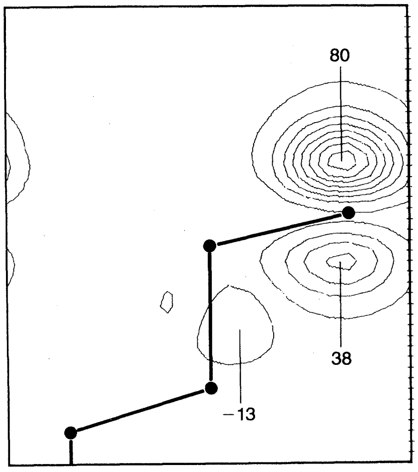
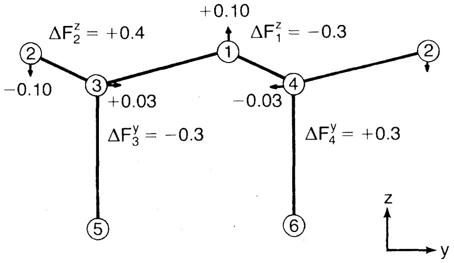


FIG. 2. Contour plot of valence spin density in the (110) mirror plane for the minimum-energy nonbuckled antiferromagnetic surface. The contour spacing is 10 units of electrons/(3376 a.u.) (Ref. 3).

ferromagnetic surface (geometry 3 in Fig. 1), the calculated interlayer distances for the first six layers are 1.11, 4.46, 1.41, 4.42, and 1.46 a.u. These distances may be compared to the values found with low-energy electron diffraction (LEED) by Zehner *et al.*[17] on a 1 × 1 laser-annealed surface. They obtained 1.10 and 4.58 a.u. for the first and second interlayer distances. The predicted contraction of the first interlayer spacing from 1.48 a.u. is in good agreement with experiment. The valence spin density for this geometry is shown in Fig. 2. It is nonzero only near the surface, and the bulk remains paramagnetic. The integrated spin-up minus spin-down electron density is ±0.5 electrons around the two structurally equivalent surface atoms in each cell. In principle, a very sensitive LEED experiment would detect a 2 × 1 diffraction pattern arising from the exchange interaction between the incident electron and the spin-polarized valence electrons.

We now turn our attention to the buckled geometries. Ten paramagnetic and four antiferromagnetic geometries were tested. Restricting ourselves to the paramagnetic subset, we find a local minimum (geometry 1 in Fig. 1). This structure, however, like the nonbuckled paramagnetic surface, is unstable with respect to variations in the spin density. The formation of an antiferromagnetic 2 × 1 spin-density wave lowers the energy of the surface by 0.018 eV per surface atom, and, as in the case of the nonbuckled surface, forces develop on the surface atoms. The forces indicate that a reduction in the buckling will reduce the energy. Additional buckled antiferromagnetic geometries were tested, each with a smaller amount of buckling, and in each case, the HF forces indicated that a still further reduction in the buckling was necessary. As the buckling was reduced, the charge transfer from down atoms to up atoms was reduced, and the spin transfer was increased. These two effects are responsible for the reduction in surface energy. A buckling distortion was then introduced into the stable nonbuckled antiferromagnetic geometry. This distortion is illustrated in Fig. 3 and denoted as geometry 4 in Fig. 1. It was found that the total energy increased by ~0.003 eV per surface atom,[18] and restoring forces developed on the displaced atoms. Thus, we find that no stable 2 × 1 buckled antiferromagnetic structure exists. The reason for the stability of the nonbuckled surface is that the buckling-induced charge transfer reduces the spin-wave amplitude.

Because the energy required to create a 2 × 1 distortion on the surface is small (0.003 eV per surface atom for a buckling amplitude of 0.2 a.u.), it is likely that the strain field around steps, when coupled to this soft phonon, will effect the long-range structural order. Steps on the freshly cleaved surface may provide a boundary condition which stabilizes a buckling distortion. Alternatively, it is possible to construct 2 × 1 geometries other than the buckled model which are consistent with the observed LEED patterns.



Displacements in a.u.
Restoring forces in 10^{-2} Ry/a.u.

FIG. 3. Side view [atoms projected onto (110) plane] of the 2 × 1 buckling distortion used to test the stability of the nonbuckled antiferromagnetic surface.

For single-domain 2 × 1 surfaces, Himpsel *et al.*[2] observed two occupied dangling-bond surface states. The existence of two occupied surface states, one spin-up and one spin-down, is inherent in a buckled antiferromagnetic surface.[6] For buckled antiferromagnetic surfaces, our calculations also lead to two such states. For a surface with a buckling of 0.72 a.u., the surface state of lower energy has a dispersion of +0.13 eV from Γ to J' and a dispersion from Γ to J of −0.06 eV. For the state of higher energy, the dispersion is +0.25 eV from Γ to J' and +0.15 eV from Γ to J. The energy splitting between these two occupied bands is 0.13 eV at Γ and 0.34 eV near J. These dispersions are geometry dependent, and the atomic positions on a stepped surface may be quite different from those for which these results were obtained. Experiments which detect spin polarized photoelectrons in photoemission or detect an absorption spectrum which depends on the polarization of the incident light could test the prediction of two nondegenerate spin-polarized surface bands. For the nonbuckled antiferromagnetic surface, the occupied spin-up and spin-down surface states are degenerate and disperse upwards by 0.1 eV from Γ to

J' and downwards by 0.2 eV from Γ to J.

In conclusion, these calculations imply that the buckling lattice distortion would not drive a 2×1 reconstruction on a perfect Si(111) surface. Instead, they show that a 2×1 spin-density wave is energetically favorable and induces the insulating behavior observed on both cleaved and laser-annealed Si(111). The nonbuckled antiferromagnetic surface is shown to be stable against buckling type distortions.

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[18] This energy difference changes from 0.0001 to 0.0028 eV per surface atom as the number of plane waves in the wave functions is increased from 275 to 450. For 635 plane waves, the energy difference is 0.0027 eV per surface atom. The calculations with 635 plane waves are, therefore, well convergent on the scale of relevant energy differences. All our results are obtained with 635 plane waves.

New π-Bonded Chain Model for Si(111)-(2×1) Surface

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Several qualitatively different structural models have been examined in a critical evaluation of spectroscopic and other data for the Si(111)-(2×1) surface. Within the one-electron theory, only a novel π-bonded chain model with a covalent surface, and not the generally accepted buckled model with an ionic surface, is consistent with the data.

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In spite of extensive and concerted experimental and theoretical effort, the determination of surface atomic structures of covalent semiconductors has remained one of the most outstanding problems in surface physics.[1] Of the proposed models[2-5] for the cleaved (111) surface of Si, which shows a (2×1) reconstruction, the buckling model[2] with alternate rows of surface atoms moving in and out of the surface [Fig. 1(a)] has been the most widely accepted model. Such a conclusion is based primarily on model-dependent calculations[6,7] of surface energy bands and their comparison with spectroscopic data, especially ultraviolet photoemission spectra (UPS)[7-9] and