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Atomic geometry and surface-state spectrum for Ge(111)-(2 × 1)

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The π-bonded chain model is studied for Ge(111)-(2 × 1). The minimum-energy chain geometry is found with the use of the Hellmann-Feynman forces. A buckling of the surface atoms in the chain is energetically favorable. This buckling is associated with rehybridization (sp^3 to sp^2) effects. Theoretical surface-state dispersions for this geometry are compared with recent angle-resolved photoemission experiments.

The Ge(111) surface exhibits a (2 × 1) low-energy electron diffraction pattern following cleavage at room temperature. Although the nature of the (2 × 1) reconstruction is unknown, a possible candidate is the π-bonded chain geometry recently proposed by Pandey for Si(111)-(2 × 1).[1] Because of the chemical similarity between Si and Ge, it is natural to propose that the (2 × 1) reconstructions found on both surfaces are similar. This assumption is motivated experimentally by optical reflectivity data,[2] which suggest that the surface-state spectra for the two materials are very similar. Recent photoemission experiments[3-6] also yield similar spectra, and therefore the chain model, which gives rise to surface-state bands in agreement with experiments for Si,[1,7] is proposed as a candidate for Ge(111)-(2 × 1).

We have carried out pseudopotential local density total energy calculations for Ge(111)-(2 × 1) using the Hellmann-Feynman forces to determine stable structures. The calculational scheme is similar to those which have been used before to study the structural properties of Si(111)-(2 × 1).[7] A slab of ten layers, containing 20 Ge atoms per unit cell, and with the slabs repeated in the direction perpendicular to the surface, is employed. The surfaces on neighboring slabs are separated by 12.0 a.u. Inversion symmetry is imposed on the atoms in each slab, as well as reflection symmetry through the (110) plane. This system has 20 structural degrees of freedom to determine.

The pseudopotential used in this momentum space total energy calculation[8,9] is generated with the scheme of Hamann, Schlüter, and Chiang.[10] We use the exchange correlation energy functional obtained by Perdew and Zunger[11] from the calculations of Ceperley and Alder.[12] The solutions to the Hohenberg-Kohn-Sham[13,14] equations are expanded in a basis set of plane waves containing waves with kinetic energies up to 5 Ry. Calculations of the bond length for the Ge diatomic molecule are converged to within 0.5% with this energy cutoff.[15] Calculations of the bulk lattice constant for Ge (Ref. 9) are converged to within less than 3% with an energy cutoff of 5 Ry. The surface calculations reported here are performed with the same unit-cell dimensions for each geometry, and therefore the plane-wave basis set is identical for each geometry. We therefore expect convergence of the structural properties of the surface to be obtained with a smaller plane-wave cutoff energy than in the bulk calculations, where the wavelength of the plane-wave basis functions depends on the lattice constant. The results of the Ge molecular calculation, where the basis set is also independent of structure, confirm this expectation. The Brillouin sums needed in the momentum space total energy formalism are evaluated with a weighted sum of six k points in the irreducible Brillouin zone.

In the π-bonded chain geometry,[1] the two surface atoms in each unit cell are almost equivalent; the difference in their chemical environments arises from differences in the fourth layer. In the optimum chain geometry, which is obtained by moving the atoms until the Hellman-Feynman forces on each atom go to zero, the two surface atoms exhibit two different types of coordination. This is clearly evident in the ball and stick model shown in Fig. 1. Atom 1 is sp^3 coordinated, while atom 2 is sp^2 coordinated. These two atoms differ in their displacements parallel to the surface normal by $\sim 0.5a_B$. In the ideal π-bonded chain geometry,[1] these two atoms are at the same elevation. A schematic representation of the optimum geometry is shown in Fig. 2. The length of the bond between surface atoms is $4.37a_B$, which is significantly shorter than the bulk bond length ($4.62a_B$). The distortions in the underlying layers are necessary to relieve the stress induced by the five- and sevenfold rings of bonds. We determined a qualitatively similar set of distortions for Si(111)-(2 × 1).[16]

The distortions described above influence the character of the dangling-bond surface-state dispersion. Considering the surface-state band which arises in a

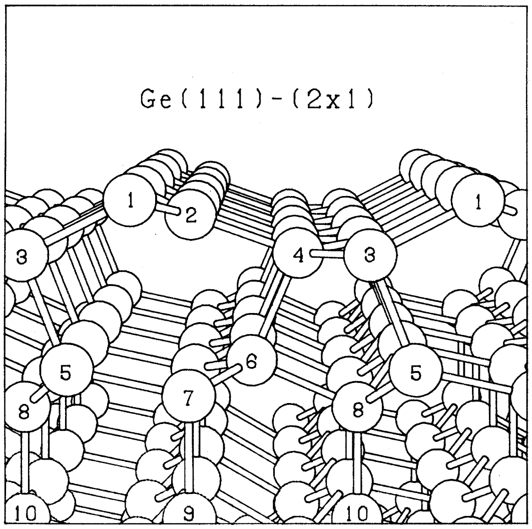

FIG. 1. Ball and stick model of the energy optimized chain geometry. Atom 1 is sp^3 coordinated; atom 2 is sp^2 coordinated.

simple one-dimensional tight-binding picture with one dangling-bond orbital per atom, one is led to a π band in which the surface-state energy is degenerate at the edge of the Brillouin zone. The degeneracy is lifted if the two surface atoms become inequivalent, and an energy gap develops at the zone edge which has a magnitude equal to the difference in the on-site orbital energies. The rehybridization which occurs in the minimum-energy geometry increases the difference in on-site orbital energies and therefore increases the energy gap. In our calculations, the rehybridization occurs naturally as the positions of the atoms are changed so that the forces on each atom vanish, i.e., the rehybridization is energetically favorable. This is in contrast to the case of the relaxed Si(111)-(1×1) surface, where electronic correlations prevent buckling induced rehybridization.[16-18]

The total energy of the optimized chain surface is ~0.32 eV/(surface atom) lower than the ideal (unrelaxed) spin-polarized [antiferromagnetic (2×1)] geometry. For Ge, as in the case of Si(111)-(2×1),[7,16,18] the chain geometry has a lower total energy than any of the ideal topology geometries tested. Local-spin-density calculations for the spin-polarized ideal topology Ge(111) surfaces are planned to be discussed in a forthcoming publication.

The theoretical surface-state dispersion and bulk projected band structure for Ge(111)-(2×1) is shown in Fig. 3. Two prominent surface states exist in gaps in the projected band structure. The π band starts as a resonance near the valence-band edge at Γ and then disperses upwards by 0.8 eV from $0.5\Gamma J$ to J. This state is flat from J to K'. A surface state with these characteristics has been observed by Nicholls *et al.*[4] The dispersion of this surface state along $\Gamma J'$ and from J' to K' is shown in Fig. 3(b). Another prominent surface state, labeled σ in Fig.

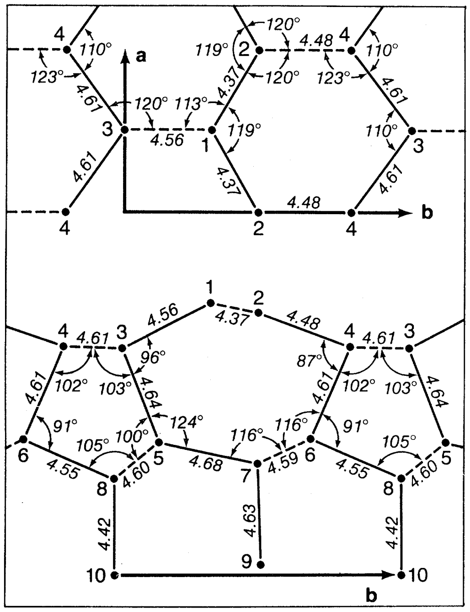

FIG. 2. Schematic view (top and side) of the predicted chain geometry. The equilibrium bond length of crystalline Ge is $4.62a_B$. The tetrahedral bond angle is 109°. Vectors a and b are primitive lattice vectors. The numbering of the atoms corresponds to Fig. 1.

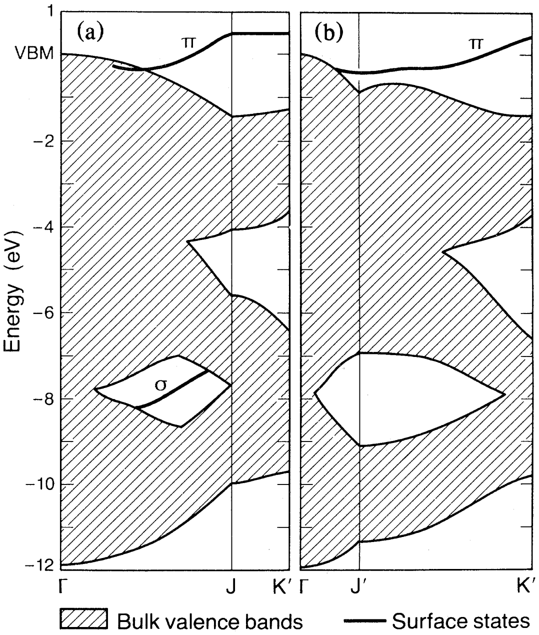

FIG. 3. Projected valence-band structure and occupied surface-state dispersion along (a) the $\Gamma JK'$ directions, and (b) the $\Gamma J'K'$ directions.

3(a), exists in a gap in the projected band structure roughly 8 eV below the top of the valence band and halfway between Γ and J. This state disperses upwards and is associated with σ bonds between the surface atoms in the chain. The presence or absence of this state in angle-resolved photoemission experiments would provide a useful check on the validity of the chain model for Ge(111)-(2 × 1).

A comparison between theory and experiment for the shape of the occupied π-band surface-state dispersion is shown in Fig. 4. Between Γ and 0.5ΓJ, the energy of the theoretical surface-state band lies within the bulk continuum, and the downward dispersion of the surface state is the same as that of the bulk states. The surface state begins to disperse upwards rapidly when it leaves the bulk continuum. The shape of the theoretical band is in good agreement with the experimental results of Nicholls *et al.*[4] The absolute position of the theoretical result is ~ 0.8 eV higher than the experimental value, but a rigid shift brings the two into reasonably good agreement.

An unoccupied π band (shown in Fig. 4) disperses downwards from Γ to J and has a small upwards dispersion from J to K'. The energy gap separating the occupied and empty π states along the line JK' is ~ 0.25 eV. The experimentally determined gap between occupied and empty surface states for Ge(111)-(2 × 1) is 0.45 eV.[2] Since the local density theory is usually unable to predict the correct excited-state energies, we are reluctant to attach a great deal of significance to the value of the calculated gap.

One source of uncertainty in the theoretical position of the surface-state energy is the interpretation of the local density eigenvalues as removal energies. The assumption that the difference between the eigenvalues of occupied states is equal to the difference in the removal energies may be invalid when comparing surface states, which are confined to two dimensions, with itinerant bulk states. The local density theory generally predicts too small a value for the ionization potential of atoms, but it generally predicts the correct ionization potential for solids. The theory may, therefore, give the surface state at too high of an energy relative to the top of the valence band.

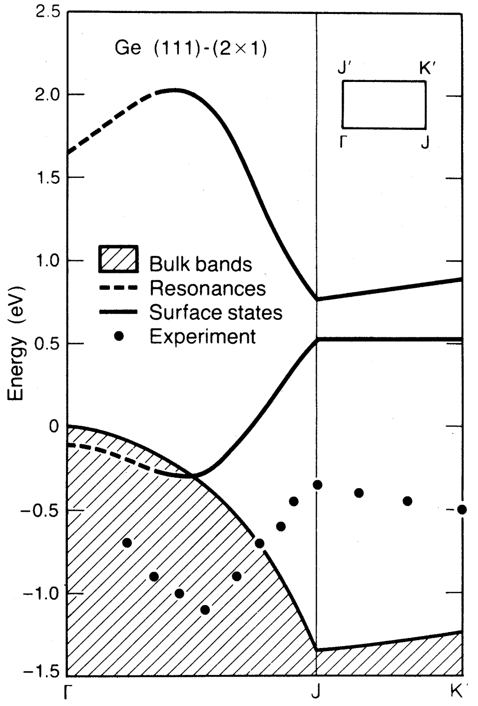

FIG. 4. Comparison between theory and experiment (Ref. 4) for the surface-state dispersion along the line ΓJK'. A rigid shift brings the two results into reasonably good agreement.

In summary, these pseudopotential local density total energy calculations demonstrate that a buckling of the surface atoms in the chain stabilizes the π bonded chain geometry. For the optimum geometry the dispersion of the π band of surface states is in qualitative agreement with experiment.[4] A surface state with σ character is predicted to exist in a gap in the valence-band structure approximately 8 eV below the valence-band maximum.

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