

Surface Vibrational Excitations on Si(001)2×1

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We present the first realistic study of the surface-phonon spectrum of a reconstructed semiconductor surface. The extensive reconstruction of the Si(001)2×1 surface is found to localize a rich spectrum of surface modes including a band localized nearly completely on a rocking motion of surface dimers and an unanticipated optical mode localized in the first two subsurface layers. With use of a tight-binding theory for structural energies, the model incorporates the effects of bond rehybridization at the surface.

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One of the more exciting developments in surface physics in recent years has been the increasing sophistication of experimental techniques for measuring surface vibrational properties. Inelastic neutral atom scattering, electron energy-loss spectroscopy (EELS), and surface infrared absorption spectroscopy have been used successfully to study vibrational excitations on the surfaces of some alkali halides, noble metals, and chemisorbed systems.^{1,2} While these techniques are beginning to be directed toward clean semiconductor surfaces, there has been virtually no theoretical work exploring the intrinsic semiconductor surface vibrations that may be accessible by these probes. In this work we demonstrate that semiconductors may indeed provide the most profitable application of such methods. We present the first realistic study of surface phonons on a reconstructed semiconductor surface, the Si(001):2×1 surface. The Si(001) surface is believed to undergo a strong relaxation in which pairs of surface atoms bind together and relax asymmetrically, producing both new surface bonds and subsurface strain propagating several layers deep. Despite the manifest complexity of this relaxation, we find that many aspects of the vibrational spectrum admit a surprisingly simple and direct interpretation in terms of the surface structural properties. In particular, we find one branch of the phonon spectrum localized nearly completely on a rocking motion of the surface dimers, providing an excitation whose character, frequency, and momentum are well suited to measurement by inelastic atom scattering. At higher frequency we find a second, unanticipated surface band dominated by an oscillation of subsurface atoms which are forced into a strained bonding geometry by the surface relaxation; this branch is potentially accessible to EELS. We demonstrate that, in any case, useful vibrational spectroscopy on this surface will require large momentum transfer in the surface plane. In this Letter we outline our computational procedure

and highlight our major results; a fuller discussion of the lattice dynamics of this surface will be deferred to a forthcoming comprehensive paper.³

To incorporate efficiently the effects of electronic rehybridization in the dynamical matrix we have coupled a tight-binding theory for the surface electronic structure with an underlying nearest-neighbor central-force elastic Hamiltonian to model the structural energies of this system. As in previous applications of this method,^{4,5} a Hamiltonian is constructed:

$$\mathcal{H} = \sum_{i,j,\sigma} h_{ij} a_{i\sigma}^\dagger a_{j\sigma} + \sum_i U_1 x_i + U_2 x_i^2, \quad (1)$$

where the $a_{i\sigma}^\dagger$ creates an electron with spin σ in the i th tight-binding orbital in the theory, and $x_i = d_i/d_0 - 1$ is the fractional deviation of the i th bond length, d_i , from the bulk equilibrium value d_0 . The parameters in the model are thus the set of hopping amplitudes (h_{ij}) and the elastic parameters U_1 and U_2 . We adopt a previously suggested set of h_{ij} which describe nearest-neighbor hopping among a set of four tight-binding valence orbitals per atomic site,⁵ and scale the amplitudes with bond length d as d^{-2} .^{6,7} The last two terms in Eq. (1) describe an effective elastic Hamiltonian which is understood to include the corrections for overcounting two-body interactions in the sum over band energies obtained from the first term in (1).⁴ U_1 (-16.3 eV) is chosen to equilibrate the crystal at the correct lattice constant and U_2 (49.3 eV) is chosen to reproduce the frequency of the zone-center optical phonon. To study lattice dynamics we require the second derivatives to the total energy at equilibrium:

$$D_{\mu\nu}(q) = \frac{\partial^2 \langle \mathcal{H} \rangle}{\partial x_{\mu,q}^* \partial x_{\nu,q}} = \frac{\partial^2 \langle \mathcal{H}_{\text{elect}} \rangle}{\partial x_{\mu,q}^* \partial x_{\nu,q}} + \frac{\partial^2 U_{\text{elast}}}{\partial x_{\mu,q}^* \partial x_{\nu,q}}, \quad (2)$$

where $D_{\mu\nu}(q)$ is the dynamical matrix whose eigen-

values are $M\omega^2(\vec{q})$, and $x_{\mu,q}$ is a displacement field for the μ th degree of freedom at wave vector \vec{q} . Here, angular brackets denote a ground-state expectation value, which is efficiently evaluated in perturbation theory^{3,8}:

$$\frac{\partial^2 \langle \mathcal{H}_{\text{elect}} \rangle}{\partial x_{\mu,q}^* \partial x_{\nu,q}} = 2 \sum_i f_i \left\langle i \left| \frac{\partial^2 \mathcal{H}_{\text{el}}}{\partial x_{\mu,q}^* \partial x_{\nu,q}} \right| i \right\rangle + 2 \sum_{i,j} \frac{f_i(1-f_j)}{E_j - E_i} \left\langle i \left| \frac{\partial \mathcal{H}_{\text{el}}}{\partial x_{\mu,q}^*} \right| j \right\rangle \left\langle j \left| \frac{\partial \mathcal{H}_{\text{el}}}{\partial x_{\nu,q}} \right| i \right\rangle, \quad (3)$$

where the f_i are Fermi factors. Despite the presence of seven parameters in the theory (five electronic and two elastic), the model is extraordinarily simple: Only U_2 is fitted to a phonon frequency which sets the overall energy scale of the vibrational spectrum, and all noncentral interactions enter through the electronic terms. The electronic terms h_{ij} are completely determined by fitting bulk Si electronic bands. Nevertheless, the description of the bulk phonon dispersion is remarkably successful, as demonstrated in Fig. 1 where we compare the bulk phonons from Eq. (2) with the experimental data from neutron scattering.⁹ The agreement is excellent over the full Brillouin zone. The principal deficiencies of the model are a systematic underestimate of the elastic constants and a slight (10%) overestimate of the zone-boundary TA modes. Similar results were obtained for elastic constants and the TA zone-boundary modes with a frozen-phonon approach.¹⁰

To extend this model to the Si (001) surface, we impose the connectivity of the 2×1 reconstructed surface, coupling pairs of Si atoms in rows along the [110] direction on both (001) surfaces of a ten-layer slab and following the Hellmann-Feynman forces prescribed by Eq. (1) to equilibrate the slab. This method is known to yield rows of asymmetric (tilted) dimers on the surface.^{5,11} This equilibrated structure is essentially that found by Chadi^{5,11} which is very similar to one obtained in the self-

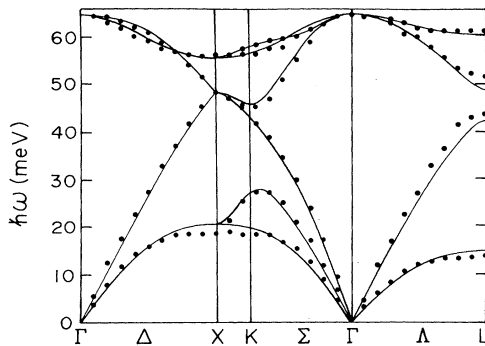


FIG. 1. Phonon bands for bulk Si derived from the present model (solid) compared with neutron-scattering data (Ref. 9) (points) along symmetry directions in the diamond-structure Brillouin zone.

consistent pseudopotential study of Yin and Cohen¹² and which agrees qualitatively with recent LEED experiments.¹³ The curvature of the total energy around this equilibrium is obtained following the scheme outlined in Eqs. (2) and (3). Eigenfunctions and band energies are computed on a mesh of six \vec{k} points in the irreducible Brillouin zone, and the polarization sum (second term) in Eq. (3) is evaluated for any \vec{q} connecting these points. The dynamical matrix is subsequently constructed for this primary set of \vec{q} 's, Fourier transformed to real space (providing the interatomic force constants), and then back-transformed onto a finer mesh of wave vectors \vec{q} to interpolate the dynamical matrix and study the dispersion of the vibrations throughout the Brillouin zone. As a check on the accuracy of the \vec{k} and \vec{q} integrations and on the convergence with respect to slab thickness we find that bulklike interatomic force constants are recovered (to within 2%) by the fifth atomic layer (slab center). It is worth noting that the force constants are considerably altered for surface atoms (by about 20%–30%) and that this is the first calculation predicting their values.³

The vibrational spectrum of the ten-layer slab is shown in Fig. 2. The cross-hatched area is the pro-

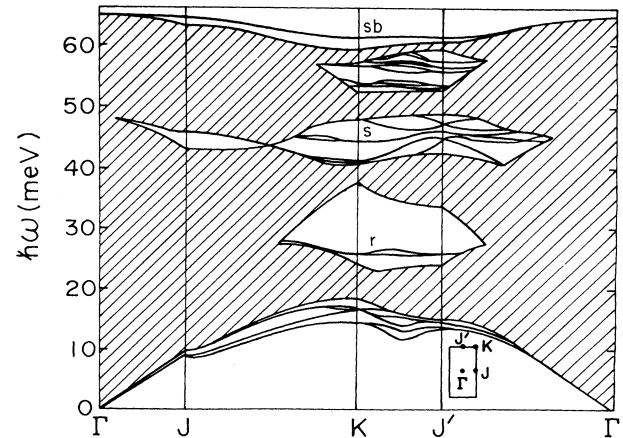


FIG. 2. Bulk phonon bands projected onto symmetry directions of the folded 2×1 surface Brillouin zone (hatched) and surface phonon bands obtained from slab calculation (solid lines).

jection of the bulk phonon bands onto the folded 2×1 surface Brillouin zone. Naturally, the most significant perturbation at the surface is the reduced coordination of the surface atoms. At long wavelengths this produces the well known Rayleigh surface wave¹ at acoustic frequencies just below the acoustic continuum. At short wavelength the character of the acoustic modes is considerably altered. Three branches (per surface) are pushed off the continuum involving motions both normal and parallel to the surface plane. The reduced coordination is also responsible for the general softening which pushes modes into the two uppermost projected gaps. In this vibrational spectrum there are three branches (r , s , and sb) which stand out as particularly informative. The first (r) extends across a projected gap at 26 meV. The displacement field for this vibration at the K point is given in Fig. 3(a). The mode involves a nearly pure rocking of the surface dimer. Notice that although it has the character of an optical phonon, the mode is found just above the bulk acoustic continuum. This softening is due to the strong screening of this vibration from virtual transitions between the dangling-bond surface bands which are split by a relaxation along this coordinate.¹⁴ The motion is therefore coupled to a charge-transfer oscillation of the surface dimer; such a mode would be strongly infrared active were it to persist at the zone center. As it is, the mode has a strong projection along the surface normal, and therefore should be particularly accessible to inelastic He scattering.

The next interesting surface branch (s) crosses the center of the next window in the projected spectrum at about 44 meV. The eigenvector of this mode at K is given in Fig. 3(b) and shows a swinging of alternate dimers 180° out of phase.

The last branch to which we call attention (sb) splits off from the *top* of the bulk TO continuum. The eigenvector at the K point is also sketched in Fig. 3(c). Remarkably, this mode has the largest amplitude on a fully coordinated subsurface atom at which the bond angles are strongly distorted, as can be seen in Fig. 3(c). In the relaxed geometry the motion of this atom projects strongly onto bond-length oscillations of two bonds in the $(1\bar{1}0)$ plane, in a manner which is impossible in the bulk. The stiffening is a geometric effect: Bond lengths are not appreciably altered from their bulk values. Thus, we predict that *any* Hamiltonian producing an equilibrium surface of asymmetric dimers, as shown in Fig. 3(c), will possess this high-frequency subsurface bond mode. As this mode is at comparatively high energy and has weaker amplitude on

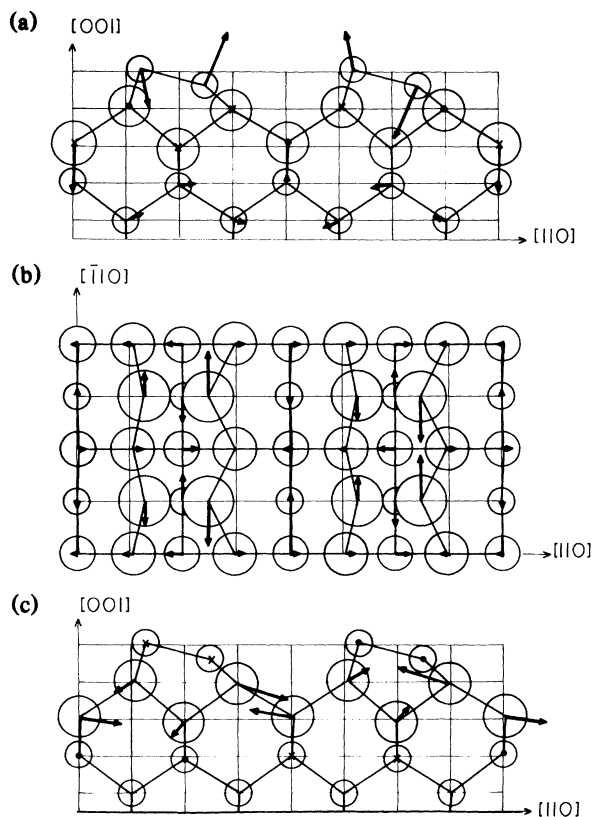


FIG. 3. Vibrational amplitudes for three localized modes (arrows are proportional to relative amplitudes) at the K point of the surface Brillouin zone. (a) A side $(1\bar{1}0)$ view of the dimer rocking mode r ($\hbar\omega = 25.7$ eV). (b) A top (001) view of a zone-boundary swing mode s ($\hbar\omega = 44.2$ eV) in which adjacent dimers swing out of phase. (c) A side $(1\bar{1}0)$ view of the subsurface bond mode sb ($\hbar\omega = 61.2$ eV) which splits off from the *top* of the bulk continuum throughout the surface Brillouin zone. The atoms mainly affected are in the second layer (largest vibrational amplitude) and in the third layer (second largest amplitude).

the surface atoms, it is a poor candidate for excitation in atom scattering. However, an intriguing possibility is that EELS, which is not quite as surface sensitive, could be used to identify such a localized subsurface vibration.

From Fig. 2 it is clear that any effective vibrational spectroscopy on this surface will require large momentum transfer in the surface plane. While this is intuitively true for any surface, it is particularly evident for Si(001) because the projected bulk spectrum is continuous at the zone center. Nonetheless, the center of the surface Brillouin zone is convenient experimentally and we are presently extending these calculations to investigate the degree to which these interesting surface vibra-

tions are reasonably broadened at the zone center.³

These calculations demonstrate that Si(001) and presumably other strongly reconstructed semiconductor surfaces possess a very rich vibrational spectrum. Surprisingly, despite the general structural complexity of this surface there are a number of branches in the vibrational spectrum which can be interpreted simply, and will yield a great deal of structural information about the bonding properties of the surface. Finally, the theoretical methods we have employed here are quite efficient and flexible, and should find increasing application for analyzing similar surface and interfacial vibrational problems.

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⁷We have investigated a number of possible scaling relations other than the d^{-2} recommended in Ref. 6, including a fit to pseudopotential band variations with hydrostatic pressure. No qualitative features of phonons we have investigated are affected.

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¹⁴Surface electronic bands before and after the asymmetric dimer relaxation are given in Ref. 5.