

Dipole Activity of Surface Phonons on Si(111)2×1

O. L. Alerhand, D. C. Allan,^(a) and E. J. Mele

Department of Physics, University of Pennsylvania, Philadelphia, Pennsylvania 19104

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We report studies of the lattice dynamics and one-phonon absorption spectrum for the π -bonded-chain model of Si(111)2×1. The surface conductivity is dominated by a localized mode near 50 meV associated with a longitudinal optical phonon on the surface chains which is coupled to charge fluctuations in the electronic surface states. The dipole activity of this feature is anomalously strong and, interestingly, polarized parallel to the surface, along the chain direction. The dipole activity polarized normal to the chains is also presented.

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Over the last several years, there has been growing evidence, both from theory and experiment, supporting an interesting structural relaxation of the Si(111)2×1 surface. The currently favored model involves the formation of π -bonded chains of Si atoms oriented along one of three equivalent $[\bar{1}10]$ directions on the surface plane.¹⁻⁷ The signature of this reconstruction is the delocalization of electrons in surface states along the chain direction. This has been confirmed by measurements of surface-state dispersion³ and by the polarization dependence of surface-state interband transitions.⁶

In this Letter we note that the π -bonded chain model also provides a very straightforward (though somewhat surprising) resolution to a long-standing question regarding the *vibrational* spectroscopy of the Si(111)2×1 surface, namely, the presence of an anomalously strongly dipole-active surface phonon in high-resolution inelastic electron-scattering spectra.^{8,9} Below we summarize results from a series of calculations which show that this feature is well described as an intrinsic longitudinal optical vibration of the surface chains and that its strong dipole activity derives nearly entirely from the coupling of this mode to large charge fluctuations in the electronic surface states. A surprising consequence of this assignment is that the dynamic dipole driven by this mode must be oriented parallel to the surface along the chain direction, rather than normal to the surface as has been commonly assumed. Our results also suggest an important experiment which can verify this assignment, namely, the rotation of the electron-energy-loss-spectroscopy scattering plane to a direction normal to the surface chains on a single-domain 2×1 surface. In this "perpendicular" geometry we anticipate the quenching of the strong Si(111)2×1 surface phonon and the appearance of a weaker spectrum with structure which could potentially provide other detailed information about the bonding properties of the surface chains. This study of the Si(111)2×1 surface illustrates the importance of the coupling of charge fluctuations to vibrational excitations on semiconductor surfaces. We believe that

similar, though possibly weaker, phenomena should be found on a variety of other semiconductor surfaces as well.

The starting point of our calculations is a total-energy expression that consists of a tight-binding Hamiltonian for the electrons and a two-body interatomic elastic potential; electron-phonon coupling is introduced through a d^{-2} scaling of the electronic hopping amplitudes with interatomic bond lengths.¹⁰ We then relax to the minimum-energy structure described by this Hamiltonian and through perturbation theory construct a dynamical matrix which we use to study vibrational excitations.¹⁰ The equilibrium geometry that we obtain for Si(111)2×1 is shown in Fig. 1.¹¹ The surface chains are tilted, with a vertical displacement d_0 between the surface atoms. In our calculation, the equilibrium value of $d_0 = 0.63$ Å which exceeds estimates from both pseudopotential total-energy calculations ($d_0 = 0.10 \pm 0.05$ Å)¹² and LEED experiments ($d_0 = 0.38 \pm 0.08$ Å).⁵ We believe that this deficiency is related to the omission of a direct electron-electron repulsion term in our model Hamiltonian; we will return to the physical consequences of this overestimate below. Notice that the second-layer atoms also form chains that are parallel to the surface chains. With respect to symmetries, the surface has a mirror plane perpendicular to the chain direction (σ_x); thus the vibrational modes with wave vector in the mirror plane fall into one of two representations; even modes with displacement parallel to the mirror plane, and odd modes polarized parallel to the surface chains.

Interesting vibrational modes which are localized on the surface and have the form of elementary excitations of the chains are found at the Brillouin-zone center (Table I). The rocking and transverse modes are transverse optical modes on the surface chains, the first one polarized normal and the second one parallel to the surface. Shown in Fig. 1 is a longitudinal optical mode along the surface chains which we will refer to as the "dimer mode"; it occurs at 53.5 meV in a symmetry gap: Projected bulk phonons with nearby ener-

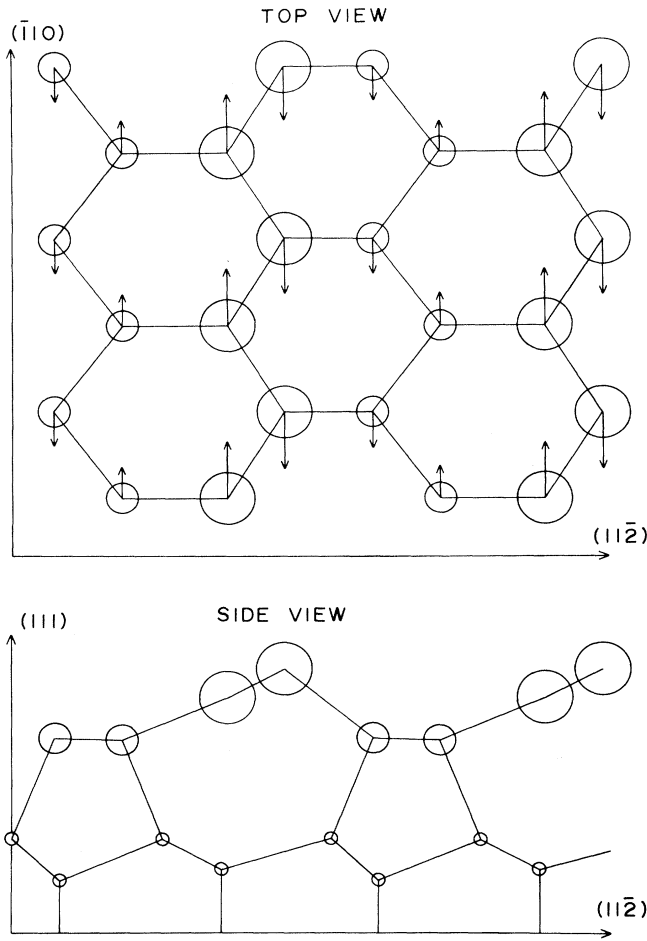


FIG. 1. Top and side views of the π -bonded chain model of the Si(111) 2×1 surface. The arrows indicate the vibrational amplitudes of a longitudinal optical mode on the surface.

gy involve displacements parallel to the (111) direction, whereas the dimer mode is transverse with respect to (111). In the dimer and transverse modes the second-layer chains move in phase with the surface chains; the subsurface modes listed in Table I correspond to the same type of vibration but with the subsurface chains moving out of phase; in this case the amplitude of the vibration is larger on the subsurface chains than on the surface chains. The appearance of these vibrational modes is a consequence of both the dramatic modification of the atomic geometry at the surface and the strong intrachain bonding of the surface Si atoms. In this respect this surface is structurally quite different from Si(100), which we have studied earlier.^{10a}

In order to study the dipole activity of the surface generated by vibrational excitations, we also calculate the linearized charge fluctuations in response to the ionic displacements and compute the dynamic charges

TABLE I. Surface vibrational features at the Brillouin-zone center.

Feature	Symmetry under σ_x	Energy (meV)
Projected bulk acoustic modes	+	0–42.3
Shear	–	17.9
Rocking	+	33.3
Transverse	+	43.5
Projected bulk longitudinal optical	+	48.7–64.3
Dimer	–	53.5
Projected bulk transverse optical	–	60.2–64.3
Subsurface dimer	–	61.6
Subsurface transverse	+	64.2

\mathbf{e}_i^* defined as

$$\mathbf{e}_i^* = i \int_0^\infty \langle [\mathbf{r}(t), h_i(0)] \rangle dt, \quad (1)$$

where $h_i = \partial H / \partial Q_i$, and Q_i denotes an ionic degree of freedom. Since the electronic states are extended to Bloch states, it is convenient to evaluate the matrix elements of the position operator with use of the identity

$$\langle n | \mathbf{r} | m \rangle = \langle n | [H, \mathbf{r}] | m \rangle / (E_n - E_m). \quad (2)$$

The dynamic charge \mathbf{e}_n carried by the n th phonon is then obtained by projection of (1) onto the displacement field of that phonon:

$$\mathbf{e}_n^* = \sum_i \mathbf{e}_i^* Q_i^{(n)}, \quad (3)$$

where $Q_i^{(n)}$ is the displacement of the i th degree of freedom in the n th normal mode. Modes that are even under σ_x have dynamic charge polarized parallel to the mirror plane, and modes that are odd under σ_x have dynamic charge polarized parallel to the surface chains. For longitudinal modes, the presence of a large dynamic charge on the surface generates an additional electrostatic term in the surface energy.¹³ We evaluate this correction by adding the potential energy of an array of surface point dipoles with effective charges given by (1) to our total-energy expression:

$$U_{\text{Coulomb}} = \frac{1}{2} \sum_{i \neq j} Q_i \left[\frac{\mathbf{e}_i \cdot \mathbf{e}_j}{r_{ij}^3} - \frac{3(\mathbf{e}_i \cdot \mathbf{r}_{ij})(\mathbf{e}_j \cdot \mathbf{r}_{ij})}{r_{ij}^5} \right] Q_j. \quad (4)$$

The shift in the phonon frequency that results from this correction is negligible in most cases, but can be as large as ~ 5 meV for exceptional modes with large \mathbf{e}_n^* . The conductivity of the surface then follows:

$$\text{Re} \sigma(\omega) = \frac{\pi}{2MA} \sum_n |e_n^*|^2 \{ \delta(\omega - \omega_n) + \delta(\omega + \omega_n) \}, \quad (5)$$

where the sum is over zone-center phonons, M is the ionic mass (28 amu), and A is the unit cell area.

In Fig. 2 we plot σ vs $E = \hbar\omega$, or the one-phonon absorption spectrum. The continuous spectra are obtained from the original discrete ones by convolution with a Lorentzian with FWHM of 5 meV, comparable to the best available experimental resolution. Figure 2(a) shows the phonon surface density of states projected onto the surface layer; the features listed in Table I can be identified with peaks on this curve. Figures 2(b) and 2(c) show, respectively, the surface conductivity polarized perpendicular to the chains (even modes) σ_{\perp} , and the surface conductivity polarized parallel to the chains (odd modes) σ_{xx} . The features with even symmetry in Table I give rise to absorption peaks in the $\sigma_{\perp}(\omega)$ spectrum, the most important being the peak at 33.5 meV, which corresponds to the rocking mode. The three curves in Fig. 2(c) are obtained for three values of the tilt parameter d_0 , which generate the three surface-state gaps listed in the inset. In our equilibrium structure the surface-state gap is quite large (0.89 eV), which is overestimated because of the exaggerated tilt mentioned earlier. The two remaining spectra correspond to reduced surface-state gaps which are obtained by imposition of a surface configuration with a reduced tilt ($d_0 = 0.14, 0.11 \text{ \AA}$)

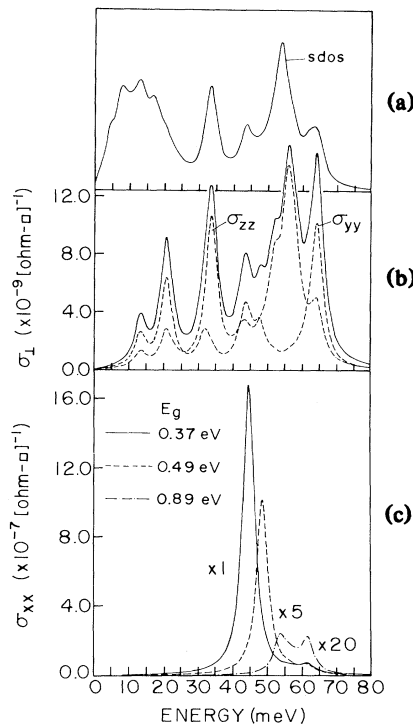


FIG. 2. (a) Phonon surface density of states projected to the surface layer. (b) Surface conductivity σ_{\perp} , polarized perpendicular to the chain, vs energy. (c) Surface conductivity σ_{xx} , polarized parallel to the chains, vs energy.

and relaxing the remaining ion coordinates. The experimentally observed direct gap ($E_g \approx 0.4 \text{ eV}$)^{6,7,14} occurs near that obtained from the latter geometry thus generated ($E_{\text{direct}} = 0.43 \text{ eV}$). We note that modes parallel to the chain do not transform under the fully symmetric representation and therefore remain stable in these “nonequilibrium” geometries. When the gap is large, σ_{xx} has two peaks; they correspond to the surface and subsurface dimer modes. As d_0 and E_g decrease, the dynamic charge associated with the surface dimer mode increases dramatically; it reaches a large value of $e^* = 1.5e$ for the smallest gap tested. The reduction of E_g also shifts the frequency of the dipole-active mode slightly. The data plotted in Fig. 2 show this mode at 53.5, 47.0, and 44.7 meV for the three geometries studied. This strong dependence on the size of the gap is in large part due to the energy denominators in Eqs. (1) and (2), which appear squared in Eq. (5). For the experimentally observed gap, the surface dimer mode completely dominates the absorption spectrum. Note that the ordinates in Figs. 2(b) and 2(c) are scaled by nearly two orders of magnitude.¹⁵ Its associated dynamic dipole is oriented *parallel* to the surface along the chains. This is rather surprising, and it would not occur on (ideal) metallic surfaces where classically the image charge exactly cancels the parallel components of the surface dipole.¹³

We conclude that in angle-resolved electron-energy-loss-spectroscopy experiments, when the surface chains project onto the scattering plane, the inelastic spectrum should be dominated by a single sharp and very strong peak near 50 meV (as reported in Refs. 8 and 9 and by Lapeyre¹⁶), but that this feature should be suppressed for scattering perpendicular to the chains. While this suppression should be complete for an ideal spectrometer with perfect angular resolution, we should note that in analysis of experimental data some care must be exercised to average the inelastic spectrum over the finite acceptance angle of any real spectrometer, since the scattering amplitude is a strong function of the incident azimuthal angle near the perpendicular geometry.¹⁷ Indeed, we have carried numerical simulations of such an experiment¹⁸ and have found that for representative acceptance parameters ($\Delta\phi = \pm 2^\circ$, $\Delta\theta = \pm 1^\circ$) the suppression of the phonon-loss peak is easily resolved for low-incident electron kinetic energy $E_i < 5 \text{ eV}$, but becomes somewhat more difficult to resolve for $E_i > 10 \text{ eV}$. With “perfect” resolution, the azimuthal dependence of the intensity of the strong surface-phonon loss peak tracks the polarization already observed for intersurface state transitions at J .

The charge fluctuations that give rise to the strong absorption peak in Fig. 2(c) are generated nearly completely by the coupling of the electronic surface state to the longitudinal optical mode of the surface chains.

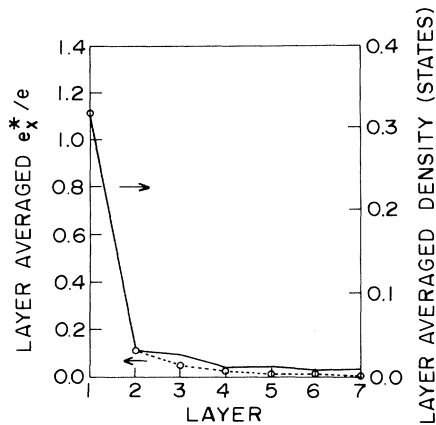


FIG. 3. Filled surface-state layer-averaged charge density and layer-averaged dynamic charge polarized in the chain direction, as a function of penetration depth into the bulk.

This can be seen from Fig. 3, where we plot the surface-state layer-averaged charge density and the layer-averaged dynamic charges of (1) as a function of penetration into the bulk. The dynamic charges are zero by symmetry in the bulk, and both quantities decay very quickly into the bulk in a correlated way, showing that the charge fluctuation is nearly entirely provided by the response of the surface-state electrons.

In summary, we find that the anomalously strong feature commonly observed in high-resolution electron-energy-loss spectroscopy from $\text{Si}(111)2 \times 1$ is well described as an intrinsic longitudinal optical phonon of the π -bonded chains on this surface; the large dynamic charge results from the response of the surface-state electrons coupled to this mode. This assignment requires that the dynamic dipole be oriented in the surface plane, parallel to the chains, contrary to most previous speculations about this feature. Experimental measurement of the azimuthal dependence of the scattering cross section for low incident-electron energies may provide an experimental verification of the assignment.

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(a)Present address: Corning Glass Works, SP-PR-22, Corning, N.Y. 14831.

¹K. C. Pandey, Phys. Rev. Lett. **47**, 1913 (1981), and **49**, 223 (1982).

²J. E. Northrup and M. L. Cohen, J. Vac. Sci. Technol. **21**, 333 (1982).

³F. J. Himpsel, P. Heimann, and D. E. Eastman, Phys. Rev. B **24**, 2003 (1981).

⁴R. M. Tromp, L. Smit, and J. F. van der Veen, Phys. Rev. Lett. **51**, 1672 (1983).

⁵F. J. Himpsel, P. M. Marcus, R. M. Tromp, I. P. Batra, M. Cook, F. Jona, and H. Liu, Phys. Rev. B **30**, 2257 (1984).

⁶M. A. Olmstead and N. M. Amer, Phys. Rev. Lett. **52**, 1148 (1984).

⁷P. Chiradia, A. Cricenti, S. Selci, and G. Chiarotti, Phys. Rev. Lett. **52**, 1145 (1984).

⁸H. Ibach, Phys. Rev. Lett. **27**, 253 (1971).

⁹E. Evans and D. L. Mills, Phys. Rev. B **5**, 4126 (1972).

^{10a}D. C. Allan and E. J. Mele, Phys. Rev. Lett. **53**, 826 (1984); E. J. Mele, D. C. Allan, O. L. Alerhand, and D. P. DiVincenzo, J. Vac. Sci. Technol. (to be published).

^{10b}D. J. Chadi, Phys. Rev. Lett. **41**, 1062 (1978).

¹¹The results that we present in this paper are for a fourteen-layer slab.

¹²J. E. Northrup, private communication.

¹³H. Ibach and D. L. Mills, *Electron Energy Loss Spectroscopy and Surface Vibrations* (Academic, New York, 1982).

¹⁴N. J. DiNardo, J. E. Demuth, W. A. Thompson, and Ph. Avovris, Phys. Rev. B **31**, 4077 (1985).

¹⁵For σ_{\perp} , there is essentially no change when d_0 and E_g are reduced; we have verified this by using the dynamic charges from a geometry with a frozen tilt (small d_0) and phonons from the equilibrium geometry.

¹⁶G. Lapeyre, private communications.

¹⁷D. Sokcevic, Z. Lenac, R. Brako, and M. Sunjic, Z. Phys. B **28**, 273 (1977).

¹⁸O. L. Alerhand and E. J. Mele, unpublished.