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Dynamics of Extensively Reconstructed Surfaces: Si(111)2×1

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We present a bond-charge-model, slab calculation of the 2×1 reconstructed Si(111) surface dynamics, which gives enlightenment on long-unexplained experimental features and provides general guidelines for the dynamical study of deeply reconstructed surfaces. This analysis is based on the concepts of geometrical folding in the surface Brillouin zone, reconstructed-to-ideal interface, and structural interpretation of the gaps that appear in the folded branches.

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Silicon has perhaps the most interesting and extensively studied surfaces both for fundamental reasons, related to their reconstruction forms and mechanisms, and for technical reasons. In particular, much effort has been concentrated on the 2×1 reconstruction of Si(111), where the formation of π-bonded atomic chains (Pandey model[1]) has been confirmed by a variety of experimental techniques[2-7] and by total-energy calculations.[8]

This is the surface where in 1971 the first microscopic surface phonon was measured, i.e., the 56-meV optical mode observed by Ibach with electron-energy-loss spectroscopy (EELS).[9] More recently, the Harten-Toennies-Wöll (HTW) helium scattering experiments[10] have revealed an isotropic low-lying optical branch at 10 meV, just above the Rayleigh wave (RW) dispersion curve. However, the dynamical structure of this surface, despite its relevance and the theoretical efforts made over many years, is not yet fully understood.

For instance, recent empirical tight-binding (TB) calculations for slab force constants by Alerhand, Allan, and Mele (AAM),[11] and by Alerhand and Mele[12,13] (AM) have associated the 56-meV EELS peak to a longitudinal variation of the topmost atomic chains, which implies a full azimuthal anisotropy of the EELS intensity. Such a prediction was apparently supported by previous experiments,[14] but is now seen to disagree with recent accurate high-resolution EELS data,[15] which have revealed a large isotropic component.

In this Letter we present a bond-charge model (BCM) slab calculation of the Si(111)2×1 surface dynamics and dipolar activity for Pandey's chain model, and provide an explanation of all salient experimental features. From the present analysis we extract three general concepts applicable to the investigation of extensively reconstructed surfaces: (i) The basic dynamical features of a reconstructed surface largely reflect those of the ideal, unreconstructed structure after the folding of the larger surface Brillouin zone (SBZ) into the smaller zone of the reconstructed phase (*folding criterion*). (ii) In the case of extensive reconstruction it makes sense to speak of an interface between reconstructed and ideal (bulk) regions and of interface modes (originating from the folding of the ideal-surface dynamics), which may be localized at the buried interface (*interface criterion*). (iii) The gaps opened along the folding lines reflect the new local arrangement of atoms in the reconstructed region and may be used to characterize the surface geometry (*gap criterion*).

As a demonstration of the folding criterion, it turns out that both the 10-meV branch and the dipole-active mode at 56 meV originate from the folding of the intrinsic surface modes existing in diatomic cubic crystals, viz., Rayleigh and Lucas modes, respectively. The 56-meV mode (not found by AAM) provides a remarkable z-polarized dipole activity at the Γ point. This interface-originated vibration turns into a true surface mode along the symmetry direction of the surface, and its presence illustrates *per se* the importance of the interface criterion. With regard to the gap criterion, we show that the experimental gap between the RW and the 10-meV mode at the zone boundary is a measure of the chain tilt, i.e., the difference in the vertical position between the two inequivalent atoms of the topmost chain. This has been experimentally derived by ion scattering[6] and LEED[7] measurements, and theoretically evaluated by total-energy calculations,[8] leading to the discrepant results of 0.39, 0.30, and 0.2 Å, respectively. Our dynamical fit of HTW data agrees with the total-energy calculation.

Our calculation is for a slab of 24 atomic layers. We adopted the adiabatic BCM,[16] which is known to give excellent agreement with experimental neutron scattering data for bulk silicon with only four parameters: (1) short-range central interaction between cores and (2) between cores and bond charges, (3) Keating angular force constants between covalent bonds, and (4) screened Coulomb potentials for cores and bond charges. The atomic positions at the surface are given as input data and taken from the fit of LEED measurements by Himpsel *et al.*[7] The bond charges are always located at the bond midpoints, even along the tilted chains, in agreement with charge-density maps from *ab initio* calculations.[8] In particular, such calculations show that no sizable amount of charge is present above the surface atoms where the dangling bonds are located; the charge redistribution leads to an evident increase of charge density around the midpoint of the chain bonds. Each bond charge between chain atoms now includes an additional π-bond electron and has altogether three electrons. The presence of the π electron would shift the bond-charge center slightly away from the chain plane; this kind of perturbation, however, is seen to have negligible effects on dynamics and dipolar activity and has been omitted.

Despite the large rearrangement of surface atoms, the interatomic distances remain almost the same as in the bulk, and no change of radial force constants has to be made at the surface. Note that the π state of the third electron has a nodal plane passing through the neighboring atoms and its overlap with the atomic core states is not modulated by small radial displacements. On the contrary, π-bound shear displacements do modulate such overlap. Thus the corresponding shear force constants, i.e., the first derivatives of *bond-charge–core* central interactions at the surface, are different from their bulk values, and are obtained from the new equilibrium conditions for the tilted-chain configuration. Moreover, the extensive change in bond angles is accounted for by the geometrical part of the Keating force constants. Thus no parameter is disposable in the present calculation. The BCM is actually the simplest model containing the basic physics of the electron-phonon interaction which permits a parameter-free calculation of the chain dynamics. An important aspect of our BCM approach to the surface vibrations is that the slab dynamical matrix is directly constructed in the full (core plus bond charge) coordinate space, the bond-charge coordinates being eliminated via the adiabatic condition only after the surface perturbation has been applied.

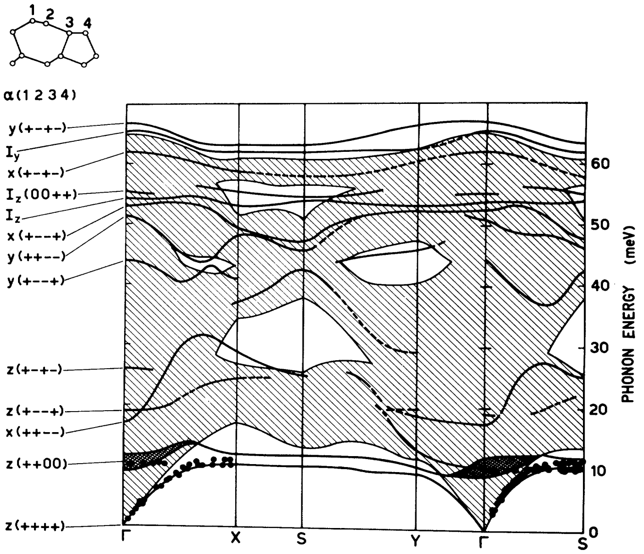

FIG. 1. Surface projection of the bulk bands (shaded areas) and surface modes (solid lines) along the borders of the irreducible part of the surface Brillouin. Broken lines represent weak resonances; black dots are experimental data from Ref. 10. The hatched areas correspond to the broad resonances produced by the 10-meV mode entering the bulk bands. On the left side are schematically displayed the displacement patterns of the topmost atoms (1,2,3,4) for surface and interface (I_a) modes.

In Fig. 1 we display the surface projection of the bulk bands (shaded area) and the calculated dispersion curves of the surface phonons (solid lines) along the symmetry directions of the SBZ. The polarization (x is the chain direction, y is normal to the chain, and z is normal to the surface) and phases of the four surface atom displacements (in parentheses, ordered as in the inset) are schematically indicated for the zone-center modes. Besides the expected twelve modes, we find three more modes (I_a) localized at the interface, having large displacements at the second and third atomic layers. Clearly we have here more surface modes than in AM. The optical x-polarized mode indicated by AAM as responsible for dipole activity is here $x(+--+)$ and falls at 52.5 meV.

The broad resonance $z(++00)$ at 10 meV and the interface mode $I_z(00++)$ at 55.1 meV are the z-polarized modes originating from the folding of the M-point Rayleigh and Lucas mode of the ideal 1×1 surface,[17-19] respectively, and correspond very well to the experimental frequencies determined by He scattering[10] and EELS.[9] We note the complementary displacement pattern of these modes: In the 10-meV mode the top chain is moving alone, whereas in the 55.1-meV mode the top chain is practically at rest and the vertical oscillation is concentrated on the lower chain and underlying interface atoms. Actually, the z-polarized *interface* modes are so high in frequency, as compared to *surface* z-polarized modes, because they involve deformations of the stiff fivefold rings spanning the interface. There is a clear separation between modes where chains move almost rigidly (below 30 meV) and those where chain bonds are stretched (above 40 meV). The largest stretch of bonds occurs for the $y(+-+-)$ mode, whose frequency falls above the bulk spectrum. This mode, and even more the localized I_y mode, also involves extensive stretching of fivefold ring bonds. Such stiff modes above the bulk maximum frequency appear to be a peculiarity of chain-reconstructed surfaces and have also been found by AM in both (111) (Ref. 13) and (100) (Ref. 20) Si surfaces.

The calculated RW dispersion curve is in very good agreement with He scattering data (dots). With regard to the dispersion of optical modes we note that only in the ΓY direction is there specular symmetry with respect to the sagittal plane. In the other directions all polarizations are admixed and relevant hybridization occurs between surface modes. Large anticrossing gaps appear in the low-symmetry directions ΓX and ΓS, between

$x(++--)$ and $y(+--+)$ modes, and between $z(++00)$ and $z(+-+-)$. The latter case is rather interesting because the X-point mode at 25 meV is y polarized (shear horizontal) and both $x(++--)$ and $z(++00)$ resonances acquire a y (shear) component when moving from Γ to X. Beyond the anticrossing region, however, the lower mode recovers its dominant z polarization as expected for a folded RW. This ensures that all the $z(++00)$ branch should be observable in He scattering experiments, as actually is the case. Yet, the experimental 10-meV branch is flatter than the calculated dispersion curve. Since the anticrossing is provided by the dynamical coupling of the chains to a substrate of different symmetry, we argue that a better agreement would be obtained by increasing such coupling. In any case it is clear that the dynamics of the π-bonded chains cannot be separated from that of the substrate and interpreted within a polymer model as proposed by AM.[13]

The calculated zone-boundary gap between RW and the 10-meV mode is about twice the experimental value. However, the gap is practically zero for the untilted-chain model, and the HTW data would be fitted by a tilt of about 0.2 A.

The BCM also offers a natural way to compute the dynamical dipoles owing to the dynamical separation of bond electrons from ions. In Fig. 2 we plot the calculated dipole-weighted phonon densities at Γ for the slab,

$$P_{\alpha\alpha}(\Omega)=\sum_{\mu}\left|\sum_{l} Z_l W_{l\alpha}(\Gamma,\mu)\right|^2 \delta(\Omega-\Omega_{\Gamma\mu}), \tag{1}$$

where $W_{l\alpha}(\Gamma,\mu)$ is the displacement vector of the μth zone-center normal mode of frequency $\Omega_{\Gamma,\mu}$, l labels both cores (c) and bond charges (b) within the slab unit cell, Z_l are their net charges ($Z_b=Z_c/2$ for all bond charges, except for the top chain where $Z_b=3Z_c/4$ by neutrality), and $\alpha=x,y,z$. The sum runs over all surface and bulk modes, but it is clear that bulk modes contribute very little due to the bulk homopolarity. For a closer comparison to EELS spectra we replace the δ function with a Lorentzian of finite width (FWHM = 5 meV) corresponding to EELS resolution.

The z-polarized dipole density displays a large peak at 55 meV in agreement with experiment, and minor features at lower frequencies, the most prominent one being the 10-meV mode. Unfortunately, the features below the minimum at 35 meV have not yet been resolved in EELS spectra due to the large diffuse elastic intensity.[15] The x- and y-polarized components yield their major contribution in the acoustic region at the resonances $x(++--)$ and $z(+-+-)$, respectively, the latter having also a large component along y. However, the overall dipole activity of horizontal components is reduced by the squared dielectric constant[21] ($\epsilon^2 \approx 140$) and is very small.

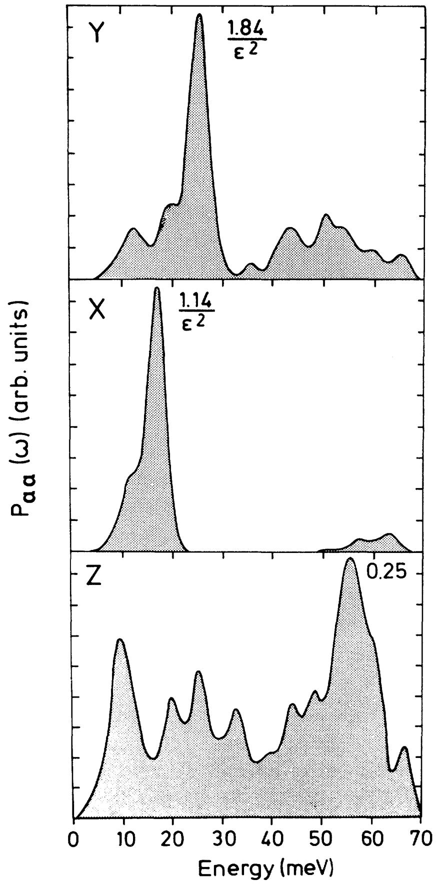

FIG. 2. Squared dipole-moment-weighted phonon density for y, x, and z components. The numerical values refer to the intensity of the highest peak in each component. The y and x components, however, have an EELS activity which is lower by a factor $1/\epsilon^2$ with respect to the z component (Ref. 21).

Moreover, the dipolar activity of the optical longitudinal mode $x(+--+)$ at 52.5 meV is practically zero (see Fig. 2, component). This mode is odd with respect to the mirror-symmetry plane normal to the chain, and could carry a dipole, but, for the untilted chain, the antiphase displacements of the two equally charged atomic rows, with the chain bond charges at rest, give an almost complete cancellation of the dipole components. Such cancellation is not exact owing to the interaction of the chain atoms with the fourth layer, but such interaction (included in the calculation) is so weak that it produces a frequency shift of less than 1% and a completely negligible contribution to the dipole moment. For the tilted chain the mirror symmetry is preserved, but the atomic rows become substantially inequivalent; however, the cancellation of the dipole components is still large and the dipole activity along x remains very small. These results agree very well with recent EELS experiments of Del Pennino *et al.*, evidencing a large isotropic (z polarized) component in the 55-meV peak.[15] In light of the present analysis the AAM prediction of a large dipolar activity from the $x(+--+)$ mode, which increases for decreasing tilt,[11] is rather puzzling because such activity should vanish for zero tilt.

In conclusion, we suggest that the application of our criteria (folding, interface, and gap) to other reconstructed surfaces may be extremely helpful, especially for a preliminary interpretation of the experimental dispersion curves.

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