

Surface reconstruction and lattice dynamics of hydrogenated Si(001):2×1

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(Received 21 December 1984)

We present a realistic calculation of the equilibrium surface structure and vibrational excitations of the hydrogenated Si(001):2×1 surface. We study a saturation monohydride coverage which is found to produce a (2×1) surface of symmetric dimers. A variety of interesting surface vibrational modes is found and discussed for this surface including a band of high-frequency vibrations associated with fivefold rings formed by the surface reconstruction. The relation between surface structure and surface vibrational modes is further elucidated by comparison with similar vibrational modes found on clean reconstructed Si(001):2×1. The results for Si-H bond bending and stretching frequencies agree with experimentally measured values for this surface.

We have performed a realistic theoretical study of structural changes and their associated modifications to the vibrational spectrum induced by chemisorption on a semiconductor surface. Surface vibrational excitations of a reconstructed semiconductor surface are sensitive to rebonding and structure in the first several atomic layers. We have already shown,^{1,2} for example, that the asymmetric dimer model of intrinsic Si(001):2×1 possesses several unique and interesting vibrational modes. In the present work we extend our calculations to consider the Si(001) surface but with hydrogen terminating the surface Si bonds. Modifications of the surface vibrational spectrum are found to provide a sensitive probe of a number of adatom-induced structural changes. Inspection of our computed force constants on the bare and hydrogenated surfaces, for example, reveals that hydrogenation reduces sublayer strain. Also we find that the tilted dimers of Si(001):2×1 become symmetric upon hydrogenation, which alters the allowed interactions and hence the spectrum of surface acoustic waves at large q . The purpose of this paper is to analyze the changes in the surface vibrational spectrum upon hydrogenation, and relate these to the accompanying structural modifications. We also compare the high-frequency bending and stretching modes of H with the measured frequencies from electron-energy-loss spectroscopy (EELS)³ and from surface infrared spectroscopy (SIS).⁴

The model for the structural energies and for the dynamical matrix, which includes bond rehybridization and electron-phonon coupling, is described in Ref. 1. The present calculation includes several new parameters which describe the Si-H bond. The electronic Hamiltonian uses a first-nearest-neighbor set of empirical tight-binding Slater-Koster⁵ parameters $\{h_{ij}\}$:

$$H_{\text{electronic}} = \sum_{ij\sigma} h_{ij} a_{i\sigma}^\dagger a_{j\sigma}, \quad (1)$$

where $a_{i\sigma}^\dagger$ creates an electron with spin σ on the i th tight-binding orbital and h_{ij} are first-nearest-neighbor hopping amplitudes. Our values for these parameters are given in Table I. The Si-Si interactions reproduce bulk Si electronic valence bands⁷ while the Si-H interactions are fit to reproduce one-electron molecular levels in SiH₄ and Si₂H₆, also given in Table I. Because the H atoms are far apart compared with the bond length of H₂ we assume no direct H-H interaction in the present model. In addition to electronic

energies, an elastic energy term is contained in the Hamiltonian with two parameters (U_1 and U_2) for each kind of bond in the system:

$$H_{\text{elastic}} = \sum_{\text{bonds } b} [U_1(b)\Delta_b + U_2(b)\Delta_b^2], \quad (2)$$

where $\Delta_b = d(b)/d_0(b) - 1$ is the fractional deviation of the length of bond b , $d(b)$, from its equilibrium length $d_0(b)$. For Si-Si bonds U_1 reproduces the crystalline Si lattice constant and U_2 reproduces the experimental Brillouin-zone center optical phonon frequency. For Si-H bonds, U_1 is fit to reproduce the Si-H bond length of 1.48 Å in SiH₄ and U_2 reproduces the a_1 vibrational mode of SiH₄ at $\hbar\omega = 271.2$ meV.⁷ Electron-phonon coupling is treated by scaling the electronic interactions between bonded atoms as d^{-2} for bond length d .^{1,2} Partly as a consequence of neglecting direct H-H interactions, the bond-bending modes of SiH₄ are predicted too low compared with experiment (Table I). This will not seriously hamper our present calculations in which we consider only monohydride H bonding. Underestimation of bond-bending forces seems to be a general feature of this model, also seen in the systematic underestimate of Si elastic constants.²

The structure for Si(001):2×1:H involves H atoms bonding to dangling bonds of Si surface dimers. In our calculation we approximate the hydrogenated surface with a slab of 10 layers of Si and a layer of H on each surface. In equilibrium we find the hydrogenated dimers to be symmetric. This is in contrast to the asymmetric dimers^{1,2} of the bare surface where a surface electronic band instability drives the asymmetric relaxation. This is not surprising because Si-H bonding removes the surface electronic bands and with them the driving force for dimer asymmetry. In the relaxed geometry we obtain $d(\text{Si-H}) = 1.48$ Å, $d(\text{Si-Si dimer}) = 2.39$ Å, and $\theta(\text{H-Si-Si}) = 110^\circ$. The dimer bond is shorter but the other parameters are the same as the result computed in Ref. 4. By directly computing the force constants for the hydrogenated slab and for bulk Si we observe that the forces among top layer Si atoms are strongly altered from bulk values (20–30%), whereas the second- and especially the third-layer force constants are close to bulk values. In contrast, both the top- and second-layer force constants are strongly altered on the intrinsic Si(001):2×1 surface with asymmetric dimers. This is an indication that hydrogenation relieves some of the sublayer strain of the asym-

TABLE I. Tight-binding Slater-Koster parameters and elastic parameters which describe Si-Si and Si-H bonds in the present model, and comparison between theoretical and experimental electron and phonon levels in SiH₄ and Si₂H₆.

Slater-Koster parameters (eV)						
$E_s(\text{Si}) = -13.08$			$E_s(\text{H}) = -10.91$			
$E_p(\text{Si}) = -6.63$						
$ss\sigma(\text{Si-Si}) = -1.94$			$ss\sigma(\text{Si-H}) = -3.37$			
$sp\sigma(\text{Si-Si}) = 1.75$			$sp\sigma(\text{Si-H}) = 2.74$			
$pp\sigma(\text{Si-Si}) = 3.05$						
$pp\pi(\text{Si-Si}) = -1.08$						
Elastic parameters (eV)						
$U_1(\text{Si-Si}) = -16.3$			$U_1(\text{Si-H}) = -14.5$			
$U_2(\text{Si-Si}) = 49.3$			$U_2(\text{Si-H}) = 43.7$			
Electronic levels (eV)			Vibrational levels (meV)			
	Experiment ^a	Theory		Experiment ^b	Theory	
SiH ₄	a_1^-	-4.1	-5.17	t_2	271.7	269.2
	t_2^-	-5.4	-4.95	a_1	271.2	271.2 (fit)
	t_2^+	-12.7	-12.59	e	121.0	71.7
	a_1^+	-18.2	-18.82	t_2	113.0	72.6
Si ₂ H ₆	a_g	-10.7	-10.93			
	e_g	-12.1	-12.38			
	e_u	13.3	-12.85			
	a_u	-17.3	-17.27			
	a_g		-19.18			

^aSee K. C. Pandey, Phys. Rev. B 14, 1557 (1976).

^bReference 6.

metric dimer structure. Experimental evidence for symmetric dimers on the hydrogenated surface is provided both by EELS³ and SIS.⁴

The projected band structure (PBS, hatched) and 10-layer slab phonon bands are plotted along symmetry directions in the (001):2×1 surface Brillouin zone (SBZ) in Fig. 1. For direct comparison of the nonhydrogenated and hydrogenated Si(001):2×1 surface vibrational modes, we reproduce the intrinsic surface bands^{1,2} in Fig. 2. Out of the apparent complexity of surface bands that derive from the complicat-

ed surface reconstruction, several are directly related to particular structural aspects and can be understood with simple physical pictures.

As expected there are a set of surface acoustic waves at low energy, split off from the acoustic continuum. These low-energy modes result from the reduced coordination number of surface atoms. The surface acoustic waves become more sensitive to the underlying surface structure at larger q. On both hydrogenated and intrinsic surfaces, three modes are seen in the K point. These are related to (K₃) surface Si atoms moving along the dimer bond, (K₁) surface Si atoms moving normal to the surface, and (K₄) second-Si-layer atoms moving normal to the surface and

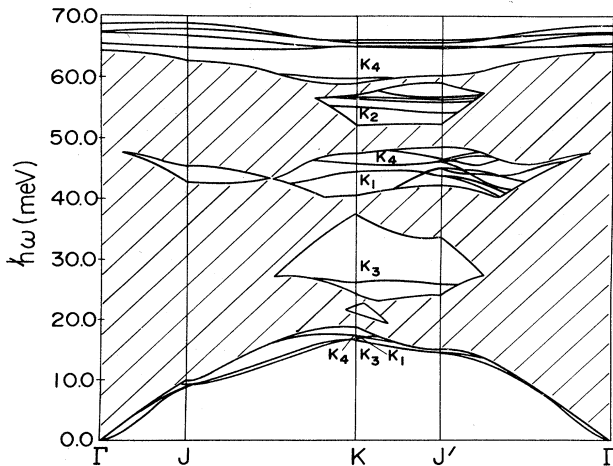


FIG. 1. Bulk Si phonon bands projected onto symmetry directions of the folded 2×1 surface Brillouin zone (cross-hatched regions) and hydrogenated Si(001):2×1 surface bands obtained from slab calculation (solid lines).

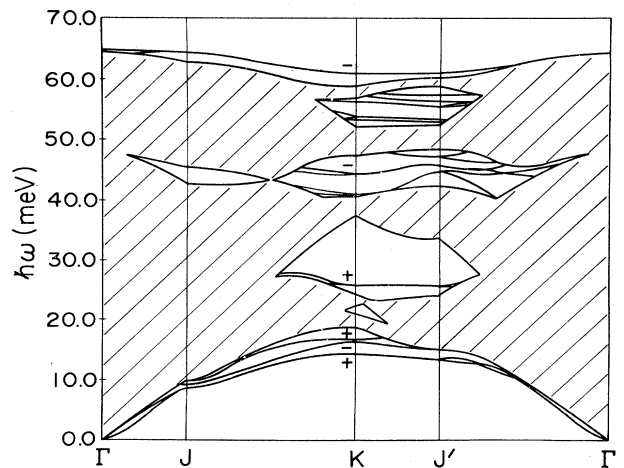


FIG. 2. Same as Fig. 1 but for the intrinsic Si(001):2×1 surface.

top-Si-layer atoms moving perpendicular to the dimer bond but in the surface plane. The symmetry labels correspond to the group C_{2v} appropriate for the symmetric dimer structure of the hydrogenated surface. Figure 1 shows that on the hydrogenated surface these modes are nearly degenerate, while Fig. 2 shows that on the intrinsic surface one mode is split off from the other two. Both surfaces share a common symmetry, the mirror plane σ containing the dimer bond. The mode K_4 is odd under σ while K_3 and K_1 are even. Thus K_4 cannot interact with K_3 and K_1 . On the hydrogenated surface the additional mirror plane σ' , which bisects the dimer bond, further distinguishes K_3 (odd under σ') from K_1 (even under σ'), and prevents their interaction. These modes are nearly degenerate on the hydrogenated surface. On the intrinsic surface, however, σ' is absent because the dimers are asymmetric. K_3 and K_1 are not proper symmetry labels for this surface; these modes interact and split to form the split-off mode (+) which is actually a mixture of K_3 and K_1 motions. Thus the symmetry of the surface partly governs where the lowest energy mode will be found along the K - J' SBZ edge.

The surface mode of next higher energy is a surface dimer rocking mode at about 26 meV in the PBS gap at the SBZ edge. This dimer rocking mode is quite similar to the r mode seen on the intrinsic surface,^{1,2} but with less screening from surface-state electrons because there are no gap electronic states on the hydrogenated surface. Table II compares screening for the intrinsic and hydrogenated rocking modes. Note first that the bare (unscreened) frequency of the dimer rocking mode is reduced on the hydrogenated surface compared with the intrinsic surface. This is partly a consequence of reduced strain on the hydrogenated surface with symmetric dimers. Also note that transitions between surface electronic states alone account for about 10% of the screening of this mode on the intrinsic surface, a direct result of the rocking-mode coupling to the dimer asymmetrization coordinate which splits the surface electronic bands and opens a gap. With the formation of Si-H bonds on the hydrogenated surface, the former surface bands become surface resonances around ± 4.5 eV from the valence-band maximum. This essentially eliminates these electronic states as a source of screening because of the larger energy denominators in the polarization sum over states, leaving the rocking mode 10% less screened on the hydrogenated

TABLE II. Comparison of electronic screening for the dimer rocking mode on intrinsic and hydrogenated Si(001):2 \times 1.

ω^2 (eV/ \AA^2 amu)	Intrinsic	Hydrogenated
Bare	0.5590	0.4104
Surface electronic		
Surface electronic state screening	-0.0376	0.0000
Full screening	-0.4011	-0.2488
Bare + screening	0.1578	0.1616
Resulting frequency		
meV	25.69	25.99
cm ⁻¹	207.2	209.6

surface than on the intrinsic surface. Combining reduced strain with reduced screening, the rocking mode ends up at nearly the same energy on both surfaces. On both the intrinsic and the hydrogenated Si(001):2 \times 1 surfaces we expect the rocking mode to be resonantly broadened at the SBZ center and the ir active, something we are presently investigating.

The complicated structure of many crossing bands in the next two projected gaps occurs partly because the optical phonon bands are fairly flat, so that small perturbations can easily localize states. Analysis of their eigenvectors is generally not helpful because each mode involves complicated motions of atoms in the outer three or four layers of the slab. The occurrence of so many interacting modes in these gaps indicates that the reconstruction of the surface has been an extensive perturbation from ideal bulk structure.

Another surface localized mode splits off the top of the bulk bands at the K point ($\hbar\omega = 59.9$ meV). This mode, shown in Fig. 3, occurs as a consequence of the fivefold ring structure of the reconstructed surface. A similar mode (the subsurface bond mode, sb) was predicted¹ for the intrinsic surface, but in that case the asymmetry of the dimers put most of the vibrational amplitude of the mode into one subsurface bond. For both the symmetric hydrogenated dimer surface and the asymmetric intrinsic surface, these high-frequency modes are dominated by subsurface atoms which remain fully fourfold coordinated but are bonded to high strain fivefold rings. We have seen similar modes in model calculations for the fivefold and sevenfold rings of the π -bonded chain reconstruction of Si(111):2 \times 1.⁸

The bond-bending modes of the Si-H bond form the bands shown above the bulk continuum in Fig. 1. Because our model predicts bond-bending forces at too low a value these modes are underestimated by about 15%; the mode we obtain at 67.4 meV is in fact seen at 78.5 meV by EELS.³

The bond-stretching Si-H modes form two nearly dispersionless (less than 0.5 meV dispersion across the SBZ) bands: the antisymmetric stretch [Fig. 4(a)] at 265.45 meV and the symmetric stretch [Fig. 4(b)] at 265.93 meV. We find the symmetric stretch at a higher frequency than the antisymmetric stretch in agreement with Ref. 4. These computed energies compare well with Chabal's SIS experimental results: 258.82 and 260.22 meV (Ref. 4) [the higher of these is seen by EELS at 260 meV (Ref. 3)]. Because there is no explicit Coulomb term in our Hamiltonian,¹ the splitting we compute includes only chemical splitting and no dipole-dipole splitting. In comparison with Chabal's⁴ obser-

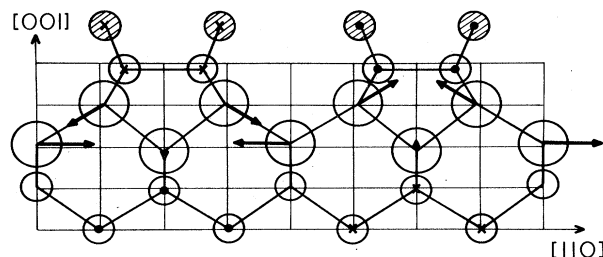


FIG. 3. The symmetric dimer structure of hydrogenated Si(001):2 \times 1 with arrows drawn proportional to the vibrational amplitudes of various atoms for the fivefold ring mode (59.9 meV) at the K point of the surface Brillouin zone.

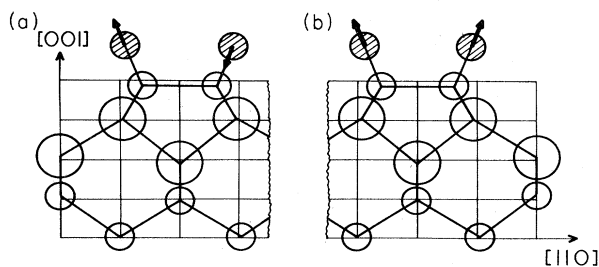


FIG. 4. (a) Vibrational amplitudes for the antisymmetric stretch mode at 265.45 meV. (b) Vibrational amplitudes for the symmetric stretch mode at 265.93 meV.

variations, we underestimate the chemical splitting by about a factor of 3. Replacing hydrogen with deuterium we predict modes at 190.2 and 191.1, comparing well with Chabal's⁴ 188.3 and 189.4 meV.

It is clear from these calculations that the strongly reconstructed Si(001):2×1:H surface has a rich vibrational spectrum. Our model confirms that the Si(001):2×1:H surface is stabilized by forming hydrogenated symmetric dimers. Out of the multitude of surface vibrational bands on this

surface we have described the simple physical interpretation for several. The symmetry (C_{2v}) of the surface *vis-à-vis* the symmetry (C_{1v}) of the intrinsic Si asymmetric dimer surface explains the relative energies of the three surface acoustic modes at the K point. A dimer rocking mode is less efficiently electronically screened on this surface than on the intrinsic Si surface but has lower unscreened frequency as well, a consequence of strain reduction upon hydrogenation. A high-frequency mode associated with fivefold rings formed by surface atom dimerization is seen just above the bulk bands at K . This is similar to fivefold ring modes we have seen on intrinsic Si(001):2×1 and on the π -bonded chain model of Si(111):2×1. We find Si-H bond-bending and bond-stretching modes in reasonable agreement with experiment, in particular with the symmetric stretch appearing above the antisymmetric stretch as observed by SIS. This calculation further demonstrates the flexibility and utility of this model for studying surface reconstruction and vibrational excitations.

This work was supported by Department of Energy Contract No. DE-AC02-83ER45037. E.J.M. gratefully acknowledges support from the Alfred P. Sloan Foundation.

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