

Adatom Vibrations on Si(111) Reconstructed Surfaces

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The vibrational electron energy-loss spectrum of the Si(111)(7×7) surface exhibits a well-defined loss at 570 cm⁻¹ and a structure at 200–270 cm⁻¹. A similar spectrum is displayed by a Si surface with a pseudo (1×1) structure. *Ab initio* calculations of the dynamical matrix show that these features are due to localized vibrations involving Si adatoms and the surface atoms lying underneath. The latter are fivefold-coordinated Si atoms exhibiting the electronic structure of an acceptor impurity localized at the surface.

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Recent studies by high-resolution electron energy-loss (EEL) spectroscopy of clean Si(111)(7×7) surfaces have found a continuum of energy losses with increasing intensities towards smaller loss energies accompanied by a large broadening of the elastic peaks.¹⁻⁴ These features, which have been interpreted to be indicative of a metallic band of surface states contributing to the surface loss function,^{1,4} have appreciably hindered the observation of intrinsic vibrations of the surface. In this Letter, we demonstrate that it is possible to suppress both the high electronic background and the broadening of the elastic reflected signal, by allowing small amounts of impurities on the surface. We have obtained Si(111)(7×7) surfaces with some carbon that exhibit a sharp loss at 570 cm⁻¹ and a broad weaker feature near 220 cm⁻¹. We have also produced Si(111) surfaces with a pseudo (1×1) low-energy electron diffraction (LEED) pattern, stabilized by traces of Ni, that display nearly the same EEL spectra, indicating that the local arrangements of the surface atoms are similar to that of the (7×7) surface. By comparison to *ab initio* calculations of the vibration spectrum of a Si₁₅ cluster we show that the observed EEL spectrum is a clear signature of Si adatoms. The 570-cm⁻¹ loss, which has an unusually high frequency for a localized Si vibration, involves the stretching of two Si–Si bonds and is thus inconsistent with tetrahedral coordination. The calculation reveals a new bond connecting the adatom with the surface Si atom lying underneath, which is therefore fivefold coordinated. This Si atom has the electronic structure of an acceptor impurity localized at the surface and we suggest that it may play a role in explaining the metallic character of the clean Si(111)(7×7) surface.

The experiments have been performed in ultrahigh vacuum (UHV), in a recipient equipped with an air-lock

system which enabled us to change the samples quickly without breaking the vacuum. For a coarse determination of the sample temperature a NiCr-Ni thermocouple was fixed to the sample holder. Figure 1(a) shows the EEL and Auger spectra of a Si(111)(7×7) surface containing small amounts of carbon. The samples, which have been cut from 400–800-Ω cm *n*-type doped Si(111) wafers, have been introduced in the recipient through air and flashed to 800 °C in UHV in order to remove the oxide. The Auger spectrum shows that besides some carbon ($I_{C272}/I_{Si92}=0.014$) no other contaminants were on the surface, which displayed a clear (7×7) LEED pattern. The EEL spectrum exhibits a sharp peak at 570 cm⁻¹ and a structure at about 200 cm⁻¹. Notice that, as a result of the carbon contamination, the inelastic background is absent and there is no appreciable broadening of the elastic line beyond the resolving power of the spectrometer, of about 50 cm⁻¹.

Figure 1(b) shows the EEL and Auger spectra of a Si(111) surface with a (1×1) structure. These samples have been obtained from the ones in Fig. 1(a) by an additional treatment of several cycles of sputtering and heating between 950 °C and 1100 °C, in order to remove the residual carbon. The Auger spectrum reveals traces of Ni ($I_{Ni848}/I_{Si92}=0.009$), probably evaporated from the thermocouple during the annealings. These nickel contaminations gave rise to an impurity-stabilized phase displaying an apparent (1×1) LEED pattern with strongly enhanced diffuse background. The EEL spectrum is very similar to that of the (7×7) surface of Fig. 1(a), although the high-frequency loss is lowered to 555 cm⁻¹ and the low-frequency structure is better resolved.

Under off-specular scattering conditions the EEL spectra of Fig. 1 became strongly suppressed, indicating that they arise from dipole scattering of totally sym-

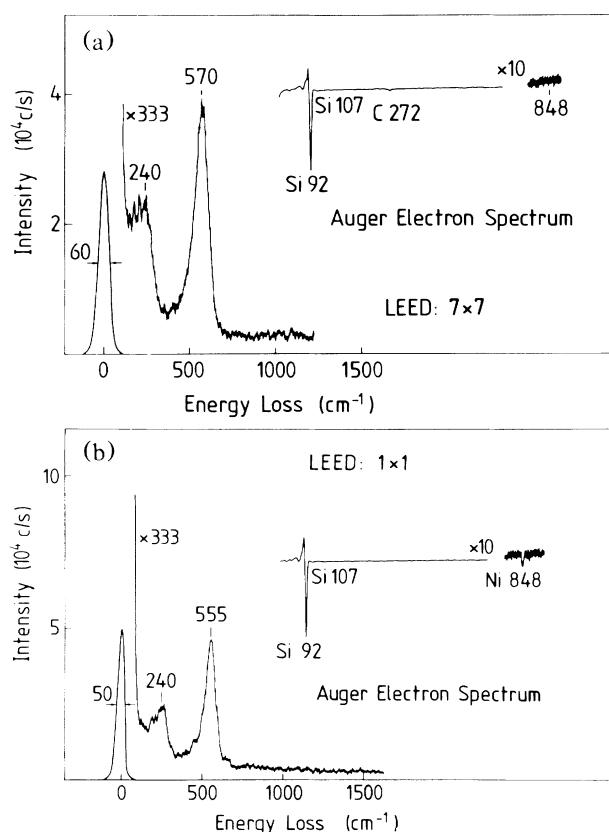


FIG. 1. (a) Electron-energy-loss and Auger spectra of a Si(111) surface with a (7×7) structure, containing small amounts of carbon. (b) Electron-energy-loss and Auger spectra of a Si(111) surface with a pseudo (1×1) structure stabilized by a small amount of Ni. The impact energy was 4.7 eV.

metric vibrations at the center of the surface Brillouin zone. Since the sample of Fig. 1(a) was free of nickel and that of Fig. 1(b) free of carbon, the losses are obviously not due to the contaminations. Instead they are intrinsic vibrational features of the Si(111) surfaces. It is furthermore obvious that the vibration spectrum is not very sensitive to the presence of long-range order. Rather it appears to be indicative of a particular local arrangement of Si-surface atoms which we shall identify below as Si adatoms. This result is consistent with recent scanning-tunneling microscopy results of Becker *et al.*,⁵ who observed a clean Si(111) (1×1) surface containing (5×5) , (7×7) , and (9×9) structural units characterized by the authors in terms of the dimer-adatom-stacking fault model.⁶ Since adatoms are present in all these structures, the resemblance of the vibrational spectra in Figs. 1(a) and 1(b) is explained if we assume that our impurity-stabilized (1×1) surface likewise contains structures with adatoms having the same local structural and electronic environment.

Previous authors have also occasionally observed a

high-frequency loss on clean Si(111) (7×7) surfaces, under different conditions which also reduced the electronic background. By decreasing the temperature to 20 K, Demuth and co-workers obtained an EEL spectrum with a sharp peak at 510 cm^{-1} , which was tentatively attributed to a surface phonon.⁴ Backes observed dominant losses at 510 and 530 cm^{-1} on surfaces inclined, respectively, by 7.5° and 10° with respect to the $[\bar{1}\bar{1}2]$ direction, and at 530 cm^{-1} on a well-oriented surface treated with a chemical etching process in order to produce atomic steps.⁷

Phonon modes and reconstructions at semiconductor surfaces have been successfully explained in terms of band-structure methods.⁸ However, for localized vibrations, as the ones revealed by our spectra, the cluster method is more appropriate. We have performed *ab initio* total-energy cluster calculations using the Kohn-Sham scheme⁹ with the local-density approximation for exchange and correlation,¹⁰ and a localized muffin-tin orbital basis¹¹ that included *s*, *p*, and *d* functions on all sites. The core electrons, although kept frozen, were explicitly incorporated in the calculation of the potential. We have investigated several clusters simulating different local geometries of the dimer-adatom-stacking surface unit cell. All the calculations yielded oscillation frequencies much lower than the observed 570-cm^{-1} vibration,¹² with the only exception of that for the adatom site. This site was studied with use of the Si_{15} cluster of Fig. 2(a), which includes all first- and second-nearest neighbors of the adatom (atom 1) and of the surface atom lying underneath (atom 2). By relaxing the vertical position of these atoms, we obtained an adatom binding energy of 4.6 eV and an equilibrium geometry with atom 2 displaced downwards by 0.30 bohr and the adatom lying 4.38 bohrs above it. As far as we know, no experimental determination of the height of the adatom has been reported, except for a crude estimate from the scanning-tunneling-microscopy experiment of Binnig *et al.*, suggesting that the adatoms lie 1.4 ± 0.2 bohrs above the average level of the surface.¹³ If we set this level at the plane of atoms type 3, this adatom height would be appreciably smaller than our calculated value of 2.45 bohrs. However, as we show below, the charge density above the adatoms is much more contracted than that of other surface atoms having dangling bonds, and this may alter the apparent height difference between them, as measured by scanning-tunneling microscopy. For comparison, pseudopotential calculations on an extended surface yielded an even larger value for the height of the adatom (4.70 bohrs above atom 2).¹⁴

The adatom has a pronounced effect on the surface electronic structure for it reduces the symmetry of atom 2 from T_d to C_{3v} . Its four *sp* orbitals make four bonding states with hybrids centered in neighboring atoms: One of them, an *sp_z* hybrid with *a₁* symmetry, points towards atom 4; the other three (another *a₁* state and a doubly

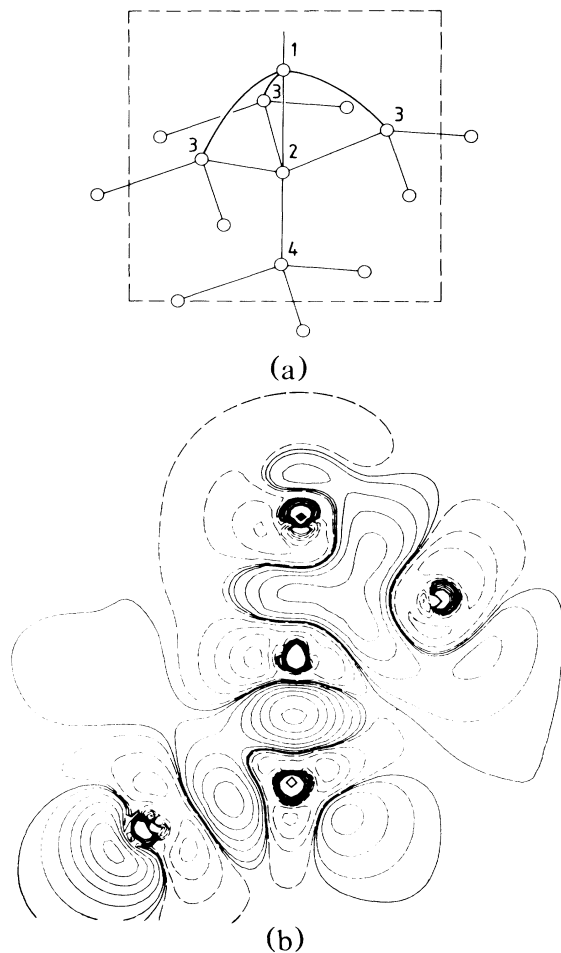


FIG. 2. (a) Si_{15} cluster employed to simulate the local environment of an adatom (denoted 1) on a $\text{Si}(111)$ surface. (b) Charge-density difference $\Delta\rho$ on the plane containing atoms 1, 2, 4, and one of type 3, indicated by the dashed line in (a). The continuous ($\Delta\rho > 0$) and dashed ($\Delta\rho < 0$) contour lines represent densities given by $n^2 \times 0.1 e/\text{bohr}^3$, for $n=1, 2, \dots, 10$.

degenerate e state involving only $p_{x,y}$ orbitals) are distributed over atoms 1, 2, and type 3. Thus all five nearest neighbors are truly bonded to atom 2. The electronic charge-density difference

$$\Delta\rho = \rho(\text{Si}_{15}) - \sum_{k=1}^{15} \rho_{\text{atom}}(\text{Si}_k),$$

shown in Fig. 2(b), displays the bonding ($\Delta\rho > 0$) and antibonding ($\Delta\rho < 0$) regions of the cluster. Notice the piling up of charge between atoms 1 and 2, that results from the direct orbital interaction between these two atoms.¹⁵ The 1–2 bond forms at the expense of the strengths of the six 1–3 and 2–3 bonds, now taken care of by only two doubly degenerate e states centered on atoms 1 and 2. As a rough estimate of the bond

strengths between two atoms, i and j , we calculated overlap populations (or bond charges) $Q_{i,j}$ derived from standard population analysis.¹⁶ We found $Q_{1,2}=0.52e$, $Q_{1,3}=0.46e$, and $Q_{2,3}=0.50e$, indicating that the 1–2, 1–3, and 2–3 bonds are roughly the same strength and appreciably weaker than bulk Si–Si bonds, for which $Q_{i,j} \approx 1.0e$.

It is also apparent in Fig. 2(b) that the charge density above the adatoms is very contracted.¹⁷ This charge density arises on adatom orbitals that lie higher in energy than those of other surface atoms. One of these adatom orbitals, an a_1 state partially delocalized on atoms 2 and type 3, is singly occupied, in accord with the observation of an adatom surface state very close to E_F , recently reported by Hamers, Tromp, and Demuth using current-imaging tunneling spectroscopy.¹⁸ This state is also consistent with the band of adatom surface states Σ_1 found by Northrup.¹⁴

In order to apply the formalism of lattice dynamics we calculated the variation of the total energy as a function of the appropriate symmetry coordinates of the cluster. As mentioned above, only the totally symmetric vibrations need to be included in the vibrational analysis. In a first step we considered merely the largest elements of the dynamical matrix, which arise from the vertical departures z_1 and z_2 of atoms 1 and 2 from their equilibrium positions, and fitted the total energy by a harmonic form

$$V = V_0 + \frac{1}{2} (k_{1,1}z_1^2 + k_{2,2}z_2^2 + 2k_{1,2}z_1z_2).$$

For the diagonal force constants we obtained $k_{1,1}=0.10$ a.u. and $k_{2,2}=0.27$ a.u. (1 a.u. = 1.56×10^6 dyn/cm), which correspond to frozen oscillation frequencies of $\omega_{01}=330 \text{ cm}^{-1}$ and $\omega_{02}=539 \text{ cm}^{-1}$, respectively. By the inclusion of the off-diagonal term $k_{1,2}=0.09$ a.u., the first frequency shifts down to $\omega_1=262 \text{ cm}^{-1}$ and the second up to $\omega_2=575 \text{ cm}^{-1}$, in good agreement with the experimental spectra reported above. In a more extensive calculation we evaluated also the variation of the total energy as a function of the coordinates of atoms of type 3 and found that the oscillation frequency ω_1 changed by only about 10 cm^{-1} , indicating that the high-energy mode is strongly localized on atoms 1 and 2. Because of its much larger frequencies it couples weakly to other modes of the cluster. We therefore expect that the vibration spectra of our cluster is also a good representation of adatom units on an extended surface.

The large oscillation frequency of the high-energy mode arises on the force constant $k_{2,2}$ related to the motion of atom 2 perpendicular to the surface. This motion involves the simultaneous stretching of the 1–2 bond and contraction of the 2–4 bond, giving rise to a much larger force constant than in fourfold-coordinated Si, where only one bond stretching occurs. Another unexpected result of the vibrational analysis was the large value of $k_{1,2}$, which turned out to be almost equal

to $k_{1,1}$. This result can be explained by our noting that both force constants are essentially determined by the stretching of the same 1–2 bond (the bending of the 1–3 bonds have a much smaller contribution to $k_{1,1}$). The vibrational eigenvectors are given by $u_1 = 0.92\hat{z}_1 + 0.39\hat{z}_2$ and $u_2 = -0.39\hat{z}_1 + 0.92\hat{z}_2$, which correspond to a motion of the two atoms in phase and against each other, respectively, and yield dynamical dipoles $q_1^* = 0.16$ a.u. and $q_2^* = -0.32$ a.u. (1 a.u. = 2.54 D) for the two modes. The larger dipole of the ω_2 mode is due to the variation of the bond charge $Q_{1,2}$ when atoms 1 and 2 move with opposite phase and is consistent with the larger intensity observed for the high-energy loss.

It may be interesting to point out that the fivefold coordination of atom 2 represents the actual realization of an object recently proposed by Pantelides¹⁹ in the context of amorphous Si. He pointed out that a fivefold-coordinated Si atom should have one unpaired electron in a state that he calls “floating bond” (by analogy to the dangling bond) and is essentially a linear combination of sp^3 hybrids pointing towards a center. The floating bond is more delocalized than the dangling bond and would therefore be a more appropriate candidate to explain the metallic character of the clean surface.

Summing up, we have shown that the vibration spectra illustrated in Fig. 1 are a spectroscopic signature of Si adatoms bonding on closed threefold sites and reveal a direct bond between the adatom and the Si atom lying underneath.

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