Raman Studies of Steric Hindrance and Surface Relaxation of Stepped H-Terminated Silicon Surfaces

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Polarized, angle-resolved Raman spectra of the Si-H stretching vibrations on stepped H-terminated Si(111) surfaces confirm the constrained orientation of the step dihydride derived from *ab initio* cluster calculations. They further show that the step normal modes involve little concerted motion of the step atoms, indicating that step relaxation reduces the steric interaction much further than predicted.

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Because reactions at defect sites often dominate the chemistry of semiconductor surfaces [1], the characterization of different surface sites, not just the average surface site, is of fundamental importance. Vibrational spectroscopies may be the most powerful probes of adsorption at defects, as the spectral features from molecules bound to different sites are easily identifiable and, in general, well resolved. Additionally, the polarization and angle dependence of *optical* techniques can be exploited to determine the (site-specific) orientation of adsorbates.

In this Letter, we show that the absolute orientation of hydrogen bound to step defects on a Si(111) surface can be obtained from Raman spectra of the Si-H stretching modes. Once the geometry has been determined, the character of the step normal modes can be extracted. Because these normal modes are determined by the relative strengths of the surface-adsorbate bond and any interadsorbate forces, they are a sensitive probe of steric hindrance and structural relaxations. Here, we show that surface stress from a severely hindered step edge induces a relaxation of the underlying structure that is much larger than predicted by *ab initio* calculations.

The aqueous fluorine etching of Si(111) surfaces is extremely site specific [2], and preferential etching leads to the formation of level H-terminated silicon surfaces. In particular, the etching of vicinal surfaces miscut in the $\langle\bar{1}\bar{1}2\rangle$ direction produces ideally monohydride-terminated (111) terraces separated by atomically straight dihydride-terminated bilayer steps (see diagram in Fig. 1). Infrared absorption studies using polarized radiation [3] have shown that the dihydride unit lies in a plane perpendicular to the step edge and that strong forces at the step result in the appearance of three step vibrational modes involving the Si-H stretch motion, instead of two modes as expected for a dihydride. *Ab initio* cluster calculations [4] attribute the appearance of a third mode to strong steric interactions between one of the dihydride hydrogens (H_B in Fig. 1) and the nearest monohydride (H_A) located on the terrace below the step. This interaction is predicted to rotate the dihydride unit 22° away from the lower terrace. Although these calculations qualitatively agree with the infrared experiments, there are serious discrepancies in both the frequency splittings and the polarization ratios.

Unenhanced, nonresonant Raman spectra of H-terminated silicon surfaces miscut from the (111) plane by 9° in the $\langle\bar{1}\bar{1}2\rangle$ direction were obtained using 600 mW of 514.5 nm light from an Ar^+ laser. The chemically prepared [3] H-terminated silicon samples were mounted in a high vacuum cell (base pressure $\approx 10^{-7}$ torr). The excitation laser was incident on the sample at 60° from the surface normal and focused to a 45×90 μm elliptical spot. Scattered radiation was collected at 60° from the surface normal in a plane perpendicular to the laser incidence plane. The light was dispersed in a 0.64 m monochromator and detected with a liquid N_2 cooled charge coupled device camera. Reported spectra represent an average of three 6 min integrations. "Cosmic ray" events

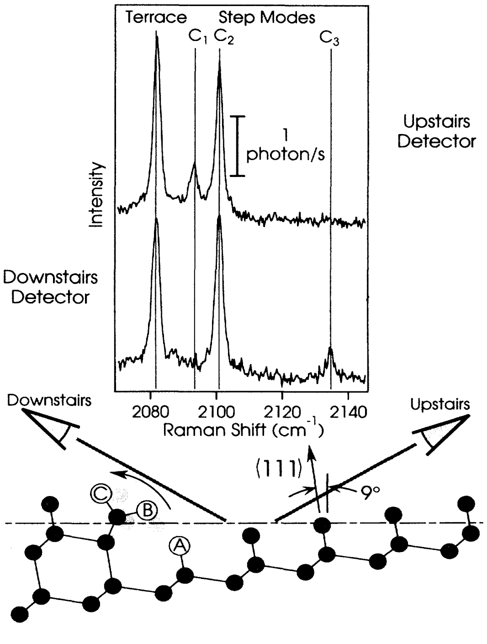

FIG. 1. Raman spectra of H-terminated vicinal Si taken with two different detector orientations and the *p*-polarized laser incident along the step edge. The sketch below shows the H atoms in grey with the most relevant labeled ($A \equiv H_A$, etc.). The center line of the detector is oriented 60° from the surface normal; the orientation with respect to the steps is shown in the sketch.

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were removed prior to averaging.

Figure 1 shows two Raman spectra of the same H-terminated Si sample taken with the (p-polarized) excitation laser pointing along the step edge. In the bottom spectrum, the detector is pointing "down the stairs" (see diagram). In this orientation, three Si-H stretching modes are observed. The low frequency band at 2082 cm^{-1} corresponds to the in-phase terrace vibration [3]. The features at 2093 and 2101 cm^{-1} were previously assigned to out-of-phase (C_2) and in-phase (C_3) combinations of the interacting step and terrace H atoms (H_B and H_A) on the basis of the cluster calculations [4]. Interestingly, *the fourth Si-H stretch mode (C_1), which was assigned to the Si-H_C stretch vibrations, is not detected.* In the top spectrum of Fig. 1, the detector is pointing "up the stairs." In this orientation, the missing C_1 mode appears at 2093 cm^{-1}; however, the C_3 mode is now unobservable.

These data may be qualitatively understood by comparing the orientation of the Si-H_C bond to the spectra of the C_1 mode. When the detector points in the downstairs direction, it is more or less aligned with the Si-H_C bond axis; this is an inefficient orientation to detect radiation from the C_1 mode. On the other hand, when the detector points up the stairs, it is perpendicular to the Si-H_C bond, and the C_1 mode is easily detected.

A similar effect is observed when the polarization of the excitation laser is varied. Figure 2 shows six spectra taken with different incidence polarizations and an upstairs pointing detector. The intensity of the C_1 mode is clearly related to the relative alignment of the incident polarization and the Si-H_C bond. The C_3 mode is absent from all spectra in Fig. 2, because the detector is unfavorably oriented for detection of this mode.

The quantitative interpretation of surface vibrational spectra is a challenging problem. The local electric field at the surface and the Raman response of the Si-H bond must be measured before any information on adsorbate orientation can be derived. We have parametrized the surface response to both the incident electric field and the radiating dipoles at the surface with a three-layer dielectric model [5]. The adsorbate layer is assumed to be an infinitely thin, isotropic dielectric medium, characterized by an *experimentally determined*, real dielectric constant $\varepsilon_{\mathrm{ads}}$. This layer is bounded on one side by vacuum and on the other side by a semi-infinite, isotropic dielectric medium with a complex, frequency-dependent dielectric constant characteristic of bulk silicon ($\varepsilon_{\mathrm{Si}} \approx 18+0.5i$) [6]. The self-consistent response of this model to an incident plane wave and a radiating surface dipole can be calculated with the appropriate Green's functions [7].

The (normalized) dynamic polarizability of the jth normal mode, α_j', is assumed to be of the form

$$\alpha_j' = \sum_i c_{ij} R^{-1}(\phi_i,\theta_i,\chi_i) \begin{pmatrix} \delta & 0 & 0 \\ 0 & \delta & 0 \\ 0 & 0 & 1 \end{pmatrix} R(\phi_i,\theta_i,\chi_i) \,,$$

where c_{ij} is the weight (and phase) of the ith bond in the jth normal mode, R is the unitary rotation operator, and (ϕ_i,θ_i,χ_i) are the Euler angles that describe the orientation of the ith bond reference frame with respect to the surface reference frame. The bond anisotropy δ is defined to be $\alpha_\perp'/\alpha_\parallel'$, the ratio of the dynamic polarizability perpendicular and parallel to the Si-H bond, and the z axis of the bond reference frame coincides with the Si-H bond axis. The coefficients c_{ij} are constrained by

$$\sum_i c_{ij} c_{ik} = 0 \text{ for } j \neq k$$

to preserve orthogonality. A full description of this model will be presented in a forthcoming publication [8].

These two parameters, $\varepsilon_{\mathrm{ads}}$ and δ, may be determined from the polarized, angle-resolved Raman response of a

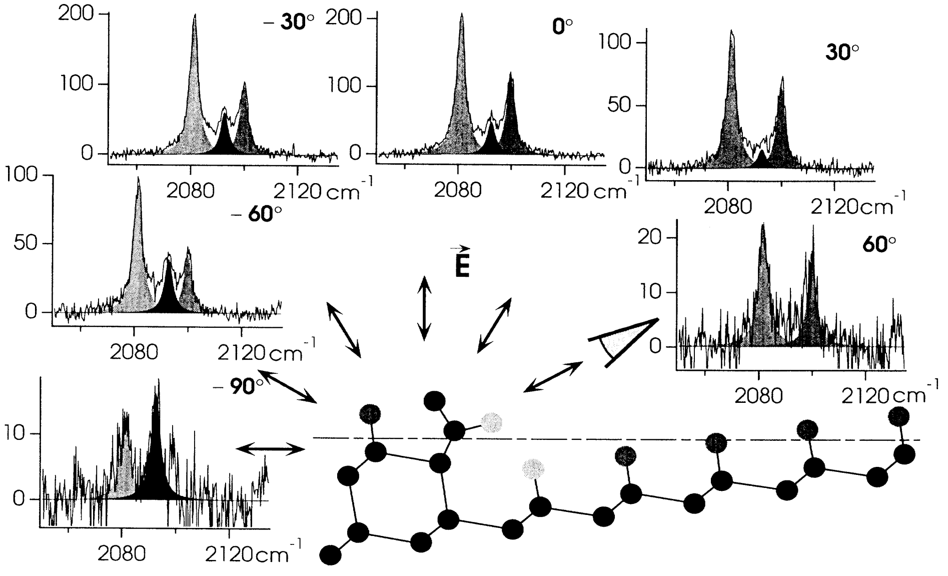

FIG. 2. Raman spectra of H-terminated vicinal Si taken with six different polarization angles [$\gamma = -90°(s)$, $-60°$, $-30°$, $0°(p)$, $30°$, and $60°$]. The detector was in the upstairs pointing configuration. The shaded areas are best fit Lorentzians to the terrace, C_1, and C_2 vibrations. The C_1 mode (darkest Lorentzian) is due to vibration of the dark H in the sketch.

bond of known orientation [9] such as the in-phase terrace mode. The terrace mode is known to lie along the ⟨111⟩ direction which is 9° away from the (macroscopic) surface normal (see Fig. 1). Relative Raman intensities (integrated over the line shape) from sixty different combinations of incident polarizations and detector angles were fitted to a unique $\varepsilon_{\mathrm{ads}},\delta$ pair using the Levenberg-Marquardt algorithm. From this analysis, we extracted an adsorbate dielectric constant of 3.78 ± 0.20 and a bond anisotropy of 0.263 ± 0.028. The quoted error bars correspond to $\pm 2\sigma$ under the assumption of normally distributed errors.

This Si-H bond anisotropy is in excellent agreement with the literature value [10] of 0.25 determined from the $\nu_2(e)$ mode of $SiH_4(g)$. Because Raman spectroscopy is sensitive to all components of the electric field, this agreement strongly supports our use of a simple three-layer model. An independent check of our analysis is especially important in light of previous concerns with dielectric models. As pointed out by Feibelman [11], these models have a number of difficulties at the microscopic level. In particular, the physical origin of $\varepsilon_{\mathrm{ads}}$ is unclear. Although this quantity has been related to the polarizability of the adsorbate (here, the Si-H bond) using the Lorentz oscillator model [12], the dielectric response of such a thin layer is expected to be nonlocal. Within the Lorentz oscillator model, our observed adsorbate dielectric constant would correspond to an Si-H bond polarizability that is an order of magnitude larger than observed for SiH_4 in the gas phase [10]. This suggests that the "adsorbate layer" polarization contains some contribution from the underlying Si-Si bonds.

Having parametrized the surface Raman response, the geometry of the dihydride unit can be determined. On the basis of *ab initio* cluster calculations [4], the C_1 mode was assigned to a stretch of the Si-H_C bond. If we tentatively accept this assignment, the orientation of the step dihydride can be determined from the Raman spectra of the C_1 mode. For this analysis, we fitted relative Raman intensities from 31 different combinations of incident polarization and detector angle. Figure 3 shows the results of this fit (dot-dashed curve) for data taken in the upstairs detector configuration. We find that the dihydride unit is rotated 37 ± 4° from the surface normal. This corresponds to a rotation of 28° from the bulk-terminated position and is 6° larger than the 22° predicted by the cluster calculations. Additionally, this fit correctly predicts that the C_1 mode cannot be detected in the downstairs-pointing detector configuration with our detection sensitivity (see lower dot-dashed curve in Fig. 3).

The 6° (± 4°) discrepancy between theory and experiment indicates that either the cluster geometry is slightly wrong or the C_1 mode has a small contribution from other Si-H bonds. Given the experimental error bars, further analysis to distinguish between these two possibilities is not worthwhile. Instead, we first assume that the discrepancy is due to the composition of the C_1 normal mode, and then compare this to the alternative possibility.

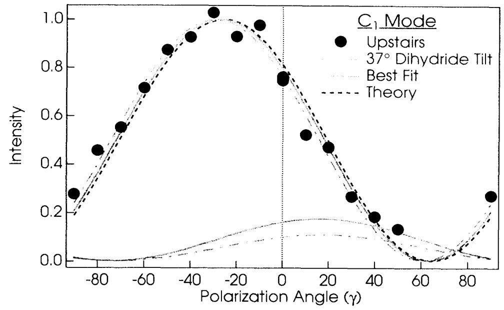

FIG. 3. Polarization dependence of C_1 mode with upstairs detector. The dot-dashed line represents the best fit to an isolated Si-H_C stretch (see text); the solid line represents the best global fit to all step modes, and the dashed line represents the theoretical prediction. Predicted intensities for the downstairs orientation are also shown.

Once the dihydride geometry is known, the composition of the step normal modes can be extracted from the Raman spectra if two assumptions are made. First, we assume that the contributions to the step modes from the terrace mode are negligible. Recent calculations [13] on this system have shown that dipole coupling between the step and terrace modes is small. This is a result of the modest dynamic dipole of the Si-H bond and the large mode splittings on this surface. Second, to obtain a unique fit, we also assume that the C_1 mode does not include any motion of the Si-H_A bond. This is justified by the large spatial separation and indirect coupling of H_A and H_C. These assumptions would not be necessary if isotopic dilution studies could be performed; however, we have not been able to prepare surfaces of the requisite perfection.

The composition of the step normal modes was simultaneously determined from a global fit of all C mode data (≈ 100 data points) assuming the dihydride tilt is 31° from the surface normal. Figures 3 and 4 show the results of this fit for the C modes in the most interesting detector orientations.

Our normal mode analysis shows that the vibrational energy for each step mode is highly localized on one type of Si-H bond [14]. More than 98% of the vibrational energy of the C_3 mode is localized on the Si-H_B bond, while more than 99% of the vibrational energy of the C_1 and C_2 modes is localized on the Si-H_C and Si-H_A bonds, respectively. If the dihydride unit were actually 37° from the surface normal (as the preceding analysis suggested), the vibrational modes would be even more localized.

The character of the C_2 and C_3 normal modes is quantitatively very different from that predicted by the *ab initio* cluster calculations (see Fig. 4). In the initial cluster calculation, the vibrational energy in the C_2 and C_3 modes was split 66%:34% between the H_B and H_A stretches [15]. This concerted H atom motion was due to

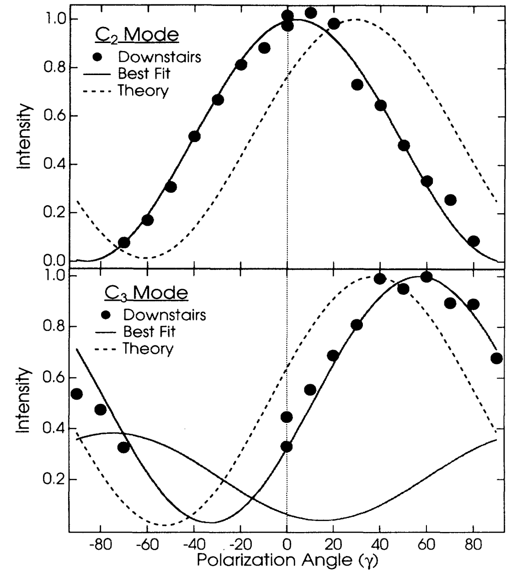

FIG. 4. Polarization dependence of C_2 (upper panel) and C_3 (lower panel) modes with downstairs detection. See Fig. 3 for explanation of legend.

steric interactions between H_A and H_B. When a large (0.15 Å), *ad hoc* motion of the second-layer step Si atoms was introduced into the calculation [4], the coupling between H_A and H_B decreased; however, the vibrational energy was still more delocalized than observed in this experiment.

The absence of energy delocalization in the observed normal modes indicates that these steric interactions are much smaller than predicted. Because quantum chemical techniques accurately describe *local* intractions, this discrepancy is most likely due to a long range relaxation of the step edge [16]. The relaxation presumably increases the distance between H_A and H_B, thereby reducing the H_A-H_B repulsion.

Surface stress has been shown to induce large scale surface relaxations [17,18] that may be stabilized by step formation [19]. In light of this, it was previously suggested [4] that tensile stress in the monohydride-terminated terraces may drive relaxation at the dihydride-terminated step edge; however, local density approximation calculations [20] have shown that the flat H/Si(111) surface is essentially stress free (0.21 eV/unit cell). A more important source of stress in this system is the sterically constrained dihydride step itself. These steric forces would result in a compressive stress at the step edge that could be relieved by any relaxation that increases the separation between H_A and H_B. Because stress-induced relaxations on other surfaces have been shown to extend many layers into the bulk [20,21], the inability of the cluster calculation to accurately predict this effect (and hence the normal modes) is most likely ascribable to the size of the theoretical cluster, rather than the precision of the calculation.

Although relaxations can redistribute localized surface stresses [19], it is likely that there is some residual stress at the step edge. This may explain the enhanced reactivity of stepped surfaces to aqueous fluorine etching, as stress has been implicated in a number of reactions on silicon surfaces [22].

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[1] For example, Ph. Avouris and D. Cahill, Ultramicroscopy **42–44**, 838 (1992); J. Wintterlin and Ph. Acouris, Surf. Sci. **286**, L529 (1993).

[2] Y. J. Chabal, Mater. Res. Soc. Symp. Proc. **259**, 349 (1992).

[3] P. Jakob and Y. J. Chabal, J. Chem. Phys. **95**, 2897 (1991).

[4] K. Raghavachari, P. Jakob, and Y. J. Chabal, Chem. Phys. Lett. **206**, 156 (1993).

[5] S. A. Francis and A. H. Ellison, J. Opt. Soc. Am. **49**, 131 (1959); R. G. Greenler, J. Chem. Phys. **44**, 310 (1966); J. D. E. McIntyre and D. E. Aspnes, Surf. Sci. **24**, 417 (1971).

[6] D. F. Edwards, in *Handbook of Optical Constants of Solids*, edited by E. D. Palik (Academic, Orlando, 1985), pp. 564,565.

[7] C. E. Reed, J. Giergiel, J. C. Hemminger, and S. Ushioda, Phys. Rev. B **36**, 4990 (1987).

[8] M. A. Hines, Y. J. Chabal, T. D. Harris, and A. L. Harris (to be published).

[9] If this bond is normal to the surface, ε_{ads} and δ cannot be determined uniquely.

[10] R. S. Armstrong and R. J. H. Clark, J. Chem. Soc. Faraday Trans. 2 **72**, 11 (1976).

[11] P. J. Feibelman, Prog. Surf. Sci. **12**, 287 (1982).

[12] Y. J. Chabal, Surf. Sci. Rep. **8**, 211 (1988).

[13] A. L. Harris, K. Kuhnke, M. Morin, P. Jakob, and Y. J. Chabal (to be published).

[14] We cannot determine whether this energy is localized on one bond or delocalized across many bonds of the same type.

[15] K. Raghavachari (private communication).

[16] Part of this discrepancy may be due to neglect of electron correlation in the *ab initio* calculation.

[17] F. K. Men, W. E. Packard, and M. B. Webb, Phys. Rev. Lett. **61**, 2469 (1988).

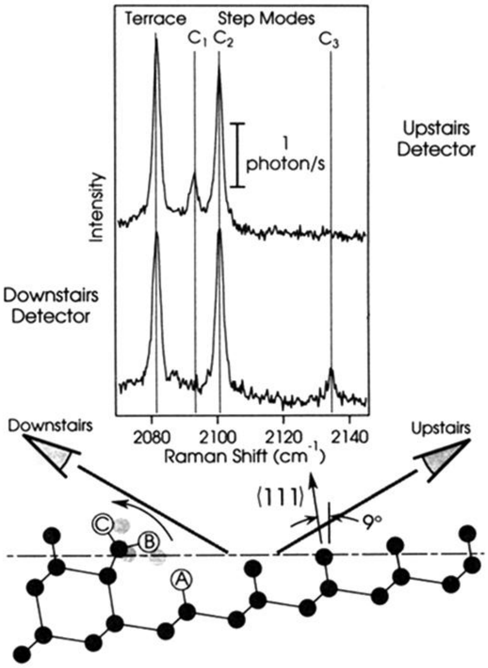
[18] O. L. Alerhand, D. Vanderbilt, R. D. Meade, and J. D. Joannopoulos, Phys. Rev. Lett. **61**, 1973 (1988).

[19] T. W. Poon, S. Yip, P. S. Ho, and F. F. Abraham, Phys. Rev. Lett. **65**, 2161 (1990); Phys. Rev. B **45**, 3521 (1992).

[20] S.-P. Li and D. Vanderbilt, Phys. Rev. Lett. **69**, 2543 (1992).

[21] H.-J. Gossman, J. C. Bean, L. C. Feldman, E. G. McRae, and I. K. Robinson, Phys. Rev. Lett. **55**, 1106 (1985).

[22] For example, P. J. Chen, M. L. Colaianni, and J. T. Yates, Jr., Surf. Sci. **274**, 605 (1992); J. J. Boland, Surf. Sci. **261**, 17 (1992).



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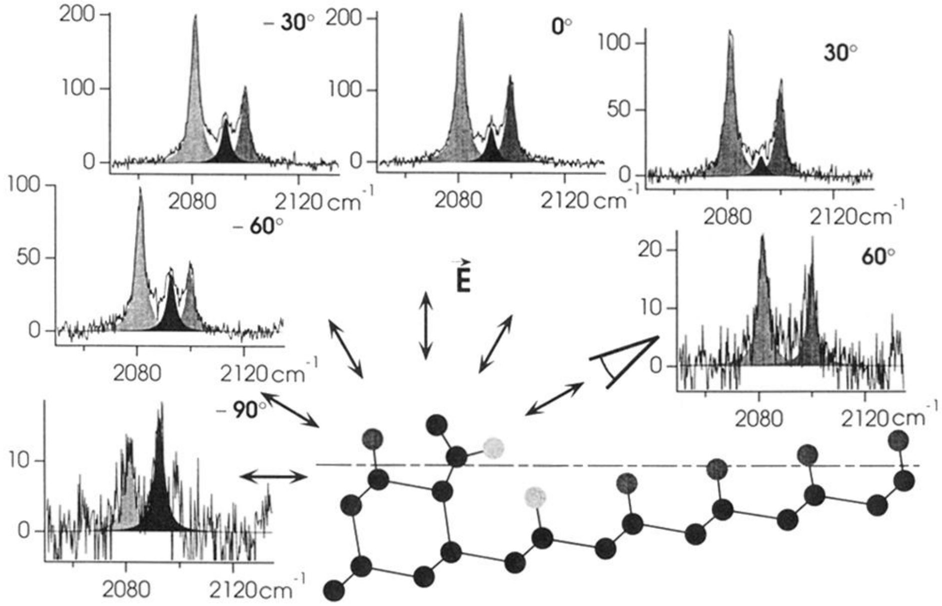

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