

Coupling of an Adsorbate Vibration to a Substrate Surface Phonon: H on Si(111)

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We report high-resolution infrared-reflection-absorption measurements of an unreconstructed, ideally H-terminated Si(111) surface. The marked width and frequency variations of the Si-H stretching vibration with temperature are completely accounted for by a *weak* anharmonic coupling of this mode to a Si surface phonon band centered at $210 \pm 25 \text{ cm}^{-1}$. A decrease in Si-H stretch intensity, observed as the temperature is increased above 300 K, suggests a *strong* anharmonic coupling between the Si-H stretching and bending modes.

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Adsorbate-substrate interactions control surface processes such as adsorption, desorption, diffusion, and reaction. Characterizing such processes is therefore central to understanding gas-surface phenomena. Despite numerous studies,¹⁻³ the microscopic mechanisms of these interactions are not well understood because of the complex nature of the adsorbate-substrate couplings (electronic and vibrational). In addition, surface disorder (defects, domains, structural rearrangements) often complicates the interpretation of experimental observations.

In this paper, we report infrared-absorption measurements of the Si-H stretching vibration on a *homogeneous*, unreconstructed and ideally H-terminated Si(111) surface. The surface perfection makes it possible to perform spectroscopic measurements over a large range of linewidths ($0.1\text{--}3.6 \text{ cm}^{-1}$) and temperatures (130–560 K), without the influence of inhomogeneous broadening. As a result, this extensive set of data yields the first direct evidence, using a simple model for anharmonic interactions, for a *weak* coupling to a substrate phonon mode (at 210 cm^{-1}) located well below the top of the silicon phonon band. In contrast, the range of previous temperature-dependence studies was limited by adsorbate rearrangement^{3,4} and/or substrate inhomogeneities,⁵ making it impossible to uncover the effects of *substrate phonons*.

The preparation of these surfaces is accomplished using a novel chemical treatment based on anisotropic silicon etching in high-pH HF solutions.^{6,7} The key step is the final dissolution of a thin chemical oxide in a 40% NH_4F solution ($\text{pH} = 7.8$ for 6.5 min). During this time, the thin surface oxide is removed and the bare silicon surface is slowly and preferentially etched, exposing large (111) planes ideally terminated with hydrogen. In contrast to the broad spectra ($\sim 100 \text{ cm}^{-1}$) obtained upon atomic H dosing of clean Si(111) surfaces,⁸ the infrared spectrum associated with the present surface is characterized by a *single* Si-H stretching mode at 2083.7 cm^{-1} , polarized perpendicular to the surface, and a narrow linewidth at room temperature (0.9 cm^{-1}).⁶

Analysis of *s*-polarized spectra (E field parallel to the surface) places an upper limit of 10^{-3} for the defect or impurity density.⁹ At this level, the defect density corresponds to the step density resulting from sample miscut rather than defects on the (111) terraces.

The *n*-doped ($\rho \sim 100 \text{ } \Omega \text{ cm}$) silicon samples ($0.5 \times 19 \times 38 \text{ mm}^3$) are beveled at each end, thus making it possible for the ir beam to bounce a total of 75 times (internal reflection angle $= 45^\circ$).¹⁰ For the temperature-dependence studies, the sample is introduced into an ultrahigh-vacuum (UHV) chamber ($P = 1 \times 10^{-10}$ Torr) by means of a load lock system.¹¹ A Chromel-Alumel thermocouple is pushed against Ta clips holding the sample, as it is introduced. The reading of that thermocouple is calibrated before and after the UHV runs by sticking a second thermocouple to the sample with silver paint, pumping the chamber to 10^{-8} Torr, and performing a cooling cycle. The absolute and relative error bars are ± 7 and ± 1 K, respectively. Careful monitoring of the surface species with ir spectroscopy shows that less than 3% ML [1 ML (monolayer) $\equiv 7.8 \times 10^{14}$ sites/ cm^2] hydrogen is lost (mostly replaced by hydrocarbons) during evacuation. These results are a marked departure from previous electron-energy-loss studies of HF-treated silicon surfaces in which a substantial hydrocarbon contamination was detected,¹² but are consistent with the observations of Fenner, Biegelsen, and Bringans.¹³

A sampling of the spectra obtained in the 2100-cm^{-1} region (Si-H stretch frequency) is shown in Fig. 1. The instrumental resolution (nominally 0.3 cm^{-1} using a square apodization) is calibrated during the runs using a CO gas cell. It is found to vary between 0.32 and 0.42 cm^{-1} depending on the sample alignment. As the temperature is lowered from 560 to 130 K, the natural linewidth decreases *continuously* from 3.6 to 0.1 cm^{-1} ,¹⁴ and the line position (wave number) increases from 2079.2 to 2085.5 cm^{-1} . In addition, the line intensity (integrated area) decreases as the temperature is raised above room temperature (by 20% at 560 K).

Since there is no structural rearrangement as a function of temperature (the system retains a sharp 1×1

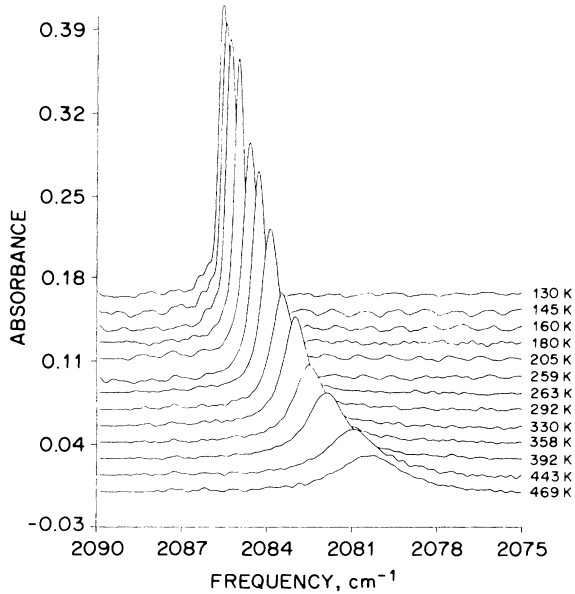


FIG. 1. Infrared-absorption spectra (p polarization) of the ideally H-terminated Si(111) surface as a function of substrate temperature. The absorbance is $A(\omega) = -\ln[I(\omega)/I_0(\omega)]$, where I and I_0 are the transmitted intensities after 75 internal reflections ($\theta_{\text{int}} = 45^\circ$) with and without hydrogen, respectively. The instrumental resolution is 0.4 cm^{-1} .

LEED pattern and single Si-H stretching vibration over the whole range), an upper limit of 0.1 cm^{-1} can be set for the inhomogeneous broadening of the Si-H stretch mode. Furthermore, its lifetime has recently been measured¹⁵ and the lifetime (T_1) broadening found to be negligible ($\sim 0.007 \text{ cm}^{-1}$). Therefore, the observed temperature dependence of the line shape must arise from phase relaxation, due to anharmonic coupling to lower-frequency vibrational modes, such as through the quartic term (u^2v^2 , where u and v are the H and Si displacements, respectively).^{1,3,16} Previous theoretical studies^{3,16} have shown that simple predictions can be made if a number of assumptions are met as described below.

If the Si-H stretching mode is coupled to a single phonon band (with frequency ω_0 and width γ) by a coupling constant $\delta\omega$ (in cm^{-1}) such that $|\delta\omega| \ll \gamma$ (weak-coupling limit), then the Si-H stretch absorption has a Lorentzian form, with a center frequency (Ω) shifted from the zero-temperature frequency (Ω_0). Its full width at half maximum, Γ , and frequency shift, $\Delta\Omega \equiv \Omega - \Omega_0$, have the following temperature dependence:³

$$\Gamma = [2(\delta\omega)^2/\gamma] e^{\hbar\omega_0/kT} (e^{\hbar\omega_0/kT} - 1)^{-2}, \quad (1)$$

$$\Delta\Omega = (\delta\omega)(e^{\hbar\omega_0/kT} - 1)^{-1}. \quad (2)$$

While both quantities vary as $e^{-\hbar\omega_0/kT}$ at low temperatures ($kT \ll \hbar\omega_0$) their dependence is more complex at higher temperatures. On the other hand, the quantity

$$\Gamma/(\Delta\Omega)^2 = (2/\gamma)e^{\hbar\omega_0/kT} \quad (3)$$

has a very simple dependence over the whole tempera-

ture range. Indeed, the logarithm of $\Gamma/(\Delta\Omega)^2$ will increase linearly with increasing $1/T$ as long as the anharmonic coupling is dominated by only one mode.

The data [Γ , $\Delta\Omega$, and $\Gamma/(\Delta\Omega)^2$] are shown in Figs. 2(a)-2(c) with the solid lines representing independent least-squares fits using Eqs. (1)-(3), respectively. Clearly, all three sets of data are well fitted with the simple model described above. Most importantly, the high quality of the linear fit over the whole temperature range of $\Gamma/(\Delta\Omega)^2$ in Fig. 2(c) indicates that the dephasing contribution can be explained by coupling to a single mode centered at 210 cm^{-1} , i.e., a silicon phonon. Using the three independent fits as starting points, a set of parameters is then obtained to give the best overall fit [indistinguishable from the lines in Figs. 2(a)-2(c)]. The results are $\delta\omega = -5(\pm 0.05) \text{ cm}^{-1}$, $\omega_0 = 210$

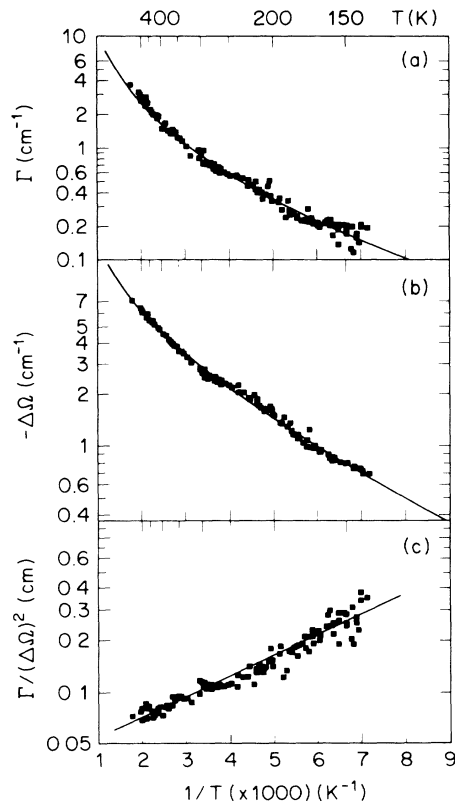


FIG. 2. Plots of (a) the natural linewidth Γ , obtained after deconvolution of the instrumental linewidth, (b) the frequency shift $\Delta\Omega$, and (c) $\Gamma/(\Delta\Omega)^2$, as a function of $1/T$. The frequency at zero degree, Ω_0 , is determined by extrapolating a least-squares linear fit to Γ vs Ω in the low-temperature regime ($T < 200 \text{ K}$), yielding $\Omega_0 = 2086.25(\pm 0.15) \text{ cm}^{-1}$. The best fits (solid lines) are obtained using (a) Eq. (1) with $2(\delta\omega)^2/\gamma = 1.015(\pm 0.015) \text{ cm}^{-1}$ and $\omega_0 = 215(\pm 25) \text{ cm}^{-1}$; (b) Eq. (2) with $\delta\omega = -5.025(\pm 0.05) \text{ cm}^{-1}$ and $\omega_0 = 210(\pm 10) \text{ cm}^{-1}$; and (c) Eq. (3) with $2/\gamma = 0.039(\pm 0.001) \text{ cm}$ and $\omega_0 = 210(\pm 10) \text{ cm}^{-1}$. The best overall fits use $\omega_0 = 210 \text{ cm}^{-1}$, $\delta\omega = -5 \text{ cm}^{-1}$, and $\gamma = 52 \text{ cm}^{-1}$ and are indistinguishable in the figure.

(± 25) cm^{-1} , and $\gamma = 52(\pm 1.5)$ cm^{-1} . The large error bars associated with the phonon frequency (ω_0) arise from the uncertainty in the line shape¹⁴ and in the determination of Ω_0 (i.e., ± 0.15 cm^{-1}), the value of which strongly affects the fits of $\Delta\Omega$ and $\Gamma/(\Delta\Omega)^2$. Note that the weak-coupling approximation ($|\delta\omega| \ll \gamma$) is well justified. The values of $\delta\omega$ are close to that estimated ($\delta\omega = -\omega_0\Omega/4E_0 \sim -4$ cm^{-1}) using a Morse potential with $E_0 = 3.5$ eV for the H binding energy.³

Insight into the nature of this phonon band at 210 cm^{-1} can be gained by considering the recent calculations of Miglio *et al.*,¹⁷ who used the bond-charge model to map out the vibrational manifold of the ideally H-terminated Si(111) surface. These calculations show distinct surface modes (in gaps of the projected bulk density of states) in the vicinity of 210 cm^{-1} (26 meV) at the edges of the irreducible surface Brillouin zone: a flat band in the vicinity of 26 meV that runs between \bar{M} and \bar{K} (210 cm^{-1} at \bar{K} and 214 cm^{-1} at \bar{M}) with some mixing with bulk states near \bar{K} ; and a smaller band at 23 meV (185 cm^{-1}) in the vicinity of \bar{K} . These two surface bands have recently been measured (at the calculated positions in the surface Brillouin zone) using inelastic helium scattering,¹⁸ at 27.4 ± 0.4 and 23.7 ± 0.4 meV, respectively. All the other surface modes (Lucas modes above 56 meV, a 38-meV mode at \bar{K} , and the Raleigh wave below 14 meV) are well outside the error bars and therefore do not contribute to the observed dephasing width of the Si-H stretching mode.

At \bar{K} , the 26-meV mode is elliptical in plane (mixture of shear horizontal and longitudinal displacements) while both the 26.5-meV mode (at \bar{M}) and the 23-meV mode (at \bar{K}) are essentially shear vertical.¹⁷ The in-plane mode involves a parallel displacement of the top Si atoms with respect to the essentially static deeper layers and results in a modulation of the H-H distance (with substantial bending of the Si-H bond). The other two modes involve a vertical displacement of the top Si atoms with no effect on either the H-H distance or the Si-H orientation. In the latter case, Persson and Ryberg³ and more recently Langreth and Persson¹⁶ have argued that the contribution of shear-vertical phonons to the dephasing of a high-frequency vertical polarized mode is negligible because most anharmonic bonds get flexed very little. However, in both cases the H-Si-Si angle is changed and a modulation of the Si-H stretching frequency is possible. In fact, the large error bars on ω_0 (26 ± 3 meV) make it impossible to rule out a contribution from both bands (measured at 27.4 and 23.7 meV)¹⁸ to the projected phonon density of states on the anharmonic coordinates of the Si-H stretch mode. Indeed, the value of the phonon width parameter, $\gamma = 52$ cm^{-1} (6.5 meV) assuming one phonon frequency only, could be due to the two modes measured at 27.4 and 23.7 meV, each one with a smaller width. Lower-temperature and higher-resolution studies will reduce the scatter in the low-temperature data points¹⁴ in Fig. 2(c), and may restrict

the possibilities.

Finally, we consider the decrease of the Si-H stretching-mode intensity observed as the temperature is increased. The effect is reversible and is not predicted by the weak-coupling theory. Such a temperature-dependent variation in the zero-phonon band of the Si-H stretch vibration could be accounted for by the thermal population of a mode which is *strongly* coupled to the Si-H stretch motion, giving rise to sidebands.¹⁹ To get some insight about this other mode, the logarithm of the normalized intensity loss is plotted as a function of $1/T$ in Fig. 3. A straight-line fit of the points gives an activation energy of $1275(\pm 50)$ cm^{-1} , i.e., twice the bending-mode frequency ($\nu_{\text{bend}} = 637$ cm^{-1}). At this time, possible sidebands at 2084 ± 1275 cm^{-1} cannot be investigated because of silicon absorption below 1400 cm^{-1} and interference from water absorption above 3200 cm^{-1} . However, this large intensity loss (20%) should be indicative of a very strong coupling,¹⁶ which is consistent with the fact that the Si-H bending mode is probably long-lived compared with the Si phonons.²⁰ Thus, any anharmonic coupling between the Si-H stretch and Si-H bend modes will be reflected in a complex spectrum (with sidebands) rather than a broadening of a particular normal mode. Note that the lack of sidebands at $\pm \nu_{\text{bend}}$ is due to symmetry: The displacement of the Si-H bend mode is orthogonal to that of the Si-H stretch mode, leading to a negligible cubic term (of the form $u^2\theta$, where θ is the bend angle).¹⁹ Higher-order terms, on the other hand, can contribute, resulting in a decrease of the zero-phonon-band intensity.

In summary, the extremely high degree of homogeneity of this surface has made it possible to identify anharmonic coupling of an adsorbate-substrate stretching vi-

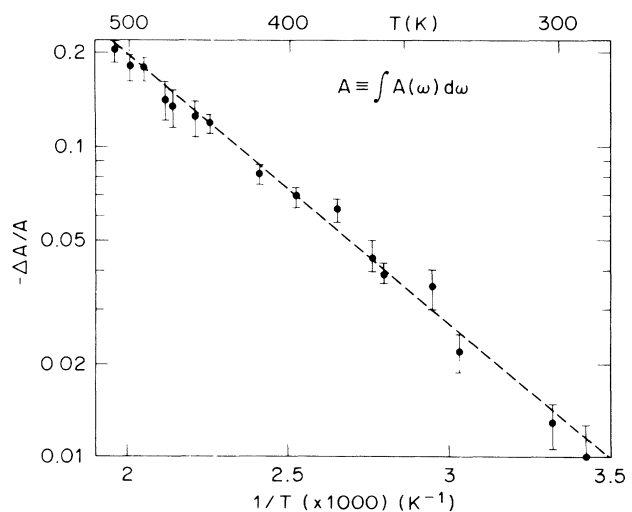


FIG. 3. Loss of integrated intensity, $\Delta A \equiv A - A_0$ (where A_0 is the integrated intensity measured at low temperatures, i.e., below 200 K), of the Si-H stretch absorbance as a function of $1/T$. The slope of the linear fit (dashed line) corresponds to 1275 cm^{-1} .

bration to a substrate phonon band centered at 210 cm^{-1} . The present results show that dephasing can be dominated by one or two *zone-boundary phonons*. In addition, the observed temperature dependence of the Si-H stretch intensity suggests that this mode may have a *strong* anharmonic coupling with the Si-H bend mode. Direct detection of vibrational sidebands is required to support this hypothesis. Yet, together with the lifetime measurements,¹⁵ and with the support of the inelastic-He-scattering data,¹⁸ these results constitute a complete enough experimental description of the vibrational dynamics associated with the Si-H stretching vibration to motivate a number of important theoretical and experimental studies.

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¹For example, see the review of J. W. Gadzuk and A. C. Luntz, *Surf. Sci.* **144**, 429 (1984); B. N. J. Persson, *J. Phys. C* **17**, 4741 (1984).

²B. N. J. Persson and R. Ryberg, *Phys. Rev. Lett.* **54**, 2119 (1985); B. N. J. Persson, F. M. Hoffmann, and R. Ryberg, *Phys. Rev. B* **34**, 2266 (1986).

³B. N. J. Persson and R. Ryberg, *Phys. Rev. B* **32**, 3586 (1985), from where Eqs. (1) and (2) of this paper are taken. See also B. N. J. Persson and R. Ryberg, *Phys. Rev. B* **40**, 10273 (1989).

⁴D. Hoge, M. Tushaus, E. Schweizer, and A. M. Bradshaw, *Chem. Phys. Lett.* **151**, 230 (1988); R. Ryberg, *Phys. Rev. B* **40**, 865 (1989); **40**, 5849 (1989); I. J. Malik and M. Trenary, *Surf. Sci.* **214**, L237 (1989).

⁵J. C. Tully, Y. J. Chabal, K. Raghavachari, J. M. Bowman, and R. R. Lucchese, *Phys. Rev. B* **31**, 1184 (1985).

⁶G. S. Higashi, Y. J. Chabal, G. W. Trucks, and K. Raghavachari, *Appl. Phys. Lett.* **56**, 656 (1990).

⁷The thick thermal oxide ($\sim 1000 \text{ \AA}$) is removed in buffered HF (7:1 $\text{NH}_4\text{F}:\text{HF}$, $\text{pH}=5.0$). Then, oxidation for 10 min in a solution of $\text{H}_2\text{O}:\text{H}_2\text{O}_2:\text{HCl}$ (4:1:1) maintained at 80°C produces $\sim 20 \text{ \AA}$ of clean SiO_2 .

⁸Y. J. Chabal, G. S. Higashi, and S. B. Christman, *Phys. Rev. B* **28**, 4472 (1983).

⁹The infrared spectrum associated with H bound to any defect Si (adatom or step atom) has a strong component parallel to the surface [see Y. J. Chabal *et al.*, *J. Vac. Sci. Technol. A* **3**, 1448 (1985); **7**, 2104 (1989)]. A large shift in the Si-H stretch frequency is observed when these silicon atoms are

chemically backbonded to impurities such as oxygen [see, e.g., J. A. Schaefer *et al.*, *Surf. Sci.* **139**, L209 (1984)], carbon, or fluorine.

¹⁰Details of the experimental geometry have been given in Refs. 6 and 8, and in V. A. Burrows *et al.*, *Appl. Phys. Lett.* **53**, 998 (1988).

¹¹A procedure has been developed to pump down the introduction chamber without contaminating the surface with hydrocarbons: thorough baking prior to introduction, dry N_2 venting followed by rapid ($< 2 \text{ min}$) sample mounting, and very slow ($\sim 5 \text{ Torr/min}$) pumping through a leak valve by a sorption pump. When the pressure is below 10^{-2} Torr , a gate valve is opened, allowing pumping by a well-baked 150-liter/s turbomolecular pump.

¹²M. Grundner and R. Schultz, *J. Vac. Sci. Technol. A* **7**, 808 (1989).

¹³D. B. Fenner, D. K. Biegelsen, and R. D. Bringans, *J. Appl. Phys.* **66**, 419 (1989).

¹⁴Gaussian deconvolution was used to extract the natural linewidth. Although the instrumental line shape is measured to be Gaussian, the natural line shape is likely to be Lorentzian. Deconvolving a Lorentzian line shape with a Gaussian leads to smaller widths at low temperatures than plotted in Fig. 2(a). We have taken this uncertainty of line shapes into account in determining the error bars associated with the phonon frequency ω_0 quoted in the text. Note that these widths are an order of magnitude narrower than observed for any other chemisorbed atom or molecule on any surface, confirming that the defect density is very low. Indeed, since the weak dynamic dipole moment ($e^*/e \sim 0.1$) precludes dipole narrowing [see, e.g., Z. Schlesinger *et al.*, *Phys. Rev. B* **32**, 2721 (1985)], the shift associated with backbonding to a defect Si would be detectable and can be estimated. For a strained backbond (0.16 \AA) such as in $\text{Si}(100)-(2 \times 1)\text{H}$, the Si-H stretch frequency is $\sim 10 \text{ cm}^{-1}$ higher than that of the relaxed Si-H-bond [see Y. J. Chabal and K. Raghavachari, *Phys. Rev. Lett.* **54**, 1055 (1985)], yielding 0.6 cm^{-1} for 0.01-\AA strain of the Si backbond. Since neighboring adatoms or defect atoms produce a larger strain than 0.01 \AA , their presence gives a distinct contribution to the spectrum of neighboring Si-H units. For instance, strain due to adatom neighbors in the 7×7 unit cell yields shifts of order $6\text{--}7 \text{ cm}^{-1}$ (see Refs. 6 and 8).

¹⁵P. Guyot-Sionnest, P. Dumas, Y. J. Chabal, and G. S. Higashi, *Phys. Rev. Lett.* **64**, 2156 (1990).

¹⁶D. C. Langreth and M. Persson (to be published).

¹⁷L. Miglio, P. Ruggerone, G. Benedek, and L. Colombo, *Phys. Scr.* **37**, 768 (1988); U. Harten *et al.*, *Phys. Rev. B* **38**, 3305 (1988).

¹⁸R. B. Doak, Y. J. Chabal, G. S. Higashi, and P. Dumas (to be published).

¹⁹Z. Y. Zhang and D. C. Langreth, *Phys. Rev. Lett.* **59**, 2211 (1987).

²⁰Analogy with localized vibrations of H^- in alkali halides indicates that the Si-H-bend lifetime width is less than 0.5 cm^{-1} . See R. J. Elliott *et al.*, *Proc. Roy. Soc. London A* **289**, 1 (1965).