

## Hydrogen Vibration on Si(111)7×7: Evidence for a Unique Chemisorption Site

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The vibrational spectrum of hydrogen chemisorbed on Si(111)7×7 is studied with high-resolution infrared spectroscopy. A unique chemisorption site characterized by a dangling bond perpendicular to the surface is identified for the first time and assigned to a silicon atom at the bottom of a deep hole formed by long-range reconstruction.

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For over twenty years the clean Si(111)7×7 surface has motivated a great deal of experimental work<sup>1-3</sup> and theoretical speculation.<sup>4-9</sup> Models fall into two general classes: one involving small modifications of the surface atoms such as buckling, commonly referred to as weak reconstruction,<sup>4,5</sup> and the other involving chemical changes such as the formation of dimers and the presence of vacancies.<sup>6-9</sup> Recent ion channeling,<sup>10,11</sup> atom scattering,<sup>12</sup> low-energy-electron diffraction analysis,<sup>13</sup> photoemission,<sup>14</sup> noble-gas physisorption,<sup>15</sup> and electron tunneling microscopy<sup>16</sup> experiments all point to the second class of reconstruction, i.e., a strong reconstruction. In particular, Ref. 16 directly shows the presence of a deep hole at the corner of the 7×7 unit cell. From the available data, the details of the surface geometry are still not unambiguously resolved, as conflicting models are proposed.

In contrast to all the above-mentioned techniques, infrared spectroscopy of semiconductor surfaces gives direct information on the number, position, and *polarization* of dangling bonds. So far, however, poor surface sensitivity to the relevant substrate/adsorbate vibrational modes has made it impossible to carry out such studies on well-characterized single-crystal semiconductor surfaces. In this Letter the first high-resolution (< 2-cm<sup>-1</sup>) vibrational study of hydrogen on Si(111)7×7 obtained with a newly designed, sensitive surface spectrometer is presented. The data clearly show that there is a unique adsorption site per surface unit cell with a dangling bond perpendicular to the surface. Screening of this mode strongly suggests that this site is located below the outermost layer. This is the first experimental evidence for such a deep-lying dangling bond.

The experimental apparatus<sup>17,18</sup> is composed of a modified Nicolet 6000 interferometer coupled to an ultrahigh-vacuum chamber equipped with CsI windows. The system covers the frequency region from 200 to 15000 cm<sup>-1</sup> with an ultimate

resolution of 0.1 cm<sup>-1</sup>. Sensitivity to weak vibrational modes is increased by use of a multiple-internal-reflection geometry with 50 reflections on the surface under investigation<sup>17,19</sup> (Fig. 1). The sensitivity of the system is  $\Delta R/R = 5 \times 10^{-5}$  per reflection with 1-cm<sup>-1</sup> resolution, allowing detection of  $\frac{1}{100}$  monolayer of a weak dipole absorber such as SiH.<sup>20</sup> However, the study of modes below 1000 cm<sup>-1</sup> is not possible *with this geometry for silicon* because of a weak lattice absorption.<sup>21</sup> An important property of nonmetallic samples is the possibility of studying, with *equal sensitivity*, vibrational modes parallel and perpendicular to the surface<sup>22</sup>; *p*-polarized light probes both parallel and perpendicular modes while *s*-polarized light is *only* sensitive to parallel modes (Fig. 1). The surface (*p*-type Si,  $\rho = 1700 \Omega \text{ cm}$ ) was prepared by mild grazing-incidence argon-ion sputtering at room temperature (3 min at 0.5 kV,  $i = 10 \mu\text{A/cm}^2$ ) to remove the oxide on the front surface followed by extended annealing at 800 °C (~ 1 h), which preserved the back-surface native oxide (~ 15 Å thick). The U shape allowed a uniform resistive heating ( $\Delta T < 10^\circ$ ) of 90% of the area under study. Laser annealing was alternatively used to clean the front surface without any effect on the results. Auger

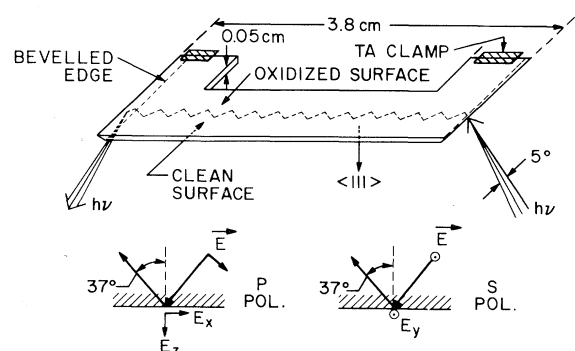


FIG. 1. Schematic representation of the sample geometry. The field distribution is shown at the bottom for the two polarizations used.

analysis performed with a single-pass cylindrical-mirror analyzer (0.1% monolayer sensitivity for the common contaminants) showed that only about 0.3% monolayer of carbon was present over the *full* area of the front surface.<sup>23</sup> Atomic hydrogen exposures were made by filling up the chamber with  $2 \times 10^{-7}$  Torr of molecular hydrogen and heating to 2000 K a tungsten ribbon ( $1 \times 2 \text{ cm}^2$ ) placed 4 cm in front of the sample. CO and H<sub>2</sub>O partial pressures remained less than  $1 \times 10^{-10}$  Torr during exposures. The residual pressure, mostly hydrogen, was less than  $1 \times 10^{-10}$  Torr during the runs.

Calibration of the coverage was done in two independent ways. Firstly, the LEED patterns obtained for various exposures were compared with the calibrated patterns of Culbertson, Feldman, and Silverman<sup>24</sup> who used nuclear microanalysis for absolute coverage measurement. From 0.4 monolayer to saturation coverage (1.25 monolayers), the comparison could be made with 10% accuracy. Below 0.4 monolayer, extrapolation assuming a simple Langmuir dependence yielded 15% accuracy. Secondly, the total integrated infrared absorption of the Si-H stretch mode associated with saturation coverage was measured. Under the assumption that the dynamic dipole moment of the SiH mode does not change with coverage, the coverage can thus be determined with 10% accuracy for lower exposures. Possible variations of the dynamic dipole moment can be estimated by measuring the infrared absorption on the hydrogen-saturated Si(100) surface, which is known to form a dihydride<sup>17, 25</sup>; that situation provides a typical local rearrangement of the top silicon atoms, which is likely to change the dynamic dipole moment. Again, the absolute coverage on Si(100) is accurately known from nuclear microanalysis.<sup>26</sup> The absorption strength per SiH unit was found to be 15% weaker. Therefore, an upper limit of  $\pm 20\%$  error can be assigned to the absolute coverage obtained with use of the integrated absorption of the vibrational mode. The agreement of the two methods (LEED with microanalysis and infrared absorption) is well within the error bars.

Figure 2 shows data for the lowest exposures. Curve *a* corresponds to 1.5% monolayer coverage. Two distinct adsorption peaks are observed at 2073 and 2077  $\text{cm}^{-1}$ , each with a strength corresponding to 0.25 and 0.35 atom per unit cell, respectively. Each peak corresponds to the Si-H stretching vibration for H chemisorbed at different sites. The formation of SiH<sub>2</sub> at these low

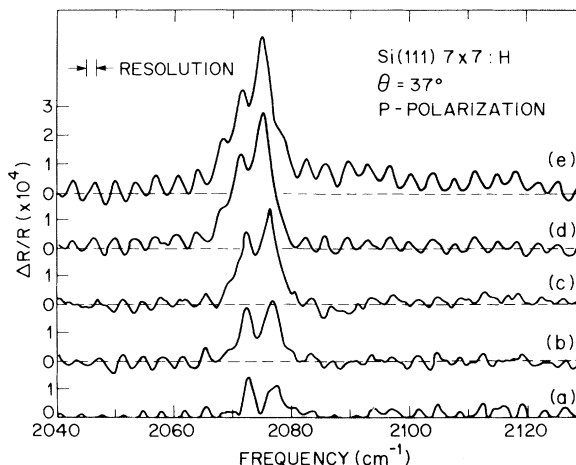


FIG. 2. Raw data (unsmoothed)—reflectivity change (per reflection) for various coverages. The nominal resolution is  $1 \text{ cm}^{-1}$ . The Happ-Genzel apodization used effectively increases the resolution by 50% for narrow lines. The coverages are (curve *a*) 0.01, (*b*) 0.02, (*c*) 0.05, (*d*) 0.07, and (*e*) 0.09. The oscillations present in some spectra are due to slight temperature variations of the sample during data taking, resulting in a small expansion and contraction causing optical interference upon spectra ratioing.

coverages does not take place as *no absorption parallel* to the surface is observed.<sup>17</sup> As more hydrogen is added (curves *b* to *e*), the 2073- $\text{cm}^{-1}$  peak saturates to a value corresponding to  $1 \pm 0.2$  atom per unit cell, i.e., 1 per 49 atoms. This is obtained by resolving the asymmetric peak in curve *e* into a peak at 2073  $\text{cm}^{-1}$  and a peak at 2077  $\text{cm}^{-1}$  by a Fourier-deconvolution method.<sup>27</sup> The higher-frequency peak saturates to a value corresponding to  $3.5 \pm 0.7$  atoms per unit cell. The total hydrogen coverage for that exposure is about 15% of a monolayer, with 5% residing in inhomogeneous sites, giving rise to a broad infrared absorption. At higher coverages ( $\theta > 0.15$ ), the peak height at 2077  $\text{cm}^{-1}$  is *reduced* while the background, located primarily on the high-frequency side of the lines, increases. Corresponding to this broadening of the infrared line, the LEED pattern begins to show a decrease of the intensity of the  $\frac{3}{2}$  and  $\frac{4}{2}$  spots. This indicates that further exposure to hydrogen induces the silicon surface atoms to rearrange, but in an inhomogeneous way. Because of this inhomogeneous rearrangement of the surface at higher coverages,<sup>28</sup> this paper focuses on the very-low-coverage regime ( $\theta < 0.15$ ) where unambiguous assignments can be made.

Since the vibrational peak associated with a

unique site lies within  $5 \text{ cm}^{-1}$  of other vibrations, there may be a concern that dipole coupling<sup>29</sup> will cause energy from this lower-frequency peak to be transferred into the higher-frequency peaks, thus giving an apparently lower integrated strength. This mechanism is negligible in this case because (a) the dynamic dipole moment is extremely weak ( $e^*/e = 0.02$ ), and (b) the average distance between Si-H oscillators at such coverages is very large ( $\sim 30 \text{ \AA}$ ).

It is now argued that this unique chemisorption site is recessed from the outermost plane. The frequency of the unique SiH vibrator is  $4 \text{ cm}^{-1}$  lower than that of other *perpendicular, noninteracting* SiH vibrators. Two mechanisms can account for this lower frequency: (a) screening by the silicon environment and (b) weaker bonding of the H to that site. The latter is unlikely since this site saturates *first* (see Fig. 2) at room temperature,<sup>30</sup> indicating a larger binding energy relative to the other chemisorption sites. Screening from the substrate must therefore take place. Topologically, only a hole with a dangling bond at the bottom could satisfy this constraint. This conclusion is particularly appealing considering the very recent evidence from both physisorption experiments<sup>15</sup> and electron tunneling microscopy<sup>16</sup> that a deep hole is present on the  $7 \times 7$  unit cell. The presence of a lone dangling bond at the bottom of the hole is consistent with the twelve-membered ring hole at the corner of the  $7 \times 7$  unit cell proposed by McRae.<sup>31</sup>

To gain insight regarding the nature of this unique site, the Si(111) surface was laser annealed, resulting in a  $1 \times 1$  reconstruction. Details of the experiments will be published elsewhere.<sup>32</sup> Of interest here is the fact that the laser-annealed surface is mostly *disordered* with no long-range reconstruction,<sup>33</sup> yet displays a *local* structure very similar to that of the  $7 \times 7$  surface.<sup>11</sup> The induced absorption resulting from a 5% coverage is shown in Fig. 3 and compared with that on the  $7 \times 7$  surface. Although the line is slightly broadened, it is clearly symmetrical with a maximum at  $2077 \text{ cm}^{-1}$ . The *low-frequency contribution is absent*. Given the signal-to-noise ratio, it can be established that 80% of the surface does not contain the special site characteristic of the  $7 \times 7$  surface. This observation strongly suggests that the unique adsorption site is a result of *long-range rearrangement*.<sup>31</sup>

In contrast, the mode at  $2077 \text{ cm}^{-1}$ , which saturates just as some structural rearrangement of the silicon surface takes place, is still present

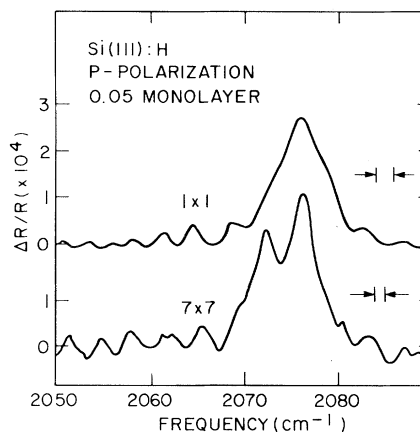


FIG. 3. Raw data (unsmoothed)—reflectivity change (per reflection) for 0.05 monolayer coverage on the laser-annealed  $1 \times 1$  and the thermally annealed  $7 \times 7$  surfaces. Note the change of resolution.

on the laser-annealed surface, and therefore is only sensitive to the local geometry of a small subunit. Its strength and polarization indicate that only three to four such subunits have a dangling bond perpendicular to the surface distinguishable from the remaining bonds ( $> 45$ ) in the  $7 \times 7$  unit cell. This is *not* predicted by any of the models proposed so far.<sup>4-9,13,16</sup>

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