

Surface Infrared Study of Si(100)-(2×1)H

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Combination of high-resolution surface infrared spectroscopy on single-domain Si(100)-(2×1)H and *ab initio* cluster calculations provides a complete determination of the geometry and vibrational parameters for the monohydride structure.

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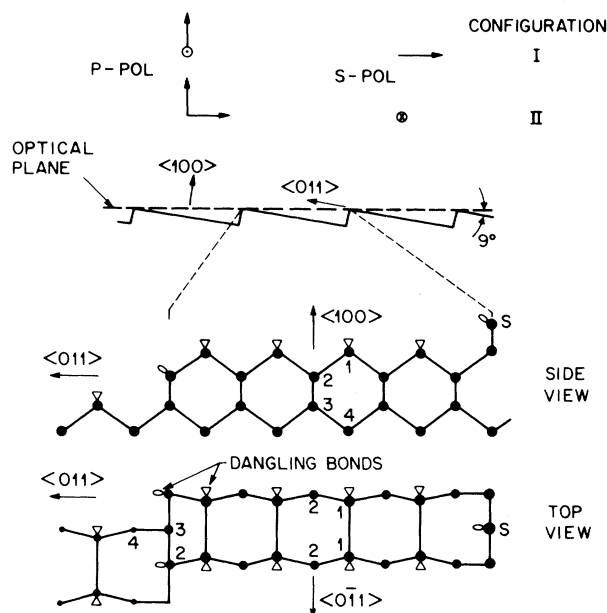
The observation of substrate/adsorbate vibrational modes with high resolution on single crystal surfaces is very recent.¹⁻³ Although such measurements promise to yield important dynamic⁴ and structural³ information, there has been no theoretical effort to assess the potential of a generally difficult spectroscopy. The aim of this Letter is to show that high-resolution infrared measurements of the Si(100)-H surface combined with accurate *ab initio* calculations give a *complete* structural and dynamic description of the system through the determination of the adsorbate geometry and its vibrational (chemical and dipole) interactions.

The ideal Si(100) surface with two broken bonds per surface atom is unstable, and pairs of atoms are believed to move together and dimerize.⁵ Although an asymmetric dimer model^{6,7} for the clean Si(100)2×1 surface accounts for numerous experimental results,⁸⁻¹⁰ the length of the dimer is still a subject of controversy.^{6,11} The analysis is further complicated by the presence of two domains with differently oriented dimers and the observations of higher-order reconstructions.^{12,13} A logical extension of the dimer model is the formation of a "monohydride" phase¹⁴ characterized by one H per surface silicon atom and by a *symmetric* dimer. Indeed, H chemisorption produces a sharp 2×1 low-energy electron diffraction (LEED) pattern^{12,15,16} with no higher-order reconstruction. In particular, saturation coverage on a substrate at 350 °C yields the sharpest 2×1 LEED pattern.^{16,17} Yet the structure of the experimentally well defined and theoretically more tractable monohydride phase has not been established. In this paper we utilize the fact that *single-domain* Si(100)-(2×1)H can be prepared on vicinal surfaces to measure the IR spectrum associated only with the monohydride or monodeuteride phase; i.e., contributions from H adsorbed on step atoms or from other forms of hydrides are clearly separated. Theoretically, we use *ab initio* cluster calculations¹⁸ since they are well suited for the study of semiconductor surfaces for which delocalization effects are usually not significant. Optimized geometries are calculated by ener-

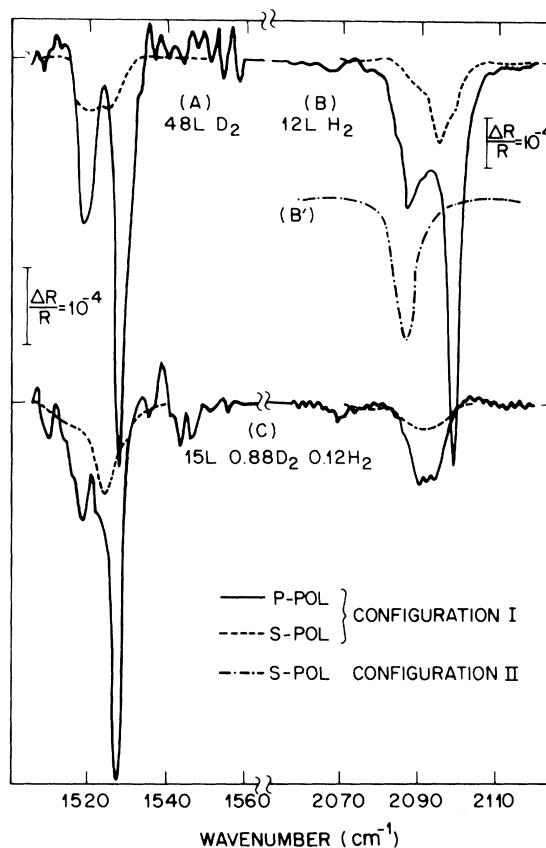
gy minimization procedures and vibrational frequencies evaluated with analytical gradient techniques.¹⁹ The small frequency splittings due to chemical interactions, the frequency shifts resulting from isotopic substitution, and the dynamic dipole moments associated with the normal modes are evaluated¹⁹⁻²¹ and found to be in excellent agreement with the experimental results, thus confirming the calculated geometry.

The features of the experimental apparatus and sample preparation are described in Ref. 3. Extensive measurements on flat Si(100) have revealed that the infrared spectra of chemisorbed H are complex,²² seemingly dependent on the surface preparation. This motivated the study of vicinal surfaces for which the dimers are all aligned along the step edges.²³ Kinematical LEED analysis of samples cut at 9° off the (100) plane about the $\langle 0\bar{1}1 \rangle$ axis shows the formation of a uniform array of double-layer steps with four dimers on each terrace (Fig. 1). The LEED patterns of the vicinal surfaces showed no change upon H chemisorption at 250 °C except for small *intensity* variations. The dimers all remain parallel to the step edge. Figure 1 shows how modes of H on the (100) terraces can be unambiguously distinguished from step modes by polarization studies. Studies with configurations I and II allow the determination of modes associated with step atoms *even if the frequencies are identical with those associated with terrace atoms.*

Selected results for D and H adsorption are summarized by Fig. 2 (curves A, B, and B'). The main terrace modes occur at 2087.5 and 2098.8 cm⁻¹ for H and at 1519 and 1528 cm⁻¹ for D. The step modes (dashed curves) occur in between the terrace modes at low coverages (e.g., at 2094 cm⁻¹ for H in Fig. 2, curve B) and shift to lower frequency as the coverage increases (e.g., see the two peaks at 1524 and 1519 cm⁻¹ for 0.5 monolayer D in Fig. 2, curve A) as confirmed by *p*-polarization data in configuration II (not shown). For saturation coverage the step modes were found at 1519 cm⁻¹ (2087.5 cm⁻¹) for D (H), clearly interfering with intensity measurements on flat surfaces where two



domains are present and step modes cannot be distinguished from polarization studies. Hence, by varying the coverage and probing the vicinal surface with both configurations, we can establish that the terraces are characterized by two modes, one polarized parallel to the surface along the dimer direction (M_{\parallel}) and the other perpendicular to the surface (M_{\perp}). The strengths of these modes yield a constant ratio $I_{\parallel}/I_{\perp} = 0.67/\epsilon_{\infty}^2$ after correction for field amplitudes and the 9° inclination, where ϵ_{∞} is the electronic screening.²⁴ To establish that M_{\parallel} and M_{\perp} are associated with *one local* structure and are not due to two *different* chemisorption sites with equal sticking coefficients and to determine the origin of the frequency splitting, isotopic-mixture experiments were performed. A surface exposed to a dilute amount of H in a D-rich mixture exhibits *only one mode* at 2092 cm^{-1} associated with H (Fig. 2, curve C).²⁵ Spectra obtained with configuration



II show that this mode is a terrace mode parallel to the step edge with a screened ratio $I_{\parallel}/I_{\perp} \sim 0.7$. Hence, the two-site hypothesis can be ruled out since a parallel mode would have no dipole interaction with a neighboring perpendicular mode. Measurements over the largest range of coverages for which M_{\parallel} and M_{\perp} could be seen showed that the chemical interactions are $\Delta_{\text{chem}}(\text{H}) = 9 \text{ cm}^{-1}$ and $\Delta_{\text{chem}}(\text{D}) = 7.5 \text{ cm}^{-1}$ while constant-coverage isotopic experiments showed that the largest dipole/dipole interaction is 3 cm^{-1} for H and 2 cm^{-1} for D. The measured dipole/dipole splitting and absolute absorption in both M_{\parallel} and M_{\perp} for a wide range of coverages give $\epsilon_{\infty} = 1.4 \pm 0.05$ yielding the *unscreened* ratio of the dynamic dipole moments associated with M_{\parallel} and M_{\perp} , $\mu_{\parallel}/\mu_{\perp} = 0.6 \pm 0.1$.

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We now show that M_{\parallel} and M_{\perp} are the antisymmetric and symmetric stretching modes of the

monohydride phase. The first report of H adsorption on Si(100) assigned M_{\parallel} and M_{\perp} to the dihydride phase²² because they persisted upon high exposures as the LEED turned into a 1×1 and because the magnitude of the chemical splitting ($\sim 10 \text{ cm}^{-1}$) was typical of that matrix-isolated SiH_2 .²⁶ However, the deuterium data clearly rule out this assignment since cluster calculations presented below and gas-phase²⁷ show that the dideuteride is characterized by M_{\parallel} being at a *higher* frequency than M_{\perp} . Further, we have determined that M_{\parallel} and M_{\perp} sharpen and persist upon annealing to 350°C where the LEED is a sharp 2×1 and no dihydride scissor mode can be seen with electron energy-loss spectra (EELS).¹⁷ Finally, the dihydride modes were recently observed²⁴ upon H_2O dissociation on Si(100) at 2106 and 2116 cm^{-1} .

The cluster models used in the calculations are shown in Fig. 3. The Si_9H_{14} cluster^{18,28} was used with the double-zeta 3-21G basis set,²⁹ reliable in predicting geometries,³⁰ to obtain the principal geometrical features. The third- and fourth-layer silicons were held rigidly at the ideal crystal positions and the hydrogens labeled H_3 , H_4 , and H_5 , representing the truncated cluster bonds, were held rigidly along the ideal crystal directions with a bond length of 1.48 \AA . The first- and second-layer silicons and the two added hydrogens were free to move along the x and z directions and the hydrogens H_1 were relaxed. Total-energy minimization subject to the above constraints yields $d_{\text{Si}_1-\text{Si}_1} = 2.54 \text{ \AA}$, $d_{\text{Si}_1-\text{Si}_2} = 2.41 \text{ \AA}$, $d_{\text{Si}-\text{H}} = 1.49 \text{ \AA}$, and $\theta(\text{H}-\text{Si}-\text{Si}) = 110^\circ$, with all the directions of the relaxations consistent with those in Ref. 5. Effects of electron correlation and of larger basis sets (includ-

ing d function on Si) were evaluated with the smaller clusters [Fig. 3(b)]. Our best projected values are $d_{\text{Si}_1-\text{Si}_1} = 2.51 \text{ \AA}$, $d_{\text{Si}_1-\text{Si}_2} = 2.38 \text{ \AA}$, $d_{\text{Si}-\text{H}} = 1.48 \text{ \AA}$, and $\theta = 110^\circ$.

Next, the splitting of the vibrational frequencies of the monohydride (monodeuteride) due to chemical interactions was evaluated by use of $\text{Si}_2\text{H}_2\text{D}_4$ ($\text{Si}_2\text{D}_2\text{H}_4$) clusters. The complete harmonic force field and the frequencies were calculated at several levels of theory with analytical gradient techniques.¹⁹ Though the absolute calculated frequencies were usually different for different levels of theory and about 10% higher than experiment,¹⁹ the *frequency splitting* was found to be remarkably *independent* of the level of theory used. Electron correlation effects on the splitting were small. With use of the large 6-31G** basis set,³¹ including d functions on Si and p functions on H, a splitting of $+11 \text{ cm}^{-1}$ ($+9 \text{ cm}^{-1}$) was calculated for the monohydride (monodeuteride). In both cases, the symmetric frequency was *higher* than the antisymmetric one, in agreement with experiment. This was not the case for the dihydride where the splitting calculated in the simple SiH_2D_2 model was $+5 \text{ cm}^{-1}$ (-14 cm^{-1}) for the dihydride (dideuteride) in agreement with experimental isotopic studies.²⁷ Further calculations for SiH_2F_2 , SiH_2Cl_2 , and Si_3H_8 showed that, for these dihydride-containing species and in agreement with experimental data,³² a similar deuterium shift was present.

Finally, the Si_2H_6 cluster was used to compute the dynamic dipole moments for both M_{\parallel} and M_{\perp} . The 6-31G** basis set was used and electron correlation effects were included by means of Moller-Plesset perturbation theory through fourth order.³³ The dynamic dipole moments were evaluated by taking finite steps along the symmetric and antisymmetric mode directions, yielding 1.36 D/\AA and 0.80 D/\AA , respectively. The ratio $\mu_{\parallel}/\mu_{\perp}$ was thus calculated to be 0.59, in remarkable agreement with the experimentally determined unscreened ratio. Consideration of the larger Si_6H_{14} cluster gave less than 10% change in the value of the computed dynamic dipole moments. Note that the back projection of μ_{\parallel} and μ_{\perp} along the Si-H bond does not give the *same value* for the dynamic dipole moment. Hence, the geometric angle of an adsorbate cannot, in general, be deduced by polarized infrared data *alone* without some knowledge of the relative strengths of the dynamic dipole moments associated with the normal modes. It should also be kept in mind that for metal substrates parallel modes are not infrared active, and cluster calculations are less accurate. However, this Letter demonstrates that

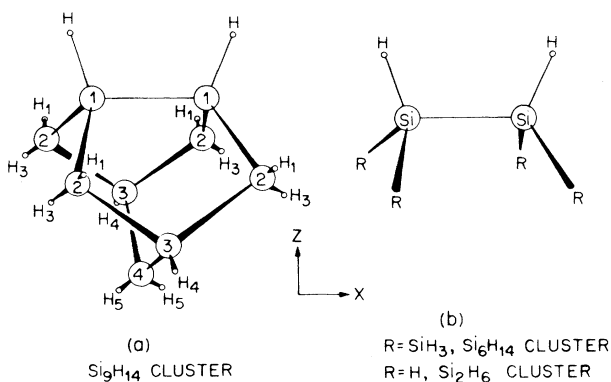


FIG. 3. Cluster models and axes used in this study. The silicons (large circles) and hydrogens (small circles) are numbered according to the layer to which they belong. The twelve hydrogens representing truncated cluster bonds are shown with shorter bond lengths for clarity.

extremely small splittings can be resolved with infrared spectroscopy and interpreted to yield very accurate geometries for adsorbates on semiconductor surfaces.

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