Supporting Information:

Transfer of Electron Density and Formation of Dative Bonds in Chemisorption of Pyrrolidine on Si(111)-7×7

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Schematic of electron density distribution in (100) semiconductor surface dimers and Layer-by-layer Reconstruction of A Si(111)7×7 unit cell

See Figures S1 and S2.

Top and Side Views of the Three-dimensional Structure of a Si(111)-7×7 Unit Cell.

See Figure S3.

Construction and Optimization of a Si₉H₁₂ Cluster Containing an Adatom and an Adjacent Rest Atom from A Large Cluster with Three 7×7 Unit Cells

See Figure S4.

Observation of Weak Vibrational Feature due to Si-H Stretching

Figure S5 replots Figure 3 by shrinking the X-axis (vibrational frequency) for a clearer view of the Si-H vibrational feature. The weak vibrational feature at ~ 2100 cm⁻¹ can be found in the region of 2000-2200 cm⁻¹ in Figure S5.
Assignment of Vibrational Feature at $\sim$578 cm$^{-1}$

Figure S6 shows the spectra of a chemisorbed monolayer collected at both specular and off-specular geometries. Only vibrational spectra in the region of 200-1900 cm$^{-1}$ are shown for a clearer comparison. Figure S6a is the spectrum of a chemisorbed monolayer collected at a specular geometry. Figures S6b and S6c are spectra of the same sample collected at two off-specular geometries. Notably, the intensity of the peak at $\sim$578 cm$^{-1}$ is significantly decreased in the off-specular geometry of 50° ($\Delta \theta = -10°$), suggesting a major contribution from dipole scattering for the excitation of this vibrational mode. Surprisingly, it disappears at an off-specular geometry of 45°. A disappearance of a vibrational mode at off-specular geometry is unusual because in principle the impact scattering should still contribute to the intensity to some extent$^{1,2}$. Obviously, the rate of decrease in the peak intensity at $\sim$578 cm$^{-1}$ is much greater than for all the other peaks such as those at $\sim$1476, $\sim$1324, and $\sim$918 cm$^{-1}$. If the vibrational peak at $\sim$578 cm$^{-1}$ in the spectra of the chemisorbed monolayer results from a ring-deformation mode which can be identified at $\sim$630 cm$^{-1}$ in the physisorbed multilayers (Figures 3c and 3d), it should have a rate of decrease in peak intensity similar to the peaks at $\sim$1476, $\sim$1324, and $\sim$918 cm$^{-1}$, and at least it should be observable at an off-specular geometry of 45°. Thus, it is suggested that the peak at $\sim$578 cm$^{-1}$ in Figure S6a cannot be assigned to the ring-deformation mode. Alternatively, it may be attributed to the stretching mode of the N···Si dative bond. Because the N···Si dative bonds are buried below the dative-bonded molecules, the relatively large C$_4$H$_8$N ring could prevent the incoming electron beam from scattering from the vibrational motion of the buried N···Si dative bond.
through an impact scattering mechanism\textsuperscript{1,2}. Thus, in the spectrum of the off-specular geometry with a large off-specular angle, the vibrational feature at \textasciitilde578 cm\textsuperscript{-1} disappears.

References


**Figure S1.** Scheme illustrating the unequal distribution of electron density between the two atoms of a surface dimer on the (100) surfaces of elemental semiconductor single crystals (Germanium, Silicon, and Diamond). The red dashed line marks the position of the surface dimer without tilting.
**Figure S2.** Layer-by-layer construction of a Si(111)-7×7 unit cell. (a) Base layer with 49 silicon atoms. (b) Dimer layer. (c) Rest-atom layer; Balls marked with red color represent rest atoms. (d) Adatom layer. Solid pink lines mark the borders of a Si(111)-7×7 unit cell. Dashed pink line marks the border between two halves of one 7×7 unit cell.
Figure S3. Three-dimensional structure of a Si(111)-7×7 unit cell.

(a) Top view. (b) Side view. The pink solid lines mark the borders of a unit cell. The pink dashed line marks the border of a half unit cell.
Figure S4. Constructed and Optimized Clusters I, II, III.
Figure S5. HREELS spectra of pyrrolidine adsorbed on a clean Si(111)-7×7 at 85 K as a function of pyrrolidine exposure.
Figure S6. Spectra of a chemisorbed monolayer collected at both specular (a) and off-specular (b and c) geometries.