

Supporting Information:

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

Feng Tao[†], Yinghui Cai[‡], Yuesheng Ning[‡], Guo-Qin Xu[‡] and Steven L. Bernasek^{†*}

Department of Chemistry, Princeton University, Princeton, New Jersey 08544 [†]

Department of Chemistry, National University of Singapore, 10 Kent Ridge, Singapore, 119260 [‡]

**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 $\sim 578\text{ cm}^{-1}$

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 $\sim 578\text{ cm}^{-1}$ is significantly decreased in the off-specular geometry of 50° ($\Delta\theta = -10^\circ$), 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 $\sim 578\text{ cm}^{-1}$ is much greater than for all the other peaks such as those at ~ 1476 , ~ 1324 , and $\sim 918\text{ cm}^{-1}$. If the vibrational peak at $\sim 578\text{ cm}^{-1}$ in the spectra of the chemisorbed monolayer results from a ring-deformation mode which can be identified at $\sim 630\text{ cm}^{-1}$ in the physisorbed multilayers (Figures 3c and 3d), it should have a rate of decrease in peak intensity similar to the peaks at ~ 1476 , ~ 1324 , and $\sim 918\text{ cm}^{-1}$, and at least it should be observable at an off-specular geometry of 45° . Thus, it is suggested that the peak at $\sim 578\text{ cm}^{-1}$ in Figure S6a cannot be assigned to the ring-deformation mode. Alternatively, it may be attributed to the stretching mode of the N \cdots Si dative bond. Because the N \cdots Si dative bonds are buried below the dative-bonded molecules, the relatively large $\text{C}_4\text{H}_8\text{N}$ ring could prevent the incoming electron beam from scattering from the vibrational motion of the buried N \cdots Si dative bond.

through an impact scattering mechanism^{1,2}. Thus, in the spectrum of the off-specular geometry with a large off-specular angle, the vibrational feature at $\sim 578\text{ cm}^{-1}$ disappears.

References

- (1) Ibach, H. *Electron Energy Loss Spectrometers: The Technology of High Performance*, Springer-Verlag, Berlin, **1990**.
- (2) Ibach, H. *Electron Spectroscopy for Surface Analysis*, Springer-Verlag, Berlin, **1977**.

Figure S1

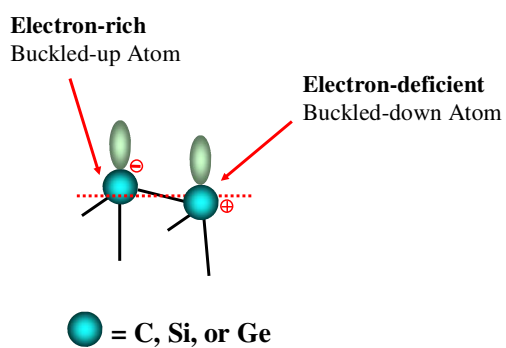


Figure S1. Scheme illustrating the unequal distribution of electron density between the two atoms of a surface dimer on the (100) surfaces of elemental semiconductor single crystals (Germanium, Silicon, and Diamond). The red dashed line marks the position of the surface dimer without tilting.

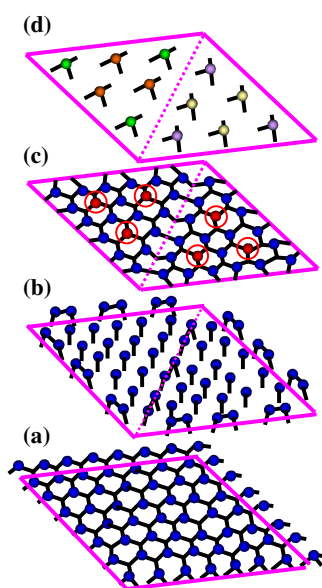


Figure S2. Layer-by-layer construction of a Si(111)-7 \times 7 unit cell. (a) Base layer with 49 silicon atoms. (b) Dimer layer. (c) Rest-atom layer; Balls marked with red color represent rest atoms. (d) Adatom layer. Solid pink lines mark the borders of a Si(111)-7 \times 7 unit cell. Dashed pink line marks the border between two halves of one 7 \times 7 unit cell.

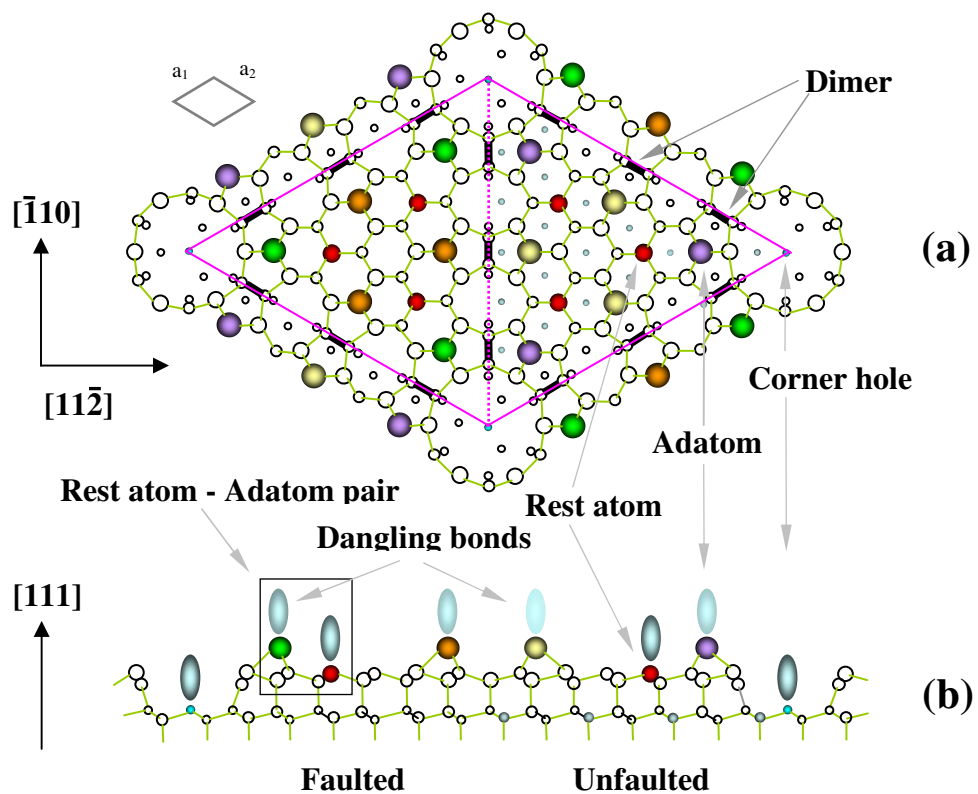


Figure S3. Three-dimensional structure of a Si(111)-7×7 unit cell.

(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

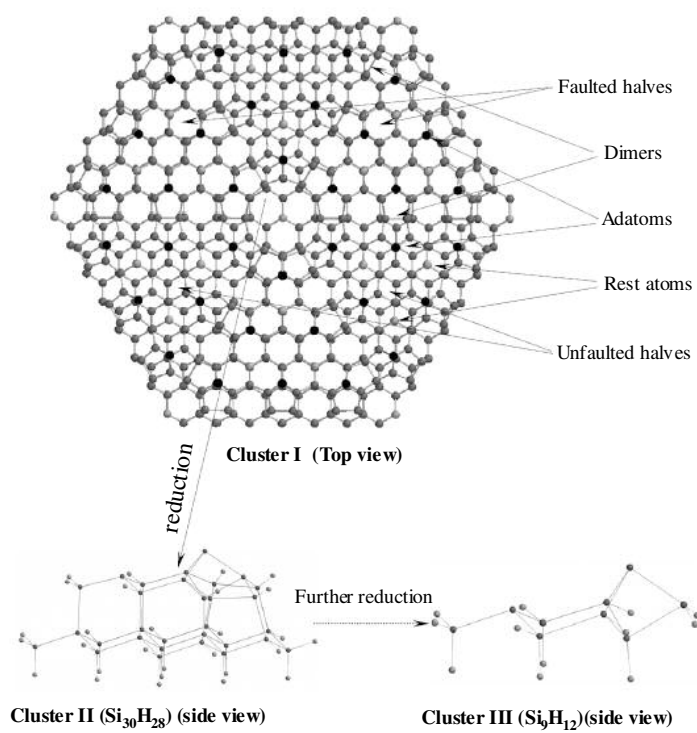


Figure S4. Constructed and Optimized Clusters I, II, III.

Figure S5

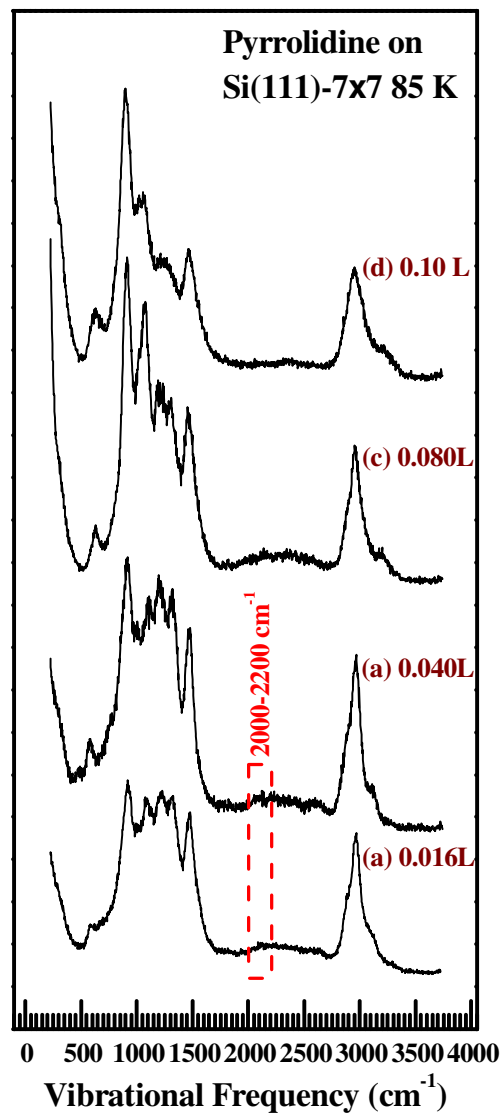


Figure S5. HREELS spectra of pyrrolidine adsorbed on a clean Si(111)-7x7 at 85 K as a function of pyrrolidine exposure.

Figure S6

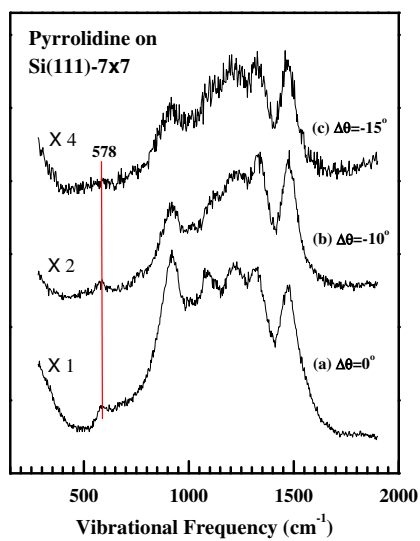


Figure S6. Spectra of a chemisorbed monolayer collected at both specular (a) and off-specular (b and c) geometries.