

Semiconductor Surface States & Surface Structures

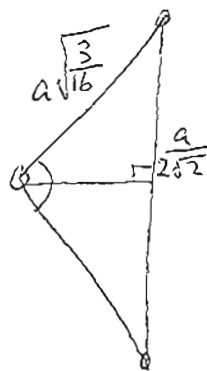
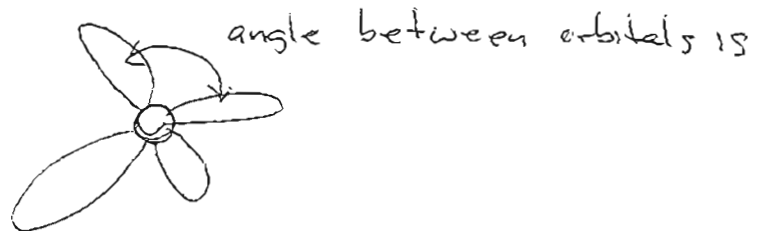
Silicon : Si = [Ne] 3s² 3p²

2 s electrons

2 p electrons

bonding is of form sp³

s and p orbitals hybridize to form sp³ orbitals



$$\theta = \arcsin \frac{\frac{a}{2\sqrt{2}}}{\frac{a}{\sqrt{3}}}$$

$$= 109.47^\circ \dots$$

$$109.4712206$$

sp^3 hybridization responsible for tetrahedral bonding
 \Rightarrow diamond crystal structure (Si, Ge, C)
 \Rightarrow zinc-blende crystal structure (GaAs, ... other III-V compounds)

Silicon (111)
 cleaved at $T < 20\text{K}$ \Rightarrow 1×1 surface structure
 cleaved at RT \Rightarrow 2×1 reconstruction
 annealed to $T > 700\text{K}$ \Rightarrow 7×7 reconstruction

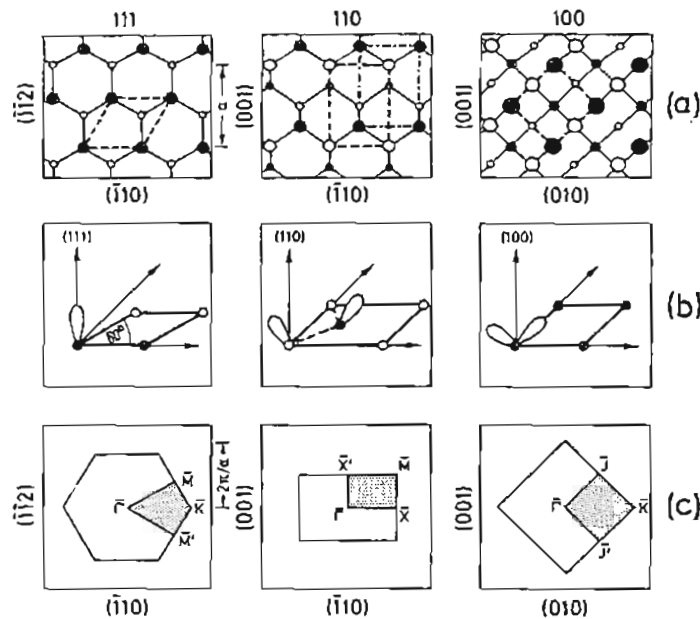


Fig. 6.30a-c. Crystallography of the non-reconstructed three low-index surfaces of the zincblende lattice (sp^3 -bonded). The diamond lattice of Si and Ge would be obtained if all atoms were of the same species. (a) Top view, smaller symbols denote deeper lying atoms. Possible unit meshes are indicated by broken lines. (b) Schematic plot of the dangling-bond orbitals occurring on the different surfaces. (c) Corresponding ideal surface Brillouin zone with conventional labeling [6.33]

$\frac{1}{2}$ -filled dangling band of the 1×1 surface is a very high energy state and reconstruction is highly favored.

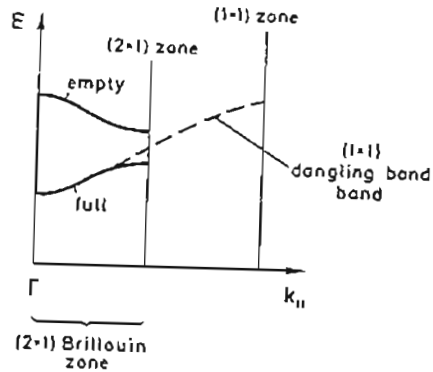
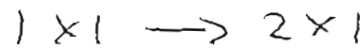


Fig. 6.31. Schematic illustration of the energy gain due to the formation of a (2×1) dangling bond surface reconstruction. The shrinking of the Brillouin-zone dimension by a factor of two in one direction causes the half-filled dangling bond surface state band (broken line) to be folded back into the new (2×1) zone and split at the zone boundary, thus leading to a reduction of the total electronic energy

Lüth, p.303

Various techniques and theories were applied to determine the model for the 2×1 of $S_2(111)$.

- A. Buckling model
- B. π -bonded chain model

Notice that the 2×1 of $\text{Si}(111)$ has a rectangular unit cell.

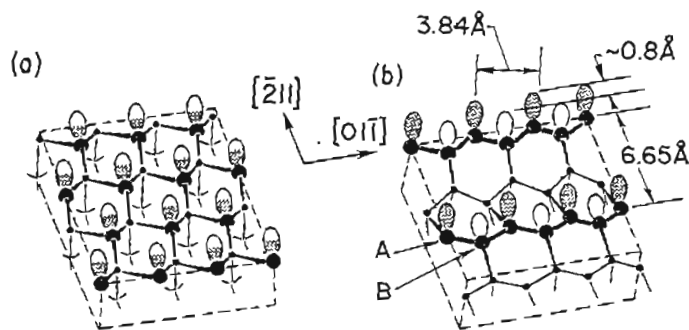


Fig. 1.11. The nascent $\text{Si}(111)$ surface and its reconstruction. (a) The nascent $\text{Si}(111)$ surface has a threefold symmetry, with nearest-neighbor atomic distance 3.84 Å. (b) The $\text{Si}(111)$ surface reconstructs immediately at room temperature to a metastable $\text{Si}(111)\text{-}2 \times 1$ surface, which has a lower symmetry. Two rows of dangling bond states are formed: One is filled, another is empty.

Sulian Chen, p. 13

Second-layer Si moves up to become first layer. A bond must be broken to do this.

Charge is transferred from one surface Si to the next one. ... filled

~~From~~
 From side-view, the π -bonded model looks like:

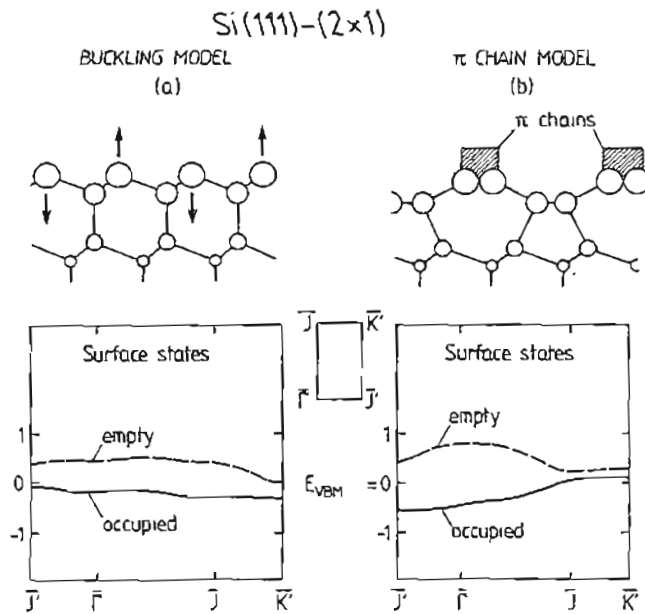


Fig. 6.32. Calculated dispersion of the dangling-bond surface-state bands for Si(111)-(2x1) [6.36] (a) for the buckling model shown in the upper part; (b) for the π -bonded chain model shown in the upper part. See also Fig. 3.6

Lith, p. 304

Notice the larger amount of dispersion for the π chain model.

Energy difference at \bar{J} is less than 0.5 eV

Electrons of low energy ~~at the surface~~ can lose energy to the transition between these surface state bands. Presumably they lose energy by exciting ~~an electron~~ another electron to make the transition.

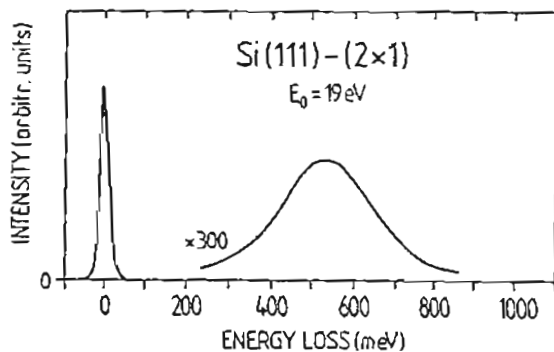


Fig. 6.34. High-Resolution Electron Energy Loss Spectrum (HREELS) of a clean, cleaved Si(111)-(2x1) surface for specular reflection (70°) and with a primary energy E_0 of 19 eV [6.40]

Lith, p. 305

After annealing to $> 700\text{ K}$ (400°C), $\text{Si}(111)$ reconstructs to 7×7

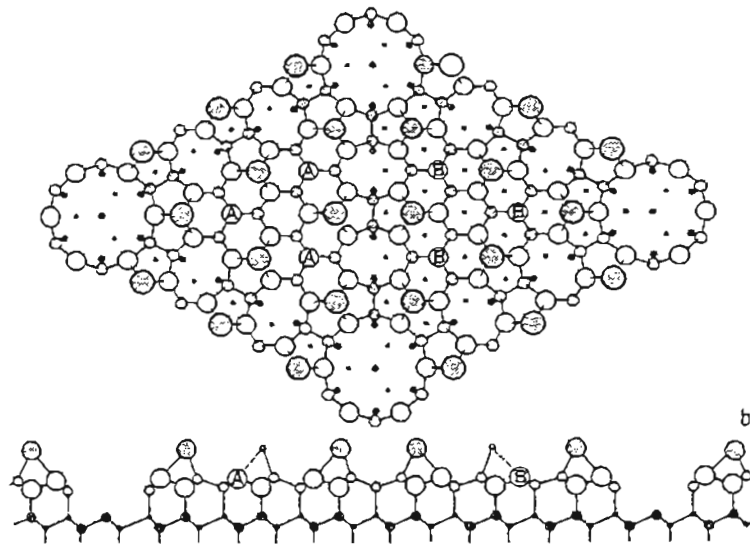


Fig. 6.37a,b. Dimer-Adatom Stacking fault (DAS) model for the $\text{Si}(111)-(7 \times 7)$ surface. (a) Top view: Atoms in (111) layers at increasing depth are indicated by circles of decreasing sizes. The heavy circles represent the 12 adatoms. The circles marked by A and B represent the rest atoms in the faulted and unfaulted half of the unit cell, respectively. (b) Side view: Atoms in the lattice plane along the long diagonal of the surface unit cell are shown with larger circles than those behind them [6.44]

Lith, p. 307

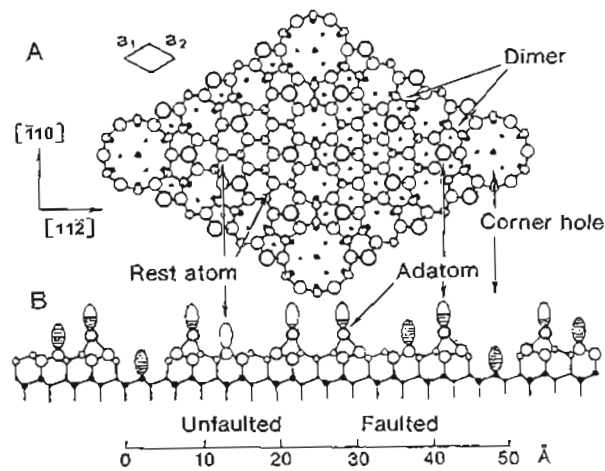
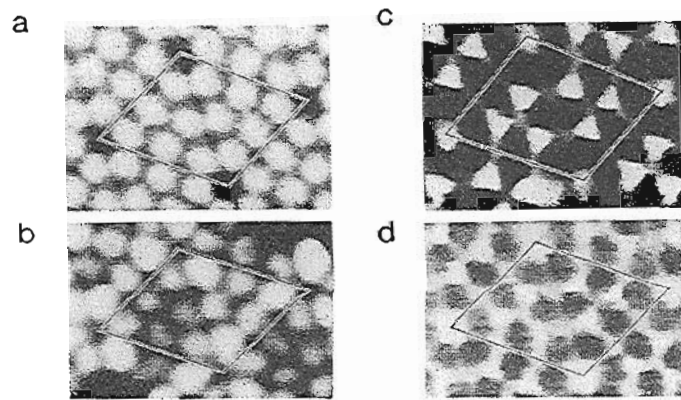


Fig. 1.14. Electronic states and DAS model of Si(111)-7 \times 7. Upper, electronic states on Si(111)-7 \times 7 mapped by STM. (a) Topographic image, taken at a bias of +2 V. (b) Current image at -0.35 V. The two sets of dangling-bond states on the faulted half and the unfaulted half become different. (c) Current image at -0.8 V. The dangling bonds at the rest atoms and the corner holes become apparent. (d) Current image at -1.8 V. The "back-bond" states are observed. (Reproduced from Hamers et al., 1987, with permission.) Below, the DAS model. In each unit cell, there are 9 dimers, 12 adatoms, and a stacking-fault layer. There are 19 dangling bonds in each unit cell. As shown, all 19 dangling bonds and their energy levels have been identified by STM experiments. (After Takayanagi et al., 1985.)

It's interesting that the large unit cell of 7×7 results in many times of zone-folding, resulting in many surface states in the band gap.

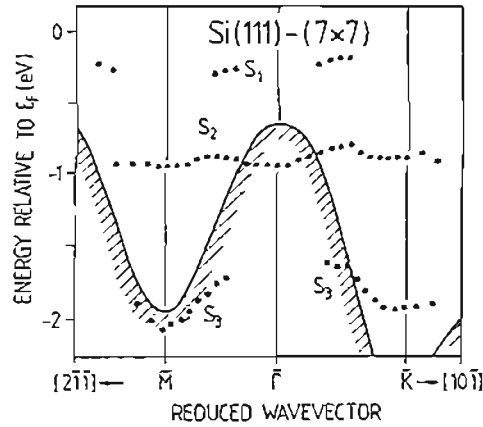


Fig. 6.38. Experimentally determined dispersion of surface state bands (S_1 , S_2 , S_3) on the clean Si(111)-(7x7) surface (points). The projected bulk valence band is indicated by its shaded upper boundary [6.47]

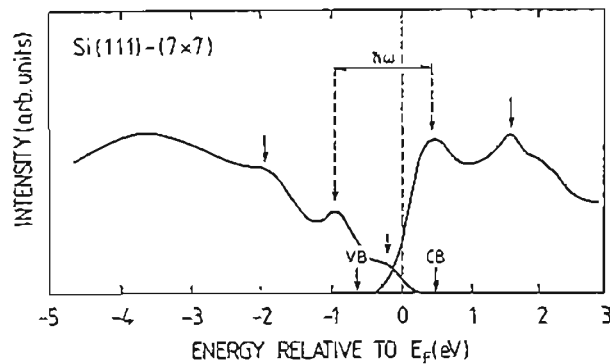


Fig. 6.39. Schematic distribution of occupied and empty surface states of the Si(111)-(7x7) surface. The curves are constructed from several sets of experimental data [6.45-6.49]. The arrow marked $\hbar\omega$ represents an electron energy loss observed experimentally. Other tic marks show occupied and empty surface states as revealed by UPS and inverse photoemission experiments [6.50]