morphology and structure

morphology means shape

structure is more specific, implies atomic structure

for example, the detailed arrangement of the surface atoms

What determines the morphology or structure?

$= \text{ the surface free energy } \gamma$

$$\int \gamma dA = \text{ minimum}$$

idea being that the surface will always attain the lowest energy configuration
Origin of Surface Free Energy

For details, follow discussion in H. Liith, Surfaces and Interfaces of Solid Materials, Section 3.1.

Begun with a consideration of pressure and force.

![Section view diagram]

Pressure is the same across any plane "parallel" to the surface plane.

![Perspective view diagram]

Force perpendicular to surface may be different compared to bulk.

\[ f_\perp = p b t - \gamma b \]

\( \gamma \) = force/length = tension, interface or surface
The surface or interface tension plays a role in the thermodynamics.

For a homogeneous bulk phase,

$$dF = -SdT - pdV + \sum \mu_i dn_i$$

For the surface/interface region

$$dF^s = -S^s dT - pdV^s + \gamma dA + \sum \mu_i dn_i$$

For $dT = 0$, one can get to:

$$F^s = -pV^s + \gamma A + \sum \mu_i n_i^s$$

can see that

$$\gamma = \text{surface tension}$$

can be regarded as an excess free energy per unit area

$$[\gamma] = \frac{\text{force}}{\text{length}} = \frac{\text{energy}}{\text{length}^2}$$

But, $\gamma = \gamma(hkl)$

$\gamma$ depends on the crystalline orientation
Different hkl planes exposed at the surface lead to some planes with larger $\gamma$, some with smaller $\gamma$

\[ \Delta A \to \min \]

A given surface may form "facets" in order to minimize the total excess free energy due to the surface

\[ \int_\mathcal{A} \gamma \, d\mathcal{A} \to \min \]

Wulff construction is a polar coordinate plot allowing to determine the shape of a crystal based on which facets have the lowest $\gamma$

\[ \hat{\mathbf{n}}_1 \quad \text{high } \gamma \text{ surface} \]

\[ \hat{\mathbf{n}}_2 \]

$\gamma(\hat{\mathbf{n}}_2) < \gamma(\hat{\mathbf{n}}_1)$

\[ \rightarrow \text{ formation of pyramids} \]

\[ \rightarrow \text{ faceting} \]

\[ \rightarrow \text{ integrated total excess free energy can be lower} \]
Surface Relaxation, Reconstruction, Vacancy Formation

Allows surface energy to be minimized by relaxation of surface atom displacement, but usually involves vertical displacement as well.

Reconstruction: lateral surface atom rearrangement of surface atoms of a simple cubic lattice with lattice constant a.

Fig. 3.6a-c: Schematic side view of the characteristic near-reconstructed surface atomic structure of a surface as seen in a (a) relaxed and a (b) near-reconstructed state of the topmost atomic layer. A surface atom moves to a position above the second layer. (c) Missing row reconstruction, where an atom is missing in the topmost surface plane.

GoAs (110) – (1x1)

Non-Reconstructed

Relaxed

(a) Top View

(b) Side View

(c) Sphere Model (Side View)

Fig. 3.6a-c: Atomic positions of the GoAs(110) surface, ideal, non-reconstructed and relaxed as it appears after cleavage in SFV. (a) Top view: the (1x1) unit cell is plotted as a function of the sphere model. (b) Side view: GoAs sphere model. (c) Sphere model: GoAs sphere and shaded circles As. Smaller circles lattice plane, larger circles As. Larger circles lattice plane.

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Of course, the surface may not always be able to achieve the state of lowest energy due to kinetic limitations. The ball is trapped in the higher energy well unless it can gain enough kinetic energy to get over the barrier.

Example: Si (111) surface. This surface can be cleaved at RT but it adopts the metastable 2×1 reconstruction.

\[
\text{Si: } \text{cleave to produce (111) face } \rightarrow 2\times1 \text{ structure}
\]

By heating the Si (111) 2×1, it is possible to overcome the energy barrier and the surface will go to the more stable 7×7 structure.
Surface facetting begins with atomically smooth surfaces.

\[ \text{heat} \]

Resulting in a larger total surface area.

but \( \Delta G \) is perhaps smaller for other facets.

\[ \Rightarrow \text{overall smaller total surface energy} \]

The heating process allows mass transport to occur and thus the surface can attain a lower energy.
The size of the surface unit cell does not necessarily have to be different compared to the bulk-like surface unit cell, even if there is a reconstruction. Example: GaAs (110)-(1x1)

Reconstructions which change the size of the surface unit cell

\[ \text{Ex. Si (001)} \]

In fact, it gets yet more complicated for Si (001) as temperature is lowered, dimers appear in STM images to go from symmetric to buckled.
Dimers on the Si(001) Surface

Unbuckled

Buckled
The Influence of the Defects:
Two Basic Categories:

1. Symmetrical-Type
   - missing dimer defects
   - buckling appears to terminate
   - buckling doesn’t appear to be induced

2. Asymmetrical-Type
   - "C-type" defects
   - buckling doesn’t appear to terminate
   - bucking appears to be induced

202 K
Data Analysis: Counting Buckled Dimers

(a) Topographic Image

(b) Curvature Image

Identification of Buckling

Si(001) Surface Reconstructions

Unbuckled Dimers

2x1

Buckled Dimers

p(2x2)  c(2x4)
but after heating above a certain critical temperature, the structure transitions irreversibly to the 7x7 reconstruction.
FIGURE 5. The dimer-adatom-stacking fault (DAS) model by Takayanagi et al. Top view: atoms in (111) layers at increasing depth are indicated by circles of decreasing sizes. The shaded circles represent the 12 adatoms per unit cell, and the 6 rest atoms are shown as solid circles. The left half of the unit cell contains the stacking fault. 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.

The $S_1$ surface state has a peak position that is $\leq 0.2$ eV from the Fermi level, and the high-energy cut-off is very similar to the Fermi edge of a metal surface. This metallic character of the $7 \times 7$ surface has also been found in electron-energy-loss measurements, where it results in a very strong broadening of the elastic peak. The emission intensity of the $S_1$ surface state has a characteristic variation with the parallel wavevector, $k_y$, i.e., the emission intensity has a maximum approximately halfway between the $\bar{\Gamma}$-point and the SBZ boundary. It has been suggested that the $S_1$ structure results from extrinsic effects, since it was seen with very low intensity in some studies. It is interesting to note that in those studies the published spectra were all obtained at emission angles for which the inten-
Math: Notation for Si (001)

bulk unit cell

\[ \mathbf{r}_b = m \mathbf{a}_1 + n \mathbf{a}_2 \quad \mathbf{a}_1 = [110] \]
\[ a_2 = [110] \]

\[ \mathbf{b}_1 = m_1 \mathbf{a}_1 + m_2 \mathbf{a}_2 \]
\[ \mathbf{b}_2 = m_{21} \mathbf{a}_1 + m_{22} \mathbf{a}_2 \]

\[ \mathbf{b}_1 = \mathbf{a}_2 \Rightarrow m_{11} = 1 \quad m_{12} = 0 \]
\[ \mathbf{b}_2 = 2 \mathbf{a}_1 \Rightarrow m_{21} = 0 \quad m_{22} = 2 \]

\[ M = \begin{pmatrix} 1 & 0 \\ 0 & 2 \end{pmatrix} \]

\[ \det M = 2 \]

\[ \Rightarrow \mathbf{B} = 2 \mathbf{A} \]