

SURFACE STRUCTURE

Where atoms are can have huge effect on properties (e. g., graphite vs. diamond) through changes in electronic structure.

Two types of structure:

Macroscopic (dislocations, roughness)
Arrangement of neighbors (crystallinity, vacancies, interstitial atoms)

Surfaces smooth to the eye are microscopically rough.

Mismatch between atomic planes (dislocations) produce terraces

Dislocation densities:

$10^6 - 10^8 / \text{cm}^2$ metals, ionic crystals
 $10^4 - 10^6 / \text{cm}^2$ semiconductors, insulators

Atoms in terrace = atomic density / dislocation density

$$(10^{15} / \text{cm}^2) / (10^8 / \text{cm}^2) = 10^9 \text{ atoms}$$



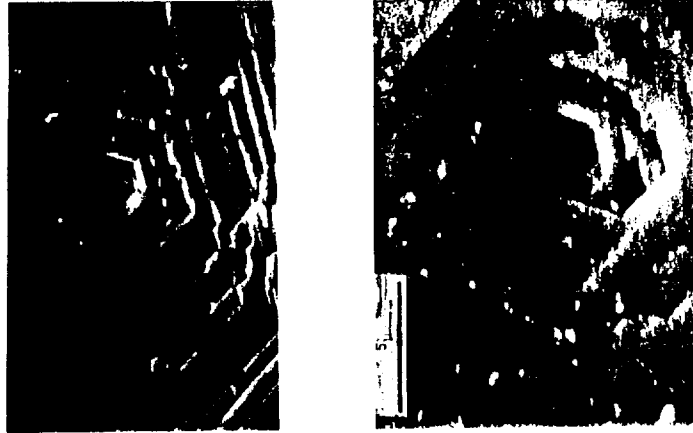


Figure 2.3. Scanning electron microscope picture of a zinc crystal surface at two different magnifications.

40 THE STRUCTURE OF SURFACES

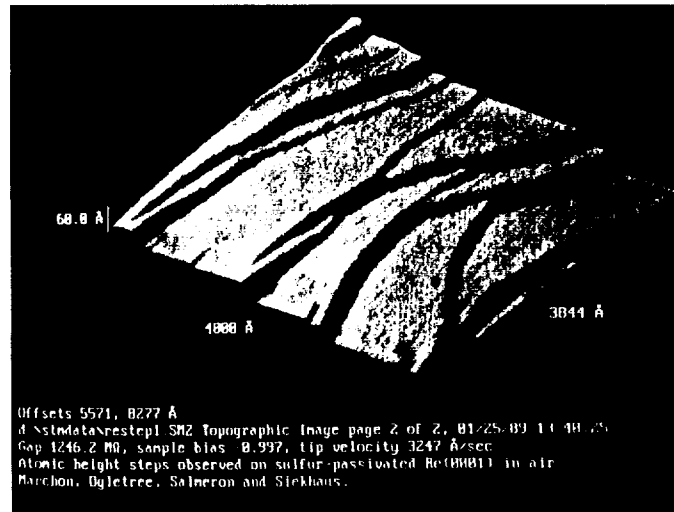


Figure 2.4. Scanning tunneling microscope (STM) picture of the (0001) face of rhenium over a $4000\text{-}\text{\AA}^2$ area.

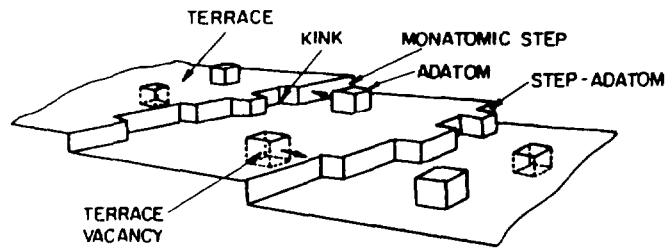


Figure 2.6. Model of a heterogeneous solid surface depicting different surface sites. These sites are distinguishable by their number of nearest neighbors.

Important aspect of structure is number of neighbors at each site (degree of bond saturation).

Rough surfaces have typically

**10 - 20 % atoms in step sites
5 % atoms in kink sites**

Vacancies and adatoms (thermally generated) are < 1 %, even at melting temperature.

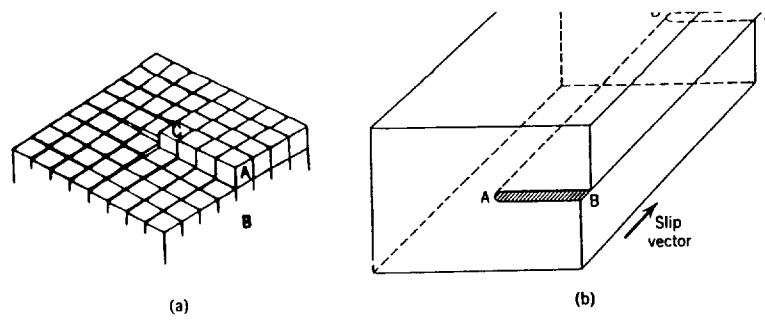


Figure 2.2. One type of screw dislocation giving rise to (a) atomic steps at the surface and (b) the slip plane that produces the dislocation and, ultimately, the defects at the surface (steps and kinks).

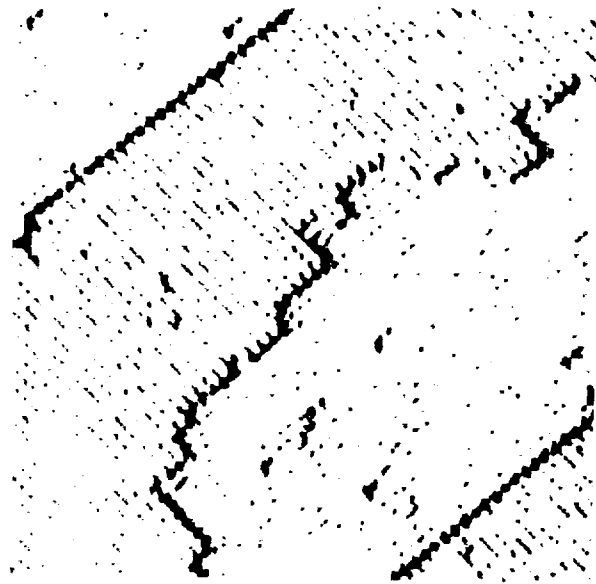
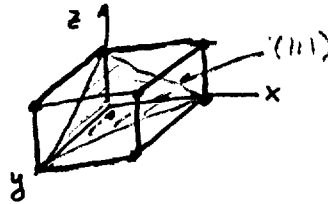


Figure 1.19 STM topograph of an Si (100) 2×1 reconstructed surface, showing monatomic height steps and the dimer rows formed in the reconstruction. (Source: B.S. Swartzentruber, Y.-W. Mo, R. Kariotis, M.G. Lagally, and M.B. Webb, *Phys. Rev. Lett.* 1990; 65:1913. Reprinted with permission.)

CRYSTALLOGRAPHY

3D



Miller indices

$[hkl]$ direction, e.g., $[111]$

$\langle hkl \rangle$ set of equivalent directions

e.g., $[100]$, $[010]$, $[00\bar{1}]$

(hkl) plane, indicates reciprocal of intercepts of planes with the three axis

For cubic lattices, (hkl) is \perp to $[hkl]$

For hexagonal lattice:

Miller Bravais indices $hkil$



Surfaces: only 5 different Bravais nets,

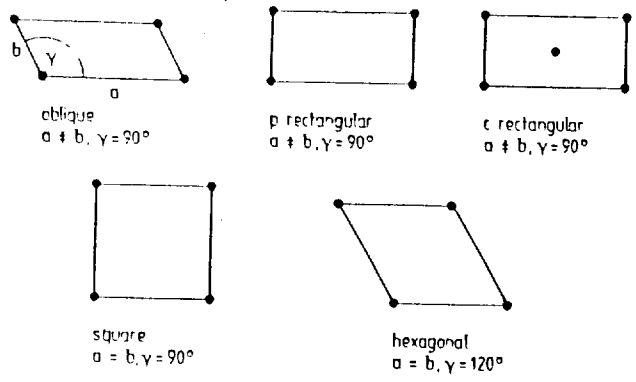


Fig. 3.9. Five possible two-dimensional (2D) Bravais lattices

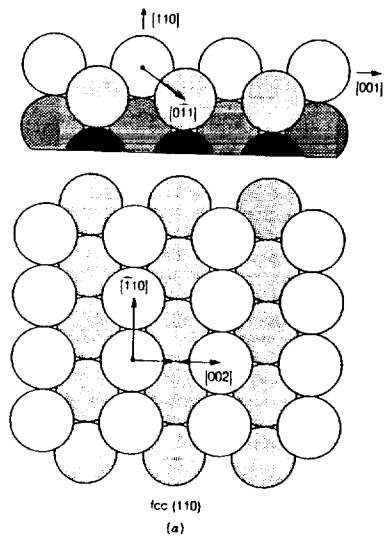
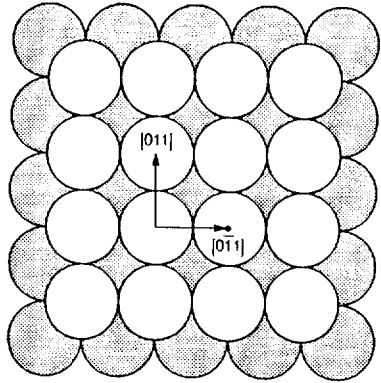
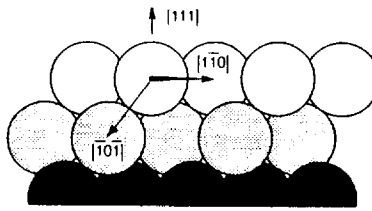
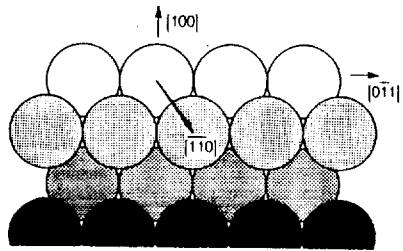
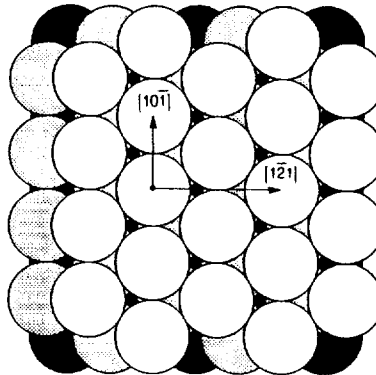


Figure 2.8. Top views and side views of the face-centered cubic (fcc) crystal surfaces: (a) (110), (b) (100), and (c) (111)

fcc (110)



fcc (100)
(b)

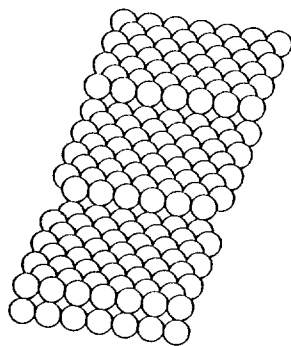


fcc (111)
(c)

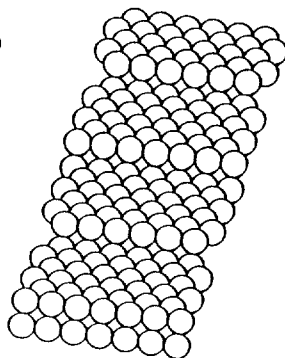
(100)

fcc

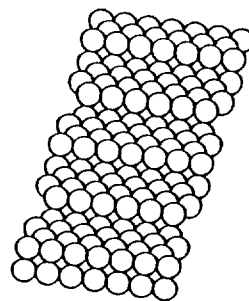
(111)



fcc {977}



fcc {755}



fcc {533}



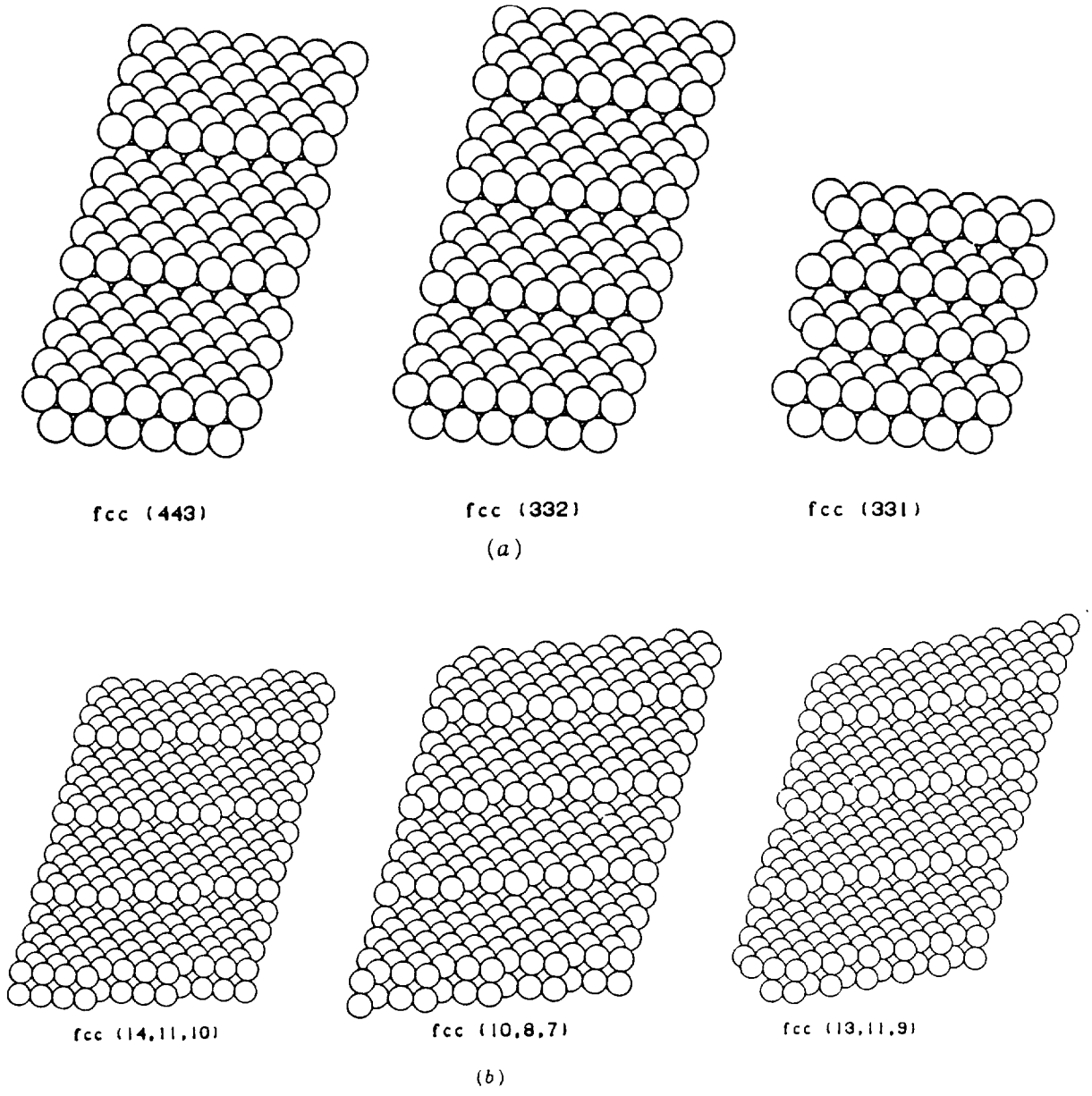


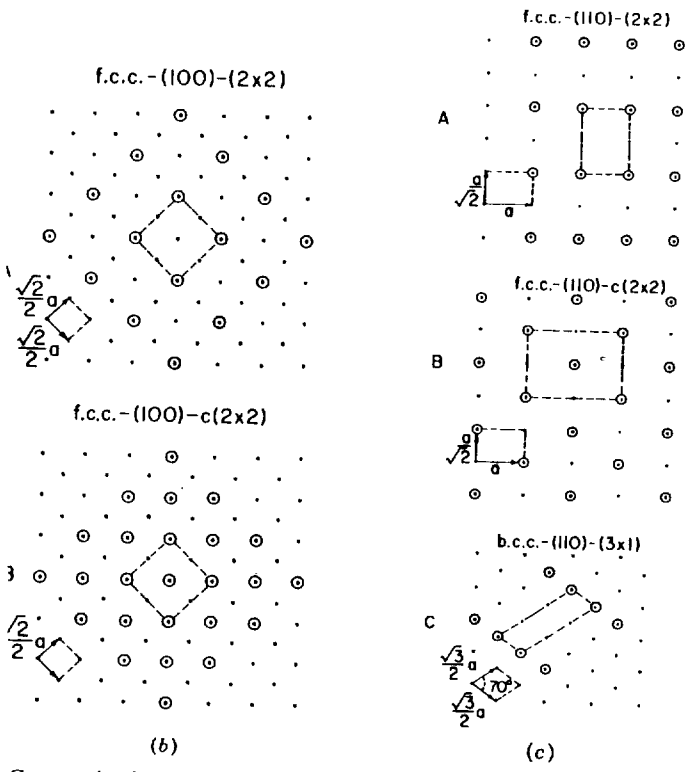
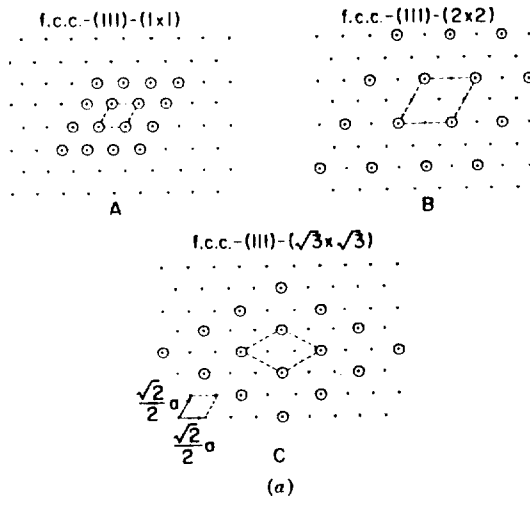
Figure 2.11. Schematic representation of the surface structures of several stepped (a) and kinked (b) crystal faces deduced from the bulk unit cell. Contraction of interlayer spacing and other modes of restructuring that are commonly observed are not shown.

Species in surface layer is appended to notation

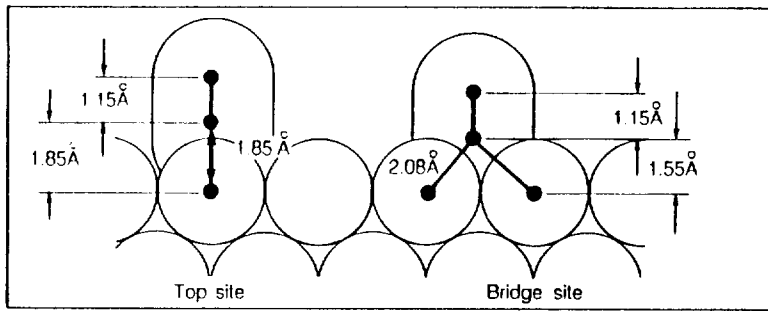
Rotation is denoted by: *R*angle (deg.)

Examples: W(211)-(2 x 2)-H

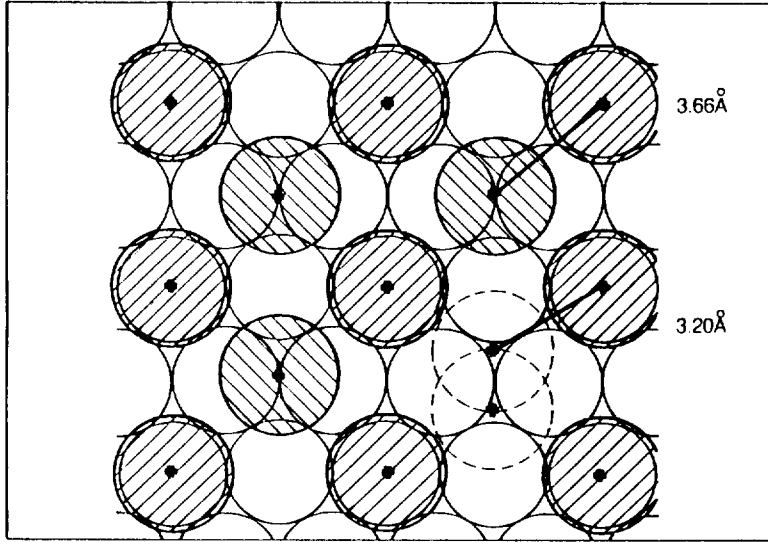
Pt(100)-($\sqrt{2}$ x $\sqrt{5}$)*R*45° - CO



Commonly observed unit cells of adsorbate surface structures on (a) the fcc(111) (b) the fcc(100) crystal face, and (c) the fcc(110) crystal face.



Side view



Top view

Pt (111)- c (4x2) - 2 CO
LEED Structure

**SOLID SURFACES ARE HETEROGENEOUS
AT ATOMIC LEVEL**

Terrace-step-kink model not right. Atoms do not stay at position expected from just the continuation of the bulk.

Rather, atom positions are shifted (relaxed)

- 1** _____
- 2** _____
- 3** _____
- 4** _____
- 5** _____

Relaxation: increases for more open (atomically rougher) surfaces

propagates a few layers into the bulk

occurs also at edges

can be induced by chemisorption

Another form of relaxation is reconstruction, where the surface has a different type of unit cell

It occurs particularly with covalent bonded solids.

Most semiconductor surfaces reconstruct (e. g., Si, Ge, GaAs, InSb)

Ex: Si(111)-(7x7)

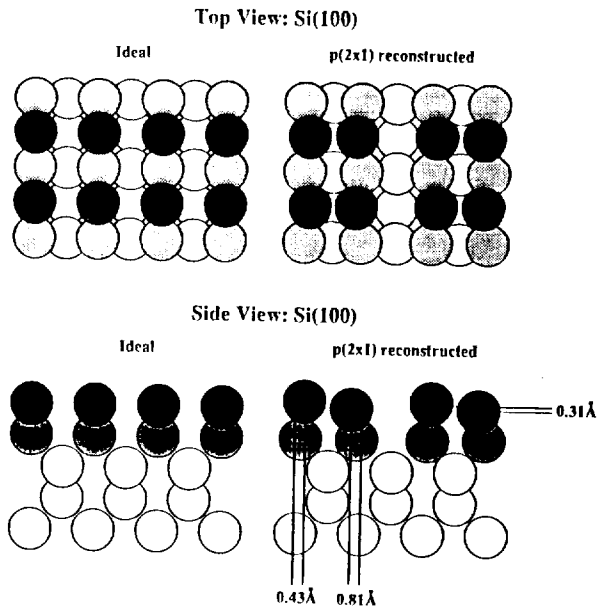


Figure 2.13. The reconstructed silicon (100) crystal face as obtained by LEED surface crystallography. Note that surface relaxation extends to three atomic layers into the bulk [166

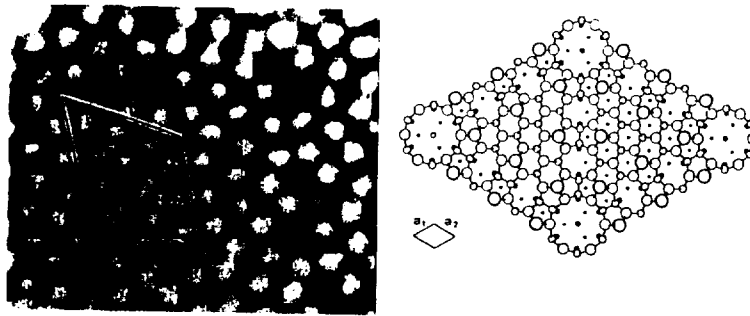
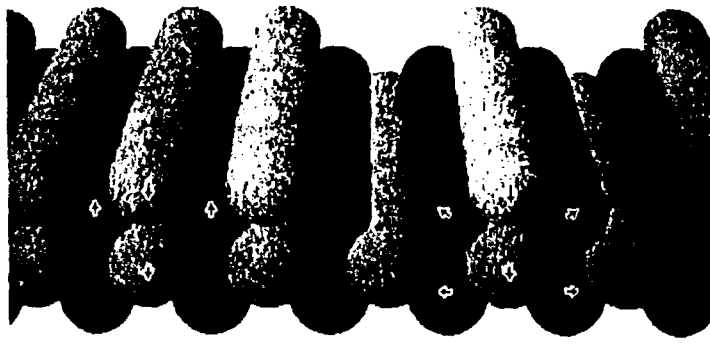


Figure 1.18 The Si (111) 7×7 surface as revealed by scanning tunneling microscopy. (a) STM image. The rhombic unit cell is outlined. The letters *F* and *U* refer to the faulted and unfaulted halves of the unit cell, as indicated in the accompanying model. (Source: R.J. Hamers, R.M. Tromp, and J.E. Demuth, *Phys. Rev. Lett.* 1986; 56:1972. Reprinted with permission.) (b) Schematic representation of surface. The adatoms are indicated by heavy circles; a stacking fault runs vertically across the center of the diagram. (Source: K. Takayanagi, Y. Tanashiro, S. Takahashi, and M. Takahashi, *Surface Sci.* 1985; 164:367. Reprinted with permission.)



fcc (110) (1x1) vs. (1x2)

Figure 2.15. The reconstructed iridium (110) crystal face obtained by LEED surface diffraction. Every second row of atoms is missing. Note that relaxation extends to the first few layers toward the bulk [169].

missing-row reconstruction in (110) surfaces

Many metal surfaces also reconstruct

Chemisorption can induce reconstruction

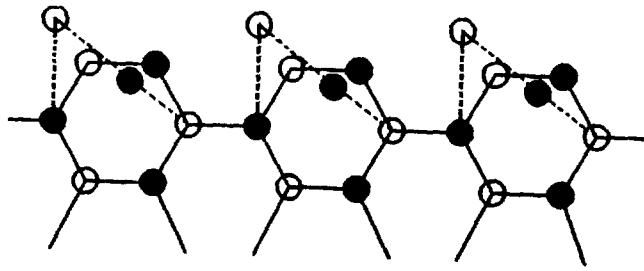


Figure 1.16 Reconstruction of the GaAs (110) surface. Solid line, ideal surface. Dotted line, reconstructed surface. (Source: C.B. Duke, *J. Vac. Sci. Technol.* 1976;13:761. Reprinted with permission.)

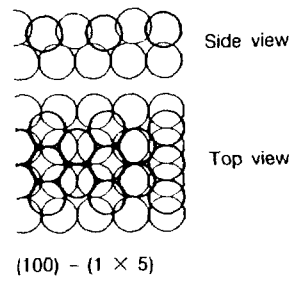
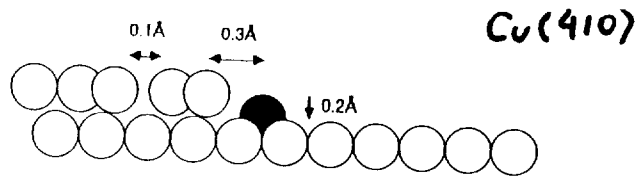
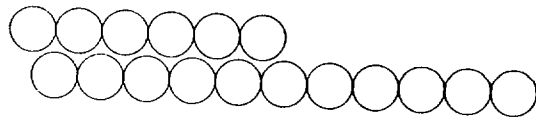


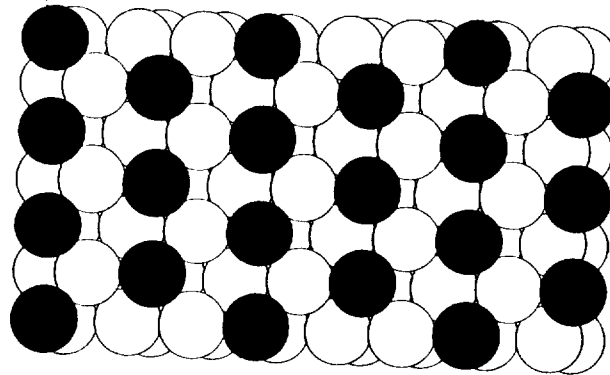
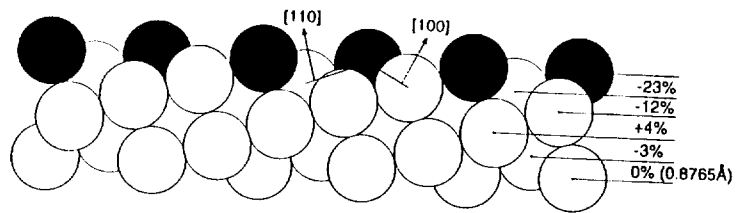
Figure 2.14. The structure of the reconstructed iridium (100) crystal face obtained from LEED surface crystallography. Hexagonal packing in the surface layer induces buckling. The second layer retains its square unit cell [167, 168].

2.5 RECONSTRUCTION



"Cracks" open close to the step edges

Each atom attempts to optimize its coordination



Pt (210)

(b)

Pt(210)

Figure 2.16. Relaxation at two different stepped surfaces: (a) Cu(110) [110]; (b) Pt(210) [111].

STRUCTURE OF ADSORBATE LAYERS

Determined by:

- **adsorbate-substrate interactions**
- **adsorbate-adsorbate interactions**

Depends on coverage θ ($0 < \theta < 1$). Ratio of number of adsorbate atoms to number of atoms in outer layer of substrate.

Low θ : adsorbates mobile - diffuse. If adsorbate-adsorbate interaction is:

- **attractive, they tend to form 2D clusters**
- **repulsive, they form disordered layers**

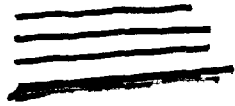
High θ : when adsorbate-adsorbate distance decreases to 5 - 10 Å, adsorbate-adsorbate interactions tend to form symmetric arrangements with some preferred energetically over others.

Higher exposure (Langmuir = 10^{-6} Torr sec) does not increase θ , but may result in incorporation and diffusion into bulk

**Case of physisorption (physical adsorption):
adsorbate-adsorbate interaction stronger than adsorbate-substrate interactions.
Produces incommensurate 2D structures.**

**Case of metallic overlayers:
stronger interactions
epitaxy possible
interdiffusion possible**

Growth modes on metal surfaces



Layer by layer (Frank - von der Merwe growth). 2nd layer does not begin until first is completed



Monolayer plus 3D islands (Stranski - Krastanov growth)



3D islands from the beginning (Volmer - Weber growth)

CHARACTERIZATION OF SURFACE STRUCTURE

Diffraction techniques

<u>LEED</u>	Low Energy Electron Diffraction
<u>RHEED</u>	Reflection High Energy Electron Diffraction
<u>XPD</u>	X-ray Photoelectron Diffraction
<u>SEXAFS</u>	Surface Extended X-ray Absorption Fine Structure
<u>AD</u>	Atom or Helium Diffraction
<u>XRD</u>	X-ray Diffraction

Scattering techniques (steering effects)

<u>MEIS</u>	Medium Energy Ion Scattering and Channelling
<u>ISS/LEIS</u>	Ion Scattering Spectroscopy/Low Energy Ion Scattering

Direct imaging techniques

<u>FIM</u>	Field ion Microscope
<u>STM</u>	Scanning Tunneling Microscope
<u>AFM</u>	Atomic Force Microscope