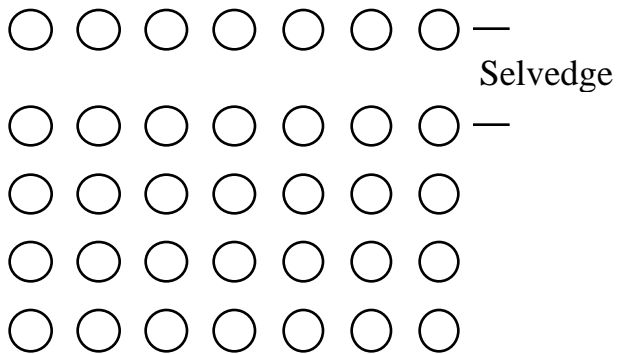
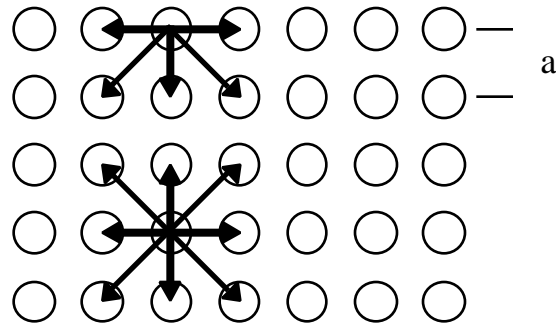


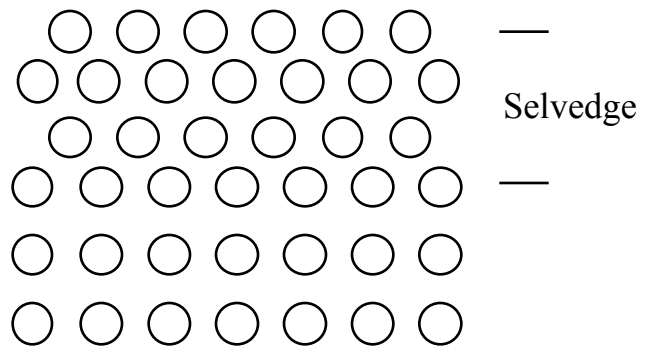
2.4 Real Surfaces

2.4.1 Surface Relaxation and Reconstruction

Atoms at surface experience different bonding environment than bulk - causes *relaxation* and *reconstruction*



Relaxation



Reconstruction

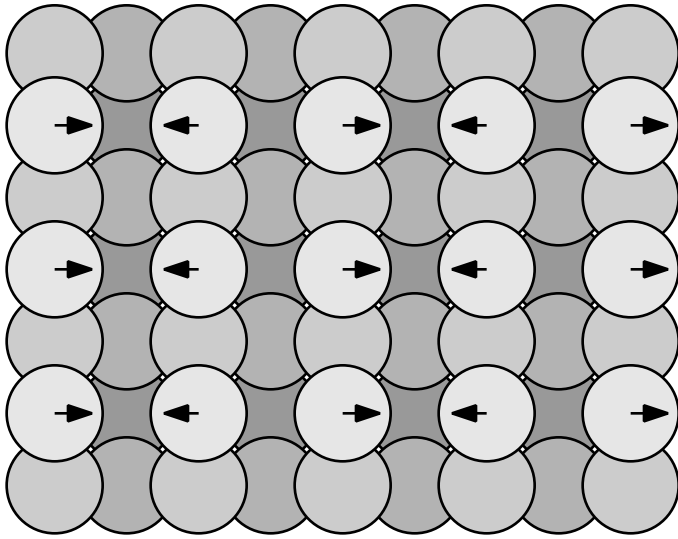
Surface	Bulk Spacing (Å)	Layer Spacing (Å)	Expansion (%)
Ag(110) FCC	1.44	1.33	-7.6
		1.50	4.2
Ag(111) FCC	2.35	2.35	0.0
Al(100) FCC	2.02	2.02	0.0
Al(110) FCC	1.43	1.30	-8.8
		1.50	4.8
		1.40	-1.8
Fe(100) BCC	1.43	1.41	-1.6
Fe(110) BCC	2.02	2.04	0.5
Fe(111) BCC	0.83	0.70	-15.4
Fe(210) BCC	0.64	0.50	-21.9
		0.57	-10.9
		0.61	-4.7
		0.64	0.0

Driving force is each atom attempts to minimize energy/maximize coordination.

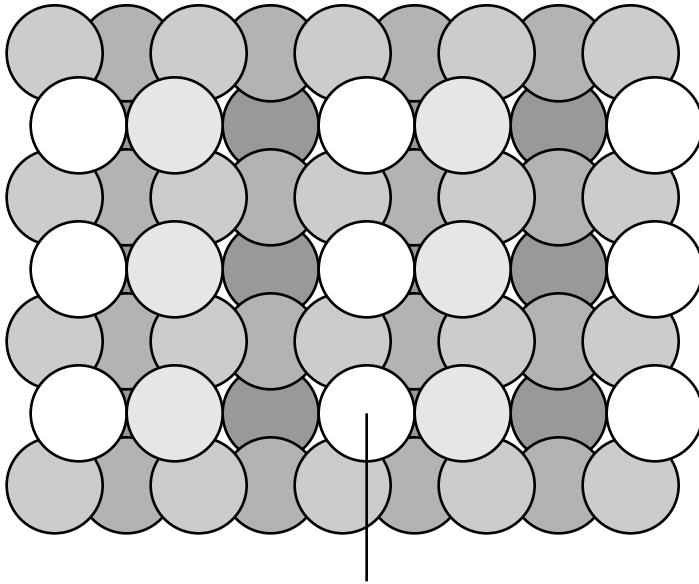
"Open" surfaces (stepped, BCC(100), BCC(110)) show more relaxation and reconstruction. Only minor for close-packed FCC(111), FCC(100)

Reconstruction can also occur in-plane of surface

0.43 Å — — 0.81 Å

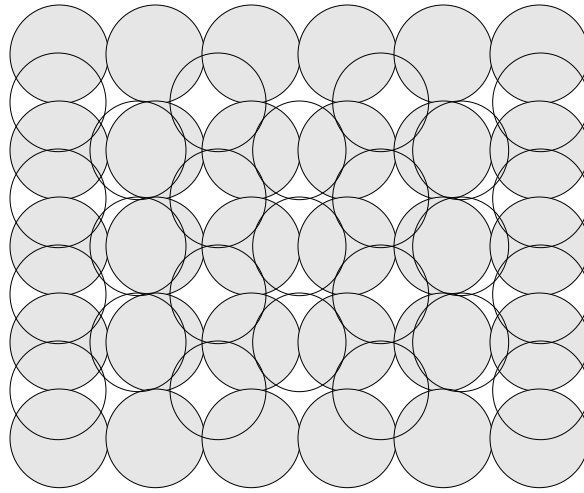


Si(100) Top View
Bulk termination



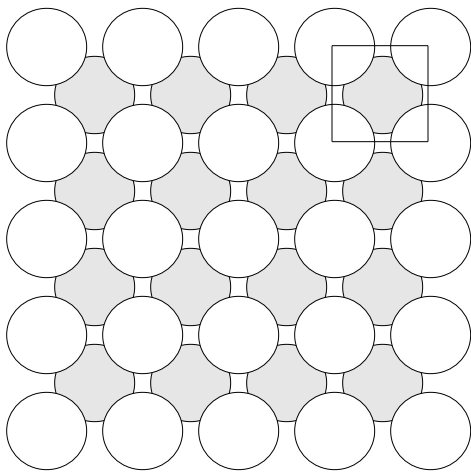
Si(100) Top View
(2x1) Buckled dimer
row reconstruction

0.31 Å higher

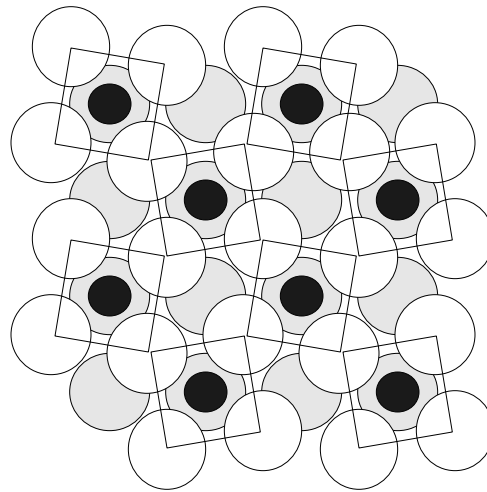


Ir(100) - (1x5) reconstruction

Adsorbed molecules can induce reconstruction - *adsorbate induced reconstruction*. Again, open or rough surface reconstruct more readily.



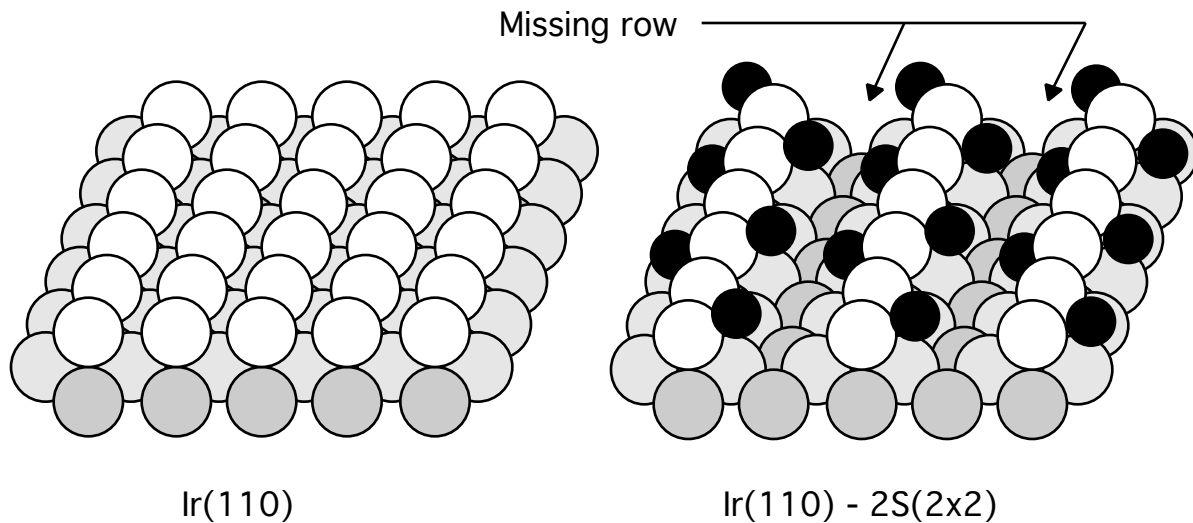
Ni(100)



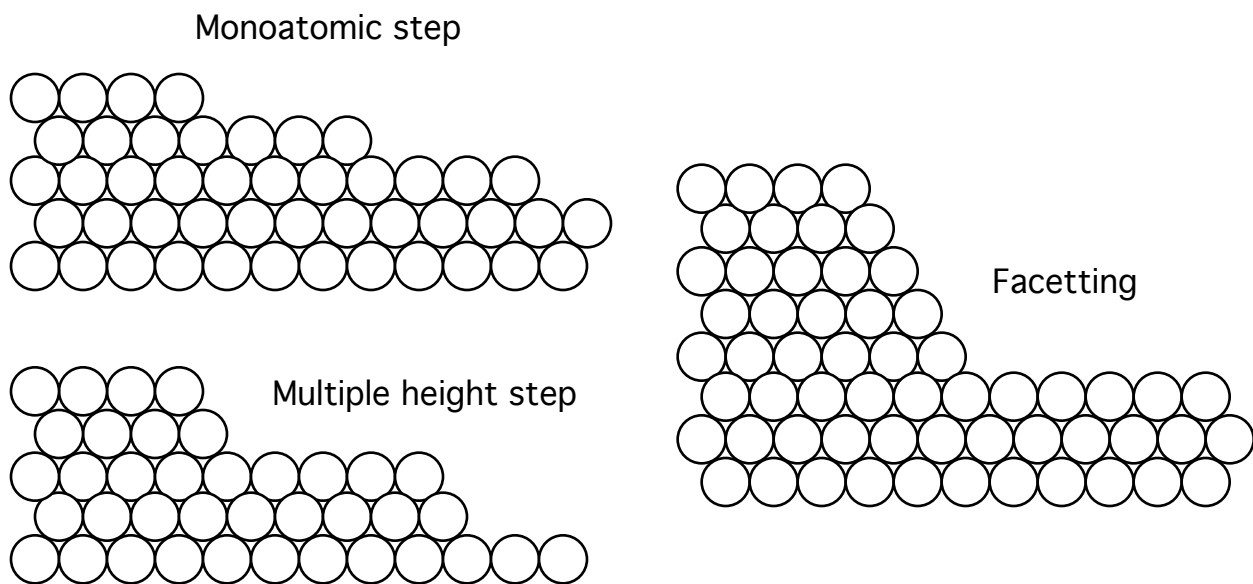
Ni(100) distorted c(2x2)-CO

Driving force is adsorbate-substrate bonding that is comparable or stronger than substrate-substrate.

Missing row reconstruction is quite common - adsorbates form rows in troughs created by missing row.



In extreme cases (adsorbate-induced or clean) may get *facetting*



2.5 Surface Defects

A defect is a break in periodicity (lattice or basis)

Any real crystalline material will contain defects

In close-packed metals, defects 10^{-2} - 10^{-4} % at room temp.

In some alloys (carbides), vacancy defects may approach 50 % at room temp.

Energy required to create defect is offset by entropy gain

When enthalpy and entropy are equal - equilibrium

$$n_{\text{defects}} = n_{\text{lattice points}} \exp \frac{-E_{\text{defect}}}{kT}$$

Purposely added impurities called *dopants*

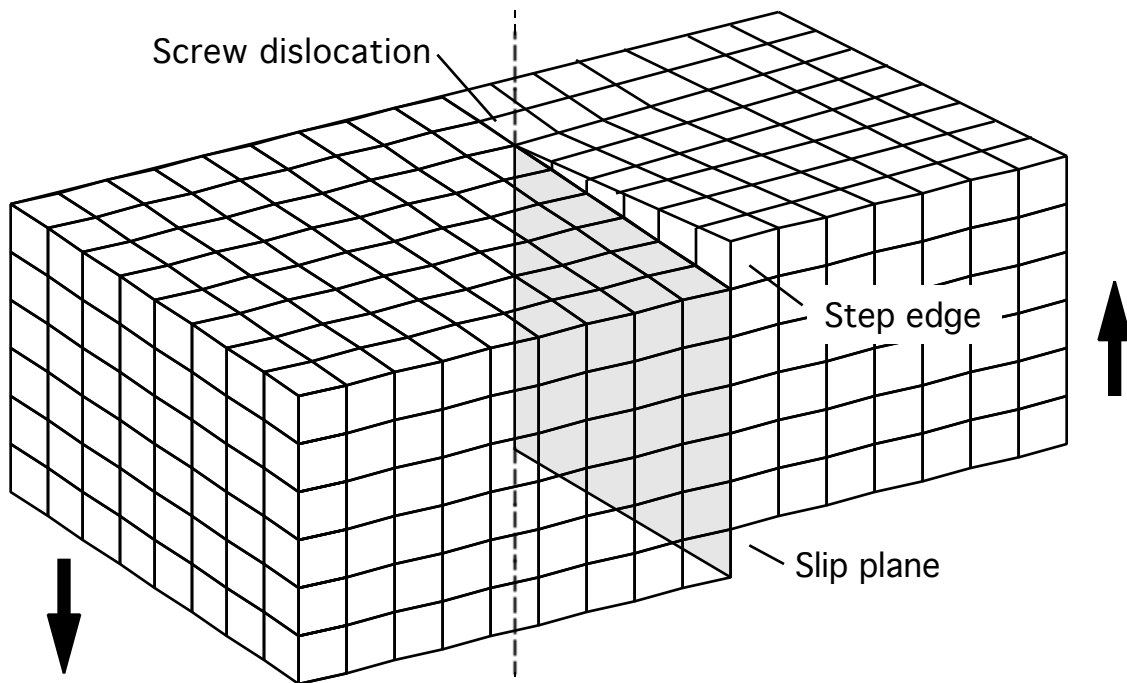
Several types of defect

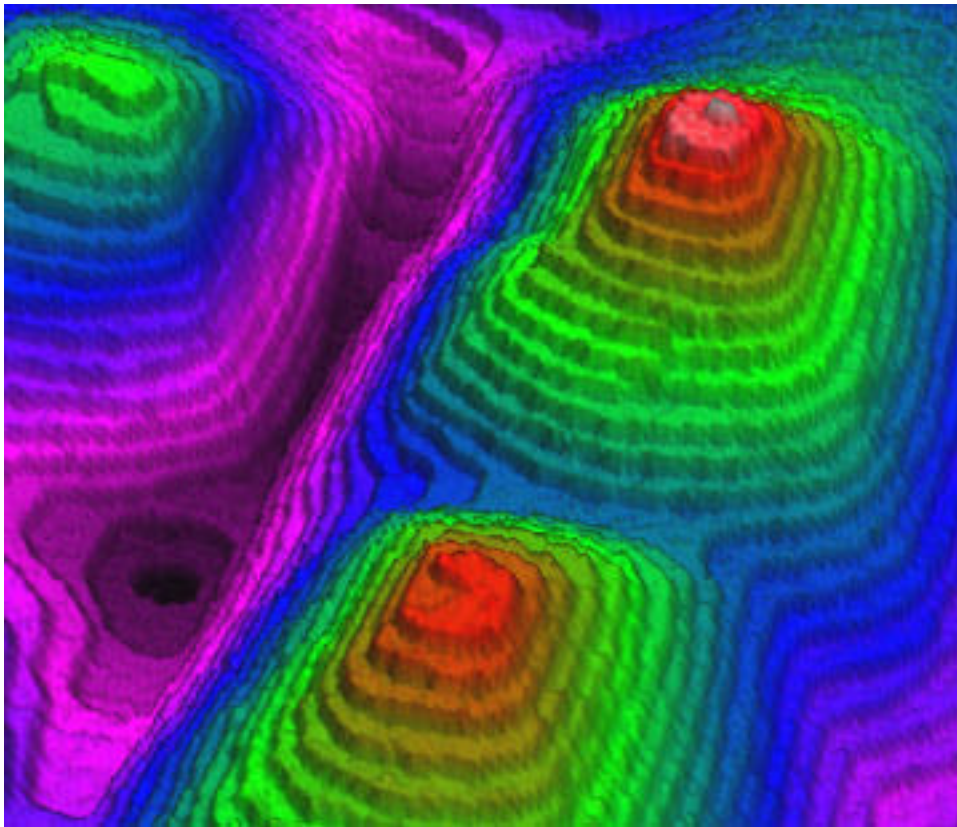
some have origins in bulk

some have origins at surface

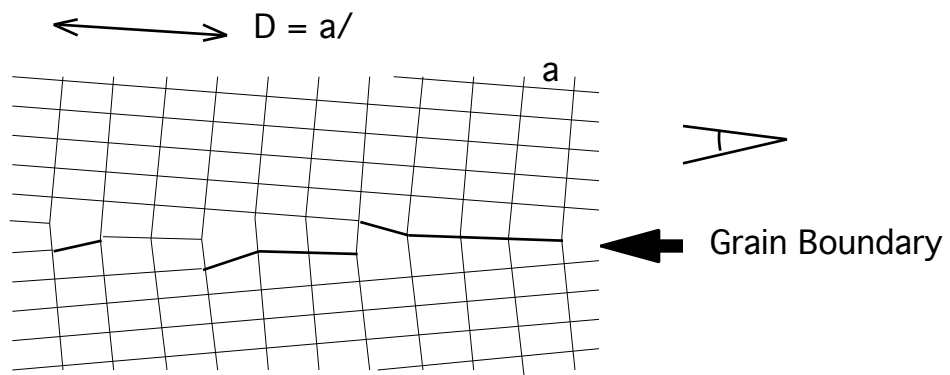
2.5.1 Bulk Defects

May be (i) extended or (ii) point





10 μm x 10 μm GaSb screw dislocations (3 \AA high steps)



2.5.2 Surface Defects

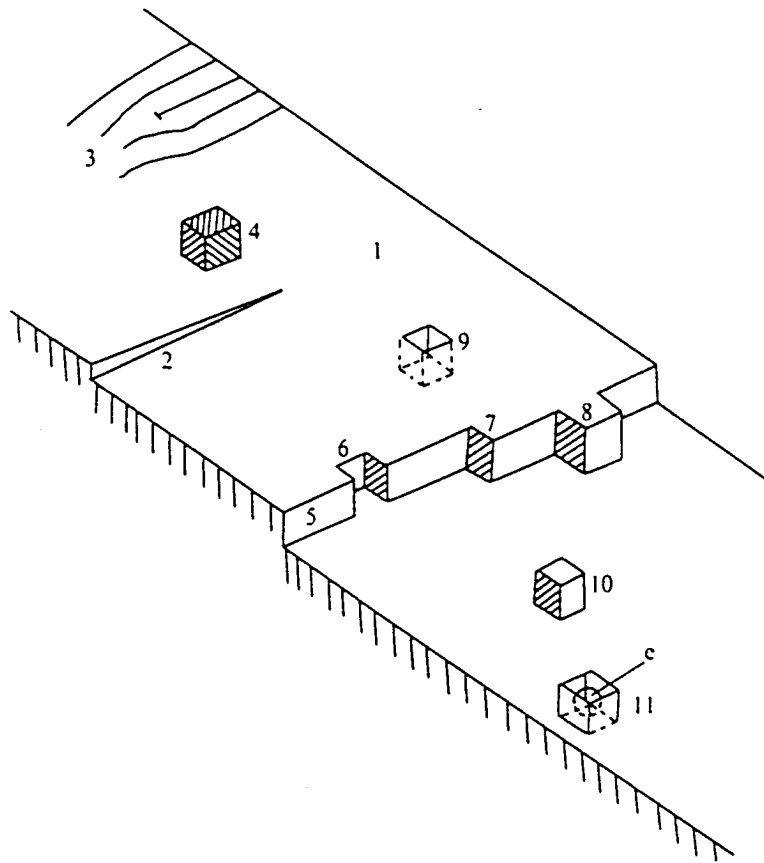


FIG. 5.4. Some simple defects that are often found on a low-index crystal face. 1. The perfect flat face itself – a terrace; 2. an emerging screw dislocation; 3. the intersection of an edge dislocation with the terrace; 4. an impurity adatom (adatoms are discussed in Chapter 6); 5. a monatomic step in the surface – a ledge; 6. a vacancy in the ledge; 7. a step in the ledge – a kink; 8. an adatom of the same kind as the bulk atoms situated upon the ledge; 9. a vacancy in the terrace; 10. an adatom on the terrace; 11. a vacancy in the terrace where an electron is trapped – in an alkali halide this would be an F-centre.

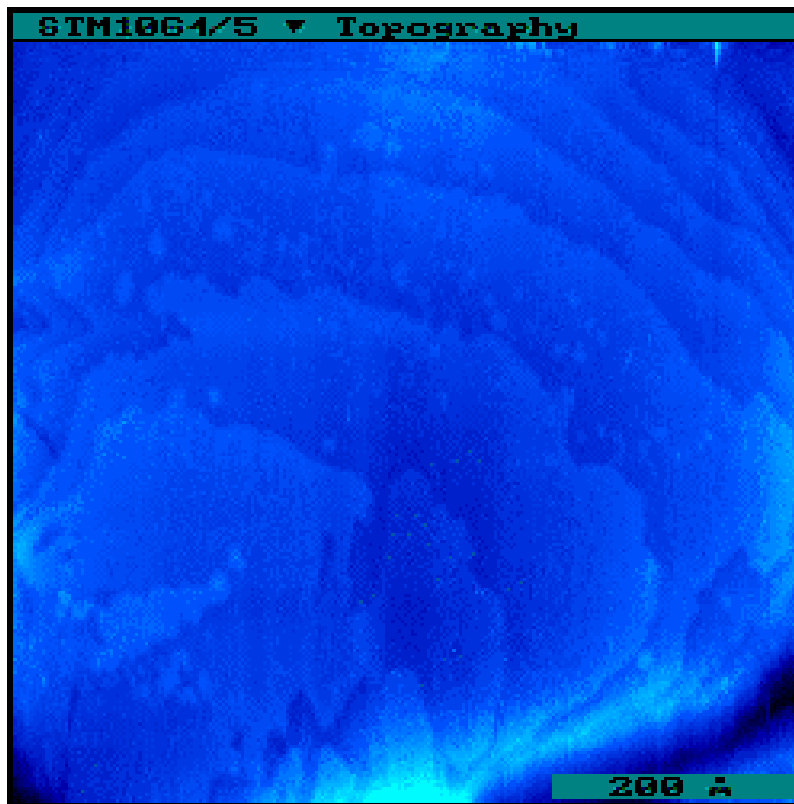
All real surfaces show *defects*

Surfaces may show *domain structure* - often observed for ordered monolayers

Vicinal (stepped) surface structure is an "average"

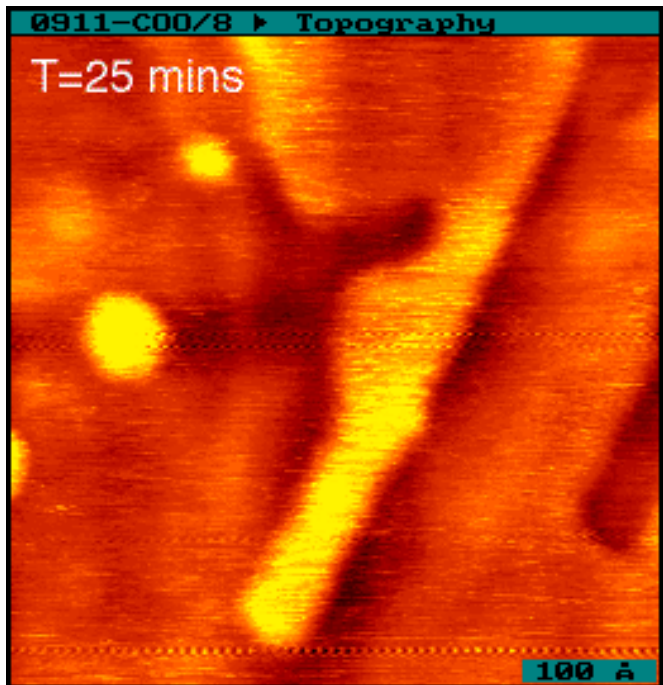
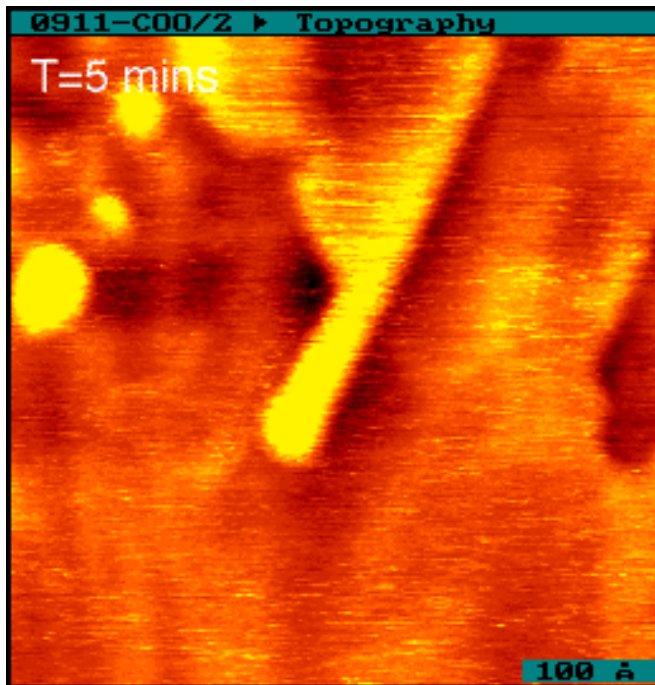
Step edges often "repel" each other - steps are sites of extra electron density

A well-prepared low-index metal surface contains 0.1-1 % defects



Defects are sites of high reactivity - may dominate surface chemistry

Adatoms often diffuse to step edges or vacancies - surface may be quite dynamic - $E_a(\text{diffusion})$ 15 (metals)-30 (insulators)% $E_a(\text{desorption})$



Au(111) surface self-diffusion at room temperature

2.6 Surface Preparation

UHV ensures that gaseous species will not contaminate surface during experiment

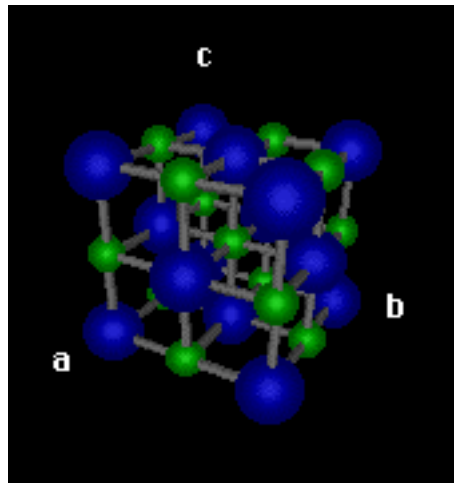
But, surface often must be cleaned (<few % foreign atoms) *ex* or *in situ* and well-ordered (minimize defects)

Mechanical means (scraping, polishing) can remove gross surface layer but usually leave surface microscopically rough and/or contaminated

Electrochemical (CV cycling) techniques can be used to clean surface but not compatible with UHV hardware

2.6.1 Cleavage

Some materials possess natural cleavage planes (mica, graphite, alkali halides, some oxides (MgO), layered semiconductors (GaAs), layered inorganics)



NaCl cleaves along equivalent (001), (010) and (100) planes

Simple method to produce large flat areas

Limited control over surface plane

Act of cleaving in air may produce transient reactive sites

Cleavage may produce metastable surface compared with heated surface (Si(111)7x7 reconstruction)

Unreliable

Cleavage in vacuum difficult

Limited number of cleaves

2.6.2 Heating

Heating in vacuum may desorb some weakly bound surface species - some carbonaceous materials, oxides, water:

W oxides decompose/desorb near melting point

Carbonaceous material desorbs/decomposes at 250 °C for NaCl, LiF

Graphite can be prepared by cleaving in air followed by heating (annealing) in vacuum at up to 750 K

Annealing minimizes number of defects by increasing bulk and surface diffusion rates:

Heat at 50-80 % of melting point

Surface melting may occur considerably before melting point of bulk

Rapid bulk evaporation creates rough surfaces

Heating may create irreversible surface structures (Si(100)-2x1 buckled dimer rows) or reconstruction (Au(111)-23x 3)

Heating may *increase* contamination at surface - surface segregation:

S in Fe

Ca in MgO

C, O in Ti

One component of alloy

Once removed, cleaning time is greatly reduced

2.6.3 Ion Bombardment (Sputtering)

Bombardment of surface by Ar (Xe, Ne, He) ions

500-5000 eV KE, 10^{-2} - 10^3 μ A

Beam is defocussed to cover entire sample or rastered

Sputtering is quite efficient - $S > 1$

$$S = \frac{\text{number of atoms removed}}{\text{number of incident ions}} \quad \text{Sputtering Yield}$$

S varies by material - f(cohesive energy):

Difficult to calibrate sputtering rate

In multielement materials get preferential sputtering

Large fraction of incident energy deposited in near-surface region - disorder, mixing, embedded noble gas atoms

Surface must be annealed - repeated segregation?

Require cycles of sputtering and annealing until segregants are depleted and removed from bulk

2.6.4 Chemical Treatment

Heating in partial pressure (10^{-7} - 10^{-5} mbar) of reactive gas

O₂ for carbide/hydrocarbon removal

H₂ for O removal

Successful in specific cases only (carbon on refractory metals)

2.6.5 Film Deposition

Evaporation or sputtering of atoms from material of interest and deposition onto new substrate

Some materials undergo stoichiometry changes during evaporation/sputtering

If lattice size/symmetry of deposited material and substrate not compatible get little control of film morphology

Islanding, polycrystallinity, strained structures, rough surfaces

Epitaxial (pseudomorphic) growth occurs when substrate acts as a template (controls) geometric growth of deposited film.

