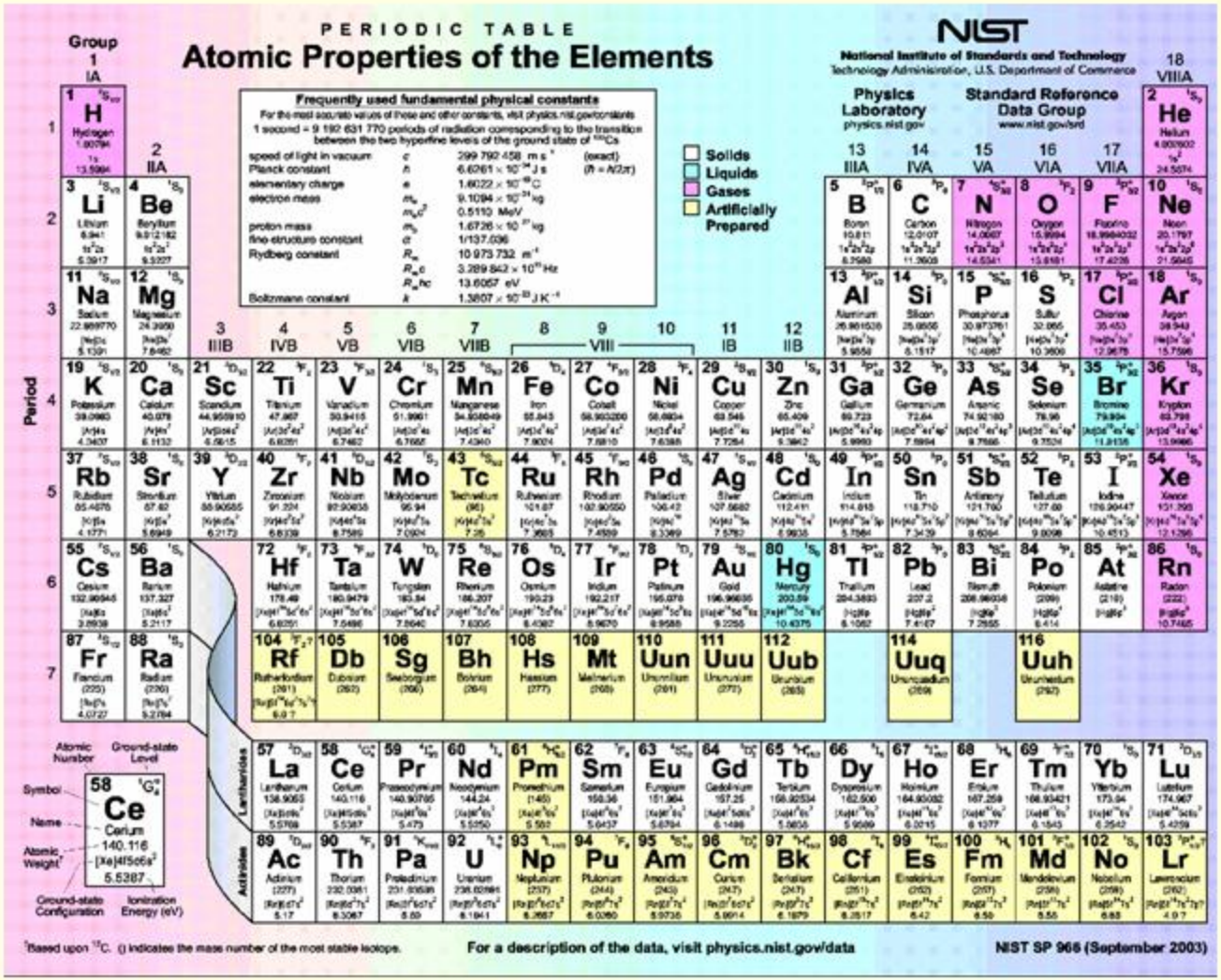
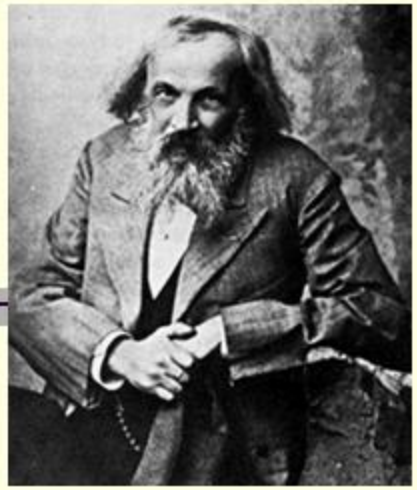
Material Science

Basic Concepts

Periodic Table

D. Mendelejeff, *Zeitschrift für Chemie* **12**, 405-6 (1869)





Dimitri Mendeleev
(1834-1907)

Classification of Solids

- Atomic structure (geometry)
- Electronic structure (bonding)
- Chemical composition
- Morphology (defects)

- Physical and chemical properties

Classification of Solids

- **Atomic structure (geometry)**
- Electronic structure (bonding)
- Chemical composition
- Morphology (thin films)

SOLID

CRYSTALLINE

7 symmetry groups

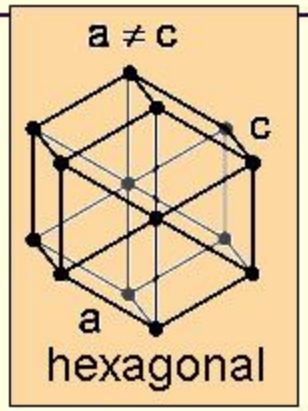
polycrystalline
(most of solid-state materials)

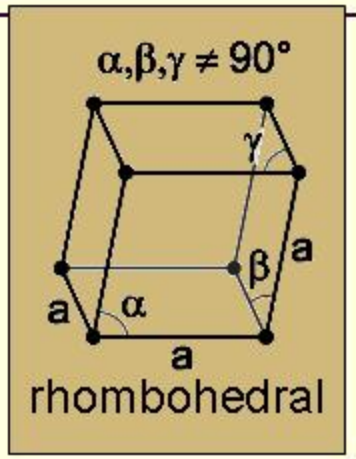
NON-CRYSTALLINE

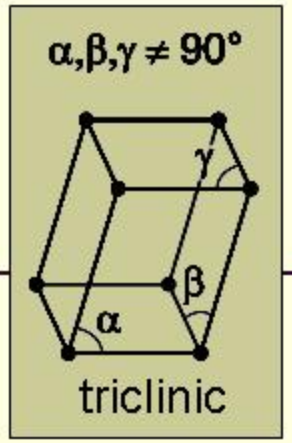
amorphous (glass)

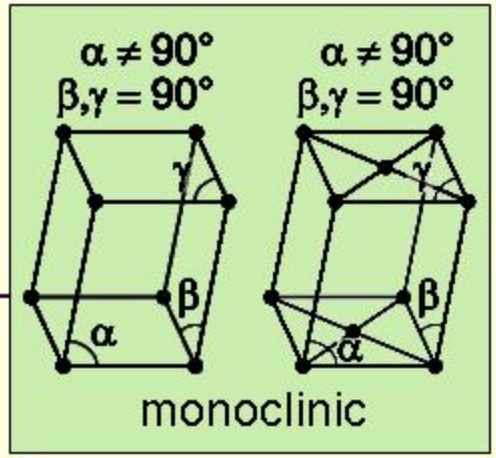
7 Crystal Systems

14 Bravais lattices

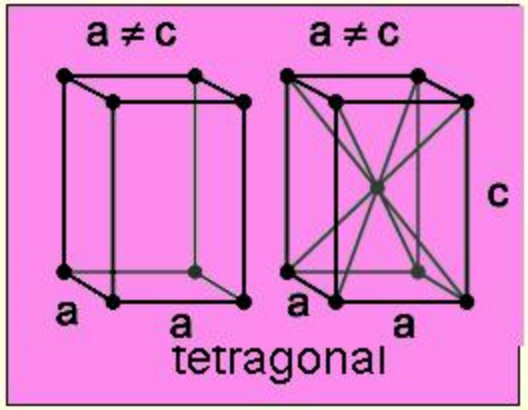


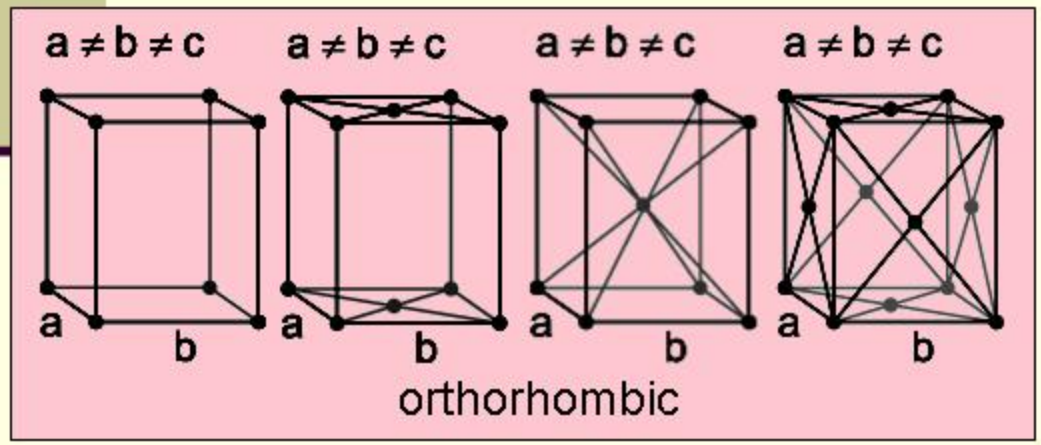


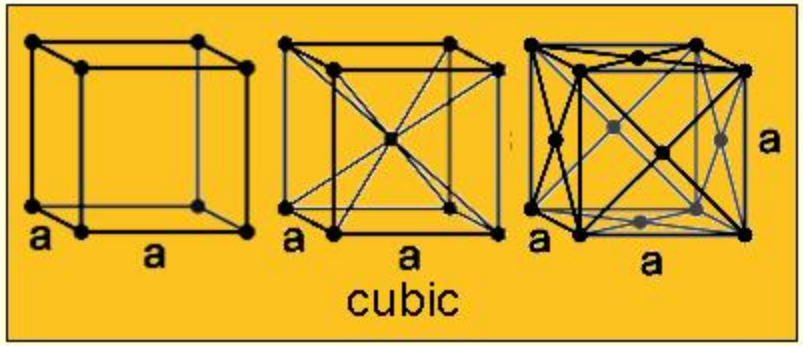




Unit cells







http://www.answers.com/topic/crystal-structure

Crystallographic Planes

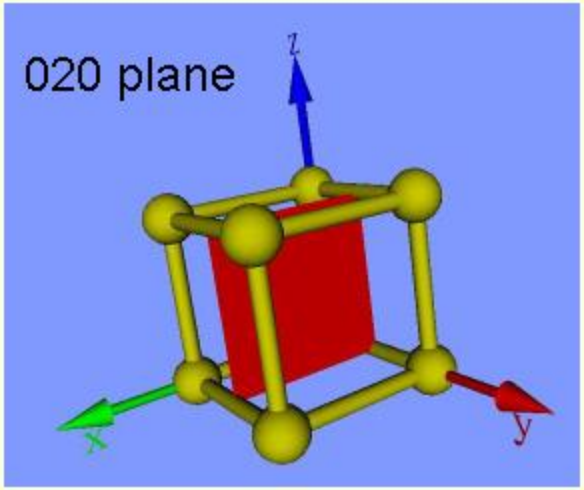
Miller Indices **are used to identify planes in a crystal:**

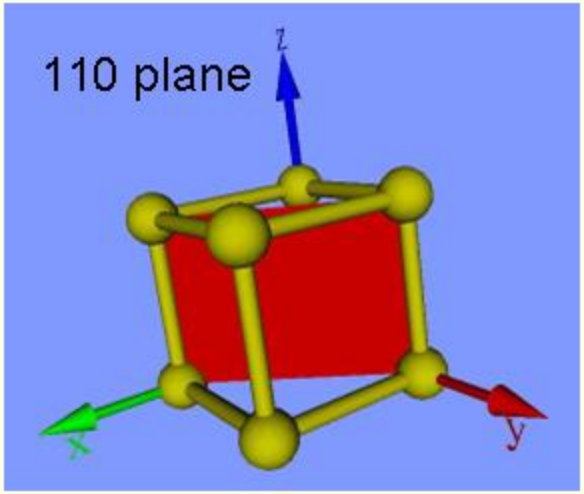
- **Determine the points at which the plane intercepts the x, y, and z coordinates. If the plane passes through the origin, shift the origin of the coordinate system.**
- **Take reciprocals of the intercepts.**
- **Clear fractions by reducing to the lowest integers by a common factor.**
- **Negative numbers should be written with a bar over the number.**

$x = \infty$

$y = \frac{1}{2}$

$z = \infty$





$x = 1$

$y = 1$

$z = \infty$

http://www-vrl.umich.edu/project2/miller/

Crystallographic Planes

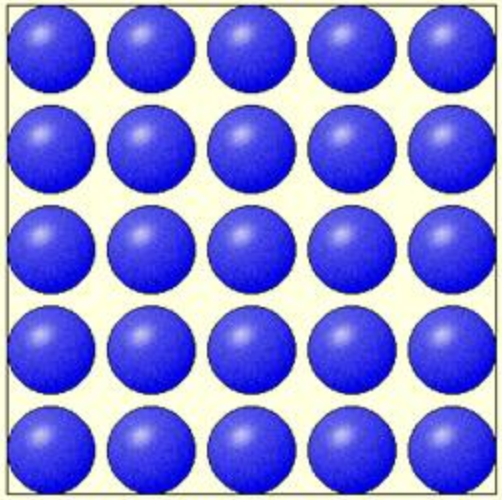
In the cubic system the (*hkl*) plane and the vector [*hkl*], defined in the normal fashion with respect to the origin, are normal to one another but this characteristic is unique to the cubic crystal system and does not apply to crystal systems of lower symmetry.

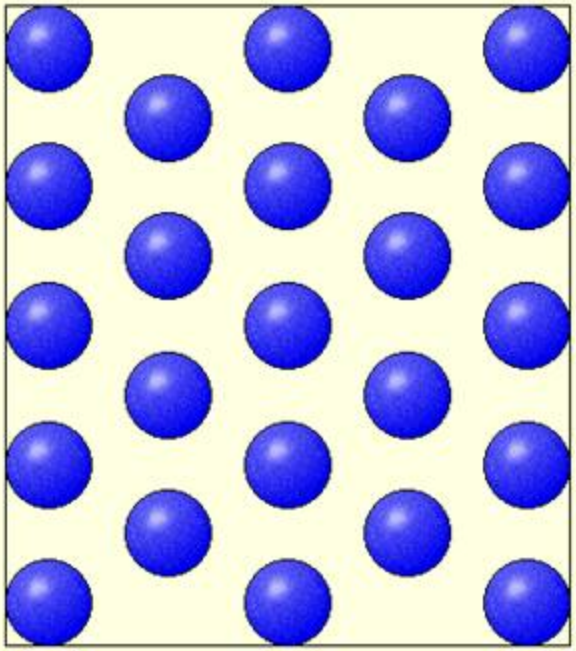
Crystallographic Planes

Crystallographic planes have different atom layouts

= different bond strength = anisotropy

BCC 001



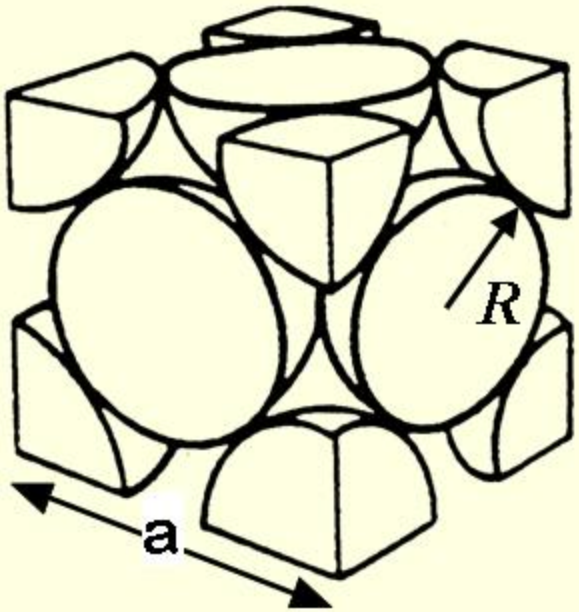


BCC 111

Surface explorer by Klaus Hermann & Fritz Rammer; http://w3.rz-berlin.mpg.de/~rammer/surfexp_prod/SXinput.html

Packing Ratio

$$PR = \frac{\text{volume occupied by atoms}}{\text{unit-cell volume}}$$



- diamond 0.34
- cubic 0.52
- BCC 0.68
- FCC 0.74
- Hex. 0.74

$$a = 2R \cdot \sqrt{2}$$

FCC unit cell contains 4 atoms

volume of the atom

FCC

$$PR = \frac{4\,\frac{4}{3}\pi R^3}{a^3} = \frac{4\,\frac{4}{3}\pi R^3}{8R^3\,2\sqrt{2}} = 0.74$$

Theoretical Density

atoms/unit cell

atomic weight, g/mol

$$\rho = \frac{n\,A}{V\,N_A}$$

unit-cell volume

Avogadro's number, 6.023e23 atoms/mol

Example: Copper

- crystal structure = FCC: 4 atoms in the unit cell (n)
- atomic weight A = 63.55 g/mol
- lattice constant a = 3.61 Å (can be measured by X-rays)

Result: 8.97 g/cm^3

Electronic Structure: Type of Bonds

SOLIDS

METALS

Metallic Bond

One or more of the valence electrons in each atom become separated from the parent atom and move throughout the crystal. These electrons are not localized near the ions and the wave functions extend over many atoms.

- neither localized nor directional
- high plasticity
- low resistivity & high thermal conductivity

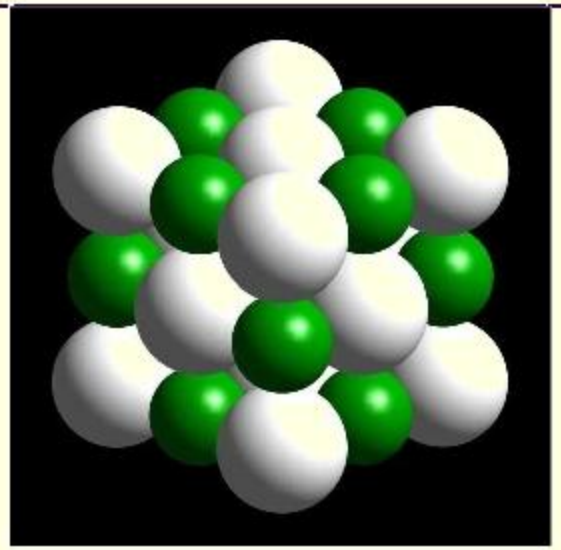
NON-METALS

Ionic Bond
Covalent Bond
Van der Waals Bond
Hydrogen Bond

Ionic Bonds

NON-METALS

Ionic Bond
Covalent Bond
Van der Waals Bond
Hydrogen Bond



- localized electrons (good dielectrics)
- not directional

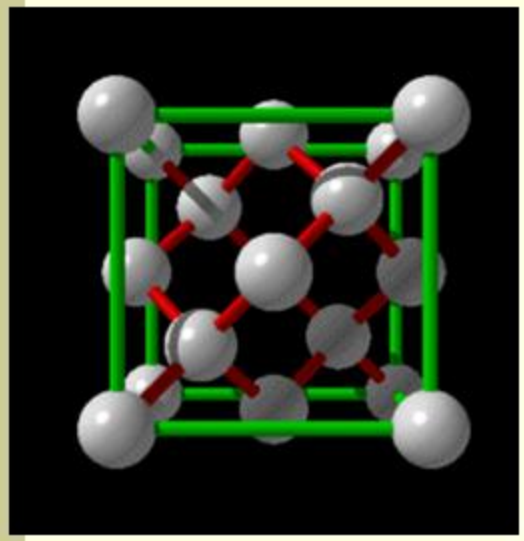
The ionic bond results from the Coulomb attraction of oppositely charged ions. The atoms of metallic elements, e.g., those of Na, lose their outer electrons easily, while the atoms of nonmetals, e.g., those of Cl, tend to gain electrons. The highly stable ions that result retain their individual structures as they approach one another to form a stable molecule or crystal. In an ionic crystal like NaCl, no discrete diatomic molecules exist; rather, the crystal is composed of independent Na+ and Cl- ions, each of which is attracted to neighboring ions of the opposite charge. Thus the entire crystal is a single giant molecule.

Covalent Bonds

NON-METALS

Ionic Bond
Covalent Bond
Van der Waals Bond
Hydrogen Bond

diamond structure



- the same or neighboring elements (III-V)
- strong directional bonding
- strongly bonded hard materials (diamond)

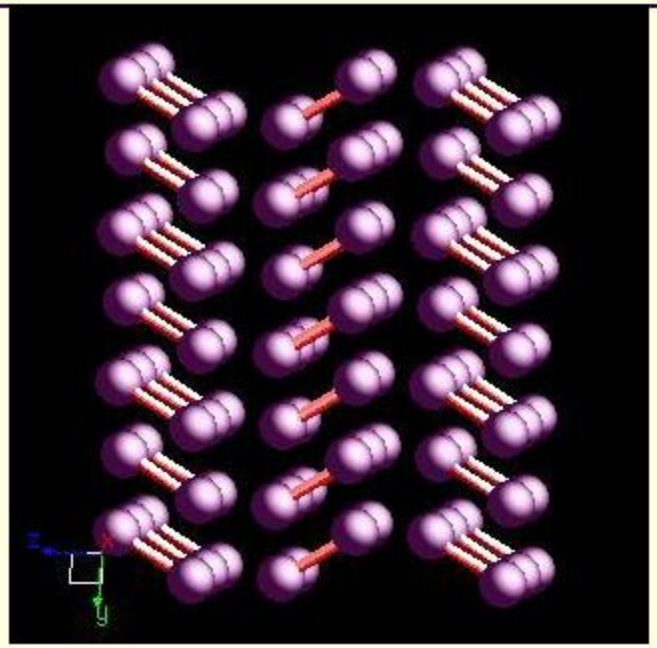
Two interleaving FCC cells offset by 1/4 of the cube diagonal

A single covalent bond is created when two atoms share a pair of electrons. There is no net charge on either atom; the attractive force is produced by interaction of the electron pair with the nuclei of both atoms. If the atoms share more than two electrons, double and triple bonds are formed, because each shared pair produces its own bond.

NON-METALS

Van der Waals Bonds

Ionic Bond
Covalent Bond
Van der Waals Bond
Hydrogen Bond



- low melting temperature
- mechanically weak

I_2

relatively weak electric forces that attract neutral molecules to one another due to

i) natural fluctuations of electron density or

ii) existence of a permanent electric dipole within the molecule

Acts in liquefied and solidified gases, and in almost all organic liquids and solids.

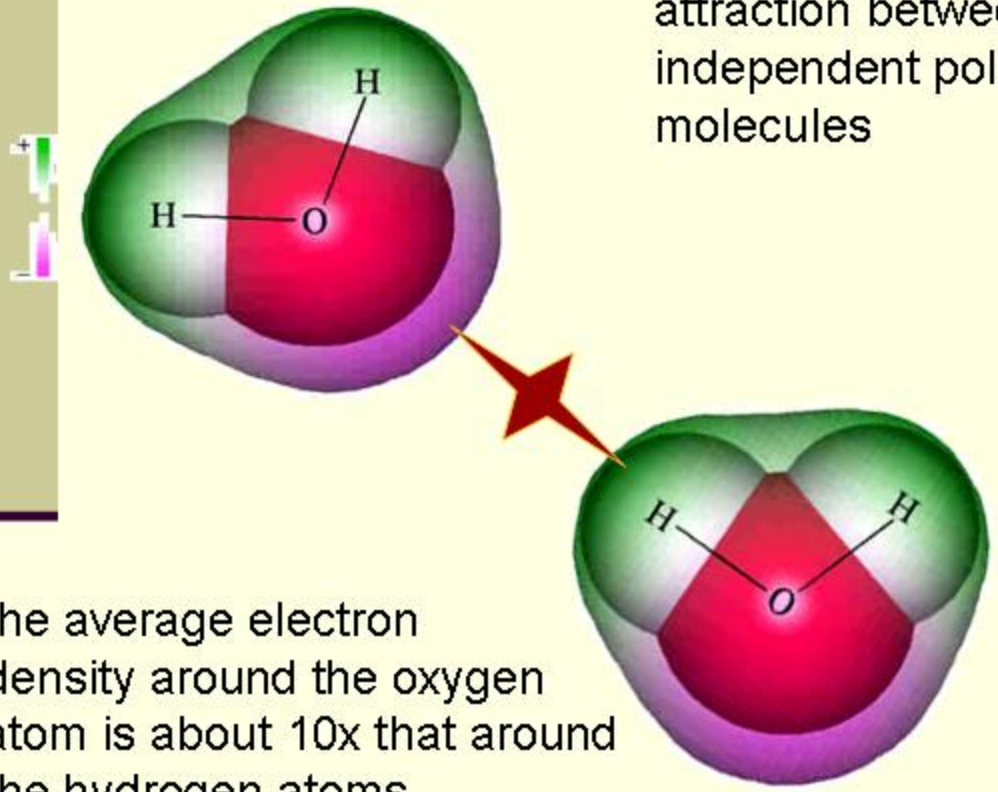
Hydrogen Bonds

NON-METALS

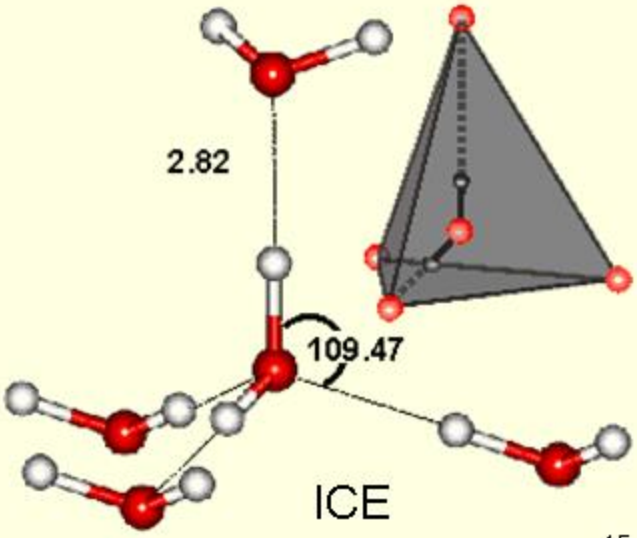
Ionic Bond
Covalent Bond
Van der Waals Bond
Hydrogen Bond

A-H-A

Hydrogen bonding is a strong electrostatic attraction between two independent polar molecules



the average electron density around the oxygen atom is about 10x that around the hydrogen atoms.



ICE

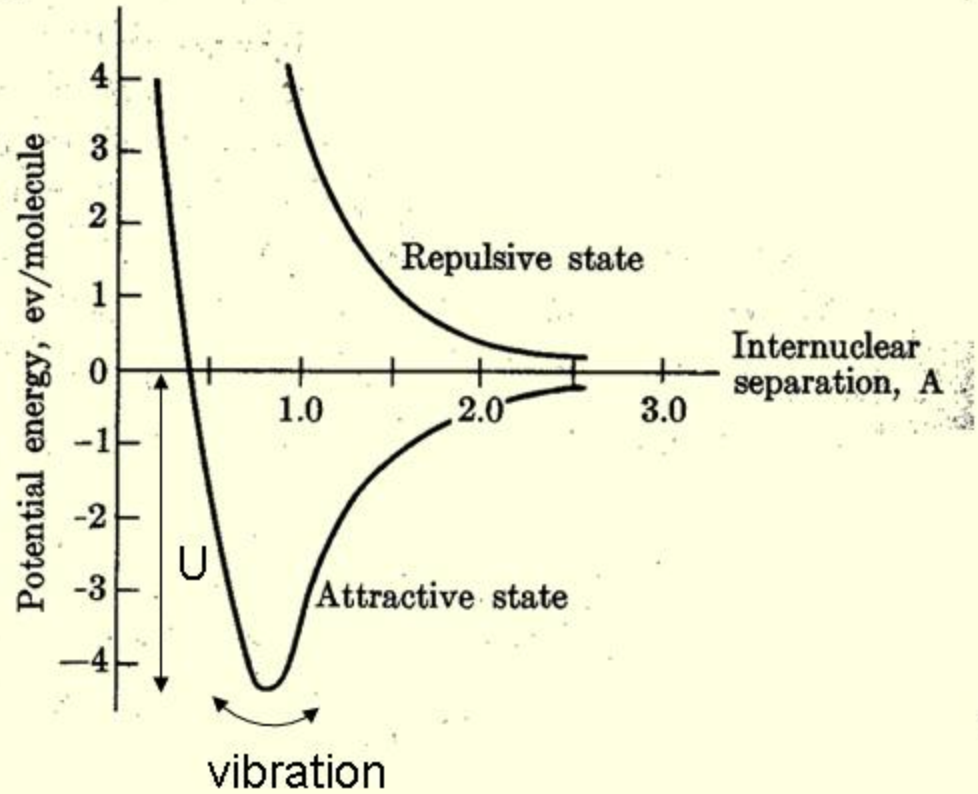
http://www.lsbu.ac.uk/water/hbond.html

Bonds

- U determines the melting temperature
- Curvature determines the elastic stiffness
- Anharmonicity (well is not parabolic) determines the thermal expansion

$$f = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

effective "spring constant" of a single bond $k = 500$ N/m

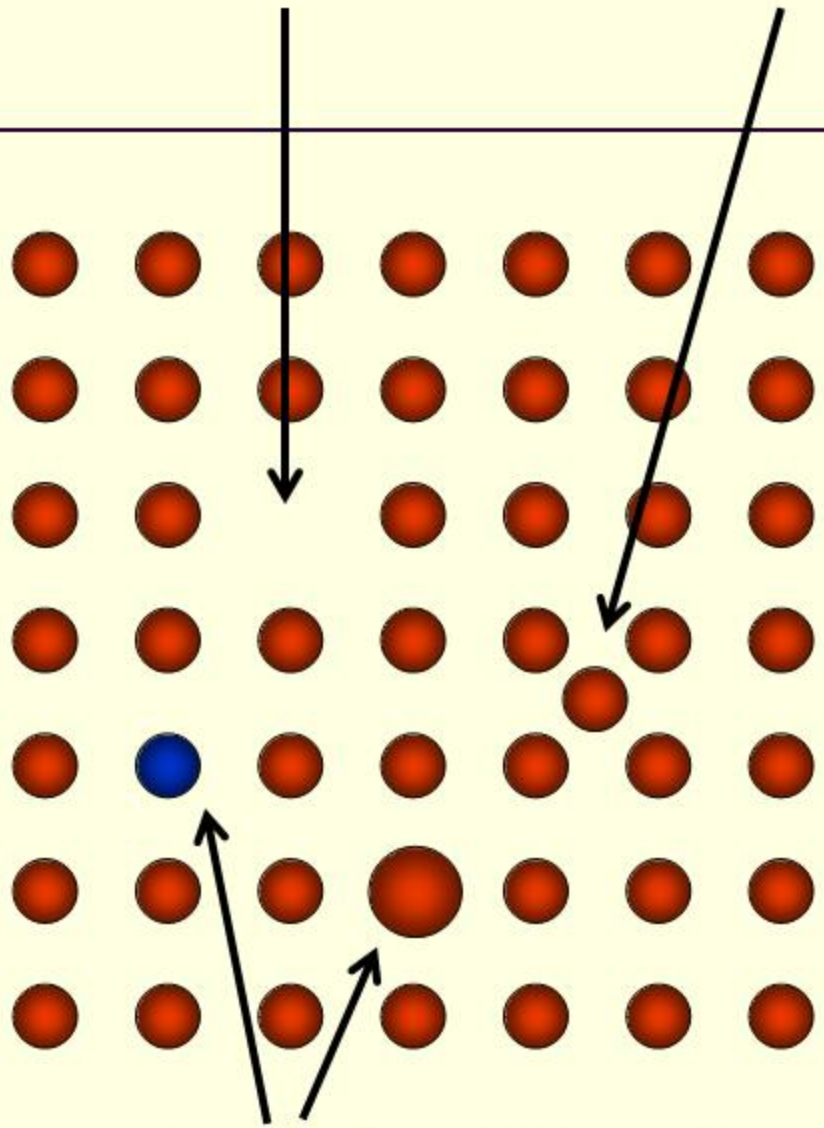


Defects in Solids

an interruption of the periodicity of the structure of a crystalline solid

- 0D: Point defects
  - vacancies
  - interstitials
  - impurities, weight and atomic composition
- 1D: Dislocations
  - edge
  - screw
- 2D: Grain boundaries
  - tilt
  - twist
- 3D: Bulk or Volume defects
- Atomic vibrations

Vacancies & Interstitials



energy of vacancy formation

$$n_{\text{vac}} = n_{\text{tot}} \exp\left(-\frac{E_{\text{vac}}}{k_{\text{B}}T}\right)$$

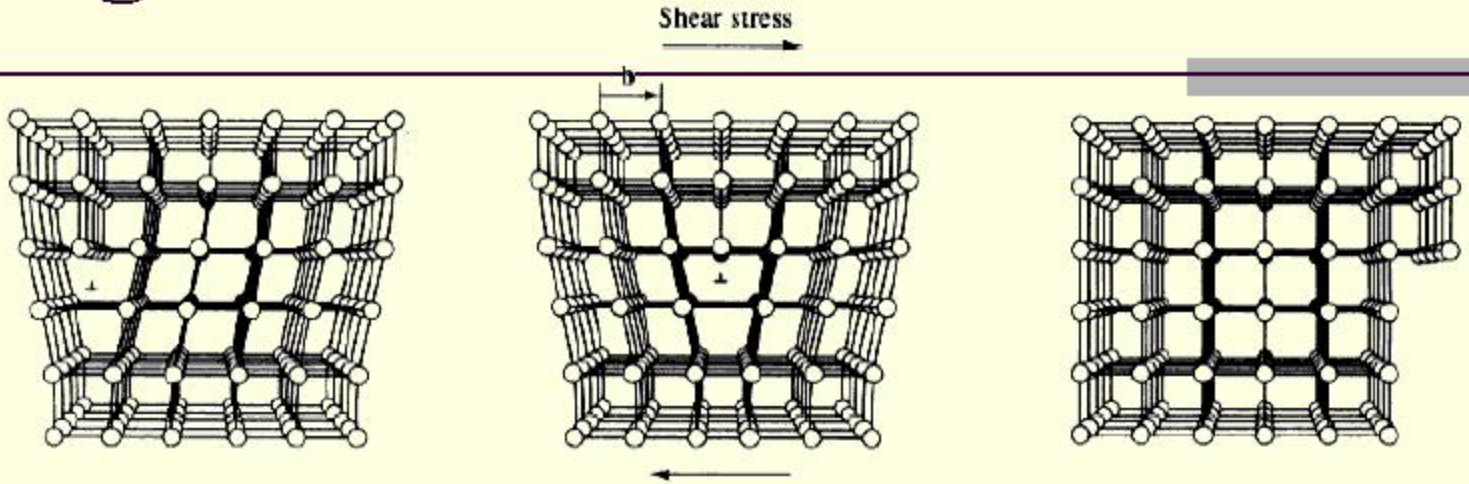
$$E_{\text{vac}} \sim 1\,\text{eV};\ T \sim 300\,\text{K};$$

$$n_{\text{tot}} \sim 10^{23}\ \text{cm}^{-3}$$

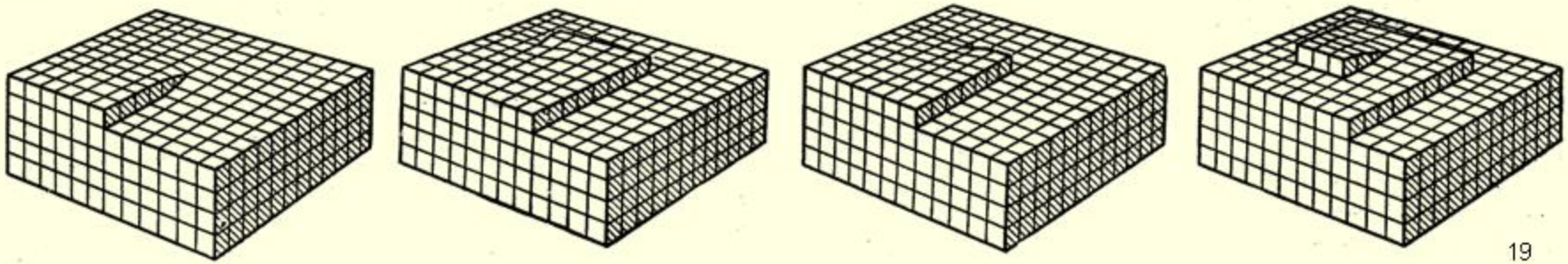
$$n_{\text{vac}} \sim 10^{6}\ \text{cm}^{-3}$$

impurities (different atoms, isotopes)

Edge & Screw Dislocations

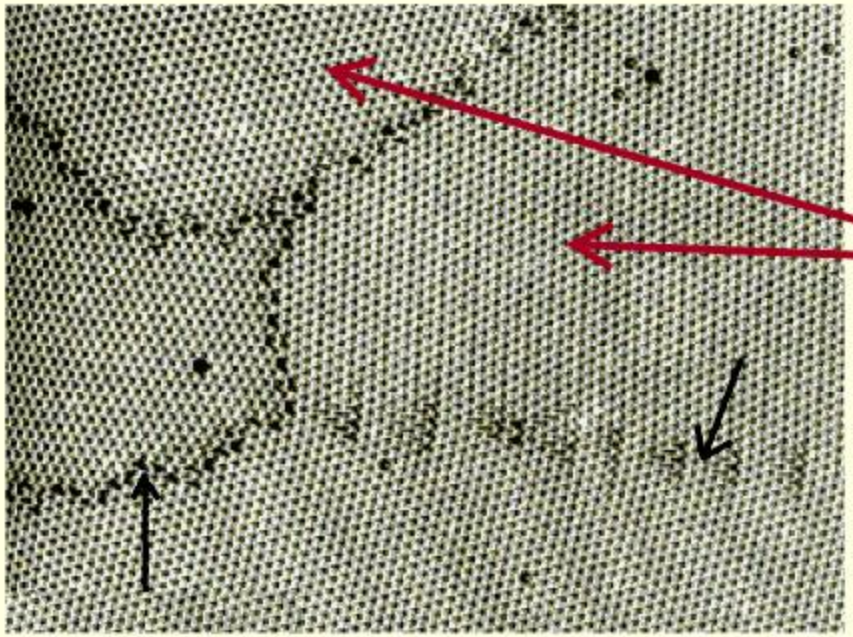


Slip - the process by which a dislocation moves and deforms a material.
Motion of dislocations determines the plasticity of metals



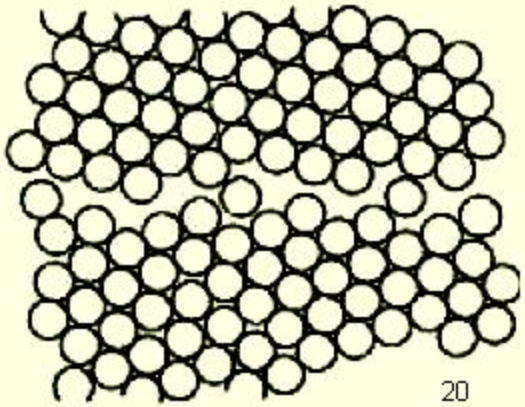
screw dislocation

Grain Boundaries



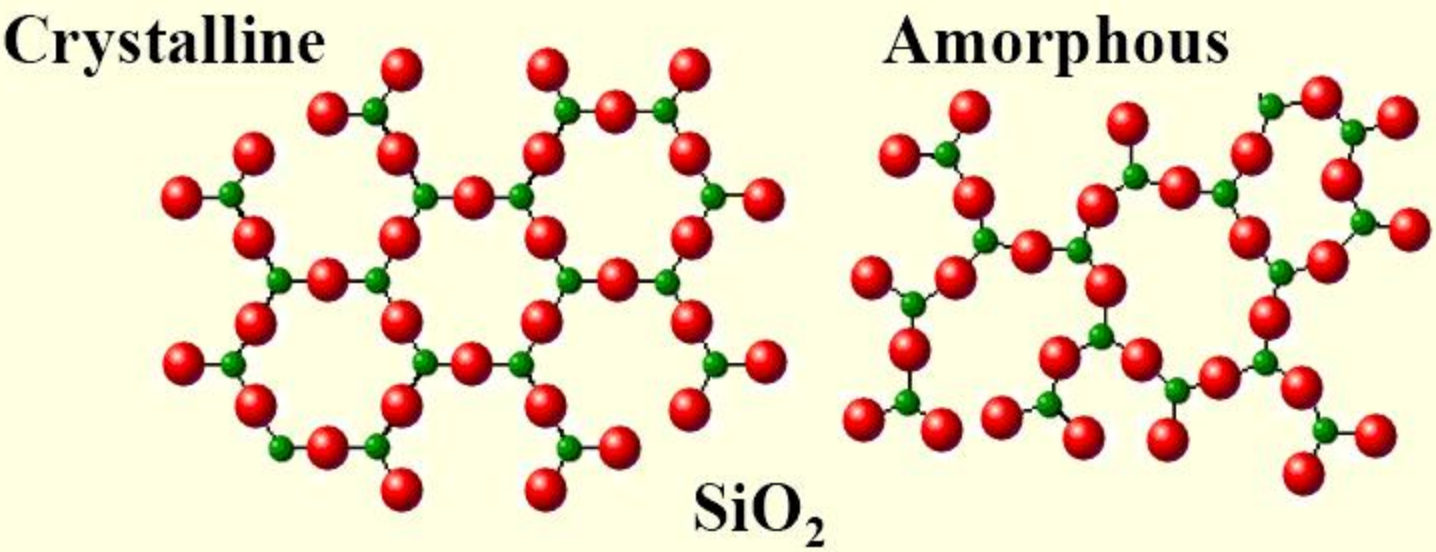
single-crystalline grains
but different orientations

easier diffusion along
grain boundaries



Amorphous Solids

- glass
- polymers
- inorganic oxides
- good absorbers
- small roughness



Thermodynamics of Materials

- Oxidation, $Si \rightarrow SiO_2$
- Chemical vapor deposition (CVD)
- Thin-film nucleation
- Materials stability
- Surface reactivity
- ...

Gibbs free-energy function:

$$G = H - TS$$

H – the enthalpy; *S* – the entropy; *T* – the temperature

Thermodynamics of Materials

- Spontaneous reacting occurs when

$$\Delta G = \Delta H - T\,\Delta S < 0$$

- The concept of minimization of free energy – a criterion for stability of a system and forward change of a reaction. Central in Material Science.

Thermodynamics of Materials

(1) $Si + O_2 \rightarrow SiO_2;\ \Delta G^0_{SiO_2} = -175\ \text{kcal}$

(2) $\frac{4}{3}Al + O_2 \rightarrow \frac{2}{3}Al_2O_3;\ \Delta G^0_{Al_2O_3} = -230\ \text{kcal}$

(3) $2Cu + O_2 \rightarrow 2CuO;\ \Delta G^0_{CuO} = -45\ \text{kcal}$

---

(2) - (1) :

$$\frac{4}{3}Al + SiO_2 \rightarrow \frac{2}{3}Al_2O_3 + Si;\quad \Delta G^0 = -55\ \text{kcal}$$

(3) - (1) :

$$2Cu + SiO_2 \rightarrow 2CuO + Si;\quad \Delta G^0 = +130\ \text{kcal}$$

Conclusion: Al thin films tend to reduce SiO_2
Cu – not.

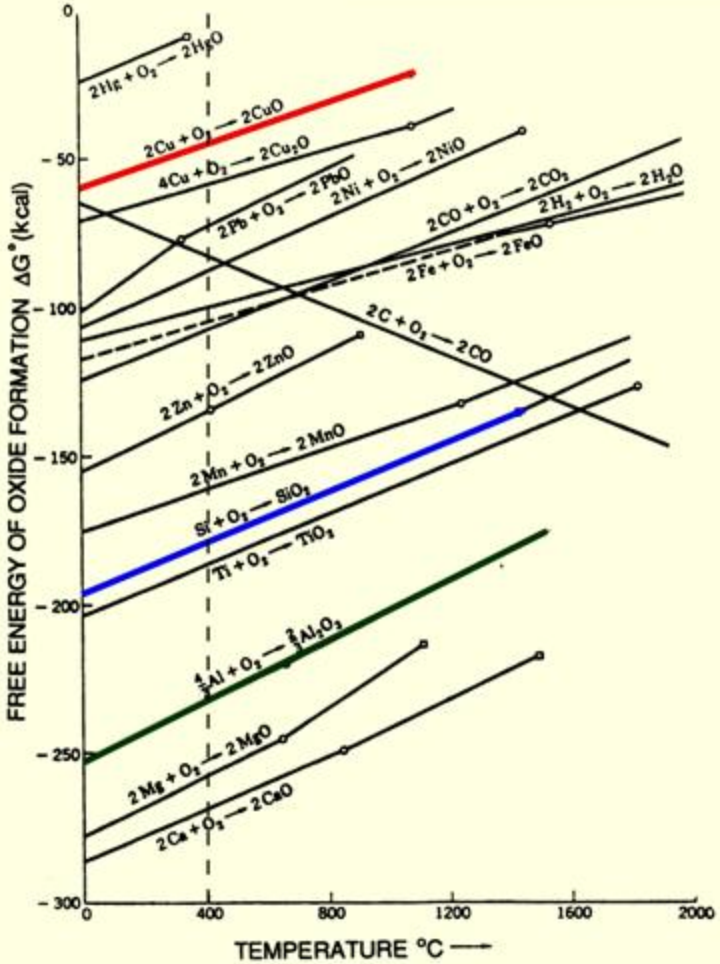


Figure 1-11 Standard free energy of oxide formation vs temperature: ○, melting point of metal; □, boiling point of metal (1 atm). Reprinted with permission from A. G. Guy, *Introduction to Materials Science*, McGraw-Hill, New York, 1972.

Phase Diagrams

- The Gibbs phase rule:

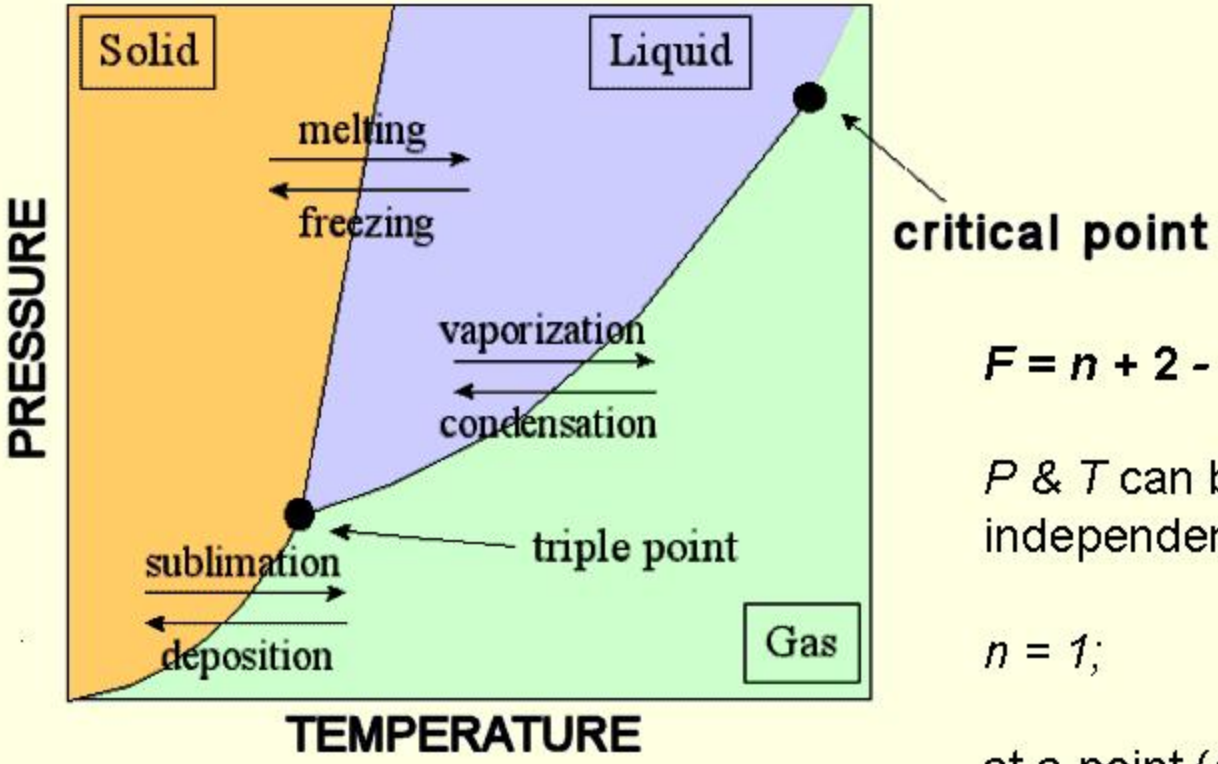
$$F = n + 2 - \psi$$

The number of phases

The number of atomic species

The number of variables that can be independently varied without changing the phase equilibrium

Phase Diagrams



$F = n + 2 - \psi$

P & *T* can be independently varied;

$n = 1$;

at a point (*P* & *T* fixed) there are *maximum* 3 coexisting phases

Phase Diagrams Multi –Component Systems

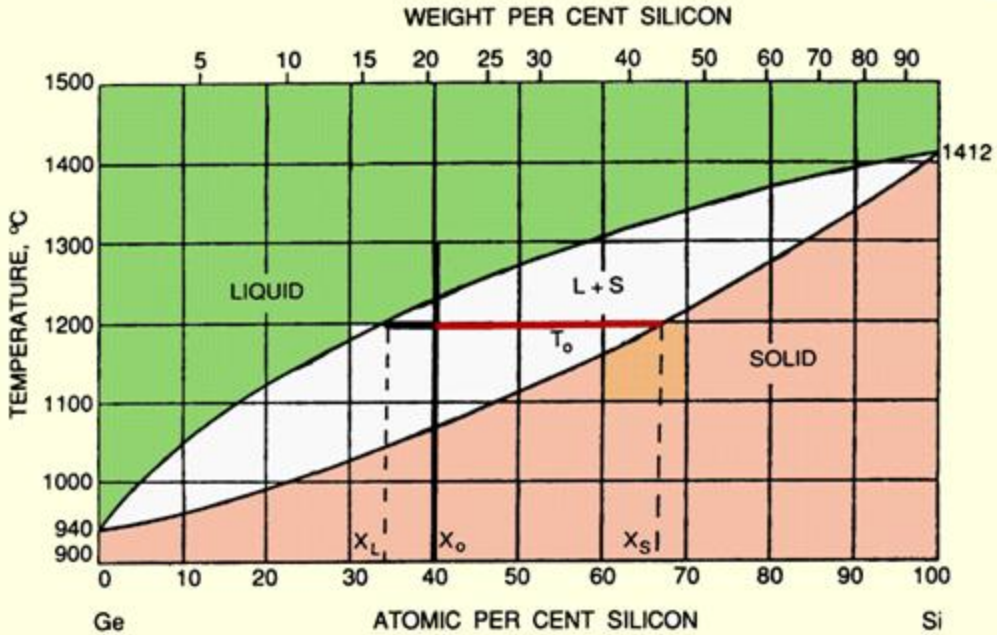


Figure 1-13 Ge–Si equilibrium phase diagram. Reprinted with permission. From M. Hansen, *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.

Level rule (2-component systems only):

$$\%L = \frac{X_S - X_0}{X_S - X_L} \cdot 100; \qquad \%S = \frac{X_0 - X_L}{X_S - X_L} \cdot 100$$

Film Structure

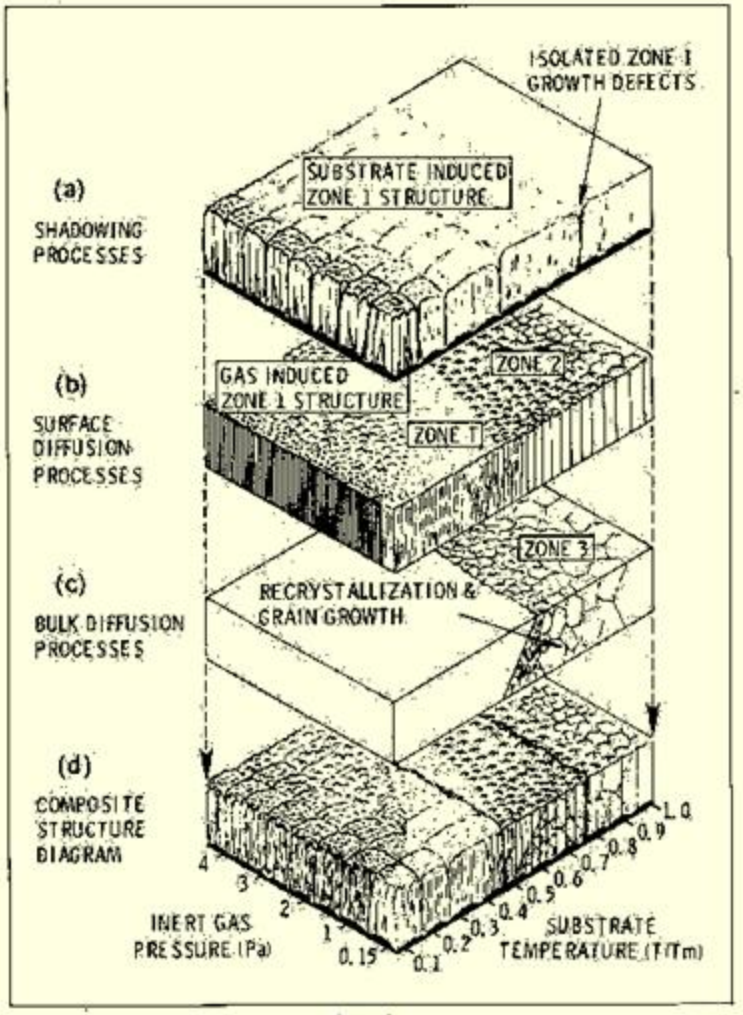
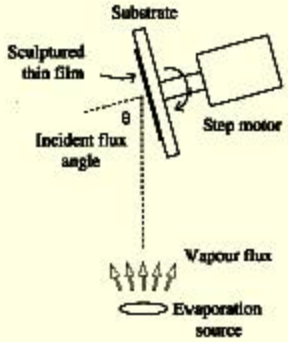
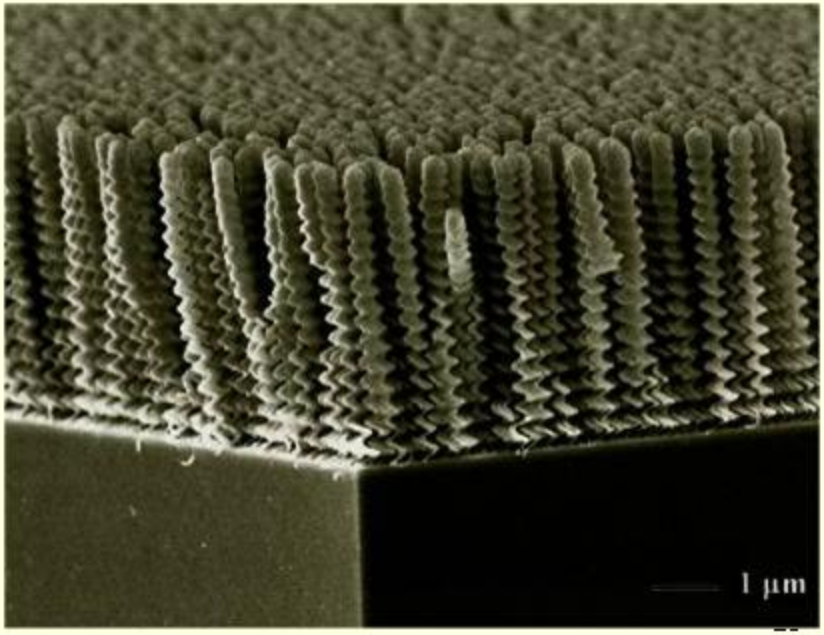


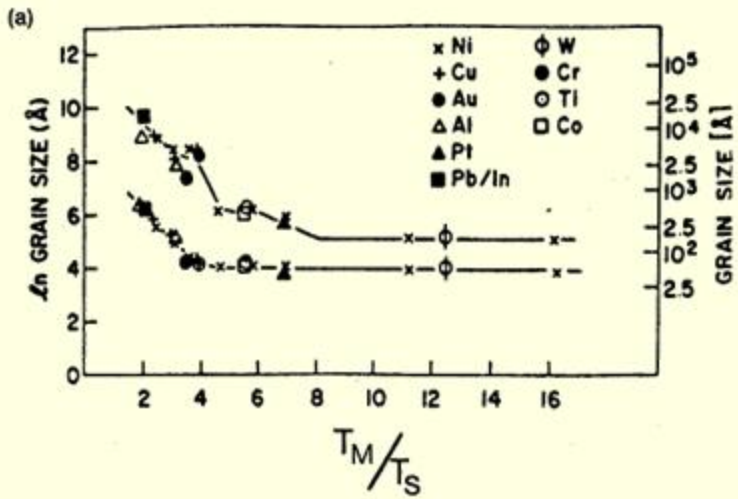
Figure 1

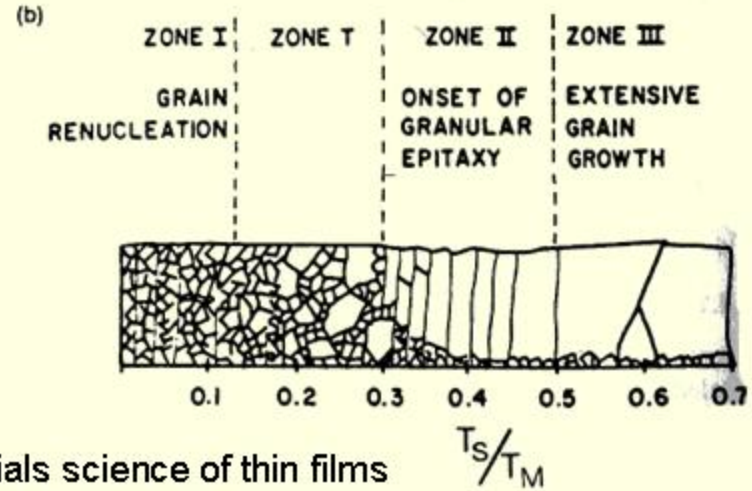


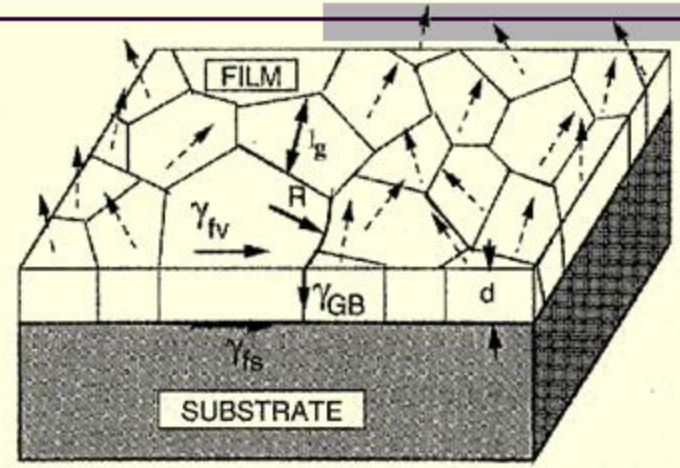


K. Robbie and M. J. Brett J.Vac.Sci.Technol. **15**, 1460 (1997)

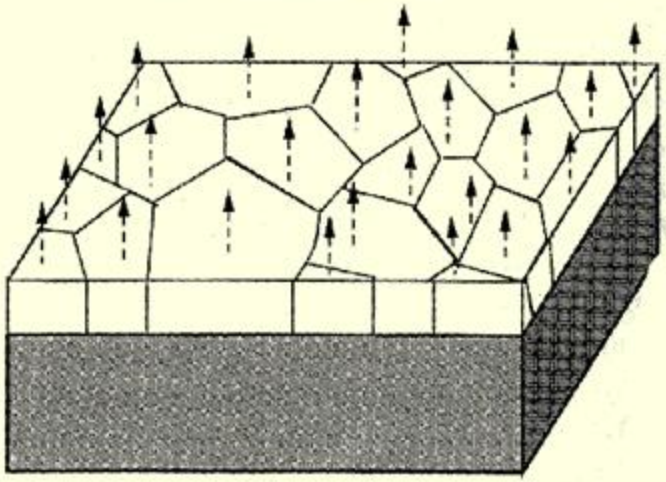
Film Structure







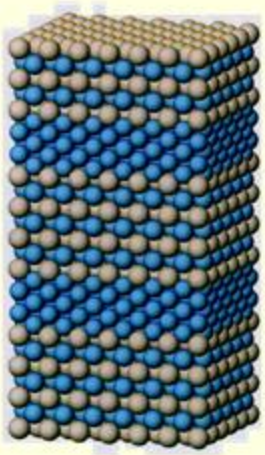
RANDOM ORIENTATION



PREFERRED ORIENTATION (TEXTURE)

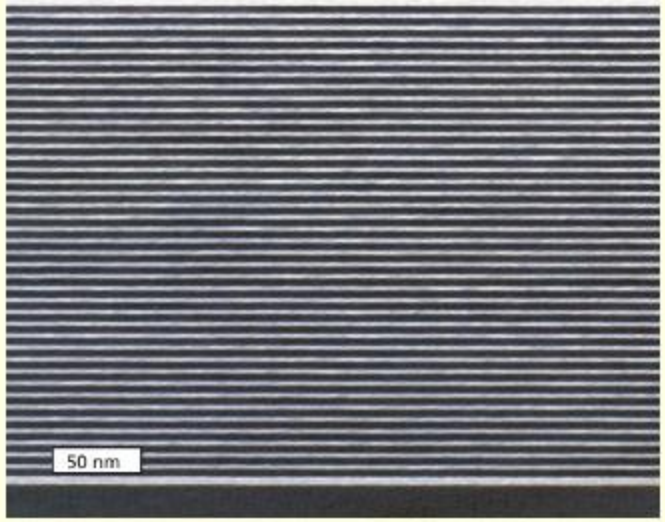
M. Ohring, Materials science of thin films

Interdiffusion & Transformations in Thin Films



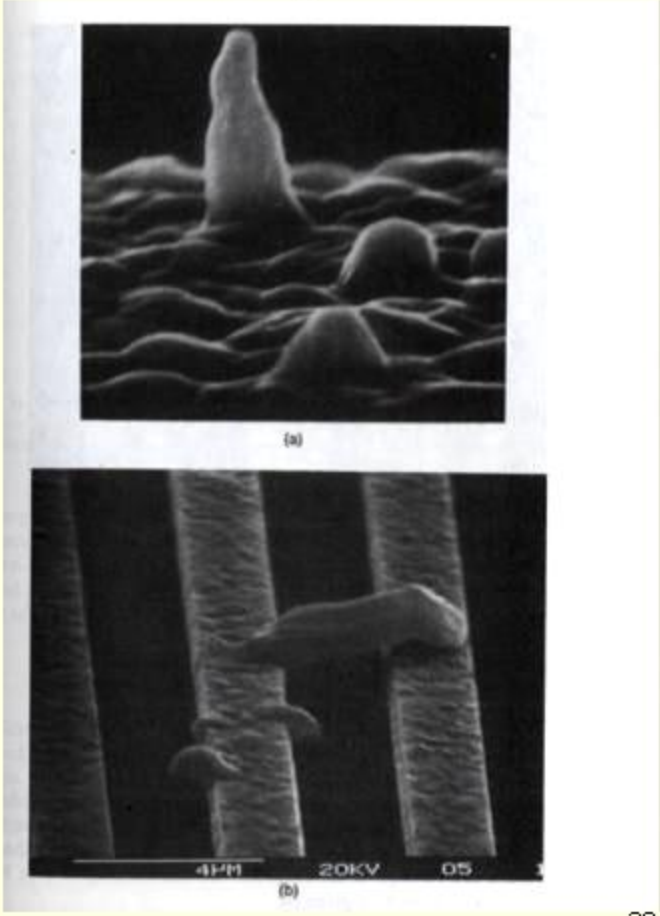
Interdiffusion is crucial in multilayers

MoSi multilayers



- EUV lithography
- EUV metrology
- EUV microscopy
- synchrotron optics
- x-ray astronomy
- soft x-ray lasers
- element analysis
- plasma physics

Electro-migration



http://www.iof.fraunhofer.de/departments/optical-coatings/

M. Ohring: Materials Science of thin films