Chapter 6: Imperfections in Solids

- **ISSUES TO ADDRESS...**
  - What are the solidification mechanisms?
  - What types of defects arise in solids?
  - Can the number and type of defects be varied and controlled?
  - How do defects affect material properties?
  - Are defects undesirable?

- **There is no such thing as a perfect crystal.**
  - What are these imperfections?
  - Why are they important?

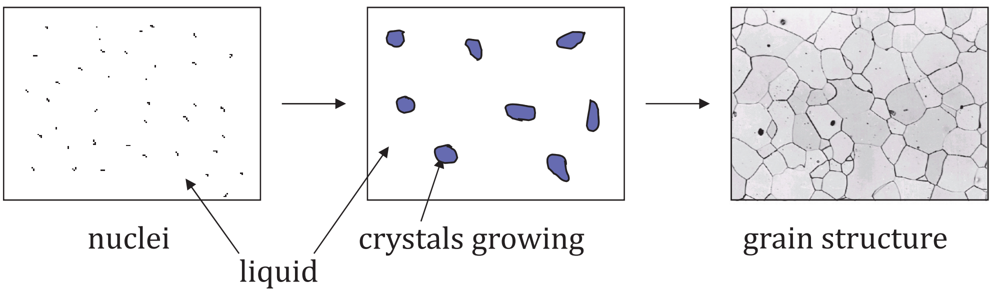
- **Many of the important properties of materials are due to the presence of imperfections.**

- **Types of Imperfections**
  - Point defects: Vacancy atoms, interstitial atoms, substitutional atoms, etc.
  - Line defects: Dislocations, etc.
  - Area defects: Grain boundaries, phase boundaries, twin boundaries, stacking faults, etc.
  - Volume defects: Pores, cracks, foreign inclusions, other phases, etc.

Imperfections in Solids

- **Solidification- result of casting of molten material**
  - 2 steps
    - Nuclei form
    - Nuclei grow to form crystals – grain structure

- **Start with a molten material – all liquid**

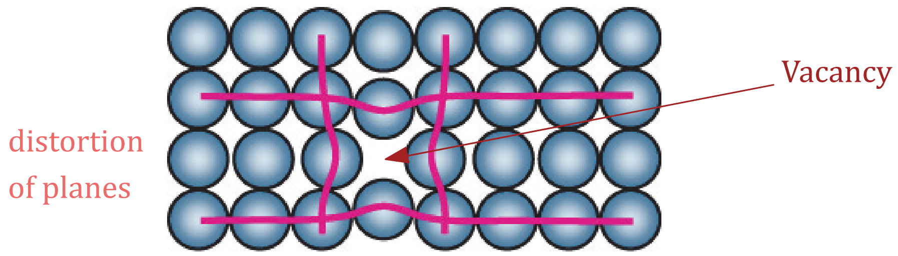


Adapted from Fig. 6.20 (b), *Callister & Rethwisch 9e.*

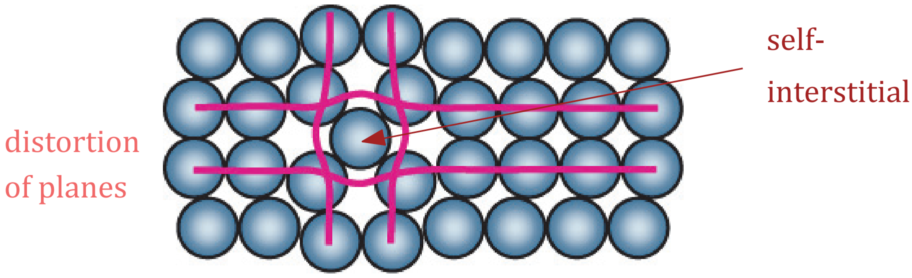
- **Crystals grow until they meet each other**

6.2 Point Defects in Metals

- **Vacancies: vacant atomic sites in a structure.**



- **Self-Interstitials: "extra" atoms positioned between atomic sites.**

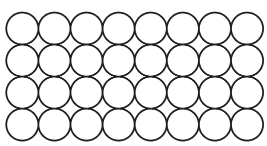


Equilibrium Concentration: Point Defects

- **Equilibrium concentration varies with temperature!**

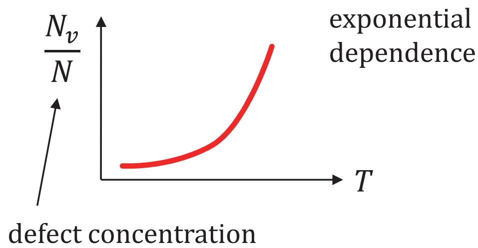
$$\frac{N_v}{N} = exp\left(\frac{-Q_v}{kT}\right)$$

- N_v: Number of defects
- Q_v: Activation energy
- N: Number of potential defect sites
- T: Absolute temperature
- k: Boltzmann's constant (1.38×10^{-23} J/atom-K)

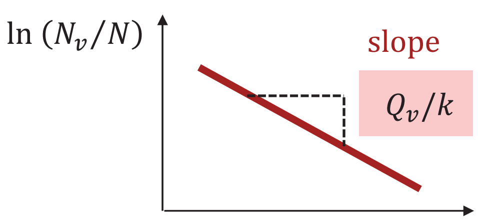


Each lattice site is a potential vacancy site.

- **Measuring activation energy, Q_v**
  - We can get Q_v from an experiment.

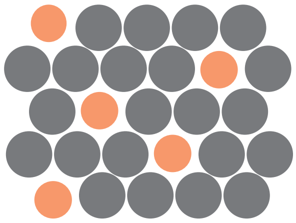


  - Replot it.



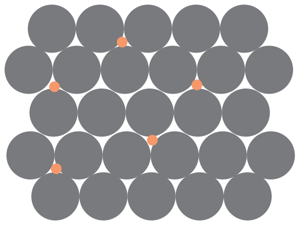
6.4 Impurities in Solids

- **Two outcomes if impurity (B) added to host (A):**
  - Solid solution of B in A (i.e., random distribution of point defects)



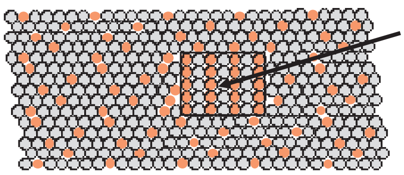
Substitutional solid solution
(e.g., Cu in Ni)

OR



Interstitial solid solution
(e.g., C in Fe)

  - Solid solution of B in A plus particles of a new phase (usually for a larger amount of B)



Second phase particle
- different composition
- often different structure.

6.4 Impurities in Solids

- **Conditions for substitutional solid solution (S.S.)**

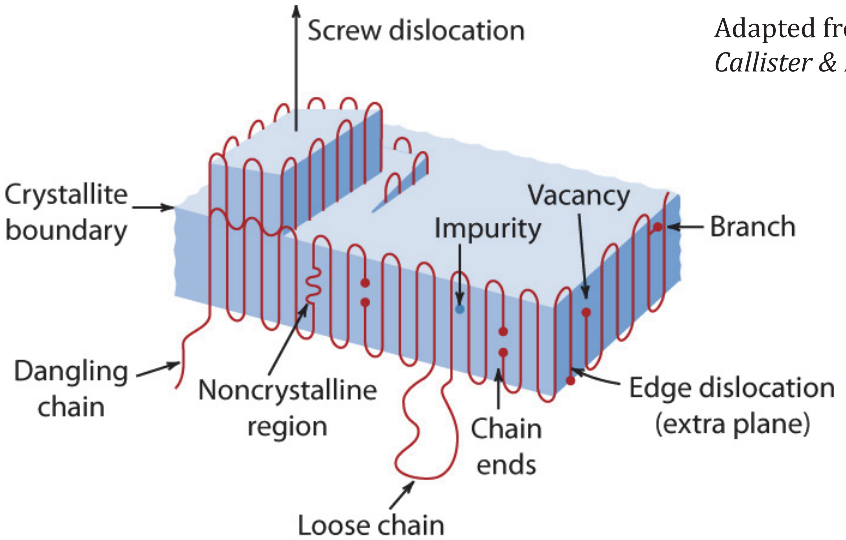
- **W. Hume – Rothery rule**
  1. Δr (atomic radius) < 15%
  2. Proximity in periodic table, i.e., similar electronegativities
  3. Same crystal structure for pure metals
  4. Valency: All else being equal, a metal will have a greater tendency to dissolve a metal of higher valency than one of lower valency

- **Application of Hume–Rothery rules – Solid Solutions**
  - 1. Would you predict more Al or Ag to dissolve in Zn?
  - 2. More Zn or Al in Cu?

Element	*Atomic Radius (nm)*	*Crystal Structure*	*Electro-negativity*	*Valence*
Cu	0.1278	FCC	1.9	+2
C	0.071			
H	0.046			
O	0.060			
Ag	0.1445	FCC	1.9	+1
Al	0.1431	FCC	1.5	+3
Co	0.1253	HCP	1.8	+2
Cr	0.1249	BCC	1.6	+3
Fe	0.1241	BCC	1.8	+2
Ni	0.1246	FCC	1.8	+2
Pd	0.1376	FCC	2.2	+2
Zn	0.1332	HCP	1.6	+2

6.5 Point Defects in Polymers

- **Defects due in part to chain packing errors and impurities such as chain ends and side chains**



Adapted from Fig. 6.8, *Callister & Rethwisch 9e ISV.*

6.6 Specification of Composition

- **Weight percent**

$$C_1 = \frac{m_1}{m_1 + m_2} \times 100$$

- m_1 = mass of component 1
- m_2 = mass of component 2

- **Atom percent**

$$C_1' = \frac{n_{m1}}{n_{m1} + n_{m2}} \times 100$$

- n_{m1} = number of moles of component 1
- n_{m2} = number of moles of component 2

- **Composition Conversions**
  - Conversion of weight percent to atom percent (for a two-element alloy)

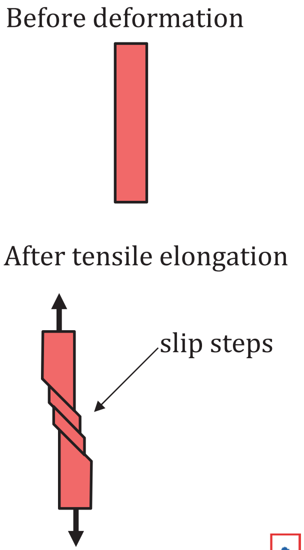
$$C_1' = \frac{C_1 A_2}{C_1 A_2 + C_2 A_1} \times 100$$

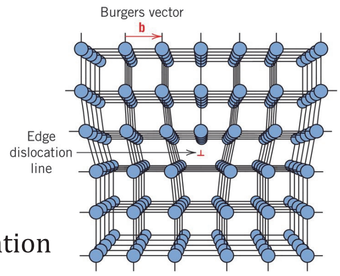
$$C_2' = \frac{C_2 A_1}{C_1 A_2 + C_2 A_1} \times 100$$

- C_1 & C_2: Weight percent
- C_1' & C_2': Atom percent
- A_1 & A_2: Atomic weight

6.7 Dislocations-Linear Defects

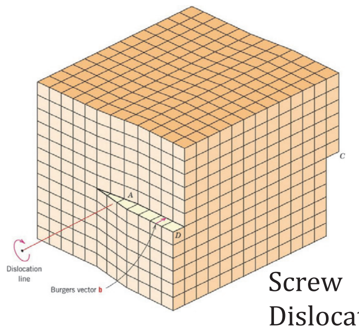
- **Linear Defects (Dislocations)**
  - are one-dimensional defects around which atoms are misaligned,
  - slip between crystal planes result when dislocations move,
  - produce permanent (plastic) deformation.
- **Edge dislocation:**
  - extra half-plane of atoms inserted in a crystal structure
  - **b** perpendicular to dislocation line
- **Screw dislocation:**
  - spiral planar ramp resulting from shear deformation
  - **b** parallel to dislocation line





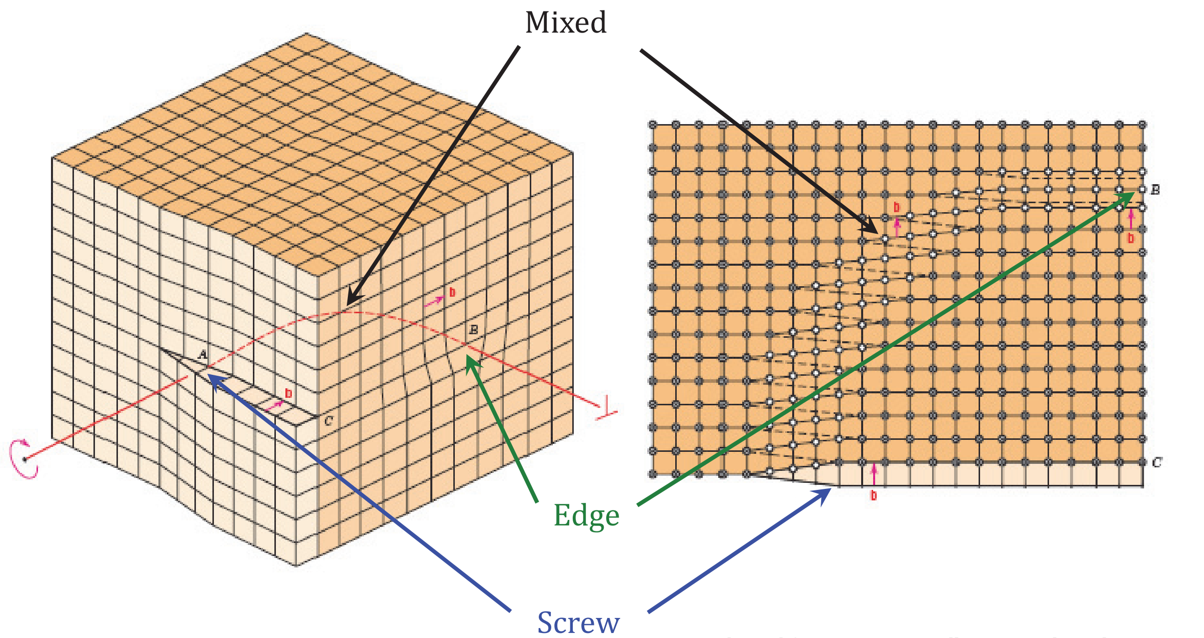
Edge Dislocation

Adapted from A. G. Guy, Essentials of Materials Science, McGraw-Hill Book Company, New York, NY, 1976, p. 153.



Screw Dislocation

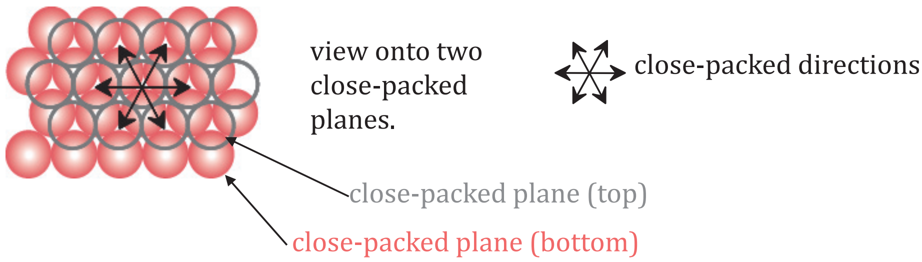
Edge, Screw, and Mixed Dislocations



Adapted from Fig. 6.11, *Callister & Rethwisch 9e.*
[Figure (b) from W. T. Read, Jr., Dislocations in Crystals, McGraw-Hill Book Company, New York, NY, 1953.]

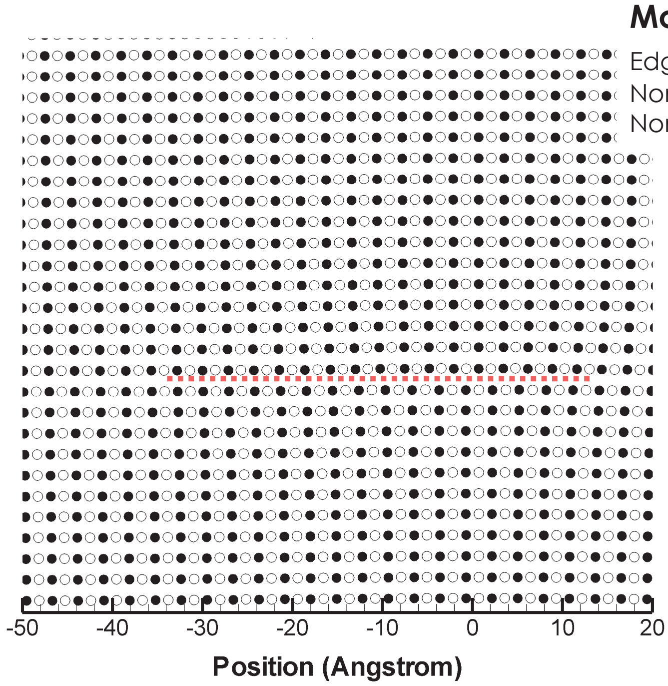
Dislocations & Crystal Structures

- **Structure: close-packed planes & directions are preferred.**



- **Comparison among crystal structures:**
  - FCC: many close-packed planes/directions;
  - HCP: only one plane, 3 directions;
  - BCC: none
- **Specimens that were tensile tested.**

Molecular Dynamics Simulation of a Dislocation



Molecular dynamics simulation

Edge Dislocation in Aluminum
Non-local and non-linear
Non-uniform field of long-range interaction

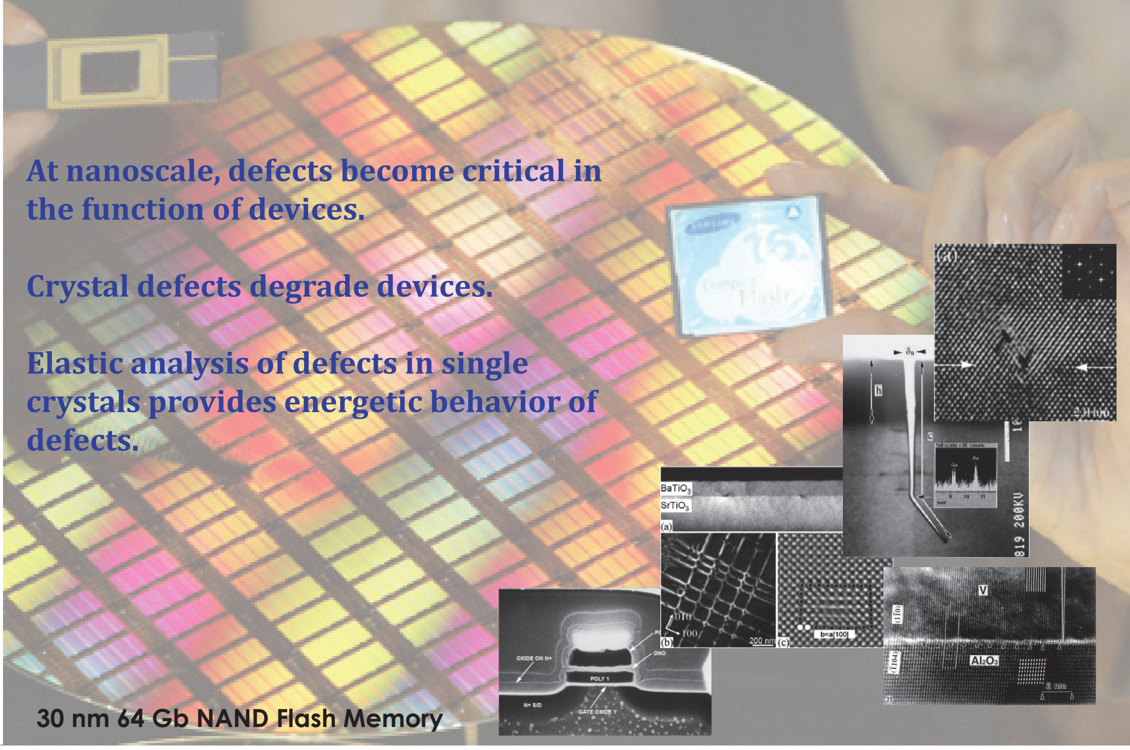
$$\frac{1}{2}\langle 110\rangle \rightarrow \frac{1}{6}\langle 211\rangle + \frac{1}{6}\langle 12\bar{1}\rangle$$

Defects in Electronic Devices

At nanoscale, defects become critical in the function of devices.

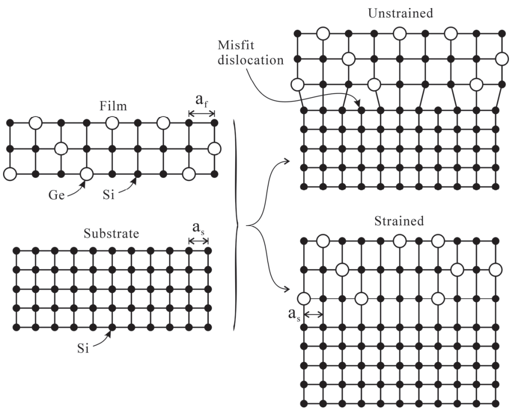
Crystal defects degrade devices.

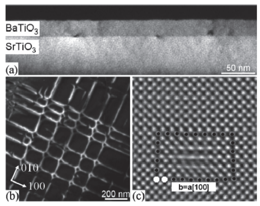
Elastic analysis of defects in single crystals provides energetic behavior of defects.



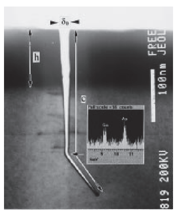
Defects in Thin Films

How can we deal with the mechanical behavior of defects in thin films and layered structures?

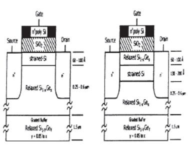


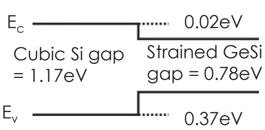


Dislocation cores at the 20 nm $BaTiO_3/SrTiO_3$ (Sun et al., Appl. Phys. Lett., 2004)



Wu and Weatherly, Acta Mat. (1999)



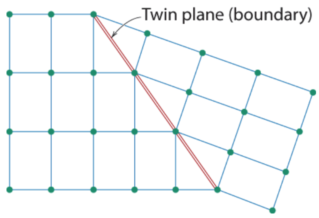


Band alignments for $Ge_{0.2}Si_{0.8}$ on unstrained Si(100) substrate

Misfit strain due to lattice mismatch affects the energy bandgap.
Misfit dislocations degrade devices

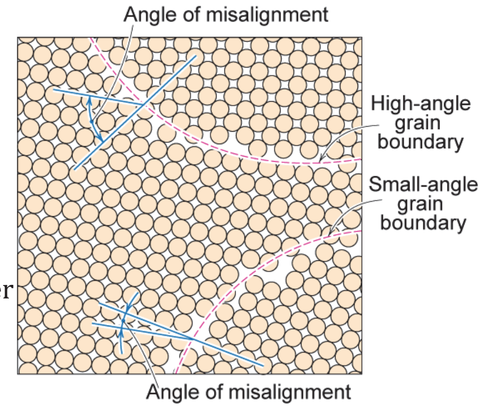
Planar Defects in Solids

- **One case is a twin boundary (plane)**
  - Essentially a reflection of atom positions across the twin plane.



Adapted from Fig. 6.15, *Callister & Rethwisch 9e.*

- **Stacking faults**
  - For FCC metals an error in ABCABC packing sequence
  - Ex: ABCABABC
- **Grain Boundaries**
  - regions between crystals
  - transition from lattice of one region to that of the other
  - slightly disordered
  - low density in grain boundaries
    - high mobility
    - high diffusivity
    - high chemical reactivity



Adapted from Fig. 6.14, *Callister & Rethwisch 9e.*

Catalysts and Surface Defects

- **A catalyst increases the rate of a chemical reaction without being consumed**
- **Active sites on catalysts are normally surface defects**

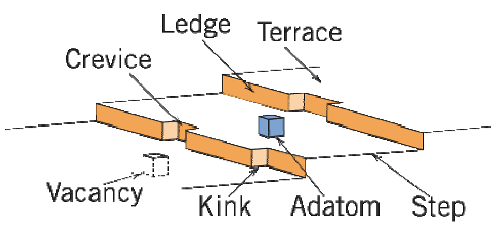


Fig. 6.16, *Callister & Rethwisch 9e.*

Single crystals of $(Ce_{0.5}Zr_{0.5})O_2$ used in an automotive catalytic converter

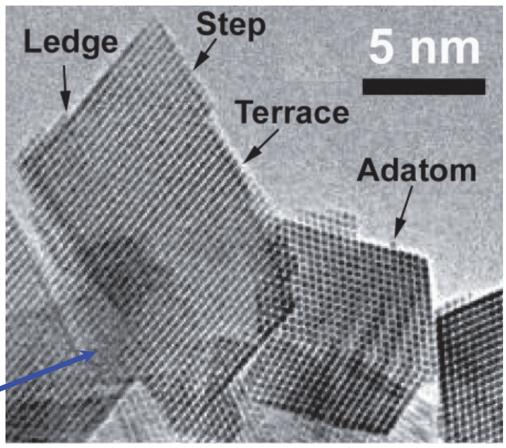


Fig. 6.17, *Callister & Rethwisch 9e.*
[From W. J. Stark, L. Mädler, M. Maciejewski, S. E. Pratsinis, and A. Baiker, "Flame Synthesis of Nanocrystalline Ceria/Zirconia: Effect of Carrier Liquid," Chem. Comm., 588–589 (2003). Reproduced by permission of The Royal Society of Chemistry.]

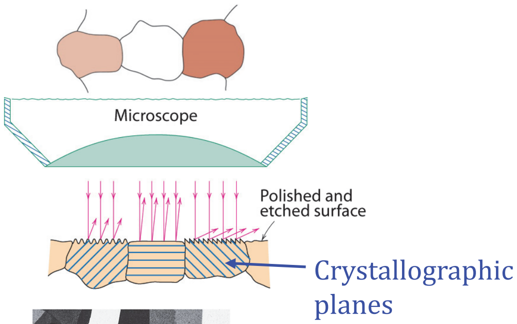
6.11 Basic Concepts of Microscopy

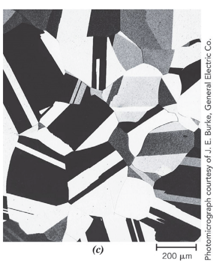
- **Crystallites (grains) and grain boundaries vary considerably in size.**
- **Crystallites (grains) can be quite large.**
  - Ex: Large single crystal of quartz or diamond or Si
  - Ex: Aluminum light post or garbage can - see the individual grains
- **Crystallites (grains) can be quite small (mm or less)**
  - Necessary to observe with a microscope.
- **Two features of microstructure: Grain size and shape**
- **Microscopy**
  - Optical Microscopy
  - Scanning Electron Microscopy (SEM) & Transmission Electron Microscopy (TEM)
  - Scanning Probe Microscopy

6.12 Microscopic Technique: Optical Microscopy

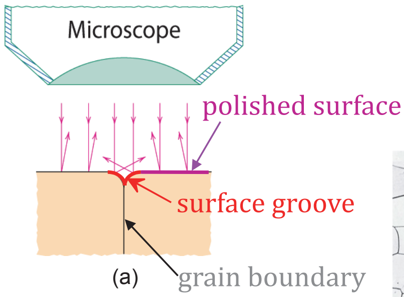
- Useful up to 2000× magnification.
- Polishing removes surface features (e.g., scratches)
- Etching changes reflectance, depending on crystal orientation.

- **Grain boundaries**
  - are imperfections,
  - are more susceptible to etching,
  - may be revealed as dark lines,
  - change in crystal orientation across boundary.

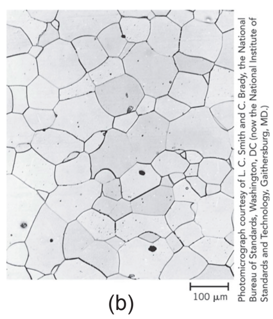




Micrograph of brass (a Cu-Zn alloy)



(a)



(b)

6.12 Microscopic Technique: Electron Microscopy

- **Optical resolution: 0.1 μm = 100 nm**
  - Diffraction of visible light limits the ability to resolve fine details. The extent and magnitude of the diffraction patterns are affected by both the wavelength of light (λ), the refractive materials used to manufacture the objective lens and the numerical aperture (NA) of the objective lens. There is therefore a finite limit beyond which it is impossible to resolve separate points in the objective field, known as the diffraction limit. Assuming that optical aberrations in the whole optical set-up are negligible, the resolution d, can be stated as:

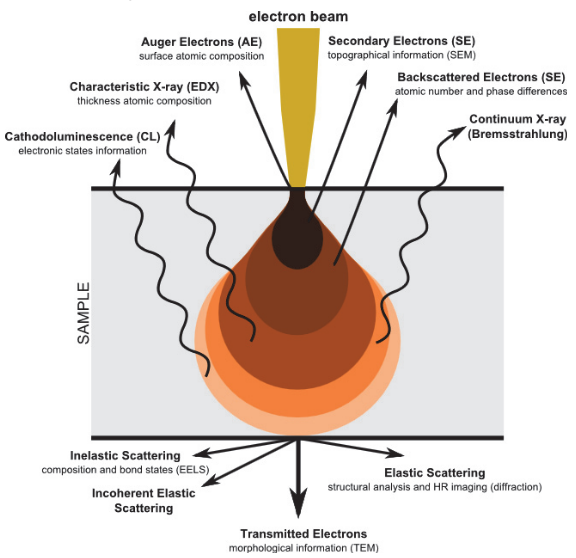
$$d = \frac{\lambda}{2NA} \cong \frac{\lambda}{2}$$

  - Usually a wavelength of 550 nm is assumed, which corresponds to green light. With air as the external medium, the highest practical NA is 0.95, and with oil, up to 1.5. In practice the lowest value of d obtainable with conventional lenses is about 200 nm.

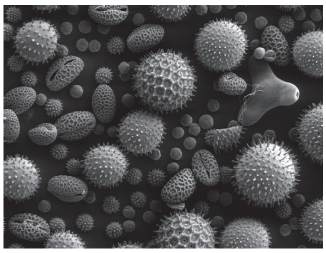
- **For higher resolution need higher frequency**
  - X-Rays? Difficult to focus.
  - Electrons
    - Wavelengths: 3 pm (0.003 nm) (Magnification - 1,000,000X)
    - Atomic resolution possible
    - Electron beam focused by magnetic lenses.

6.12 Microscopic Technique: Electron Microscopy

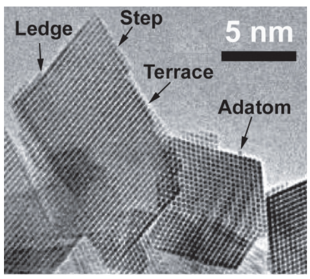
- Transmission electron microscopy (TEM) is a microscopy technique in which a beam of electrons is transmitted through an ultra-thin specimen, interacting with the specimen as it passes through it. An image is formed from the interaction of the electrons transmitted through the specimen;
- A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that contain information about the sample's surface topography and composition.



https://en.wikipedia.org/wiki/Scanning_electron_microscope



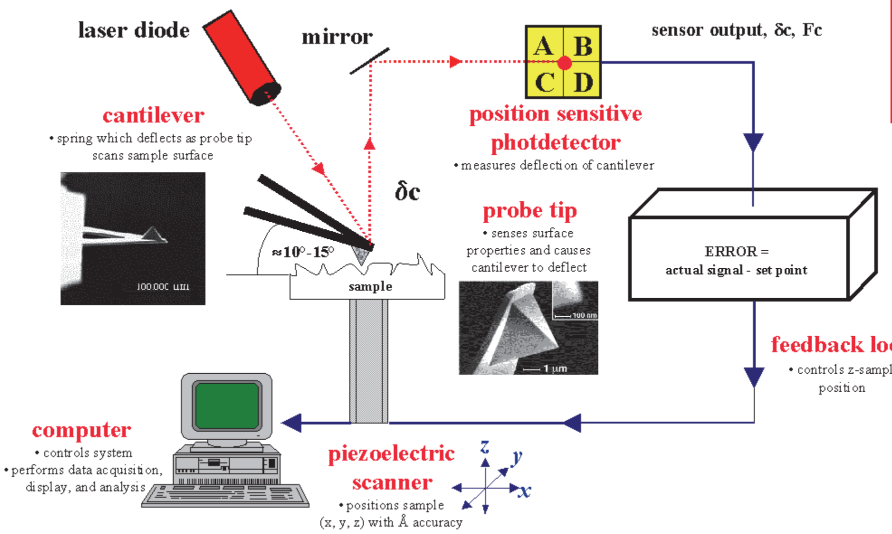
Example of a SEM image

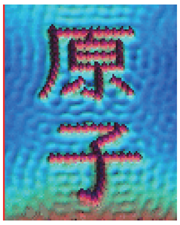


Example of a TEM image

6.12 Microscopic Technique: SPM

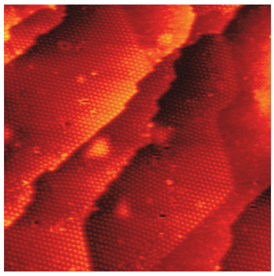
- **Scanning Probe Microscopy (SPM)**
  - Forms images of surfaces using a physical probe that scans the specimen.
  - Uses a tiny probe with a very sharp tip.
  - Atoms can be arranged and imaged!





Iron atoms arranged on a copper (111) surface.

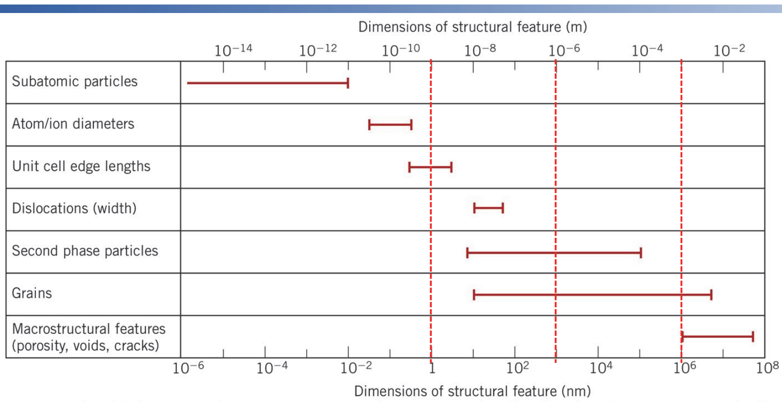
Photos produced from the work of C.P. Lutz, Zeppenfeld, and D.M. Eigler. Reprinted with permission from International Business Machines Corporation, copyright 1995.



Graphene on Ru(0001)

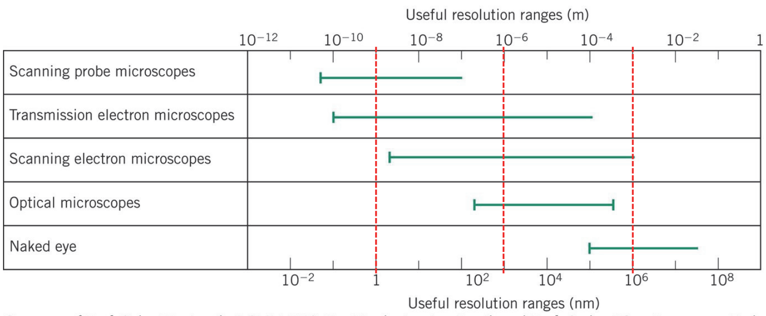
http://www.specs.de/cms/front_content.php?idart=552

6.12 Microscopic Technique



Courtesy of Prof. Sidnei Paciornik, DCMM PUC-Rio, Rio de Janeiro, Brazil, and Prof. Carlos Pérez Bergmann, Federal University of Rio Grande do Sul, Porto Alegre, Brazil.

Size range of several structural features



Courtesy of Prof. Sidnei Paciornik, DCMM PUC-Rio, Rio de Janeiro, Brazil, and Prof. Carlos Pérez Bergmann, Federal University of Rio Grande do Sul, Porto Alegre, Brazil.

Useful resolution range for four microscopic techniques