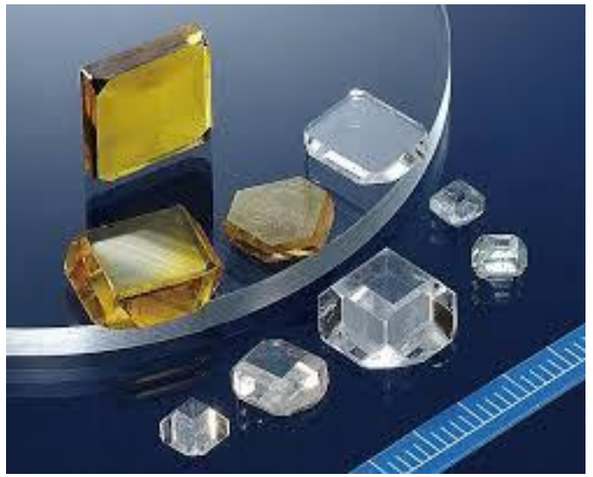
Chapter 4

Defects
(Imperfection in Crystals)

Dr. Zhe Cheng

Types of Imperfections (or Defects) in Crystals

- NO perfect crystals! → Defects or imperfection always exist



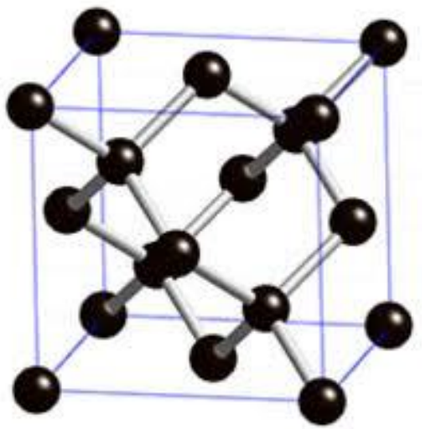
https://sumitomoelectric.com/id/dna/v16

Point (0D) defects

- Vacancy
- Interstitial atoms
- Substitutional atoms
- Others…

Line (1D) defects

- Dislocation



Planar (2D) defects

- Surfaces
- Grain boundaries
- Interfaces

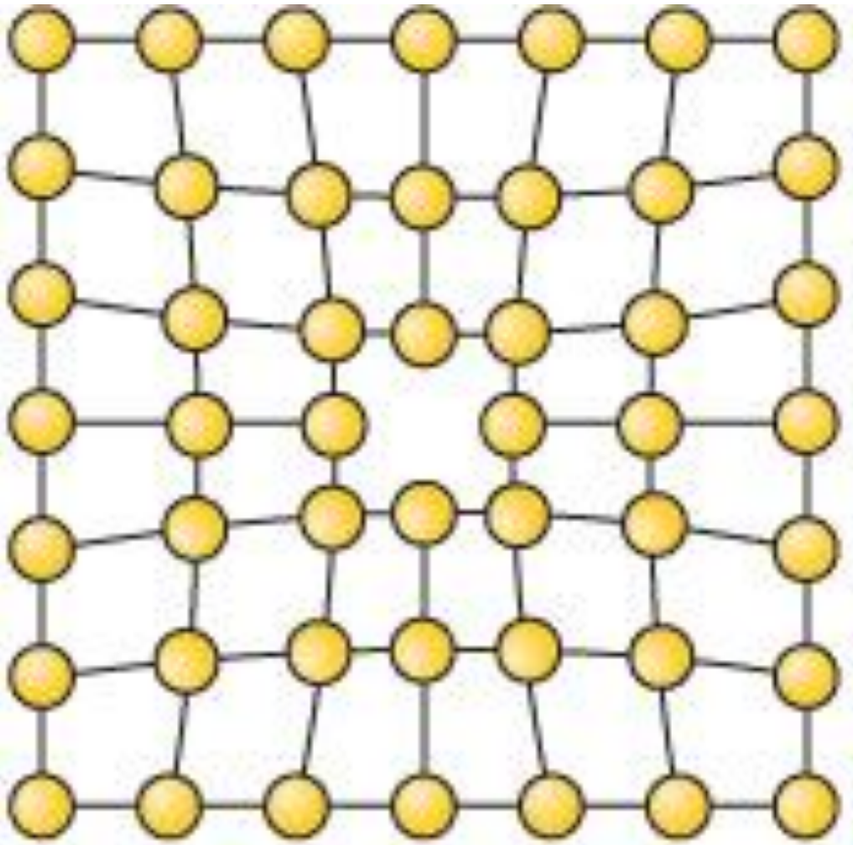
Volume (3D) defects

- Foreign inclusion/secondary phase
- Void or pores

- Many of materials properties are influenced or even determined by defects

Point Defect: Vacancy

- A vacant atomic lattice site in a structure
- Need energy to form (by breaking bonds) vacancies
- Form naturally, may occur at any atom site



Equilibrium fraction of vacancy X_V

$$X_V = \frac{n_V}{n} = \exp\left(-\frac{Q_V}{RT}\right)$$

n_V Vacancy volume concentration, unit cm^{-3}

n Atom volume concentration, unit cm^{-3}

Q_V Vacancy formation energy (a positive value), unit J/mol

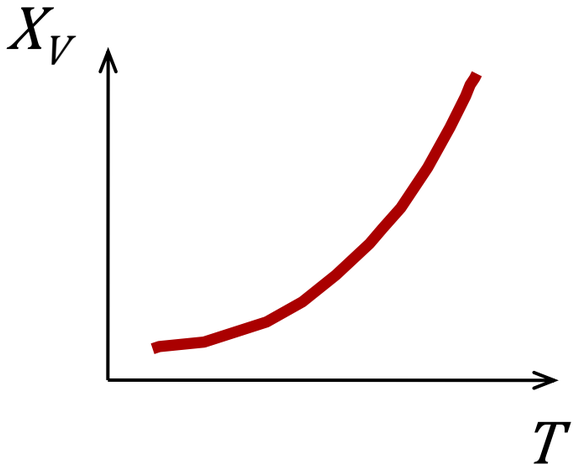
R Gas constant, 8.312 J/(mol • K)

T Absolute temperature, unit K

Change of Vacancy Fraction X_V with Temperature

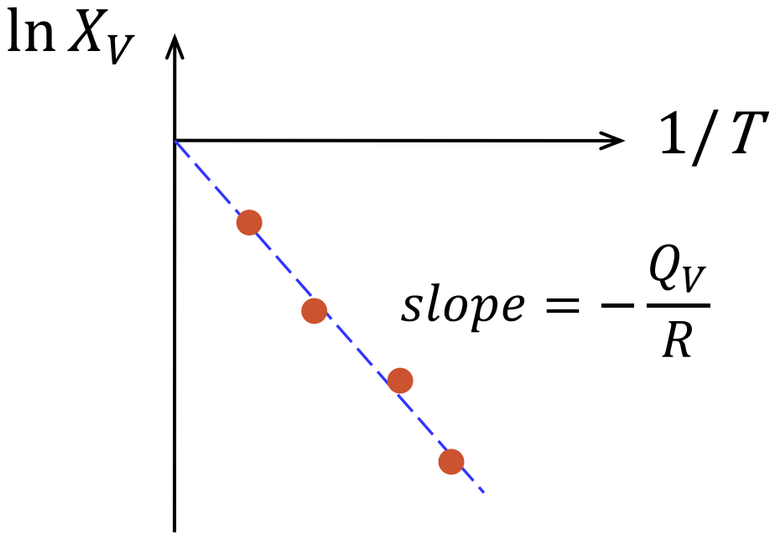
$$X_V = \frac{n_V}{n} = \exp\left(-\frac{Q_V}{RT}\right)$$

- Fraction of vacancy X_V increases "exponentially" with T



- If vacancy fraction X_V at different T are known, vacancy formation energy Q_V can be obtained by fitting:

$$\ln X_V = -\frac{Q_V}{RT} = -\frac{Q_V}{R} \cdot \frac{1}{T}$$



Estimating Equilibrium Vacancy Fraction (1)

Estimate equilibrium vacancy fraction for copper at 1050°C and at 25°C, respectively.

(Assuming vacancy formation energy is constant of 0.9 eV per atom)

Knowing $1\ \text{eV} = 1.602 \times 10^{-19}\ \text{J}$

Converting vacancy formation energy from eV per atom to J/mol:

$$Q_V\left(\text{in unit of } \frac{\text{eV}}{\text{atom}}\right) = 0.9\ \frac{\text{eV}}{\text{atom}} = 0.9 \times 1.602 \times 10^{-19}\ \frac{\text{J}}{\text{atom}}$$

$$Q_V\left(\text{in unit of } \frac{\text{J}}{\text{mol}}\right) = 0.9 \times 1.602 \times 10^{-19}\ \frac{\text{J}}{\text{atom}} \times \left(6.02 \times 10^{23}\ \frac{\text{atom}}{\text{mol}}\right) = 86796\ \frac{\text{J}}{\text{mol}}$$

Equilibrium fraction of vacancy at 1050°C:

$$X_V = \exp\left(-\frac{Q_V}{RT}\right) = \exp\left[-\frac{86796\ \frac{\text{J}}{\text{mol}}}{8.314\ \frac{\text{J}}{\text{mol}\cdot\text{K}} \times (1050 + 273)K}\right]$$

$$= \exp(-7.9) = 3.74 \times 10^{-4}$$

or 0.0374% or 1 in every ~2670 Cu atoms

Estimating Equilibrium Vacancy Fraction (2)

Continue from before:

Similarly, equilibrium fraction of vacancy at 25°C:

$$X_V = \exp\left(-\frac{Q_V}{RT}\right) = \exp\left[-\frac{86796\,\frac{\mathrm{J}}{\mathrm{mol}}}{8.314\,\frac{\mathrm{J}}{\mathrm{mol}\cdot\mathrm{K}} \times (25+273)K}\right]$$

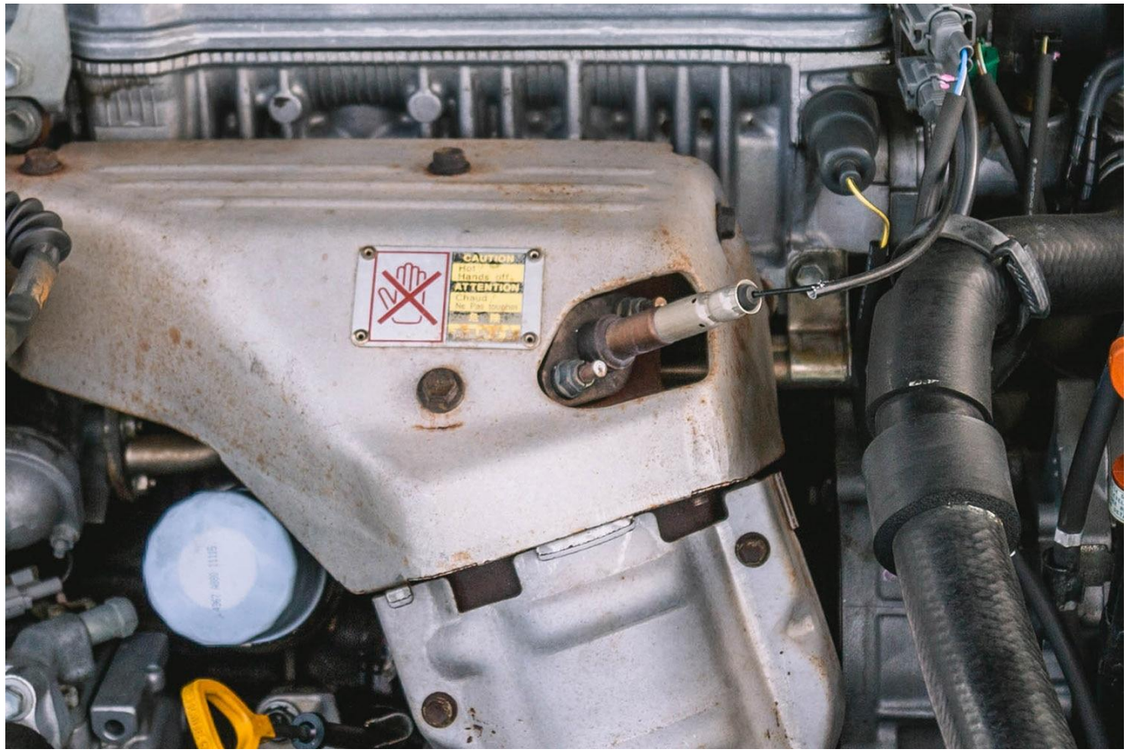
$$= \exp(-35.0) = 6.1 \times 10^{-16}$$

or or 1 in every ~1.64x10^{15} Cu atoms!

Practical Examples involving Vacancies

Desirable:

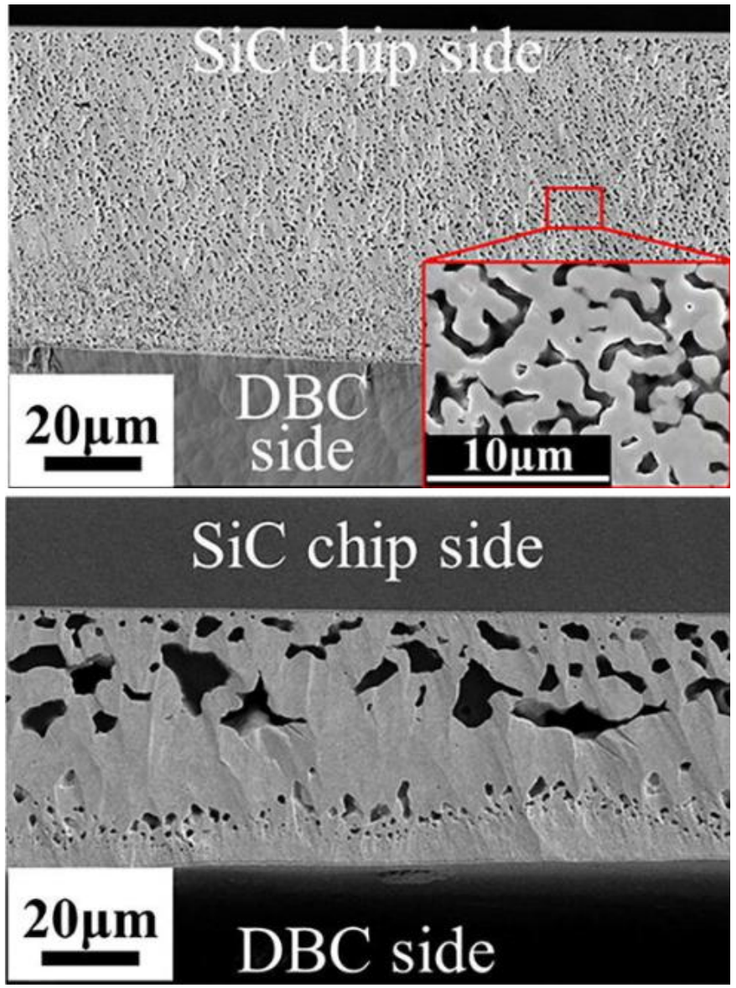
- Oxygen sensor at high temperature:
  vacancies help ion conduction and sensing



https://www.capitalone.com/cars/learn/finding-the-right-car/what-to-know-about-oxygen-sensors-in-cars-and-how-to-replace-them/2808

Undesirable:

- Voiding of materials upon processing
  (e.g., in direct bonded copper, DBC)

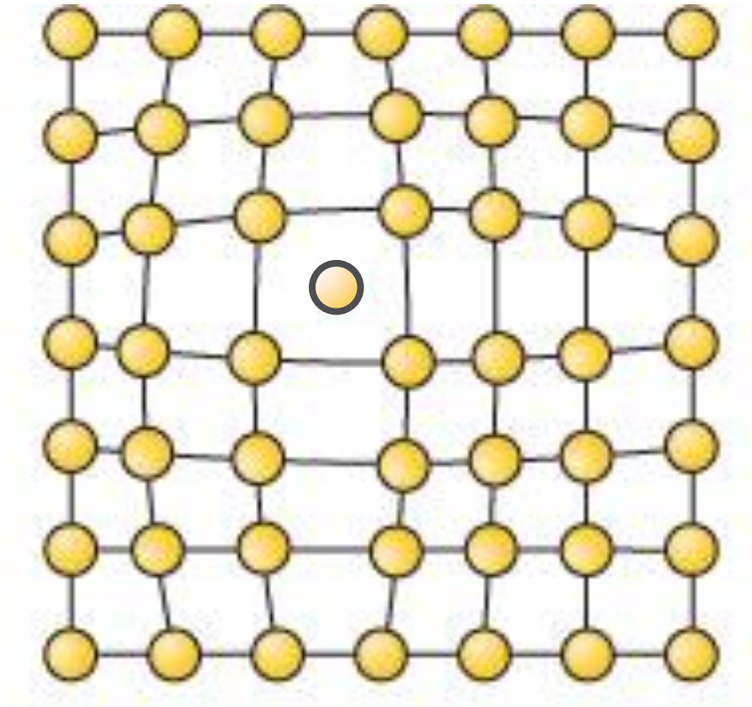


Zhao et al., Materials Letters, v228, p168 (2018)

Point Defect: Interstitial Atom

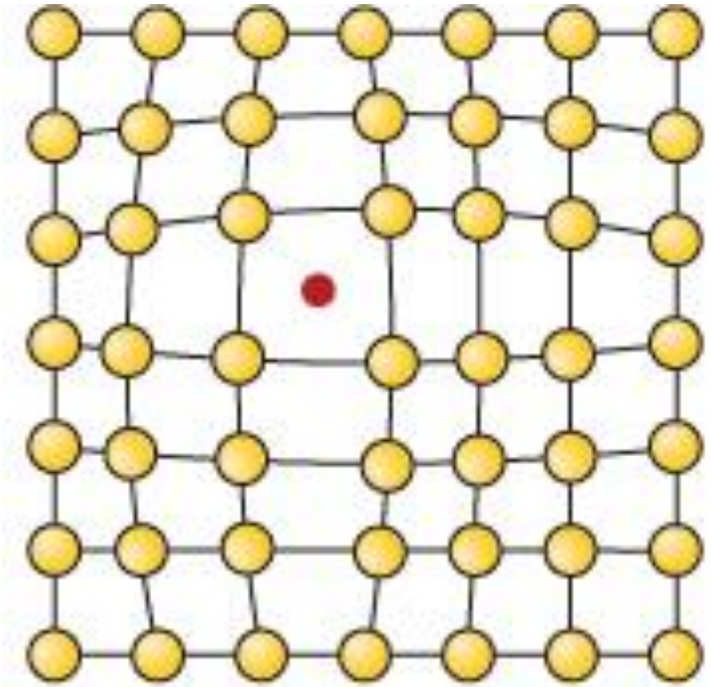
Interstitial atom: atom "goes" to a position in-between normal atoms' lattice positions

Self interstitial atom



Rare, typically accompanied with a neighboring vacancy, as in Frenkel defect

Foreign/Impurity interstitial

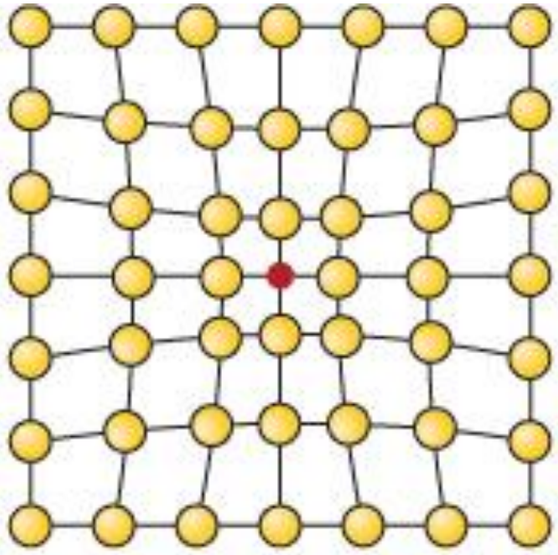


Common when the impurity atom is much smaller than host atom:
e.g., C in Fe

Point Defect: Substitutional Atom

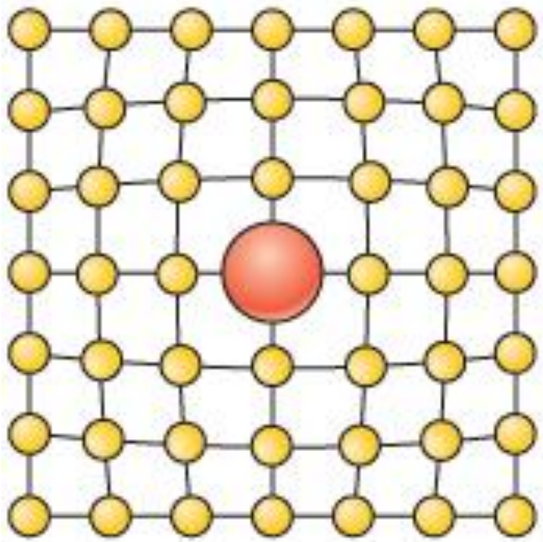
- When impurity atom **size is similar** to host atom, impurity atom will form point defect of **substitutional atom**, replacing/substituting the host atom at their positions, and the substance is called **substitutional solid solution**
- No matter larger or smaller, substitutional atom will cause **lattice distortion**

*Impurity atom **slightly smaller** than host atoms*



If much smaller than host atoms, impurity atoms tend to go into interstitial sites

*Impurity atom **slightly larger** than host atoms*

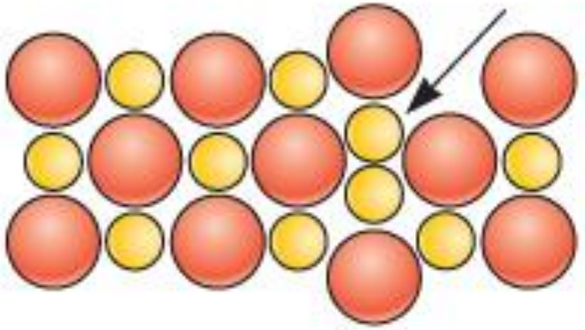


If much larger than host atoms, impurity atoms tend to cluster together and form its own crystal (or phase or substance)

Point Defect: Others

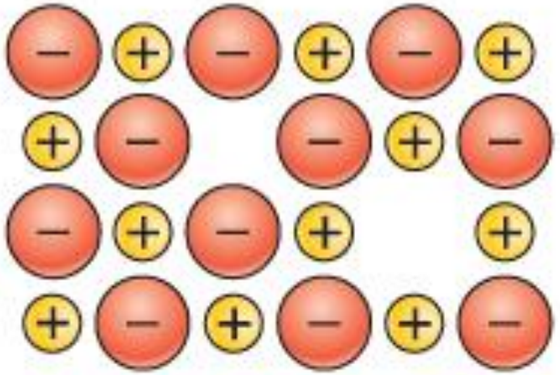
Frankel defect

Interstitial – vacancy pair

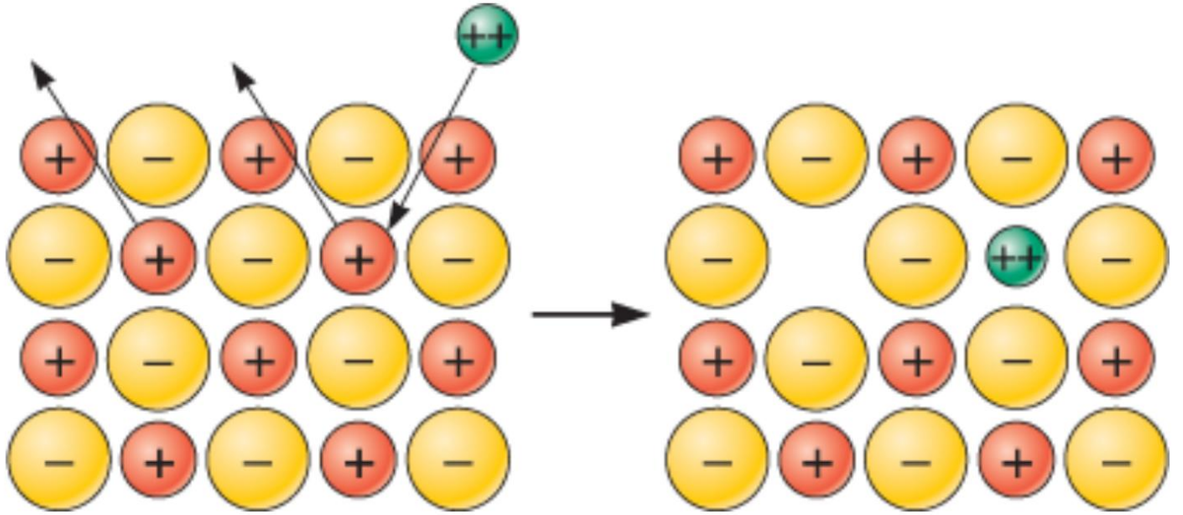


Schottky defect

A pair of positive ion & negative ion



Substitutional atom-vacancy pair



Examples involving Impurity Atoms

Desirable:

- Doping of Si with P or B for semi-conductivity

https://www.mmtc.co.jp/en/products/silicon-s.html

- Adding Zn to Cu to improve strength

https://www.orientalartauctions.com/object/art3003204-a-chinese-bronze-sword-western-han-dynasty-206-bc-24-ad

Undesirable:

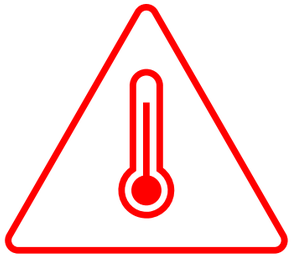
- Fe or Ni contaminants in Si wafer

https://solarmuseum.org/cells/polycrystalline-123/

Control of Point Defects

Common Factors influencing point defects (vacancy, interstitial, substitutional atoms)**:**

- **Temperature**
  - Higher T → more vacancy/interstitial



- **Impurity**
  - More (unwanted) impurity → more point defects

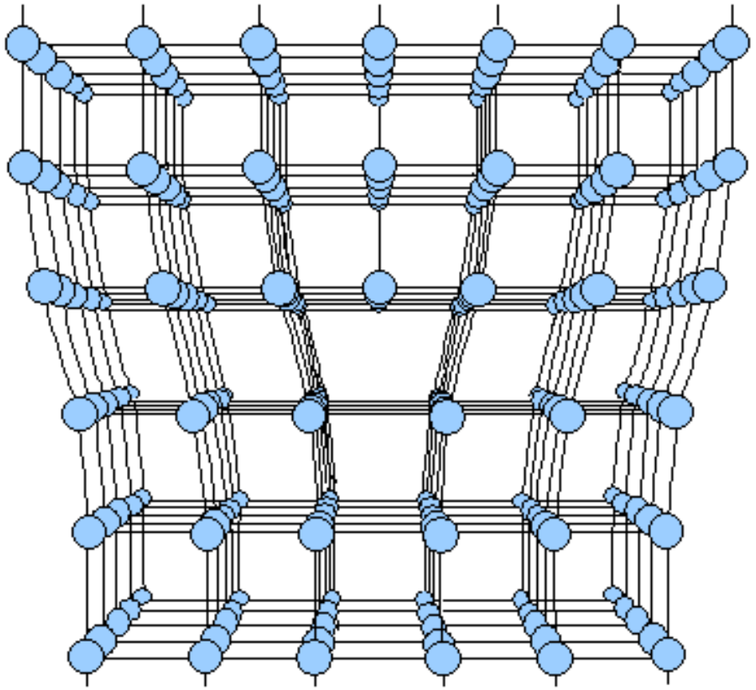
- **Doping/alloying**
  - Purposefully adding special impurity element (alloying or doping) to create certain (desired) point defects

Line (1D) Defects - Dislocation

- Dislocation: 1D defect around which atoms are misaligned
- Can be straight, but NOT necessary

Edge dislocation

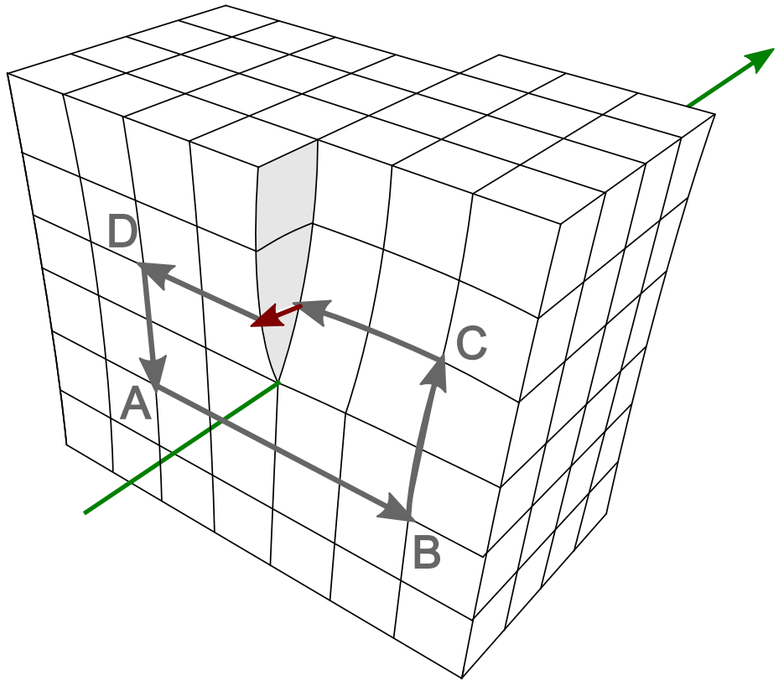
Extra half-plane of atom, inserted into a crystal structure



https://www.tf.uni-kiel.de/matwis/amat/iss/kap_5/backbone/r5_4_1.html

Screw dislocation

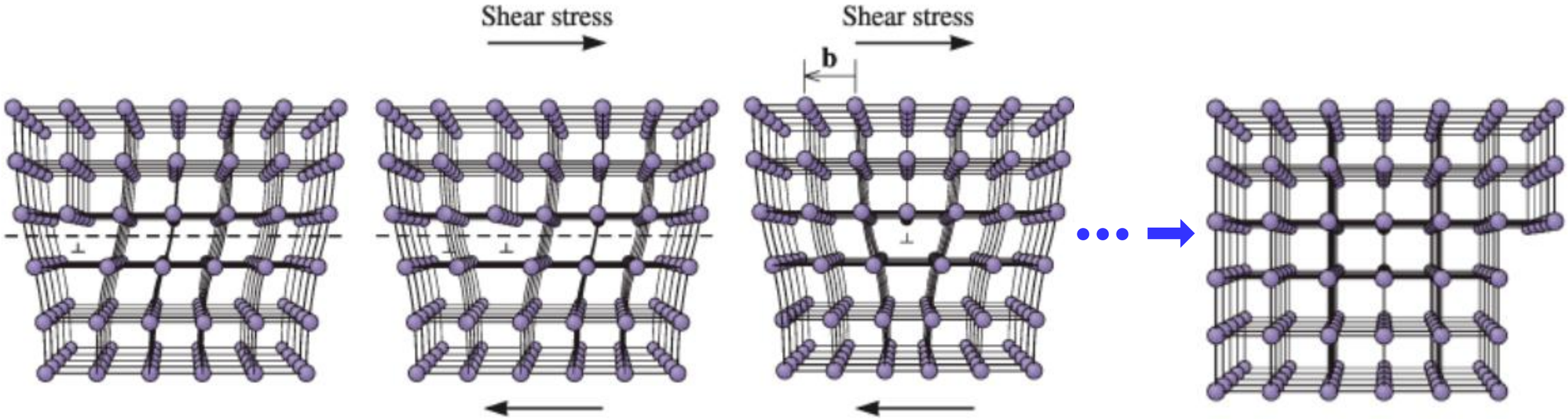
Crystal partially “cut” and the two sides shifted along the cut line



By Martin Fleck - Own work, CC BY-SA 4.0, https://commons.wikimedia.org/w/index.php?curid=96858277

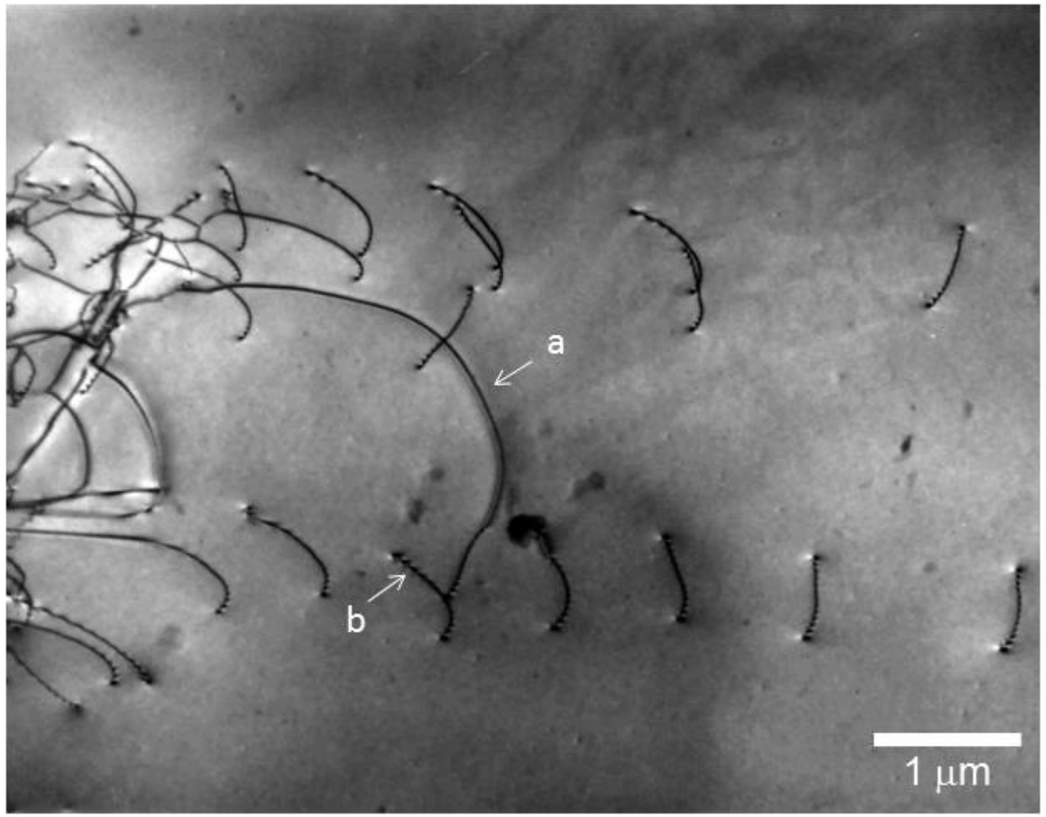
Dislocation & Plastic Deformation

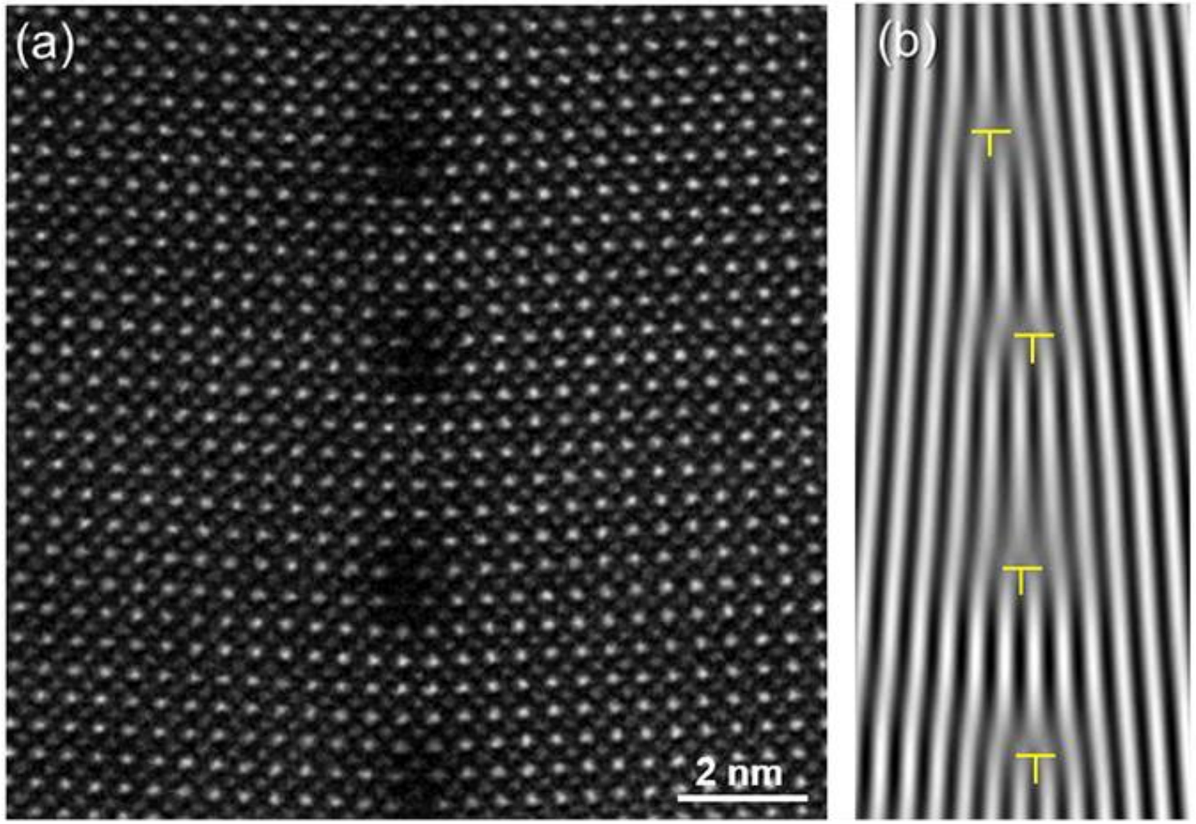
- Dislocations naturally occur in crystals
- Dislocation motion is associated with (and the reason for) **plastic or permanent deformation** of crystalline materials, especially metals



Observation of Dislocations

- Dislocations have been observed extensively using transmission electron microscopy (TEM) and related techniques





https://www.jeol.com/words/emterms/20121023.064858.php#gsc.tab=0

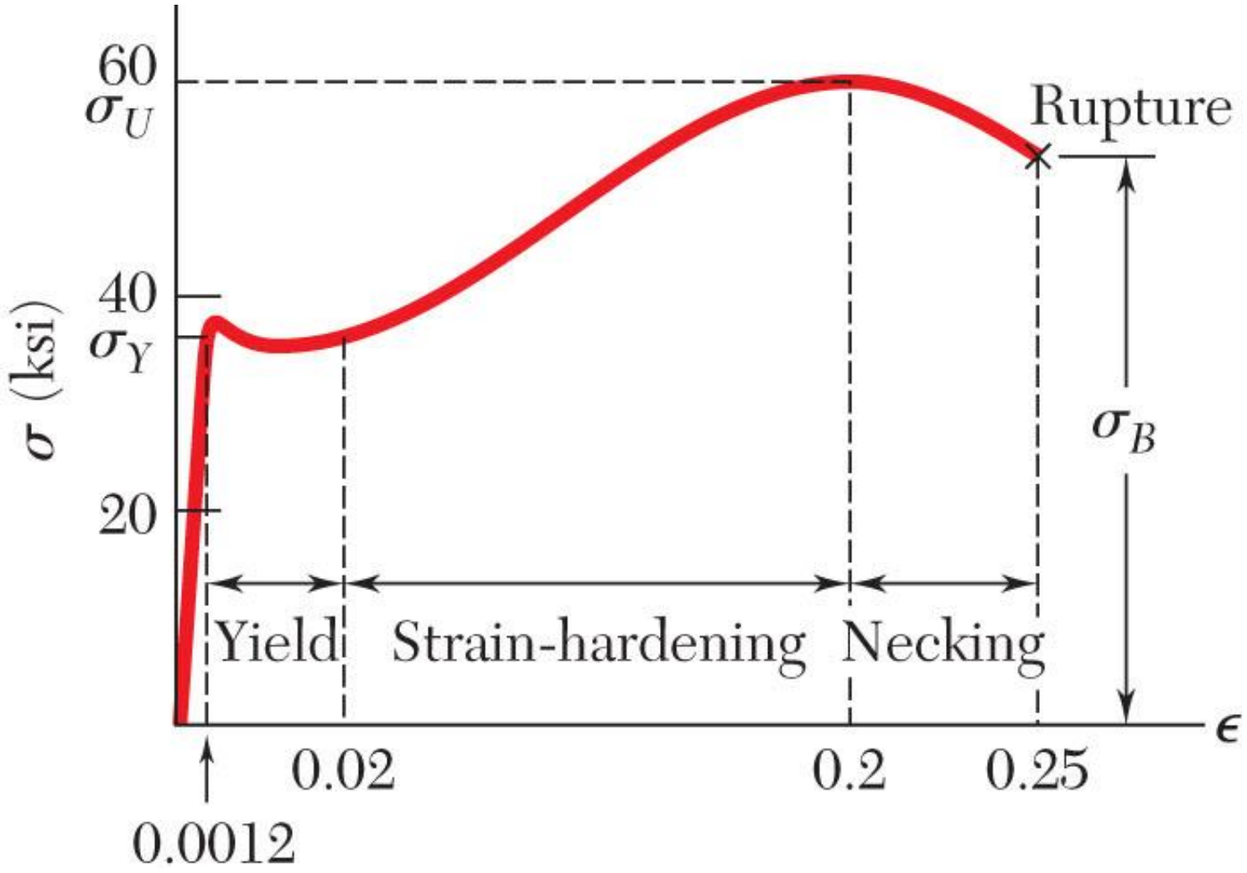
Examples involving Dislocations

Desirable:

- Strain hardening of materials:
  Formation & accumulation of dislocations in metals improve mechanical strength

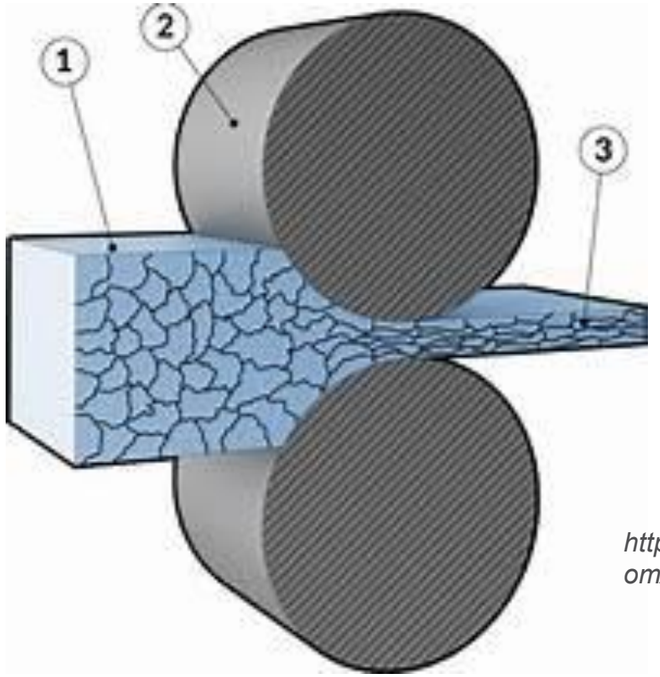
Undesirable:

- Dislocation in polycrystalline Si for solar cells: dislocations cause degradation of carrier lifetime and decrease solar cell efficiency



Creation & Elimination of Dislocations

- **To create/increase:**
  - Plastically deformation of metals
  - Introducing alloying elements
  - Introduce grain boundaries by reducing grain size)



https://www.manufacturingguide.com/en/cold-rolling-sheets

- **To eliminate or reduce:**
  - Controlled growth of single crystals or aligned crystals
  - Heat treatment (e.g., annealing)
  - Improve materials' purity

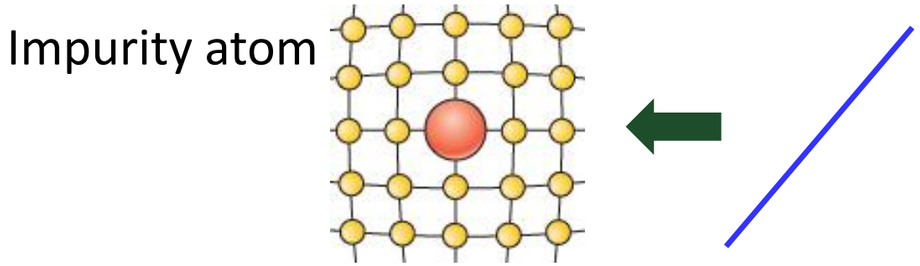
E. Dornberger, PhD Dissertation (1997)

Strengthening of Metals by Impeding Dislocation Motion

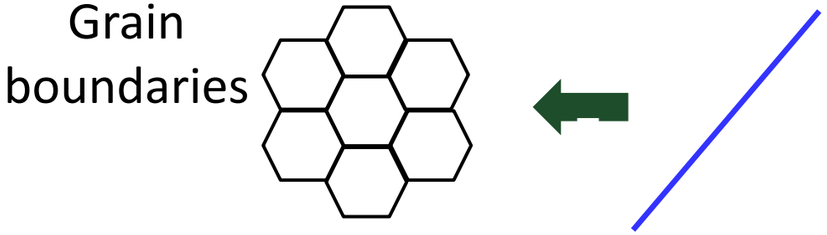
(Metal) plastically deform by dislocation motion → Strengthen metals by impeding dislocation motion, in different ways

- **Strain** hardening
  - Entangled dislocations hamper dislocation motion

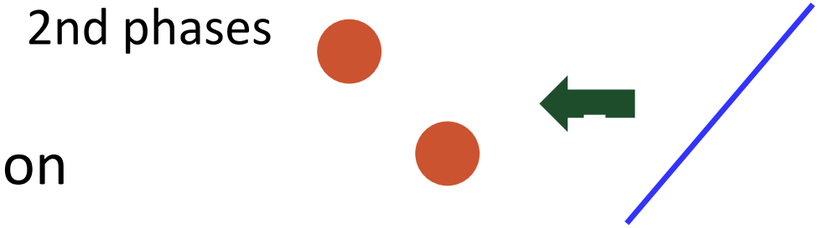
- **Solid solution** strengthening
  - Lattice distortion from impurity atoms hampers dislocation motion



- **Grain boundary** strengthening
  - Grain boundaries hamper dislocation motion



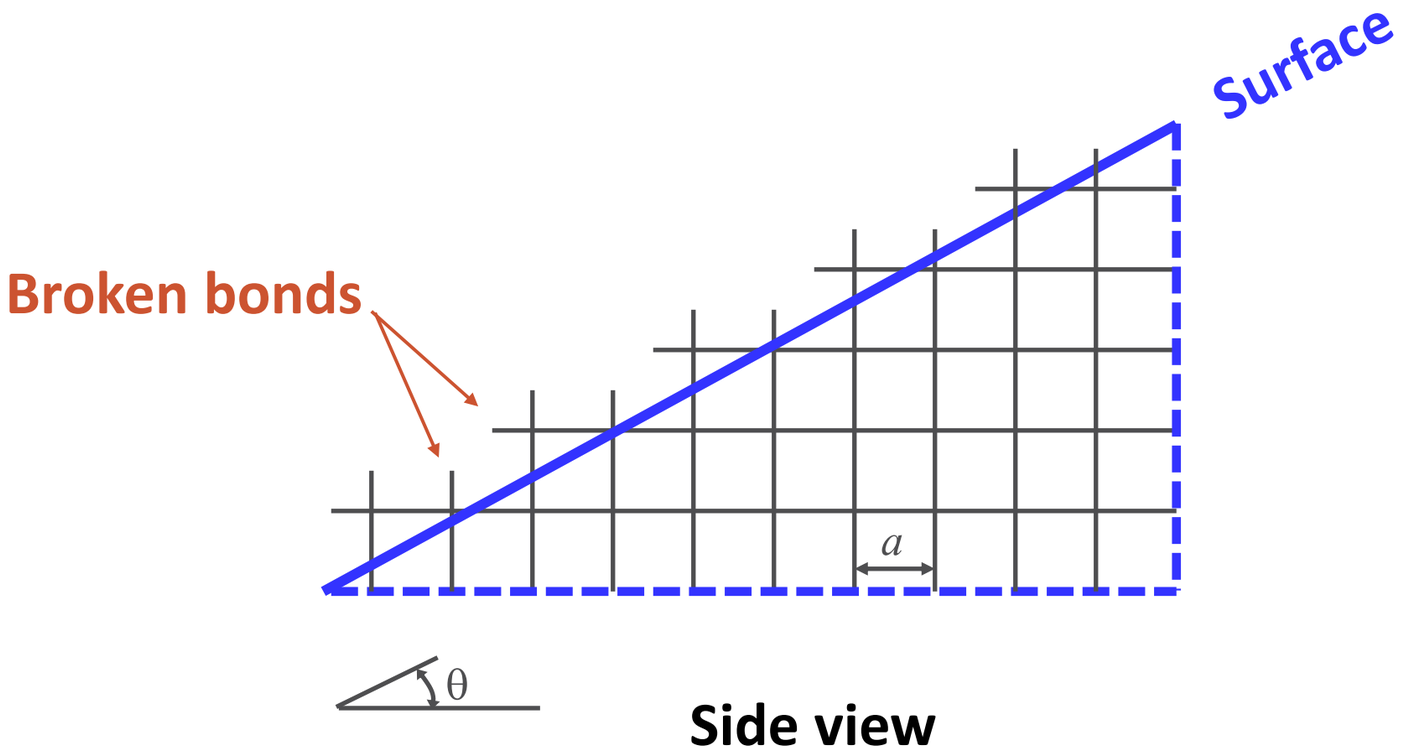
- **Secondary-phases** (e.g., precipitation) strengthening
  - Hard second phases or precipitates hampers dislocation motion



Plane (2D) Defects - Surface

➢ Surface

For perfect, infinite crystal, surface can be viewed as 2D defects with many broken bonds!

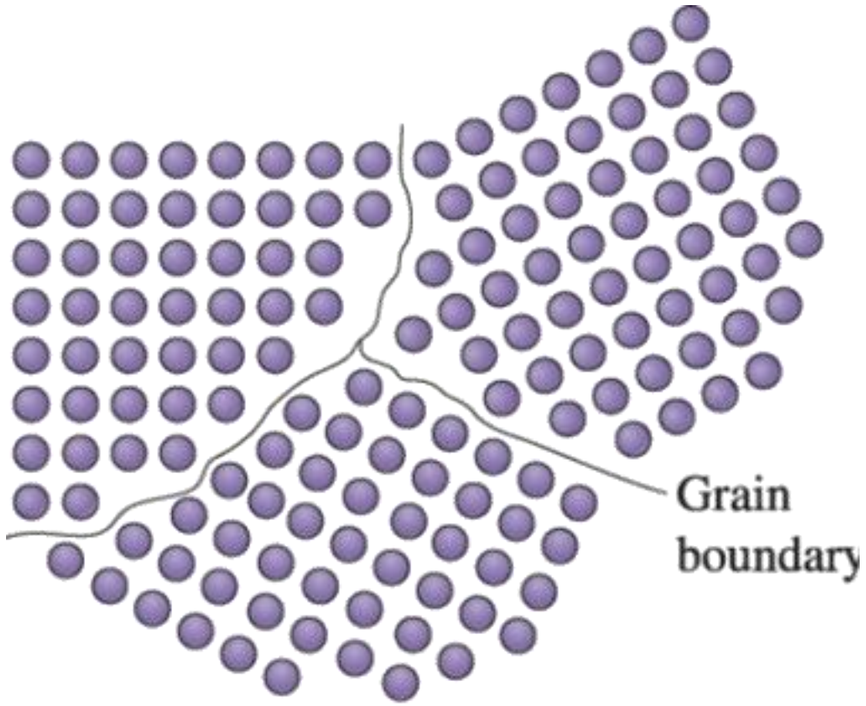


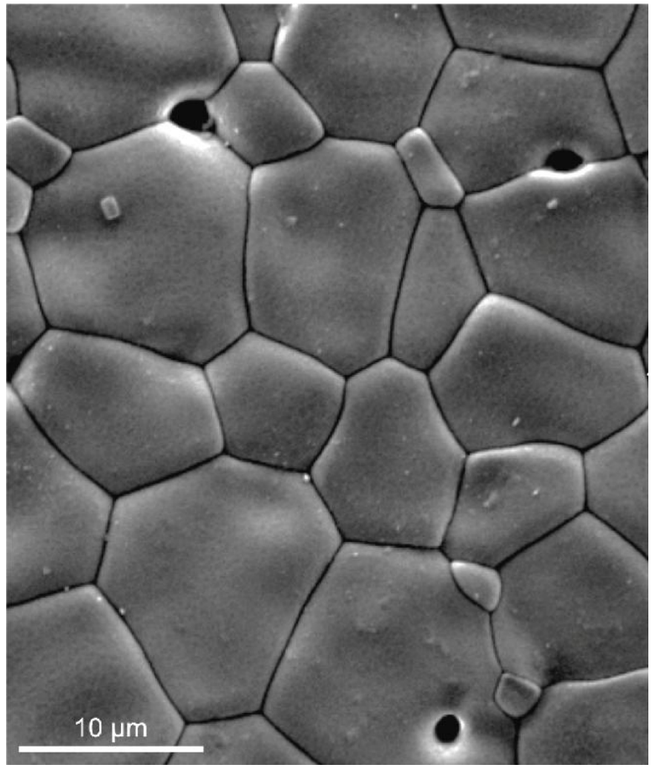
Side view

Plane (2D) Defects - Grain Boundaries (GB)

➢ Grain Boundaries (GB)

- Regions between individual crystals or grains of the same substance - transition from one ordered region to another
- Slightly disordered w/ lower packing density than in crystals or grains
- Higher mobility & higher (chemical) reactivity



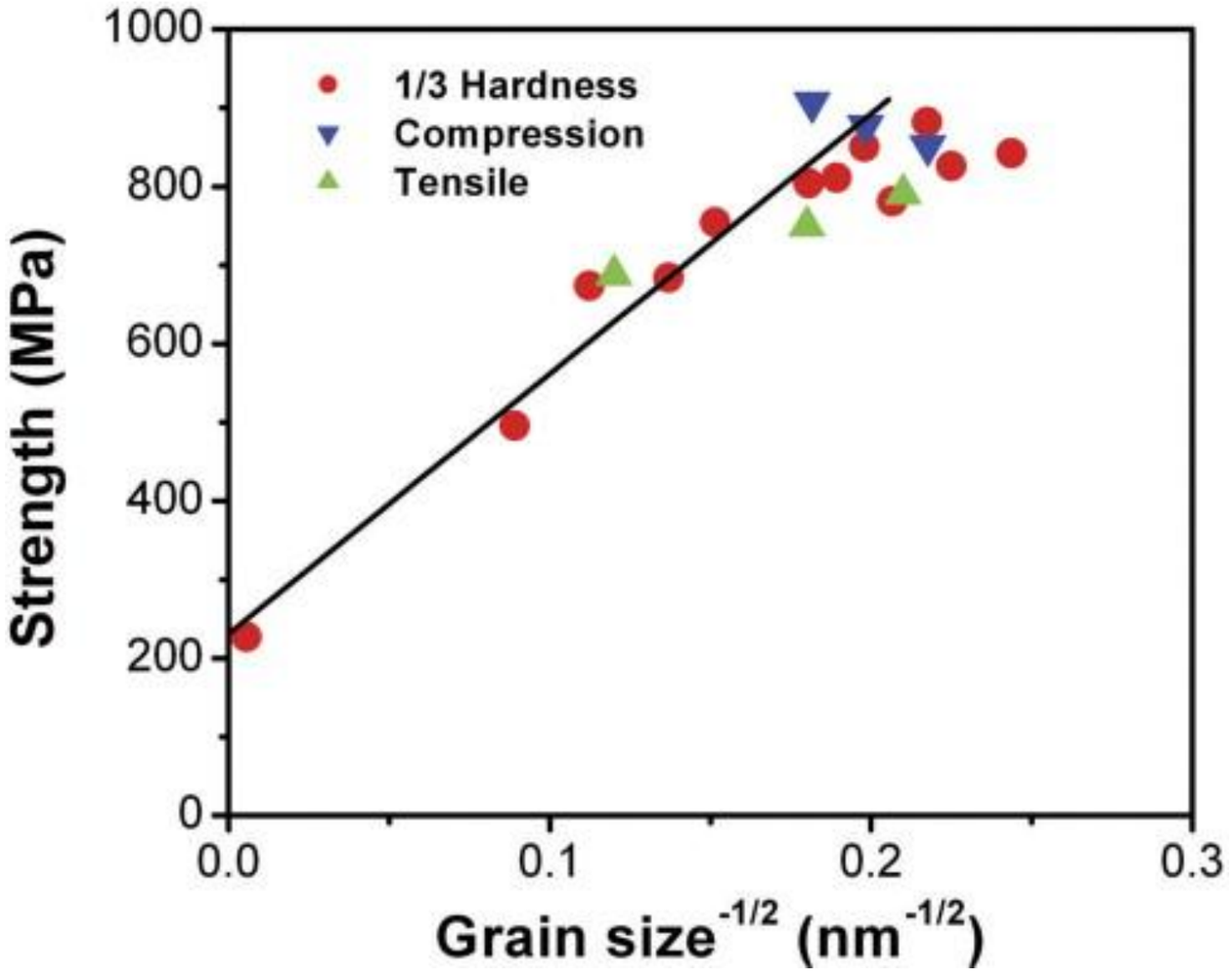


WJ Bowman, PhD Dissertation, ASU (2016)

Examples involving Grain Boundaries

Desirable:

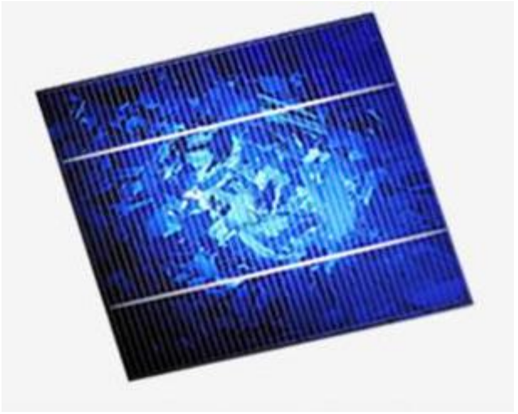
- Grain size reduction for improved strength



H Van Swygenhoven and Julia R. Weertman, Materials Today, v9(5), p.24 (2006)

Undesirable:

- Grain boundaries in polycrystalline Si for solar cell wafers decrease carrier lifetime and lowers conversion efficiency



Polycrystalline Si solar cell
Lower efficiency

Single crystalline (monocrystalline) Si solar cell
Higher efficiency

END

Homework 4.0

Carefully review chapter 4 lecture slides and, if time allows, read textbook sections (Askeland chapter 4; some sections, such as 4.5, can be neglected) and give an honor statement confirming the reading

Homework 4.1

Calculate the equilibrium fraction of atom sites that are vacant for lead (Pb) at its melting temperature of 327°C (600 K). Assume vacancy formation energy is 0.55 eV/atom

Leadbetter, A. J. et al., The Philosophical Magazine: A Journal of Theoretical Experimental and Applied Physics, 13(122), 371–377. *https://doi.org/10.1080/14786436608212615*

Homework 4.2

Cu and Ni form substitutional solid solution with face centered cubic (FCC) crystal structure, meaning Cu and Ni would randomly occupy the lattice sites. For a 60 wt% Cu-40 wt.% Ni alloy, what is the fraction of atom sites that are occupied by Ni?

Homework 4.3

Niobium (Nb) and tungsten (W) form a substitutional solid solution with body centered cubic (BCC) crystal structure, meaning Nb and W would randomly occupy the lattice sites. Knowing a particular Nb-W alloy has a lattice constant of 0.32554 nm, and its density is 11.95 g/cm^3, please estimate atomic percentage of Nb and W in the Nb-W alloy.

Hints:

Please refer to Chapter 3 class example about

- BCC structure to get the number of atoms within the unit cell
- How density is calculated based on structure and the type of atoms within it

Also need atomic mass A for both Nb and W

Homework 4.4

Given the following chemical reaction:

$2NaCl + 2H_2O = 2NaOH + Cl_2 + H_2$

Knowing that the atomic mass values

Na 22.99 g/mol

Cl 35.45 g/mol

H 1.00 g/mol

O 16.00 g/mol

- To produce **one mole** of NaOH, at least how many grams of NaCl would be needed?
- How many moles of chlorine gas (Cl_2) will be produced, under ideal condition?
- How many liters of hydrogen gas (H_2) can be produced, under standard condition?