

## Chapter 1 Introduction

Properties of materials can be determined by:

1. Composition (atomic structure)
2. Microstructure (location of atoms, amorphous vs. crystalline)

Crystalline microstructure:

- Can be described by a “unit cell” that can be repeated to describe a full 3-dimensional crystal space

Three types of properties of materials:

1. Thermochemical properties
  - How does a material respond to heat or the presence of different atoms?
2. Electromagnetic properties
  - How does a material respond to light?
3. Mechanical properties
  - How does a material respond to forces?

Microstructure

- Roughly  $10^{22} / \text{cm}^3$  atoms in a solid material
- Difficult to describe the position of every single atom – this rises to approximations for describing the material
  - o Crystalline (ordered) vs. amorphous (random)
- Amorphous materials will have isotropic properties (same in all directions) whereas crystalline materials could have anisotropic properties (different depending on crystal direction)

## Chapter 2 Bonding

- Electrons surrounding atoms can be classified as core or valence electrons
- Materials condense and form bonds in order to minimize the potential energy of atoms
- Pauli exclusion principle: no two electrons can have the same quantum numbers. The rapid rise in potential energy is a result of this.

### Bond Model

Energy vs Intermolecular Separation:

$r_0$  is the ideal intermolecular separation.

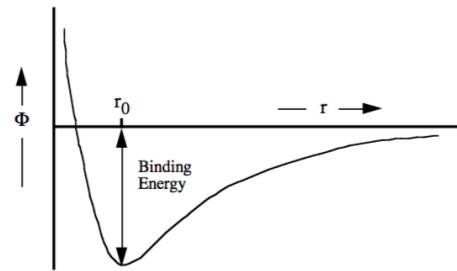


Fig. 2.1: Schematic drawing of the binding potential between two atoms as a function of their internuclear separation.

### Bonding

Bond/Molecular model: This model is poor in describing principles like conductivity (if electrons are shared, how can they move?)

Band model: Better at describing electrical conductivity. Can be used to describe metals and malleable materials. Electrons as waves in a material.

### Types of bonding:

1. Covalent bonding: saturated bonds, sharing of electrons. Strong, directional bonds, poor conductors (insulators and semiconductors), not malleable. Directional bonding means that atoms are fixed (leading to brittle materials), cannot be bent.

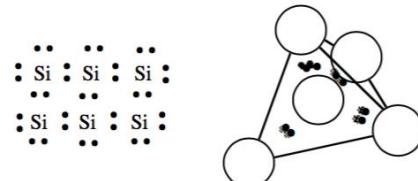


Fig. 2.3: Two-dimensional representation of covalent bonding in silicon, and the tetrahedral coordination of Si atoms in three dimensions.

2. Metallic Bonding: High electrical conductivity, non-directional, unsaturated bonds. Malleable.

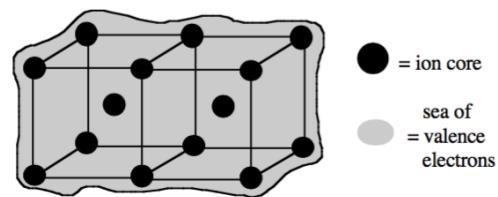


Fig. 2.4: Illustration of metallic bonding. Valence electrons bind a distribution of ion cores.

3. Ionic bonding: Electron transfer, strong, insulators, valence electrons localized and tightly bound to individual ions. Non-directional.

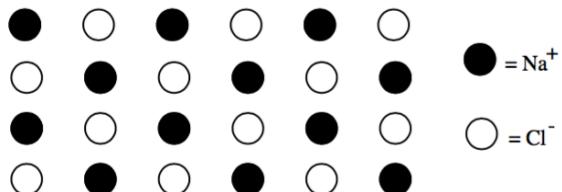


Fig. 2.5: Schematic illustration of bonding in NaCl.

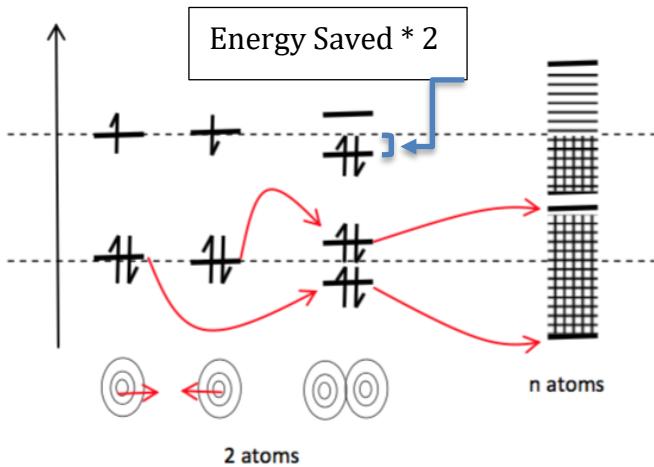
**4. Dipole Bonding:** Caused by differences in electronegativity of atoms in the molecule.  
Source: distribution of charge in neutral atom/molecule. Non-directional.

4.1 Hydrogen Bonding: H with N, O, F.

4.2 Van der Waals: dipoles caused by electronic cloud distribution induce similar dipoles in neighboring atoms, resulting in attractive force

### Band Model

As atoms are brought together, orbital splitting occurs, whereas the energy level will split into a higher and lower level. The average of these energy levels remains stable. As atoms are brought closer together, the energy level band gets larger and has more states to fill. Due to the small differences in energy states, we can consider them as a band of allowable energies.



Question: Are 2 Na<sup>+</sup> atoms more stable or are 2Na more stable? Answer: From the figure, when 2 atoms are joined, the two energy levels split, and the lower energy level will be filled.

- Full orbital: full band
- Half-filled orbital: half-filled band, full bottom half

Valence Band: Highest Occupied Molecular Orbital

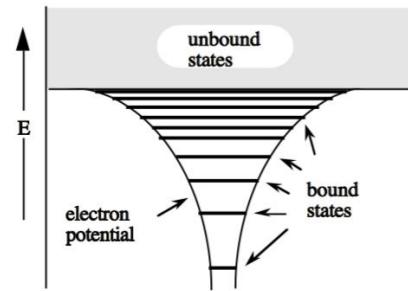


Fig. 2.7: Schematic diagram of the electron energy states in an isolated atom.

When E = 0 eV, the electron is free.

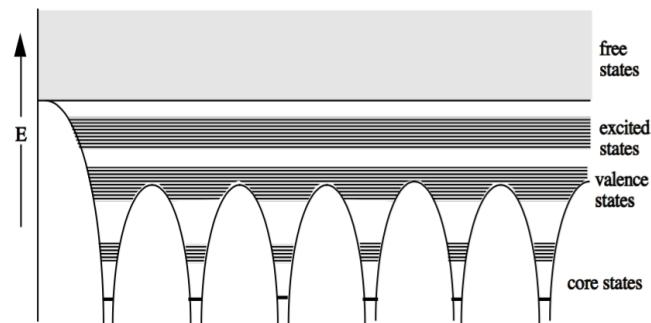


Fig. 2.8: Schematic diagram of the potential and the electron energy states along a line of atoms in a solid. The atom at the left lies at the solid surface.

When cascading many atoms together, the free electron regions create a band of shared electrons in the material. Electrons can move throughout the solid when they are in this higher energy state.

**The Fermi energy, E<sub>F</sub>,** is the energy of a state that has probability 1/2 of being filled by an electron. At T = 0K, the Fermi Energy level is the highest occupied state.

### 1. Monovalent Metal

- Everything in the leftmost of periodic table excluding H. Good conductors, shells are partially filled.
- Valence band is half-filled, easy to excite and create free electrons. The Fermi Energy level would be within the VB.

Conduction Band: Lowest Unoccupied Molecular Orbital

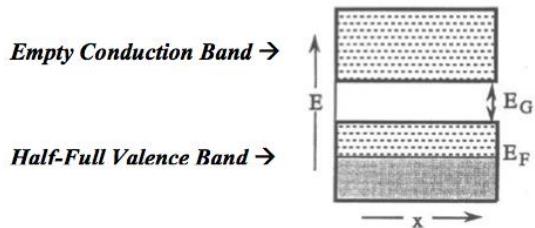


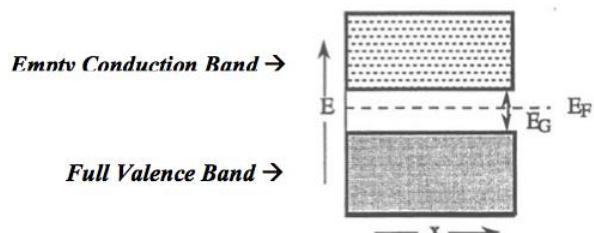
Fig. 7: A monovalent material, such as **Lithium or Sodium**<sup>2</sup>

## 2. Semi-conductor vs Insulator

- For insulator or semi-conductor, the valence band is full. The Fermi energy level is located in the band gap between the conduction band and the valence band. For this reason, much energy is required to excite an electron to the conduction band.

Energy gap  $\geq 2$  eV: Insulator

Energy gap  $< 2$  eV: semi-conductor



## 3. Divalent Metals

Conduction band overlaps the valence band. No matter where the Fermi Energy level is located, the material would be a conductor. However, they are worse conductors than Monovalent Metals, where the valence bands are half-full and electrons move freely. Second column of the periodic table.

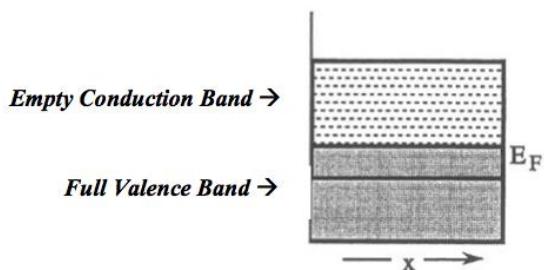
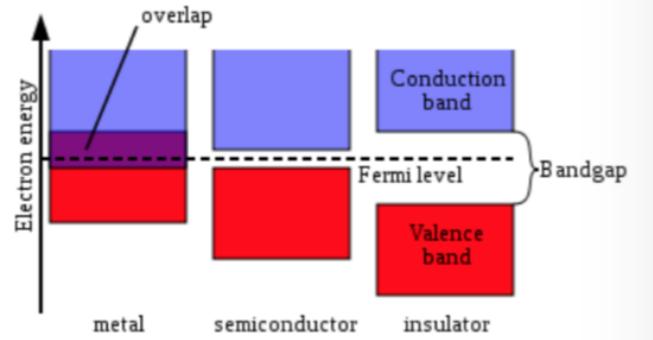


Fig. 9: A divalent metal, such as **Magnesium**<sup>4</sup>



Elements that have odd valence are inevitably metallic (empty spots within the band).

## Chapter 3 Crystal Structure

- The material can be a perfect crystal
- Or amorphous (random)

### 2-d Crystal Structures

**Lattice Point:** A point within the crystal with same environment

**Crystal Structure:** Combination of lattice points and atoms associated with those lattice points

**Unit Cell:** A cell that tiles space

**Primitive Cell:** The unit cell of a structure that contains a net of one atom/lattice point per cell.

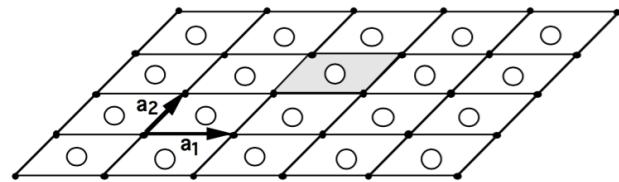


Fig. 3.2: An alternate crystal lattice and unit cell for the atom configuration shown in Fig. 3.1.

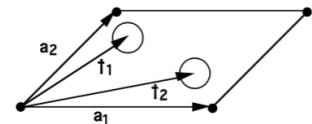
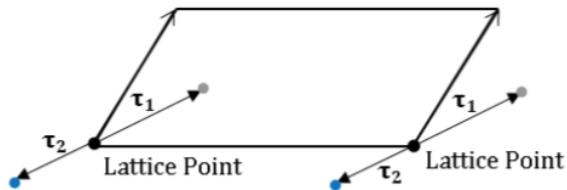


Fig. 3.4: The unit cell of the structure in Fig. 3.2, showing how basis vectors are used to locate the two atoms in the unit cell.

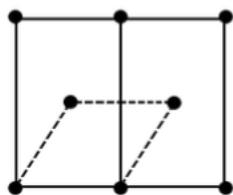
Locating the atoms from lattice points using vectors. The lattice point is arbitrary and can be placed anywhere.



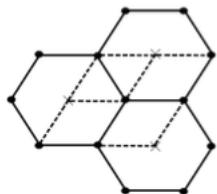
$$\vec{R} = m\vec{a}_1 + n\vec{a}_2 + \tau_1 \text{ (Carbon atom shown in grey)}$$

2D Crystal Structure: (All are shapes that allow complete tile of space without rotation)

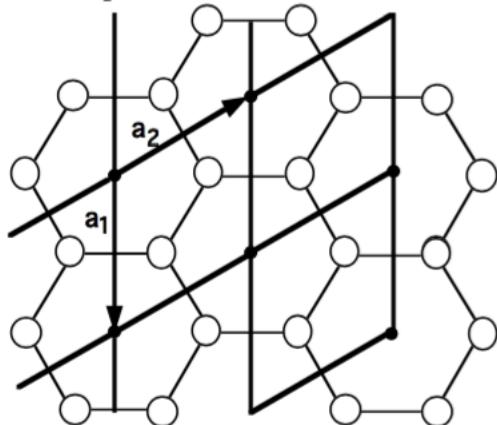
1. Square (Primitive)
2. Parallelogram (Primitive)
3. Rectangle (primitive)
4. Face-centered Rectangle (Not primitive): 2 lattice points per cell. Can be thought of parallelograms but right angles are easier to work with.



5. Hexagon (Primitive)



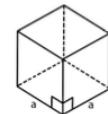
Used by graphite.



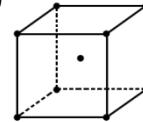
The atom has to be in the center of the hexagon in order to maintain the same environment for each cell.

### 3-d Crystal Structures

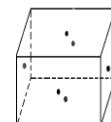
1. Simple Cubic (SC)
  - Lattice at corners
  - 1 lattice point/cell



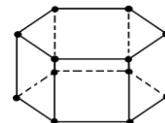
2. Body Centered Cubic (BCC)
  - 2 lattice points/cell



3. Face Centered Cubic (FCC)
  - 4 lattice points/cell



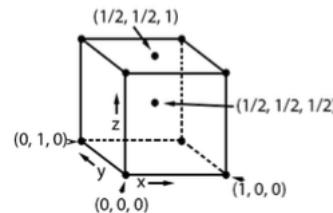
4. Hexagonal
  - 2 lattice points/cell



### Miller Indicies

Points:

- Family of points: {x,y,z}
- Points: (x,y,z)



Ex) {0,0,0}, {0,1,0}, ...

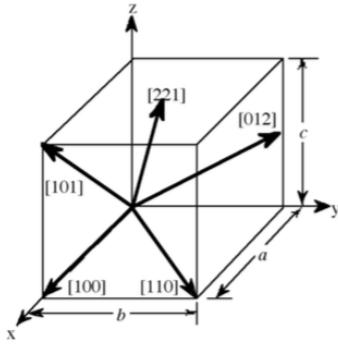
The above 2 family of points are equivalent.

Family of points are equivalent if their environment remains the same (i.e. an observer would notice no change in his view on any of these points.)

The family  $\{\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\}$  would include all center points of our cubes, and  $\{\frac{1}{2}, \frac{1}{2}, 0\}$  would include all the points in the face centers.

Directions:

- Family of directions:  $\langle h k l \rangle$
- Single directions:  $[h k l]$



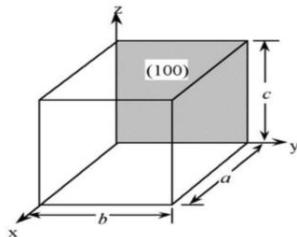
$h$ ,  $k$ , and  $l$  must be integers.

A family of directions is shown as  $\langle h k l \rangle$  and it includes all directions that are equivalent by symmetry to the direction  $[h k l]$ . So there are only 3 types: sides, face diagonals, cube diagonals.

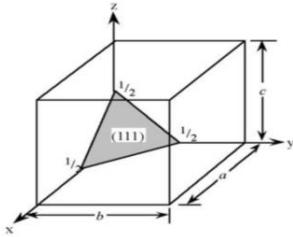
### Planes:

- Planes:  $(h k l)$

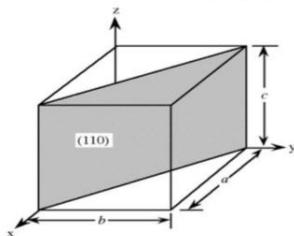
Invert to find tips of planes



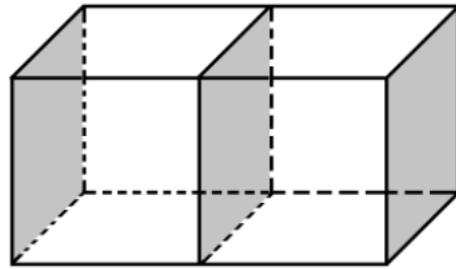
$$\begin{matrix} h & k & l \\ \frac{1}{1}, \frac{1}{\infty}, \frac{1}{\infty} \end{matrix} = (100)$$



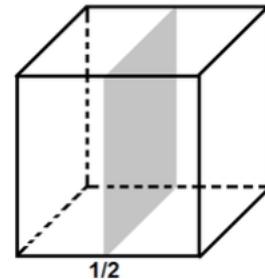
$$\begin{matrix} h & k & l \\ \frac{1}{2}, \frac{1}{2}, \frac{1}{2} \end{matrix} = (222) = (111)$$



$$\begin{matrix} h & k & l \\ \frac{1}{1}, \frac{1}{1}, \frac{1}{\infty} \end{matrix} = (110)$$



The planes are all  $\{100\}$



But this is  $\{200\}$ , not equivalent to the plane on sides.

For cubic systems:

The direction  $[hkl]$  is perpendicular to the plane  $(hkl)$ . This can be used to calculate the angle between two planes using the dot product.

$$\vec{a} \cdot \vec{b} = |a||b| \cos \theta$$

Then the angle between two planes:

$$\theta = \cos^{-1} \left( \frac{[hkl]_1 \cdot [hkl]_2}{|hkl|_1 \times |hkl|_2} \right)$$

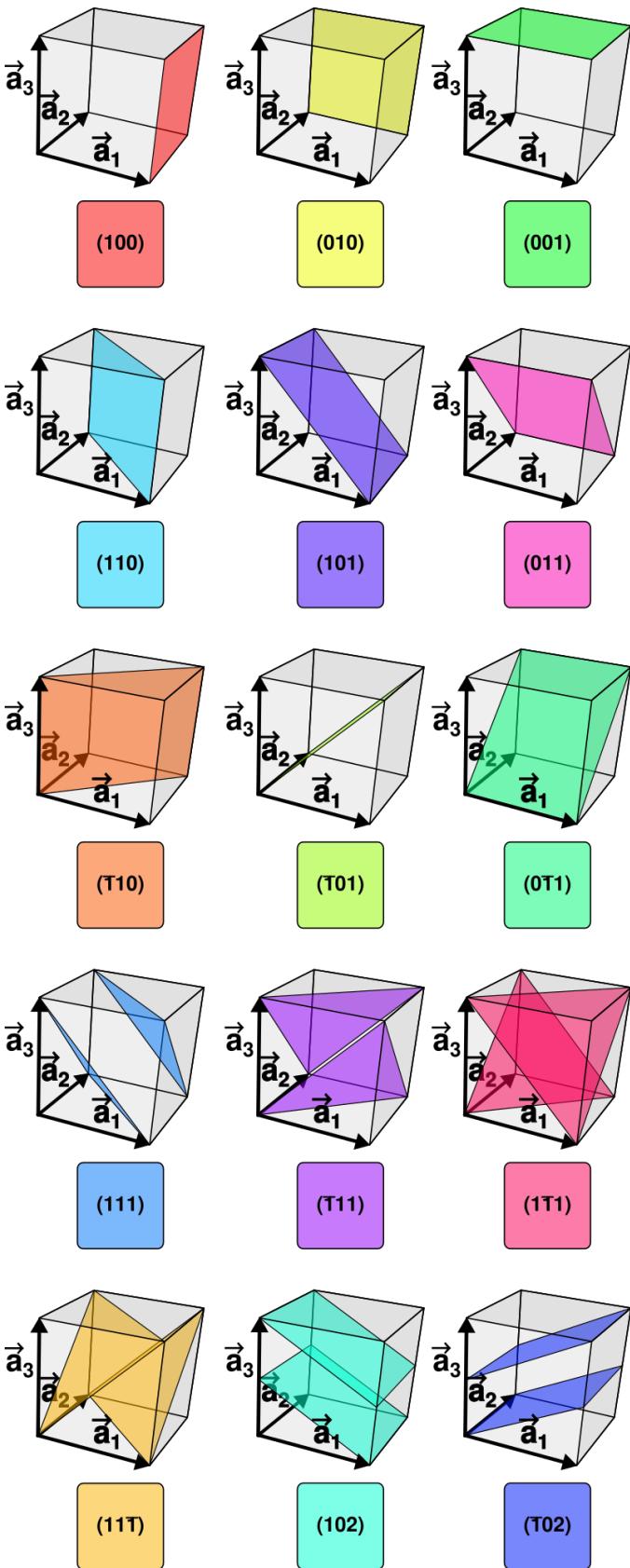
Distance between parallel planes:

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

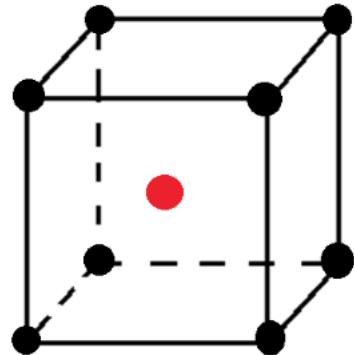
where  $a$  is side length of cube

Use Miller Indices to describe planes

Family of Planes: all crystallographically equivalent parallel planes have same  $\{hkl\}$



- Not a close-packed structure
- All BCC are metallic conductors



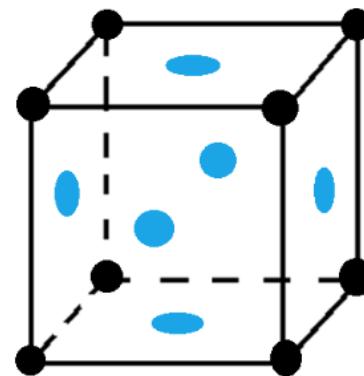
Family of corner lattice points (black dots) : {0, 0, 0}  
Family of center lattice point (red dot) : {1/2, 1/2, 1/2}

Family is related by symmetry. Every corner is part of the same family, because every corner can rotate to get to another corner position.

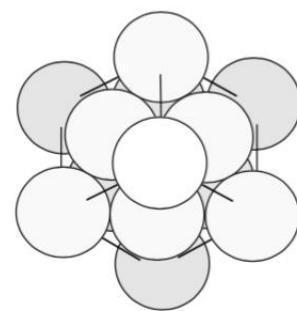
**Close-Packed Structures:** Spherical atoms packed together as tightly as possible.

### FCC

- ABCABC... stacking
- A total of 4 lattice points



Family of corner lattice points (black dots) : {0, 0, 0}  
Family of face centered lattice points (blue dots) : {1/2, 0, 1/2}



View of the FCC cell along its diagonal showing the cube axes.

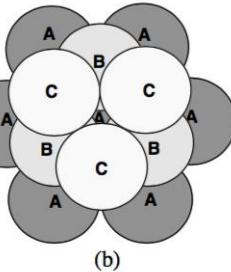
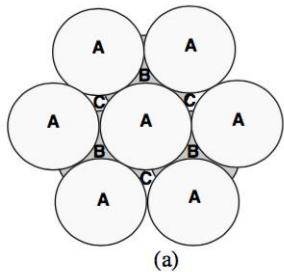
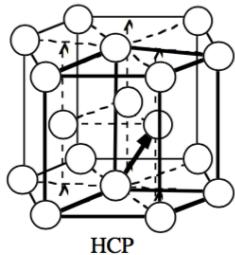
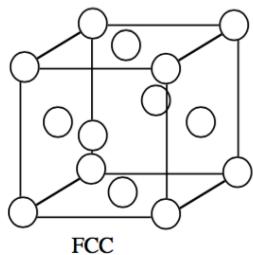
## Crystal Structures

### BCC

- Lattice points at all corners and at center of cube

## HCP (Hexagonal Close-Packed)

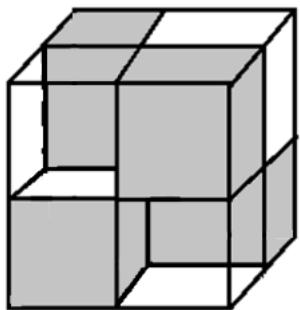
- ABABAB... stacking
- A total of 6 lattice points



.3.26: The two possible types of three-layer stacking of equal-sized spheres: (a) ABA (the A-sites in the third plane obscure those in the first plane); (b) ABC.

## DC (Diamond Cubic)

- A variation of FCC. Half of the tetrahedron voids have atoms.

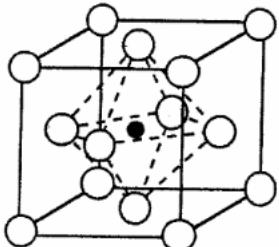


## Voids

- Empty spaces in the structure that additional atoms may fill

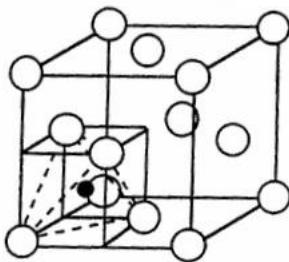
### Octahedral Void

- Center is equidistant from 6 neighboring atoms.



### Tetrahedral Void

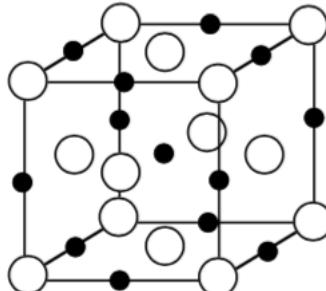
- Center is equidistant from 4 neighboring atoms.



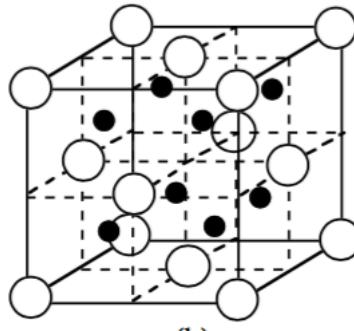
## **Voids in Crystal Structures**

### 1. FCC

- 4 octahedral voids

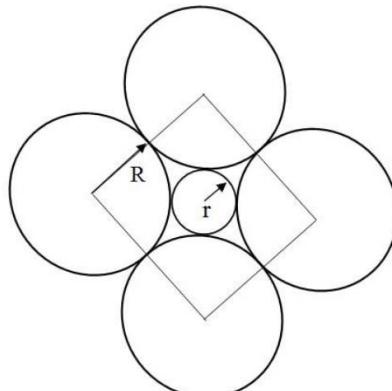


- 8 tetrahedral voids



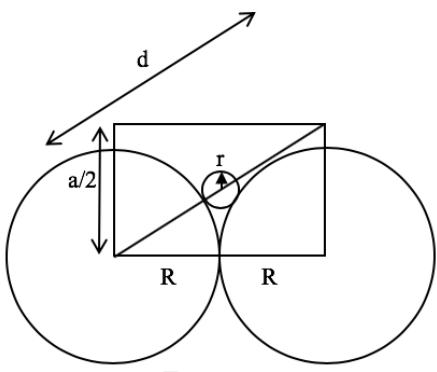
### Void size in FCC:

- Octahedral void:

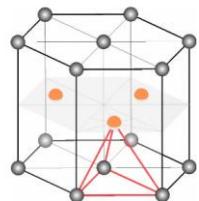


$$r = \frac{2\sqrt{2}R - 2R}{2} = (\sqrt{2} - 1)R$$

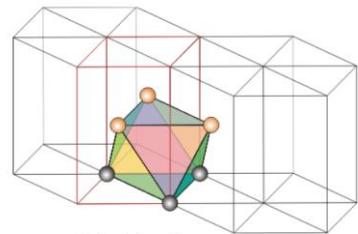
- Tetrahedral void:



$$\text{Hence: } r = R(\frac{\sqrt{6}}{2} - 1)$$



Tetrahedral voids



Octahedral voids

## Mixture of material

- No real material is 100% pure
- pseudo-atoms: average the properties of the substitutional species by having uniform, arbitrary atoms.

Substitutionally: Atoms replace regular ones in the crystal lattice

Interstitially: Atoms occupy empty spaces (voids) in the crystal lattice

## Ordered Solutions

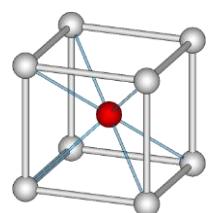
	Substitutional	Interstitial
BCC	CsCl	Nb <sub>3</sub> Sn
FCC	Cu <sub>3</sub> Au	NaCl, β-ZnS
HCP		α-ZnS
DC	β-ZnS	

## Criterias:

- Metallic: Unsaturated bonds
- Ionic: Nearest neighbors all opposite type
- Covalent: ≤ 4 nearest neighbors

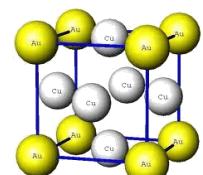
## 1. CsCl

- BCC substitutional
- 1 lattice point
- Metallic, ionic, not covalent



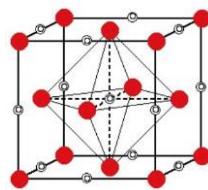
## 2. Cu<sub>3</sub>Au

- FCC substitutional
- 1 or 3 lattice points
- Metallic, not ionic, not covalent



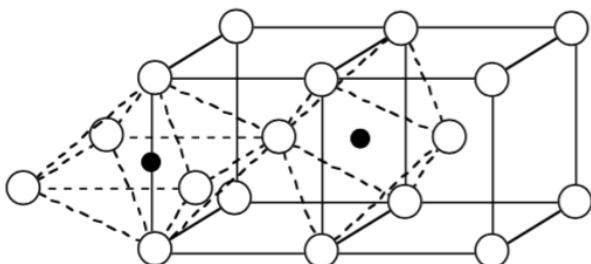
## 3. NaCl

- FCC interstitial - octahedral
- Metallic, ionic, not covalent
- Cl<sup>-</sup> larger – occupy FCC atoms
- Na<sup>+</sup> smaller – occupy voids



## 2. BCC

- Octahedral voids and tetrahedral voids in BCC are distorted
- 6 octahedral voids



- 12 tetrahedral voids, not true tetrahedrons

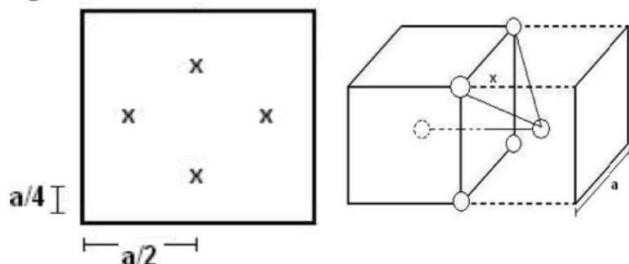
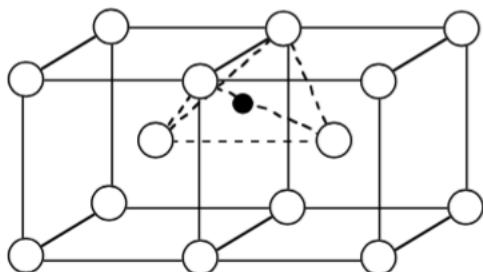


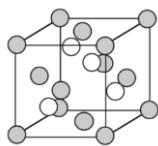
Figure 4: Tetrahedral voids in BCC crystal

## 3. HCP

- 6 octahedral and 12 tetrahedral voids

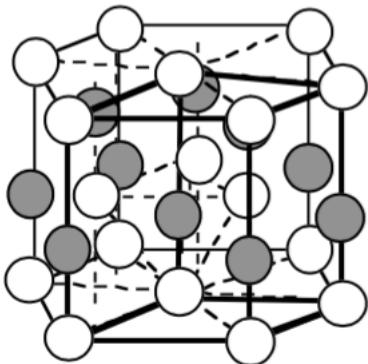
#### 4. $\beta$ -ZnS

- DC substitutional/FCC interstitial – tetrahedral
- Metallic, ionic, covalent
- Compound semiconductors (GaAs)



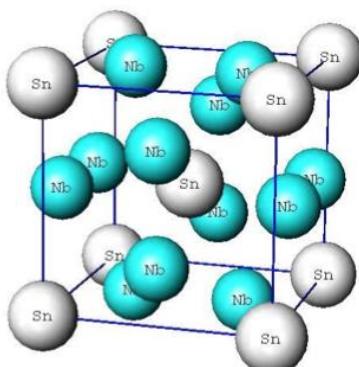
#### 5. $\alpha$ -ZnS

- HCP interstitial
- Metallic, ionic, covalent
- Ex. GaN, InN
- Fills half of all tetrahedral voids



#### 6. $\text{Nb}_3\text{Sn}$

- BCC Interstitial
- A15 Superconductor ( $\text{A}_3\text{N}$ )
- Separated chains of interstitial atoms provide easy pathway for current flow. Good isotropic conductor
- Half of tetrahedral voids filled



### Predicting Crystal Structures

#### Solid Solutions:

- Generally concentrated solid solutions cannot exist unless the size difference between the atoms is less than 15%

- Elements that are widely separated in the periodic table do not ordinarily form solid solutions

- When two elements do form a solid solution, look at average valences:

- $z = 1$ : FCC
- $z = 1.5$ : BCC
- $z = 1.75$  HCP

#### Substitutional Compounds:

- Similar in size
- Not too different in electronegativity

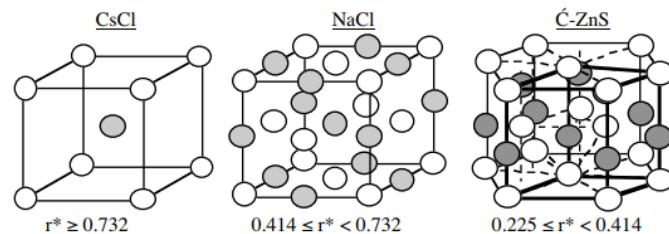
#### Ionic Interstitial Compounds:

- It is easy to determine the crystal structure but hard to predict the crystal structure a material will take. It is because the condensation energy is much greater than the crystal energy.

$$E_{\text{total}} = E_{\text{crystal}} + E_{\text{condensing}}$$

$$E_{\text{condensation}} \gg E_{\text{crystal}}$$

We define  $\alpha = \frac{r^+}{r^-}$  where  $r^+$  and  $r^-$  represent radii of positively and negatively charged atoms respectively. The structure of an ionic crystal can then be predicted using the following rules:



### Chapter 4 Defects

- 0D Point Defects (vacancy or interstitialcy)
- 1D Line Defects (dislocation)
- 2D Surface Defects (grain boundary)
- 3D Volume Defects (precipitate)

#### Point Defect

Intrinsic Defect: Formed when an atom is missing from a position that ought to be filled in the crystal

Two types of point defects: **vacancy** and **interstitialcy** (high energy defect)

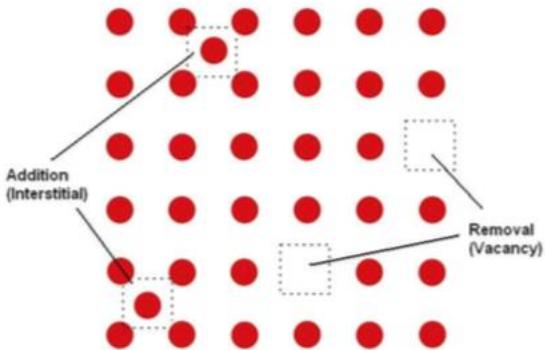
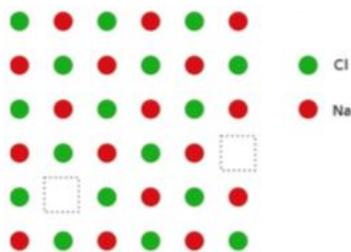


figure 3: Intrinsic defects in non-ionic compounds

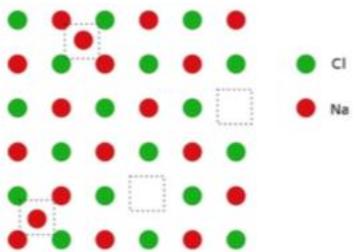
#### For Ionic Materials:

- Defects that are charge neutral

- **Schottky Defect:** Removing two atoms of opposing charges

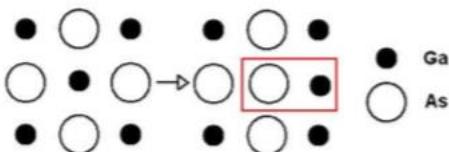


- **Frenkel Defect:** Atom creates a vacancy in the lattice and becomes an interstitial by lodging in a nearby location



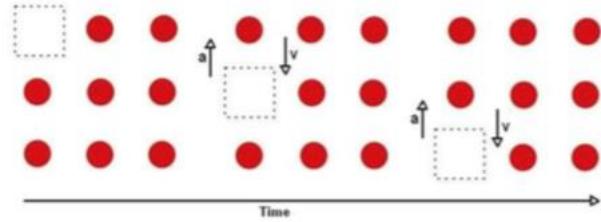
#### For Covalent Materials:

- **Anti-site Defect:** Two atoms of opposite charges exchange places

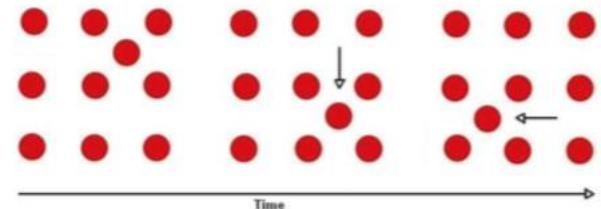


- Diffusion: Vacancies allow diffusion, more likely to happen.

- Vacancy diffusion: Movement of vacancies



Interstitial diffusion: Movement of interstitials

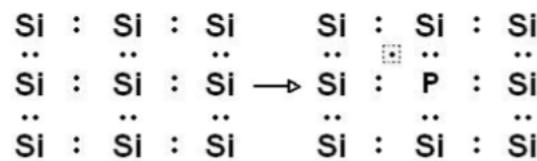


Extrinsic Defect: A foreign atom occupy space in lattice. Doping Silicon wafers with Boron or Phosphorous. They are called **solutes** if they are intentionally added to the material and **impurities** if they are not.

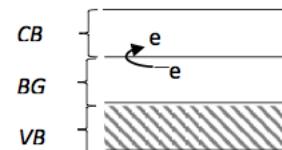
- Substitutional solute (impurity): occupy a lattice site

- Interstitial solute: occupy an interstitial site

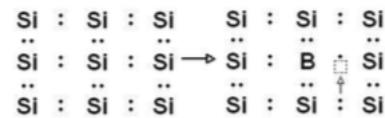
- **Phosphorous Doping:** Replace the central Si with a P atom. An extra electron is added. Electron is loosely bounded. N-type semiconductor (negatively charged).



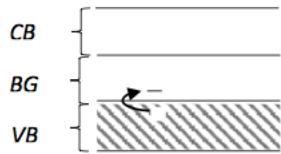
Electron promotion is easy.



- **Boron Doping:** Replace the central Si with a B atom. There is one less electron, a vacancy, hole, is present. P-type semiconductor (positively charged).



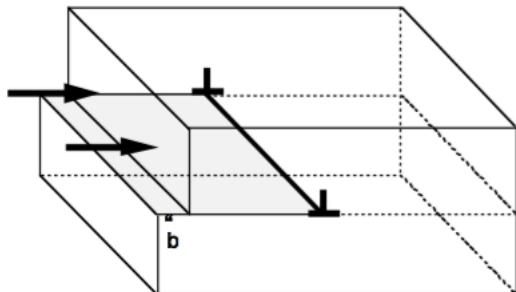
Electrons are easily obtained. The hole is promoted.



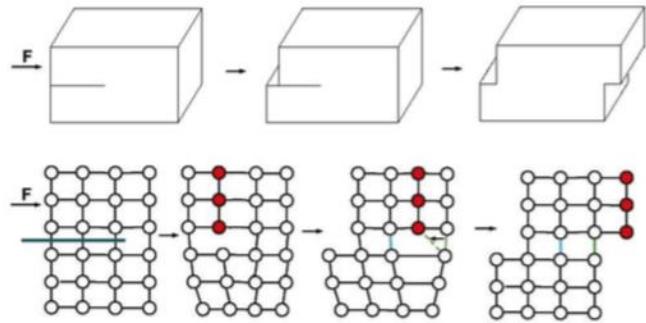
- Extrinsic Semiconductor: Semiconductors whose electrical properties are controlled by electrically active solutes; number of free electrons and number of holes never equal; high electrical conductivity; depends on T and doping
- Intrinsic Semiconductor: Has no impurity atoms; number of free electrons and number of holes exactly equal; low electrical conductivity; depends on T alone
- A conductor is not transparent because photons are absorbed to excite electrons
- An insulator is transparent because photons are not absorbed but passes through

### Line Defect

- Edge Dislocation: When Burgers vector is perpendicular to dislocation line  
An edge dislocation is a defect where an extra half-plane of atoms is introduced midway through the crystal. As force is applied to the crystal, the half-plane of three atoms moves throughout the structure, forcing a single row of bonds to break at a time.



Eventually leads to deformation of material.



Elastic deformation: Crystal structure maintained – moved atoms go back into place

Plastic deformation: Permanently change the crystal structure

### The Slip Plane

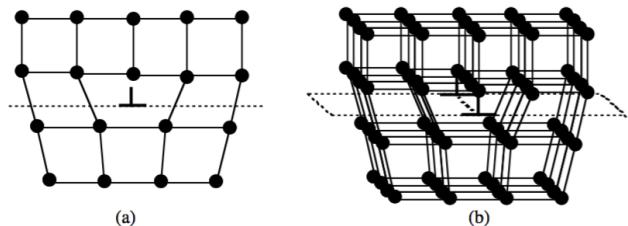
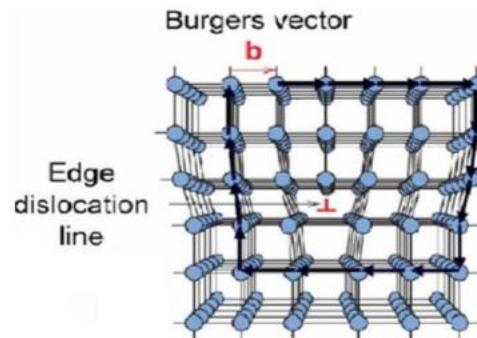


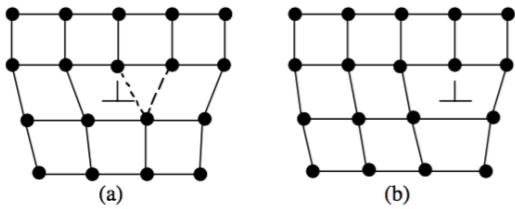
Fig. 4.10: An edge dislocation in a simple cubic structure. The dotted plane is the slip plane.

### Finding Burgers Vector



### Glide

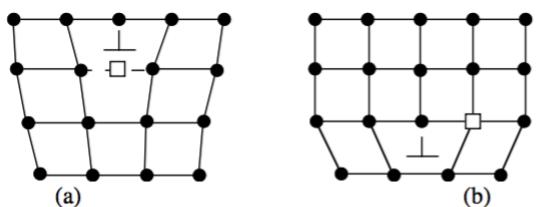
- Breaking one bond at a time, the dislocation glides through the crystal along its slip or glide plane. The slip plain must contain both the Burgers vector and the dislocation line



4.12: Glide of an edge dislocation. Only a single bond must be broken per plane for each increment of glide.

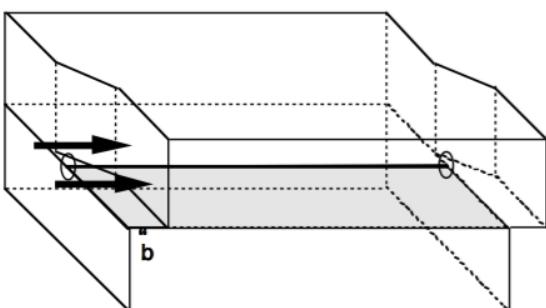
### Climb

- Dislocation climb up: Need vacancies; movement up out of slip plane; elimination of atoms by vacancies, need many vacancies to move entire plane up.
- Dislocation climb down: Need addition of atoms by interstitials
- More likely to climb up. Dislocation climbs normally occur at high temperatures since the number of vacancies is proportional to the temperature



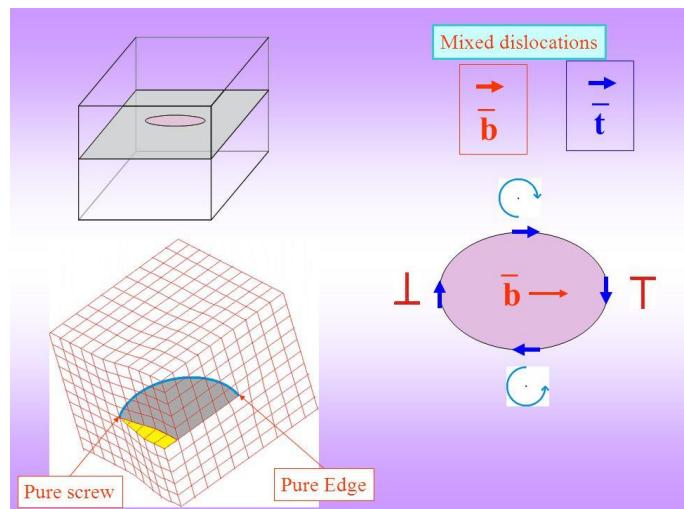
13: Climb of an edge dislocation. Movement up out of the plane requires the elimination of atoms by vacancies. Movement down requires the addition of atoms.

Screw Dislocation: When Burgers vector is parallel to dislocation line



### Mixed Dislocations

- Everywhere dislocations will have same  $b$
- $l$  is tangent to loop
- When  $l$  and  $b$  are perpendicular, edge dislocation
- When  $l$  and  $b$  are parallel, screw dislocation
- Mixed character dislocations elsewhere



### Surface Defects

#### Grain Boundary

- The interface between two different crystallites of a polycrystalline material
- Formed by disorientation of the crystal grains

#### Surface Energy

- For simple metals, the surface tension is nearly isotropic, preferred shape is spherical which minimizes the surface area for a given volume
- For ionic or strongly covalent crystals, they usually have a faceted shape because neutral planes have significantly lower energy

#### Stacking Fault

- Defects in the sequence of planes of atoms in a crystal. Ex. FCC stacking: ABCABA**C**A**B**C. The extra A is the stacking fault.
- Fairly low energy defects

### Volume Defects

3D aggregates of atoms or vacancies

- Voids: Break in the structure and an absence of atoms (cluster of vacancies). Introduced by gases that are trapped during solidification or by vacancy condensation in solid state. Undesirable. Decrease mechanical strength and promote fracture at small loads.
- Precipitates: Small particles that are introduced into the system by solid state reactions.
- Dispersants: Larger than precipitates; they behave as second phase, but also influence the behaviour of primary phase. They may be large precipitates, grains, or polygranular particles distributed through the microstructure.

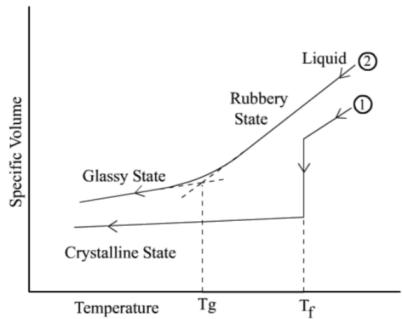
- inclusions: Foreign particles or large precipitate particles. Disturbs the geometry of microstructure.

## Chapter 5 Glasses

- Crystalline Structure: Atoms or molecules distributed in a perfectly regular way, ordered
- Amorphous Material: "glass", atoms or molecules distributed in a random way

### Amorphous Materials:

- Isotropic behaviour: same property in all directions
- Glassy state is not in equilibrium
- Usually achieved by quenching (fast cooling) to trap atoms/molecules in an irregular configuration



If the amorphous material is cooled quickly (2), it transitions smoothly from a liquid, to a rubbery state, and finally to a glassy state.  $T_g$  is the transition temperature between the glassy and liquid state.

If the amorphous material is cooled slowly, its volume drops discontinuously at  $T_f$ , and it assumes a stable crystalline state.

**Thermosetting:** Network polymer, strengthens and hardens upon heating  
**Thermoplastic:** Amorphous polymer, melts upon heating, not networked

### Isotropic Materials:

- Amorphous solids and glasses
- Cubic crystal structures
- Polygranular materials that are aggregates of many crystalline grains with random orientations

## Configuration of polymer types A, B:

- Random: ABAABBBBABAB
- Regular: ABABABABAB
- Block Co-polymer: AAAAABBBBBBB

## Configuration of R-groups on a polymer:

- Isotactic: all R groups are on the same side
- Syndiotactic: R groups alternate
- Atactic: arbitrary location

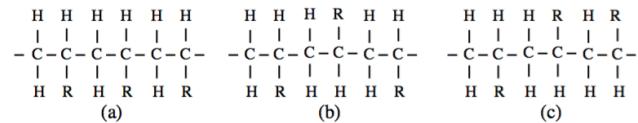
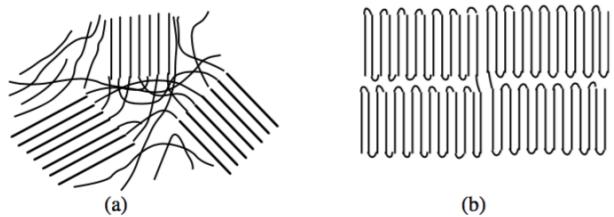


Fig. 6.5: Relative orientations of asymmetric monomers: (a) isotactic; (b) syndiotactic; (c) atactic (random).

**Partial Crystallinity:** Having some place ordered and other place amorphous (a)



### Shape of Polymers:

- (a) is folded; (b) is fringed
- Fringed is stronger; folded is more flexible

Crystalline polymers are stronger than amorphous polymers, but harder to form. Amorphous polymers are easy to shape and mold. The crystallization of a polymer generally increases its strength and rigidity with respect to the amorphous state.

## Linear Polymers and Network Polymers

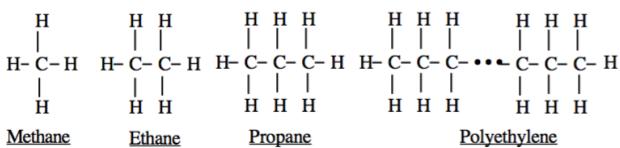
Linear: Joined by covalent bonds in a long chain (polyethylene)

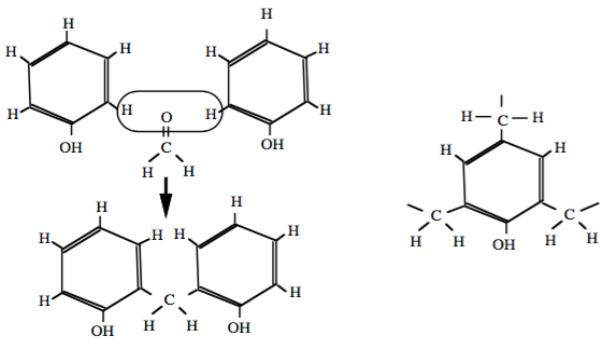
Network: Chain polymers with crosslinks

## Network Polymers

- Thermosetting, hardens upon heating
- Due to multi-directional bonds:

Ex. Bakelite: Network of Benzene rings





**Due to crosslinks:** Covalent bonds between linear polymers. Vulcanized rubber is an example.

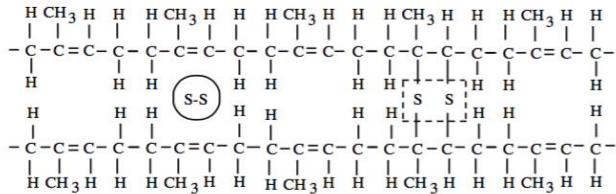


Fig. 6.11: The vulcanization of rubber. Sulfur atoms react with the C=C double bonds on adjacent chains to create cross-links.

Natural rubber: No crosslinks, able to shear and stretch. Deformation due to stretching comes back but due to shearing does not.

Vulcanized rubber: Sulfur links, no shearing present, only stretching and recovers. An example of Elastomer.

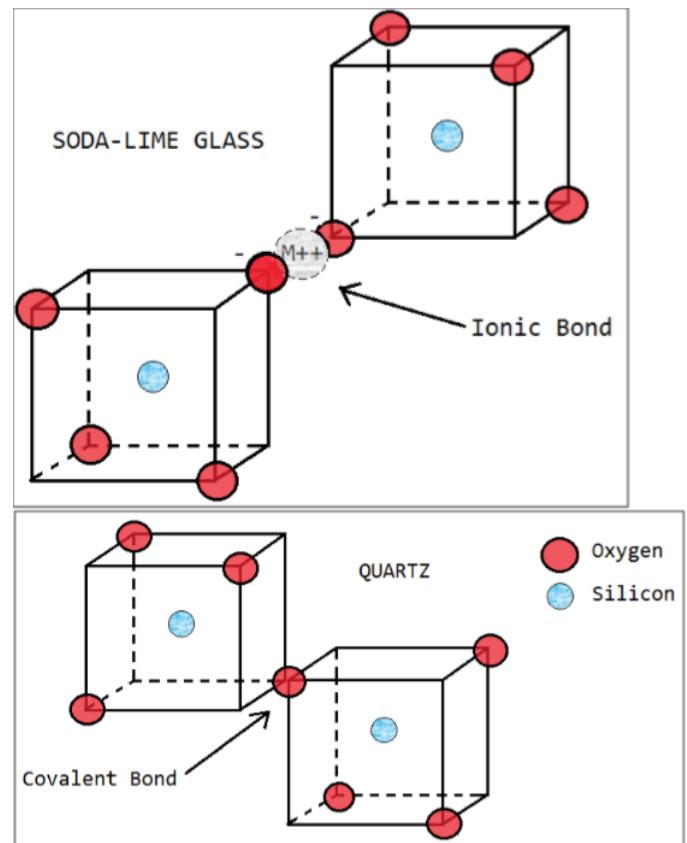
**Elastomer:** Polymers that have highly kinked chains in the isolated state, like rubber, made into very flexible materials by introducing a relatively low density of crosslinks.

## Silicates

$\text{SiO}_2$ : 3D network structure of quartz, made of  $\text{SiO}_4^{4-}$  tetrahedrons.

Silicate glasses are thermoplastic.

Bonded to divalent and monovalent cations.



The addition of these cations such as Na, Ca, Mg, is beneficial because they: decrease the working temperature (disrupts crystal lattice energies), allow amorphous state = isotropy, less brittle and more tough.

## Artificial Fibers

- Glass fiber: Strong and flexible
- Carbon fiber: Light and strong

Graphite: Sheets with weak Van der Waal bonds between.

## Chapter 7 Entropy

- Entropy is a measure of disorder that occurs due to systems trying to achieve thermodynamic equilibrium.
- Entropy can be characterized by mixing and more introduced randomness.
- Entropy is associated with: evolutionary time, heat, and randomness

- For an adiabatic process:  $dS \geq 0$
- $dS = 0$ : reversible process
- $dS > 0$ : irreversible process

## Thermodynamic Laws

1. Energy is conserved
2. Entropy, S, only increases
3. At T = 0K, S = 0, Degeneracy  $\Omega = 1$   
- implies completely pure material

## Entropy

### Entropy and Heat

Entropy  $S = f(E, V, \{N\})$  a function of Energy, volume, and number of particles.  
- S is continuous, differentiable, additive

### First derivatives of S:

$$\begin{aligned}\frac{dS}{dE} &= \frac{1}{T} \\ \frac{dS}{dV} &= \frac{P}{T} \\ \frac{dS}{dN_k} &= \frac{-\mu_k}{T}\end{aligned}$$

- Where  $\mu_k$  is the chemical potential of the k<sup>th</sup> particle. And  $N_k$  is the mole number of the k<sup>th</sup> component.

$$dS = \frac{dS}{dE} dE + \frac{dS}{dV} dV + \sum_k \frac{dS}{dN_k} dN_k$$

$$dE = TdS - PdV + \sum_k \mu_k dN_k$$

-  $TdS$  is thermal work =  $dQ$

-  $PdV$  is mechanical work =  $-dW$

When heat is added reversibly:

$$dS = \frac{dQ}{T}$$

### Entropy and Degeneracy:

Statistical  $S(E, V, \{N\}) = k_B \ln \Omega(E, V, \{N\})$   
- Degeneracy is the number of ways we can arrange something that would still achieve the same energy

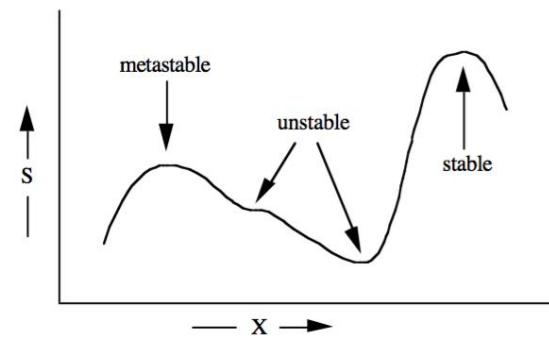
### Types of Entropy

1. Electronic Entropy: Number of ways an electron can be distributed (Free electrons in VB and CB)  
-  $S_{\text{conductor}} > S_{\text{insulator}}$
2. Vibrational Entropy: Energy from vibration; increases with openness of structure.
3. Configurational Entropy: Number of ways atoms can be distributed

## Equilibrium

### Equilibrium for Isolated System:

- Stable, metastable, unstable



7.2: Illustration of four kinds of equilibrium: metastable, unstable (inflection point), unstable (minimum), and stable equilibrium.

- At equilibrium,  $\frac{dS}{dx} = 0$ .
- At stable equilibrium,  $\frac{dS}{dx} = 0$  and  $dS \leq 0$

### Internal Equilibria

#### Thermal Equilibrium

Conditions: Hold V and  $\{N\}$  const,  $dE_2 = -dE_1$

Use Equation:  $dS = dS_1 + dS_2$

Result:  $T_1 = T_2$

#### Mechanical Equilibrium

Conditions: T,  $\{N\}$  const,  $dV_2 = -dV_1$

Use Equation:  $dS = dS_1 + dS_2$

Result:  $P_1 = P_2$

#### Chemical Equilibrium

Conditions: E, V const,  $dN_{K_2} = -dN_{K_1}$

Use Equation:  $dS = dS_1 + dS_2$

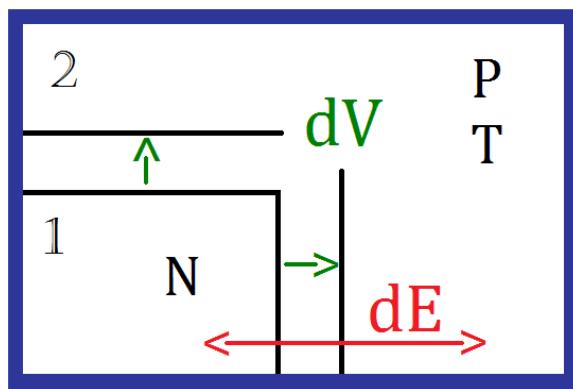
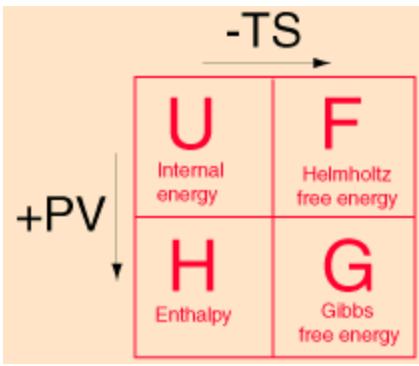
Result:  $\mu_{k_1} = \mu_{k_2}$

### Non-equilibrium Examples

- Semiconductor: islands of concentrated electrically active solutes
- Polygranular crystalline solid: migration of grain boundaries
- Crystalline solids with dislocations:  
Dislocations annihilate each other

### Thermodynamic Potentials

- Maximization of S is equivalent to the minimization of E

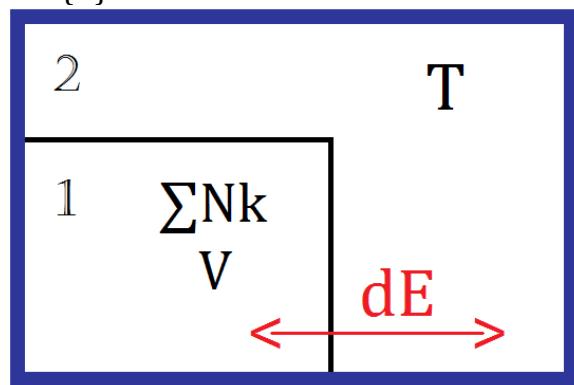


### Helmholtz Free Energy

Material interacts thermally with the environment

$$F = E - TS$$

- Governs the behavior of a system with fixed V and {N} in reaction with a T reservoir



- Conditions:  $dE_2 = -dE_1$

- Use equation:  $dS = dS_1 + dS_2$

$$F = F(T, V, \{N\})$$

$$dF = -SdT - PdV + \sum \mu dN$$

$$dF = \left[ \frac{\partial \tilde{F}}{\partial T} \right] dT + \left[ \frac{\partial \tilde{F}}{\partial V} \right] dV + \sum_k \left[ \frac{\partial \tilde{F}}{\partial N_k} \right] dN_k$$

### Gibbs Free Energy

Material interacts thermally and mechanically with the environment

$$G = E - TS + PV$$

- Governs the behavior of a system with fixed {N} in reaction with a T and P reservoir

- Conditions:  $dV_2 = -dV_1; dE_2 = -dE_1$
- Use Equation:  $dS = dS_1 + dS_2$

$$G = G(T, P, \{N\})$$

$$dG = -SdT - VdP + \sum (\mu) dN$$

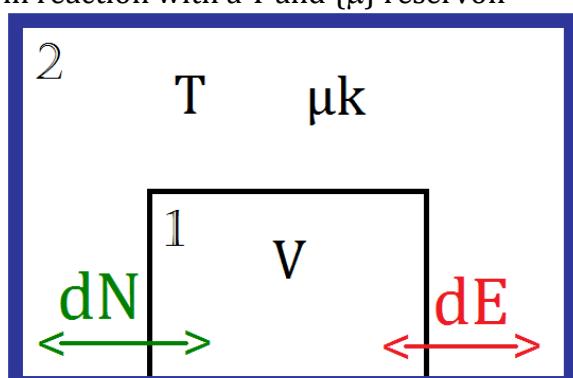
$$dG = \left[ \frac{\partial \tilde{G}}{\partial T} \right] dT + \left[ \frac{\partial \tilde{G}}{\partial P} \right] dP + \sum_k \left[ \frac{\partial \tilde{G}}{\partial N_k} \right] dN_k$$

### The Work Function

Material interacts thermally and chemically with the environment

$$\Omega = E - TS - \sum \mu N$$

- Governs the behavior of a system with fixed V in reaction with a T and {\mu} reservoir



- Conditions:  $dE_2 = -dE_1; dN_{K_2} = -dN_{K_1}$

- Use equation:  $dS = dS_1 + dS_2$

$$\Omega = \Omega(T, V, \{\mu\})$$

$$d\Omega = -SdT - PdV - \sum (\mu) dN$$

$$d\Omega = \left[ \frac{\partial \tilde{\Omega}}{\partial T} \right] dT + \left[ \frac{\partial \tilde{\Omega}}{\partial V} \right] dV + \sum_k \left[ \frac{\partial \tilde{\Omega}}{\partial \mu_k} \right] d\mu_k$$

### Second Derivatives

- Isobaric Specific Heat:

$$\left[ \frac{\partial^2 \tilde{G}}{\partial T^2} \right] = \frac{\partial}{\partial T} \left[ \frac{\partial \tilde{G}}{\partial T} \right] = - \left[ \frac{\partial S}{\partial T} \right]_{P\{N\}} = - \frac{C_P}{T}$$

- Coefficient of Thermal Expansion:

$$\left[ \frac{\partial^2 \tilde{G}}{\partial T \partial P} \right] = \frac{\partial}{\partial T} \left[ \frac{\partial \tilde{G}}{\partial P} \right] = \left[ \frac{\partial V}{\partial T} \right]_{P\{N\}} = V\alpha_T$$

## Thermodynamics of Interfaces

- Two crystals separated by an interface



Figure 1

- There is excess energy near the surface. Crystalline structures must have lower energy, or the solid would be driven to have more surfaces than the inside bulk.

$$E = E_V^\alpha V^\alpha + E_V^\beta V^\beta + E_S A$$

$E_V^\alpha$ : Energy / unit Volume  $\alpha$

$E_S$ : Energy / unit Area surface

## Work Function ( $\Omega$ )

$$\Omega_{total} = \Omega_V^\alpha V^\alpha + \Omega_V^\beta V^\beta + \Omega_S$$

$$\Omega_S = \sigma A$$

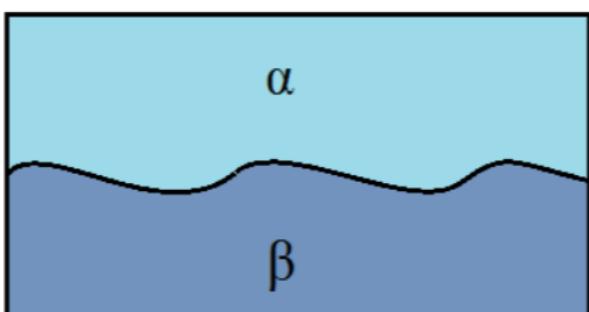


Figure 2  $\Omega_S$  is larger due to bigger Area of Interface

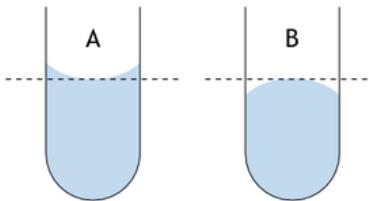
## Surface Tension

-  $\sigma$ : The force that resists the extension of the surface

- If  $\sigma$  constant: spheres (water, liquid, amorphous)

- If  $\sigma$  not constant: faceting (NaCl)

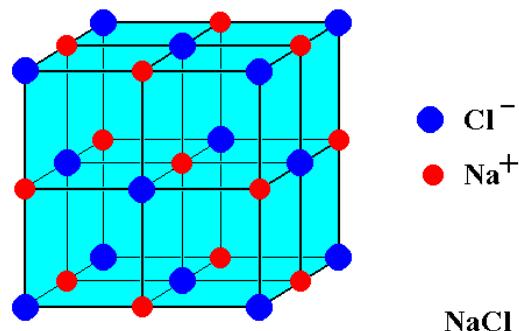
## 1. Constant $\sigma$



- For the hydrophilic surface in concave meniscus A,  $\sigma$  is low

- For the hydrophobic surface in convex meniscus B,  $\sigma$  is high

## 2. Not constant $\sigma$



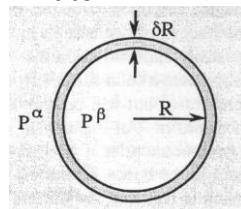
- Ionic crystal

- Low energy surfaces are charge neutral

- Non-charge neutral planes in crystal are high energy. (111) plane.

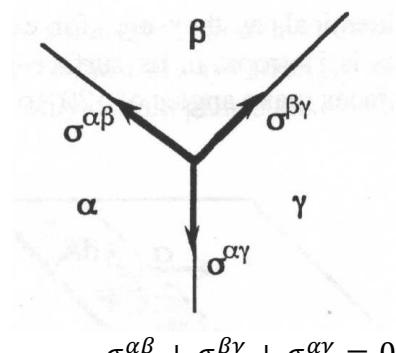
## Interface that ends on itself:

- Water

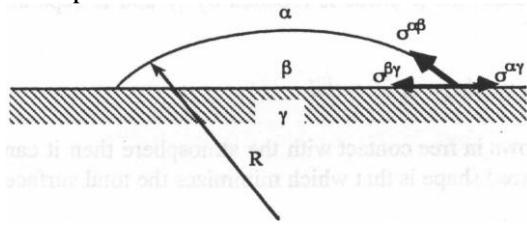


## 3 Interfaces:

- 3 Component: Neumann Triangle



- Droplet of water:



- Sitting on a rigid surface

- Young Equation

$$\cos(\theta) = \frac{\sigma^{\alpha\gamma} - \sigma^{\beta\gamma}}{\sigma^{\alpha\beta}} = \kappa$$

- As  $\kappa$  approaches 1,  $\theta$  approaches 0 degrees: wetting
- As  $\kappa$  approaches -1,  $\theta$  approaches 180 degrees: dewetting

## Chapter 8 Simple Solids

- Total energy is the sum of the net binding energy at  $T = 0K$ , the vibrational energy, and the electronic energy

### PERFECT CRYSTAL

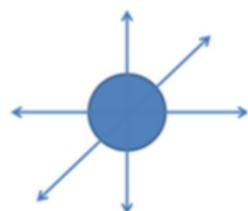
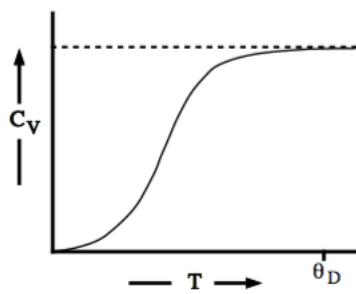
- Assume net binding energy = 0

## Thermal Conductivity

- The transport of heat. Heat travels via electrons and phonons
- Heat Capacity,  $C_V$ , the heat needed to raise the temperature of a system by one degree. Related to how many things and ways these things can move (atoms, electrons).
- Heat Capacity  $C_V = \text{constant} * T^3$

## Debye Temperature

- Temperature at which all vibration modes are available
- An atom can move along three directions in space (3 modes per atom)
- The Debye Temperature depends on the material.



## Dulong-Petit Law

- Low temperature ( $T < \frac{\theta_D}{2}$ ):

$$C_V \propto T^3$$

- High temperature ( $T > \theta_D$ ):

$$C_V \approx 3Nk$$

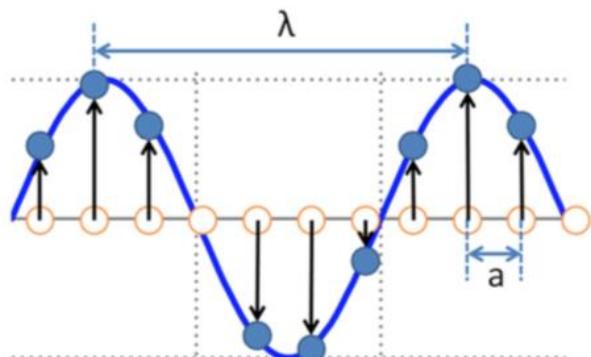
## Phonon

Quantum of vibrational energy in the lattice

$$dS = \frac{dQ}{T} = \frac{dE}{T} = \frac{C_V dT}{T}$$

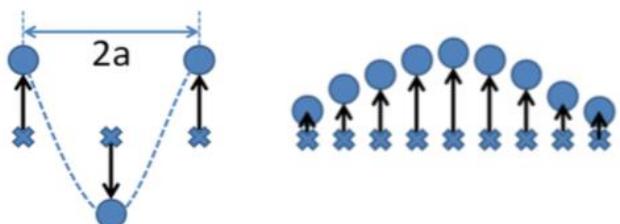
Electrons and Phonons contribute to Heat Capacity and Thermal Conductivity. Electrons conduct heat better than phonons because they travel at the speed of light.

### Transverse Vibrations



$$\text{Wave Vector: } k = \frac{2\pi}{\lambda}$$

Highest  $k$  ( $\lambda_{\min} = 2a$ )      Low  $k$  (note that  $\lambda_{\max} \rightarrow \infty$ )



$$2a < \lambda < \infty$$

$$w = 2\pi f = kV, \text{ where } V = \text{velocity}$$

Energy of a perfect crystal is the sum of:

- Net binding energy at zero temperature
- The vibrational energy
- The electronic energy

The vibrational and electronic energies increase with temperature, and this increase measured by  $C_V$

## Electronic Contribution to the Specific Heat

- Electrons excited to high energy states
- Electron contribution tends to be less than the vibrational contribution (principal source).
- Only electrons that are very close to Fermi energy can be excited (Pauli Exclusion Principle).
- The electrons excited to VB is very few and accounts for only about  $\sim 1\%$  of  $C_V$  at normal T
- The electronic contribution is only observable at very low T where  $T \gg T^3$

$$C_V \propto T$$

## Fermi-Dirac Distribution Function

- Probability of finding an electron at energy E
- Fermions are distributed over the set of states available
- The expected number of particles is given by:

$$\langle n(E) \rangle = \frac{1}{e^{(E-E_F)/kT} + 1}$$

The Fermi Energy is the energy at which the probability that a state is occupied is exactly 1/2.

## Three Cases

1. If  $E - E_F \gg kT$

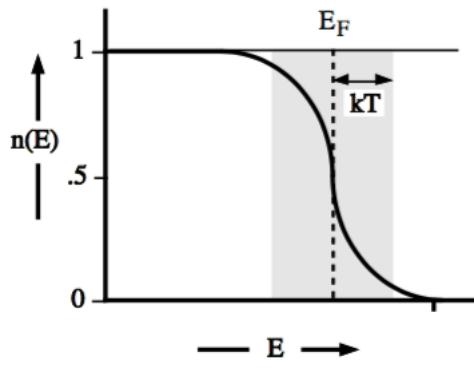
$$\langle n(E) \rangle \cong e^{-\frac{E-E_F}{kT}} \rightarrow 0$$

2. If  $E = E_F$

$$\langle n(E) \rangle = \frac{1}{2}$$

3. If  $E_F - E \ll kT$

$$\langle n(E) \rangle \cong 1 - e^{\frac{E-E_F}{kT}} \rightarrow 1$$



## The Vibrational Energy

- Energy is absorbed in atomic vibrations
- Phonons are elementary quantized excitations of lattice vibrations. Phonon motion is

independent on temperature. Energy of phonons:

$$E = (n + 1/2)\hbar\omega$$

$$\hbar = h / 2\pi, h \text{ is Planck's constant}$$

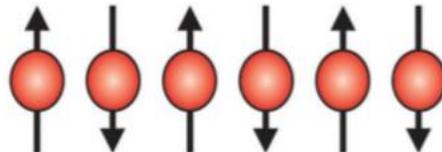
n = Integer

$\omega$  = angular frequency

## Bose-Einstein Distribution and Phonons

Two types of quantum properties:

1. Fermions (half integer spin)



- Fermions follow the Pauli Exclusion Principle (electron).

- Bosons follow Bose-Einstein statistics which states that two particles can be in the same state (phonons).

Expected number of phonons (level of excitation):

$$n(\omega, t) = \frac{1}{(e^{\hbar\omega/kT} - 1)}$$

k = Boltzmann's constant

T = Temperature

## Two Cases

- 1)  $kT \gg \hbar\omega$

$$e^{\hbar\omega/kT} \cong 1 + \frac{\hbar\omega}{kT}$$

$$n(\omega, t) \cong \frac{\hbar\omega}{kT}$$

- 2)  $kT \ll \hbar\omega$

$$n(\omega, t) \cong e^{-\hbar\omega/kT}$$

The total vibrational energy:

$$E_v(T, V, N) = \sum_{\omega} (n(\omega, t) + \frac{1}{2}) \hbar\omega$$

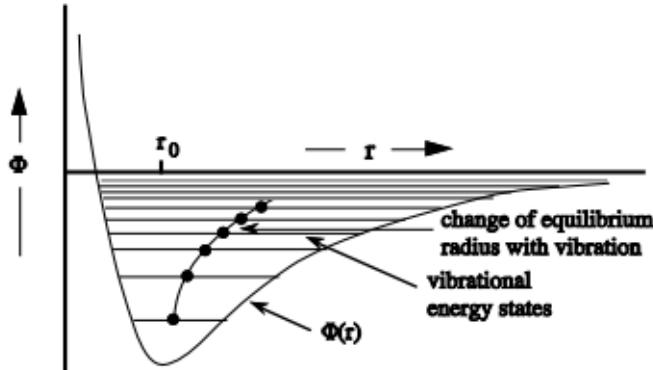
## The Vibrational Contribution to Specific Heat

- At high T: all available vibrational modes are activated, increasing T further raises the level of

activation of each of the  $3N$  modes by the same amount,  $C_V$  is constant

- At low T: only some modes are strongly activated
- Increasing T raises the energy by: raising the energy of activated modes; activating the vibrational modes that were previously quiet

## Thermodynamics: Interatomic Separation



- The physical source of the coefficient of thermal expansion lies in the anharmonicity of the atom vibrations in the solid
- The restoring force is smaller when  $r > r_0$  than when  $r < r_0$ , so the average  $r$  increases as the vibrational energy increases

### Random Solid Solution

- Bragg-Williams Model

### The Configurational Entropy

$$S = -k \ln(\Omega)$$

- $\Omega$  is the degeneracy, the number of ways you can make the same material with different atom configurations

$\Omega = 1$  means pure material

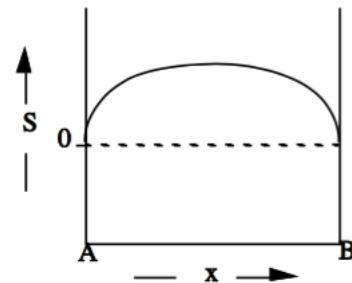
$$\Omega = \frac{N!}{N_A! N_B!}$$

$N = N_A + N_B = \text{Number of sites}$

$N_A = \text{Number of atom a (ex. Fe)}$

$N_B = \text{Number of atom b (ex. C)}$

Then the  $S_{\text{config}}$  (With Sterling's Approx):



$$S_{\text{config}} = -k \ln \left( \frac{N!}{N_A! N_B!} \right)$$

$$S_{\text{config}} = -kN \{x \ln x + (1-x) \ln(1-x)\}$$

The Holmholtz Free Energy:  $F = E - TS_{\text{config}}$

$$\lim_{x \rightarrow 0} \left( \frac{dF}{dx} \right) = \lim_{x \rightarrow 0} \left( -T \frac{d}{dx} S_{\text{config}} \right)$$

$$= \lim_{x \rightarrow 0} \left[ \ln \left( \frac{x}{1-x} \right) \right] = -\infty$$

As  $x \rightarrow 0$ , the limit approaches negative infinity. Thus: more likely to form a mixture rather than a pure material.

### The Internal Energy

- Binary solution with A and B

#### Internal Energy of Solution:

$$E = V_{AA}N_{AA} + V_{BB}N_{BB} + V_{AB}N_{AB}$$

Let  $x = N_A / N$ , which is mole fraction of A

$N$  = number of sites

$Z$  = number of nearest neighbors

$N_A$  = sites occupied by A

$N_B$  = sites occupied by B

Then,

$N_{AA} = \text{number of AA bonds} = N_A Z x (1/2)$

$N_{BB} = \text{number of BB bonds} = N_B Z x (1/2)$

$N_{AB} = \text{number of AB bonds} = N_A Z x$

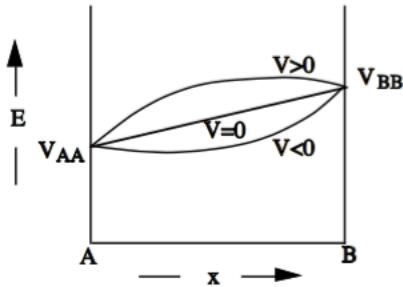
$V_{MN} = \text{binding energy between M and N}$

$$E = \frac{N_Z}{2} \{(1-x)V_{AA} + xV_{BB} + 2x(1-x)V\}$$

Where  $V$  is the relative binding energy,

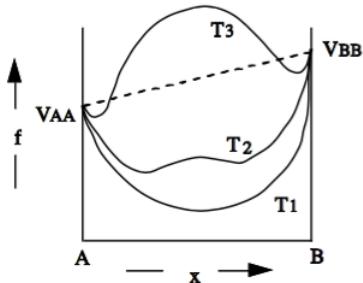
$$V = V_{AB} - \frac{1}{2}(V_{AA} + V_{BB})$$

$V$  is the difference between the energy of an AB bond and the average of the energies of AA and BB bonds



- The max/min near but not necessarily 50%
- $V = 0$  means no preference of bonding
- $V > 0$  BB and AA bonds preferred. Binding energy increase as number of AB bonds is increased
- $V < 0$  AB bonds preferred. Adding A or B in pure mixture of A/B reduces the binding energy

### Free Energy Diagram



Free energy curves for a random solution with  $V > 0$  at three temperatures,  $T_1 > T_2 > T_3$ .

$$F = E - TS_{config}$$

-TS decreases as T increases.

- This graph shows the Miscibility Gap. For certain compositions x, two or more substances do not mix, but form two independent solutions. In this case, at  $T_1$  or  $T_2$  they will always mix. At  $T_3$  they will not always mix.  $T_3$  crosses the dotted line (no preference). Example of  $T_1$  is Silicon and Germanium.
- The free energy function is always concave when x is close to 0 or 1. This is because of the singularity of the slope of the free energy at  $x = 0$  and  $x = 1$ , which is due to the singularity in the slope of  $S_{config}$ . Thus, there is always some solubility for A in B and B in A.

### The Equilibrium Vacancy Concentration

- The equilibrium concentration of vacancies that minimize Gibbs Free Energy
- Vacancies appear because of configurational entropy

$$\Delta G(n) = n\Delta G_v - TS_{config}$$

$\Delta G_v$  = energy to form vacancy

$X_v$  = fraction of vacancies in a material

$X_v \rightarrow 0$  at equilibrium

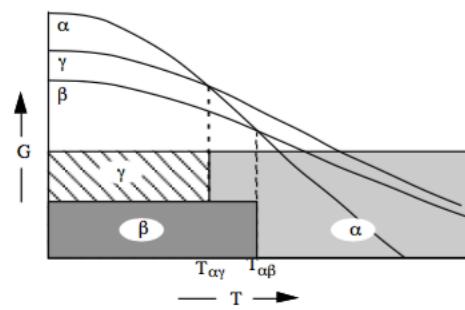
$$\ln(X_v) = \frac{-\Delta G_v}{kT}$$

$$X_v = e^{-\Delta G_v/kT}$$

### Chapter 9 Phases and Phase Equilibrium

#### One Component System

- The Gibbs Free Energy:  $G = E + PV - TS$
- $$\frac{\partial G}{\partial T} = -S$$
- the slope of the G vs T phase diagram



- The gamma phase will never be reached by looking at this diagram, but we are still able to form gamma phase as a metastable phase.
- The kinetics play a key role, if the formation of beta phase from alpha is not kinetically favorable, then the alpha phase will be retained as a metastable phase.
- If the transformation from alpha to gamma is kinetically favorable, then gamma phase will be formed.
- Beta phase: BCC structure
- Gamma phase: A HCP structure
- The BCC is more open whereas a HCP is close packed, the BCC has more space, atoms can move freely, more entropy

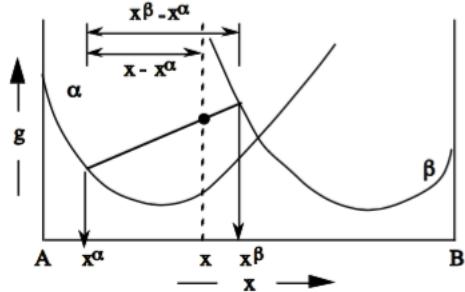
#### Two Component System

- Stability of a phase requires:  $\left(\frac{\partial^2 g}{\partial x^2}\right) \geq 0$ , the curve to be concave up

$$G = f(T, P, N_1, N_2)$$

$$g = \text{molar Gibbs Free Energy} = G/N$$

$$g = f(T, P, x)$$



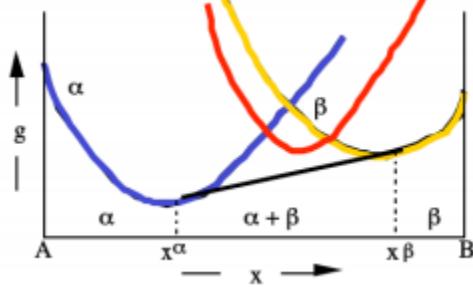
$$X = f^\alpha * X^\alpha + f^\beta * X^\beta$$

where  $f^\alpha + f^\beta = 1$

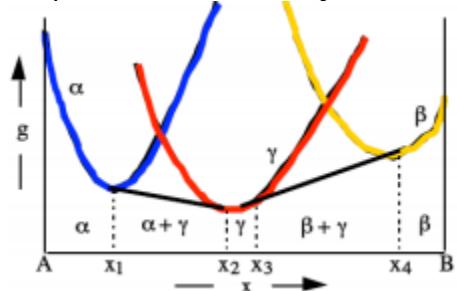
$$f^\alpha = \frac{X^\beta - X}{X^\beta - X^\alpha}$$

$$f^\alpha = \frac{X^\beta - X}{X^\beta - X^\alpha}$$

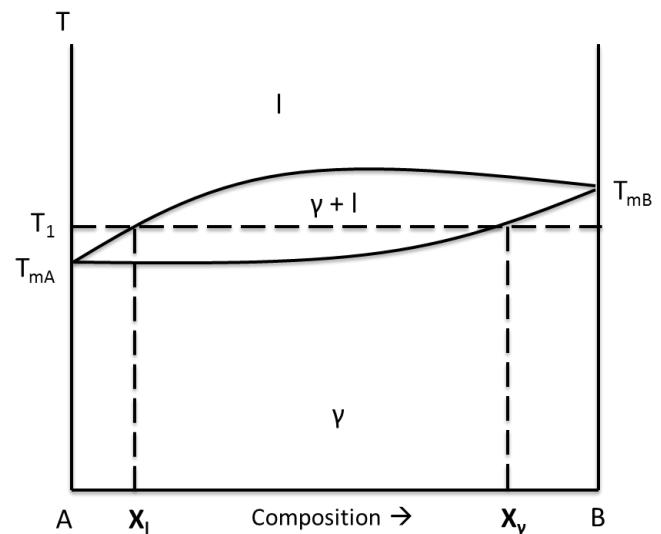
The common tangent line is the minimum free energy curve of the different phases. If a segment of the curve includes a single-phase curve, then the equilibrium state at that composition is a homogeneous state of that phase.



- The red phase does not appear
- The minimum energy is along the lower curve
- Within the two-phase region:
  - $\alpha$  has the fixed composition  $x^\alpha$
  - $\beta$  has the fixed composition  $x^\beta$



- Phase  $\gamma$  appears in the middle

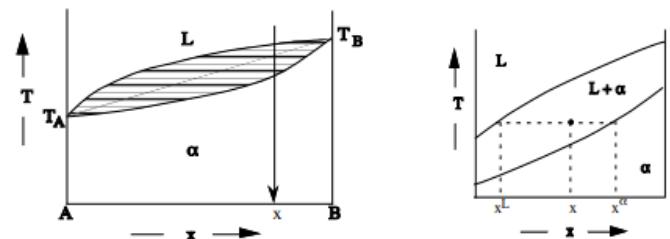


- liquid favored at higher T and solid favored at lower T. A and B are pure materials with the same crystal structure. As composition x shifts from A to B, A atoms randomly mixes into the B crystal lattice.

- 3 bits of information: 1) Phases present 2) Component of the phases 3) Fraction of each phase (lever rule)

- The liquid phase has a mole fraction  $f^l$  of the two-phase mixture and the solid phase has a mole fraction  $f^\gamma$  of the two-phase mixture

### Freezing



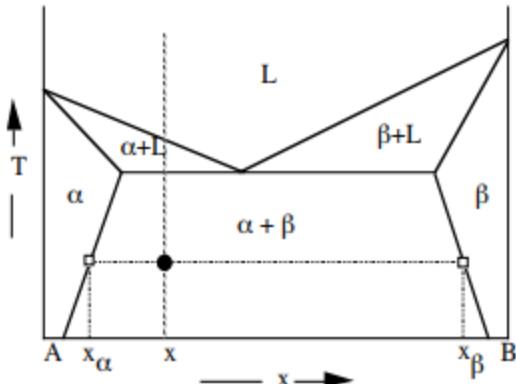
- A binary system freezes over a range of T through a gradual increase in the fraction of solid
- During freezing, T decreases. When first reaches the mixed phase, it is rich in B (high B composition but very low fraction)
- As T decreases further, more solid but less pure

(Grape Example)

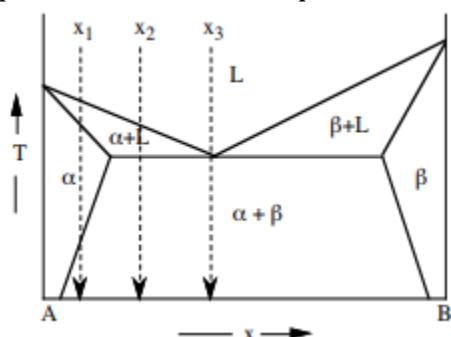
### Eutectic Phase Diagram

## Binary Phase Diagrams

### Solid Solution (Lens) Diagram



- Pure materials of different crystal structures or distinct phases come in contact with the liquid phase.
- Mixed composition of Pb and Sn would result in a lower melting T of 183.
- The composition of the two phases would be determined by a tie-line
- The fraction of each phase would be determined by the lever rule
- Eutectic point in the center: At this point, both A and B are solidified
- Pure phase solutions: alpha, beta, and Liquid
- At precisely eutectic T: 3-phase equilibrium. The compositions are given by the points at which the isotherm line at the eutectic temperature touches the  $\alpha$ ,  $\beta$ ,  $L$  single phase fields. Cannot use lever rule to determine quantities of the three phases.



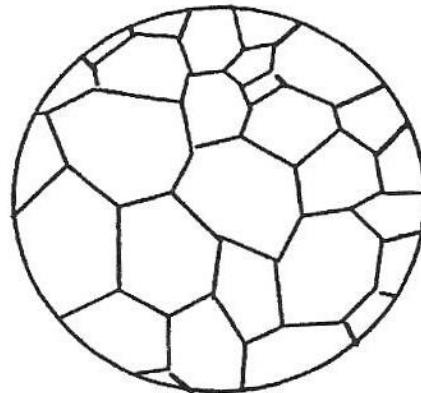
#### Paths & Precipitates:

##### 1. $L \rightarrow \alpha + L$

Isothermal line: Composition of each phase  
Lever rule: fraction of each phase present

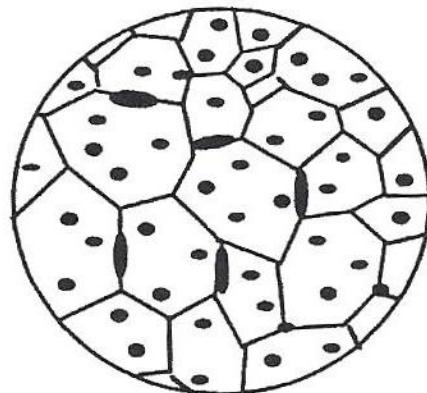
##### 2. $\alpha + L \rightarrow \alpha$

Solution solidifies into the  $\alpha$  phase until it becomes a homogeneous  $\alpha$  solution. This would have a **polygranular microstructure**.



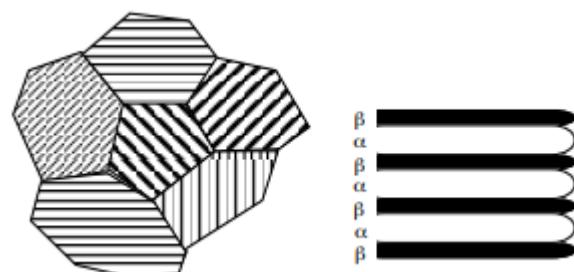
##### 3. $\alpha \rightarrow \alpha + \beta$

As we approach the  $\alpha + \beta$  line, a small amount of  $\beta$  phase that has a high B composition starts to precipitate or nucleate in the polygranular solution that has a rich A.



##### 4. $L \rightarrow \alpha + \beta$

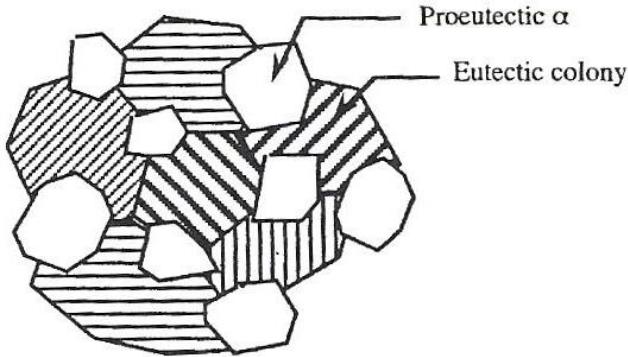
- At the eutectic point, we create a eutectic microstructure which is a continuous matrix of thin rods of A-rich  $\alpha$  and B-rich  $\beta$  phases.  
- Solidification occurs sharply at the eutectic T  
-  $\alpha$  and  $\beta$  grow as plates side by side to maintain composition at interface  
- This transformation mechanism is the easiest kinetic path



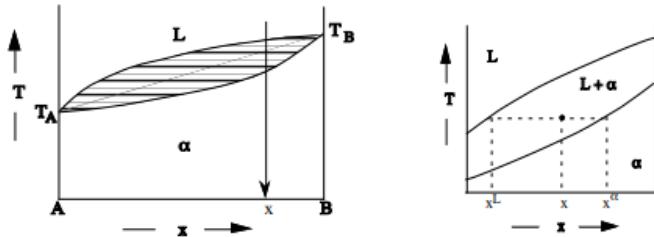
##### 5. $\alpha + L \rightarrow \alpha + \beta$

Whatever portion of the solution was liquid forms a eutectic microstructure, but the fraction of composition that was in the  $\alpha$  phase will

remain in islands, inducing a proeutectic microstructure



## Applications



Solidifying a solution:

- First solid to form is very rich in B
- As T decreases, fraction of  $\alpha$  increases, and the composition of  $\alpha$  ( $x^\alpha$ ) evolves towards  $x$
- Final  $\alpha$  has the average composition of the solution ( $x^\alpha = x$ )

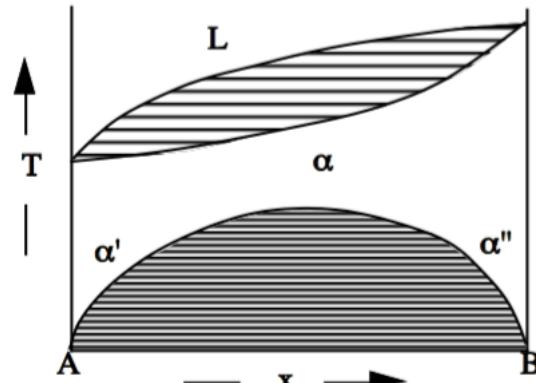
Purification:

- Cool until first solid forms (rich in B)
- Extract, re-heat and cool again (richer in B)
- Repeat until desired purity reached

## Low Temperature Behaviour

- $S \rightarrow 0$  when  $T \rightarrow 0K$
- At low T, equilibrium must be a perfectly ordered phase
- $\Omega = 1$  and  $S = 0$
- The solid solution can decompose into two terminal solutions (like bonds preferred) at low T or rearrange itself into an ordered compound (unlike bonds preferred)

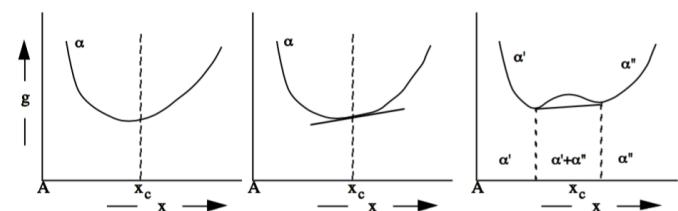
## Solid Solution Diagram with Miscibility Gap



- the system freezes into a solid solution ( $\alpha$ ) at all compositions
- At low T the solid solution spontaneously decomposes into two solid solutions, with same structure but different compositions

Reason for miscibility gap:

- miscibility gap caused by an instability in the free energy curve that develops as the temperature decreases
- which is due to a preference for bonds between atoms of like kind, so energy is lowered when the system decomposes into A-rich and B-rich solutions



- the convex region has the consequence that two points on the free energy curve are connected by a common tangent
- system decomposes into two solutions with different compositions, but the same structure
- as temperature decreases further, convex region becomes more pronounced and miscibility gap broadens
- At higher temperature, the energetic preference for decomposition is outweighed by the entropic preference for the solid solution

## Eutectic Phase Diagram

- usually system whose components have different crystal structures in the pure form
- components with different structures cannot form a continuous range of solid solutions
- there are always at least two phases in the solid state

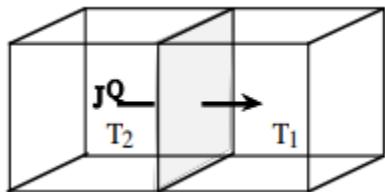
## Chapter 10 Kinetics

- Rate of change of state in response to thermodynamic driving forces
- Global equilibrium: discontinuous change; change in Gibbs Energy  $\Delta G$
- Internal equilibrium: continuous change; change in  $T$  (heat flow and conduction) and change in  $\mu$  (changing chemical potential by diffusion of atoms)

## Thermal Conductivity

- How efficient (fast) heat transfers
- Heat flows in response to a temperature gradient
- If  $T_2 > T_1$ , over time, heat ( $E$ ) will be transferred from  $T_2$  to  $T_1$ .

- The heat flux  $J^Q$  is:



Fourier's Law of Heat Conduction in 1-d:

$$J^Q = \frac{E}{A * t} = -k \left( \frac{dT}{dx} \right)$$

Where  $J^Q$  is the *heat flow across the interface per unit area per unit time*, and  $k$  is the thermal conductivity (material property) and  $\frac{dT}{dx}$  is temperature gradient.

- The materials that feel colder have a higher thermal conductivity with the same temperature gradient.

## Thermal Conductivity

- There are 3 ways to transfer energy:
  - 1) electrons (predominant carriers in metals at moderate temperature)
  - 2) phonons (predominant carriers in all materials at very low temperature && dominate thermal conductivity of insulating materials at all but very high  $T$ )
  - 3) photons (generally negligible except in transparent solids at very high temperature)

- Electrons, phonons, and photons that carry heat through a solid all behave as gas of colliding particles.
- Particles reach thermal equilibrium by collisions and transfers energy

In 1-d:

$$k = C_v v_x \langle l_x \rangle$$

In 3-d for a cubic structure:

$$\mathbf{k} = \frac{1}{3} C_v v_x \langle l_x \rangle$$

Where  $k$  is the thermal conductivity and  $\langle l_x \rangle$  is the mean path travelled by the particle

## Heat Conduction by Mobile Electrons

- In metals, electrons are the primary way of conductivity. Phonons possess higher specific heat than electrons, but there are much more electrons than phonons, and they can move freely. Electrons transfer heat at the speed of light, and phonons transfer at speed of vibration of atoms (wave). Thus, in metals, electrons make a greater contribution to thermal conductivity.
- **For metals:** conductivity from both electrons and phonons.
- **For insulators:** conductivity from mostly phonons.

Sources of electron collision:

- Collision with phonons
- Collision with defects, solute or impurity atoms

Electrical Resistivity:

$$\rho = \rho_0 + bT$$

Where  $\rho_0$  is the residual resistivity (due to solutes, impurities, and lattice defects), and  $b$  is the temperature coefficient of resistivity, due to electron collisions with lattice **phonons**.

The thermal resistivity of the crystal lattice:

- due to scattering from lattice vibrations
- determines resistivity of a pure metal
- As  $T$  increases,  $\rho$  of a metal increases linearly

The contribution of solutes and impurities:

- As  $x$  (mole fraction of solutes and impurities) increase,  $\rho$  increases linearly
- As the **cross-section** increase,  $\rho$  increases faster (steeper slope) with  $x$

## Heat Conduction by Particles

### Wiedemann-Franz Law:

$$k = LT\sigma = \frac{LT}{\rho} = \frac{LT}{\rho_0 + bT}$$

$$\rho = \frac{1}{\sigma}$$

- Where  $k$  is the thermal conductivity,  $L$  is the Lorentz factor,  $\rho$  is the resistivity, and  $\sigma$  is the electrical conductivity.
- Relates thermal conductivity  $k$  with electrical conductivity  $\sigma$

- If  $T \rightarrow 0K$ :

$$k = \frac{LT}{\rho_0}$$

For low T, the movement of electrons is reduced, thus reducing  $k$  (thermal conductivity). A low thermal energy means there is not much lattice vibration. So the residual resistivity dominates.

In practice, this equation is only satisfied with a high  $\rho_0$  value (alloys and defective metals)

- If  $T \rightarrow high$ :

$$k = \frac{L}{b} = constant$$

For high T, the thermal conductivity approaches a constant. A high thermal energy leads to increased lattice vibration, which results in increased collision and scattering of electrons, reducing their mean free path.

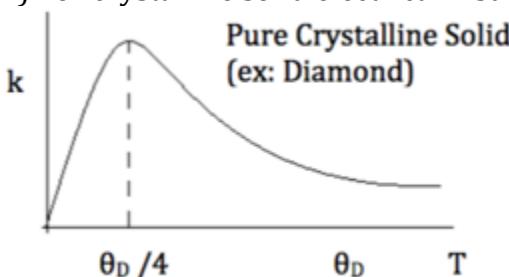
Thermal conductivity of alloys smaller than pure metals.

### **Heat Conduction by Phonons**

- Principle carriers of heat in all materials at very low T and dominate thermal conductivity in insulating materials at all but very high T

### 2 problems:

1) For crystalline solid electrical insulators



$$1. T > \theta_D : k \propto \frac{1}{T}$$

- At high T, phonons are scattering each other, thermal conductivity decreases.

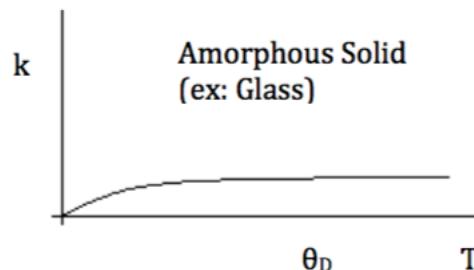
$$2. 0K \ll T < \theta_D : k \propto e^{-\frac{\theta_D}{2T}}$$

- Phonons are scattering each other

$$3. T \rightarrow 0K : k \propto T^3$$

- Mean free path for phonon-phonon collisions exceeds mean free path for phonon-defect collisions:  $\langle l \rangle$  treated as a constant.  $C_V$  varies with T following  $C_V \propto T^3$

- We have highest thermal conductivity at  $\sim 25\%$  Debye Temperature (**Crystalline**)



- For **amorphous** material there is no peak

2) At low temperature, phonons have a higher k

- Diamond is the most thermally conductive material due to its strong covalent bonds, its Debye Temperature (=2000K) is higher than most substances

Sources of phonon collision:

- One another
- With lattice defects such as solute atoms

- Mean Free Path: A long mean free path = High conductivity

- Glass, amorphous material: phonons scattered, short mean free path, low conductivity

- Point defects: impede overall movement of electrons in a certain direction

### **Chemical Diffusion**

- the ability to move atoms

$$J_B = -L \nabla \mu$$

Where J is the chemical flux, L is the mobility, and  $\mu$  is the chemical gradient.

### Fick's First Law

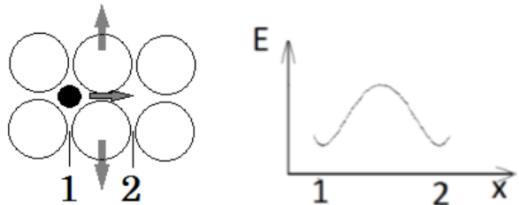
$$J = -nD \nabla c = -D \nabla n$$

Where  $J$  is the chemical flux,  $D$  is the diffusivity (easiness for atoms to move within a space), and  $n$  is the concentration.

## Mechanisms for Diffusion

### 1. Interstitial Diffusion

The atom pushes its way through two touching atoms (displaces two neighbouring atoms), leads to activation energy



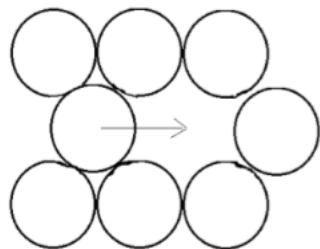
$$P_{1 \rightarrow 2} = e^{-\frac{Q_m}{kT}}$$

Where  $Q_m$  is the activation energy,  $\nu$  is the jump attempt frequency.

$$\omega = \nu e^{-\frac{Q_m}{kT}}$$

and  $\omega$  is the number of jumps made per unit time (in all directions)

### 2. Substitutional Diffusion



- Rate of diffusion depends strongly on vacancy concentration

$$X_{Vacancies} = e^{-\frac{Q_v}{kT}}$$

Where  $X_v$  is the mole fraction of vacancies

- Move the atom (activation energy)

$$P_{1 \rightarrow 2} = e^{-\frac{Q_m}{kT}}$$

- The successful jumps made per unit time is

$$w = z\nu e^{-\frac{(Q_m+Q_v)}{kT}}$$

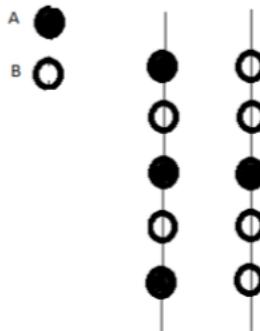
Where  $z$  is the number of nearest neighbors

- Substitutional diffusion is generally harder one to occur because there are two steps, **displacing** the neighbouring atom and having a **vacancy** nearby. Creating a vacancy creates dangling bonds that are of high energy  
 $Q_m \sim 0.5\text{eV}$     $Q_v \sim 1.0\text{eV}$

## Correlation Effect

- A reverse jump back to the original location, made after a jump
- Ignored when concerning a one-component species or when solvent and solute atoms have similar sizes

## Diffusion Plane



- The net flux:  $J_{net} = J_+ - J_-$

-  $J_+ = w_{+x} n_1$

Where  $J_+$  is the flux along the  $+x$  direction

-  $J_- = w_{-x} n_2$

Where  $J_-$  is the flux along the  $-x$  direction

-  $n_1 = n * c_1 * a$

-  $n_2 = n * c_2 * a$

Where  $n$  is the # of sites/Volume,  $a$  is the interatomic spacing, and  $c$  is the concentration

For a cubic system:

$$w_{+x} = \frac{w}{6} = w_{-x}$$

where  $w$  is the total number of successful jumps/time

$$c_2 = c_1 + \frac{dc}{dx} a$$

Where  $a$  is the interatomic spacing.

Thus,

$$J_{Total} = J_+ - J_- = -\frac{n}{6} w a^2 \frac{dc}{dx}$$

Fick's 1<sup>st</sup> law:

$$J = -nD \frac{dc}{dx}$$

$$D = \frac{1}{6} w a^2$$

## Kirkendall Effect

During diffusion, the atoms of A diffuse into B and the atoms of B diffuse into A. The atoms do

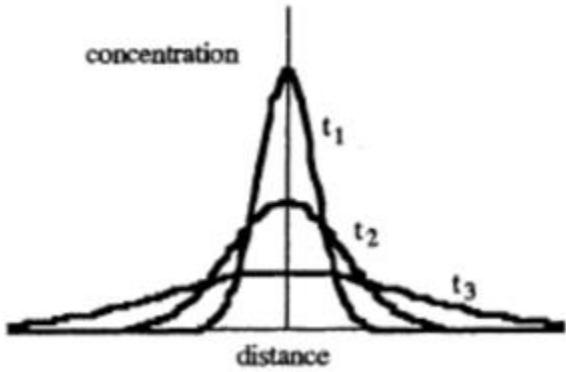
not exchange with each other, but with the vacancies. If there is a large net flux of atoms in one direction and a large net flux of vacancies in the other direction, more than which can be eliminated at dislocations and boundaries, the concentration of vacancies will be so high that eventually they will gather together and precipitate out as voids, forming a line of voids (Kirkendall voids) on the interface.

### Brownian Motion

- Random walk: Over time an atom experiences a sequence of random jumps within a uniform solid, and meanders through the solid in an aimless path
- Interstitial atoms will jump randomly in 1 of 6 directions. There can only be a net flux of atoms when there is a concentration gradient.
- Since all directions are equally likely, the vectors cancel out.

$$\begin{aligned}\langle x \rangle &= 0 \\ \langle x^2 \rangle &= 2Dt \\ \sqrt{\langle x^2 \rangle} &= \sqrt{2Dt}\end{aligned}$$

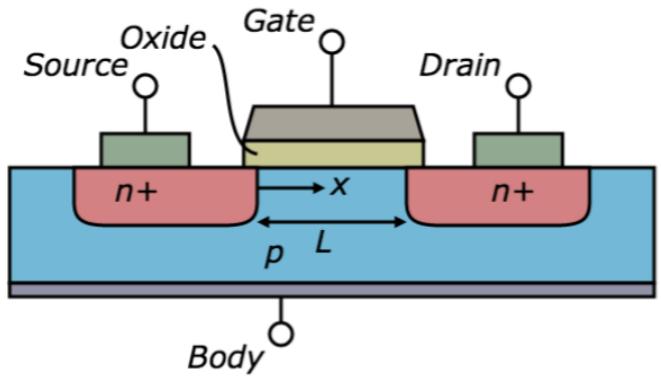
The concentration gradient causes it to go from  $t_1 \rightarrow t_2 \rightarrow t_3$



Two important applications:

1. Time needed to complete diffusion process
2. Device functional time (lifetime: time until gradient disappears; lifetime decreases exponentially with T because of the diffusivity component)

### MOSFET: Example of Gradient



From

$$\langle x^2 \rangle = 2Dt$$

We know that if

$$|x| \gg L$$

Then the device is not going to work, which means

$$t \gg \frac{x^2}{2D}$$

And the diffusivity:

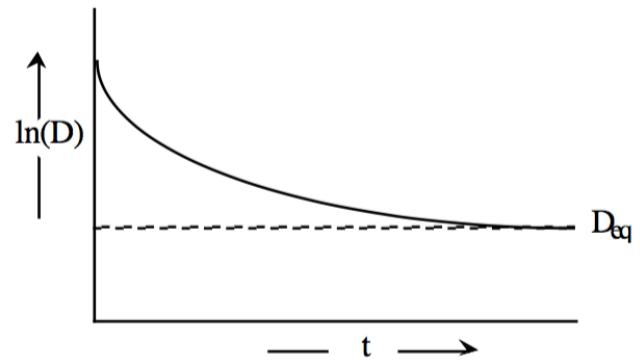
$$D \propto e^{-\frac{E}{KT}}$$

Where K is the **Boltzmann Constant**

### Vacancy Concentration in Substitutional Diffusion

#### 1. Quench from high T

Heating up the material will lead to high vacancy concentration, followed by quenching the material which will preserve the microstructure



Where  $D_{eq}$  is the equilibrium rate of substitutional diffusion, and vacancy concentration at room temperature

$$\begin{aligned}X_{Vacancies} &= e^{-\frac{Q_v}{KT}} \\ D_{substitutional} &= C_{vacancy}\end{aligned}$$

### 2. Introducing Point Defects

Example: Introducing impurity atoms,  $Mg^{++}$  to replace  $Na^+$  in a pure Na material. In order to maintain charge neutrality, two  $Na^+$  atoms will be taken out, leaving a vacancy behind.

### 3. Plastic Deformation

Increases  $X_V$ , dislocations, grain boundaries, etc.  
Interstitial species tend to accumulate near dislocations that have some edge component because the lattice beneath the extra half-plane of an edge dislocation is expanded and can better accommodate interstitial defects.

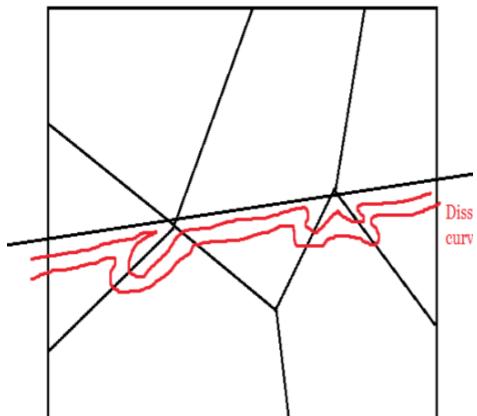
### 4. Radiation

Intense radiation knocks atoms off their lattice and creates an interstitialcy pair point defect. Vacancies increase diffusivity on lattice and interstitials are mobile through the interstitial sites

### **Short Circuit Diffusion**

#### Grain boundary diffusion

- A grain boundary is a region of disorder where adjacent crystals do not fit perfectly together, which contains a high concentration of vacancies.
- Atoms diffuse faster along grain boundaries than in bulk because of many defects



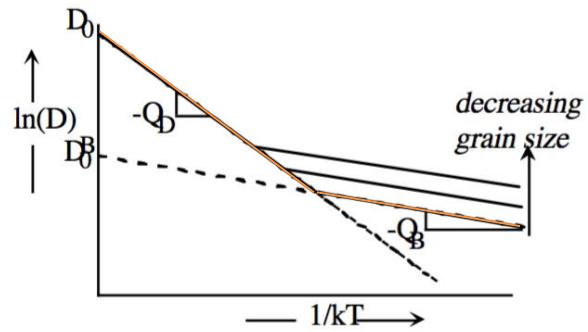
- 3 types of diffusion: pure grain boundary diffusion, pure bulk diffusion, mixture of grain boundary and bulk diffusion

#### Activation Energy

$$Q_{GB} = \frac{Q_{Bulk}}{2}$$

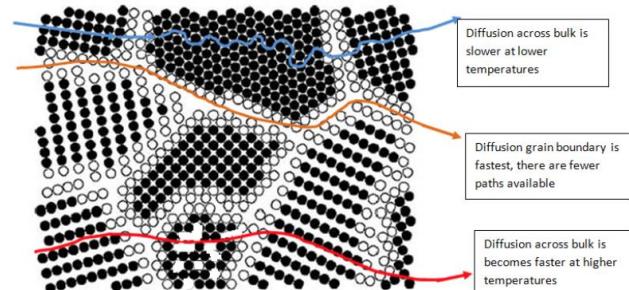
To diffuse across grain boundary

$$D = D_0 e^{-\frac{Q_{GB}}{KT}}$$



To the left is high T, to the right is low T.

- At low T, grain boundary diffusion is more predominant
- At high T, bulk diffusion is more predominant
- As the grain size decreases, there are more grain boundaries, meaning that grain boundary diffusion is prevalent at a higher T, higher  $D_0^B$



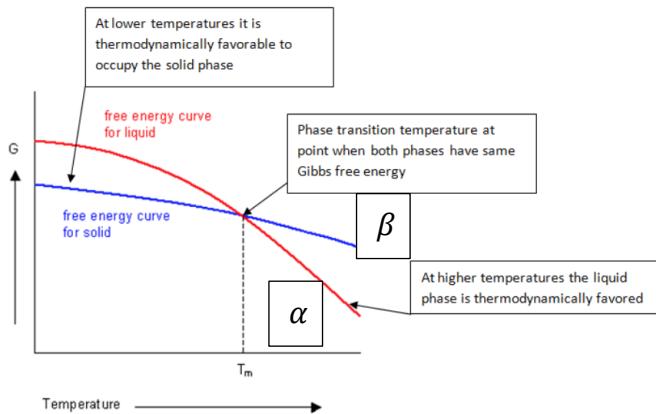
### **Chapter 11 Phase Transformation**

- Discontinuous change in the microstructure of a material
- Thermodynamics: difference in free energy is the driving force
- Kinetics: rate of transformation depends on the mechanism or path chosen

### **Nucleation**

- formation of the first nucleus of crystal of the other type
- The most favorable transformation mechanism is that which requires the smallest disturbance of the metastable phase (the formation of the nucleus or seed)
- Nucleation & growth is the usual mechanism for the transformation of a metastable phase
- Requires significant change in the original phase; can be suppressed or delayed by quenching material

- Sometimes the original phase cannot be cooled indefinitely. It becomes thermodynamically unstable (large thermodynamic driving force), which leads to termination and instability of the metastable phase: the original phase must transform



- A decrease in Gibbs Free Energy  $\Delta G_{\alpha \rightarrow \beta} = G_\beta - G_\alpha$  is the thermodynamic driving force
- At the transition point  $T_m$ :  $\Delta G = 0$
- $\Delta G$  is a function of T

$$\Delta G_V = G_\beta - G_\alpha$$

$\Delta G_V$  is the free energy change per unit volume of the nucleus

- has a negative value when  $T < T_{\alpha\beta}$

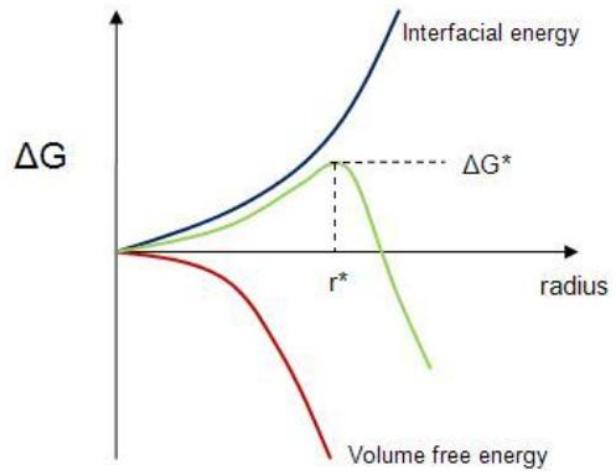
$$\Delta G = \Delta G_V V^\alpha + \sigma^{\alpha\beta} S^\alpha$$

$\Delta G$  is the thermodynamic driving force

- $V^\alpha$  is the volume of the nucleus of  $\alpha$
- $\sigma$  is the surface tension
- $S$  is the surface area of the nucleus
- The first term enhances the  $\alpha$  phase and the second term inhibits the  $\alpha$  phase. Nucleation creates a more stable region, which decreases the free energy; but an interface is also created, which increases the free energy. The total free energy is the sum of the two.

If we assume a spherical  $\alpha$  phase

$$\Delta G = \Delta G_V \frac{4\pi R^3}{3} + \sigma^{\alpha\beta} 4\pi R^2$$



- $\Delta G^*$  is the activation energy of nucleus formation
- Interfacial energy is the surface tension
- Volume free energy is the energy difference between inside the nucleus and outside. The inside of the nucleus has a lower energy than the outside, which is a less stable phase
- Since  $\Delta G_V$  is a function of T,  $\Delta G$  is a function of T. The graph is different for different T.

- The interface is of  $r^2$  and the volume is of  $r^3$ . As r increase,  $\Delta G_{\text{total}}$  changes from increasing to decreasing, then from positive to negative
- left of  $R^*$  is nucleation, right of  $R^*$  is growth
- $R < R^*$ : Requires energy to form  $\alpha$  phase
- $R > R^*$ :  $\Delta G$  decreases as more  $\alpha$  phase form (system reduces its energy)

$$\Delta G^* = \frac{16\pi\sigma^3}{3(\Delta G_V)^2}$$

$$R^* = -\frac{2\sigma}{\Delta G_V}$$

- At  $T = T_{\alpha\beta}$ ,  $\Delta G_V$  approaches 0 and  $\Delta G^*$  approaches infinity. No phase transformation occurs at this temperature.

### Thermodynamic Factor

$$P = A e^{-\frac{\Delta G^*}{KT}}$$

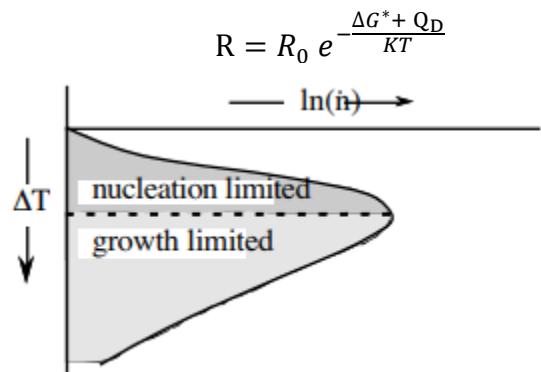
Where P is the probability that phase transformation occurs

### Kinetic Factor

$$P = A' e^{-\frac{Q_D}{KT}}$$

where  $Q_D$  is the activation energy associated with diffusion. Nucleation also depends on the assembly of materials needed for nucleation.

## Nucleation Rate

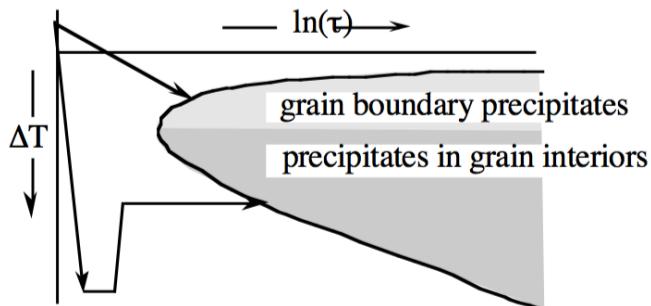


- Nucleation Rate is the product of the thermodynamic factor and the kinetic factor
- As T decreases,  $\Delta G_V$  (thermodynamic drive) increases,  $\Delta G^*$  (activation energy) decreases, which means nucleation is more likely; but as T decreases, the diffusivity also decreases
- Nucleus growth is limited by the diffusion of material required for further growth across the phase interface.
- Nucleation-limited:  $\Delta G^*$  predominant and inhibits nucleation at high T close to  $T_{\alpha\beta}$
- Growth-limited:  $Q_D$  predominant and inhibits nucleation at low T close to  $T_{\alpha\beta}$

## Tradeoff:

At high T: 1) high diffusivity since atoms move around better; 2) high activation energy  $\Delta G^*$  for nucleation to occur

The time to the next nucleation  $t = R^{-1}$



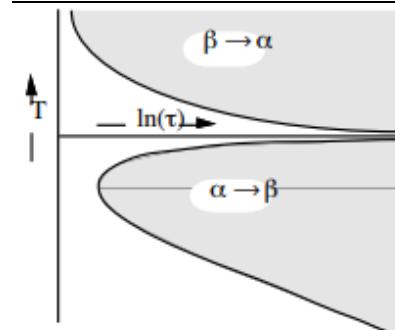
## Different types of transformations by cooling at different rates:

- Pure interior nucleation in diffusion limited growth
- Pure boundary nucleation in nucleation limited growth
- Mixture of boundary and interior nucleation

## Material Processing:

- Quench alloy to suppress nucleation on the grain boundaries, then re-heating to induce precipitation at a low temperature, where nucleation happens predominantly

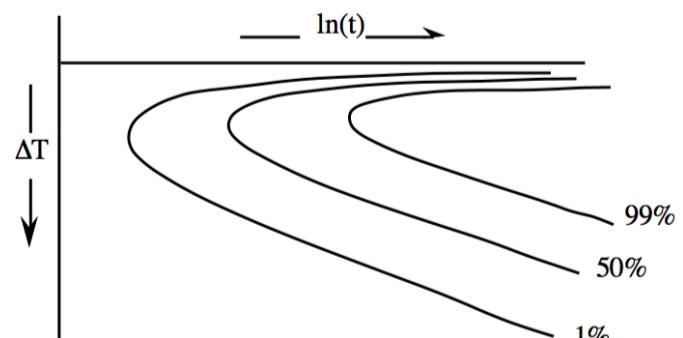
## Reverse: Phase Transformation when Heating



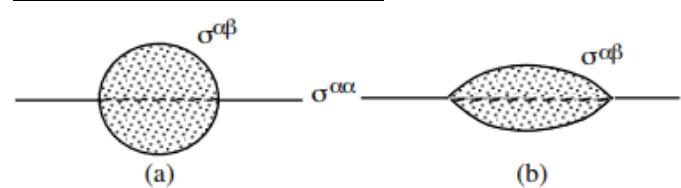
- As the material is heated above  $T_{\alpha\beta}$ , the phase transformation from  $\beta \rightarrow \alpha$  occurs and both nucleation and diffusion is easier. The nucleation rate is monotonically faster as T increases. Thus, transformation cannot be suppressed

## Growth

### Time Temperature Transformation Diagram (TTT Diagram)



## Nucleation Limited Growth



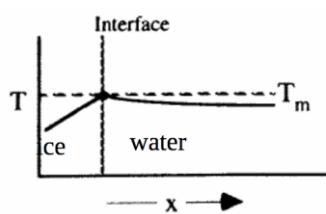
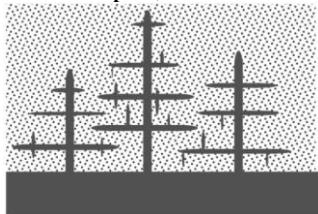
- Large precipitates on the boundary. Diffusion is not a problem. Nucleation first takes place on grain boundaries.
- *Boundary Nucleation*: Using the boundary as part of its side, only need to form part of the nucleus surface, less energy required
- *Homogeneous Nucleation*: Need to form an entire surface
- Not a preferred microstructure: brittle, introduces preferential paths for inter-granular fracture

### Diffusion Limited Growth

- Dense distribution of fine precipitates through the volume. Easy to get nucleation. But at low T, diffusion is difficult, there are no large blocks of precipitate on grain boundaries
- Preferred microstructure: strong, small precipitates inhibit dislocation glide. The compression and stretching forces around the dislocations combined creates overall isotropic pressures

### **Dendrites: Diffusion Controlled Growth**

- Liquid is supercooled and solidification is much more rapid, but unstable



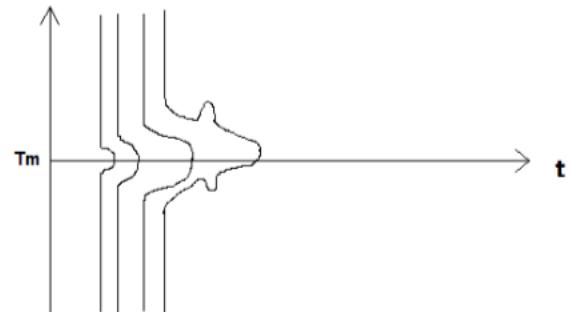
As the vapor to solid phase transformation happens, the entropy increases and heat is released. Thus, there is a higher T at the s-v interface.

Snowflakes have dendritic structures because as ice crystals form from supercooled liquid in clouds, heat is released. The heat has to be evacuated from the interface, and heat flux is proportional to the temperature gradient.

### **Dendrite Growth**

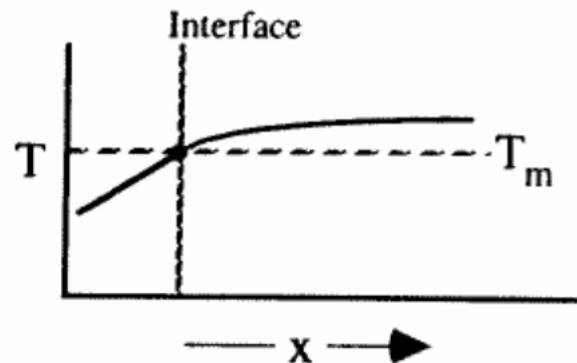
The solidification front will advance more rapidly if there is a steeper temperature drop into the liquid. A small perturbation may cause a

protrusion (bump) to form on the solidification front, the liquid sampled by the tip of the protrusion is cooler than that at the solid surface (heat creation points). Moreover, heat is conducted radially away from the tip while only  $1-d$  from the trailing solid surface



There is a protrusion due to temperature fluctuation near the interface. At the tip of protrusion, the vapor sampled is cooler than that is sensed by rest of surface. So the temperature gradient at the tip is greater than that at the surface. The region within the protrusion is of lower temperature and the region outside the protrusion is of higher temperature. Both increase the rate of growth of the protrusion.

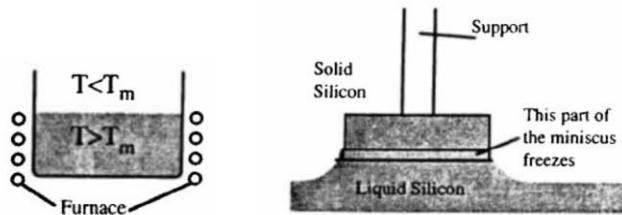
The materials solidified in this way is of polycrystalline structure with grain boundaries.



### **Single Crystal Solidification**

In the case of producing a silicon wafer, the liquid silicon is held at a higher temperature than the melting temperature of silicon; and the Silicon crystal seed is held at a temperature below the melting point of Silicon. When a protrusion occurs, the tip is melted, the surface is flat. Able to form a stable planar growth front.

Czochralski Process:

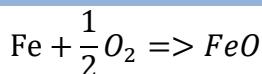


The silicon wafer is a perfect single crystal. Made by dipping the solid Silicon (seed) into the liquid Silicon, continuously spinning and pulling up the seed. A larger wafer means parallel printing and saving costs when producing chips.

## Chapter 12 Environmental Interaction

- Oxidation: Formation and growth of new compounds at the interface

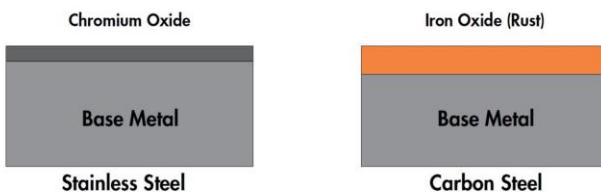
### Oxidation



- This is an exothermic reaction. FeO is more stable than Fe. Releases about 270 kJ per mole.

Iron is used in bridges, it is stable. It is also used in fireworks, it is explosive.

The oxide formed from oxidation of metal by oxygen forms a thin film, a "protective layer" which acts like a "paint" that prevents further oxidation by blocking  $\text{O}_2$  atoms from contacting Fe atoms.



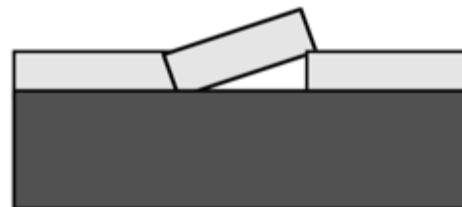
The FeO layer limits but does not completely block oxygen molecules. Oxygen molecules can diffuse through FeO layer.

### Oxidation Kinetics - Diffusion

$$x = \sqrt{2Dt}$$

- where x is the thickness, D is the diffusion

Rust is flakey. FeO has much larger volume than Fe.



Buckle/bubble: FeO has a much larger volume than Fe. This allows  $\text{O}_2$  to come in contact with Fe, leading to further oxidation.

Oxidation in Fe first follows a parabolic (square root) growth relationship, then at the point where buckling/bubbling takes place and flakes are present, the oxidation is then linear growth relationship.

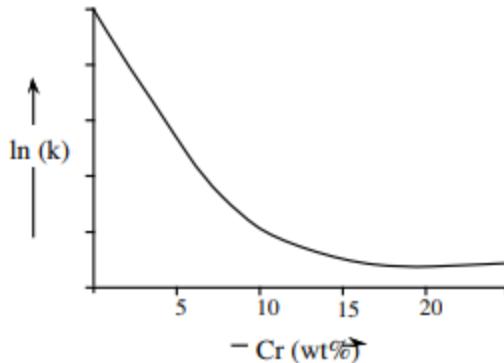
### Oxidation Resistance

**Stainless steel:** has >10.5% Cr, which is shiny and mirror-like.

**Properties of Cr:** If we were to have 100% Cr metal, in contact with  $\text{O}_2$ , we would get an oxide layer of  $\text{Cr}_2\text{O}_3$ . This oxide has a similar volume as Cr. A coherent layer that protects Cr from further oxidation.  $\text{Cr}_2\text{O}_3$  is a glass that's transparent (mostly clear), and Cr is a shiny and reflective material.

In a **mirror**, the glass protects the metal from being oxidized. Can't very well protect oxidation from the edge (brownish spots). The greenish color of Cr is due to the impurities.

In **stainless steel**, the composition is: 70% Fe, 10% Cr, 10% Ni, and 10% C. The oxide layer has **90%  $\text{Cr}_2\text{O}_3$**  and **10% FeO**. Cr is much less stable than Fe, so when Cr is exposed to oxygen, Cr oxidizes much more than iron. Most of the oxide is composed of Cr.



Cr lowers the rate constant, due to its low cation diffusivity. In conclusion, Cr, which forms  $\text{Cr}_2\text{O}_3$ , replaces the original oxide and has a low cation diffusivity, lowering the rate constant. The oxide layer also fits better with the substrate (similar volume). Oxidation is reduced.

Another strategy is the alloy addition which influence the oxidation rate by changing the cation diffusivity in the original oxide film. The alloy additions decrease the concentration of the defects that are responsible for diffusion.

## Kinetics of Oxidation

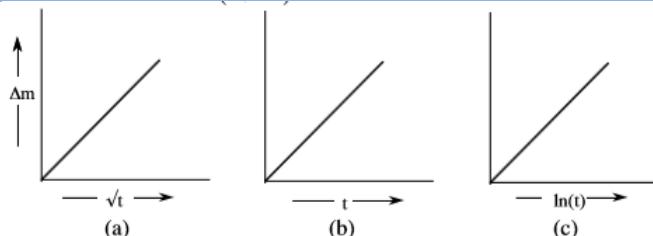
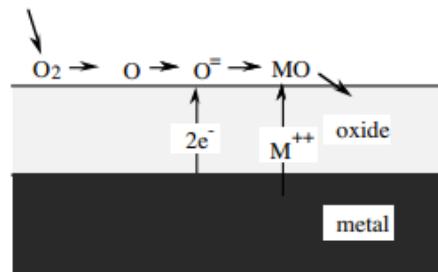
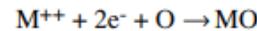


fig. 12.7: The three common kinetic relations for interfacial reactions:  
(a) parabolic growth; (b) linear growth; (c) logarithmic growth.

### 1. Parabolic growth

$$\Delta m = k\sqrt{t}$$

Where  $\Delta m$  is the mass of metal oxidized in time  $t$ . Oxide grows as a continuous film that thickens, rate of growth is limited by the rate at which the reactants can diffuse through the film



The typical mechanism of oxide film growth. Oxygen atoms adsorb, dissociate, ionize by accepting electrons from the metal, and grow oxide by combining with ions from the metal.

$$\frac{dm}{dt} = \frac{k}{2\sqrt{t}}$$

- Rate of oxidation: mass of metal consumed per unit time, decreases monotonically with time. The diffusion of metal ions through the oxide is the rate limiting step. (The square root comes from average diffusion distance by Brownian motion and random walk)

$$k = A * e^{-\frac{Q_D}{2kT}}$$

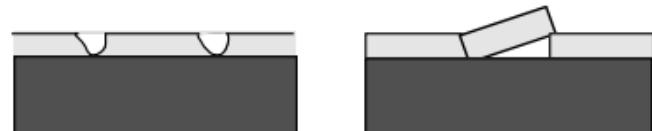
where  $k$  is the rate constant. Thus, the temperature dependence of the oxidation rate is primarily due to its dependence on diffusivity

### 2. Linear growth

- The addition of many parabolic steps  

$$\Delta m = k't$$

Rapid oxidization at high T, stress levels are developed and causing the film to crack. Exposes fresh surface to oxidizing environment



### Piling-Bedworth Ratio:

$$P = \frac{V_0}{nV_M}$$

- Where  $V_0$  is the molar volume of the oxide formed,  $V_M$  is the molar volume of the metal consumed, and  $n$  is the moles metal consumed to create a mole of oxide

- For  $P < 1$ , the volume of oxide formed is less than the volume of metal consumed. Tension is present on the interface, stretching the oxide, causing it to crack and expose fresh surface to oxidation

- For  $P > 1$ , the volume of oxide formed is greater than the volume of metal consumed. The compressive tension causes the oxide to spall, resulting in flakes

### 3. Logarithmic growth

$$\Delta m = k'' \ln(Bt + 1)$$

When a film is very thin, the electric field created from the inhomogeneous charge distribution that develops as the metal and oxygen ionize at the film surface promotes diffusion of ionic species

## **Chapter 13 Metals**

### **Conductivity & Resistivity**

$$V = iR$$

Electrons: random movement

With electric field: electrons have both random movement and drift in a direction

$j = \text{current density} = \sigma E$ , where  $\sigma = \frac{1}{\rho}$  and  $\rho$  is the resistivity.

$$R = \rho \frac{L}{A}$$

Where R is the resistance and is a geometric property. A material property is one that is not concerned with geometry.

### **Graphite**

Hexagonal crystal that has two independent conductivities. One governs current flow in the basal plane of the hexagonal cell, and the other governs flow perpendicular to the basal plane. Graphite-fiber: highly conductive in the direction parallel to the fibers, but insulating in the perpendicular direction

## **Mechanism of Electrical Conduction**

In an electric field:

- electrons accelerated by field

$$\begin{aligned} F &= ma = qE = -eE \\ a &= \frac{dv}{dt} = -\frac{eE}{m} = \frac{qE}{m} \\ v(t) &= v_{avg} + \delta_v(t) \end{aligned}$$

In random motion,  $v_{avg} = 0$

$\delta_v(t)$  is known as the **drift velocity**. For the most part, this results from the force of the electric field.

$$\int \frac{dv}{dt} dt = \delta_v(t) = \frac{Ft}{m} = -\frac{eEt}{m} = -\mu E$$

$$\mu = \text{mobility} = \frac{et}{m}$$

Recall that

$$j = ne \delta_v(t) = \sigma E$$

$$\sigma E = ne(-\mu E)$$

$$\sigma = -ne\mu$$

Where n is the density of mobile electrons, e is the electron charge, and  $\mu$  is the electron mobility.

The carrier density n is a characteristic of the material, and determines whether the material is a good or poor conductor

With defects of grain boundaries,  $\mu$  will be decreased due to scattering of electrons.

## **Conductor Type**

### **Semiconductor:**

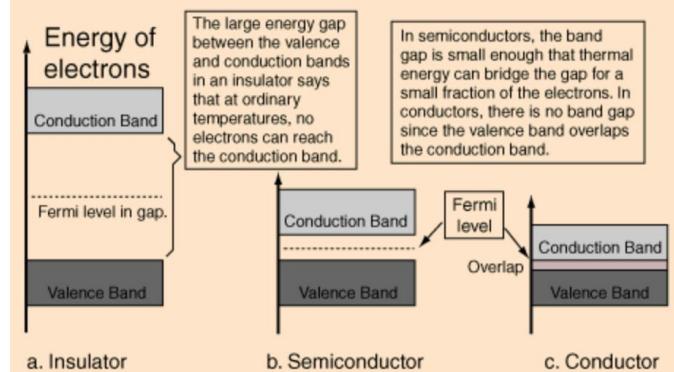
$E_F$  is halfway between CB and VB. VB filled, need to jump across bandgap. Carrier density in the CB is negligible

### **Metal:**

There are empty states arbitrarily close to the Fermi Energy.  $E_F$  is in VB, so VB is partly filled. Electrons in VB are free to respond to an E field. Mobile carrier density n is high, and electrical conductivity is appreciable

## **Chapter 14 Semiconductors**

### **Band Gaps**



For an insulator,  $E_g > 2 \text{ eV}$

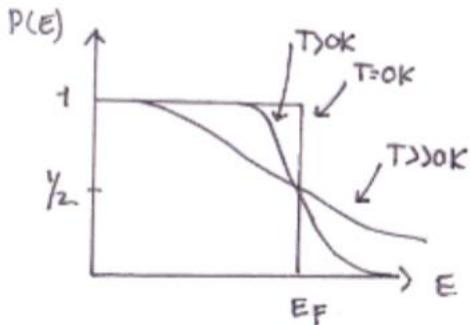
For a semiconductor,  $E_g < 2 \text{ eV}$

For a conductor, CB and VB overlap.

## Fermi Function

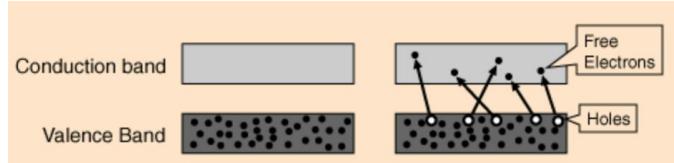
$$P(E) = \frac{1}{1 + e^{\frac{E-E_F}{KT}}}$$

- The fermi function reveals the probability of finding an electron at energy level E.
- The fermi energy level is the level at which there is exactly a probability of 0.5 of finding an electron.



## Intrinsic Semiconductor

- Fermi energy level in the middle of band gap.
- Pure semiconductors without doping present. (i.e. pure Silicon crystal)
- # of electrons in CB = # of holes in VB



**Density of States** = # of allowable states for electrons to reside.

Electron at  $E_F$ ?

Between the band gap, there is a non-zero probability for finding an electron; however, it is only a probability. Since there are no energy bands between the energy gap, the density of state = 0. We find no electrons at the fermi energy level.

We need 2 pieces of info to find out the number of electrons we can find at the fermi energy level: fermi function & density of states.

## Electron Hole in Intrinsic Semiconductor

$$n = p = N_A e^{-\frac{E_A}{KT}}$$

Where:

- $n_h$  and  $p$  is the density of holes (# holes per unit volume);
- $N_A$  is the number of acceptor atoms per volumes
- $E_A$  is the acceptor level activation energy

At just some temperature,  $p \approx N_A$  since  $E_A$  is low

## Intrinsic Carrier Density

- No dopants.  $n_i$  is a property of a given semiconductor, and holds whether or not the semiconductor is intrinsic

$$n_e n_h = np = N_C N_V e^{-\frac{E_g}{KT}} = n_i^2$$

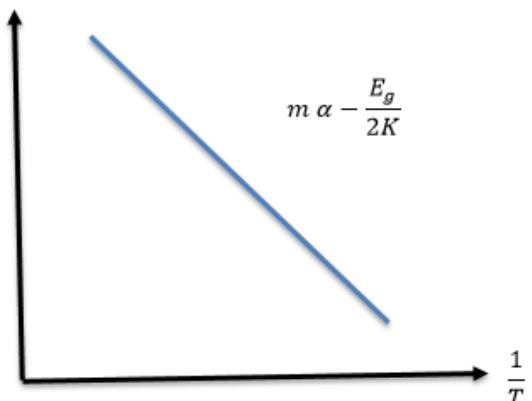
Where  $n_i$  is the intrinsic density of charge carriers (electrons or holes depending on n or p type);  $N_C$  is the density of states in CB; and  $N_V$  is the density of states in VB.

$$n = n_e = n_h = p = n_i = f(T) = \sqrt{N_C N_V e^{-\frac{E_g}{KT}}} = \sqrt{N_C N_V} e^{-\frac{E_g}{2KT}}$$

- This is only valid for intrinsic semiconductors
- We are able to express the carrier density independent of  $E_F$

## Conductivity

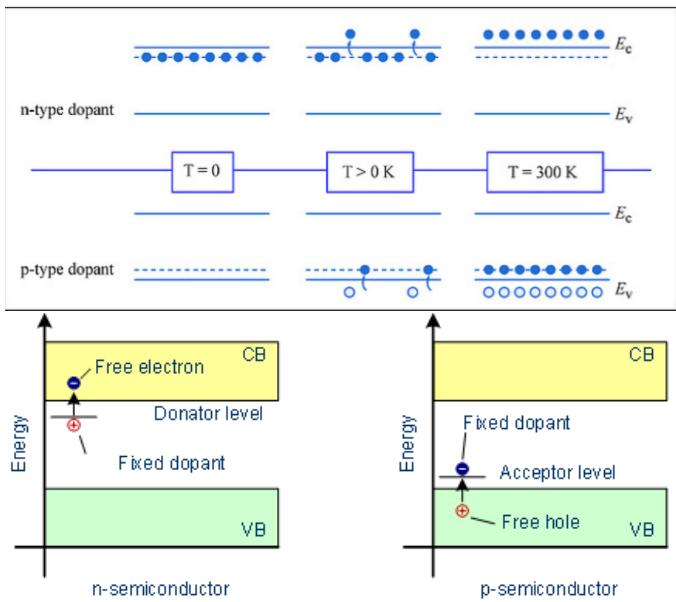
$$\ln(n_h) = \ln(p)$$



This is an i-type material

## Extrinsic Semiconductor

- n-type: negative type
- p-type: positive type



For a p-type material, the acceptor energy level  $E_A = E_F$  is closer to the VB. Because there are more holes due to doping, there is a larger probability of finding holes on VB and a smaller probability of finding electrons on CB.

For an n-type material, the donor energy level  $E_D = E_F$  is closer to the CB. Because there are more electrons due to doping, there is a smaller probability of finding holes on VB and a larger probability of finding electrons on CB.

### Extrinsic Carrier Density

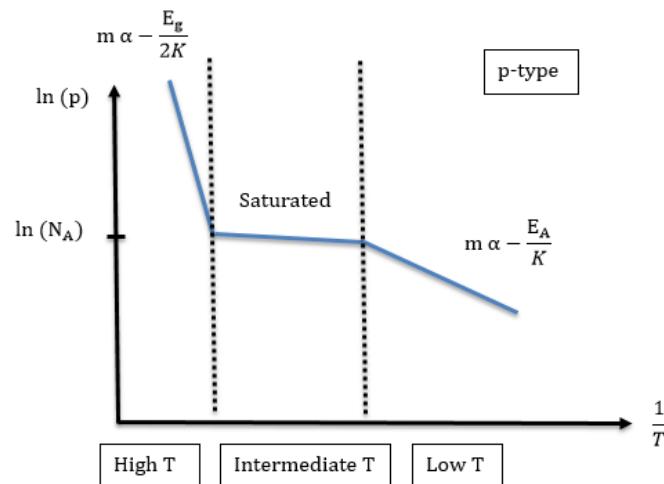


Diagram for p-type material. At low T, the slope is shallow since  $E_A$  is small. Electrons are excited and filling up the acceptor level. At intermediate T, the acceptor level is filled (saturated) and the density of holes in VB is not changing. At high T, electrons can be directly excited to CB, so there are more and more holes in VB.

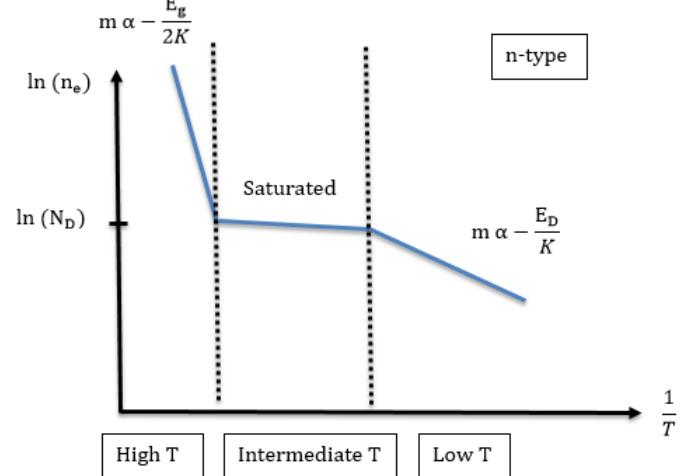


Diagram for n-type material. At low T, the slope is shallow since  $E_D$  is small. Electrons are excited and moving from the donor level to the CB. At intermediate T, the electrons on the donor level are all excited to the CB, so the charge carrier density on the CB is constant. At high T, electrons can be directly excited to CB from the VB.

$$n = n_e = N_D e^{-\frac{E_D}{KT}}$$

- where  $N_D$  is the density of donors;  $E_D$  is the donor energy level

$$n = N_D^+ + p$$

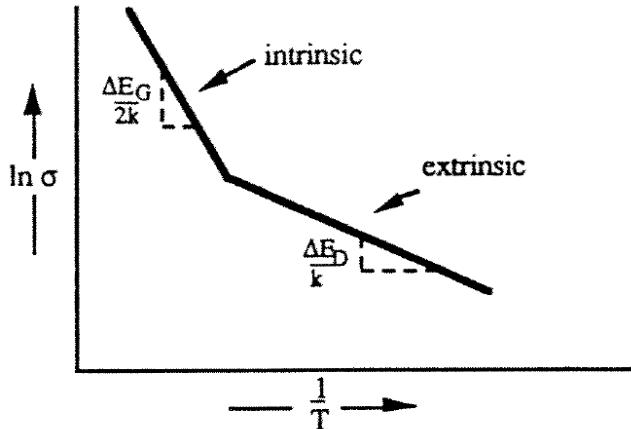
- where  $N_D^+$  is the number of ionized donors; and  $p$  is the density of holes in VB (intrinsically activated carriers)

- there are two sources for the free electrons in CB, from the ionization of the donor sites and intrinsic activation across the band gap

At  $T = 0\text{K}$ , there are no free charge carriers. For n-type semiconductors, electrons are free charge carriers; for p-type semiconductors, holes are free charge carriers.

All semiconductors are extrinsic at sufficiently low temperatures, and all semiconductors are intrinsic at sufficiently high temperatures. At very low T, most of the charge carriers are extrinsic, since the activation energy to excite an extrinsic carrier is much less than that for an intrinsic carrier; At sufficiently high T, most of the charge carriers are intrinsic, since the energy is sufficient to activate most intrinsic carriers.

## Extrinsic Semiconductor Without Saturation



- not all extrinsic semiconductors saturate
- may not be possible to ionize all active impurities (donors or acceptors) before intrinsic conduction becomes significant
- the band gap should be less or about the same as the acceptor or donor band gap

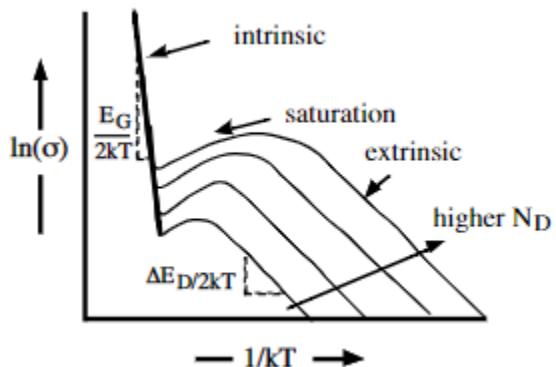
## Conductivity of Extrinsic Semiconductors

- In n-type: conductivity determined almost completely by conduction electrons

$$\sigma = ne\mu_e$$

- In p-type: conductivity determined almost completely by conduction holes

$$\sigma = pe\mu_p$$



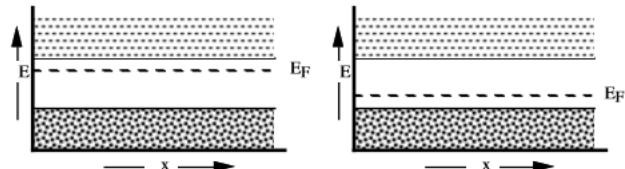
- At low T, conductivity is dominated by the exponential dependence of the carrier density (exponentially increasing conductivity)
- At medium T when the SC is saturated, the mobility decreases with T and conductivity decreases with T
- At high T, intrinsic carriers are activated and the semiconductor is intrinsic

- Devices: Transistor, diodes, LEDs, solid state lasers

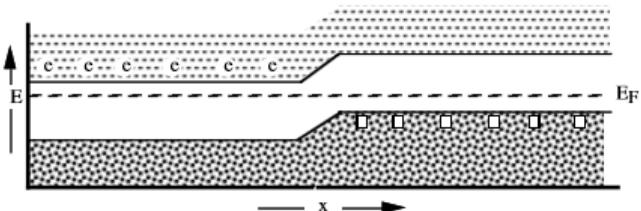
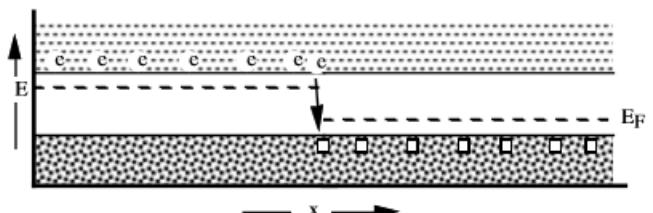
- Also a rectifier: only allowing current in one direction

- At absolute zero (0K), we expect to have all the electron states filled up until the Fermi Energy level

- The energy of electrons in n-type material > the energy of electrons in p-type material, because of the difference in their Fermi Energy levels



- Right after the two regions are joined together, there is an energy gradient present. The electrons in CB join the holes in VB.



- As electrons move away from  $n \rightarrow p$ , n becomes more positive and decreases in potential, while p becomes more negative and increases in potential, until the energy gradient decrease to 0.

- Thus, the energy levels of the p-type material are increased while the energy levels of the n-type material are decreased.

- The bottom layer of electrons and the bottom layer of holes have energy lower than the energy of the potential barrier. They are inhibited by the potential barrier and cannot move.

- The system reaches equilibrium when the mobile electrons in the n-type material have the same energy as the mobile electrons in the p-type material. They counteract each other and there is no net electron / hole flux. However, there is flux going from  $n \rightarrow p$  and from  $p \rightarrow n$ ,

## PN Junction

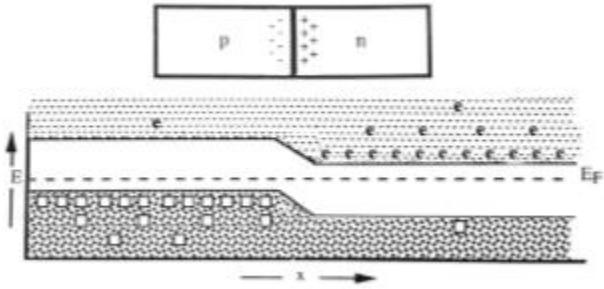
they cancel each other out. The Fermi Energy is continuous and the same on both sides.

- Contact Potential: The difference in energy between the original Fermi energies

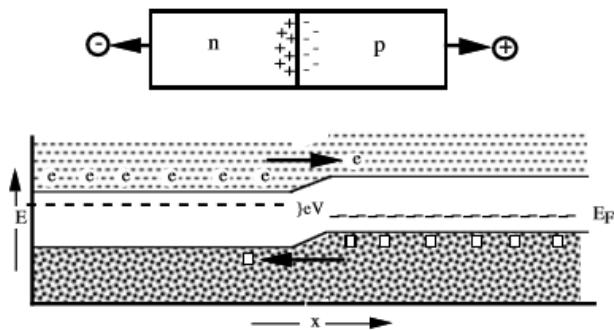
## Bias

### 1. Zero Bias

The PN Junction is at equilibrium. The electron / hole density is the same on both regions.



### 2. Forward Bias



- An external potential is applied and creates a constant potential difference.
- The **p-type** region has higher potential (+) and the **n-type** has lower potential (-).
- This creates an electric field across the PN Junction, equivalent to raising the potential of the **p-type**.
- Thus, electrons flow from **n**  $\rightarrow$  **p** and holes flow in reverse.
- The n-type band shifts up as more voltage is applied.
- There is a substantial current from p  $\rightarrow$  n because there are plenty of electrons in the n-type.
- The current is dominated by majority carriers, which are electrons in n-type or holes in p-type

Net flux of electrons across the junction:

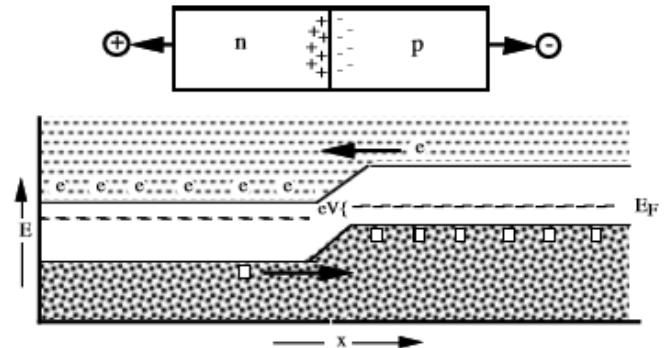
$$j_e = j_e^+ - j_e^- = j_e^0 \left( e^{\frac{eV}{kT}} - 1 \right)$$

Where  $j_e^0$  is the equilibrium flux of electrons.

Current density in the positive direction:

$$j = -2j_e = 2j_e^0 \left( 1 - e^{\frac{eV}{kT}} \right)$$

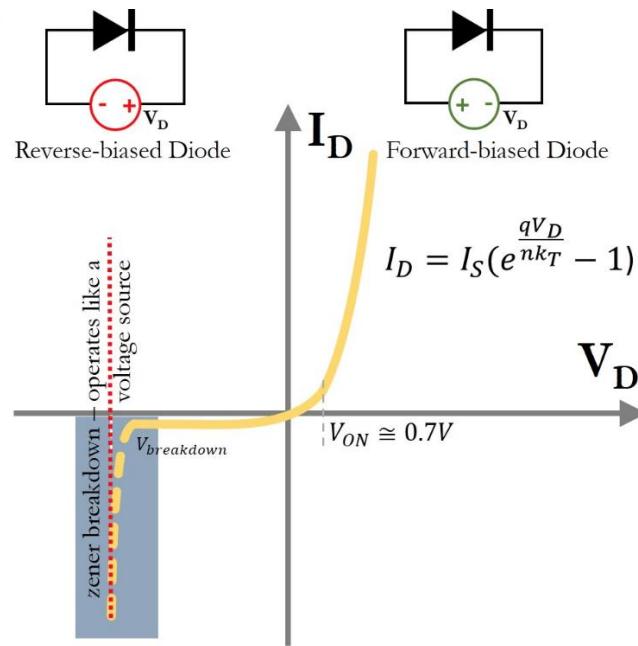
### 3. Reverse Bias



- An external potential is applied and creates a constant potential difference.
- The **n-type** region has higher potential (+) and the **p-type** has lower potential (-).
- This creates an electric field across the PN Junction, equivalent to lowering the potential of the **p-type**. A greater potential barrier.
- Thus, electrons flow from **p**  $\rightarrow$  **n** and holes flow in reverse.
- The n-type band shifts down as more voltage is applied, and creates an excess flux.
- There is little current from n  $\rightarrow$  p because there are few electrons in the p-type.
- The current is dominated by minority carriers, which are holes in n-type or electrons in p-type

## Current

For a real diode:



$$I = I_0(e^{\frac{eV_A}{KT}} - 1)$$

Where  $I_0$  is the equilibrium current;  $e$  is 1 electron charge;  $V_A$  is the voltage applied;  $K$  is the Boltzmann constant;  $T$  is the temperature. The graph intersects the origin at  $V = 0$

- For forward bias (+V): As voltage increases, an exponentially increasing fraction of the electrons in CB of the n-type material is free to move across the interface. The current is in the negative direction, and its density increases with voltage, becoming nearly exponential when  $eV \gg kT$

$$j = -2j_e^0 \left( e^{\frac{eV}{kT}} - 1 \right) \rightarrow \infty$$

- For reverse bias (-V): Due to an excess flux of minority carriers: electrons in p-type and holes in n-type. Limited by minority carriers. Current is in the positive direction, but rapidly asymptotes as  $e|V| \gg kT$

$$j = 2j_e^0 \left( 1 - e^{-\frac{eV}{kT}} \right) \rightarrow 2j_e^0$$

For an **ideal diode**:

- The device completely allows the current without any loss under forward bias, and completely blocks the current with infinite loss under reverse bias.

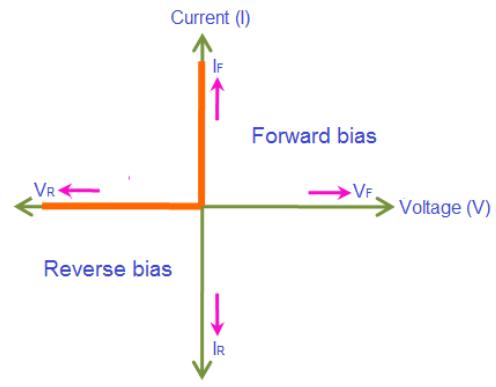
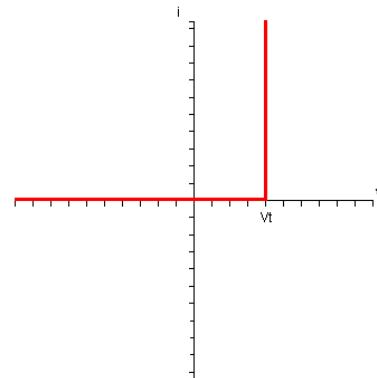


Fig: V-I characteristics of ideal diode

For a **modelled diode**:



The diode conducts after the voltage applied is greater than the knee voltage.

### LED (Light Emitting Diode)

When an electron falls to a lower energy band, and fills up (interact with) another carrier (hole), energy in the form of light is emitted.

### Semiconductor Light Absorption

There are two band gap types:

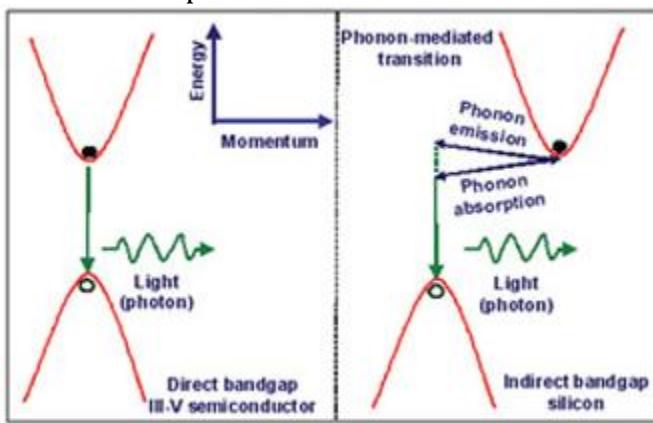
- Direct band gap
- Indirect band gap

The minimal-energy state in CB and the maximal-energy state in VB are each characterized by a certain crystal momentum (**k-vector**) in the **Brillouin zone**.

- If the **k-vectors** for electrons and holes is the **same** in both CB and VB: direct band gap
- If the **k-vectors** are **different**: indirect band gap

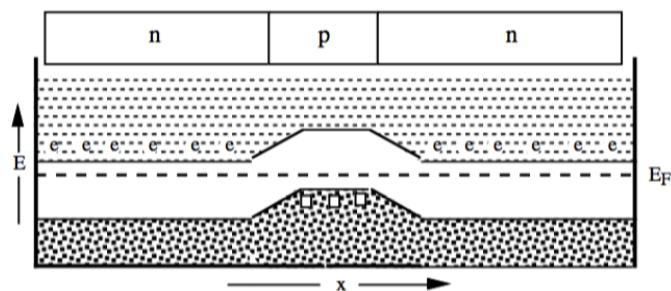
- For a **direct band gap**, an electron can directly emit a photon

- For an **indirect band gap**, a photon can be emitted but it's much less likely. There is no direct way for the charge carrier to fall from VB to CB due to the different crystal momentums ( $k$ -vectors). Without violating the conservation of momentum, the charge carrier can only fall to CB and emit a photon while accompanied by the emission of a phonon with the momentum.

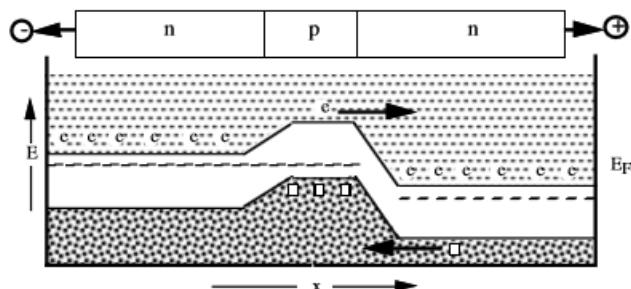


### NPN Junction

The three elements of n-p-n are called the emitter, the base, and the collector.



### Voltage applied at the collector:

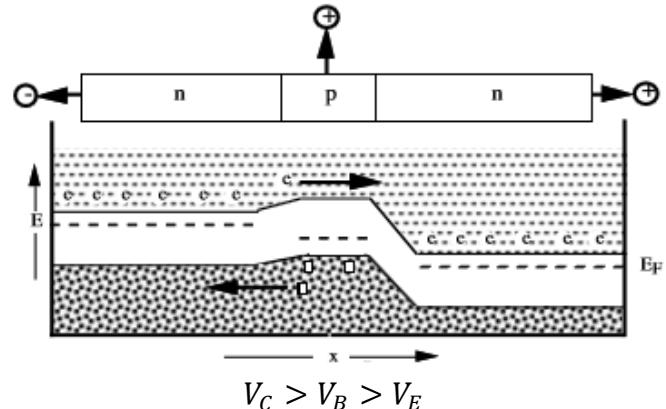


- The emitter-base junction is in forward bias while the base-collector junction is in negative bias
- Current flows easily across the emitter-base junction but only a small current flows across the base-collector junction due to the limiting minority carriers.

- The potential difference between the emitter and the base is rapidly lost due to charge transfer, and all the potential difference is concentrated at the base-collector junction

- If voltage is applied on the emitter side, the situation will be similar as described above: there will be a small current at the emitter-base junction and all the potential difference will accumulate at the emitter-base junction

### Voltage applied at the base:



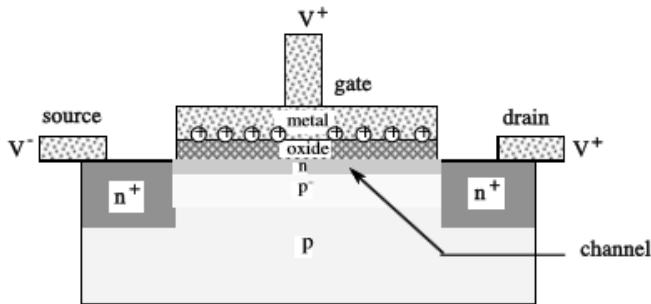
- At the emitter-base junction, electrons flow into the base and holes flow into the emitter.
- Since the voltage difference in the emitter-base junction is maintained, the current does not disappear with time. This is maintained by a combination of current from the collector and current from the device that maintains the voltage on  $V_B$
- At steady state the electrons injected into the base from the emitter combine with excess holes in the base to maintain equilibrium
- The region near the emitter-base interface is depleted of holes since they are swept into the emitter. Excess electrons move freely for some distance into the base.
- If base is relatively thin, the electrons move close to the base-collector interface and are swept into the collector by the potential difference at the base-collector junction
- Both the current at the emitter-base junction and the base-collector junction increase exponentially with the potential difference ( $\Delta V$ )
- In such scenario, the n-p-n junction behaves very much like an NP Junction in forward bias

### Applications

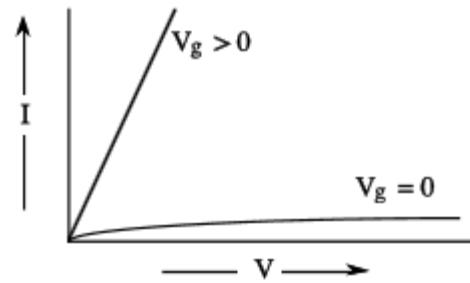
1. Memory element

Read current induced by voltage at the collector. If there is a positive voltage applied to the base, then the transistor will behave as a junction in forward bias; if there is a zero or negative voltage applied to the base, then the transistor will behave as a junction in reverse bias.

## Metal Oxide Semiconductor Field Effect Transistor (MOSFET)



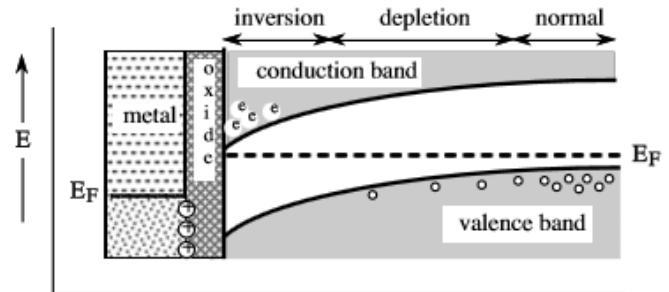
- The Metal Insulator Semiconductor (MIS) junction, a metal-oxide junction, the “gate”, is used to form or suppress a conducting channel between a source and drain for charge carriers; controls the resistivity of a line connecting two conductors.
- The gate is connected to a p-type region in a semiconducting crystal.
- Two adjacent regions of the crystal are heavily doped to n-type and are connected to metal lines that join an electrical circuit.
- The n-type at the negative terminal is called the source and at the positive terminal is called the drain
- If the gate has **no voltage** imposed, the MOSFET behaves like a NPN junction in reverse bias, with little current and is a poor conductor
- If the gate has a **suitable positive voltage** imposed, the semiconductor material just below the oxide inverts to n-type, and forms a thin, n-type channel between the two n+ terminals. The channel behaves as a simple resistor between the source and drain.



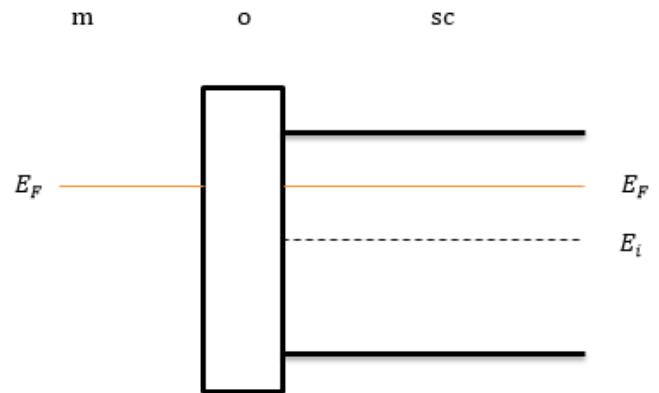
- A greater voltage applied at the gate creates a channel with more depth, which increases the conductivity. Thus, the effective resistance can be varied independently with the potential difference between the source and drain.

## Band Structure of Gate for PNP Junction MOSFET

Example of NPN inversion for p-type SC:

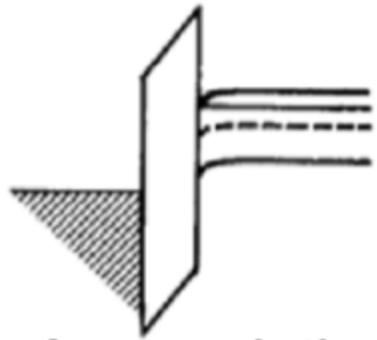


1.  $V_A = 0$  (Flat band)



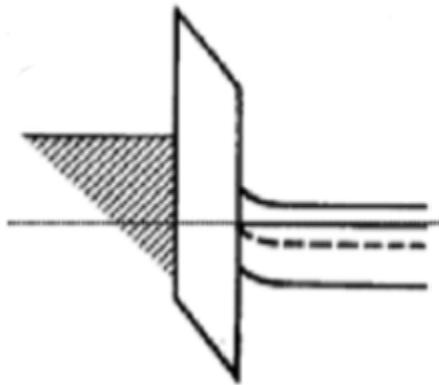
- $E_F$  is constant since there is no potential difference or current
- sc is n-type, meaning  $E_F$  is closer to CB
- Oxide limits the current

2.  $V_A > 0$  (Accumulation)



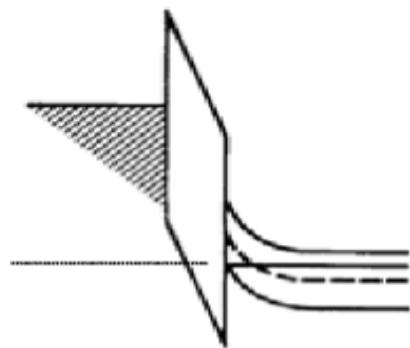
- Positive on m and negative on sc
- Since the oxide does not conduct, holes accumulate on the m-o interface and electrons accumulate on the o-sc interface.

#### 3. $V_A < 0$ (Depletion)



- Negative on m and positive on sc
- Electrons accumulate on the m-o interface and holes accumulate on the m-sc interface, the electrons in the semiconductor gets repelled
- Near the o-sc interface, the semiconductor is less n-type and more i-type

#### 4. $V_A \ll 0$ (Inversion)

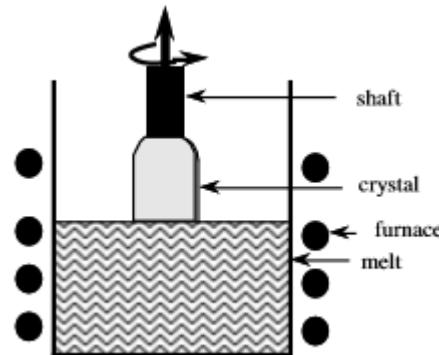


- Electrons accumulate on the m-o interface and holes accumulate on the m-sc interface, to a point where there is a significant concentration of holes at the m-sc interface

- Near the o-sc interface,  $E_F$  is close to CB, meaning that it inverted from an n-type material to a p-type material

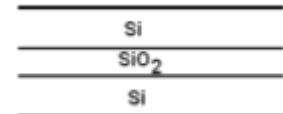
## Semiconductor Fabrication

### 1. Growth of Si Crystals



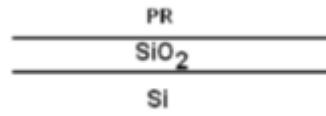
- Czochralski process: grows large Si and Ge crystals

### 2. Generate $\text{SiO}_2$ layer



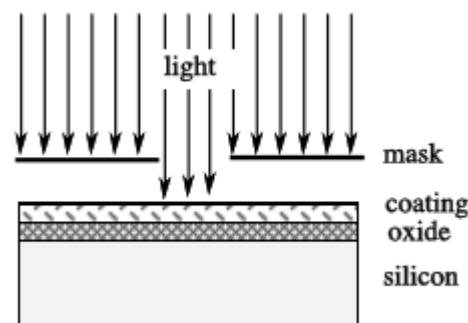
- Oxidized at 1000 degrees C under  $O_2$

### 3. Spin-on photoresistive layer



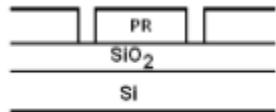
- positive photoresist: more chemically reactive after exposure
- negative photoresist: less reactive after exposure

### 4. Exposure to develop PR



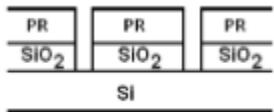
- The mask, prepared and contains a cut pattern which defines the region of the crystal surface to

be processed, is placed on the PR surface and exposed to light.



- When PR is exposed to light, its polymeric structure alters and has a chemically active pattern. The first development

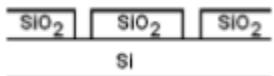
#### 5. Etching



- Then, the *SiO<sub>2</sub>* layer is etched with chemicals such as *HF*, which dissolves the *SiO<sub>2</sub>* and exposes the semiconductor in a proper pattern.

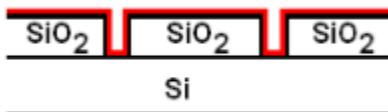
- PR protects the underlying *SiO<sub>2</sub>* from *HF*

#### 6. Removing the PR



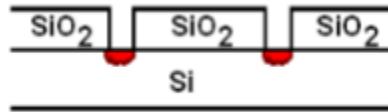
- Second development

#### 7. Doping



- The surface of the semiconductor is coated with the dopant (i.e. depositing a film of dopant from the vapor)

#### 8. Diffusion



- The sample is kept at high T to allow the dopant to diffuse in silicon. *SiO<sub>2</sub>* inhibits diffusion.