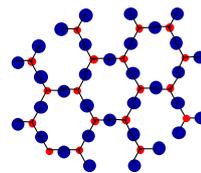# Chap. 1 A Review of Materials Science

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1.1 MATERIALS AND PACKING

Crystalline materials...
- atoms pack in periodic, 3D arrays
- typical of:
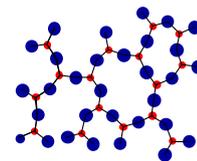 - -metals
  - -many ceramics
  - -some polymers

crystalline SiO_2
Adapted from Fig. 3.18(a), *Callister 6e.*

• Si   ● Oxygen

Noncrystalline materials...
- atoms have no periodic packing
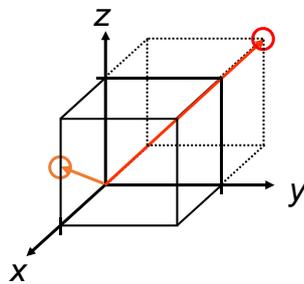- occurs for:
  - -complex structures
  - -rapid cooling

"Amorphous" = Noncrystalline

noncrystalline SiO_2
Adapted from Fig. 3.18(b), *Callister 6e.*

3

Crystallographic Directions

Algorithm

1. Vector repositioned (if necessary) to pass through origin.
2. Read off projections in terms of unit cell dimensions a, b, and c
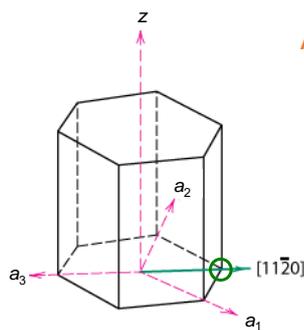3. Adjust to smallest integer values
4. Enclose in square brackets, no commas

$$[uvw]$$

ex: 1, 0, ½ => 2, 0, 1 => [201]

-1, 1, 1 => [$\bar{1}$11]   where overbar represents a negative index

families of directions *<uvw>*

HCP Crystallographic Directions

Algorithm

1. Vector repositioned (if necessary) to pass through origin.
2. Read off projections in terms of unit cell dimensions a_1, a_2, a_3, or c
3. Adjust to smallest integer values
4. Enclose in square brackets, no commas

$$[uvtw]$$

[11$\bar{2}$0]

Adapted from Fig. 3.8(a), *Callister 7e.*

HCP Crystallographic Directions

- **Hexagonal Crystals**
  - 4 parameter Miller-Bravais lattice coordinates are related to the direction indices (i.e., *u'v'w'*) as follows.

[0001]
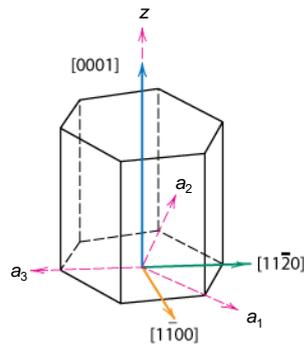
a_2

[11$\bar{2}$0]

a_3

a_1

[1$\bar{1}$00]

Fig. 3.8(a), *Callister 7e.*

$$[u'v'w'] \rightarrow [uvtw]$$

$$u = \frac{1}{3}(2u'-v')$$
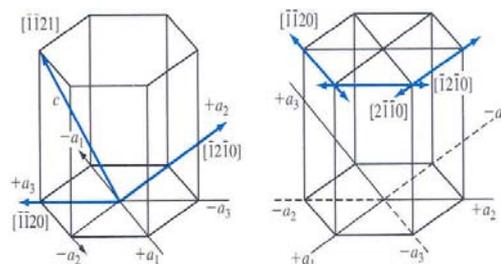
$$v = \frac{1}{3}(2v'-u')$$

$$t = -(u+v)$$

$$w = w'$$

Directions in HCP Unit Cells

- Indicated by 4 indices [uvtw].
- u,v,t and w are lattice vectors in a_1, a_2, a_3 and c directions respectively.
- **Example:-**

  For a_1, a_2, a_3 directions, the direction indices are
  [2 $\bar{1}$ $\bar{1}$ 0], [$\bar{1}$ 2 $\bar{1}$ 0] and [$\bar{1}$ $\bar{1}$ 2 0] respectively.

[$\bar{1}\bar{1}$21]

[$\bar{1}\bar{1}$20]

[$\bar{1}$2$\bar{1}$0]

$+a_2$

$-a_1$

[1$\bar{2}$1$\bar{1}$0]

$+a_3$

[$\bar{1}\bar{1}$20]

$-a_2$ $+a_1$

$+a_3$

[2$\bar{1}\bar{1}$0]

$-a_1$

$-a_2$ $+a_2$

$+a_1$ $-a_3$

Source : William F. Smith, Javad Hashemi, Foundations of Materials Science and Engineering

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Chapter 3 -

3-27

3

Crystallographic Planes

- Miller Indices: Reciprocals of the (three) axial intercepts for a plane, cleared of fractions & common multiples. All parallel planes have same Miller indices.

- Algorithm
  1. Read off intercepts of plane with axes in terms of *a*, *b*, *c*
  2. Take reciprocals of intercepts
  3. Reduce to smallest integer values
  4. Enclose in parentheses, no commas i.e., (*hkl*)

Crystallographic Planes

example		a	b	c
1.	Intercepts	1	1	∞
2.	Reciprocals	1/1	1/1	1/∞
		1	1	0
3.	Reduction	1	1	0
4.	Miller Indices	(110)		
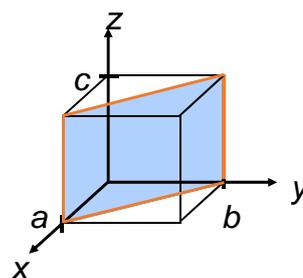
example		a	b	c
1.	Intercepts	1/2	∞	∞
2.	Reciprocals	1/½	1/∞	1/∞
		2	0	0
3.	Reduction	2	0	0
4.	Miller Indices	(200)		
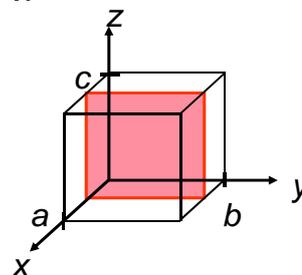
Crystallographic Planes

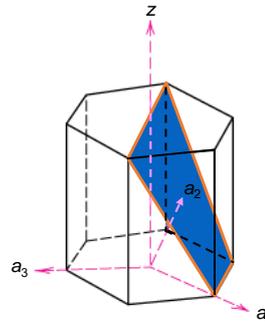|	example	a	b	c
1.	Intercepts	1/2	1	3/4
2.	Reciprocals	1/½	1/1	1/¾
		2	1	4/3
3.	Reduction	6	3	4
4.	Miller Indices	(634)		
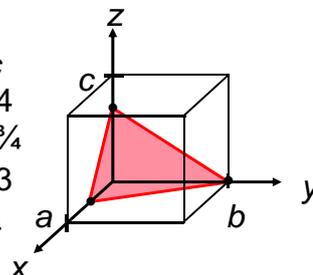
Family of Planes   {hkl}

Ex: {100} = (100), (010), (001), ($\bar{1}$00), (0$\bar{1}$0), (00$\bar{1}$)
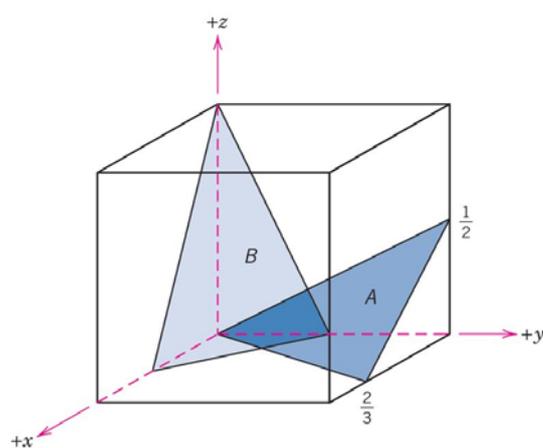
Crystallographic Planes (HCP)
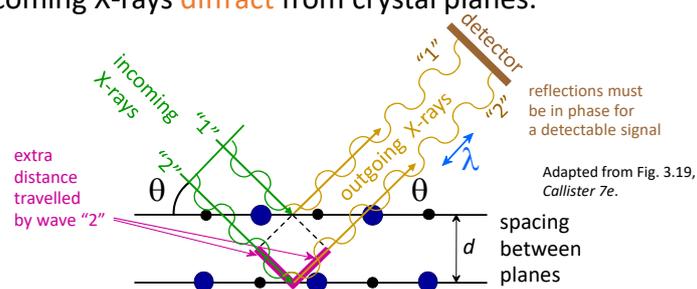
- In hexagonal unit cells the same idea is used

example		a_1	a_2	a_3	c
1.	Intercepts	1	∞	-1	1
2.	Reciprocals	1	$1/\infty$	-1	1
		1	0	-1	1
3.	Reduction	1	0	-1	1
4.	Miller-Bravais Indices		$(10\bar{1}1)$		

Adapted from Fig. 3.8(a), *Callister 7e.*

X-Rays to Determine Crystal Structure
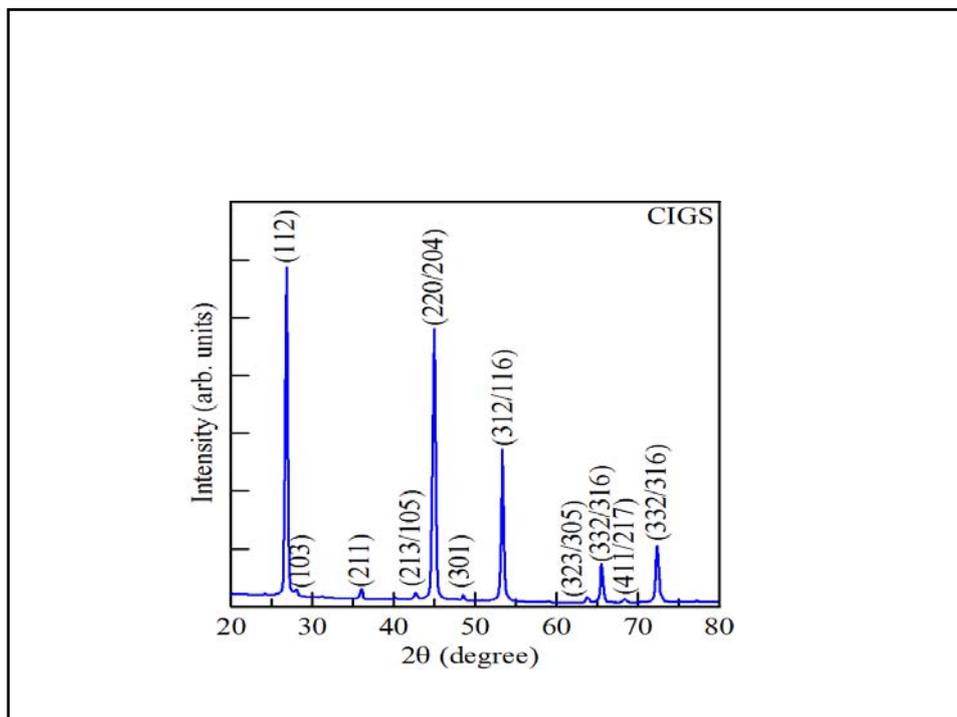
- Incoming X-rays diffract from crystal planes.

incoming X-rays

"1"

"2"

detector

outgoing X-rays

"1"

"2"

reflections must be in phase for a detectable signal

Adapted from Fig. 3.19, *Callister 7e.*

extra distance travelled by wave "2"

θ

θ

λ

spacing between planes

d

Measurement of critical angle, θ_c, allows computation of planar spacing, d.

X-ray intensity (from detector)

$$d = \frac{n\lambda}{2 \sin \theta_c}$$

θ

θ_c
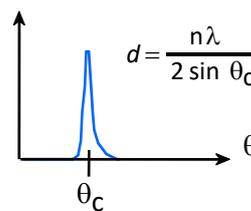
1.3. DEFECTS IN SOLIDS

- In thin crystalline films the presence of defects not only serves to disrupt the geometric regularity of the lattice on a microscopic level, it also significantly influences many film properties, such as **chemical reactivity, electrical conduction, and mechanical behavior**.
- The structural defects briefly considered in this section are **grain boundaries, dislocations, and vacancies**.

TYPES OF DEFECTS

- Vacancy atoms
- Interstitial atoms   Point defects
- Substitutional atoms

- Dislocations   Line defects

- Grain Boundaries   Area defects

1.3.1. Grain Boundaries

- **Grain boundaries** are surface or area defects that constitute the **interface between two single-crystal grains of different crystallographic orientation**.

- **This causes the grain boundary to be a heterogeneous region** where various atomic reactions and processes, such as **solid-state diffusion and phase transformation, precipitation, corrosion, impurity segregation, and mechanical relaxation**, are favored or accelerated.

GRAIN BOUNDARIES

- are boundaries between crystals.
  - are produced by the solidification process, for example.
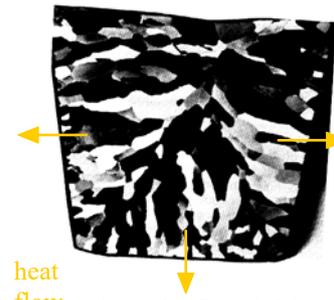 - have a change in crystal orientation across them.
  - impede dislocation motion.

Schematic

Metal Ingot

~ 8cm

grain boundaries
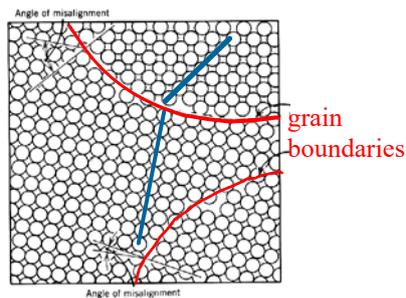
heat flow

Adapted from Fig. 4.7, *Callister 6e.*

Adapted from Fig. 4.10, *Callister 6e.* (Fig. 4.10 is from *Metals Handbook*, Vol. 9, 9th edition, *Metallography and Microstructures*, Am. Society for Metals, Metals Park, OH, 1985.)

1.3.1. Grain Boundaries

- Electronic transport in metals is impeded through , **increased scattering at grain boundaries**, which also serve **as charge recombination centers in semiconductors**.
- Grain sizes in films are typically **from 0.01 to 1 µm** in dimension and are smaller, by a factor of more than common grain sizes in bulk materials.
- Thin films tend to be **more reactive** than their bulk materials.

1.3.2. Dislocations

- Dislocations are line defects that bear a definite crystallographic relationship to the lattice.
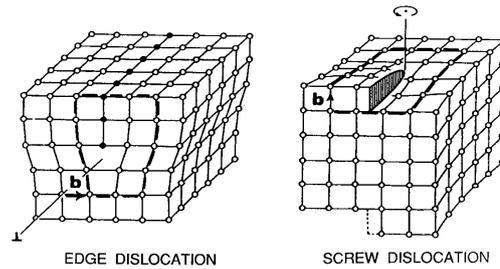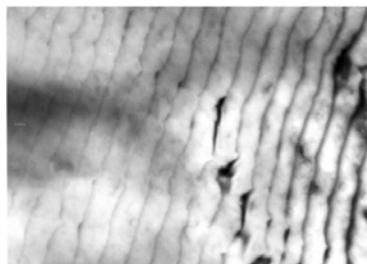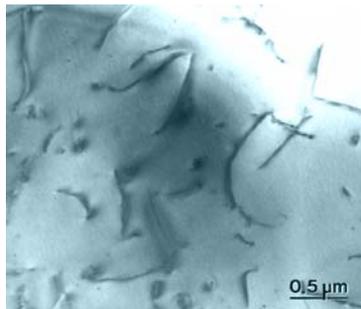- The two fundamental types of dislocations-the edge and the screw.

EDGE DISLOCATION   SCREW DISLOCATION

Figure 1-6. (left) Edge dislocation; (right) screw dislocation. (Reprinted with permission from John Wiley and Sons, H. W. Hayden, W. G. Moffatt, and J. Wulff, *The Structure and Properties of Materials*, Vol. III, Copyright © 1965, John Wiley and Sons).

DISLOCATION Image

* TEM

0.5 µm

1.3.2. Dislocations

- **Dislocations** are important because they have provided a model to help explain a great variety of mechanical phenomena and properties in all classes of crystalline solids.

- This alternative mechanism requires that dislocations undulate through the crystal, making and breaking bonds on the slip plane **until a slip step is produced**.

- **A density of as many 10^{12} dislocation lines** threading 1 cm^2 of surface area has been observed in highly deformed metals.

- **Many deposited poly crystalline metal thin films also have high dislocation densities**.
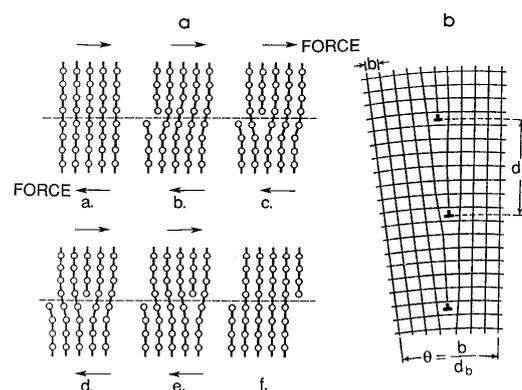
1.3.2. Dislocations

Figure 1-7. (a) Edge dislocation motion through lattice under applied shear stress. (Reprinted with permission from J. R. Shackelford, Introduction to Materials Science for Engineers, Macmillan, 1985). (b) Dislocation model of a grain boundary. The crystallographic misorientation angle θ between grains is b/d_b.

1.3.2. Dislocations

- A good match of lattice parameters is sought for epitaxial growth. **Substrate steps and dislocations should also be eliminated where possible prior to growth**.
- Grain boundaries in semiconductors, dislocations can be sites of **charge recombination** or generation as a result of uncompensated **dangling bonds**.
- Film stress, thermally induced mechanical relaxation processes, and **diffusion in films are all influenced by dislocations.**

1.3.3. Vacancies

- Vacancies are **point defects** that simply arise when lattice sites are unoccupied by atoms.

distortion of planes — Vacancy

distortion of planes — self-interstitial
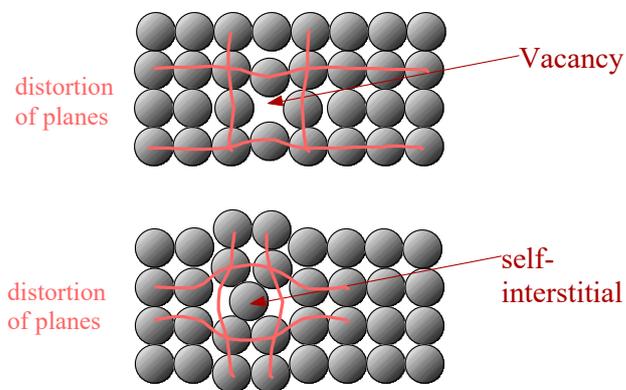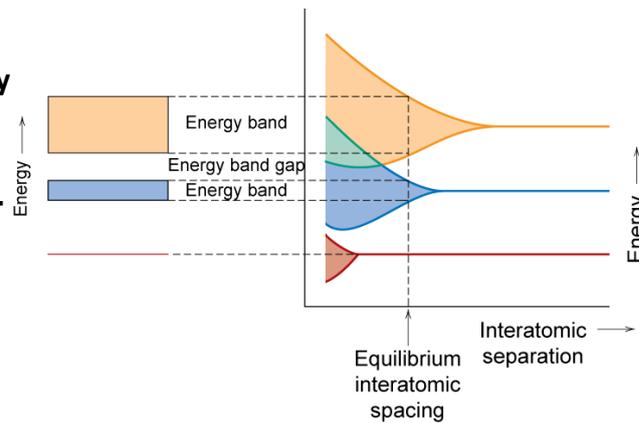
1.3.3. Vacancies

- Vacancies play an important role in all processes related to solid-state diffusion, including **recrystallization, grain growth, sintering, and phase transformations.**
- In semiconductors, vacancies are electrically neutral as well as charged and can be **associated with dopant atoms**.

1.4. BONDING OF MATERIALS
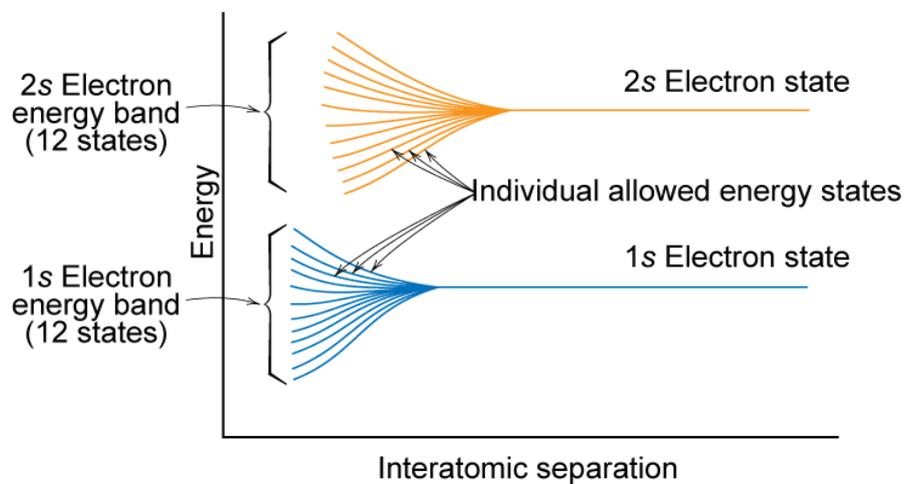
1.4. BONDING OF MATERIALS

- **Valence band – filled – highest occupied energy levels**
- **Conduction band – empty – lowest unoccupied energy levels**

Energy band

Energy band gap

Energy band

Energy

Energy

Equilibrium interatomic spacing

Interatomic separation

1.4. BONDING OF MATERIALS

(b)

REPULSIVE ENERGY

POTENTIAL ENERGY (V(r))

TOTAL ENERGY (BULK ATOMS)

TOTAL ENERGY (SURFACE ATOMS)

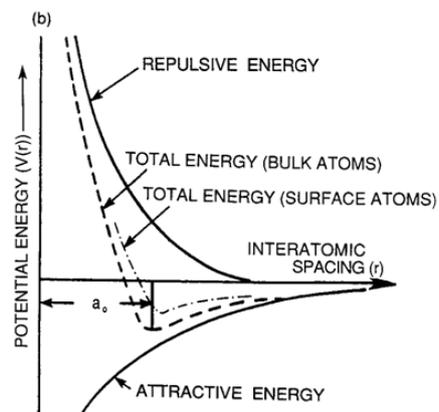INTERATOMIC SPACING (r)

a_o

ATTRACTIVE ENERGY

Figure 1-8. Splitting of electron levels (a) and energy of interaction between atoms (b) as a function of interatomic spacing. $V(r)$ vs. r shown schematically for bulk and surface atoms.
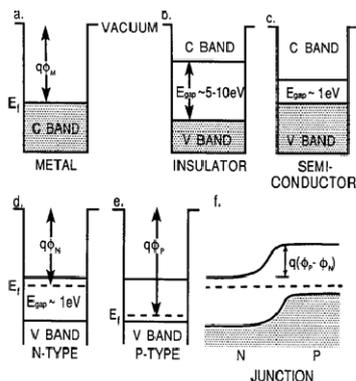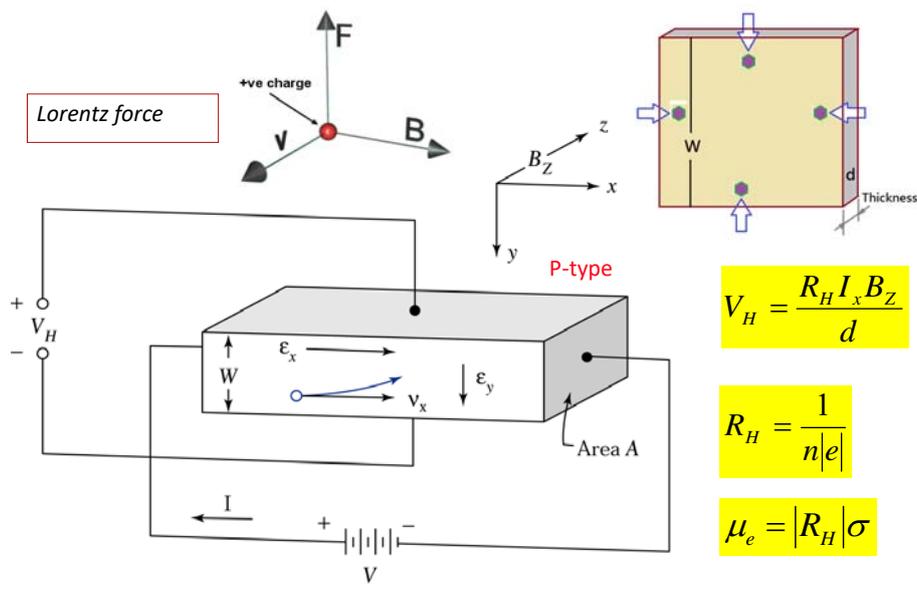
1.4.5. Energy-Band Diagrams

Figure 1-9. Schematic band structure for (a) metal; (b) insulator, (c) semiconductor; (d) N-type semiconductor; (e) P-type semiconductor; (f) P–N semiconductor junction.

The Hall Effect

Lorentz force

P-type

$$V_H = \frac{R_H I_x B_Z}{d}$$

$$R_H = \frac{1}{n|e|}$$

$$\mu_e = |R_H|\sigma$$

Ex. There is a n-type semiconductor film that is shown in figure below, (a) cite direction vectors of v_x and ε_y according to the principle of Lorentz force (b) cite the "+" and "-" terminals of V_H