

# Semiconductor Materials and Devices

## (반도체 재료 및 소자)

### Lecture 4. Introduction to Quantum Theory of Solid

**Young Min Song**

Assistant Professor

School of Electrical Engineering and Computer Science

Gwangju Institute of Science and Technology

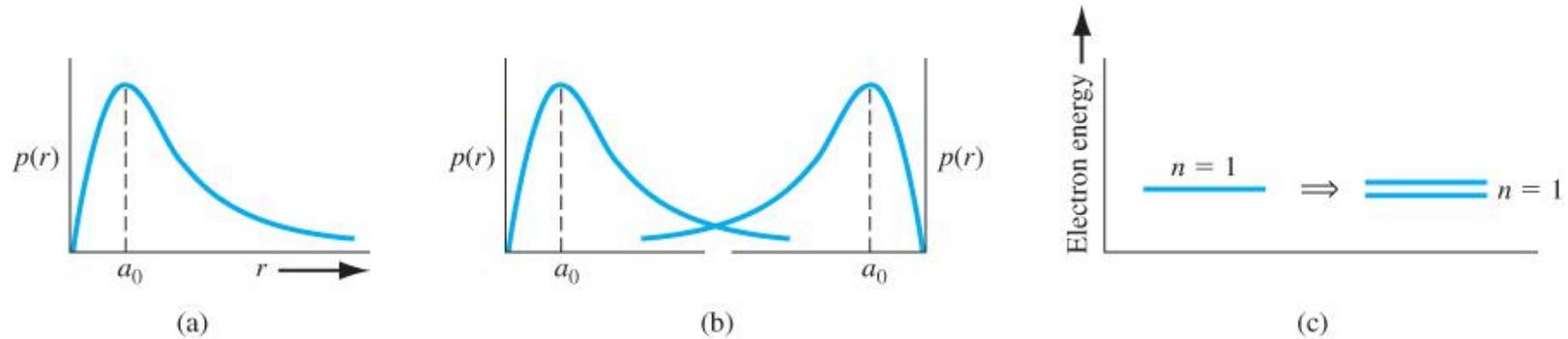
<http://www.gist-foel.net>

[ymsong@gist.ac.kr](mailto:ymsong@gist.ac.kr), [ymsong81@gmail.com](mailto:ymsong81@gmail.com)

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“To determine the electrical properties of a semiconductor material, we need to determine the properties of electrons in a crystal lattice, and need to determine the statistical characteristics of the very large number of electrons in a crystal.”

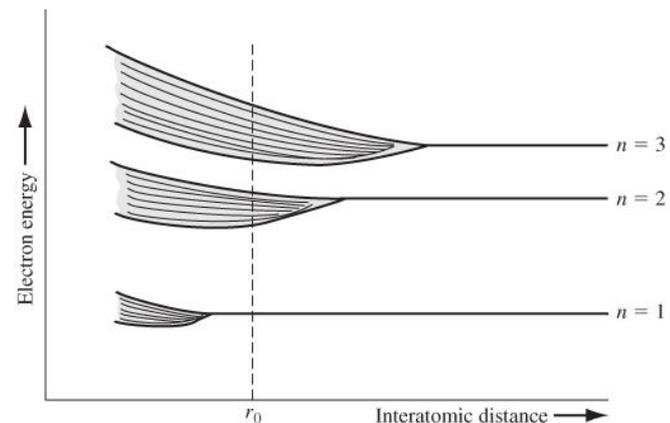
## Formation of Energy Bands



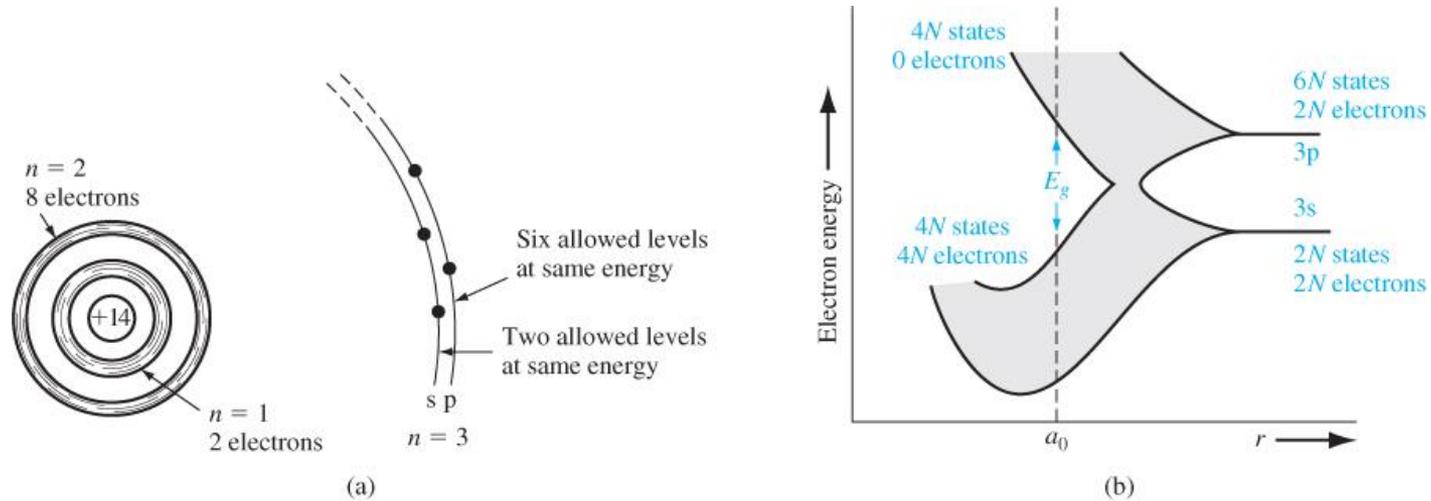
**Figure 3.1** | (a) Probability density function of an isolated hydrogen atom. (b) Overlapping probability density functions of two adjacent hydrogen atoms. (c) The splitting of the  $n = 1$  state.

Suppose the atom in the imaginary crystal contains electrons up through the  $n = 3$  energy level.

If the equilibrium interatomic distance is  $r_0$ , then we have bands of allowed energies that the electrons may occupy separated by bands of forbidden energies.



**Figure 3.3** | Schematic showing the splitting of three energy states into allowed bands of energies.



**Figure 3.4** | (a) Schematic of an isolated silicon atom. (b) The splitting of the 3s and 3p states of silicon into the allowed and forbidden energy bands.  
(From Shockley [6].)

As the interatomic distance decreases, the 3s and 3p states interact and overlap. At the equilibrium interatomic distance, the bands have again split, but now four quantum states per atom are in the lower band and four quantum states per atom are in the upper band. At absolute zero degrees, electrons are in the lowest energy state, so that all states in the lower band (the valence band) will be full and all states in the upper band will be empty.

The bandgap energy  $E_g$  between the top of the valence band and the bottom of the conduction band is the width of the forbidden energy band.

# The Kronig-Penney Model

The concept of allowed and forbidden energy bands can be developed more rigorously by considering quantum mechanics and Schrodinger's wave equation.

The Kronig-Penney model is an idealized periodic potential representing a one-dimensional single crystal, but the results will illustrate many of the important features of the quantum behavior of electrons in a periodic lattice. → energy bands (allowed/forbidden bands)

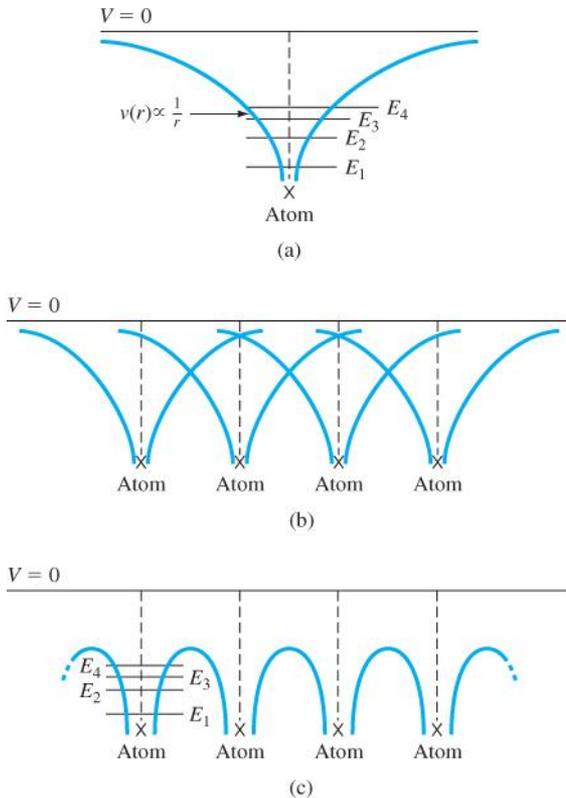


Figure 3.5 | (a) Potential function of a single isolated atom. (b) Overlapping potential functions of adjacent atoms. (c) Net potential function of a one-dimensional single crystal.

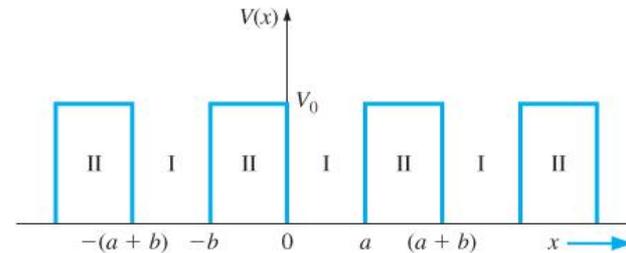


Figure 3.6 | The one-dimensional periodic potential function of the Kronig-Penney model.

$$\psi(x) = u(x)e^{jkx} : \text{Bloch's theorem. } u(x) \text{ is periodic function.}$$

$$\Psi(x, t) = u(x)e^{j(kx - (E/\hbar)t)}$$

In region I, 
$$\frac{d^2u_1(x)}{dx^2} + 2jk \frac{du_1(x)}{dx} - (k^2 - \alpha^2)u_1(x) = 0 \quad \alpha^2 = \frac{2mE}{\hbar^2}$$

In region II, 
$$\frac{d^2u_2(x)}{dx^2} + 2jk \frac{du_2(x)}{dx} - (k^2 - \beta^2)u_2(x) = 0$$

$$\frac{2m}{\hbar^2}(E - V_0) = \alpha^2 - \frac{2mV_0}{\hbar^2} = \beta^2$$

$$u_1(x) = Ae^{j(\alpha-k)x} + Be^{-j(\alpha+k)x} \quad \text{for } (0 < x < a)$$

$$u_2(x) = Ce^{j(\beta-k)x} + De^{-j(\beta+k)x} \quad \text{for } (-b < x < 0)$$

### Boundary Conditions

$$u_1(0) = u_2(0)$$

$$\left. \frac{du_1}{dx} \right|_{x=0} = \left. \frac{du_2}{dx} \right|_{x=0}$$

$$u_1(a) = u_2(-b)$$

$$\left. \frac{du_1}{dx} \right|_{x=a} = \left. \frac{du_2}{dx} \right|_{x=-b}$$

$$A + B - C - D = 0$$

$$(\alpha - k)A - (\alpha + k)B - (\beta - k)C + (\beta + k)D = 0$$

$$Ae^{j(\alpha-k)a} + Be^{-j(\alpha+k)a} - Ce^{-j(\beta-k)b} - De^{j(\beta+k)b} = 0$$

$$(\alpha - k)Ae^{j(\alpha-k)a} - (\alpha + k)Be^{-j(\alpha+k)a} - (\beta - k)Ce^{-j(\beta-k)b} + (\beta + k)De^{j(\beta+k)b} = 0$$

For a non-trivial solution of A, B, C, and D,

$$\frac{-(\alpha^2 + \beta^2)}{2\alpha\beta} (\sin \alpha a)(\sin \beta b) + (\cos \alpha a)(\cos \beta b) = \cos k(a + b)$$

For  $E < V_0$  (bounded electron)

$$\beta = j\gamma \quad \frac{\gamma^2 - \alpha^2}{2\alpha\gamma} (\sin \alpha a)(\sinh \gamma b) + (\cos \alpha a)(\cosh \gamma b) = \cos k(a + b)$$

: define the relation between  $k$ ,  $E$ , and  $V_0$

: gives the conditions for which Schrodinger's wave equation will have a solution.

For an infinite impulse potential ( $b \rightarrow 0, bV_0$ : finite)

$$P' \frac{\sin \alpha a}{\alpha a} + \cos \alpha a = \cos ka \quad P' = \frac{mV_0 b a}{\hbar^2}$$

For  $V_0=0$  ( $P'=0$ )  $\rightarrow$   
(free electron)

$$\cos \alpha a = \cos ka \quad \alpha = k$$

$$\alpha = \sqrt{\frac{2mE}{\hbar^2}} = \sqrt{\frac{2m(\frac{1}{2}mv^2)}{\hbar^2}} = \frac{p}{\hbar} = k \quad E = \frac{p^2}{2m} = \frac{k^2 \hbar^2}{2m}$$

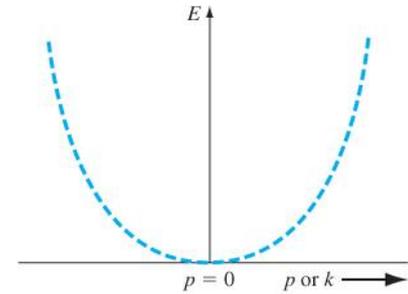


Figure 3.7 | The parabolic  $E$  versus  $k$  curve for the free electron.

For  $P' \neq 0$

$$f(\alpha a) = P' \frac{\sin \alpha a}{\alpha a} + \cos \alpha a$$

$$f(\alpha a) = \cos ka$$

For the above equation is valid, the allowed values of the  $f(\alpha a)$  function must be bounded between +1 and -1.

$\rightarrow$  the allowed values of  $f(\alpha a)$  and the allowed values of  $\alpha a$  in the shaded areas.

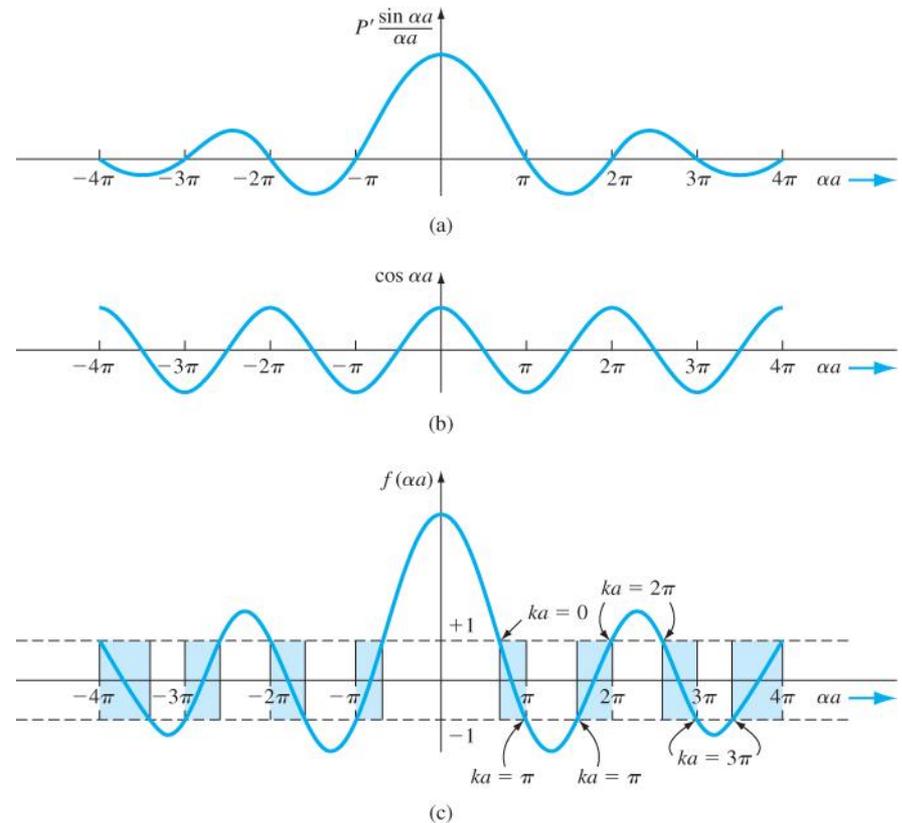


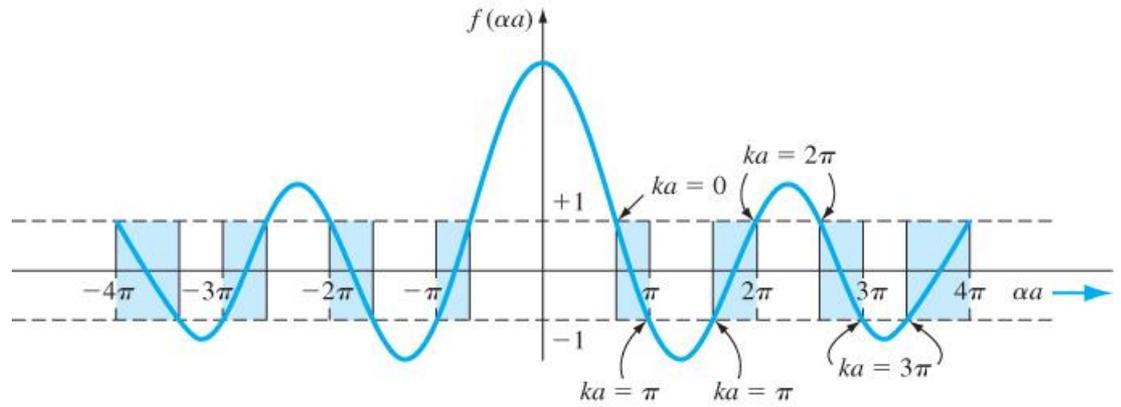
Figure 3.8 | A plot of (a) the first term in Equation (3.29), (b) the second term in Equation (3.29), and (c) the entire  $f(\alpha a)$  function. The shaded areas show the allowed values of  $(\alpha a)$  corresponding to real values of  $k$ .

### Allowed bands

$$0 < ka < \pi \rightarrow P < \alpha a < Q$$

$$\rightarrow P < \sqrt{\frac{2mE}{\hbar^2}} a < Q$$

$$\rightarrow \frac{\hbar^2 P^2}{2ma^2} < E < \frac{\hbar^2 Q^2}{2ma^2}$$

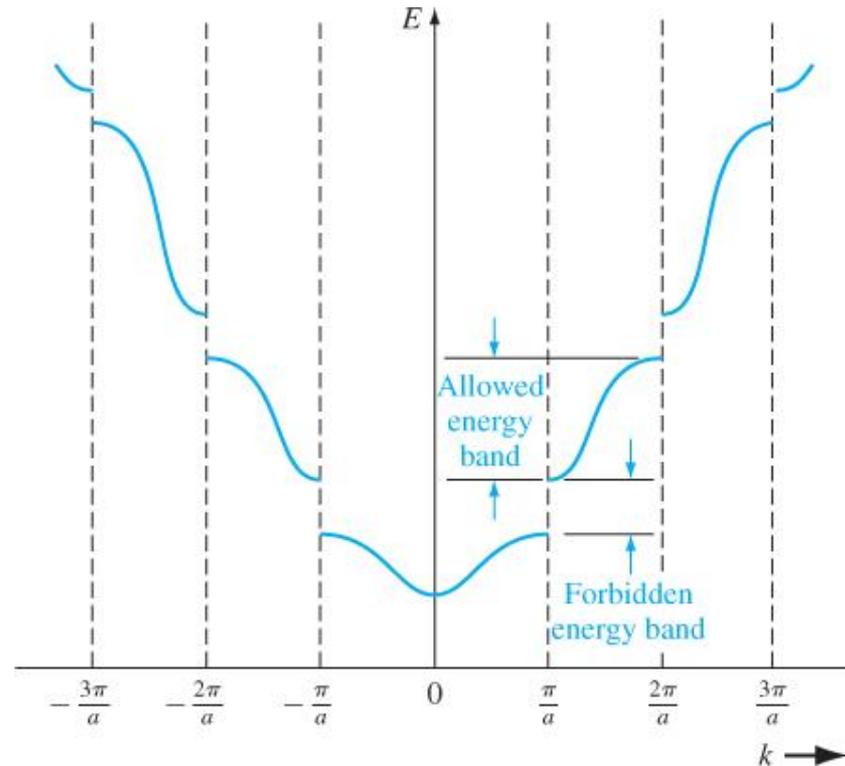


### Forbidden bands

$$ka = \pi \rightarrow Q < \alpha a < R$$

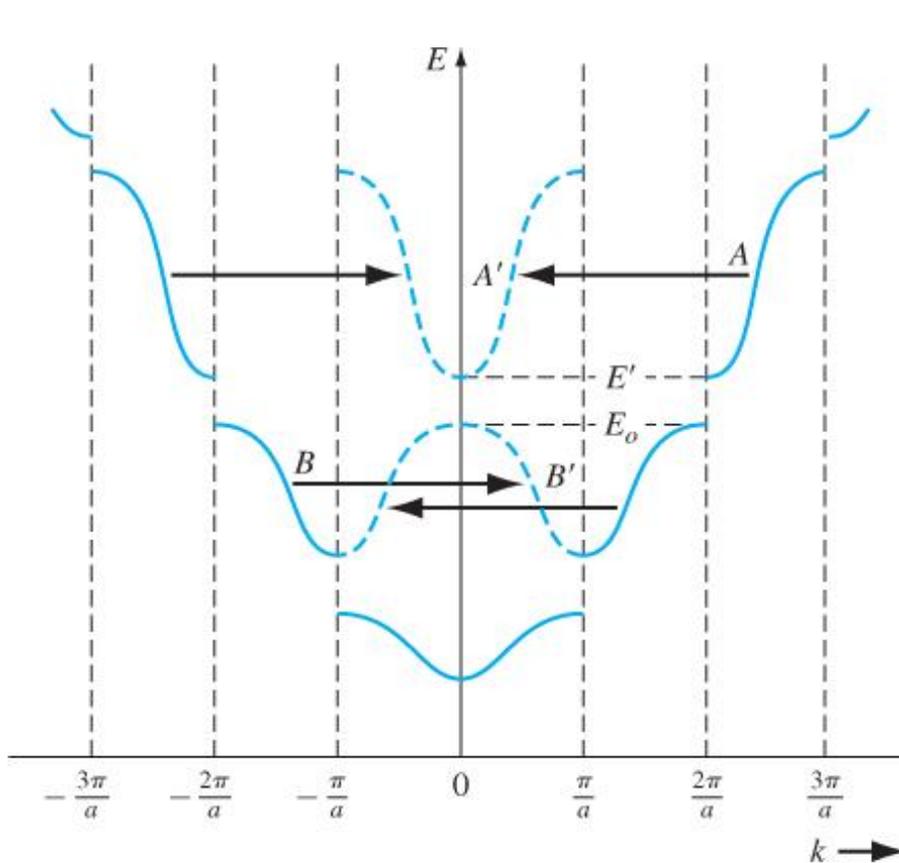
$$\rightarrow Q < \sqrt{\frac{2mE}{\hbar^2}} a < R$$

$$\rightarrow \frac{\hbar^2 Q^2}{2ma^2} < E < \frac{\hbar^2 R^2}{2ma^2}$$

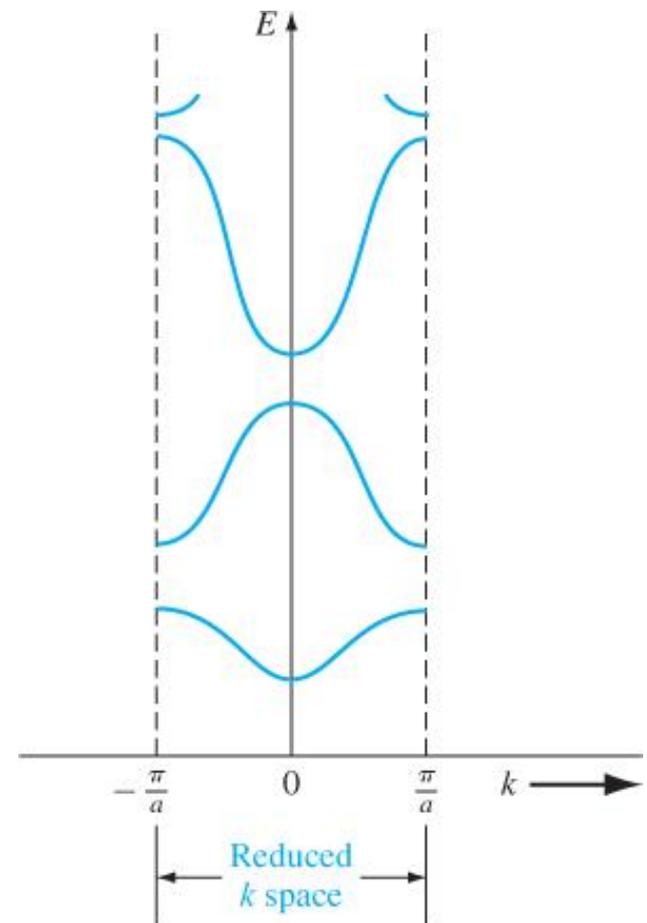


## Reduced k-space diagram

$$\cos ka = \cos (ka + 2n\pi) = \cos (ka - 2n\pi)$$

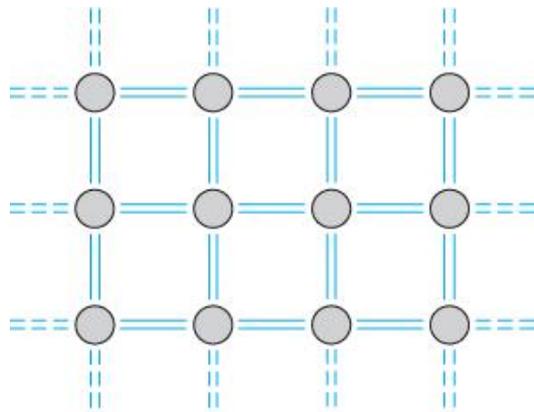


**Figure 3.10** | The  $E$  versus  $k$  diagram showing  $2\pi$  displacements of several sections of allowed energy bands.

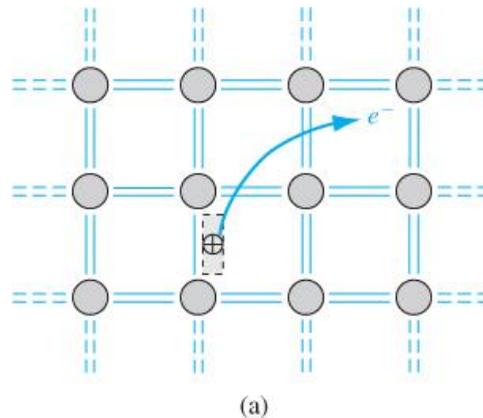


**Figure 3.11** | The  $E$  versus  $k$  diagram in the reduced-zone representation.

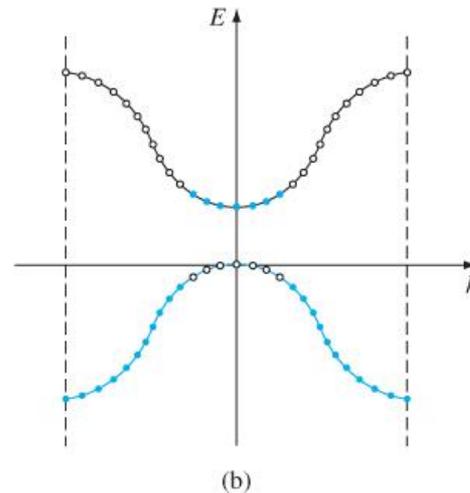
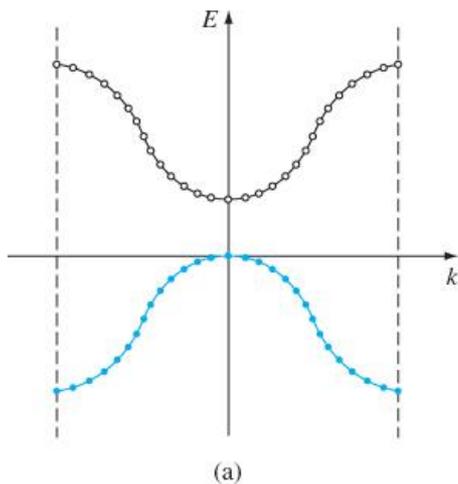
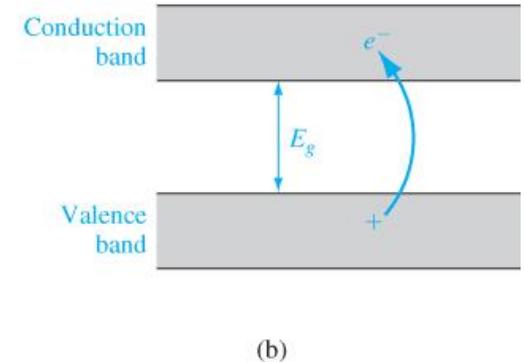
## Energy Band and Bond Model



**Figure 3.12** | Two-dimensional representation of the covalent bonding in a semiconductor at  $T = 0$  K.



**Figure 3.13** | (a) Two-dimensional representation of the breaking of a covalent bond. (b) Corresponding line representation of the energy band and the generation of a negative and positive charge with the breaking of a covalent bond.



**Figure 3.14** | The  $E$  versus  $k$  diagram of the conduction and valence bands of a semiconductor at (a)  $T = 0$  K and (b)  $T > 0$  K.

No external forces are applied so that the electron and hole distributions are symmetrical with  $k$ .

## Drift Current

Current density due to the net flow of charge

$$J = qn\mathbf{v}_d \qquad J = qn \sum_{i=1}^N \mathbf{v}_i$$

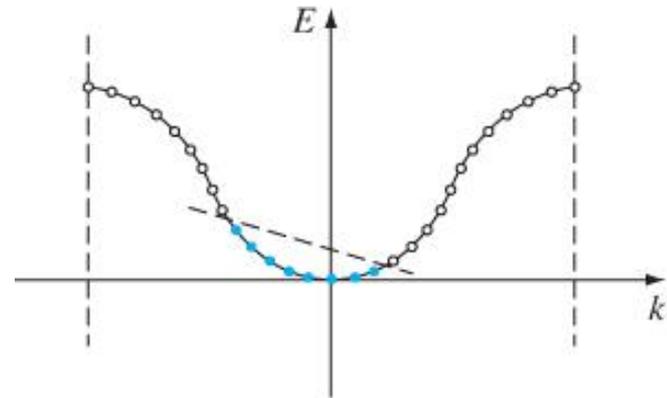
$v_d$  : average drift velocity  
 $v_i$  : velocity of  $i$  th charge

If a force is applied to a particle and the particle moves, it must gain energy,

$$dE = F dx = F v dt$$

Because of the external force, electrons can gain energy and a net momentum.

$$p = \hbar k$$



**Figure 3.15** | The asymmetric distribution of electrons in the  $E$  versus  $k$  diagram when an external force is applied.

## Electron Effective Mass

Acting on a particle in a crystal:

$$F_{\text{total}} = F_{\text{ext}} + F_{\text{int}} = ma$$

$F_{\text{int}}$  : internal forces due to the potential difference caused by the positive ions or electrons.

$m$  : rest mass,  $a$  : acceleration

$$F_{\text{ext}} = m^*a$$

Since it is difficult to take into account all of the internal forces, we define the *effective mass*  $m^*$  to take account into the particle mass and also the effect of the internal forces.

Effective mass from E-k curves,

$$E = p^2/2m = \hbar^2 k^2/2m \quad p = \hbar k$$

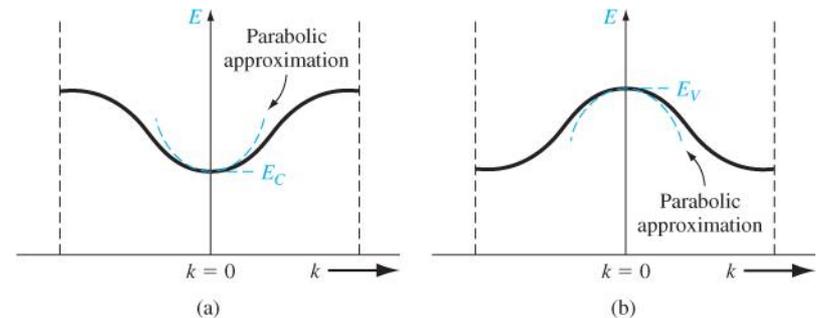
$$\frac{dE}{dk} = \frac{\hbar^2 k}{m} = \frac{\hbar p}{m}$$

$$\frac{1}{\hbar} \frac{dE}{dk} = \frac{p}{m} = v$$

$$\Rightarrow \boxed{\frac{1}{\hbar^2} \frac{d^2 E}{dk^2} = \frac{1}{m}} \quad F = ma = -eE \quad a = \frac{-eE}{m}$$

Effective mass is a parameter that relates the quantum mechanical results to the classical force equations.

The effective mass of the electron near the bottom of the conduction band is a constant.



**Figure 3.16** | (a) The conduction band in reduced  $k$  space, and the parabolic approximation. (b) The valence band in reduced  $k$  space, and the parabolic approximation.

## Concept of the Hole

$$J = +e \sum_{i(\text{empty})} v_i$$

$$v(E) = \left(\frac{1}{\hbar}\right) \left(\frac{dE}{dk}\right)$$

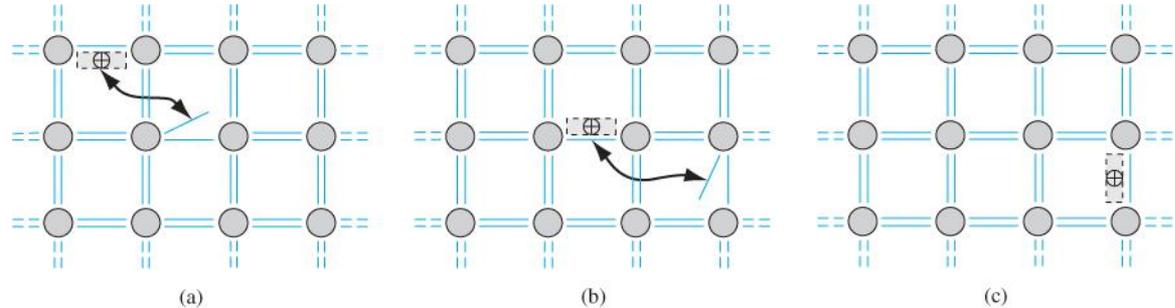


Figure 3.17 | Visualization of the movement of a hole in a semiconductor.

Placing a positively charged particle in the empty states and assuming all other states in the band are empty.

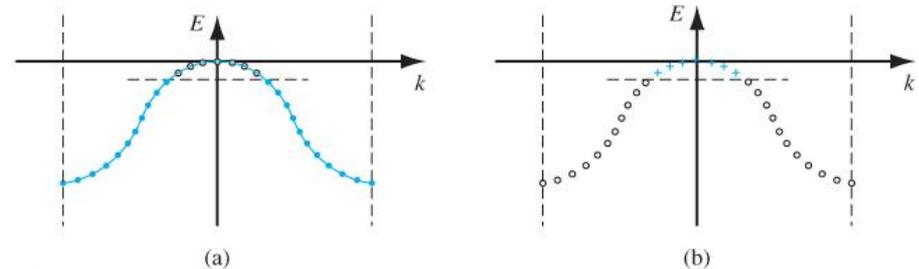


Figure 3.18 | (a) Valence band with conventional electron-filled states and empty states. (b) Concept of positive charges occupying the original empty states.

$$F = m^*a = -eE \quad a = \frac{-eE}{-|m^*|} = \frac{+eE}{|m^*|} \quad \frac{1}{\hbar^2} \frac{d^2E}{dk^2} = \frac{-2C_2}{\hbar^2} = \frac{1}{m^*}$$

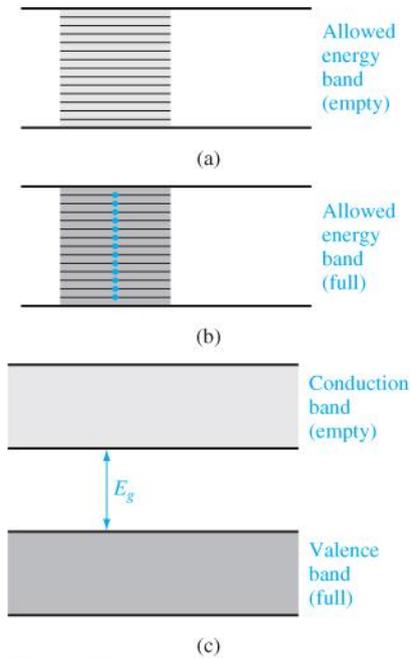
$m^*$  is a negative quantity.

An electron moving near the top of an allowed energy band behaves as if it has a negative mass.

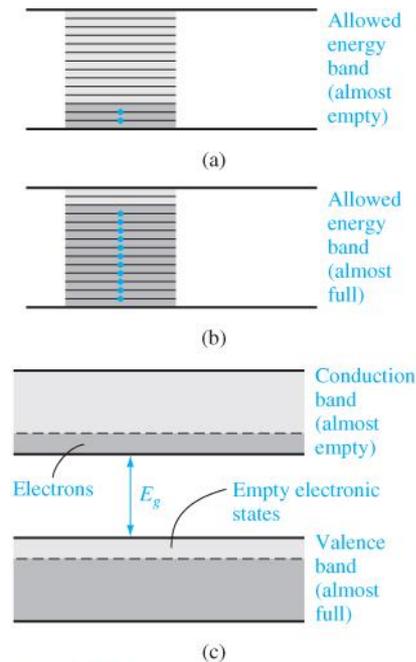
# Metals, Insulators, and Semiconductors

Complex band splitting occurs in crystals, leading to large variations in band structures between various solids and to a wide range of electrical characteristics observed in these various materials.

## Insulators



## Semiconductors



## Metals

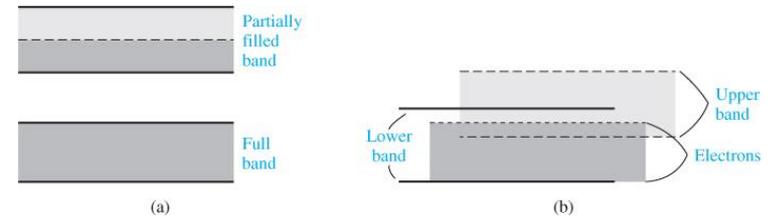


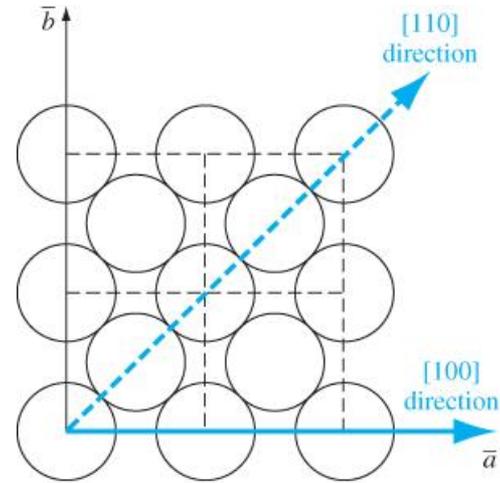
Figure 3.21 | Two possible energy bands of a metal showing (a) a partially filled band and (b) overlapping allowed energy bands.

Figure 3.19 | Allowed energy bands showing (a) an empty band, (b) a completely full band, and (c) the bandgap energy between the two allowed bands.

Figure 3.20 | Allowed energy bands showing (a) an almost empty band, (b) an almost full band, and (c) the bandgap energy between the two allowed bands.

## Direct and Indirect Semiconductors

Distance between atoms varies as the direction through the crystal changes → Electrons traveling in different directions encounter different potential patterns and therefore different  $k$ -space boundaries.



It is normal practice to plot the [100] direction along the normal  $+k$  axis and to plot the [111] portion of the diagram so the  $+k$  points to the left.

✓ Direct bandgap semiconductor

✓ Indirect bandgap semiconductor: needs momentum conservation (interaction with crystal)

Effective masses of GaAs and Silicon

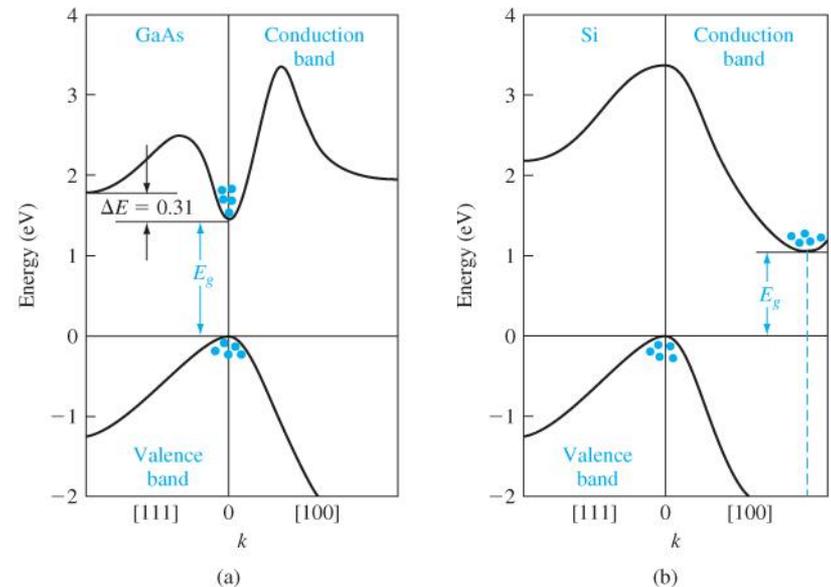
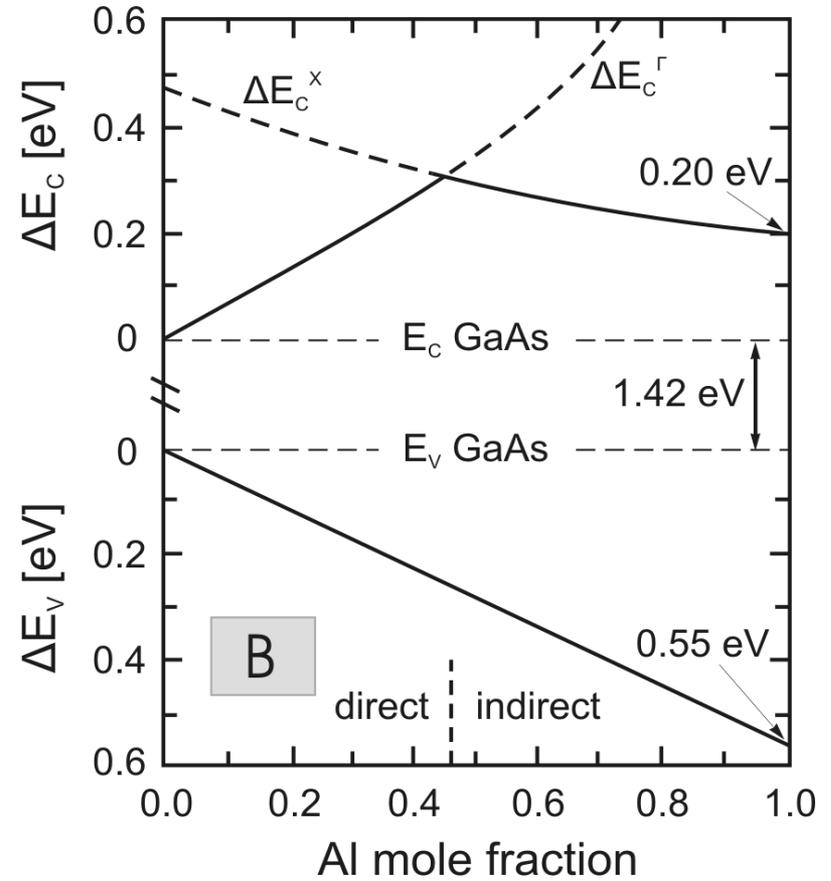
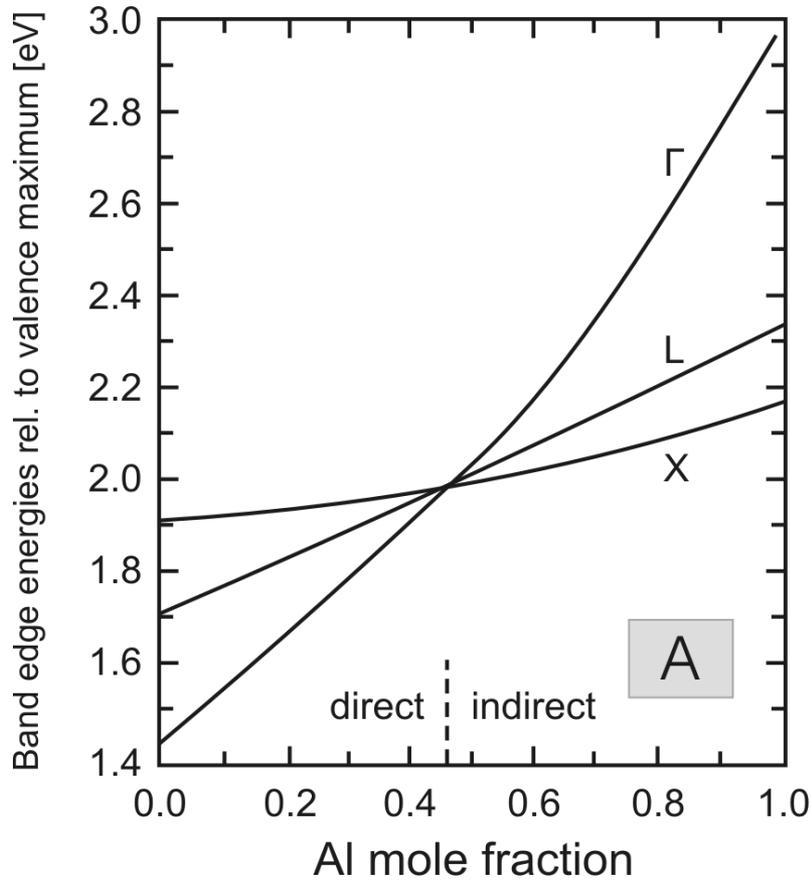
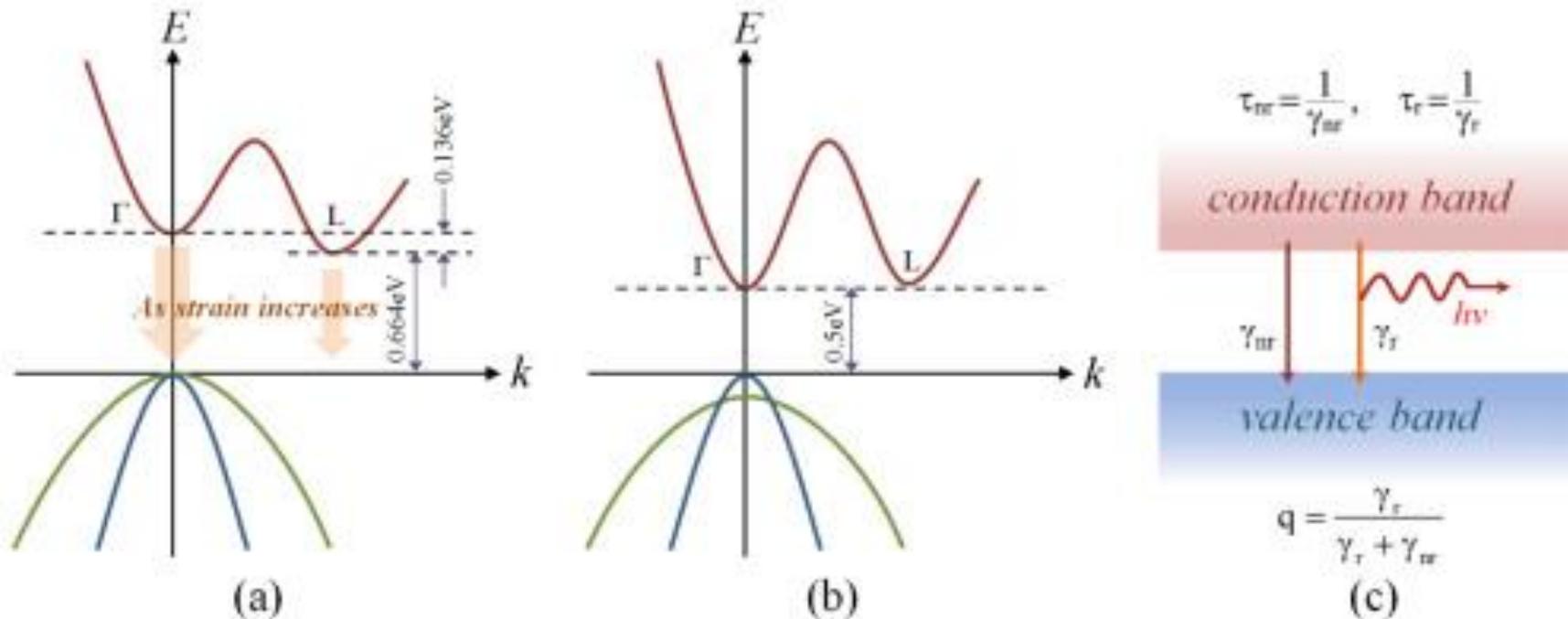


Figure 3.25 | Energy-band structures of (a) GaAs and (b) Si. (From Sze [12].)

## Bandgap energies of AlGaAs in different points versus Al concentration

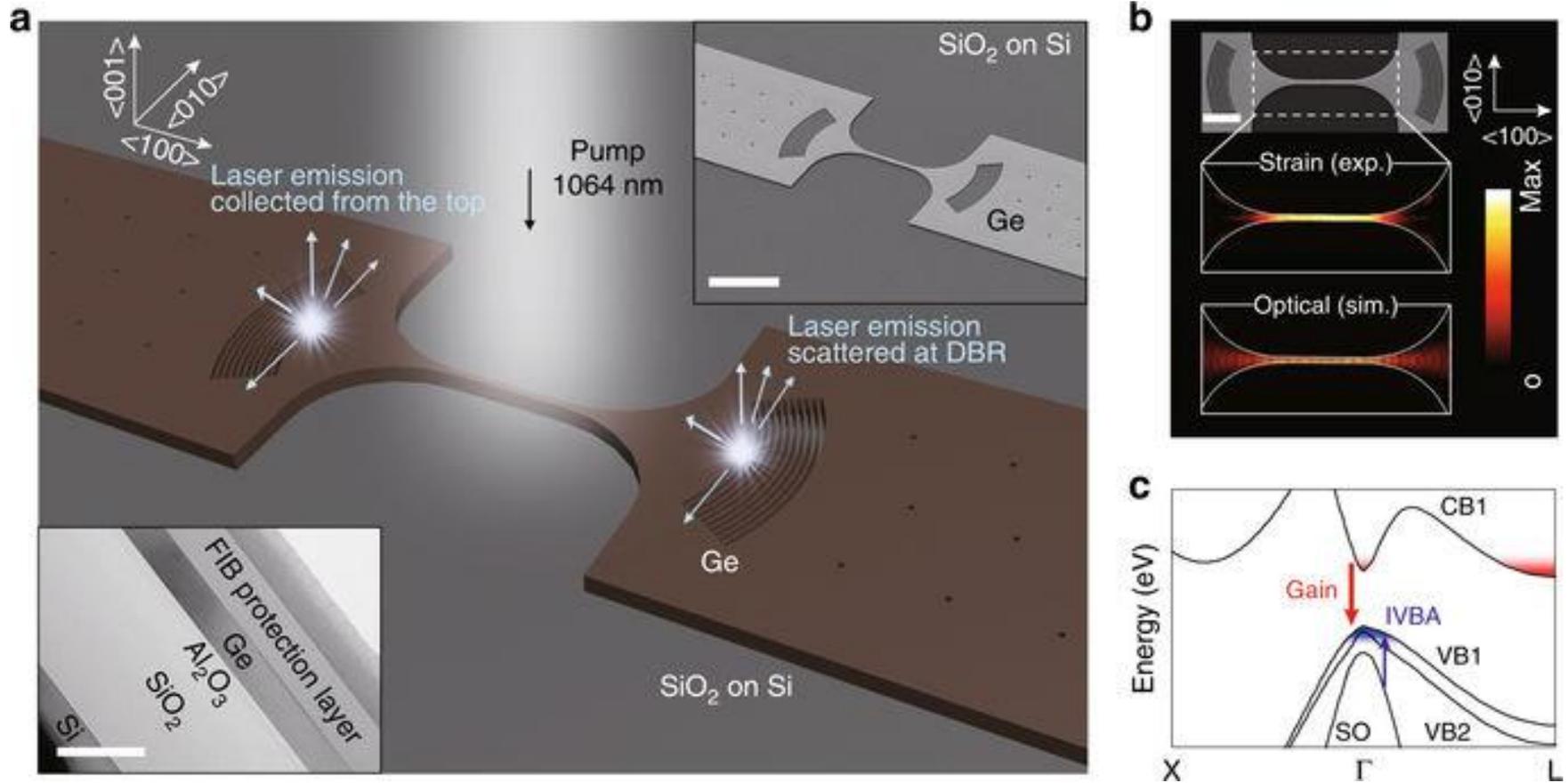


## Energy band structure of Ge under straining



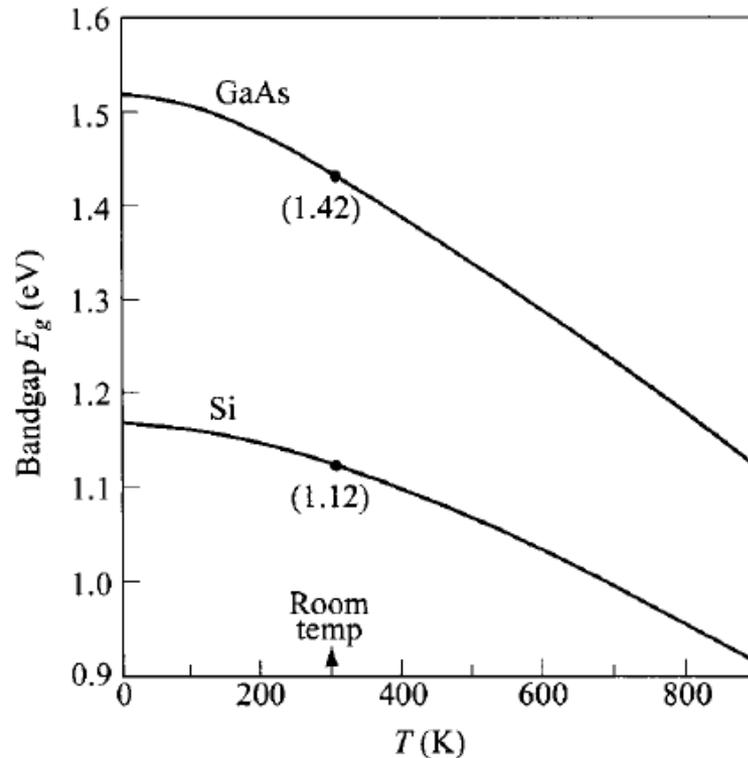
Energy band structure of Ge under straining [11]. (a) Energy band structure of unstrained bulk Ge. The band gap is 0.664 eV. It is an indirect band gap. The energy difference between the  $\Gamma$ -valley and the L-valley is relatively small (0.136 eV). By addressing tensile strain, Ge can be more direct-band-gap-like due to lowering of the  $\Gamma$ -valley. The L-valley also becomes lower, yet slower than the  $\Gamma$ -valley lowering. (b) 2% strain makes Ge a true direct band gap material by lowering the  $\Gamma$ -valley down to the L-valley level. Valence band structure also changes slightly. The band gap energy becomes much smaller. (0.5 eV)

## Low-threshold optically pumped lasing in highly strained germanium nanowires



(2017)Nat. Comm.

<https://www.nature.com/articles/s41467-017-02026-w.pdf>

Energy bandgaps of Si and GaAs as a function of temperature

	$E_g(0)$ (eV)	$\alpha$ (eV/K)	$\beta$ (K)
GaAs	1.519	$5.4 \times 10^{-4}$	204
Si	1.169	$4.9 \times 10^{-4}$	655

$$E_g(T) = E_g(0) - \frac{\alpha T^2}{T + \beta}$$

At room temperature and under normal atmospheric pressure, the values of the bandgap are 1.12 eV for Si and 1.42 eV for GaAs. These values are for high-purity materials.

- Experimental results show that the bandgaps of most of semiconductors decrease with increasing temperature.
- Near room temperature, the bandgap of GaAs increases with pressure  $P$ , while the Si bandgap decreases with pressure.

Current : flow of charges  $\propto$  the number of electrons or holes that will be available for conduction  $\propto$  **the number of available energy states  $\rightarrow$  the density of states as a function of energy.**

### Mathematical Derivation : A free electron in 3-D infinite potential box

$$V(x, y, z) = 0 \quad \text{for } 0 < x < a$$

$$0 < y < a$$

$$0 < z < a$$

$$V(x, y, z) = \infty \quad \text{elsewhere}$$

Solving Schrodinger's wave equation using the separation of variables technique.

$$\frac{2mE}{\hbar^2} = k^2 = k_x^2 + k_y^2 + k_z^2 = (n_x^2 + n_y^2 + n_z^2) \left( \frac{\pi^2}{a^2} \right)$$

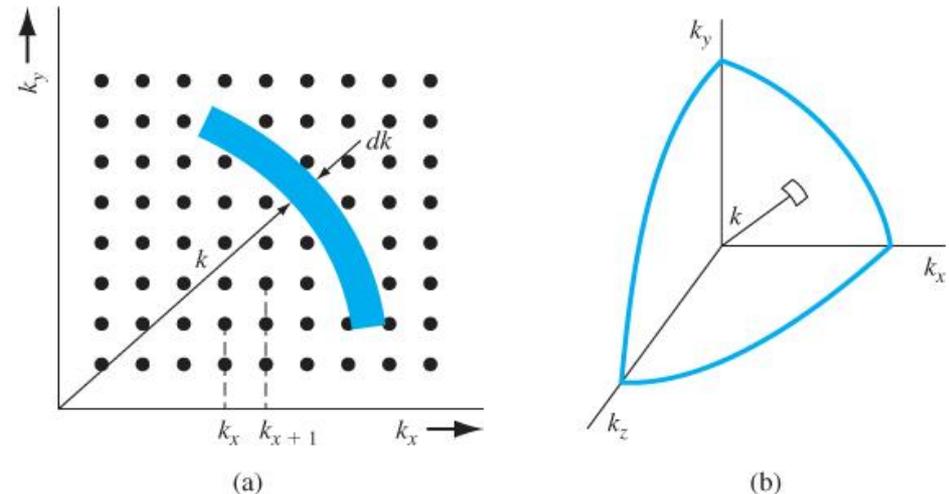
For 1-D,  $k_{x+1} - k_x = (n_x + 1) \left( \frac{\pi}{a} \right) - n_x \left( \frac{\pi}{a} \right) = \frac{\pi}{a}$

For 3-D,  $V_k = \left( \frac{\pi}{a} \right)^3$  : volume of a single quantum state in 3-D.

Density of quantum states

$$g_T(k) dk = 2 \left( \frac{1}{8} \right) \frac{4\pi k^2 dk}{\left( \frac{\pi}{a} \right)^3}$$

$$= \frac{\pi k^2 dk}{\pi^3} \cdot a^3$$



**Figure 3.26** | (a) A two-dimensional array of allowed quantum states in  $k$  space. (b) The positive one-eighth of the spherical  $k$  space.

Density of quantum states as a function of  $E$  :

$$k^2 = \frac{2mE}{\hbar^2}$$

$$k = \frac{1}{\hbar} \sqrt{2mE}$$

$$dk = \frac{1}{\hbar} \sqrt{\frac{m}{2E}} dE$$

Total number of states between  $E$  and  $E+dE$  in the crystal space volume of  $a^3$

$$g_T(E) dE = \frac{\pi a^3}{\pi^3} \left( \frac{2mE}{\hbar^2} \right) \cdot \frac{1}{\hbar} \sqrt{\frac{m}{2E}} dE$$

The density of quantum states per unit volume and per unit energy

$$g(E) = \frac{4\pi(2m)^{3/2}}{h^3} \sqrt{E}$$

## Mathematical Derivation : Extension to Semiconductors

The  $E$ - $k$  curve near  $k=0$  at the bottom of the conduction band can be approximated as a parabola :

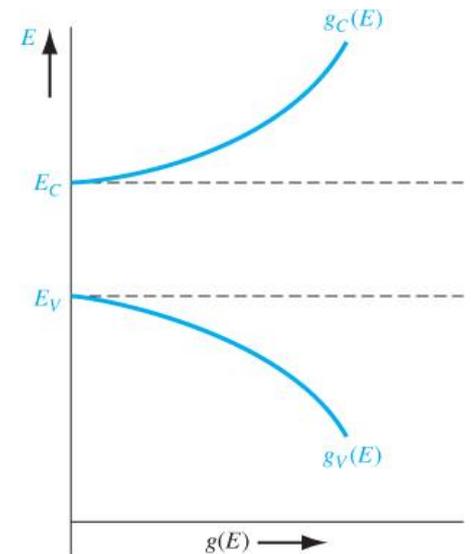
$$E - E_c = \frac{\hbar^2 k^2}{2m_n^*}$$

$$E_v - E = \frac{\hbar^2 k^2}{2m_p^*}$$

$$g_c(E) = \frac{4\pi(2m_n^*)^{3/2}}{h^3} \sqrt{E - E_c}$$

$$g_v(E) = \frac{4\pi(2m_p^*)^{3/2}}{h^3} \sqrt{E_v - E}$$

“free” conduction electron model :



## Statistical Laws

### 1. Maxwell-Boltzmann Probability Function:

$$f_{MB}(E) = A \exp\left(-\frac{E}{kT}\right)$$

- ✓ Distinguishable
- ✓ No restriction such as permitting only one particle per state at an energy E (do NOT obey Pauli's exclusion principle)
- ✓ Electrons in CB of Semiconductor

### 2. Fermi-Dirac Probability Function:

$$\frac{N(E)}{g(E)} = f_F(E) = \frac{1}{1 + \exp\left(\frac{E - E_F}{kT}\right)}$$

$N(E)$  : number of particles per unit volume per unit energy

$g(E)$  : number of quantum states per unit volume per unit energy

$f_F(E)$  : the ratio of filled states to total quantum states

- ✓ Indistinguishable
- ✓ Should obey Pauli's exclusion principle
- ✓ Quantum particles Ex. Electrons.

### 3. Bose-Einstein Probability Function:

$$f_{BE}(E) = \frac{1}{1 - A \exp\left(\frac{E}{kT}\right)}$$

- ✓ Indistinguishable
- ✓ No limit to the number of particles in each quantum state
- ✓ Photons.

# Fermi-Dirac distribution function and the Fermi Energy

$$f_F(E) = \frac{1}{1 + \exp\left(\frac{E - E_F}{kT}\right)}$$

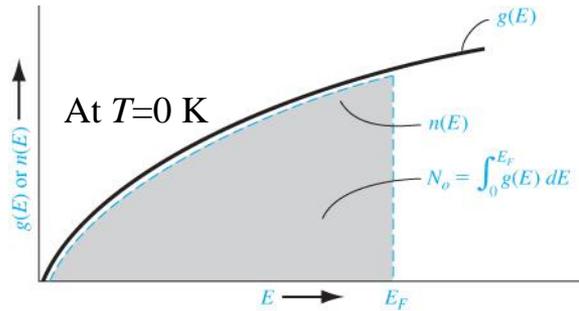


Figure 3.31 | Density of quantum states and electrons in a continuous energy system at  $T = 0$  K.

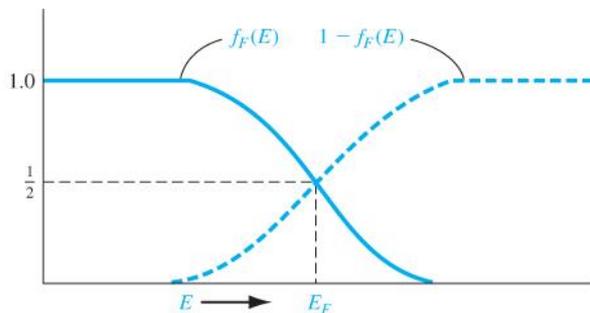
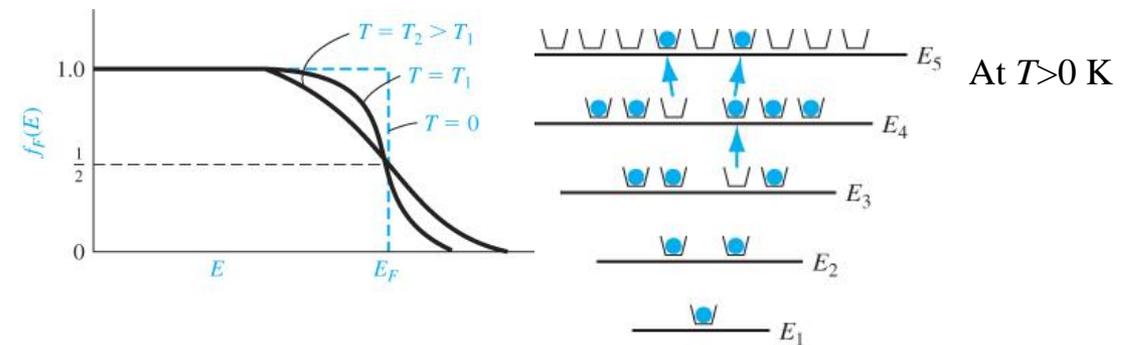
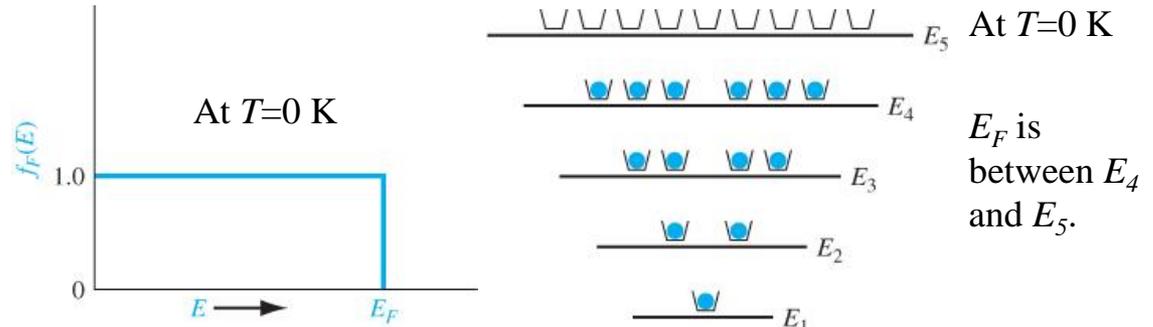


Figure 3.34 | The probability of a state being occupied,  $f_F(E)$ , and the probability of a state being empty,  $1 - f_F(E)$ .

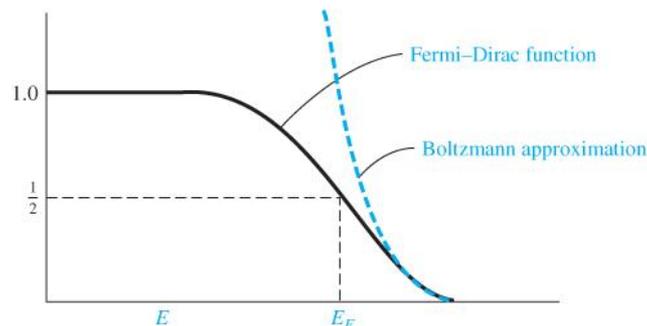


Figure 3.35 | The Fermi-Dirac probability function and the Maxwell-Boltzmann approximation.

$$f_F(E) \approx \exp\left[\frac{-(E - E_F)}{kT}\right]$$

## Examples

3.6  $T=300\text{K}$ . Determine the probability that an energy level  $3kT$  above the Fermi energy is occupied by an electron.

$$f_F(E) = \frac{1}{1 + \exp\left(\frac{E - E_F}{kT}\right)} = \frac{1}{1 + \exp\left(\frac{3kT}{kT}\right)} \quad f_F(E) = \frac{1}{1 + 20.09} = 0.0474 = 4.74\%$$

3.7 Determine the temperature at which there is a 1 percent probability that an energy state is empty. ( $E - E_F = -0.3\text{ eV}$ )

$$1 - f_F(E) = 1 - \frac{1}{1 + \exp\left(\frac{E - E_F}{kT}\right)} \quad 0.01 = 1 - \frac{1}{1 + \exp\left(\frac{5.95 - 6.25}{kT}\right)} \quad T = 756\text{ K}$$

3.8 Determine the energy at which the Boltzmann approximation may be considered valid within 5 %.

$$\frac{\exp\left[\frac{-(E - E_F)}{kT}\right] - \frac{1}{1 + \exp\left(\frac{E - E_F}{kT}\right)}}{\frac{1}{1 + \exp\left(\frac{E - E_F}{kT}\right)}} = 0.05 \quad \Rightarrow \quad \exp\left[\frac{-(E - E_F)}{kT}\right] \cdot \left\{1 + \exp\left[\frac{E - E_F}{kT}\right]\right\} - 1 = 0.05$$

$$\Rightarrow \quad \exp\left[\frac{-(E - E_F)}{kT}\right] = 0.05 \quad (E - E_F) = kT \ln\left(\frac{1}{0.05}\right) \approx 3kT$$