Lecture 5

3 ENERGY BAND OF SEMICONDUCTOR

3.1 Molecular orbitals and energies *(for illustration, not required for exam)*

- First, consider the formation of energy levels when two hydrogen atoms are brought together to form a hydrogen molecule (H_2). The H_2 molecule are bonded by the covalent bonding.

- The electronic configuration of H atoms is

$$H: \quad 1s^1$$

  - The wave function of the 1s state: Ψ_{1s}

  - The energy of the 1s state: E_{1s}

- When two hydrogen atoms, A and B, approach each other, the 1s wave function Ψ_{1s} of each individual H atom interact producing two new wave functions, Ψ_a and Ψ_b, with energies E_a and E_b respectively.

$\Psi\psi$ Psi

- The wave functions Ψ_a and Ψ_b are obtained by linear combination of the individual atomic orbitals/wave functions (LCAO)

$$\Psi_a = \Psi_{1s}(A) + \Psi_{1s}(B)$$
$$\Psi_b = \Psi_{1s}(A) - \Psi_{1s}(B)$$

(3.1)

$\Psi_{1s}(A)$ and $\Psi_{1s}(B)$ are the 1s wave function of H atoms A and B respectively.

E_a Ψ_a

Ψ_{1s} Ψ_{1s}

E_{1s} E_{1s}

ΔE bonding energy

E_b

Ψ_b

H atom
(A)

H_2 molecule

H atom
(B)

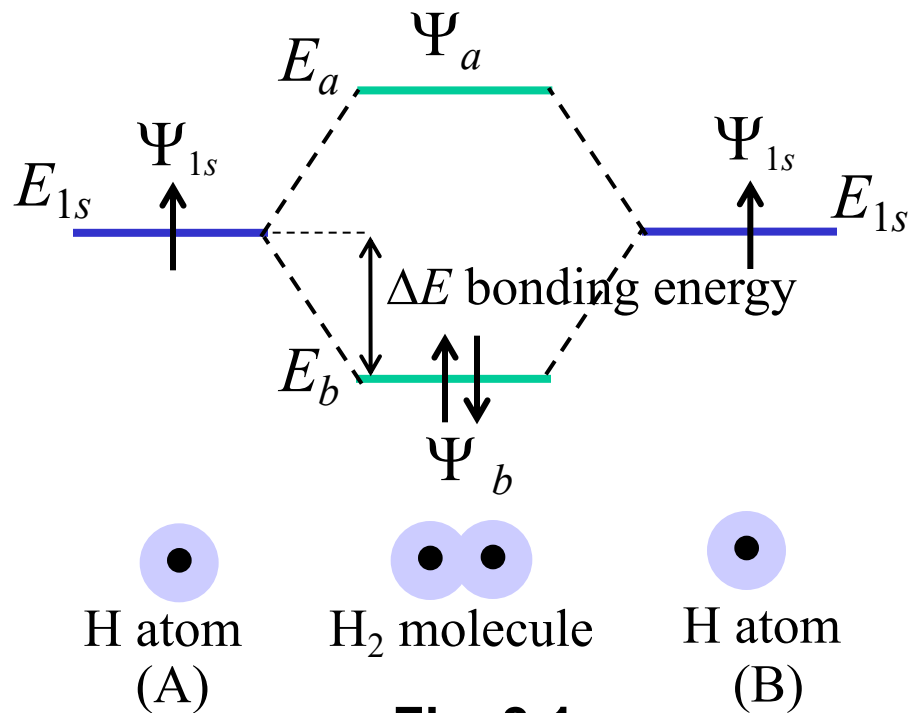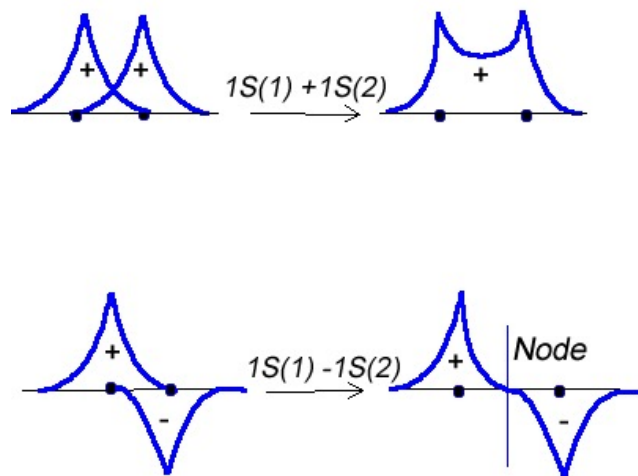**Fig. 3.1**

$1S(1) + 1S(2)$

$1S(1) - 1S(2)$

Node

- The formation of the two new wave functions Ψ_a and Ψ_b is consistent with the <u>Pauli exclusion principle</u>, that is: this means we cannot have two identical Ψ_{1s} wave functions in the H_2 molecule.

- The wave functions Ψ_a and Ψ_b are called the molecular orbital.

- Each wave function will have two distinct states: one spin up and one spin down. In other words, each wave function can accommodate two electrons.

- Before the interaction, each individual H atom has one electron in the 1s state/wave function.

- After the interaction, in the ground state, the two electrons will occupy the lowest energy wave function Ψ_b, one electron with spin up and the other electron with spin down.
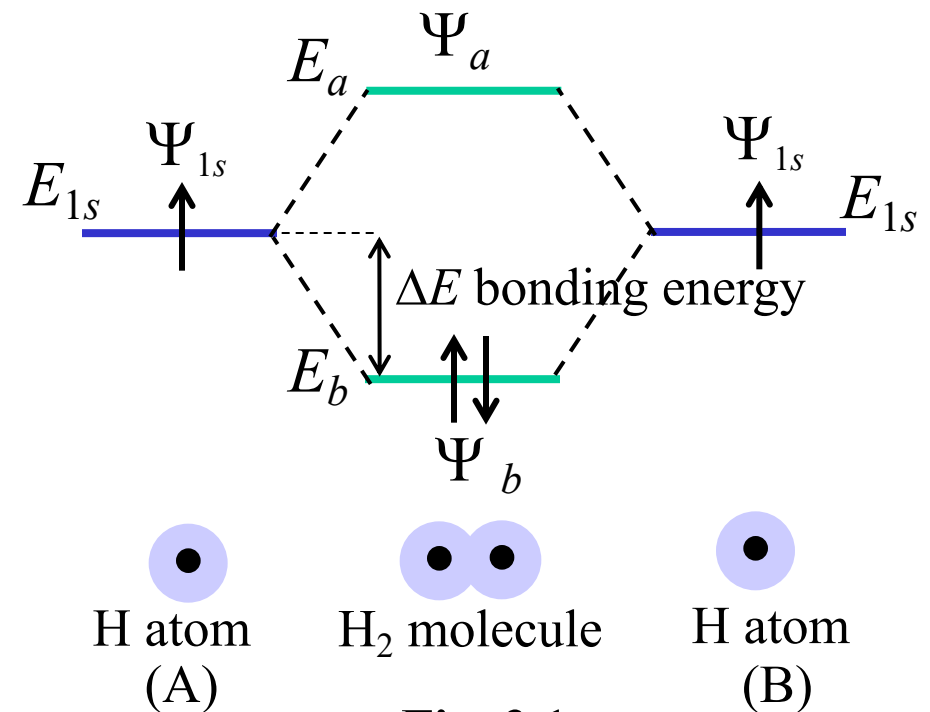

Fig. 3.1

- The lowering of the original energy before the interaction (E_{1s}) and the ground state energy after the interaction (E_b) is the <u>bonding energy</u> of the H_2 molecule (ΔE).

- The formation of E_b and E_a, from the original energy E_{1s} is referred to as <u>energy splitting</u>

- The energy splitting, in other words is the separation of E_a and E_b, varies with the inter-atomic distance r between the two H atoms as shown in Fig. 3.2
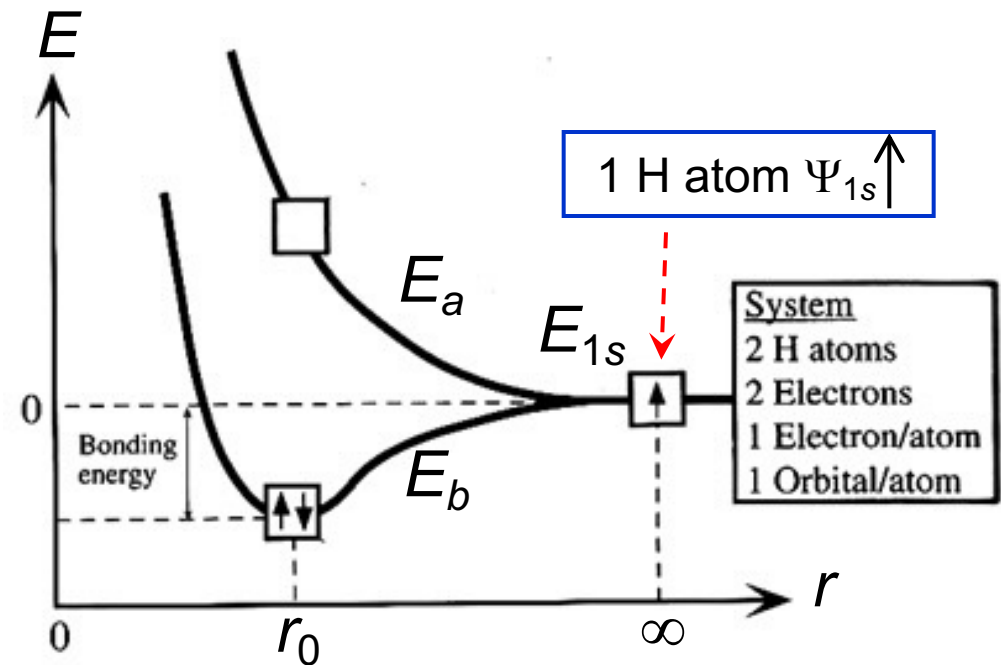

1 H atom $\Psi_{1s}\uparrow$

E

E_a

E_{1s}

0

Bonding energy

E_b

System
2 H atoms
2 Electrons
1 Electron/atom
1 Orbital/atom

0   r_0 ∞ r

Fig. 3.2

- It is important to note here that:

  - the number of quantum states before interaction = the number of quantum states after interaction

  - the number of electrons before interaction = the number of electrons after interaction

3.2 Energy band: conduction and valence bands

- We can now look into the energy band formation in semiconductor crystals.

- Consider a silicon crystal consisting of *N* silicon atoms. The electronic configuration of an isolated silicon atom is

  ^{14}Si: $1s^2 \, 2s^2 \, 2p^6 \, 3s^2 \, 3p^2$

Table 3.1

- The number of states and electrons of *N* isolated Si atoms is given in Table 3.1

States	No. of states	No. of electrons
$1s$	$2N$	$2N$
$2s$	$2N$	$2N$
$2p$	$6N$	$6N$
$3s$	$2N$	$2N$
$3p$	$6N$	$2N$

- The *N* silicon atoms are now brought together to form silicon crystal.

- Each Si atom shares its four valence electrons (2 electrons from each 3*s* and 3*p* states) with the four nearest neighbors to form stable configuration or to complete their subshells. As a result each Si atom is surrounded by 8 electrons.
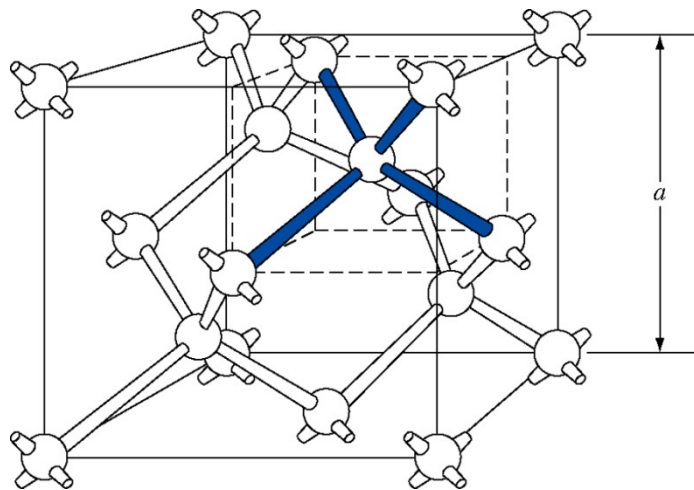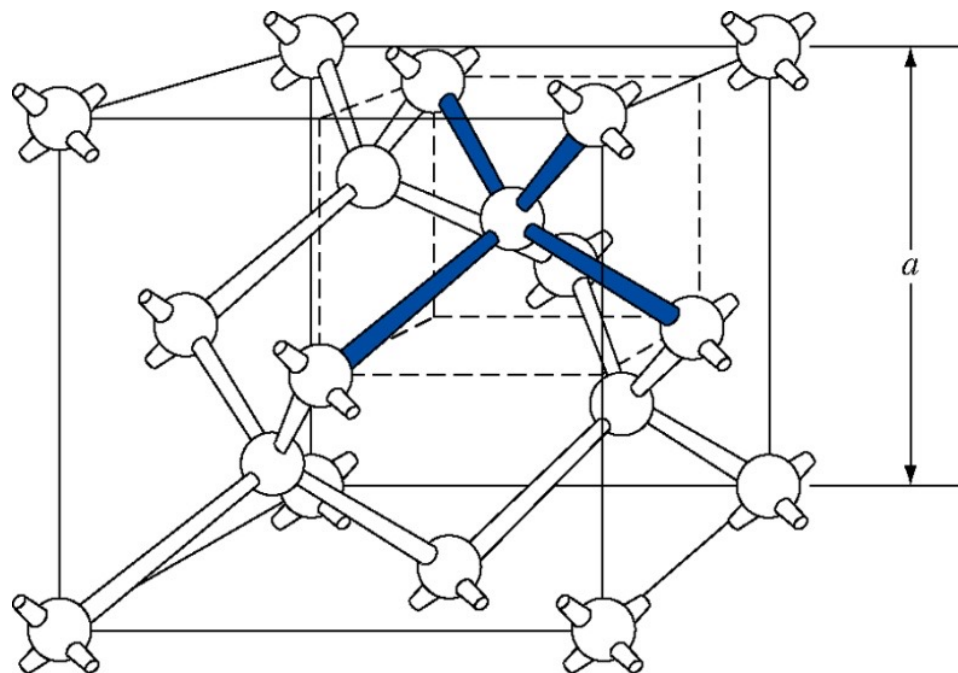

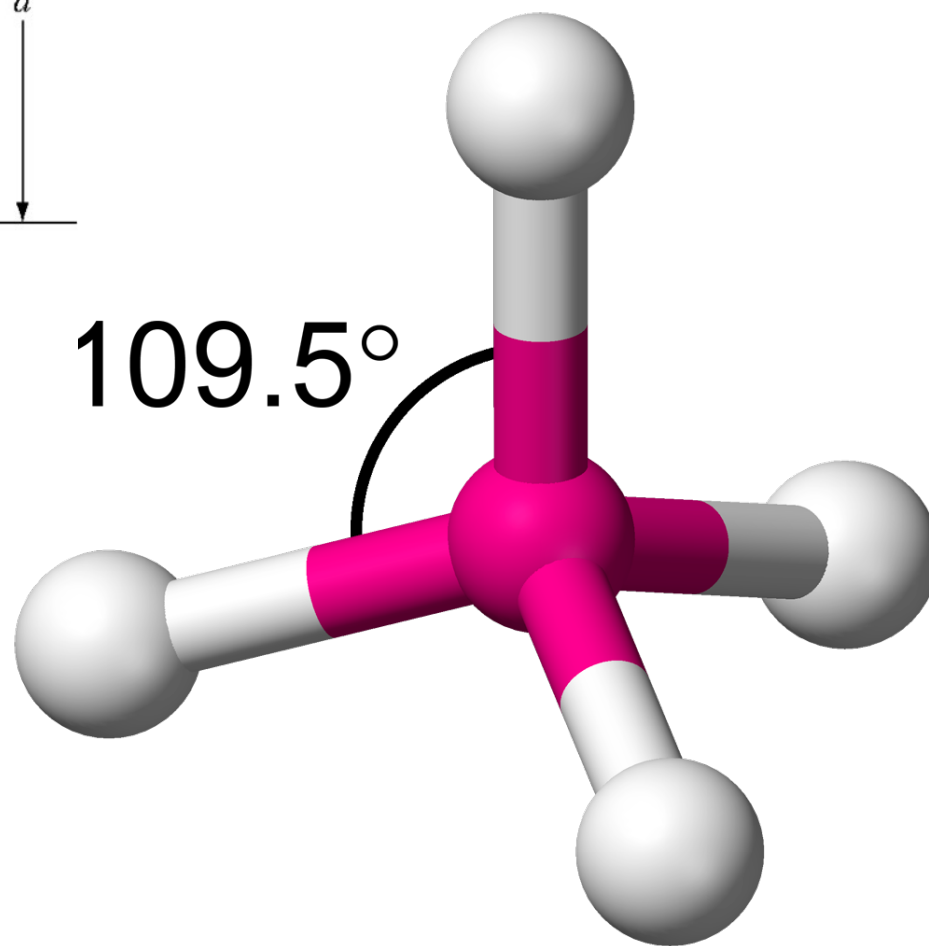(a) 3-dimensional representation of the covalent bonding in Si crystal at 0 K
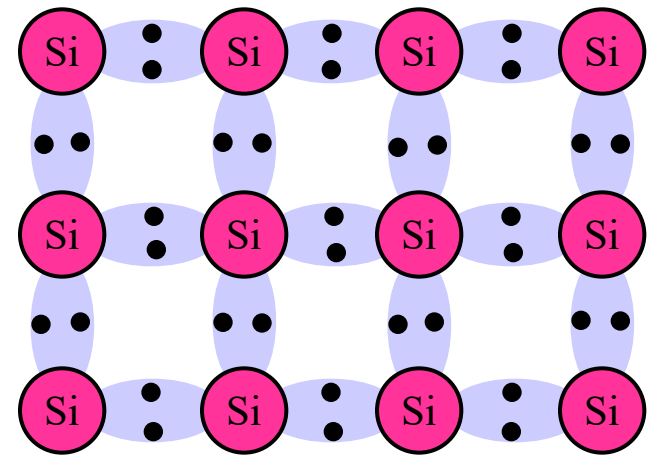
(b) 2-dimensional representation of the covalent bonding in Si crystal at 0 K

Fig. 3.3 Covalent bonding of silicon crystal

Tetrahedral

109.5°

- The formation of the energy band in Si crystal can be described as follow based on Fig. 3.4.

- As the inter-atomic distance decreases the outer shells $3s$ and $3p$ states interact:

  - The $2N$ states of $3s$ interact. The energy levels split forming $3s$ band. There are $2N$ states and $2N$ electrons in the $3s$ band.

  - The $6N$ states of $3p$ interact. The energy levels split forming $3p$ band. There are $6N$ states and $2N$ electrons in this band.

  - The degree of the energy splitting increases with decreasing inter-atomic spacing.

  - <u>Pauli exclusion principle</u>: no two electrons in a given system may have the same quantum states.

- As the inter-atomic spacing decreases further, the $3s$ and $3p$ bands grow and merge into a single band composed of mixture of energy levels. This $3s$-$3p$ band contains $8N$ states and $4N$ electrons.

- Further decreasing the inter-atomic distance, approaching the equilibrium inter-atomic spacing, the $3s$-$3p$ band splits into two bands separated by an energy gap or a bandgap E_g.

  - The upper band, called the conduction band, contains $4N$ states

  - and the lower band, called the valence band, also contains $4N$ states.

- In a perfect crystal, the are no allowed energy levels (quantum states) in the bandgap for electrons to occupy. The bandgap is also called a "forbidden band".

- At 0 K, the electrons will occupy the lowest energy states and therefore all 4N available electrons occupy all 4N states in the valence band.

- In other words, at 0 K the valence band is fully occupied and the conduction band is empty. In this state, the semiconductor is an insulator, no electrical conduction can take place.

  - for the electrical conduction to take place, electrons must be able to move into empty states. It follows that for the electrical conduction, the electrons must be excited to the conduction band.
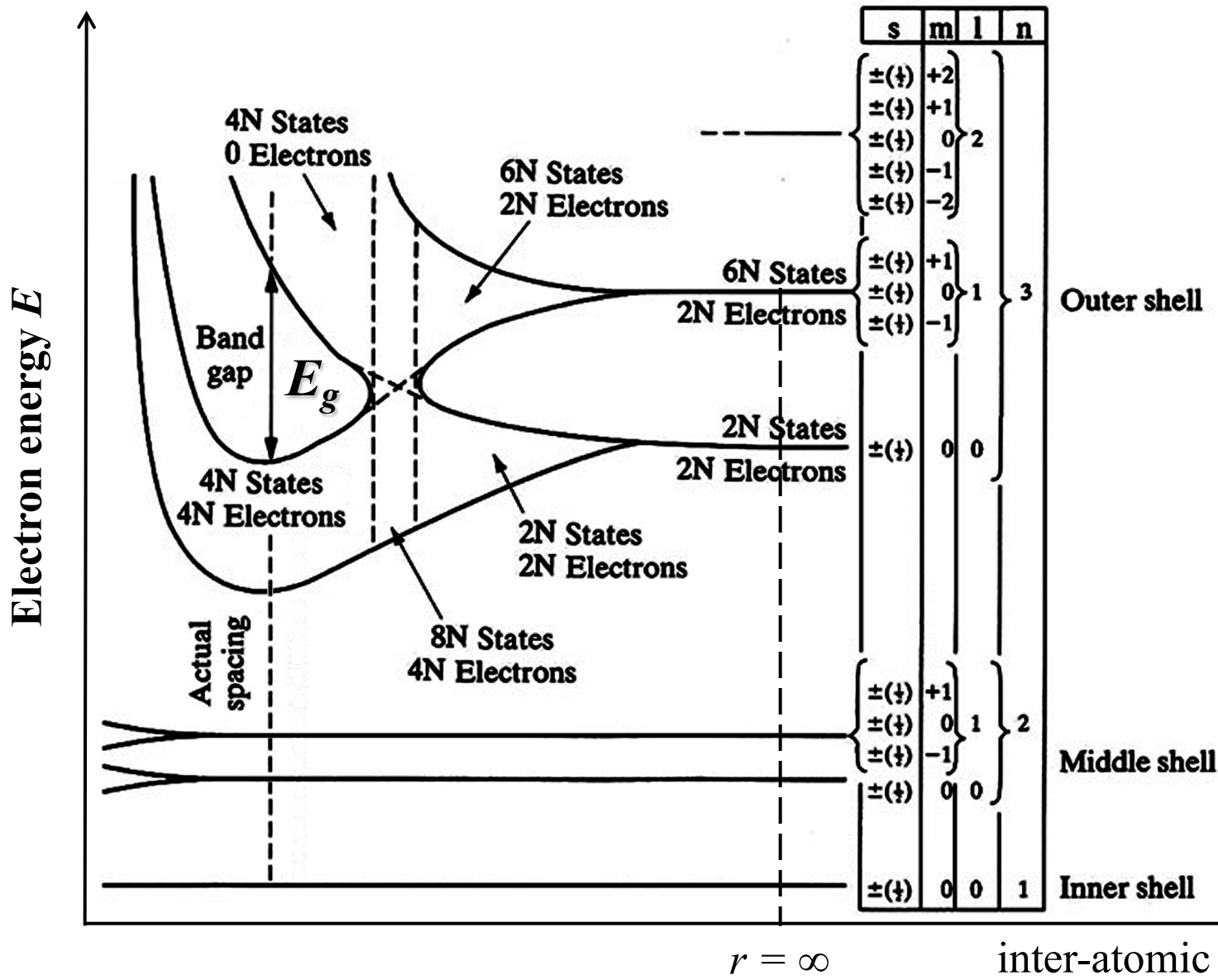
Fig. 3.4 Variation of electron energy with inter-atomic spacing

- The energy of the conduction and valence bands versus the physical distance x of the semiconductor sample can be represented by an energy band diagram as shown in Fig. 3.5

  - the energy refers to the electron energy
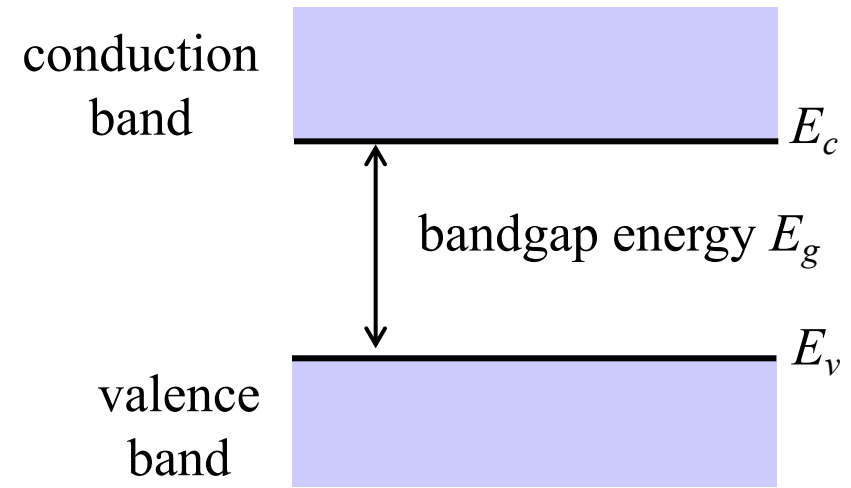
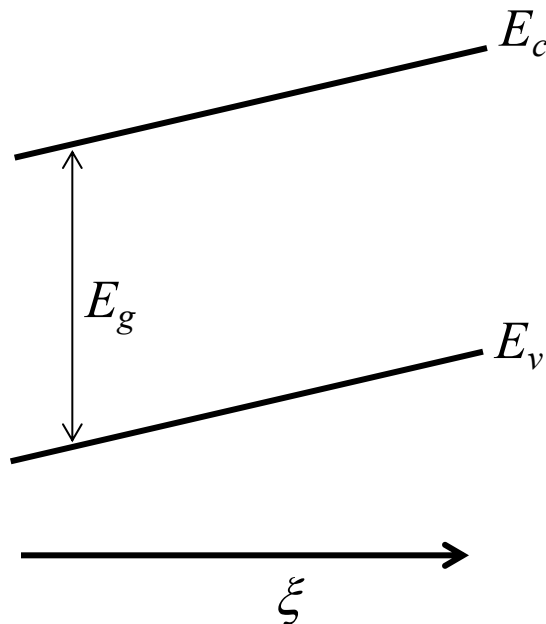 - the physical distance x is normally not indicated

Fig. 3.5

  - E_c is the energy of the bottom of the conduction band, very often called the <u>conduction band edge</u>

  - E_v is the energy of the top of the valence band, very often called the <u>valence band edge</u>
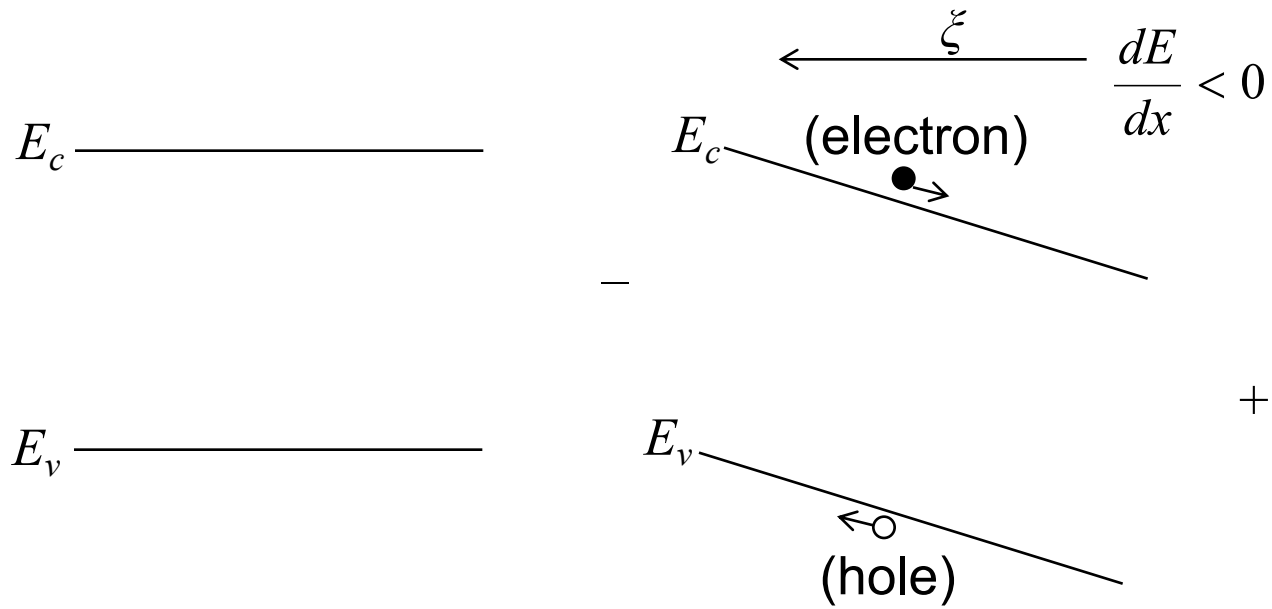
- If an electric field ξ is applied to the semiconductor sample

  - the energy band is not flat anymore

  - the energy bands will be inclined at a gradient proportional to the electric field according to equation (3.2). The energy band diagram is shown in Fig. 3.6

$$\xi = \frac{1}{q}\frac{dE}{dx} \qquad (3.2)$$

Fig. 3.6

E_c ————————————

$\xleftarrow{\hspace{3cm} \xi}$ $\dfrac{dE}{dx} < 0$

E_c (electron)

$-$

E_v ————————————

E_v

$+$

(hole)

Without electric field   With electric field ξ

$$\xi = -\frac{dV}{dx}$$

We will learn more about this in Tutorial 4

$$E = -qV$$

$$\xi = \frac{1}{q}\frac{dE}{dx}$$

3.3 Electrons and holes

- At $T = 0$ K, the valence band is fully occupied by electrons and the conduction band is empty. The semiconductor behaves like an insulator.

- The electrons in the valence band can be excited to the conduction by

  - increasing the temperature

  - illuminating crystal with light of a suitable wavelength

- As the temperature of the semiconductor is raised above 0 K, i.e. $T > 0$ K

  - some electrons in the valence band gain enough thermal energy to be excited across the bandgap to the conduction band.

  - This process corresponds to the electrons breaking the Si-Si covalent bonds leaving behind broken bonds. (Fig. 3.7)
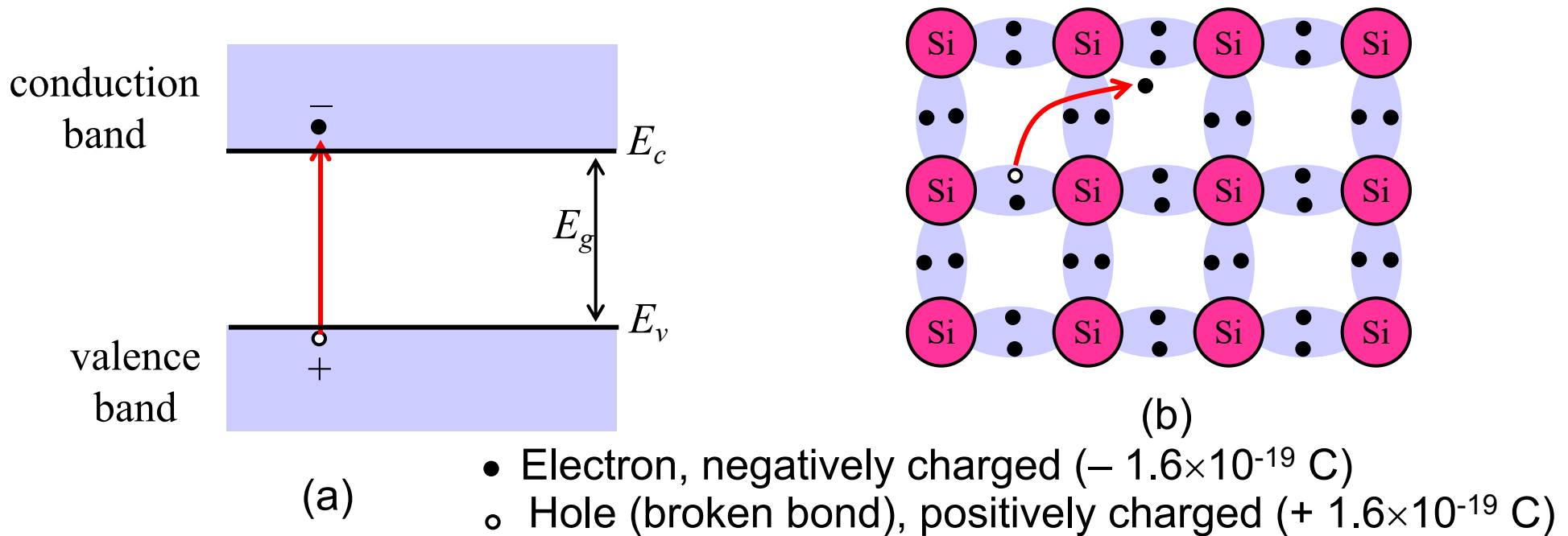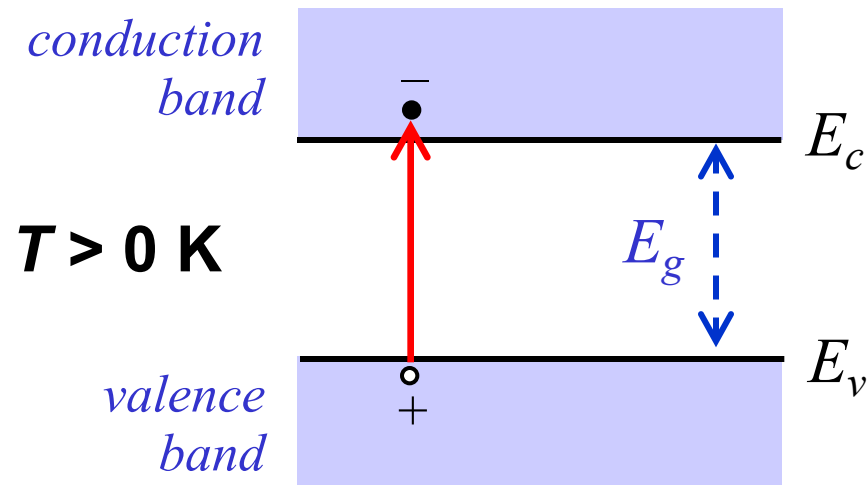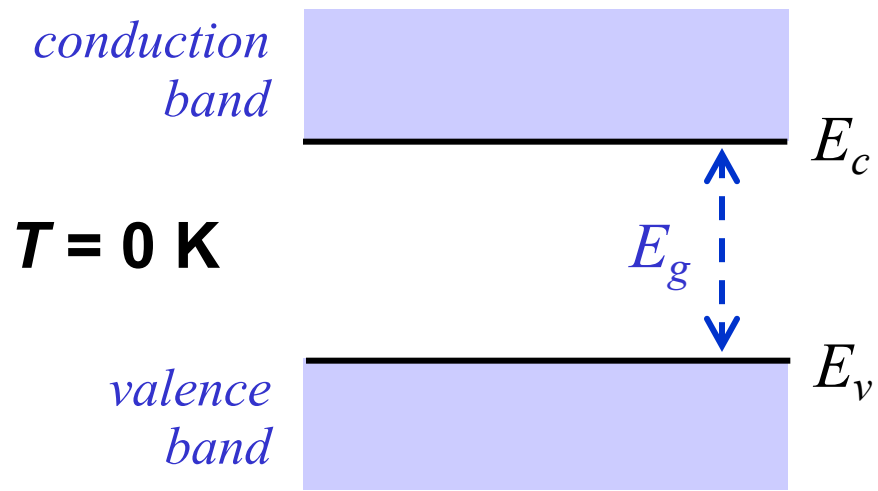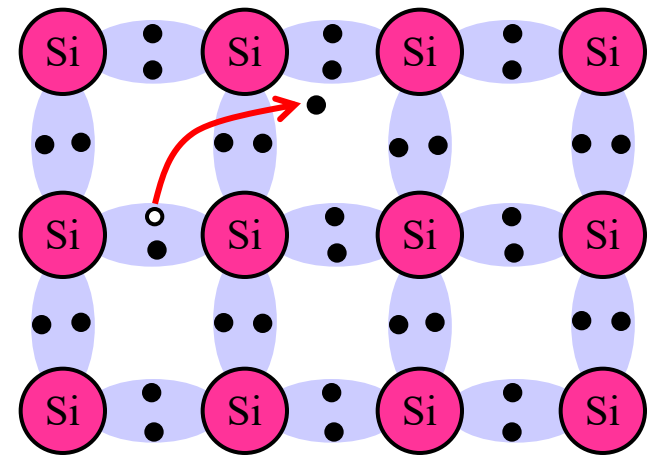
conduction band

E_c

E_g

E_v

valence band

(a)

(b)

- Electron, negatively charged (-1.6×10^{-19} C)
- Hole (broken bond), positively charged ($+1.6 \times 10^{-19}$ C)

Fig. 3.7

conduction band

$T = 0$ K

E_c

E_g

E_v

valence band

conduction band

$T > 0$ K

$-$

E_c

E_g

E_v

$\circ$
$+$

valence band
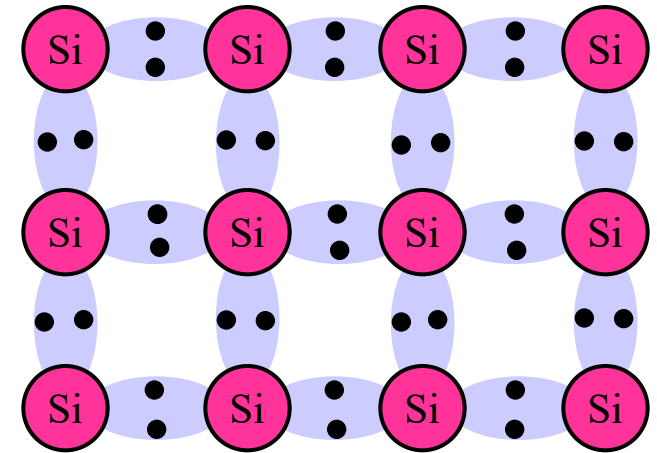
(a)

(b)

Fig. 3.7a

- Electron, negatively charged ($- 1.6 \times 10^{-19}$ C)
- Hole (broken bond), positively charged ($+1.6 \times 10^{-19}$ C)

- Some of the states in the conduction band is now occupied by electrons and some of the states in the valence band is now empty.

- An empty state in the valences band is referred to as a **hole**, it corresponds to the broken bond in the Si-Si bonding. The hole is positively charged with a value of 1.6×10^{-19} C.

- The electrons and holes can "freely" move throughout the crystal, under the influence of periodic potential formed by the atoms/ions in the crystal (compare to the real free electron in vacuum).

- The electrons and holes can only move freely for a short period of time, after which they will collide with vibrating atoms, impurity atoms and defects.

- The movement of the hole is actually the movement of the electron from the Si-Si bond to the broken bond. This is illustrated in Fig. 3.8.

- It is easier and convenient to think in terms of the displacement of holes rather than the actual displacement of electrons from Si-Si bonds to the broken bonds.
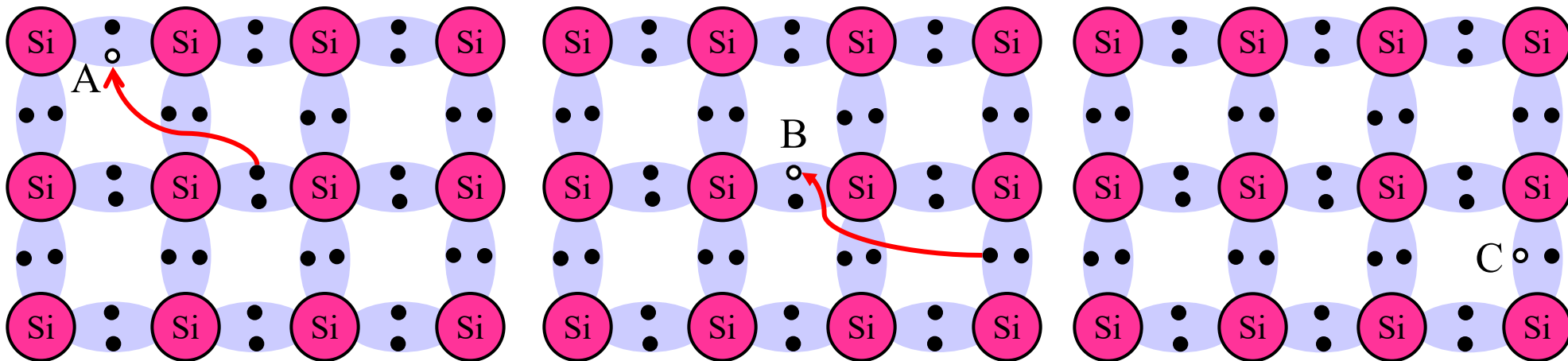

Fig. 3.8 The hole has moved from A to B to C

- The electrons and holes are created by the excitation of electrons from the valence band to the conduction band. This direct excitation of electrons from the valence band to the conduction band is referred to as <u>direct band-to-band generation</u>.

- Obviously, the number of hole in the valence band = the number of electrons in the conduction band. Since the electrons and holes are created in pair, they are also called <u>electron-hole pairs (EHP)</u>.

- There are empty states in the conduction and valence bands, therefore the electrons and holes are able to perform a directed motion under the action of an external electric field, conducting an electric current.

- The electrons in the valence band can also be excited to the conduction band, creating electron-hole pairs, by illuminating the semiconductor with light having a photon energy E_{ph} equal or greater than the bandgap energy E_g. This is illustrated in Fig. 3.9.

$$E_{ph} \geq E_g \qquad (3.3)$$

$$E_{ph} = h\nu = \frac{hc}{\lambda} \qquad (3.4)$$

$$\frac{hc}{\lambda} \geq E_g$$

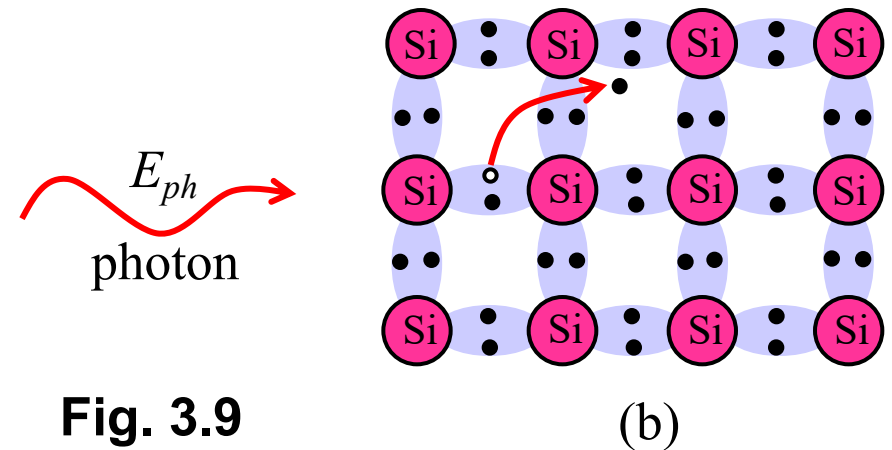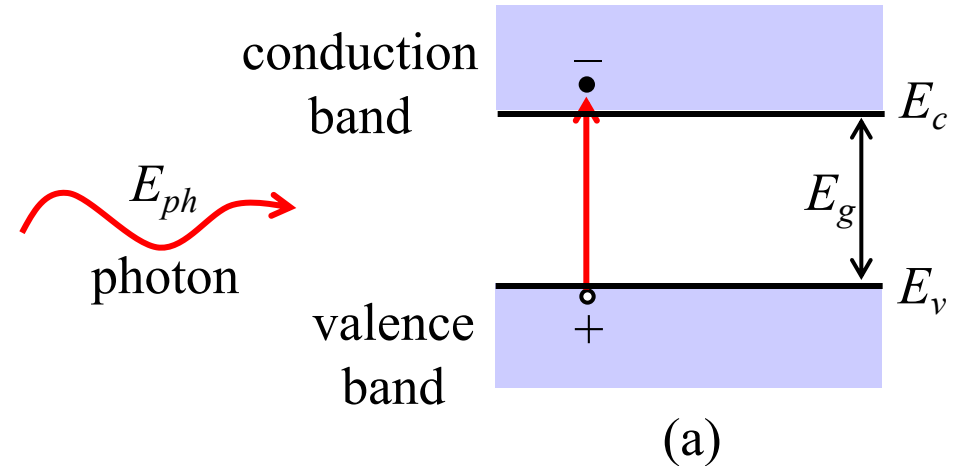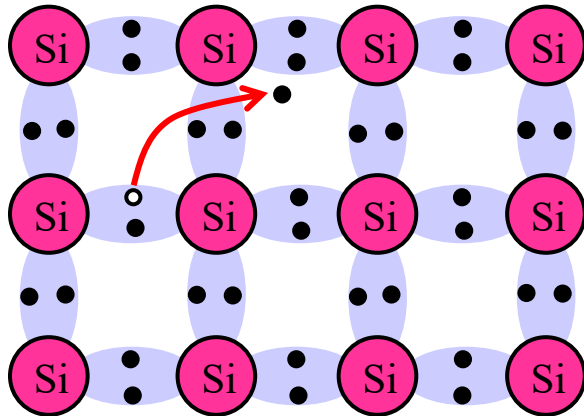$$\frac{1240}{\lambda} \geq E_g \qquad (3.5)$$
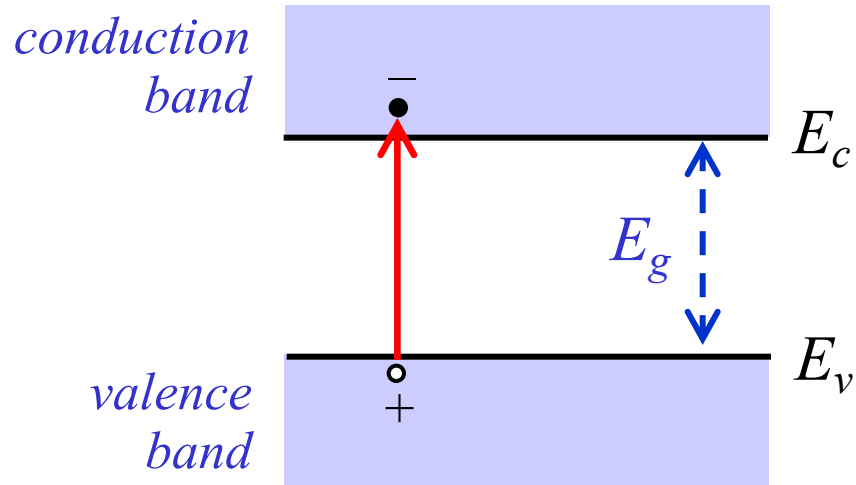
where λ in nm and E_g in eV

conduction band

E_{ph}
photon

valence band

(a)

E_c

E_g

E_v

E_{ph}
photon

(b)

Fig. 3.9

Sample at temperature *T*

conduction band

E_c

E_g

E_v

valence band

Sample subjected to light

conduction band

E_{ph}

photon

E_c

E_g

E_v

valence band

E_{ph}
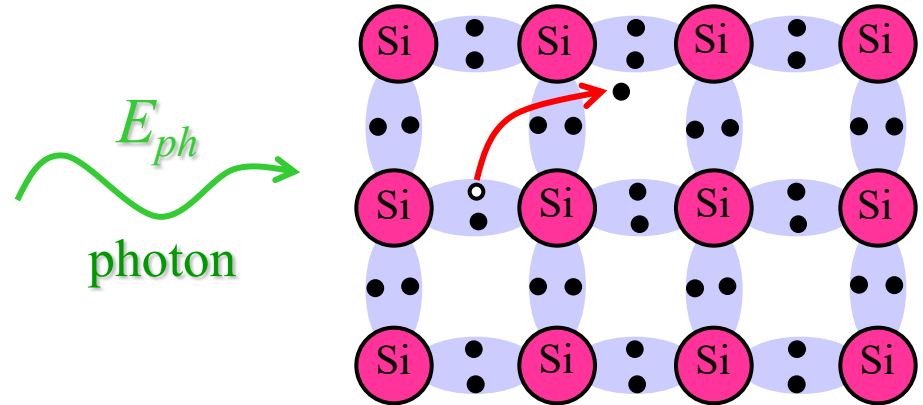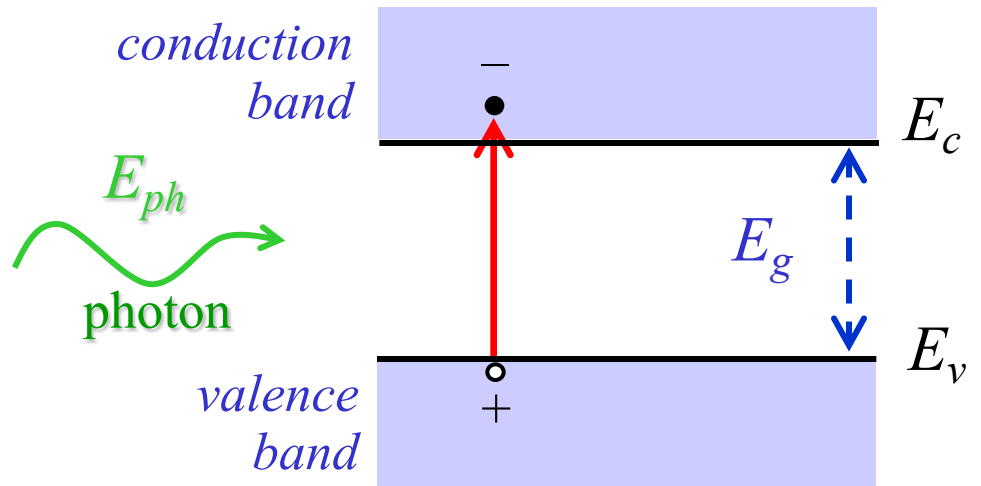
photon

Problems

Q1: Determine the energy (in eV) of a photon having a wavelength of (a) 10 nm, and (b) 450 nm. (Ex 2.1)

(a) $\quad E = h\nu = \dfrac{hc}{\lambda} = \dfrac{\left(6.625\times10^{-34}\right)\left(3\times10^{10}\right)}{100\times10^{-8}}$

$$= 1.9875\times10^{-17}\ \text{J}$$

or $\quad E = \dfrac{1.9875\times10^{-17}}{1.6\times10^{-19}} = 124\ \text{eV}$

(b) $\quad E = \dfrac{hc}{\lambda} = \dfrac{\left(6.625\times10^{-34}\right)\left(3\times10^{10}\right)}{4500\times10^{-8}}$

$$= 4.417\times10^{-19}\ \text{J}$$

or $\quad E = \dfrac{4.417\times10^{-19}}{1.6\times10^{-19}} = 2.76\ \text{eV}$

Q2: The work function of a material refers to the minimum energy required to remove an electron from the material. Assume that the work function of gold is 4.90 eV and that of cesium is 1.90 eV. Calculate the maximum wavelength of light for the photoelectric emission of electrons for gold and cesium. (2.5)

Q2: The work function of a material refers to the minimum energy required to remove an electron from the material. Assume that the work function of gold is 4.90 eV and that of cesium is 1.90 eV. Calculate the maximum wavelength of light for the photoelectric emission of electrons for gold and cesium. (2.5)

$$E = h\nu = \frac{hc}{\lambda} \Rightarrow \lambda = \frac{hc}{E}$$

Gold: $E = 4.90\,\text{eV} = (4.90)(1.6 \times 10^{-19})$ J

So,

$$\lambda = \frac{(6.625 \times 10^{-34})(3 \times 10^{10})}{(4.90)(1.6 \times 10^{-19})} = 2.54 \times 10^{-5}$$

cm

or

$$\lambda = 0.254\,\mu\text{m}$$

Cesium: $E = 1.90\,\text{eV} = (1.90)(1.6 \times 10^{-19})$ J

So,

$$\lambda = \frac{(6.625 \times 10^{-34})(3 \times 10^{10})}{(1.90)(1.6 \times 10^{-19})} = 6.54 \times 10^{-5}$$

cm

or

$$\lambda = 0.654\,\mu\text{m}$$

Key takeaways (Lecture #5)

- When Silicon atoms form covalent bonds with four nearest atoms, discrete 3s and 3p energy states form continuous conduction band and valence band, separated by a bandgap;

- At 0K, the valence bond is fully occupied by electrons, the conduction band is empty $\rightarrow$ no current conduction;

- To achieve conduction, electrons in the valence band can be excited to the conduction band (direct band to band generation):

  - increasing the temperature

  - illuminating crystal with light of a suitable wavelength

- The number of hole in the valence band = the number of electrons in the conduction band. Since the electrons and holes are created in pair, they are also called electron-hole pairs (EHP).

Lecture 6

3.3.1 Direct band-to-band generation and recombination

- If a semiconductor is subjected to a certain temperature T, or illuminated with light ($E_{ph} \geq E_g$) or both,

    - Do these generated electron-hole pairs keep increasing continuously?

    - The answer is certainly "NO", otherwise we will observe that all the covalent bonds of the semiconductor will be broken simply by putting a sample at room temperature.

- The reason is that as electron-hole pairs are generated, they also can recombine. In this process the electrons and holes are annihilated (i.e. disappear). The process is called recombination. (Fig. 3.10)

- The direct generation and recombination processes from band-to-band shown in Fig. 3.10 is called <u>direct band-to-band generation and recombination.</u>
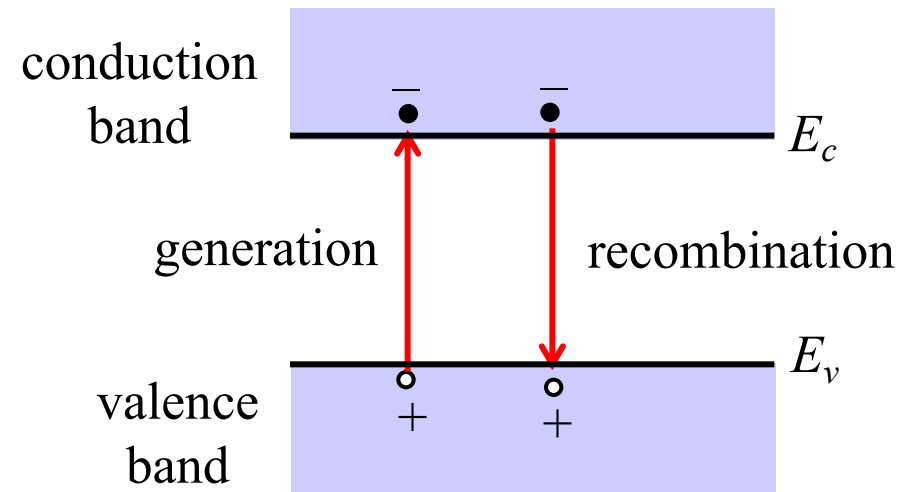

Fig. 3.10

- A steady state will be established when

  generation rate G = recombination rate R (3.6)

  - The generation rate G is the number of electron-hole pairs created per unit volume per second (units: #/cm^3-s).

    - *The generation is the sum of the thermal generation rate and the generation rate by the external excitation (if any)*

  - The recombination rate R is the number of electron-hole pairs recombining per unit volume per second (units: #/cm^3-s).

    - *It is expected that the recombination rate is proportional to the electron concentration in the conduction band and the hole concentration in the valence band.*

- Obviously, in the steady state, the electron and hole concentrations are constant with time.

- When a semiconductor is at temperature T and there is no external disturbance/excitation (e.g. external electric field, magnetic field or light illumination), the electrons and holes are solely created by thermal energy.

- An equilibrium will be established, and this equilibrium state is called **thermal equilibrium** since there is only thermal energy involved.

- In thermal equilibrium:

  - thermal generation rate G_{th} = recombination rate R

  - there exist thermal equilibrium electron and hole concentrations, n_0 and p_0 respectively.

3.4 Direct and Indirect Bandgap Semiconductors

The electron energy E can also be related to its momentum p (or, in crystal, more precisely, it is called crystal momentum). This relation will lead to direct and indirect bandgap semiconductors.

3.4.1 E versus k (E - k) for free electrons and electrons in crystals

- From appendix D [eqn (D.8)], the relation of E with p for a free electron in an one dimensional (1-D) system is parabolic and given by

$$E = \frac{\hbar^2 k_x^{\,2}}{2m} \qquad (3.7)$$

where k_x is the wave vector

and the momentum p is given by

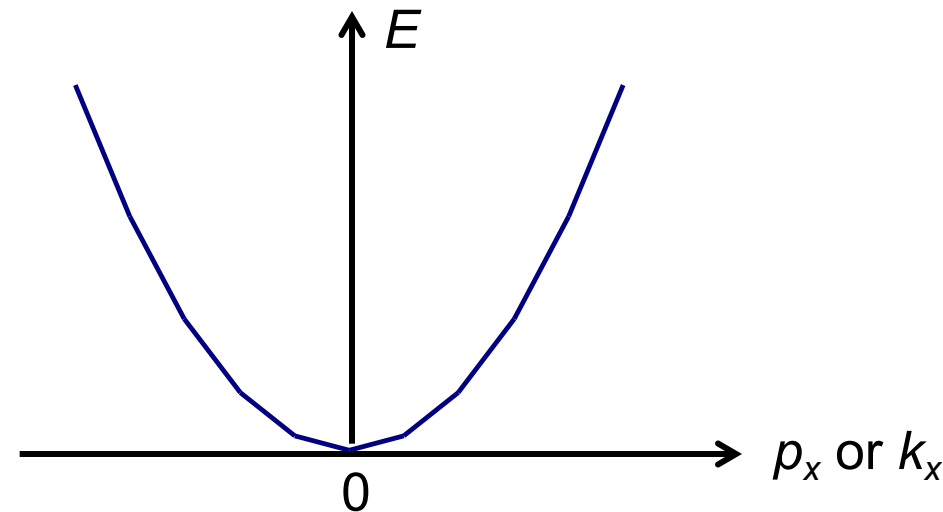$$p_x = \hbar k_x \quad (3.8), \quad \text{here } \hbar = \frac{h}{2\pi} \quad (3.9)$$

Fig. 3.11 E vs p_x or k_x is parabolic

- In crystals, there is interaction between the electrons and the periodic potential in the lattice (see Appendix D section D.2).

- Taking this interaction into account, the Schrödinger equation, as shown in eqn. (D.1), becomes

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{dx^2} + U(x)\Psi = E\Psi \qquad (3.10)$$

periodic potential energy

where $U(x)$ is periodic potential energy and given by

$$U(x) = U(x + n_x a) \qquad (3.11 \text{ or see D.9})$$

n_x is integer

- Due the interaction of the electrons with the periodic potential, the solution of the Schrödinger equation in eqn. (3.10) will lead to the forbidden energy band (energy bandgap) and allowed energy band.

- The electron energy E versus k ($E - k$) relation is shown in Fig. 3.12.a. The parameter a is the period of the lattice or the lattice constant. The E - k relation is called the energy band structure.

  - Here the quantity $\qquad p = \hbar k \qquad$ **(3.12)**

    is called crystal momentum. This is not the actual momentum of the electron in the crystal, but it describes the motion of the electron that includes the interaction between the electron and the crystal (see Appendix D, section D.2).

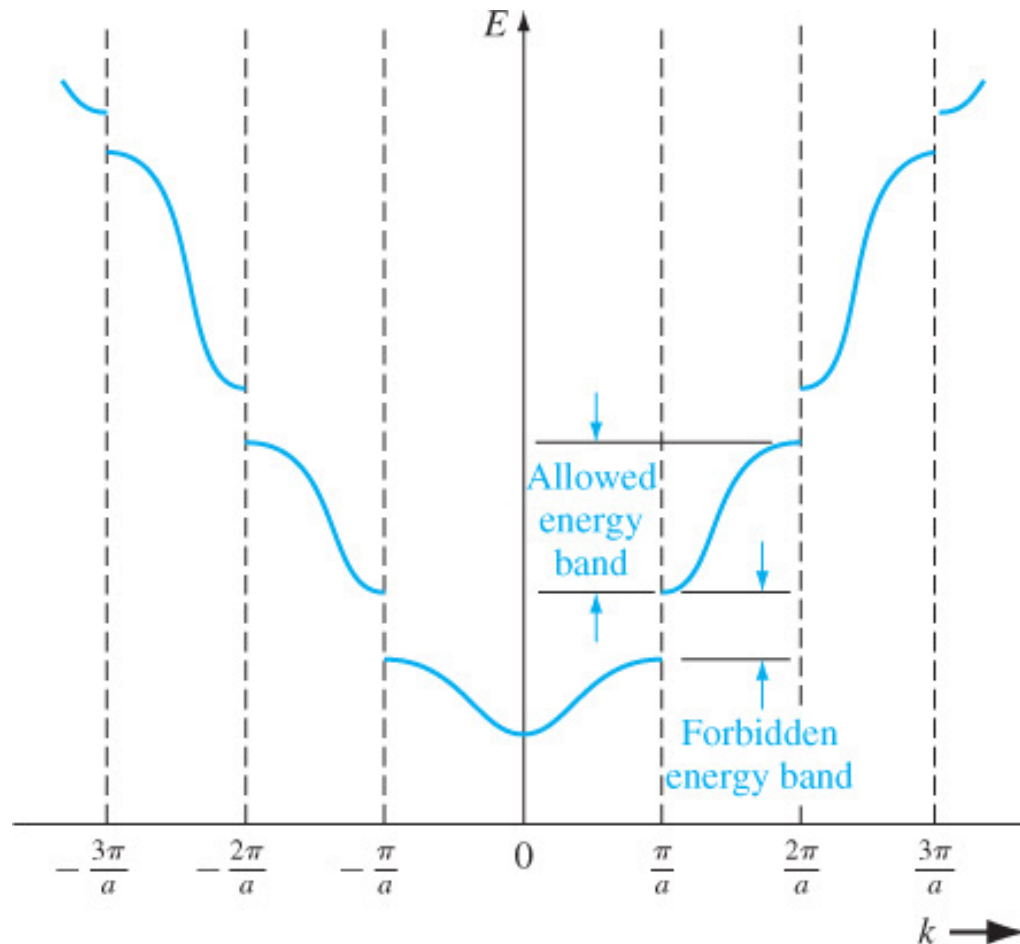- Note that the *E-k* relation is no longer parabolic as that of a free particle shown in Fig. 3.11.

Fig.3.12.a $E - k$ relation with the forbidden and allowed energy bands

- It is customary to plot the *E-k* relation within −π/a < k < π/a by displacing the curve by multiple of 2π/a. This is shown in Fig. 3.12.b & referred to as a reduced *k*-space diagram.

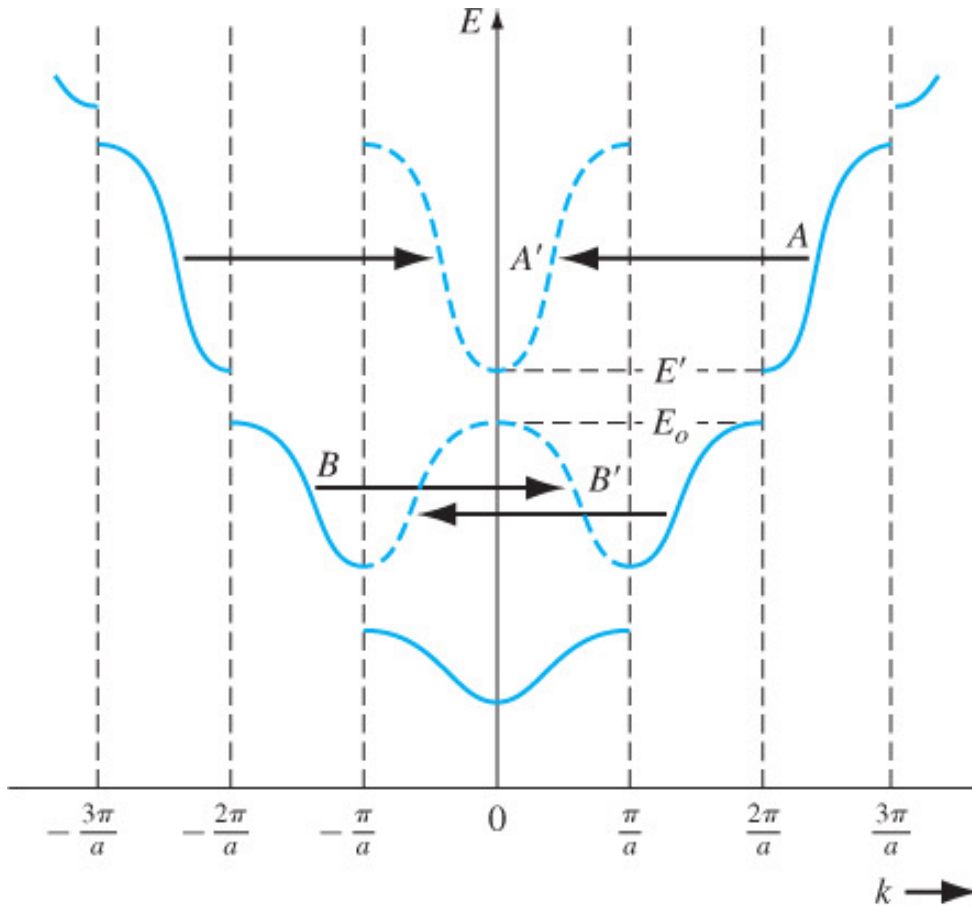**Figure 3.10** | The *E* versus *k* diagram showing 2π displacements of several sections of allowed energy bands.
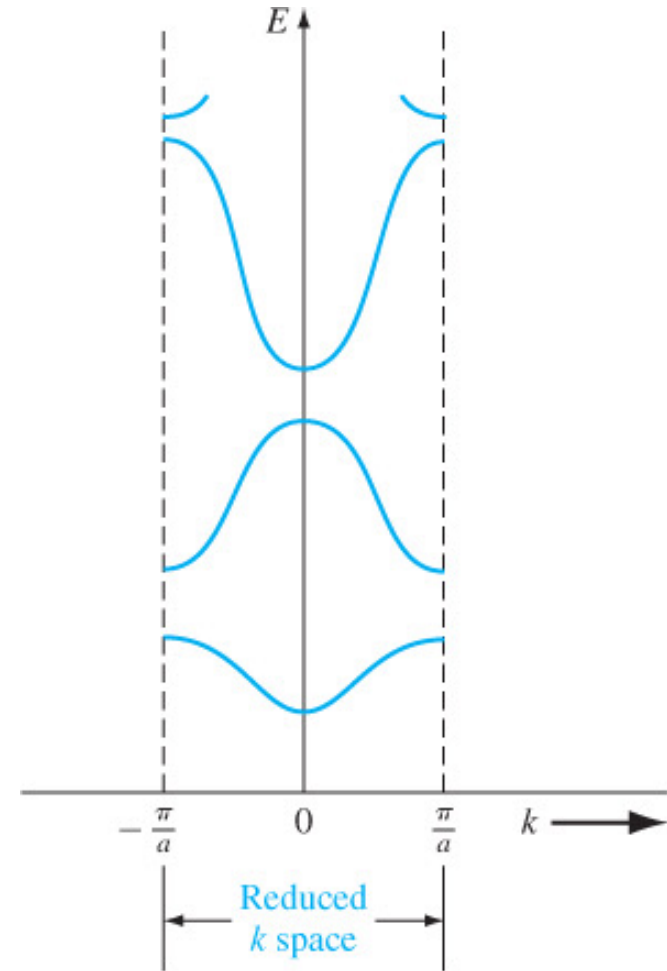
3-39

Fig.3.12.b *E-k* relation in the reduced *k*-space diagram

- We have seen that because of the interaction of the electrons with the periodic potential in the lattice, the *E-k* relation is **no longer parabolic** (see Fig.3.12) as in the free electron case.
- However, near the conduction band minima & the valence band maxima, it can be approximated by a *parabolic relation*. This is shown in Fig. 3.13.
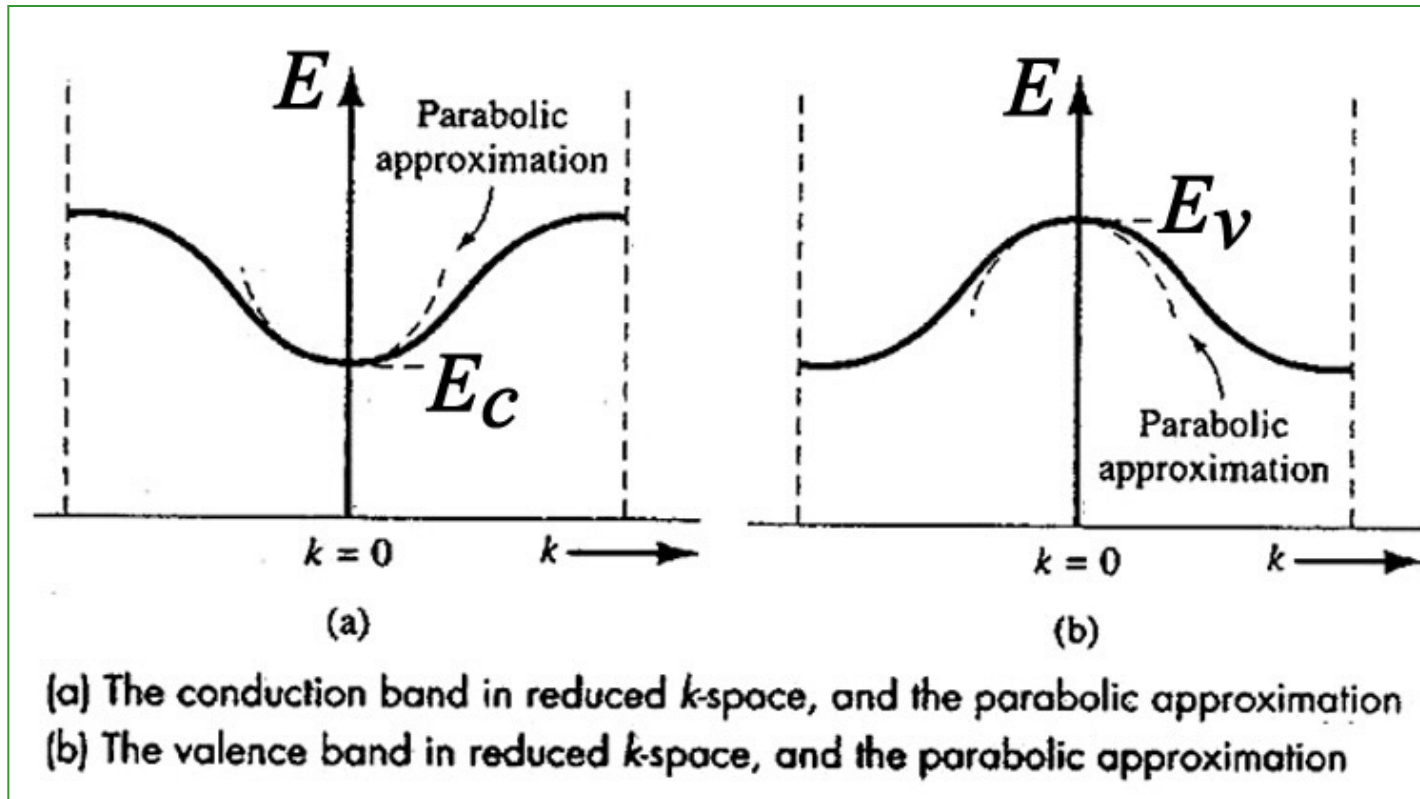

Fig. 3.13

(a) The conduction band in reduced *k*-space, and the parabolic approximation
(b) The valence band in reduced *k*-space, and the parabolic approximation

The concept of Effective Mass

- From equation (3.7),

$$E = \frac{\hbar^2 k_x^2}{2m}$$

- If we take the first and second derivative:

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

$$\frac{1}{\hbar^2} \frac{d^2 E}{dk^2} = \frac{1}{m}$$

Whereby *m* is the mass of a free particle.

- In a crystal, there are internal forces that act on the particle (such as electron) besides the external force due to positively charged ions or protons and negatively charged electrons.

- Hence, we modify the mass of the particle to an effective mass *m**, to take into account the particle mass as well as the effect of internal force. *(Anology: marbles in water and oil)*

$$\frac{1}{\hbar^2}\frac{d^2E}{dk^2} = \frac{1}{m*}$$

- Since the energy near the minimum (or maximum) of the *E-k* diagram can be approximately by a parabola, we may write the following for electron:

$$E - E_c = C_1(k^2)$$

- Whereby *C₁* is a coefficient. Hence:

$$\frac{1}{\hbar^2}\frac{d^2E}{dk^2} = \frac{1}{m*} = \frac{2C_1}{\hbar^2}$$

Problems

Q1: A simplified parabolic E vs. k curve for an electron in the conduction band is given. The value of a is 1 nm. Determine the relative effective mass. (TYU 3.3)
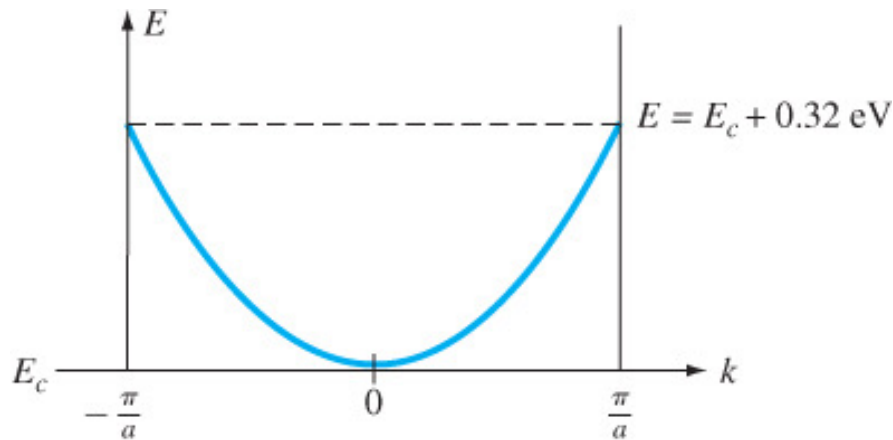

Figure 3.22 | Figure for Exercise TYU 3.3.

We have $E - E_c = C_1 k^2$

$$(E_c + 0.32 - E_c)(1.6 \times 10^{-19})$$

$$= C_1 \left(\frac{\pi}{10 \times 10^{-10}} \right)^2$$

so that $C_1 = 5.1876 \times 10^{-39}$

We have

$$m^* = \frac{\hbar^2}{2C_1} \Rightarrow \frac{m^*}{m_o} = \frac{\hbar^2}{2m_o C_1}$$

$$= \frac{\left(1.054 \times 10^{-34} \right)^2}{2\left(9.11 \times 10^{-31} \right)\left(5.1876 \times 10^{-39} \right)}$$

or

$$\frac{m^*}{m_o} = 1.175$$

Q2: Two possible conduction bands are shown in figure. State which band will result in the heavier electron effective mass and why? (3.13)
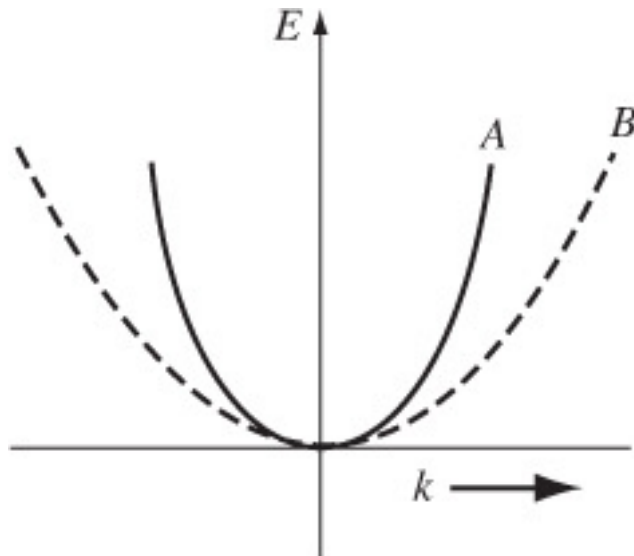

Figure P3.13 | Conduction bands for Problem 3.13.

Q2: Two possible conduction bands are shown in figure. State which band will result in the heavier electron effective mass and why? (3.13)
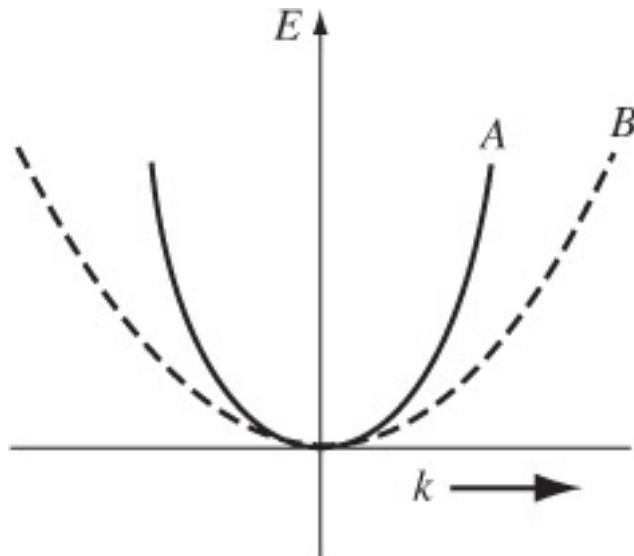

Figure P3.13 | Conduction bands for Problem 3.13.

The effective mass is given by

$$m^* = \left(\frac{1}{\hbar^2} \cdot \frac{d^2 E}{dk^2} \right)^{-1}$$

We have

$$\frac{d^2 E}{dk^2}(curve\ A) > \frac{d^2 E}{dk^2}(curve\ B)$$

so that $\quad m^*(curve\ A) < m^*(curve\ B)$

3.4.2 *E* versus *k* (*E* - *k*) for Si and GaAs

Consider the energy *E* versus *k* (*E* - *k*) for silicon and gallium arsenide (GaAs).

- *E* - *k* is symmetric in *k* and that no new information is obtained by displaying the negative axis.

- It is a normal practice to plot *E* - *k* along positive [100] direction to the right and along positive [111] direction to the left.
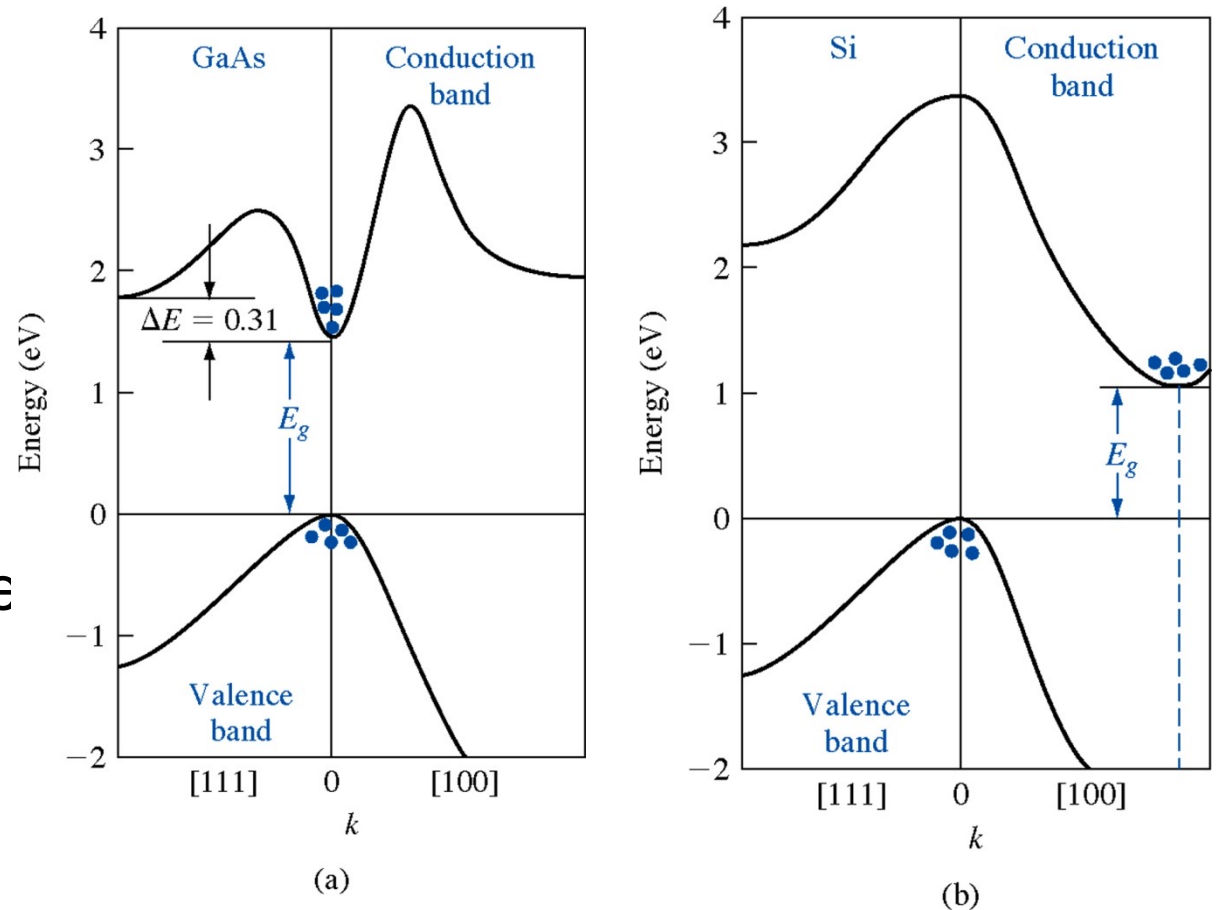

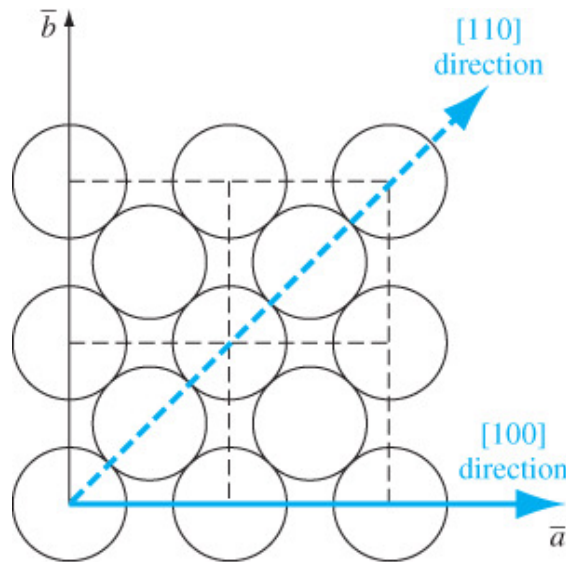**Fig.3.14** Energy band structure of (a) GaAs and (b) Si

Figure 3.24 | The (100) plane of a face-centered cubic crystal showing the [100] and [110] directions.

- In the E - k diagrams we see that

  - the majority of electrons occupy the bottom of the conduction band

  - and the majority of holes occupy the top of the valence band

  - the bandgap energy E_g is the energy difference between the conduction band minimum and the valence band maximum

- The *E - k* diagram for GaAs

  - Conduction band minimum and valence band maximum both occur at same *k*-value (in this case at *k* = 0). A semiconductor with this property is called a direct bandgap semiconductor.

  - The electron transitions from conduction band to valence band or vice versa require the <mark>conservation of energy and momentum.</mark>

  - In the direct bandgap semiconductor, the transitions do not require changes in the crystal momentum. Therefore, the transitions are very efficient. For the transitions from the conduction band to the valence band, the <mark>energy is given off as photon (light).</mark>

  - Consequently, the direct band gap semiconductors are suitable for light producing optical devices (e.g. semiconductor laser)

- The *E - k* diagram for Si

  - Conduction band minimum and valence band maximum do not occur at same *k*-value. A semiconductor with this property is called an indirect bandgap semiconductor.

  - The electron transitions from the conduction band to the valence band require changes in the crystal momentum.

  - The crystal momentum change can be satisfied, in principle, through the involvement of phonons (lattice vibration) in the transition process. Because of the need of the phonons involvement, this type of transitions are not efficient.

  - In the presence of the defect states, the transitions of electrons from the conduction to the valence band are more likely through defect states and the energy is given out as heat.

  - This is why the indirect semiconductor materials are not suitable for light producing devices.

Is Ge a direct or indirect band-gap semiconductor?
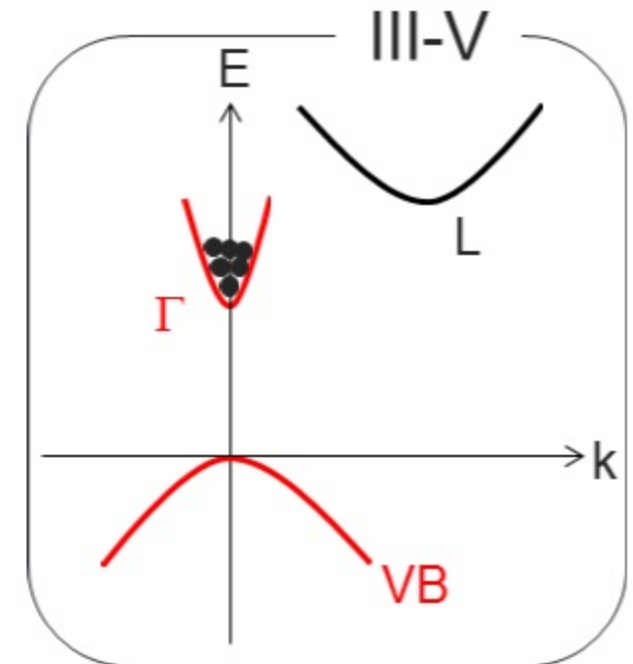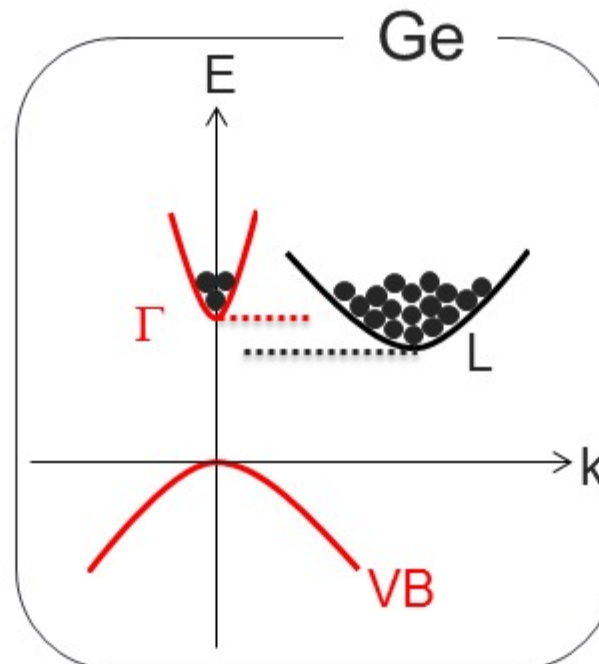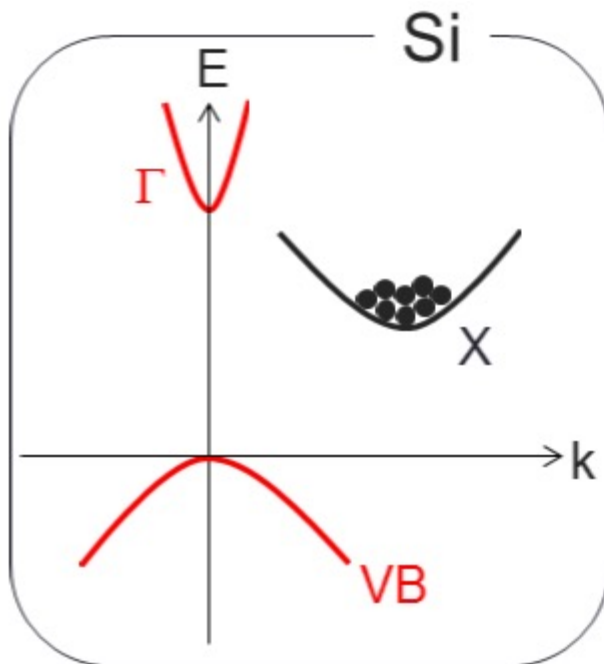
Key takeaways (Lecture #6)

- At thermal equilibrium (un-doped semiconductor):

  - thermal generation rate G_{th} = recombination rate R

  - thermal equilibrium electron and hole concentrations, $n_0 = p_0$

- *E-k* diagram for electrons in a crystal can be approximated as parabola curves around the conduction band min and valence band max;

- The effective mass of electron is inversely proportional to the curvature:

$$m^* = \left(\frac{1}{\hbar^2} \cdot \frac{d^2 E}{dk^2} \right)^{-1}$$

- Si = indirect band-gap, GaAs = direct bandgap