Fundamentals of Solid State Physics

Semiconductors - General

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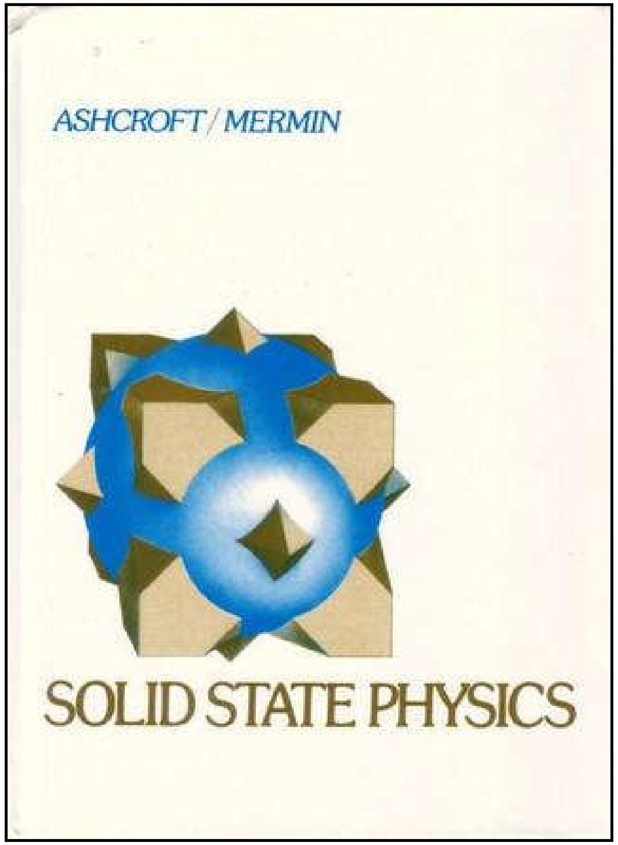
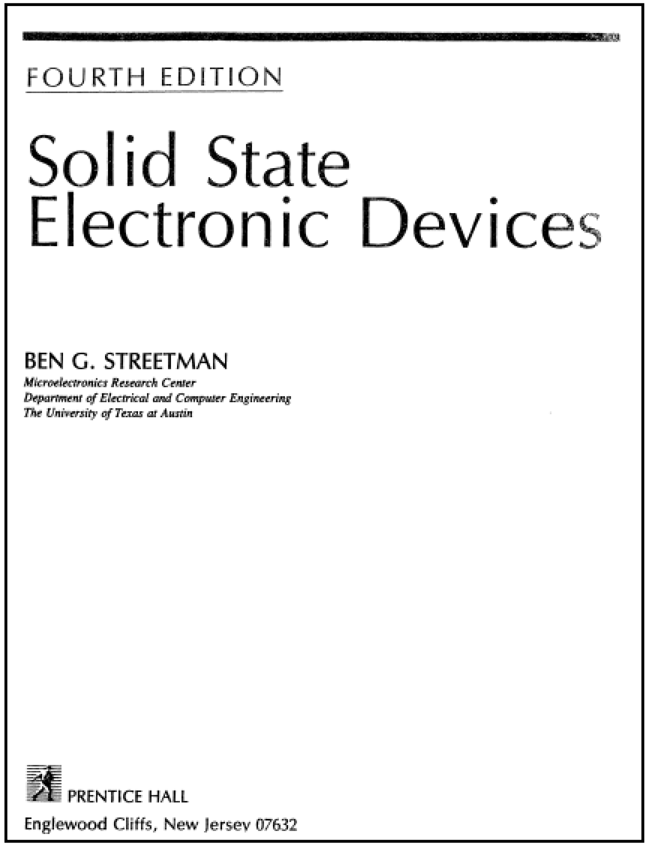
Further Reading

- **Ashcroft & Mermin, Chapter 28**
- **Solid State Electronic Devices by Streetman, Chap.3**





Electronic Properties of Materials

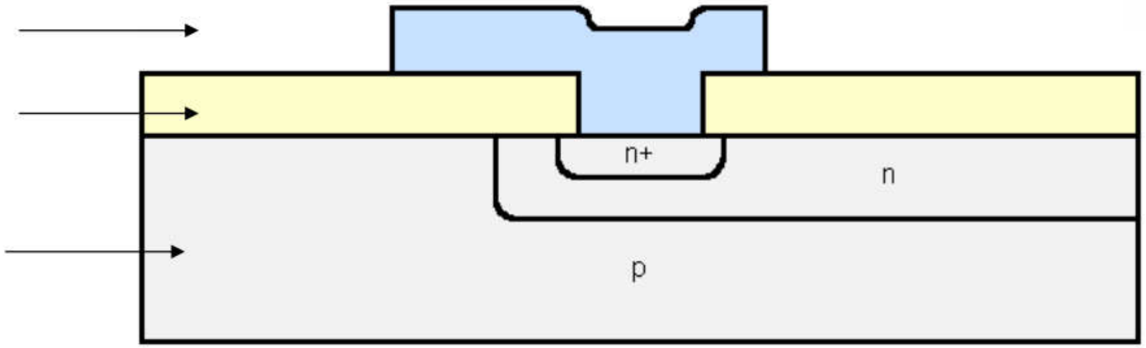
CMOS transistor

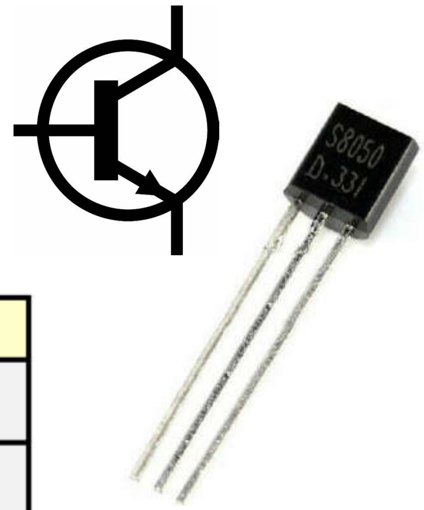
- Complementary Metal-Oxide-Semiconductor

conductor Al

insulator SiO_2

semiconductor Si



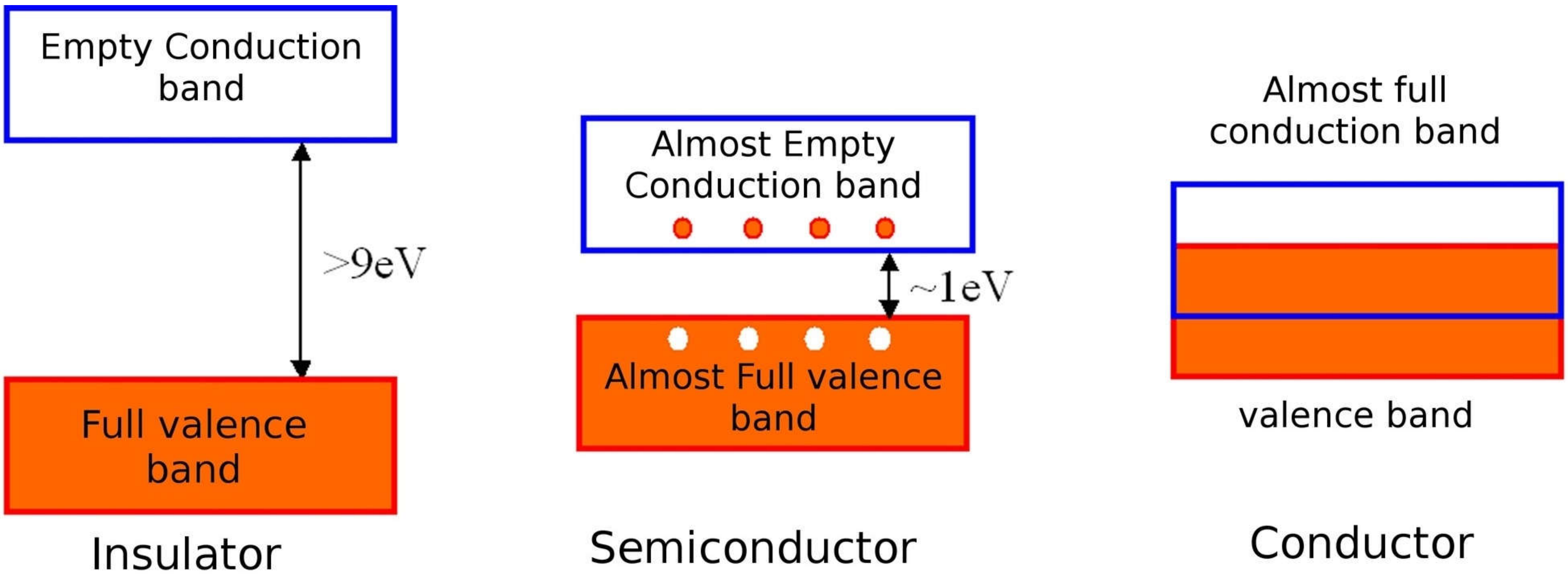


Metal

SiO_2

Silicon

Insulator, conductor, semiconductor



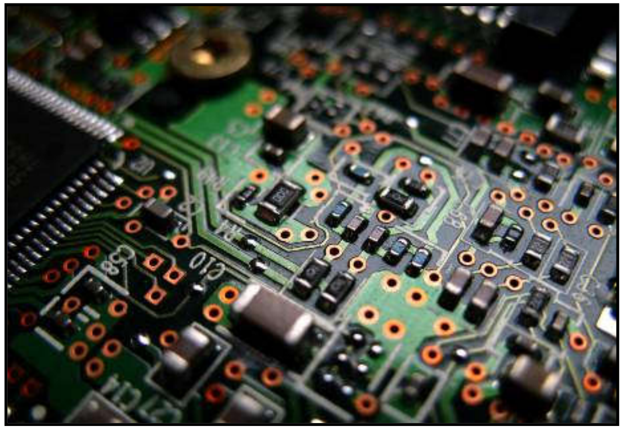
$E_g \sim 0.5\text{–}5$ eV

Semiconductors - General Concepts

- Band diagram
- Band gap E_g
- Effective mass m^*
- Holes
- Density of States (DOS) $g(E)$
- Density of Carriers
  - Mass Action Law
- Intrinsic and Extrinsic

Semiconductors - Applications

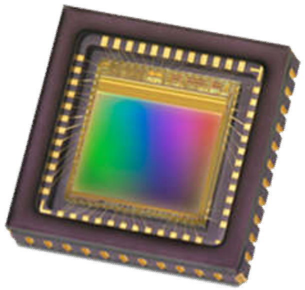
semiconductors are the basis of electronics and photonics



integrated circuits

LEDs

lasers



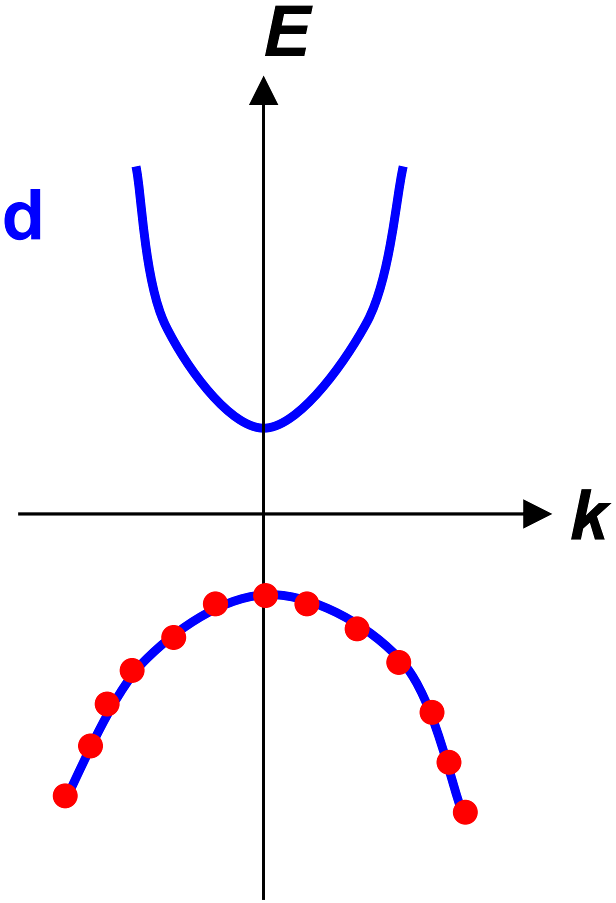
detectors

solar cells

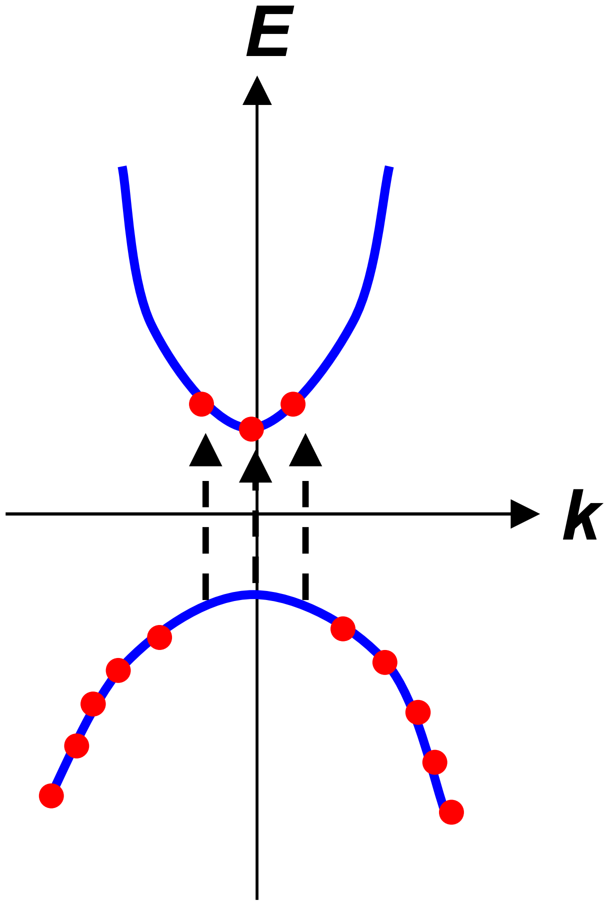
Semiconductor 半导体

conduction band
(CB) 导带

valence band
(VB) 价带



T = 0 K
CB is empty, VB is full
insulator



T > 0 K
thermalization 热激发
CB and VB are partly filled
conductor

Band Structure / Diagram 能带图

Free electrons

energy

$$E(k) = \frac{\hbar^2 k^2}{2m}$$

velocity

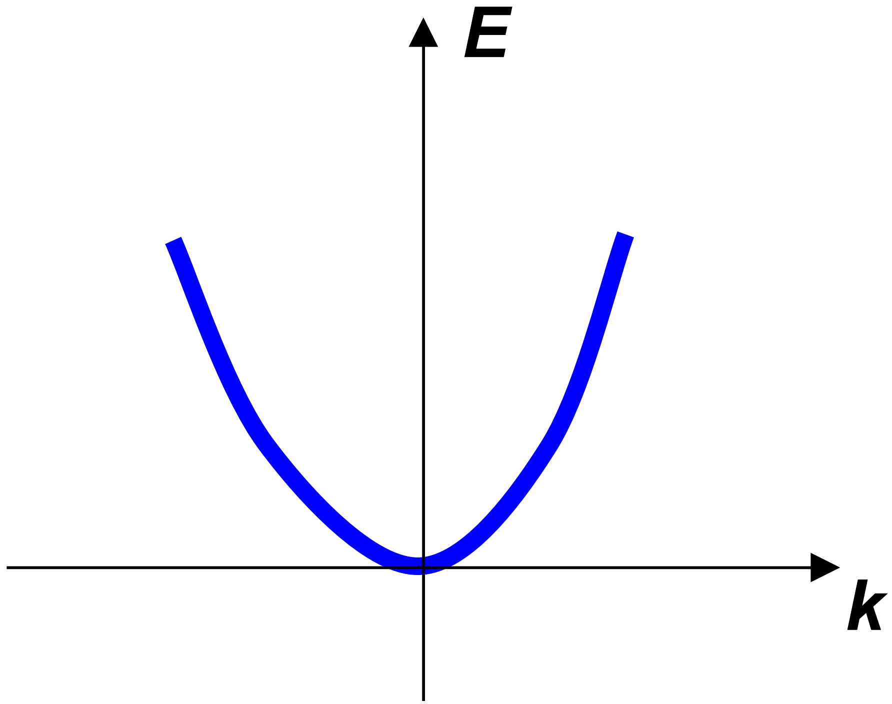
$$v = \frac{\hbar k}{m} = \frac{1}{\hbar}\frac{dE(k)}{dk}$$

momentum

$$p = \hbar k$$

electron mass

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



***E*-*k* diagram**
(energy dispersion curve)

Band Structure / Diagram 能带图

energy $E(k)$

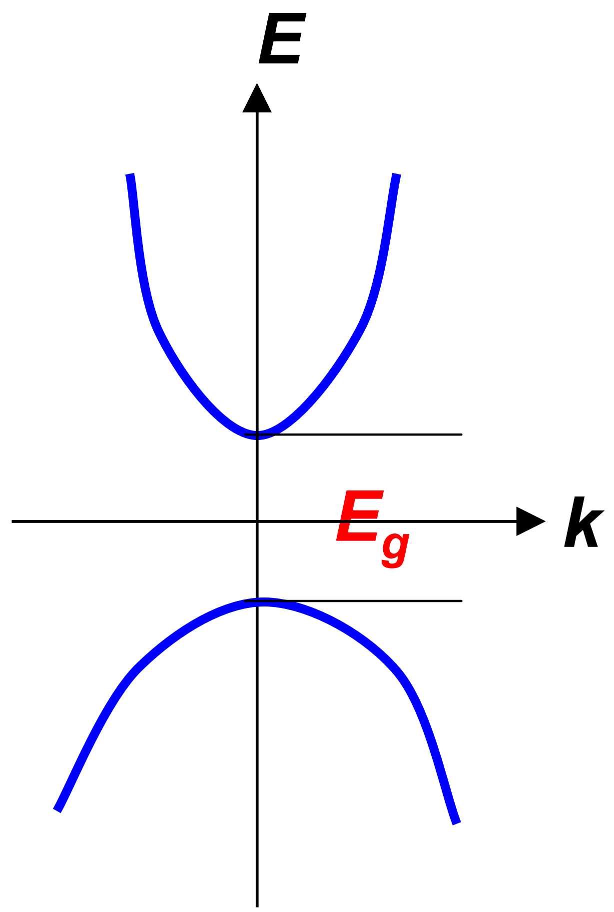
band gap E_g

crystal momentum
(*not* electron momentum) $\hbar k$

group velocity $$v_g = \frac{1}{\hbar}\frac{dE(k)}{dk}$$

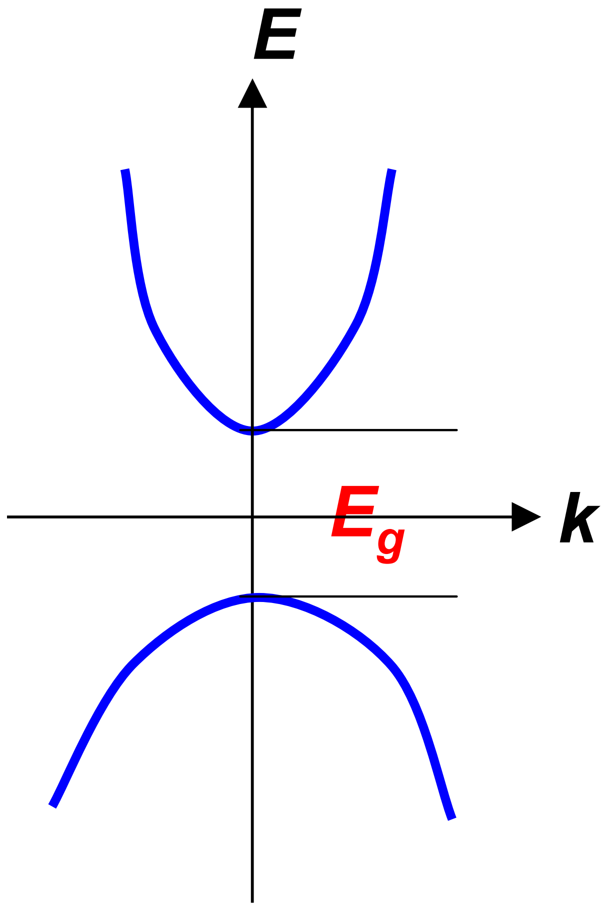
or

$$\mathbf{v} = \frac{1}{\hbar}\nabla_{\mathbf{k}} E(\mathbf{k})$$



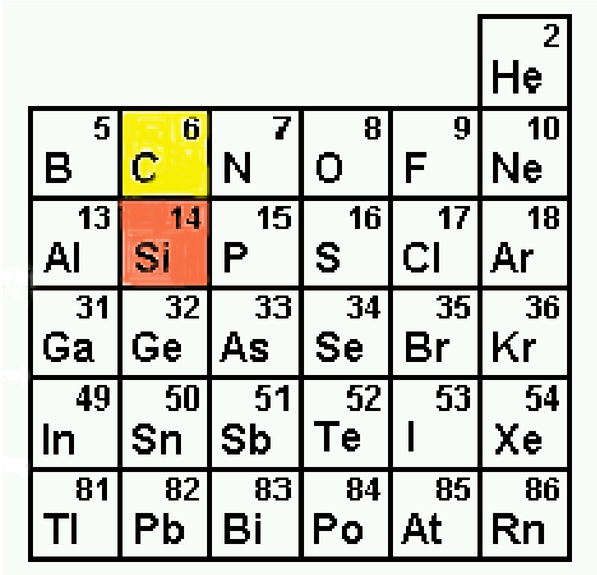
E-k diagram
(energy dispersion curve)

Band Gap E_g



$$E_g = 2V_1$$

the nearly free electron model

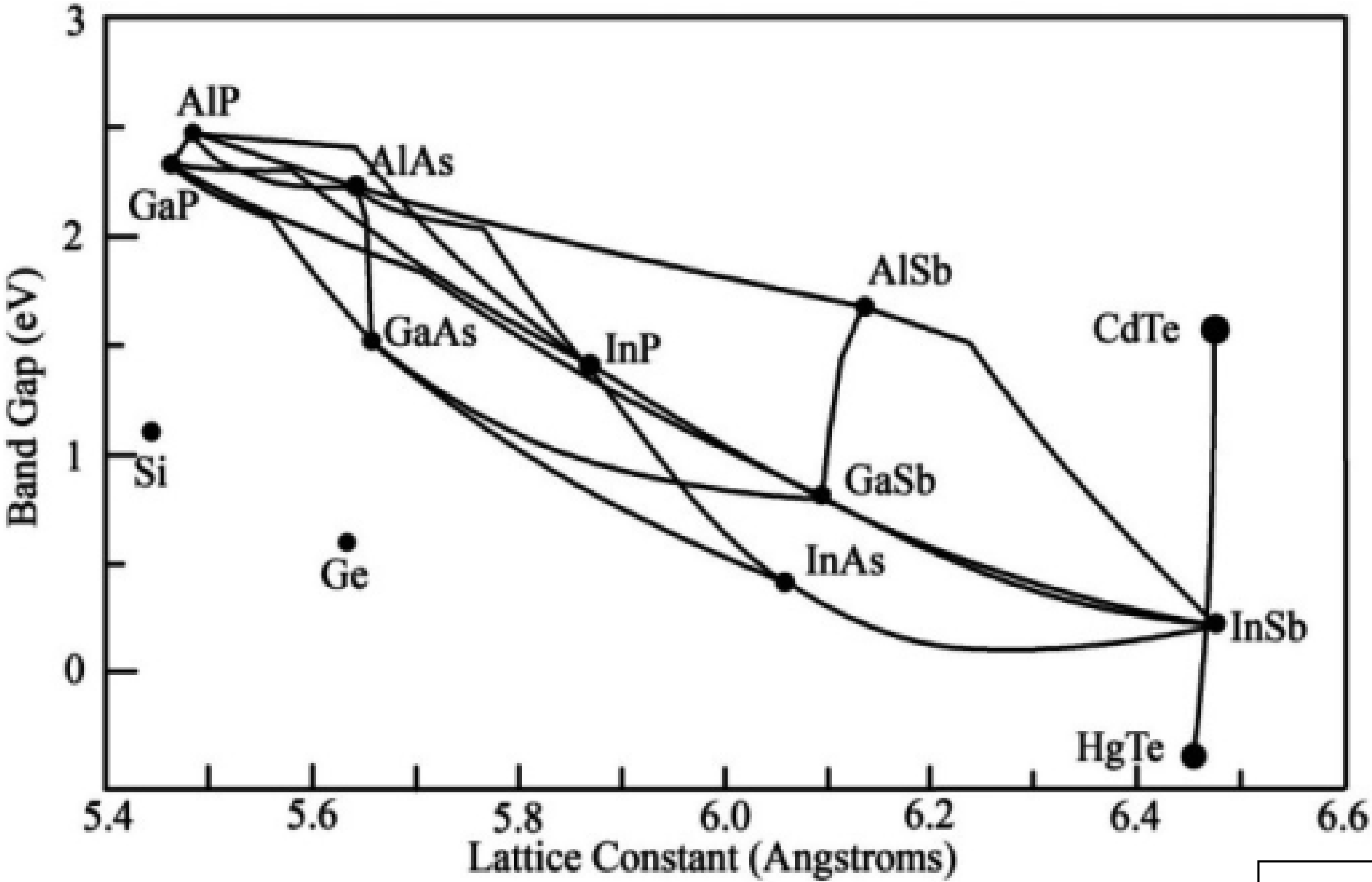


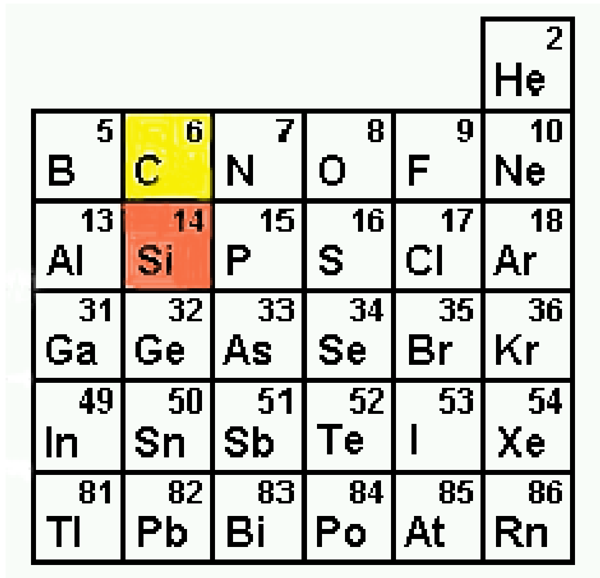
at T = 300 K

	a (Å)	E_g (eV)
C (diamond)	3.57	5.5
Si	5.43	1.1
Ge	5.66	0.66
α-Sn	6.49	0.08

Q: Why?

Band Gap E_g





Si > Ge

AlAs > GaAs > InAs

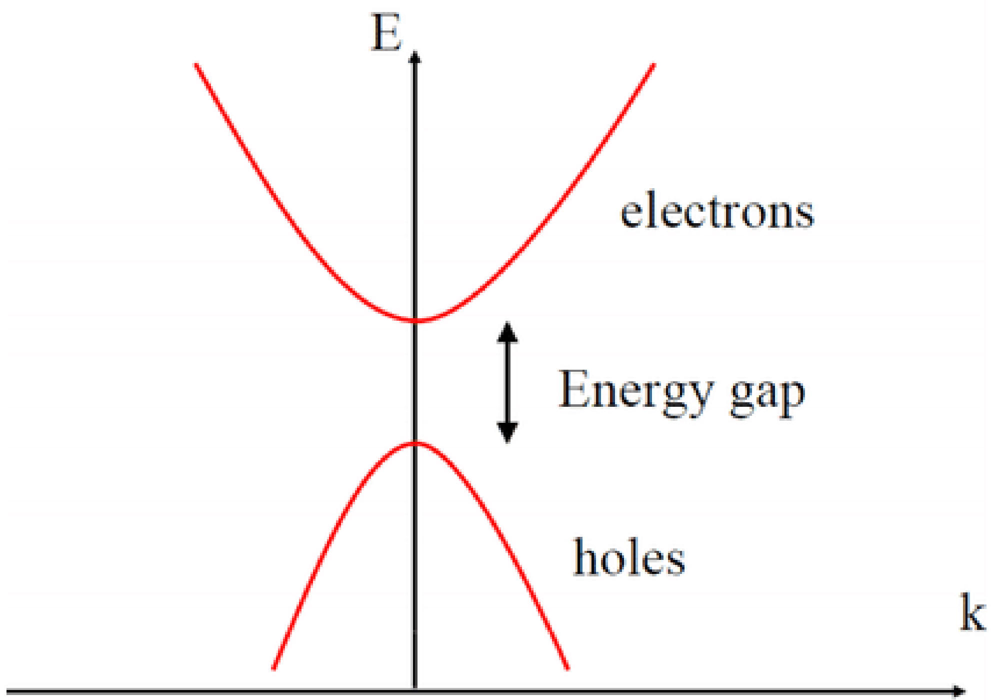
GaP > GaAs > GaSb

larger atoms

-> smaller V_1

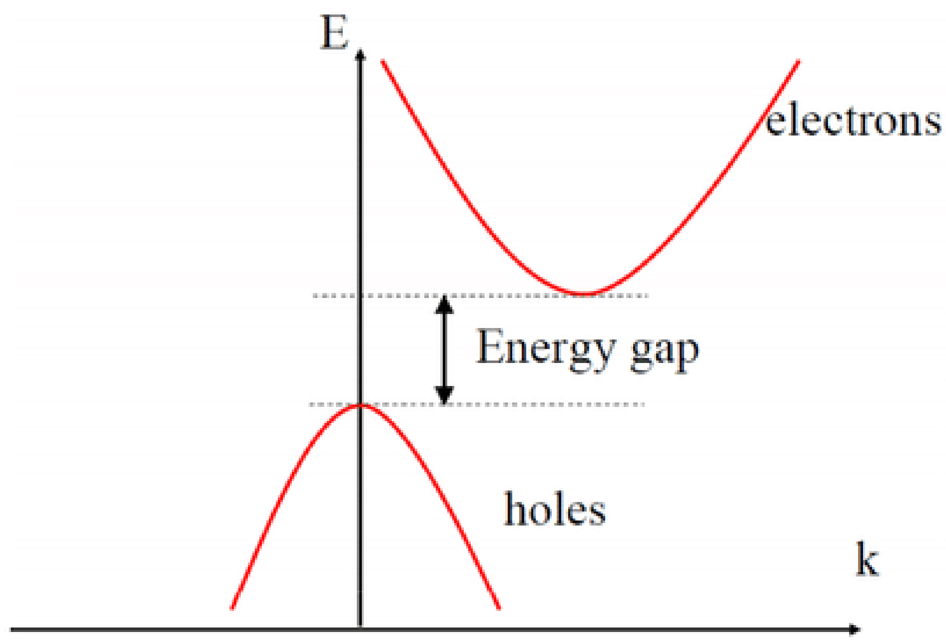
-> smaller E_g

Direct and Indirect Gaps



Direct bandgap semiconductors

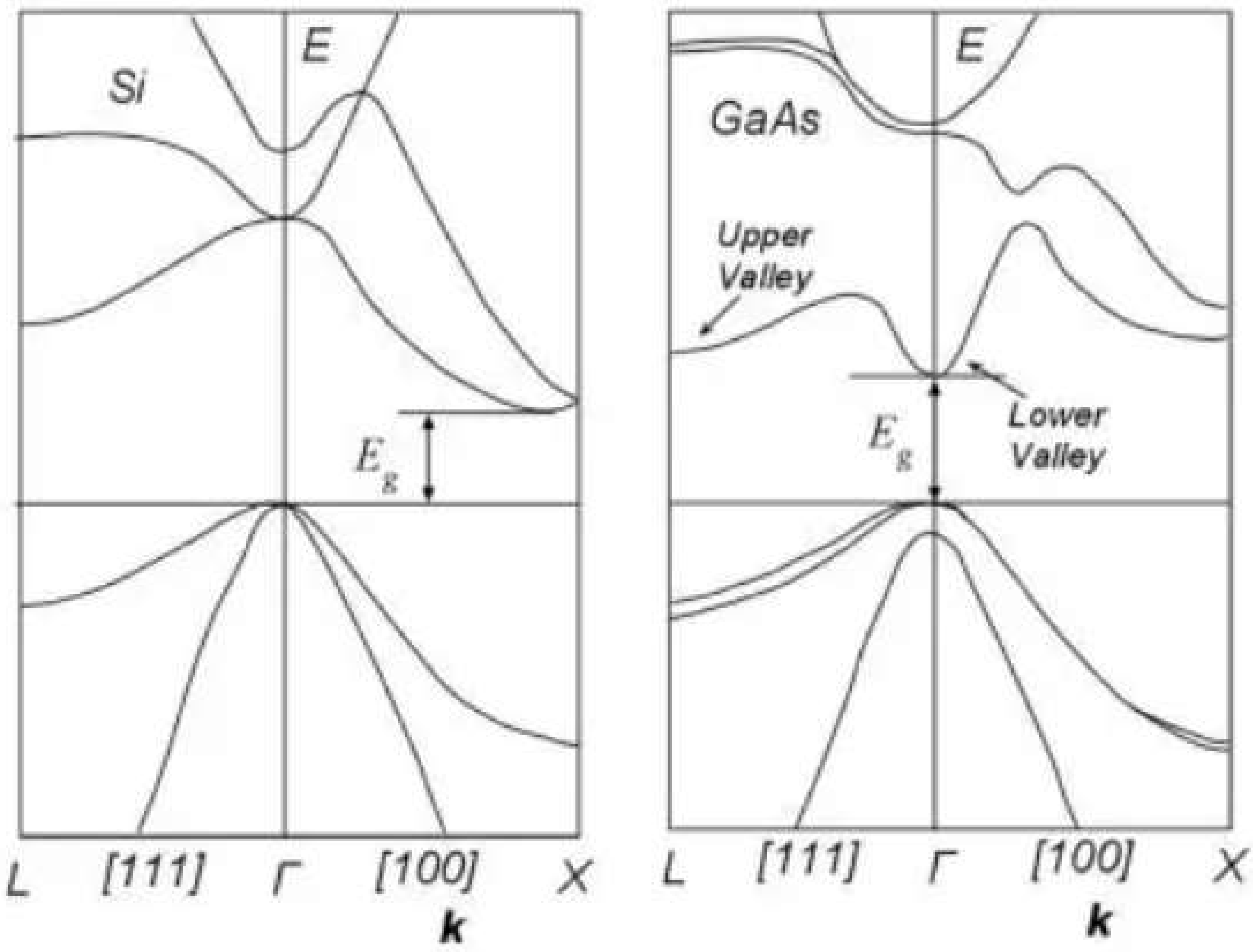
直接带隙



Indirect bandgap semiconductors

间接带隙

Direct and Indirect Gaps



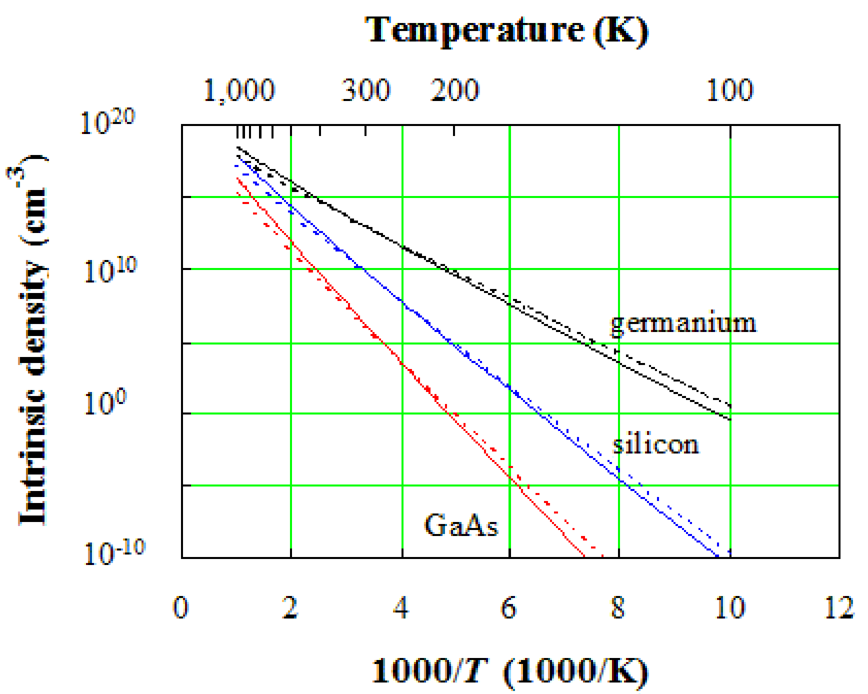
Silicon - indirect **GaAs - direct**

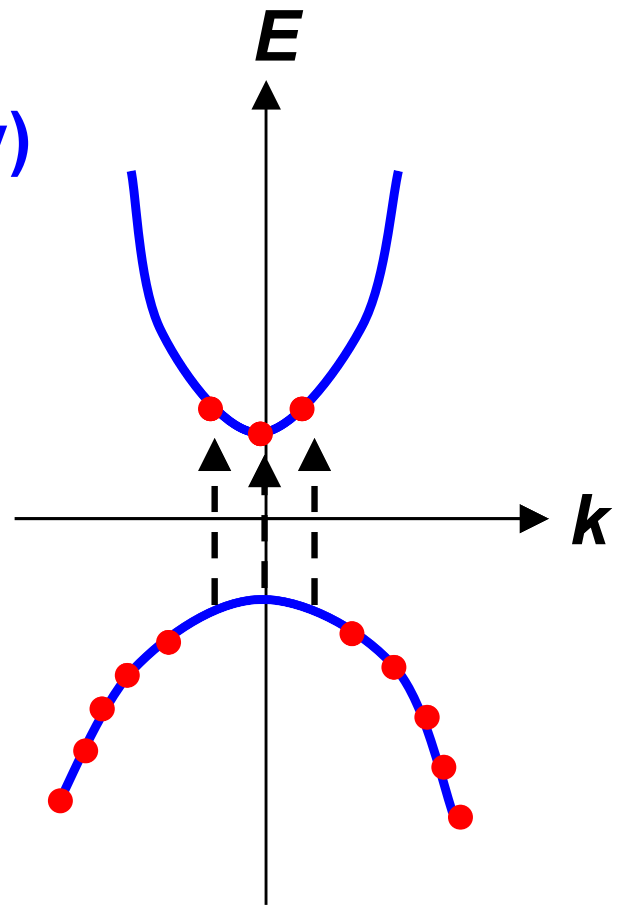
Measurement of Band Gaps

temperature dependence
of carrier concentration (or conductivity)

$$n_i \propto T^{3/2} \cdot e^{-E_g/2k_BT}$$

$$\ln n_i \sim -\frac{E_g}{2k_BT}$$

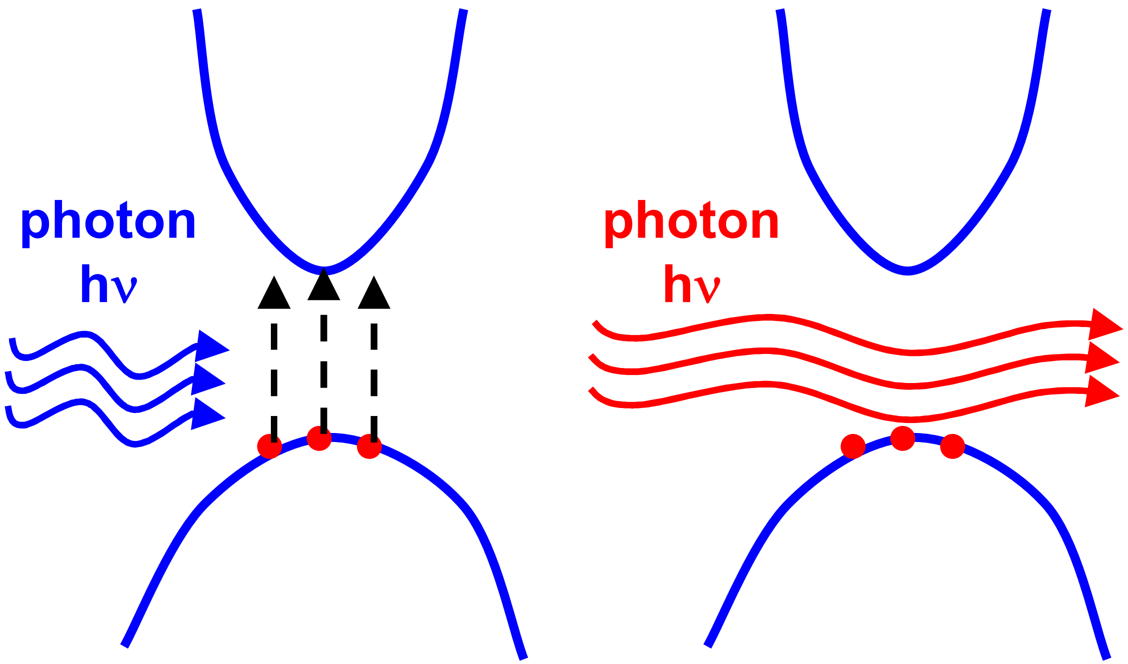




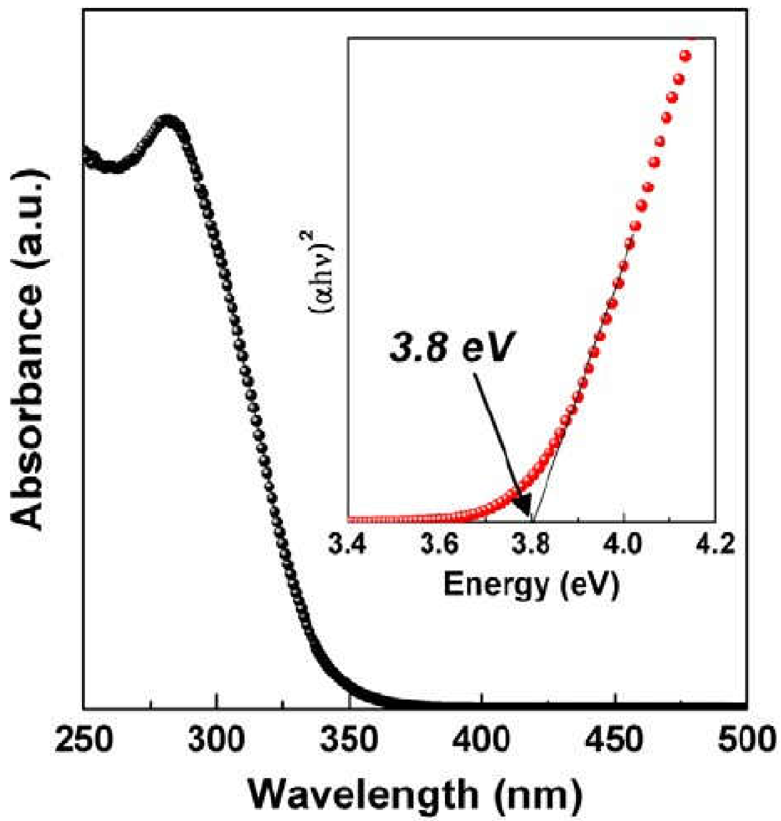
***T* > 0 K**
thermalization 热激发
CB and VB are partly filled
conductor

Measurement of Band Gaps

wavelength dependent optical absorption



Zn_2SnO_4 nanoparticles

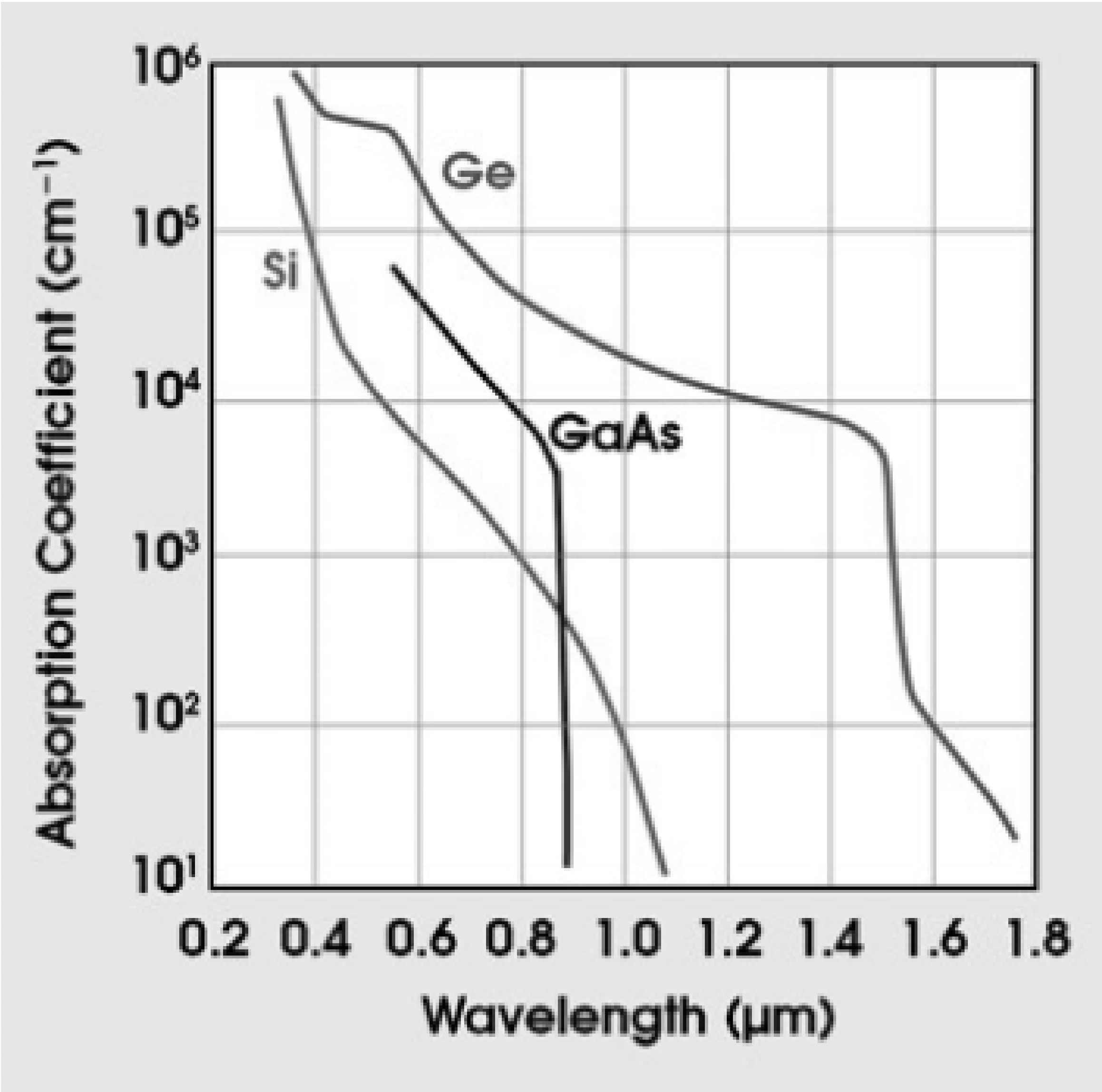


$h\nu > E_g$ ---> light absorption

$h\nu < E_g$ ---> light transmission

D. Kim, *et al*, *Nanoscale* **4,** 557 (2011)

Measurement of Band Gaps



$$E_g = \frac{hc}{\lambda_g} \rightarrow$$

$$E(\text{eV}) = \frac{1240}{\lambda(\text{nm})}$$

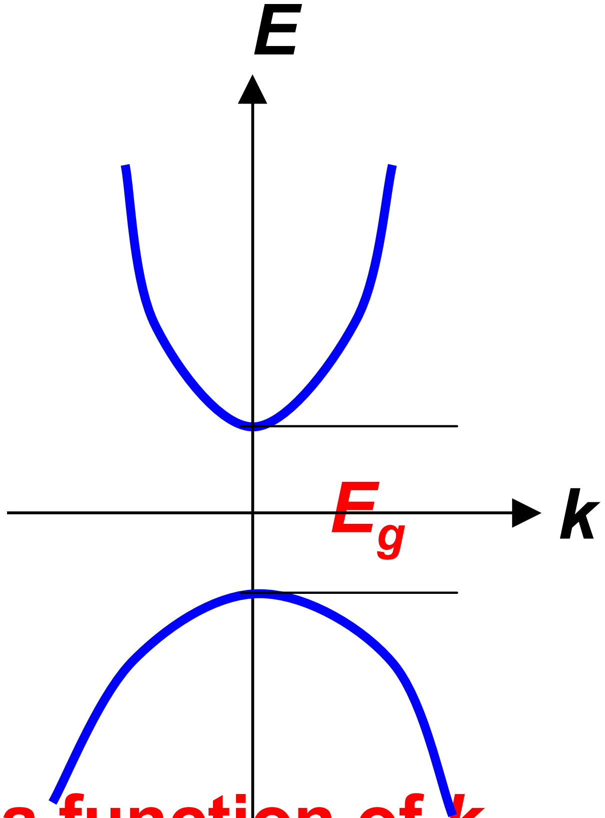
	E_g (eV)
Si	1.1
Ge	0.66
GaAs	1.43

Effective Mass 有效质量

effective mass

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

The mass that an electron "seems" to have in a solid



For 3D solids, a tensor form

$$\frac{1}{\mathbf{M}^*} = \frac{1}{\hbar^2}\begin{pmatrix} \frac{\partial^2 E}{\partial k_x^2} & \frac{\partial^2 E}{\partial k_x \partial k_y} & \frac{\partial^2 E}{\partial k_x \partial k_z} \\ \frac{\partial^2 E}{\partial k_y \partial k_x} & \frac{\partial^2 E}{\partial k_y^2} & \frac{\partial^2 E}{\partial k_y \partial k_z} \\ \frac{\partial^2 E}{\partial k_z \partial k_x} & \frac{\partial^2 E}{\partial k_z \partial k_y} & \frac{\partial^2 E}{\partial k_z^2} \end{pmatrix}$$

m^* is a function of k, can be smaller or larger than m_0, even can be negative

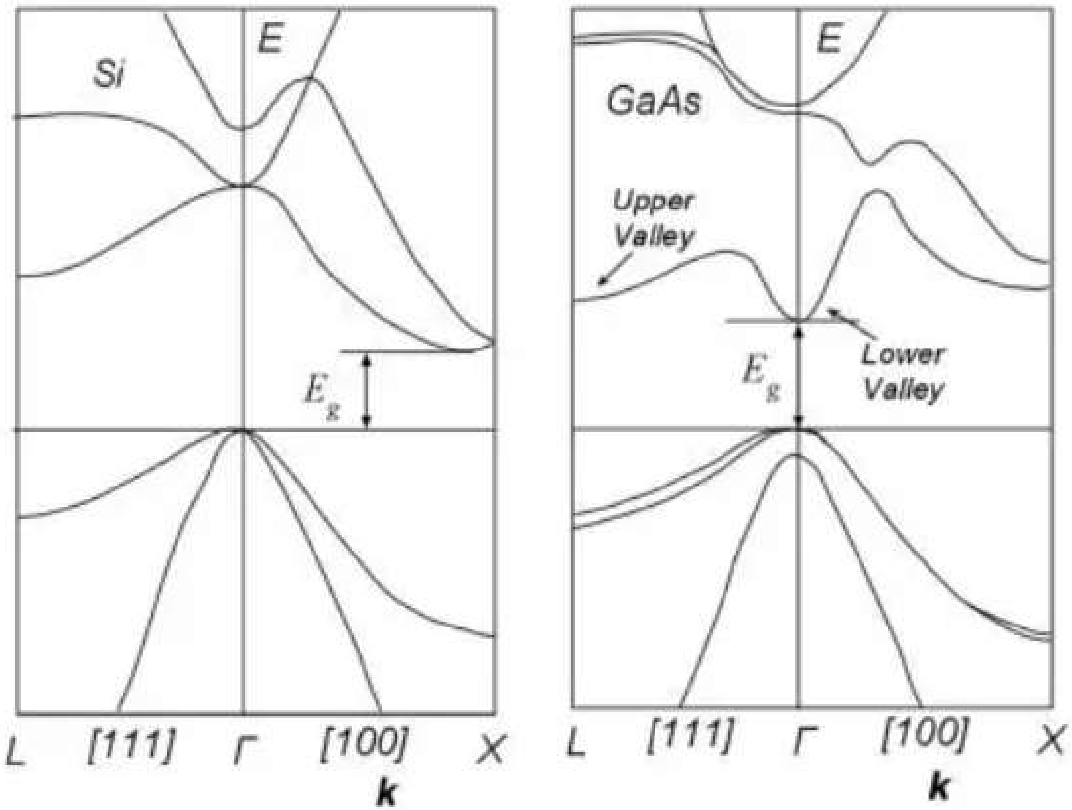
$m_0 = 9.11*10^{-31}$ kg

Effective Mass 有效质量

The actual effective mass is a tensor, depending on the location (k_x, k_y, k_z)

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

Approximation is taken for different calculations.



Effective Mass 有效质量

The actual effective mass is a tensor, depending on the location (k_x, k_y, k_z)

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

Approximation is taken for different calculations:

- Density of states calculations
- Conductivity / mobility calculations

https://ecee.colorado.edu/~bart/book/effmass.htm

Effective Mass 有效质量

The actual effective mass is a tensor, depending on the location (k_x, k_y, k_z)

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

Approximation is taken for different calculations.

	Symbol	Germanium	Silicon	Gallium Arsenide
Smallest energy bandgap at 300 K	E_g (eV)	0.66	1.12	1.424
Effective mass for density of states calculations				
Electrons	$m_{e^*,dos}/m_0$	0.56	1.08	0.067
Holes	$m_{h^*,dos}/m_0$	0.29	0.57/0.81[1]	0.47
Effective mass for conductivity calculations				
Electrons	$m_{e^*,cond}/m_0$	0.12	0.26	0.067
Holes	$m_{h^*,cond}/m_0$	0.21	0.36/0.386[1]	0.34
Free electron mass	m_0 (kg)	9.11×10^{-31}		

Table 2.3.4 Effective masses for both density of states and conductivity calculations.

Effective Mass 有效质量

effective mass

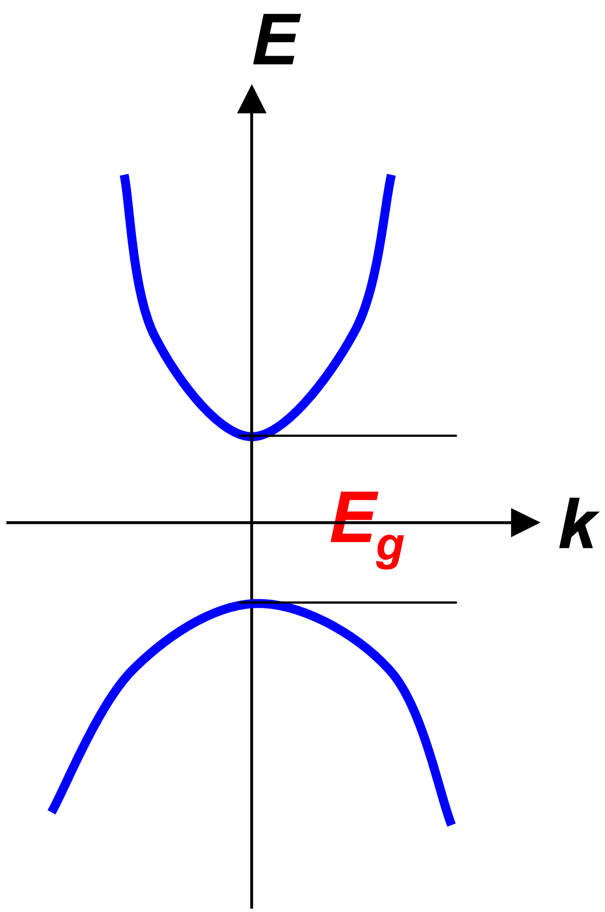
$$\frac{1}{m^*} = \frac{1}{\hbar^2}\frac{d^2E(k)}{dk^2}$$

mobility

$$\mu = \frac{v}{E} = e\frac{\tau}{m^*}$$

conductivity

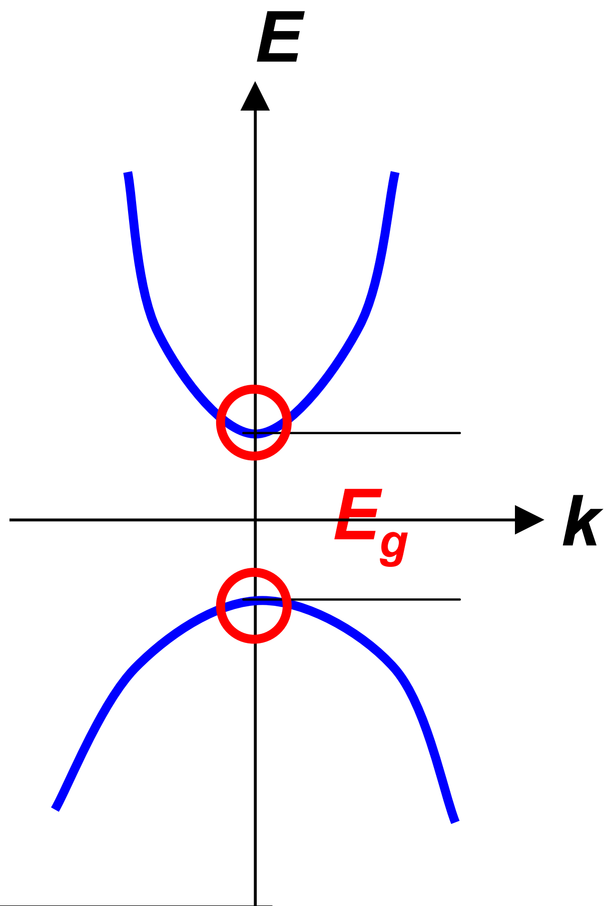
$$\sigma = ne\mu = ne^2\frac{\tau}{m^*}$$



Effective Mass 有效质量

effective mass

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



close to band minimum
parabolic approximation

$$E(k) \approx E_0 + \frac{\hbar^2}{2m^*}(k-k_0)^2$$

3D DOS

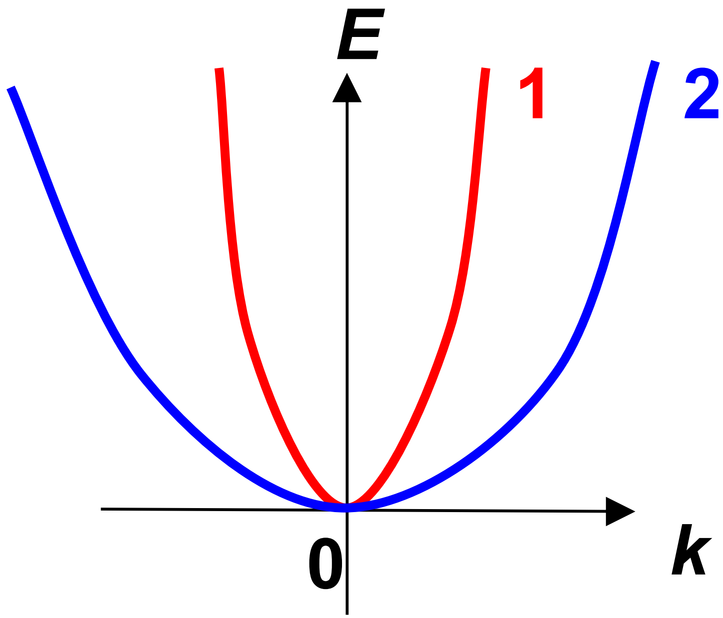
$$g(E) = \frac{dn}{dE} = \frac{1}{2\pi^2}\left(\frac{2m^*}{\hbar^2}\right)^{3/2}(E-E_0)^{1/2}$$

Effective Mass 有效质量

effective mass

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

inverse curvature of the parabolic curve



Q: $m_1 > m_2$ or $m_1 < m_2$?

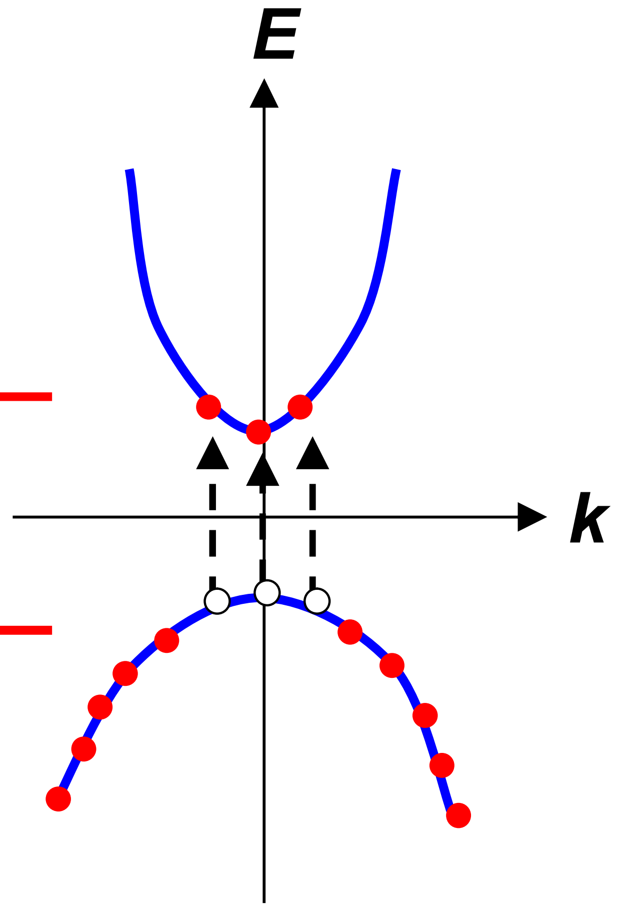
Effective Mass 有效质量

effective mass

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

$m_e^* > 0$

$m_e^* < 0$

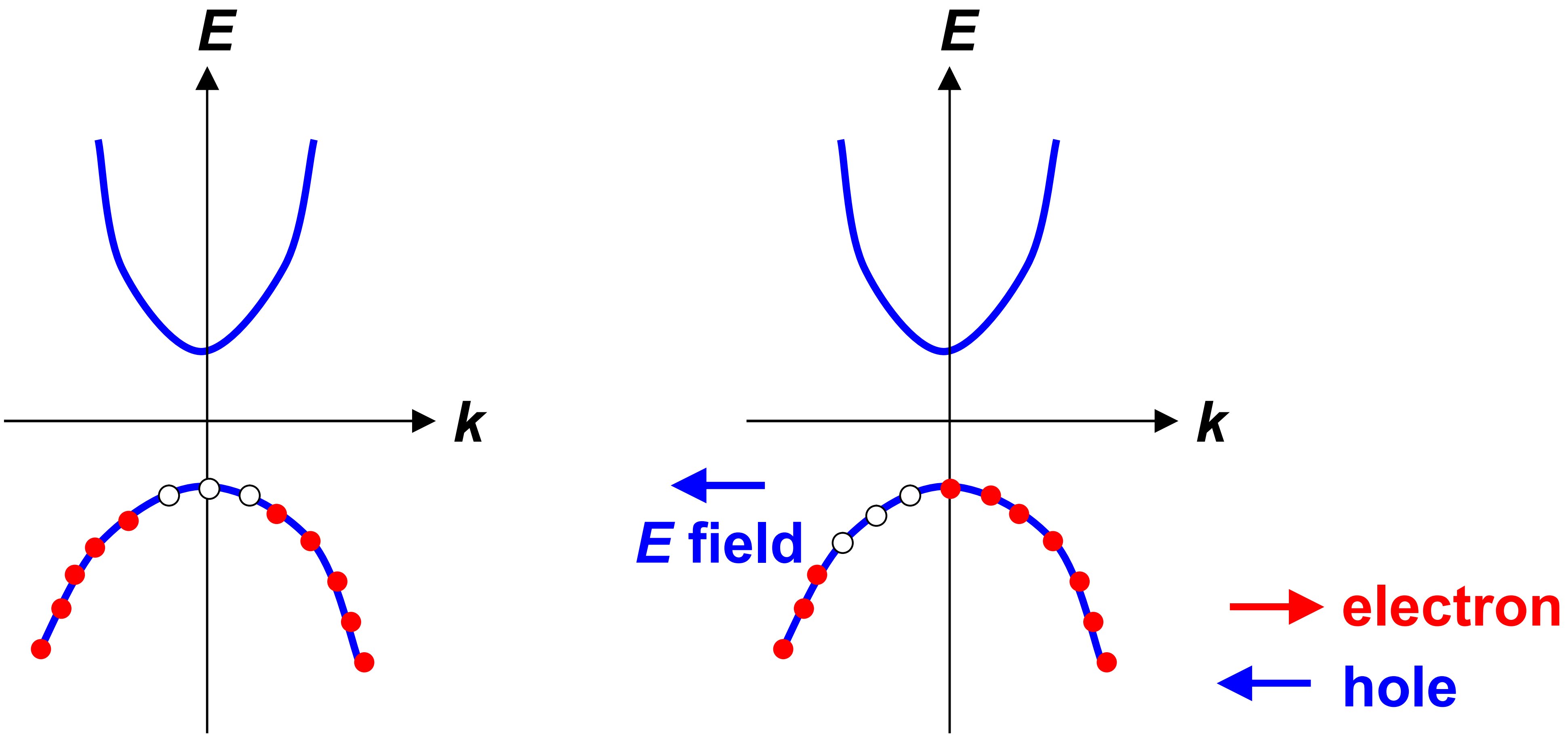


hole 空穴

$$m_h^* = -m_e^*$$

Hole 空穴

We conventionally use *holes* to analyze the electron behaviors in VB



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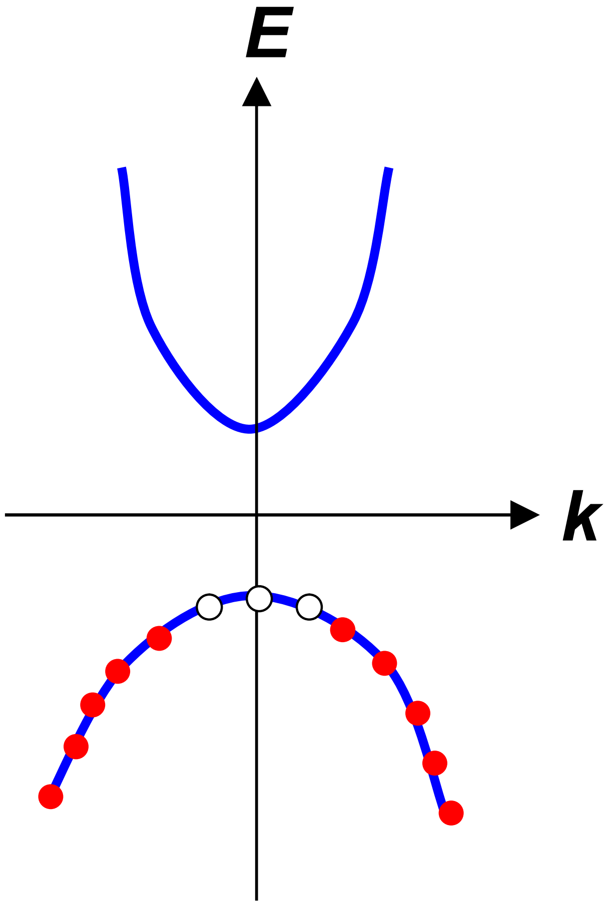

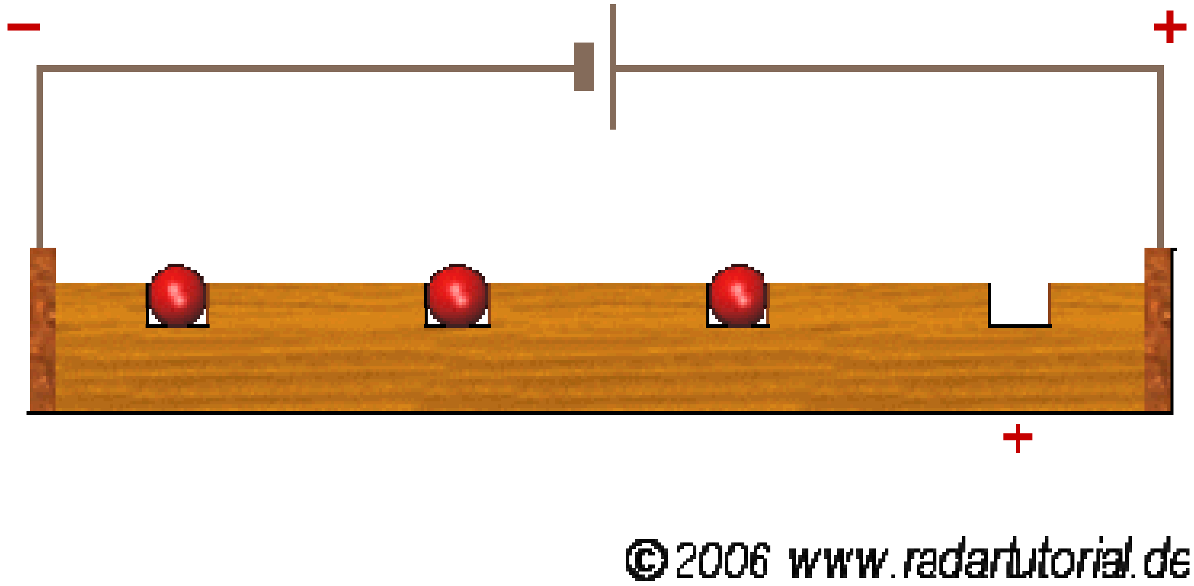

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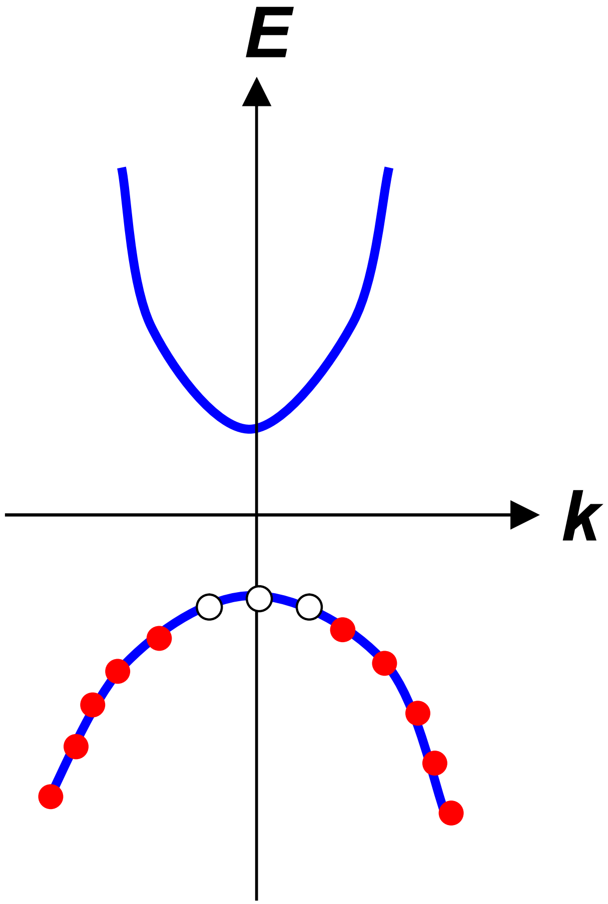
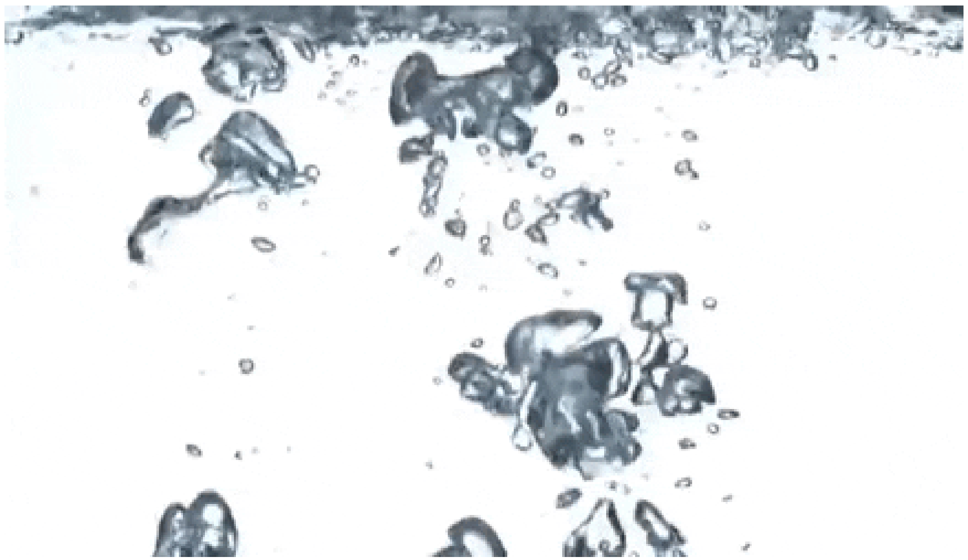
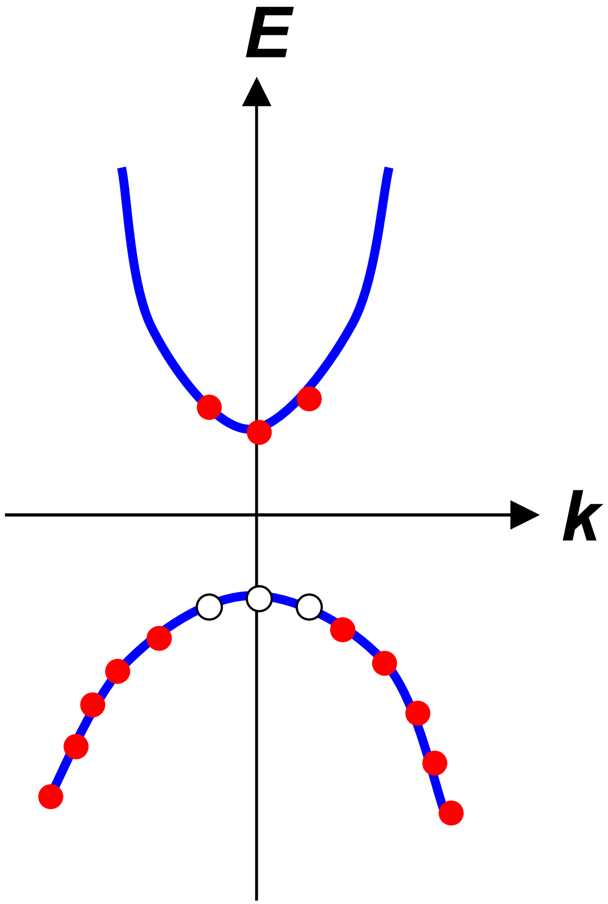




air bubbles in water

Carriers 载流子

Particles that conduct electrical current: electrons in CB and holes in VB



in CB — **electron mobility**

$$\boxed{m_e^* > 0}$$

$$\boxed{\mu_e = \frac{e^2\tau}{m_e^*}}$$

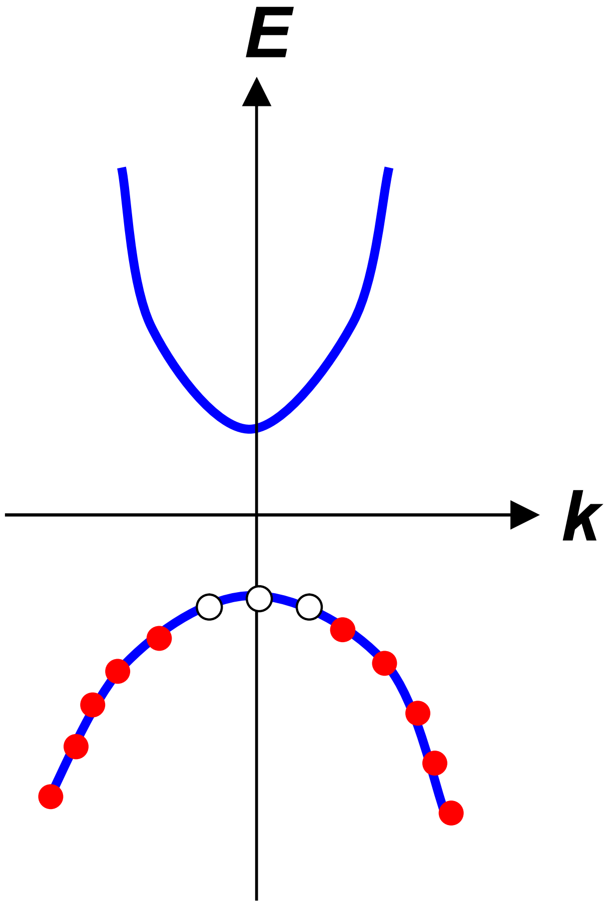
in VB — **hole mobility**

$$\boxed{m_h^* > 0}$$

$$\boxed{\mu_h = \frac{e^2\tau}{m_h^*}}$$

Hole 空穴

We conventionally use *holes* to analyze the electron behaviors in VB



effective mass $m_h^* = -m_e^*$

charge $q_h = -e$

wavevector $\mathbf{k}_h = -\mathbf{k}_e$

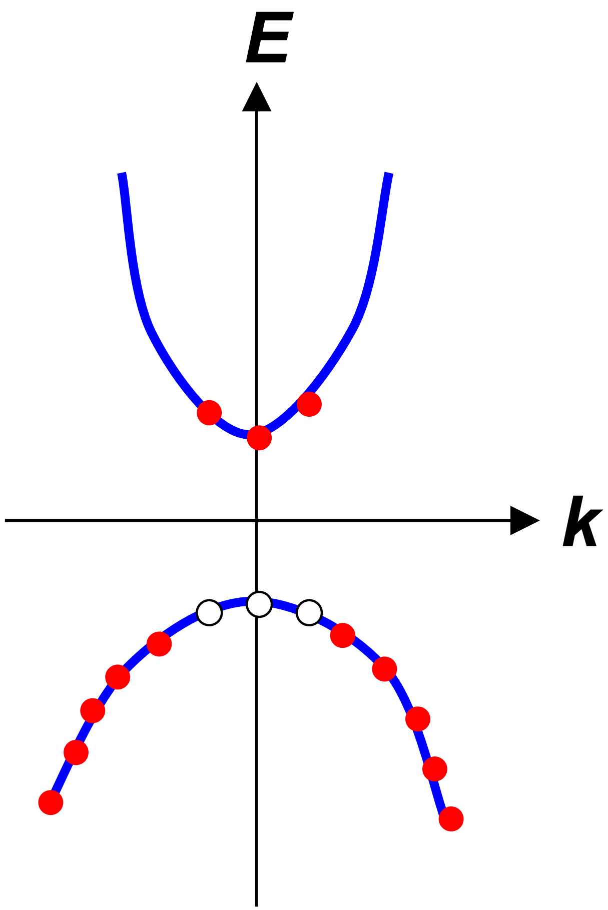
energy $E_h = -E_e$

group velocity $\mathbf{v}_h = \mathbf{v}_e$

Singleton, p45-p46

Carriers 载流子

Particles that conduct electrical current: electrons in CB and holes in VB



Q: How to calculate:
m_e^* in CB
m_h^* in VB?

The Nearly Free Electron Model

$$\begin{vmatrix} \frac{\hbar^2}{2m}(k-g)^2 - E & -V_1 \\ -V_1 & \frac{\hbar^2}{2m}k^2 - E \end{vmatrix} = 0$$

$$\rightarrow \quad \left[\frac{\hbar^2}{2m}(k-g)^2 - E\right]\left[\frac{\hbar^2}{2m}k^2 - E\right] - V_1^2 = 0$$

$$\rightarrow \quad \boxed{E_1(k), E_2(k)}$$

The Nearly Free Electron Model

Nearly Free electron → $V_1 \neq 0$ **and** $V_1 \ll \frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2$

$$\left[\frac{\hbar^2}{2m}(k-g)^2 - E\right]\left[\frac{\hbar^2}{2m}k^2 - E\right] - V_1^2 = 0$$

→ $$E_{\pm}(k) = \frac{(A+B) \pm \sqrt{(A-B)^2 + 4V_1^2}}{2}$$

$$A = \frac{\hbar^2}{2m}k^2 \qquad B = \frac{\hbar^2}{2m}(k-g)^2$$

The Nearly Free Electron Model

Nearly Free electron → $\boxed{V_1 \neq 0}$ **and** $\boxed{V_1 \ll \frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2}$

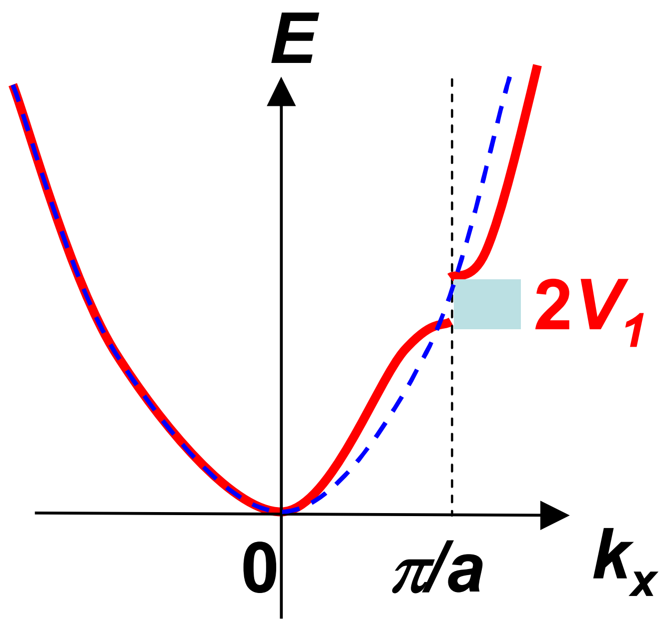
$$\left[\frac{\hbar^2}{2m}(k-g)^2 - E\right]\left[\frac{\hbar^2}{2m}k^2 - E\right] - V_1^2 = 0$$

when $k = \pi/a$

→

$$E_+\left(k = \frac{\pi}{a}\right) = \frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2 + |V_1|$$

$$E_-\left(k = \frac{\pi}{a}\right) = \frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2 - |V_1|$$



Band Gap!

The Nearly Free Electron Model

Nearly Free electron → $V_1 \neq 0$

$$\left[\frac{\hbar^2}{2m}(k-g)^2 - E\right]\left[\frac{\hbar^2}{2m}k^2 - E\right] - V_1^2 = 0$$

when $k \sim \pi/a$, $(A-B) \sim 0$, take the first order approximation

$$E_\pm(k) = \frac{(A+B) \pm \sqrt{(A-B)^2 + 4V_1^2}}{2}$$

$$\rightarrow \quad E_\pm(k) \approx \frac{A+B}{2} \pm V_1\left[1 + \frac{1}{2}\frac{(A-B)^2}{4V_1^2}\right]$$

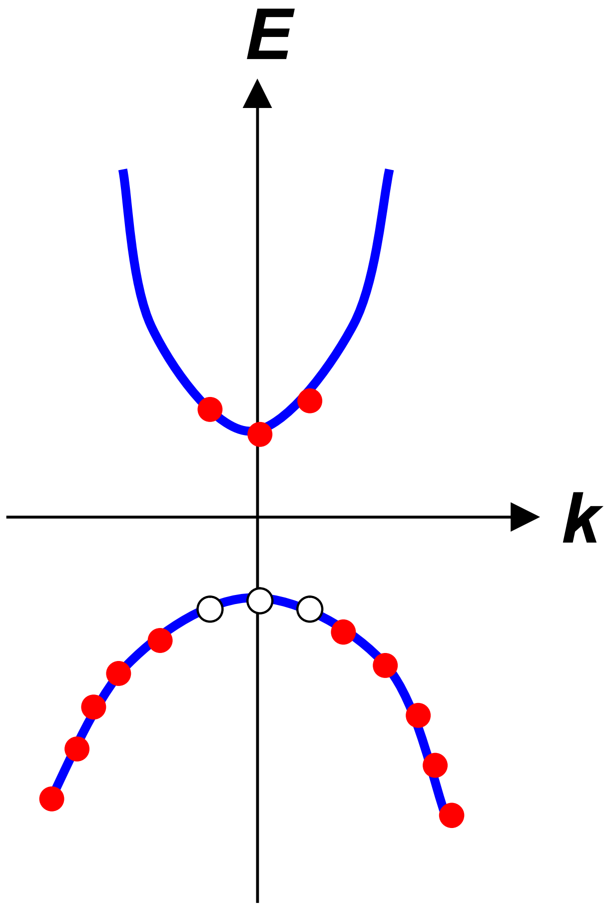
Effective Mass 有效质量

$$E_{\pm}(k) \approx \frac{A+B}{2} \pm V_1\left[1+\frac{1}{2}\frac{(A-B)^2}{4V_1^2}\right]$$

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

$$\begin{cases} \dfrac{m_e^*}{m_0} \approx \dfrac{1}{C/V_1+1} \\ \dfrac{m_h^*}{m_0} \approx \dfrac{1}{C/V_1-1} \end{cases}$$

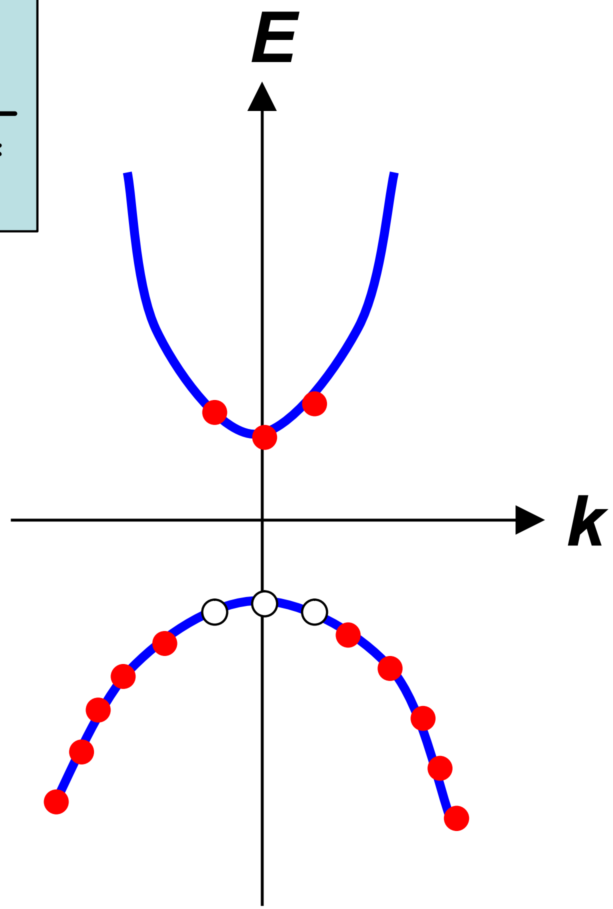
$$C = \frac{\hbar^2 g^2}{4m}$$



Effective Mass 有效质量

$$\begin{cases} \dfrac{m_e^*}{m_0} \approx \dfrac{1}{C/V_1+1} \\ \dfrac{m_h^*}{m_0} \approx \dfrac{1}{C/V_1-1} \end{cases}$$

$$\mu = e\frac{\tau}{m^*}$$



For many semiconductors, V_1 is very small (C/V_1 ~ 1–10)

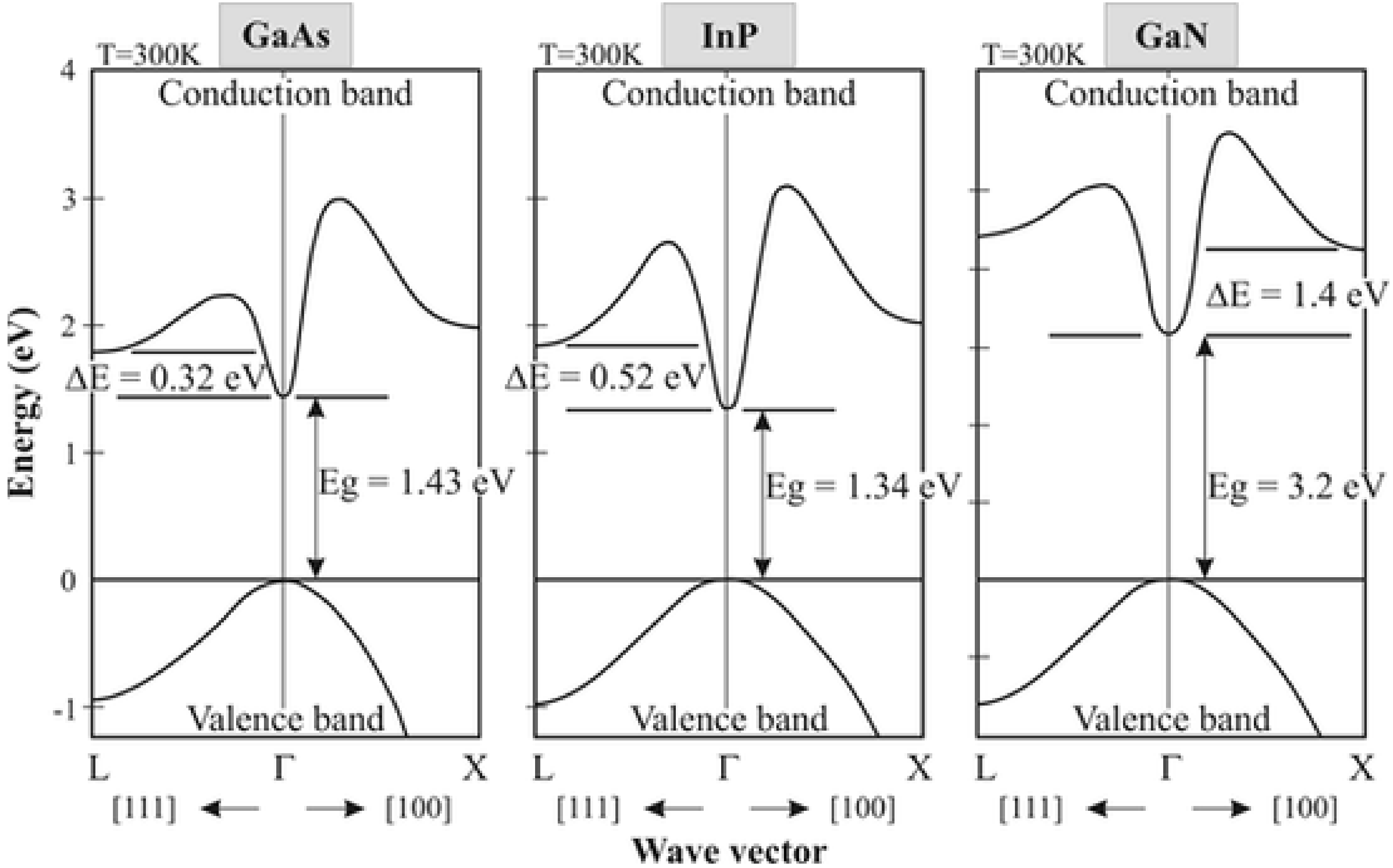
$$\rightarrow \boxed{m_e^* < m_h^* < m_0}$$

- Effective mass is smaller than real electron mass m_0

- m_e in CB is smaller than m_h* in VB*

- small V_1 ----> small m ----> large mobility μ*

Examples



m_e* in CB is smaller than m_h* in VB
(electrons have more freedom than holes)

Examples

	a (Å)	E_g (eV)	m_e^* / m_0	m_h^* / m_0	μ_e (cm^2/V/s)	μ_h (cm^2/V/s)
Si	5.43	1.1	0.26	0.38	1350	450
Ge	5.66	0.66	0.12	0.23	3900	1900
-	-	-	-	-	-	-
GaAs	5.65	1.42	0.067	0.45	8500	400
InAs	6.06	0.35	0.022	0.40	33000	450

* effective mass for conductivity

1. large a ----> small V_1 ----> small E_g
   ----> small m^* ----> large mobility μ
2. $m_e^* < m_h^* < m_0$
3. $\mu_e^* > \mu_h^*$

Examples

	a (Å)	E_g (eV)	m_e^* / m_0	m_h^* / m_0	μ_e ($cm^2/V/s$)	μ_h ($cm^2/V/s$)
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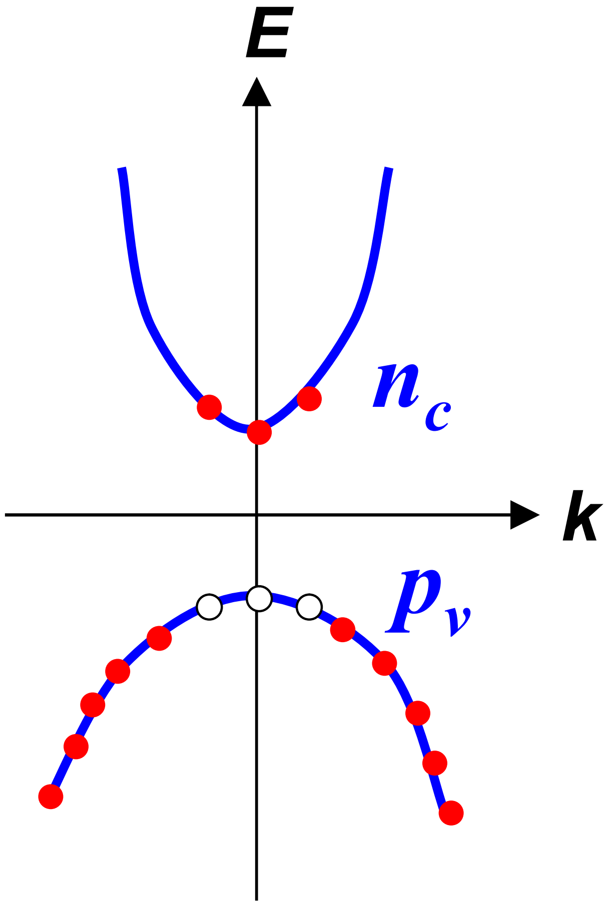
* effective mass for conductivity

larger atoms
----> electrons have more freedom
----> smaller m, move faster*

Carriers 载流子

Particles that conduct electrical current: electrons in CB and holes in VB



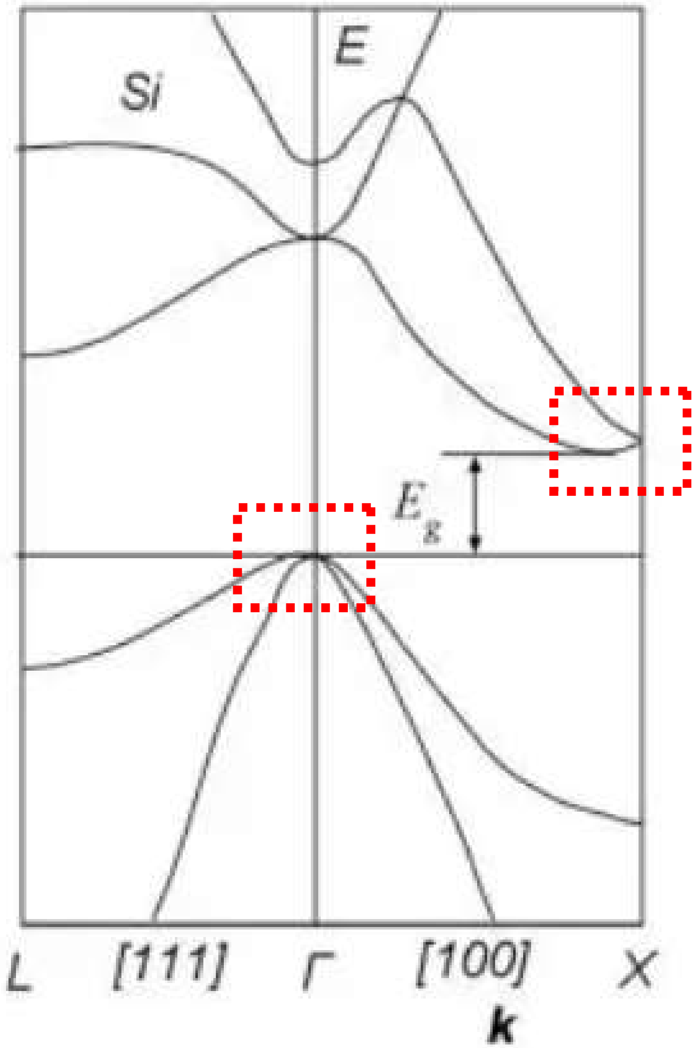
electrical conductivity

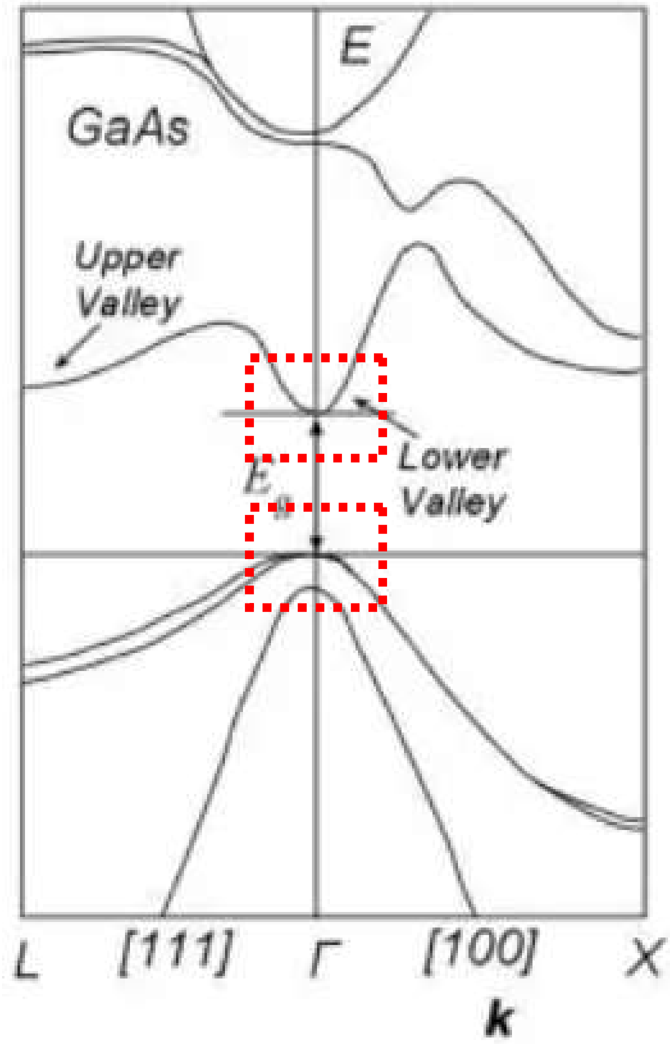
$$\sigma = n_c e\mu_e + p_v e\mu_h$$

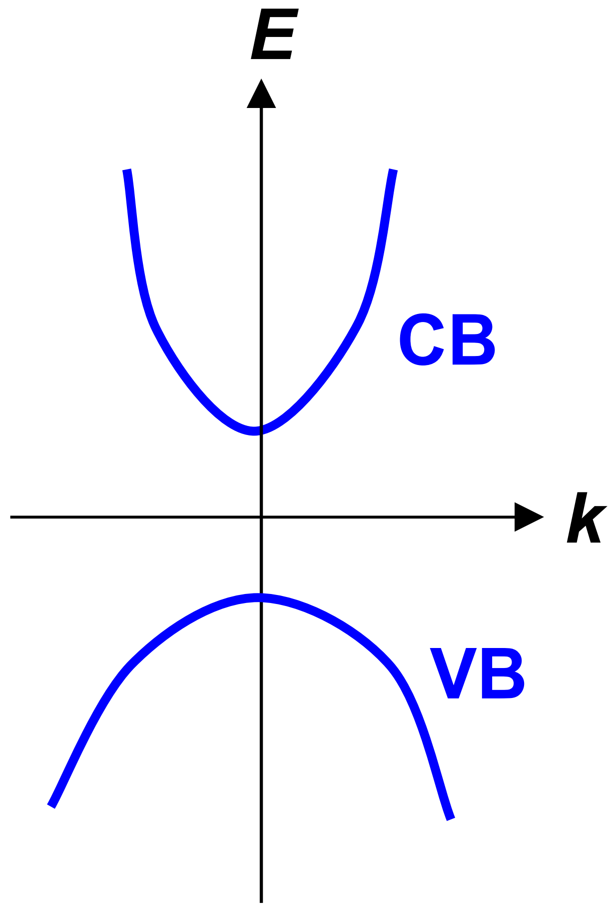
Q: How to calculate carrier densities?

n_c and p_v (#/cm^3)

Band Diagram of Semiconductors







The peaks and valleys of VB and CB can be approximately by *parabolic functions*

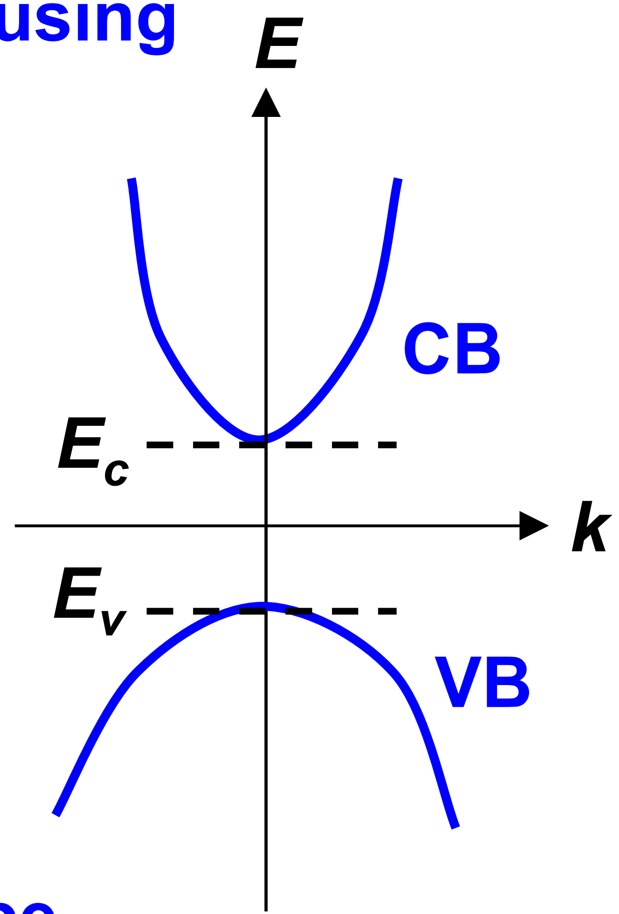
Band Diagram of Semiconductors

electrons and holes can be approximated using
free electron gas
- modify the Sommerfeld Model

$$E_c - E_v = E_g$$

$$E(k) = E_c + \frac{\hbar^2 k^2}{2m_e^*}$$

$$E(k) = E_v - \frac{\hbar^2 k^2}{2m_h^*}$$



The peaks and valleys of VB and CB can be approximately by *parabolic functions*

Q: How many electrons and holes?

Density of States (DOS) 态密度

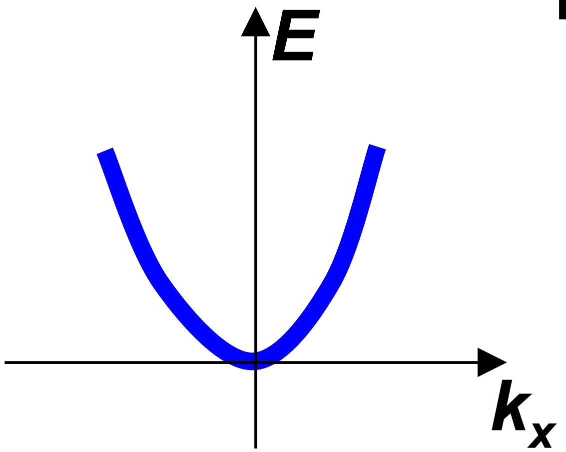
$$g(E)=\frac{dn}{dE}$$

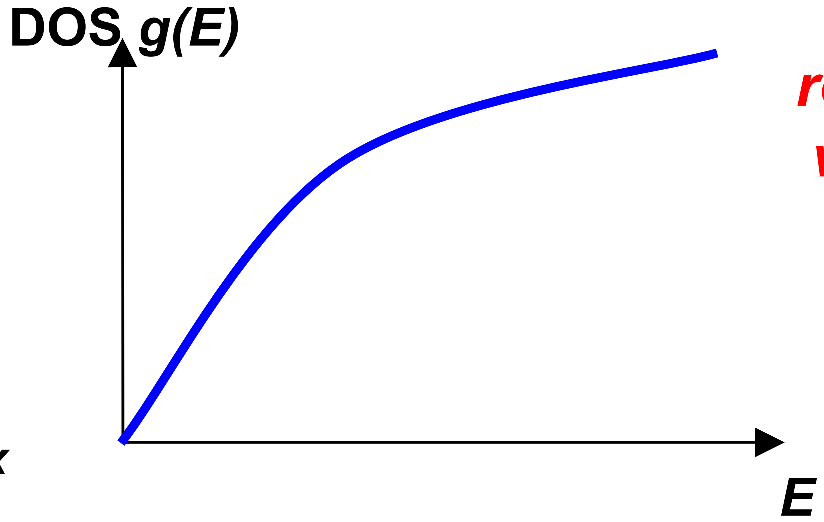
DOS - number of energy states/levels per unit energy in [*E*, *E*+*dE*], per unit volume

free electrons in 3D

$$E=\frac{\hbar^2k^2}{2m_e}$$

$$g(E)=\frac{dn}{dE}=\frac{1}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2}E^{1/2}$$





replace mass m with effective mass m*

See the Sommerfeld Model

Density of States (DOS) 态密度

$$g(E) = \frac{dn}{dE}$$

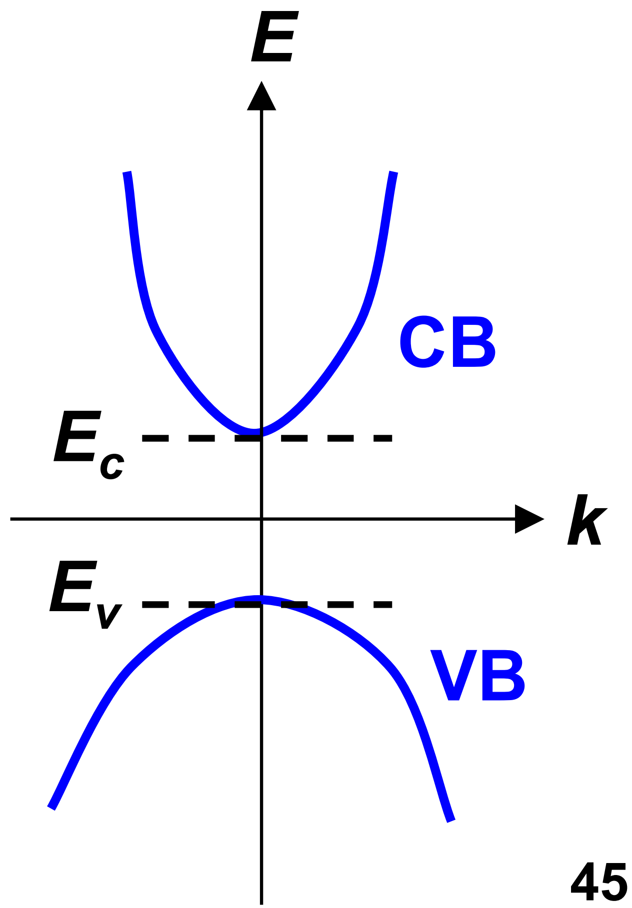
DOS - number of energy states/levels per unit energy in [*E*, *E+dE*], per unit volume

DOS for electrons in CB

$$g_c(E) = \frac{1}{2\pi^2}\left(\frac{2m_e^*}{\hbar^2}\right)^{3/2}(E - E_c)^{1/2}$$

DOS for holes in VB

$$g_v(E) = \frac{1}{2\pi^2}\left(\frac{2m_h^*}{\hbar^2}\right)^{3/2}(E_v - E)^{1/2}$$



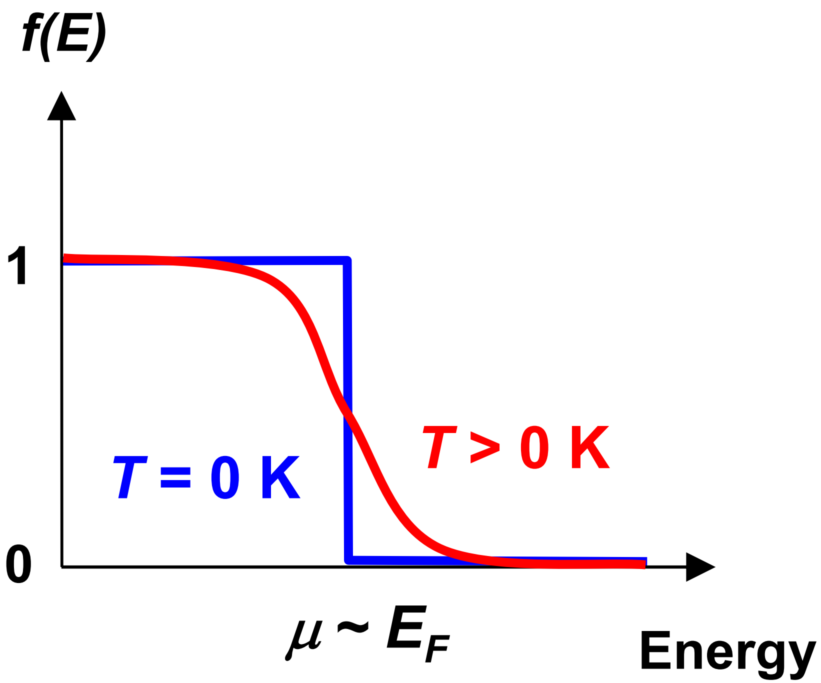
Density of Carriers

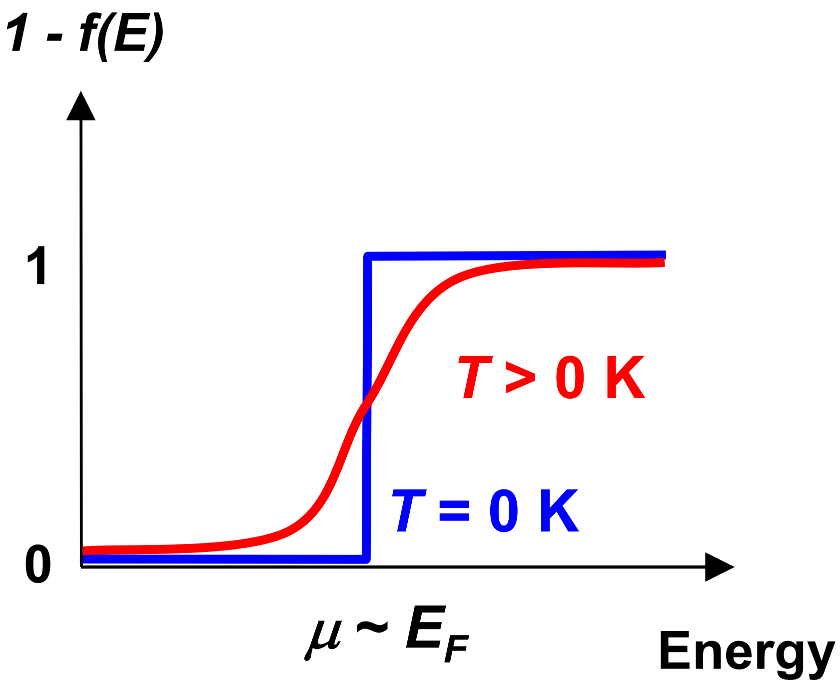
Density of electrons = DOS * probability f

Density of holes = DOS * $(1-f)$

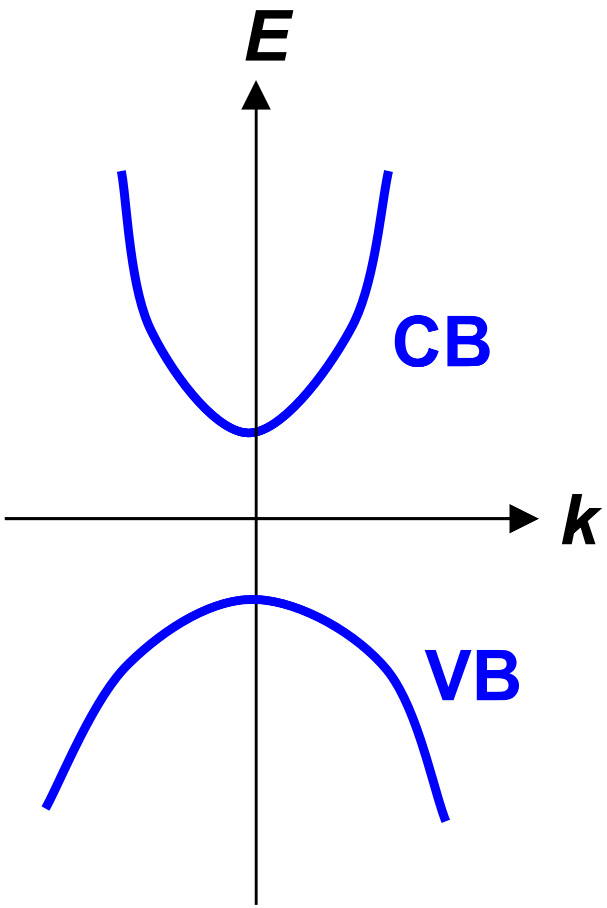
$$f(E)=\frac{1}{e^{(E-\mu)/k_BT}+1}$$

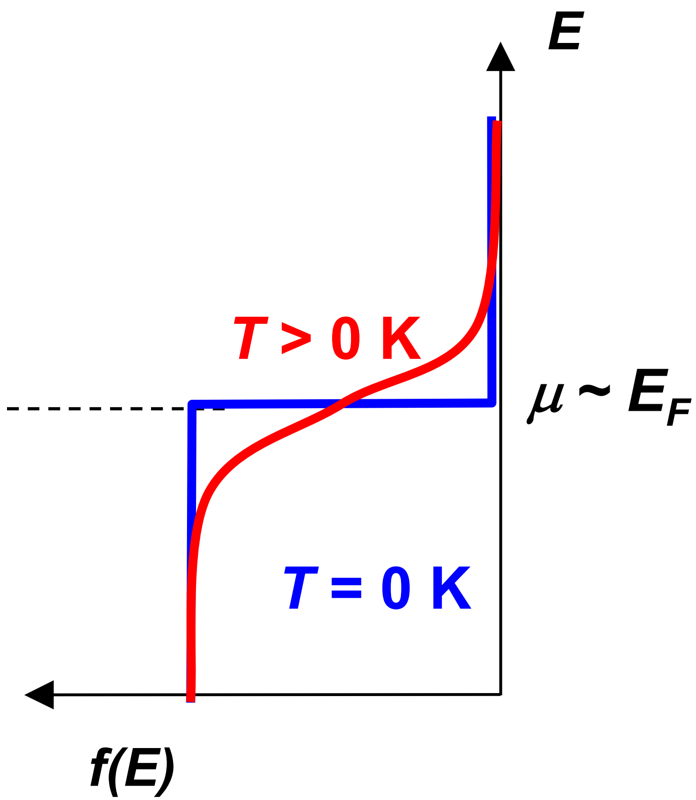
$$1-f(E)=1-\frac{1}{e^{(E-\mu)/k_BT}+1}=\frac{1}{e^{(\mu-E)/k_BT}+1}$$





Density of Carriers





For pure semiconductors (intrinsic), the chemical potential μ (Fermi level E_F) lie within the band gap.

Fermi Energy E_F - A Little Note

In metals, Fermi energy/level E_F is the highest occupied state of electrons at $T = 0$ K.

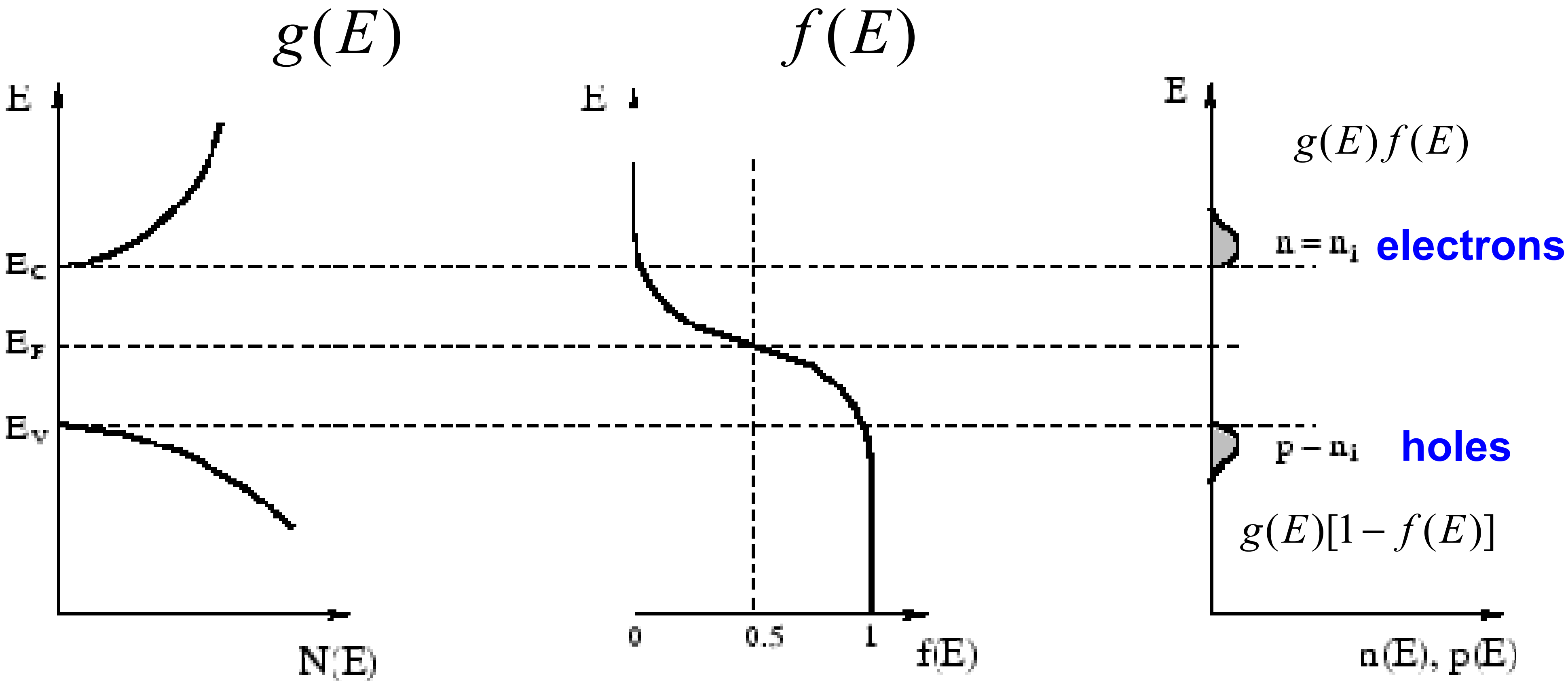
In semiconductors, Fermi energy/level E_F is referred to the chemical potential μ, which is inside the gap. No electrons at E_F !

"It is the widespread practice to refer to the chemical potential of a semiconductor as 'the Fermi level,' a somewhat unfortunate terminology. ... The term 'Fermi level' should be regarded as nothing more than a synonym for 'chemical potential,' in the context of semiconductors.

---- Ashcroft & Mermin, p573

Number of Carriers = DOS * Probability

Intrinsic



DOS

electron probability

carriers

Density of Carriers

electrons in CB

$$n_c = \int_{E_c}^{+\infty} g_c(E) \cdot f(E) dE$$

If μ is in the gap, assume

$$E_c - \mu \gg k_B T$$

$$\rightarrow \quad f(E) = \frac{1}{e^{(E-\mu)/k_B T} + 1} \approx e^{-(E-\mu)/k_B T}$$

holes in VB

$$p_v = \int_{-\infty}^{E_v} g_v(E) \cdot [1 - f(E)] dE$$

$$\mu - E_v \gg k_B T$$

$$\rightarrow \quad 1 - f(E) = \frac{1}{e^{(\mu-E)/k_B T} + 1} \approx e^{-(\mu-E)/k_B T}$$

Non-Degenerate semiconductors (非简并半导体):
Fermi-Dirac is approximated by Maxwell-Boltzmann distribution
not valid for high temperature or small band gap

Density of Carriers

electrons in CB

$$n_c = \int_{E_c}^{+\infty} g_c(E)\cdot f(E)dE$$

$$= \int_{E_c}^{+\infty} \frac{1}{2\pi^2}\left(\frac{2m_e^*}{\hbar^2}\right)^{3/2} (E-E_c)^{1/2}\cdot e^{-(E-\mu)/k_BT}dE$$

$$= \frac{1}{4}\left(\frac{2m_e^* k_B T}{\pi\hbar^2}\right)^{3/2} e^{-(E_c-\mu)/k_BT}$$

$$= N_c(T)e^{-(E_c-\mu)/k_BT}$$

$$N_c(T) = \frac{1}{4}\left(\frac{2m_e^* k_B T}{\pi\hbar^2}\right)^{3/2} = 2.5\left(\frac{m_e^*}{m_0}\right)^{3/2}\left(\frac{T}{300\ \mathrm{K}}\right)^{3/2}\times 10^{19}\ \mathrm{cm}^{-3}$$

Density of Carriers

note here we use the integral

$$\int_0^{+\infty} x^{1/2} \cdot e^{-x/a} dx = \frac{\sqrt{\pi}}{2} a^{3/2}$$

so

$$\int_{E_c}^{+\infty} (E - E_c)^{1/2} \cdot e^{-(E-\mu)/k_B T} dE$$
$$= \frac{\sqrt{\pi}}{2} (k_B T)^{3/2} e^{-(E_c-\mu)/k_B T}$$

Density of Carriers

holes in VB

$$p_v = \int_{-\infty}^{E_v} g_v(E) \cdot [1 - f(E)] dE$$

$$= \int_{-\infty}^{E_v} \frac{1}{2\pi^2} \left(\frac{2m_h^*}{\hbar^2} \right)^{3/2} (E_v - E)^{1/2} \cdot e^{-(\mu - E)/k_B T} dE$$

$$= \frac{1}{4} \left(\frac{2m_h^* k_B T}{\pi \hbar^2} \right)^{3/2} e^{-(\mu - E_v)/k_B T}$$

$$= P_v(T) e^{-(\mu - E_v)/k_B T}$$

$$P_v(T) = \frac{1}{4} \left(\frac{2m_h^* k_B T}{\pi \hbar^2} \right)^{3/2} = 2.5 \left(\frac{m_h^*}{m_0} \right)^{3/2} \left(\frac{T}{300\ \mathrm{K}} \right)^{3/2} \times 10^{19}\ \mathrm{cm}^{-3}$$

Density of Carriers

$$N_c(T) = \frac{1}{4}\left(\frac{2m_e^* k_B T}{\pi\hbar^2}\right)^{3/2} = 2.5\left(\frac{m_e^*}{m_0}\right)^{3/2}\left(\frac{T}{300\ \mathrm{K}}\right)^{3/2} \times 10^{19}\ \mathrm{cm}^{-3}$$

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effective density of states (有效态密度)

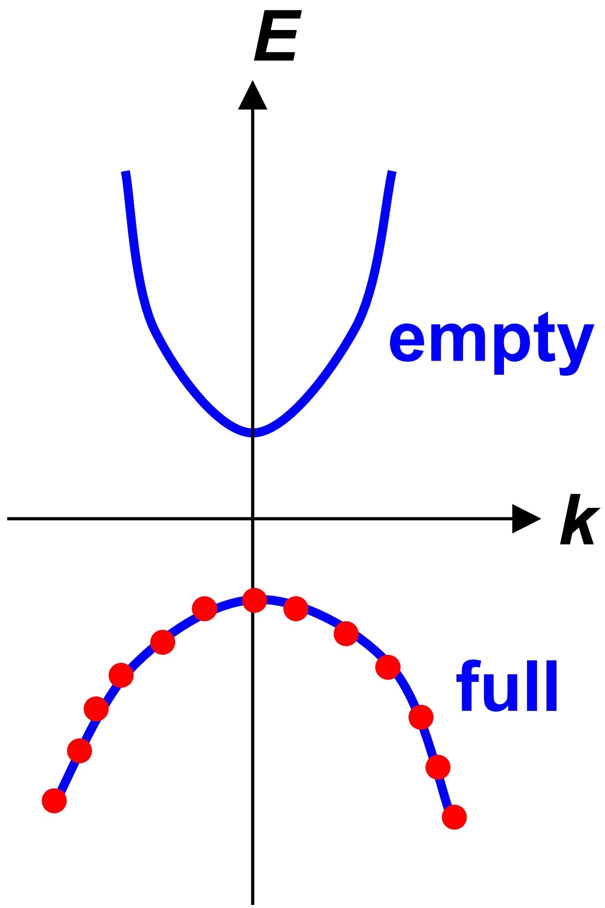
no physical meaning, just two constants

Density of Carriers

when T = 0 K

$$n_c = N_c(T)e^{-(E_c-\mu)/k_BT} = 0$$

$$p_v = P_v(T)e^{-(\mu-E_v)/k_BT} = 0$$



T = 0 K
insulator

Density of Carriers

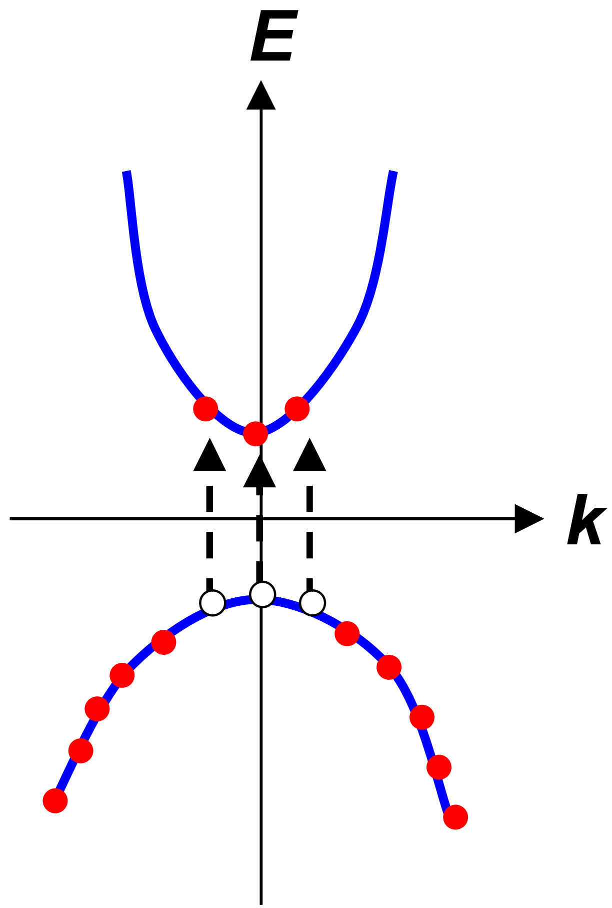
when T > 0 K

$$n_c = N_c(T)e^{-(E_c-\mu)/k_BT} > 0$$

$$p_v = P_v(T)e^{-(\mu-E_v)/k_BT} > 0$$

conductivity

$$\sigma = n_c e\mu_e + p_v e\mu_h$$



T > 0 K
thermalization 热激发
CB and VB are partly filled
conductor

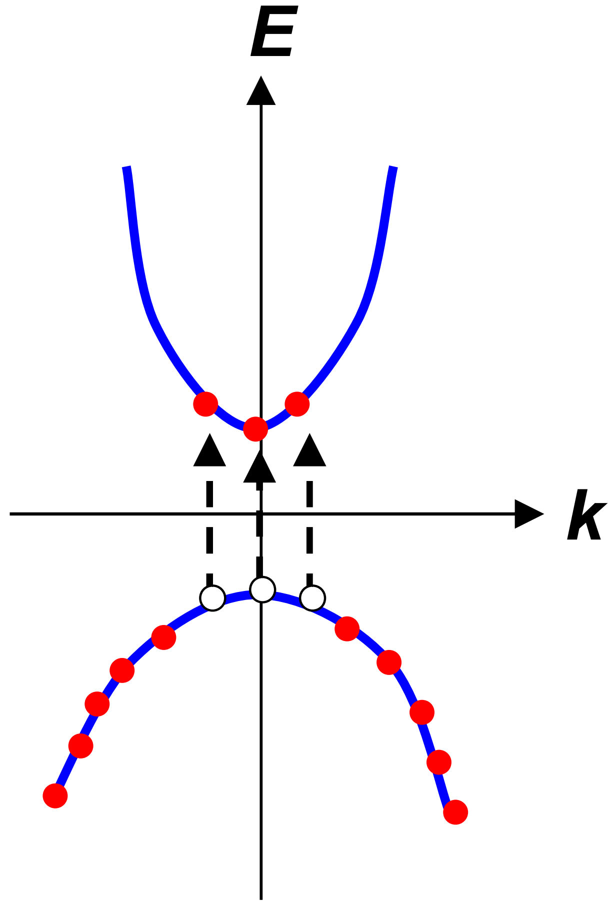
Density of Carriers

when T > 0 K

$$n_c = N_c(T)e^{-(E_c-\mu)/k_BT} > 0$$

$$p_v = P_v(T)e^{-(\mu-E_v)/k_BT} > 0$$

$$\begin{aligned} n_c p_v &= N_v(T)P_v(T)e^{-(E_c-E_v)/k_BT} \\ &= N_v(T)P_v(T)e^{-E_g/k_BT} \end{aligned}$$



mass action law

at equilibrium, $n_c p_v$ is a constant

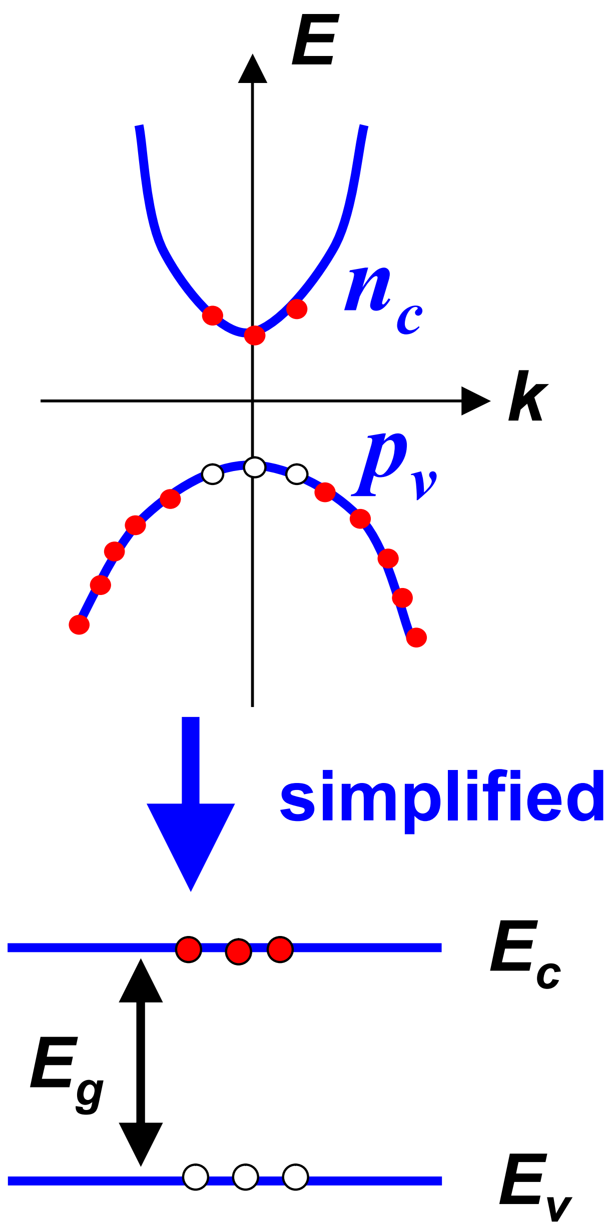
Carriers in Semiconductors

- **For calculations here, we go back to classical physics, assume:**
  - **Carriers are much fewer than DOS**

$$\boxed{f(E) \ll 1}$$

  - **Carriers are non-Degenerate (Boltzmann Distribution)**
  - **Carriers are almost in the same energies (E_c and E_v)**
  - **Carriers have the same velocities and motilities**

$$\boxed{\sigma = n_c e \mu_e + p_v e \mu_h}$$



Mass Action Law - A Little Notion

- The product of electron and hole concentrations is a constant, at a fixed temperature

$$\boxed{n_c p_v = n_i^2 = N_v(T) P_v(T) e^{-E_g/k_B T}}$$

- In water, the product of H^+ and OH^- concentrations is also a constant

$$\boxed{[\mathrm{H}^+][\mathrm{OH}^-] = K_w = 10^{-14} (\mathrm{mol/L})^2 \ \ (\text{at } 25\ °\mathrm{C})}$$

- Both are originated from classical statistics (non-degenerate, Maxwell-Boltzmann distribution), *not* related to quantum mechanics

Thank you for your attention