

Fundamentals of Solid State Physics

Semiconductors - Intrinsic and Extrinsic

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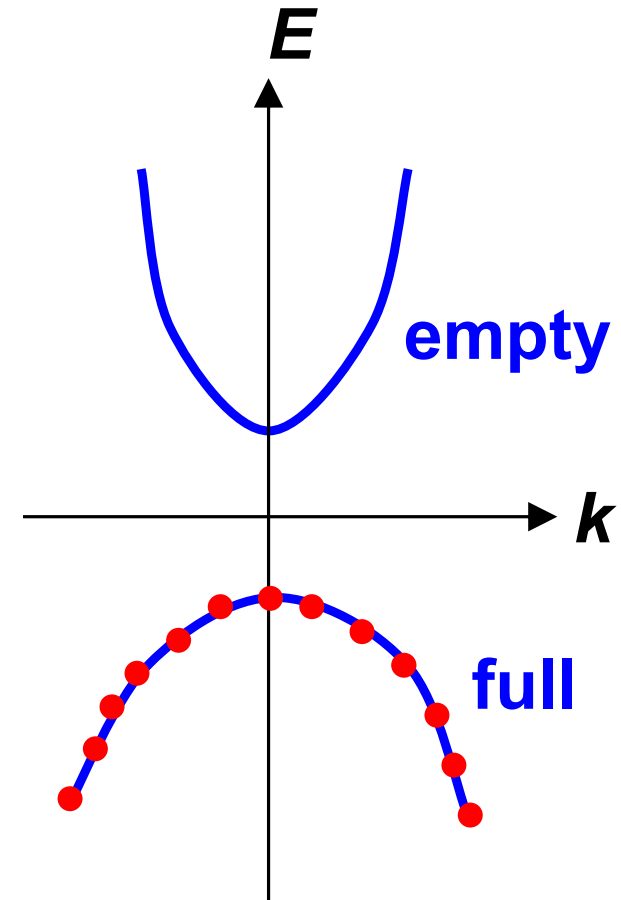
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Density of Carriers

when $T = 0$ K

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

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



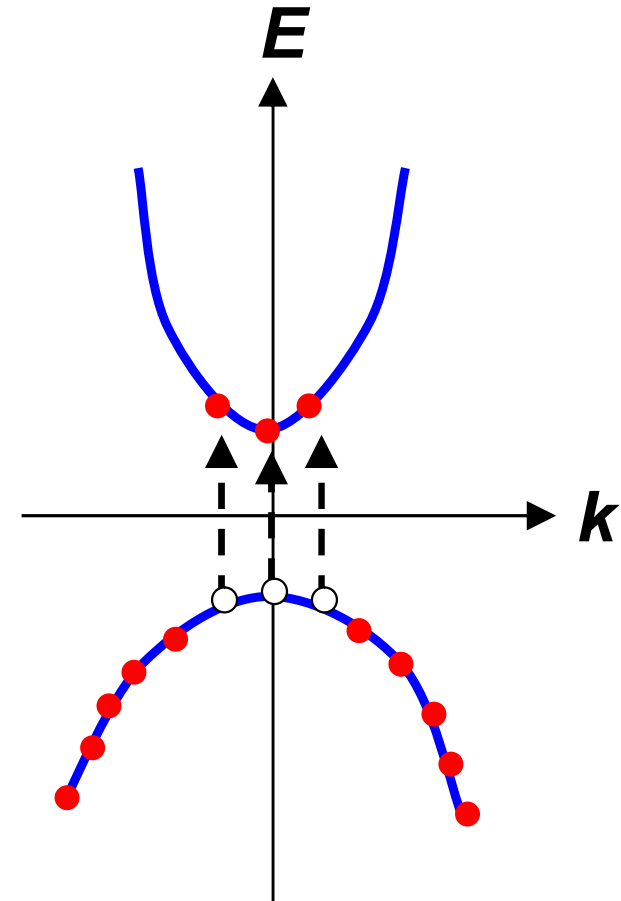
$T = 0$ K
insulator

Density of Carriers

when $T > 0$ K

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

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



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

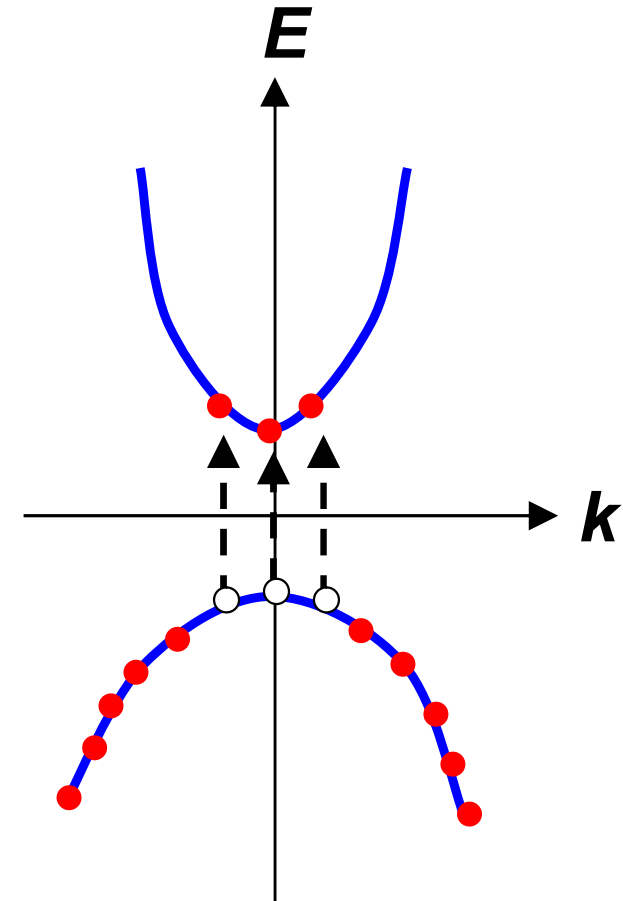
when $T > 0 \text{ K}$

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

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



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



mass action law

at equilibrium, $n_c p_v$ is a constant

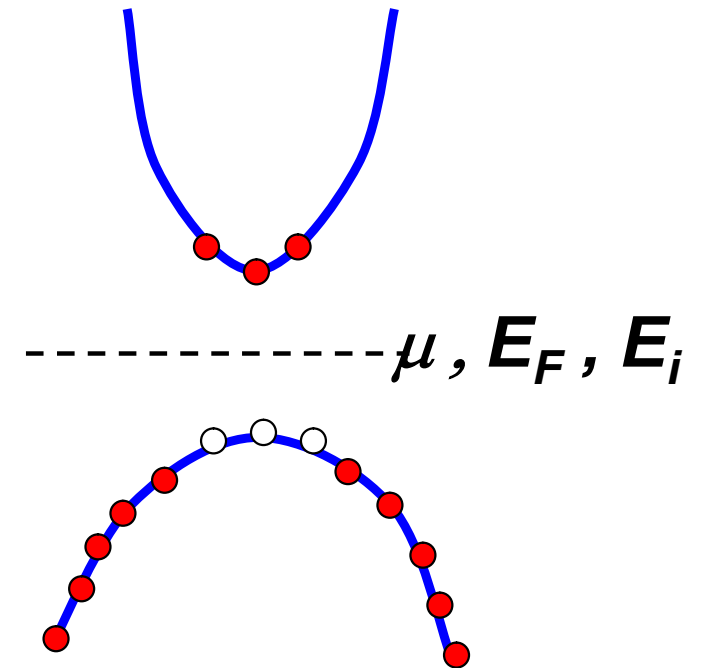
Intrinsic Semiconductor 本征半导体

pure, no impurity, charge balance

$$n_c = p_v = n_i$$

→
$$n_i = \sqrt{N_v(T)P_v(T)} \cdot e^{-E_g/2k_B T}$$

→
$$\begin{aligned} \mu &= E_F = E_i \\ &= E_c - k_B T \ln \left(\frac{N_c(T)}{n_i} \right) \\ &= E_v + k_B T \ln \left(\frac{P_v(T)}{n_i} \right) \end{aligned}$$



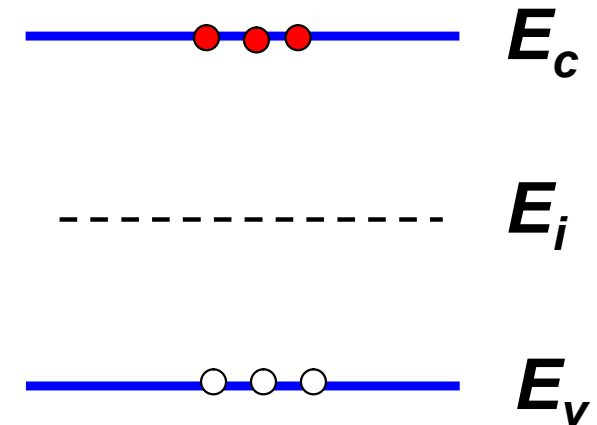
Intrinsic Semiconductor 本征半导体

pure, no impurity, charge balance

$$n_c = p_v = n_i$$

→
$$n_i = \sqrt{N_v(T)P_v(T)} \cdot e^{-E_g/2k_B T}$$

→
$$\begin{aligned} \mu = E_F = E_i \\ = E_v + \frac{1}{2} E_g + \frac{3}{4} k_B T \ln \left(\frac{m_h^*}{m_e^*} \right) \end{aligned}$$



The chemical potential / Fermi level / Intrinsic level is closed to the middle gap

Intrinsic Semiconductor 本征半导体

Example: intrinsic Si at 300 K

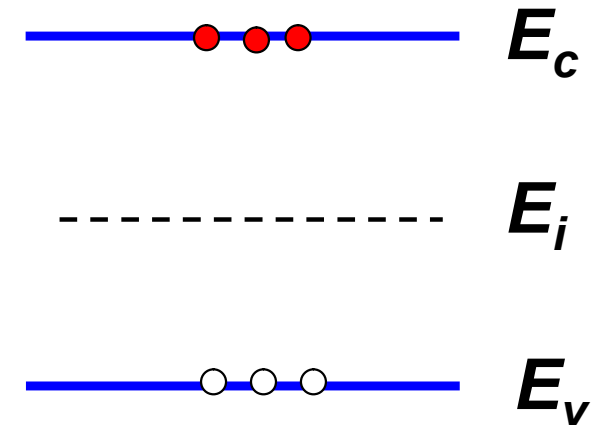
$$n_c = p_v = n_i \approx 10^{10} \text{ cm}^{-3}$$

$$\mu_e = 1500 \text{ cm}^2/\text{V/s}$$

$$\mu_h = 450 \text{ cm}^2/\text{V/s}$$



$$\sigma = n_c e \mu_e + p_v e \mu_h$$
$$\approx 10^{-6} \text{ S/cm}$$

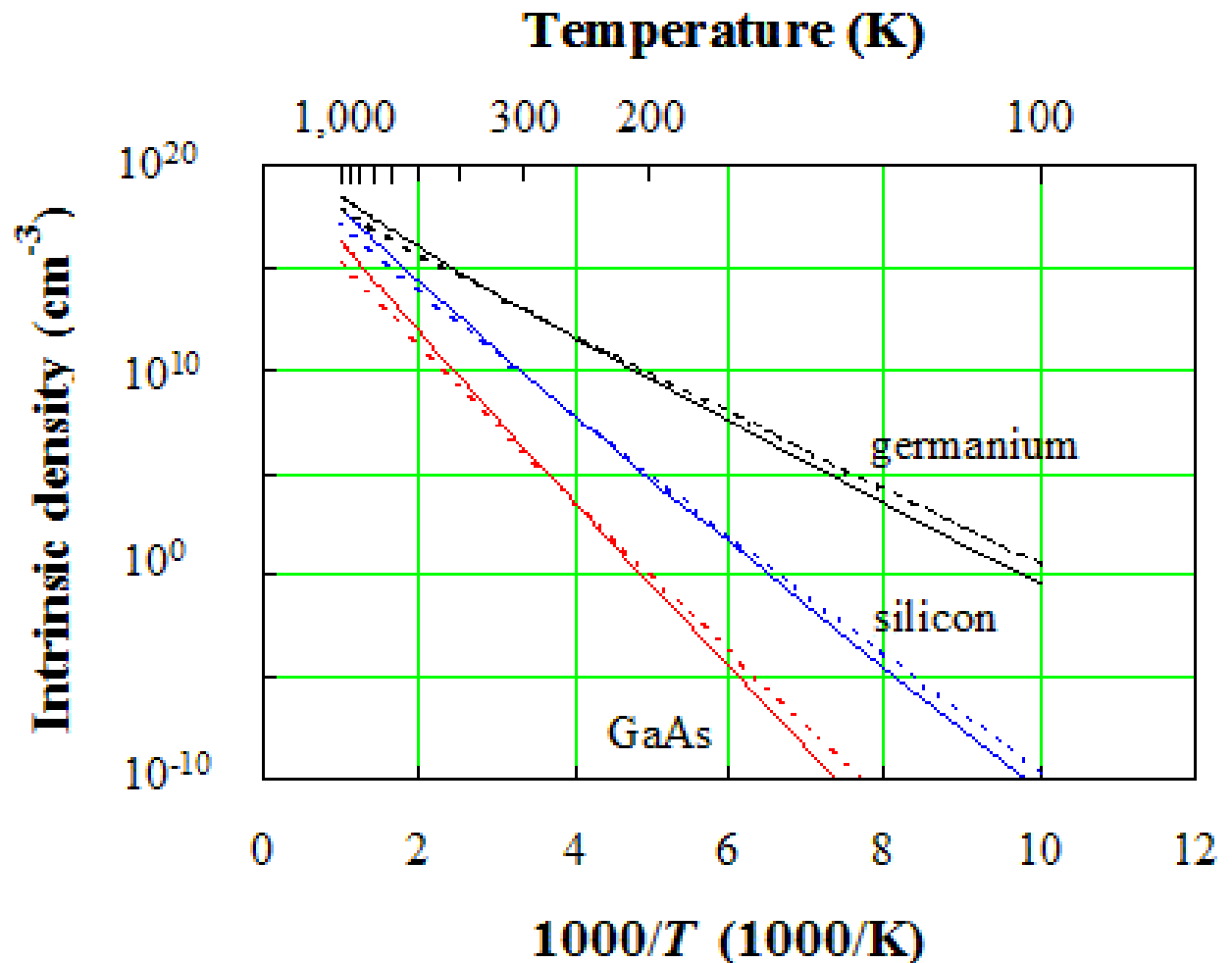


Intrinsic Semiconductor 本征半导体

temperature dependence of carrier concentration

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

$$\ln n_i \sim -\frac{E_g}{2k_B T}$$



Intrinsic Semiconductor 本征半导体

temperature dependence of carrier mobility μ

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

at low T

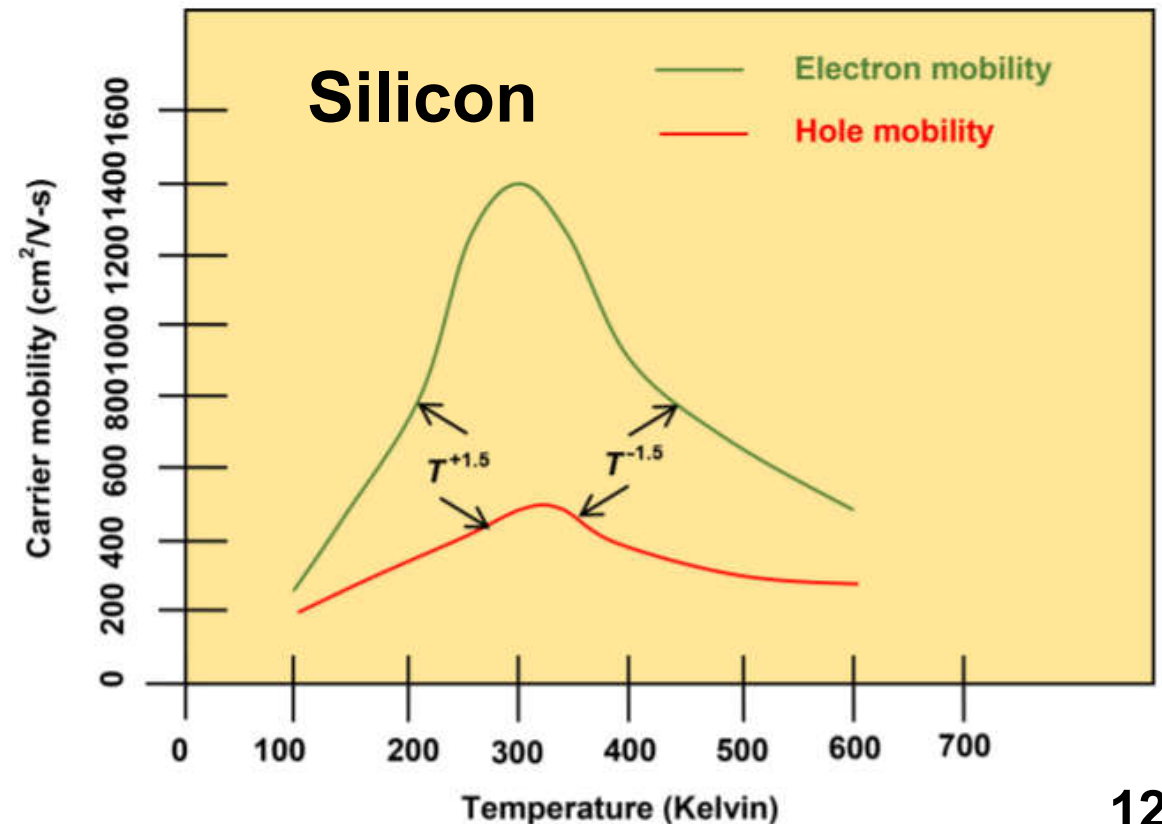
$$\mu \sim T^{3/2}$$

impurity scattering

at high T

$$\mu \sim T^{-3/2}$$

lattice scattering

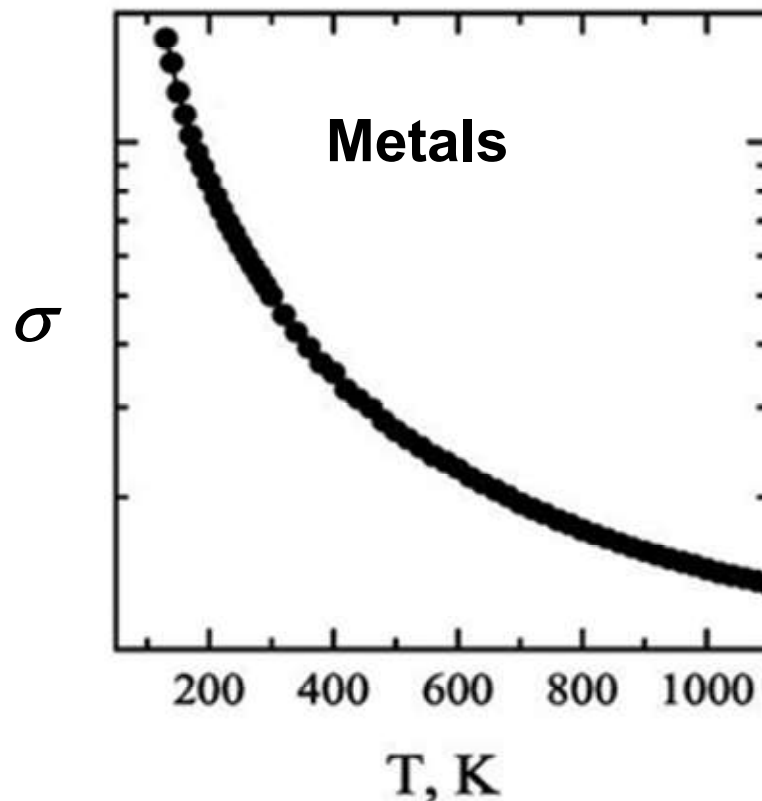


Temperature Dependence of σ

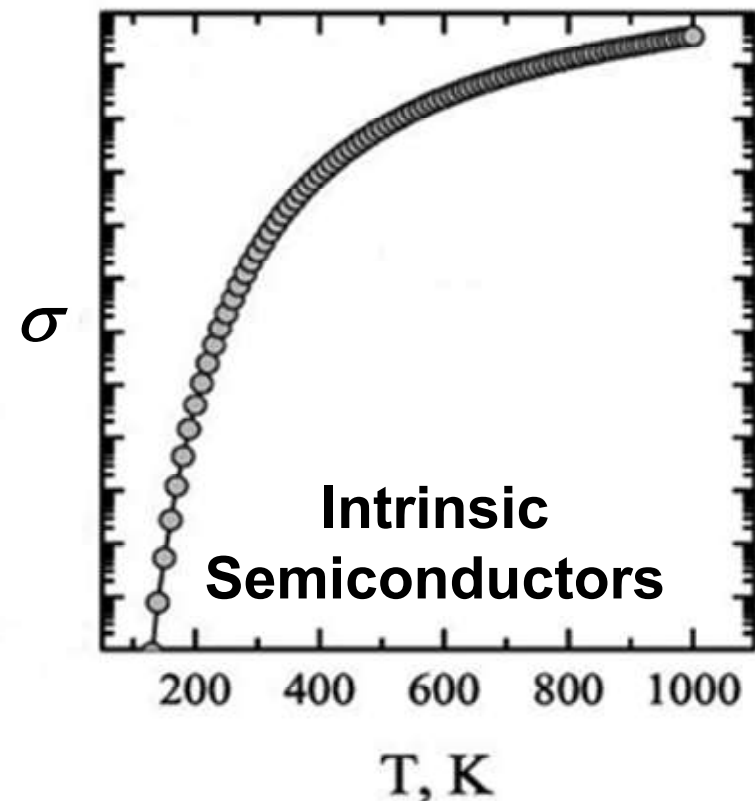
Metals and semiconductors have different temperature dependences of σ

$$\sigma = ne\mu$$

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



μ dominates



n dominates

Conductivity of Semiconductor

metals

	conductivity σ (S/m)
Ag	6.3×10^7
Al	3.5×10^7

insulators

wood	$10^{-14} \sim 10^{-16}$
glass	$10^{-11} \sim 10^{-15}$

silicon with doping

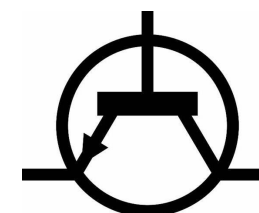
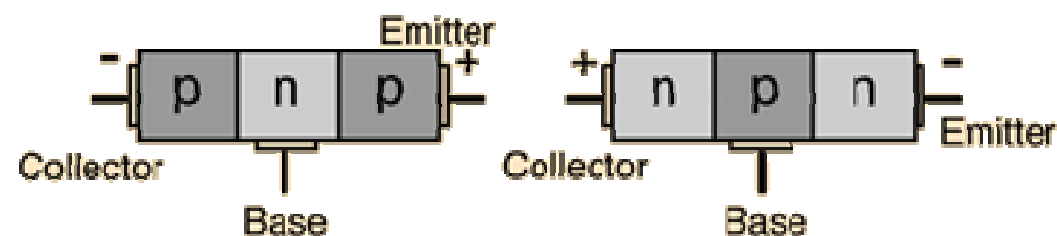
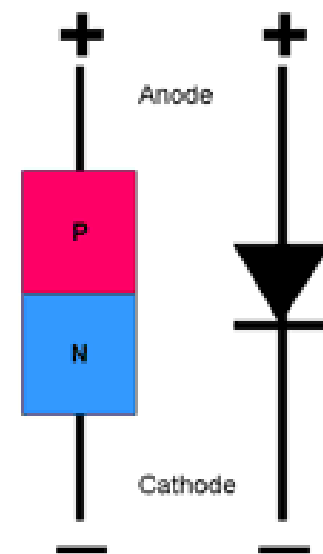
	conductivity σ (S/m)
0	10^{-6}
$1 / 10^9$	10^{-1}
$1 / 10^6$	10^2
$1 / 10^3$	10^5

at $T = 300 \text{ K}$

Doping Makes Functional Devices



ingots and wafers



Extrinsic Semiconductor 掺杂半导体

For Si and Ge (group IV)

add Group V dopants: **P, As, Sb, ...**

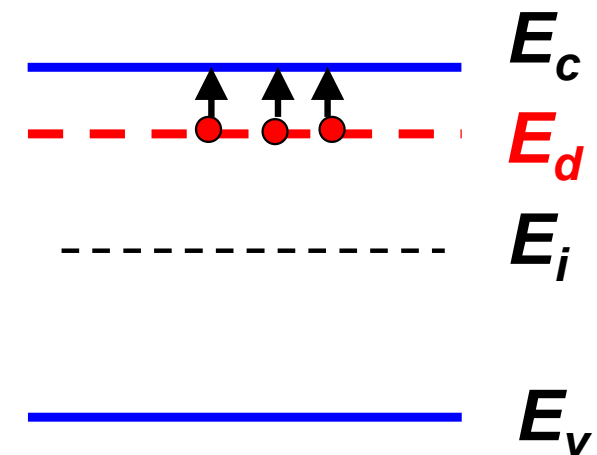
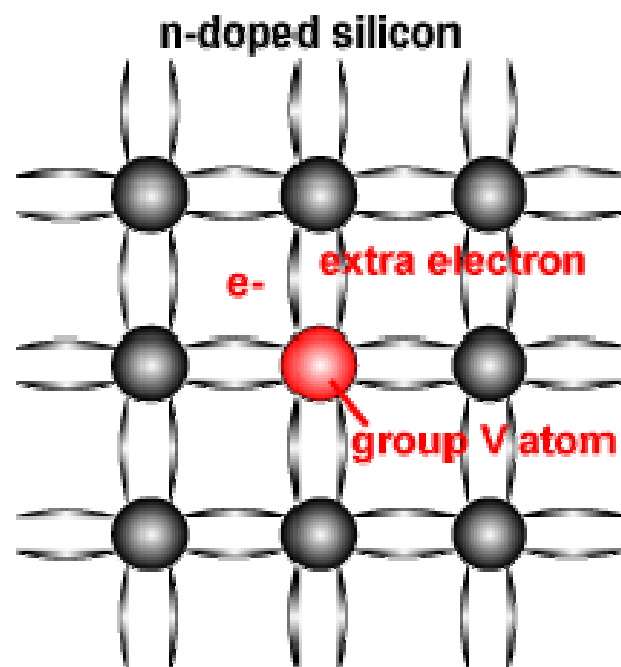
create level E_d close to E_c with **extra electrons**

these electrons can be excited at low temperature

making Si more conductive

donor 施主 ----> n-doping

					2
	5	6	7	8	9
	B	C	N	O	F
10					
13	Al	Si	P	S	Cl
18					
31	Ga	Ge	As	Se	Br
36					
49	In	Sn	Sb	Te	I
54					
81	Tl	Pb	Bi	Po	At
86					



Extrinsic Semiconductor 掺杂半导体

For Si and Ge (group IV)

add Group III dopants: **B, Al, Ga, ...**

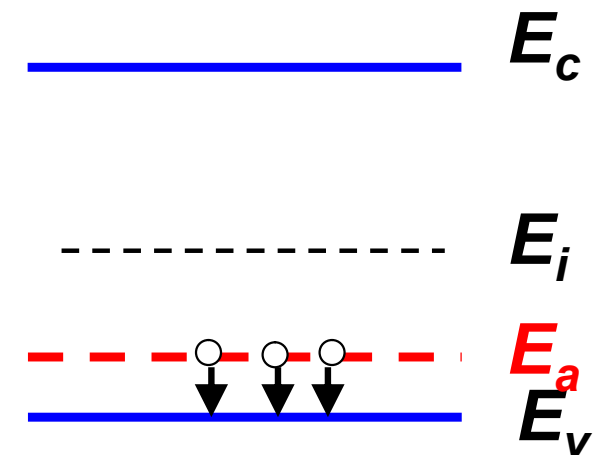
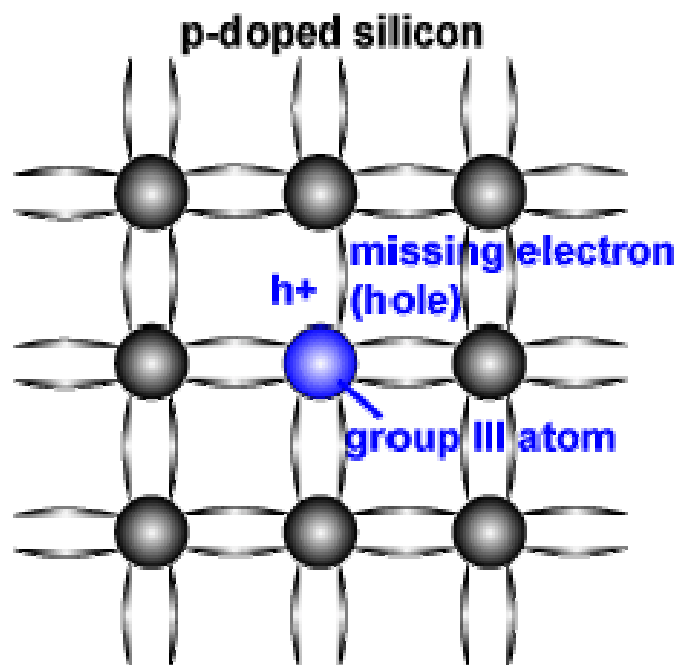
create level E_a close to E_v with **extra holes**

these holes can be excited at low temperature

making Si more conductive

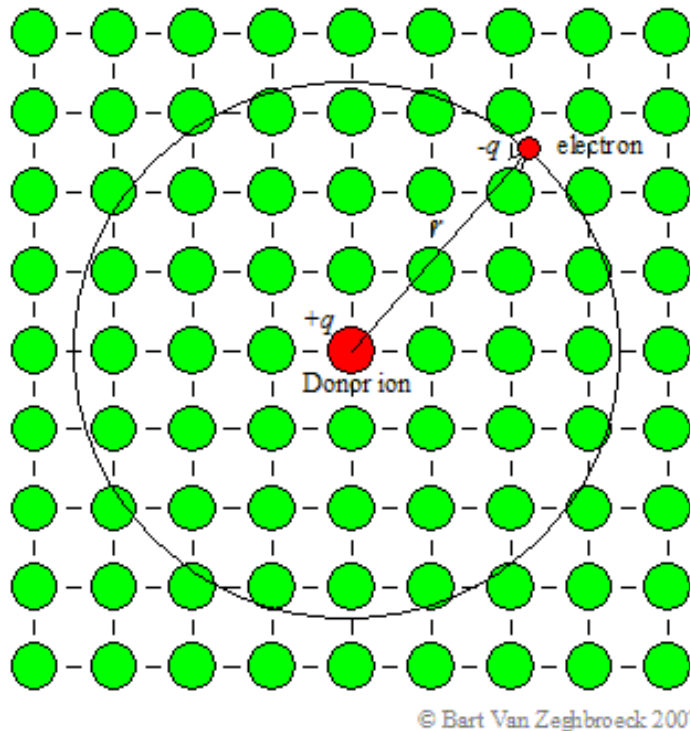
acceptor 受主 ----> p-doping

					2
	5	6	7	8	9
B	C	N	O	F	Ne
13	14	15	16	17	18
Al	Si	P	S	Cl	Ar
31	32	33	34	35	36
Ga	Ge	As	Se	Br	Kr
49	50	51	52	53	54
In	Sn	Sb	Te	I	Xe
81	82	83	84	85	86
Tl	Pb	Bi	Po	At	Rn



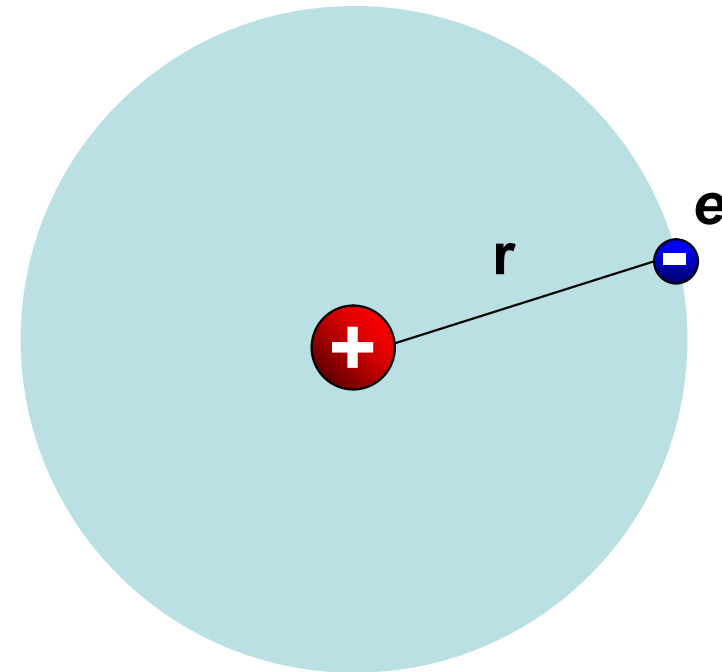
Ionization Energy of Dopants 电离能

Hydrogen-like Model



$$\Delta E = 13.6 \frac{m^*}{m_0} \frac{1}{\epsilon_r^2} \text{ eV}$$

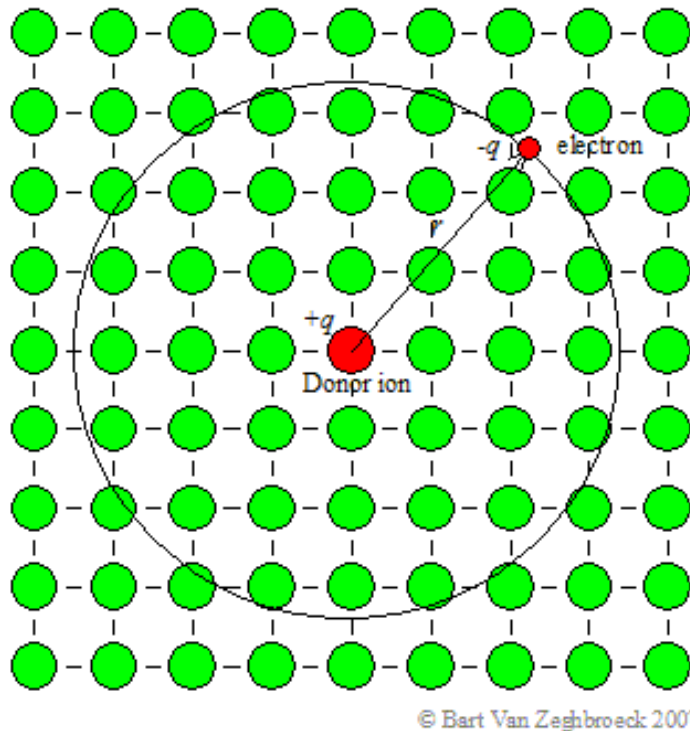
Hydrogen Atom



$$E_1 = -\frac{m_0 e^4}{8 \epsilon_0^2 h^2} = -13.6 \text{ eV}$$

Ionization Energy of Dopants 电离能

Hydrogen-like Model

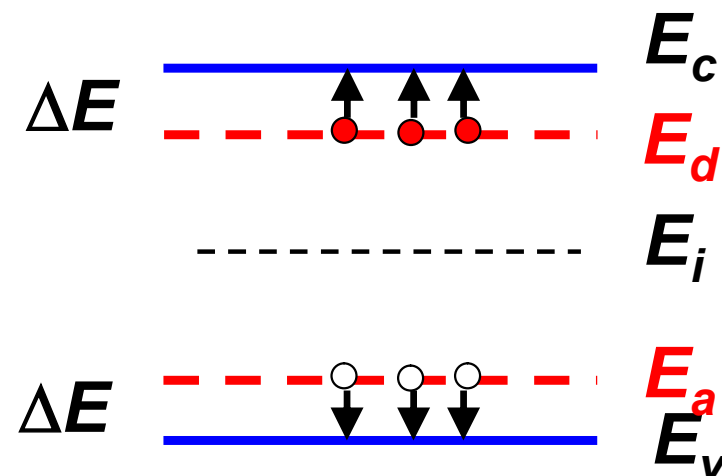


$$\Delta E = 13.6 \frac{m^*}{m_0} \frac{1}{\epsilon_r^2} \text{ eV}$$

m^* - effective mass $\sim 0.1m_0$

ϵ_r - relative dielectric constant ~ 10

→ $\Delta E \sim 0.01 \text{ eV}$



Ionization Energy of Dopants 电离能

Table 28.2

LEVELS OF GROUP V (DONORS) AND GROUP III (ACCEPTORS)
IMPURITIES IN SILICON AND GERMANIUM

GROUP III ACCEPTORS (TABLE ENTRY IS $\epsilon_a - \epsilon_v$)					
	B	Al	Ga	In	Tl
Si	0.046 eV	0.057	0.065	0.16	0.26
Ge	0.0104	0.0102	0.0108	0.0112	0.01
GROUP V DONORS (TABLE ENTRY IS $\epsilon_c - \epsilon_d$)					
	P	As	Sb	Bi	
Si	0.044 eV	0.049	0.039	0.069	
Ge	0.0120	0.0127	0.0096	—	
ROOM TEMPERATURE ENERGY GAPS ($E_g = \epsilon_c - \epsilon_v$)					
Si	1.12 eV				
Ge	0.67 eV				

Source: P. Aigrain and M. Balkanski, *Selected Constants Relative to Semiconductors*, Pergamon, New York, 1961.

Doping in Silicon

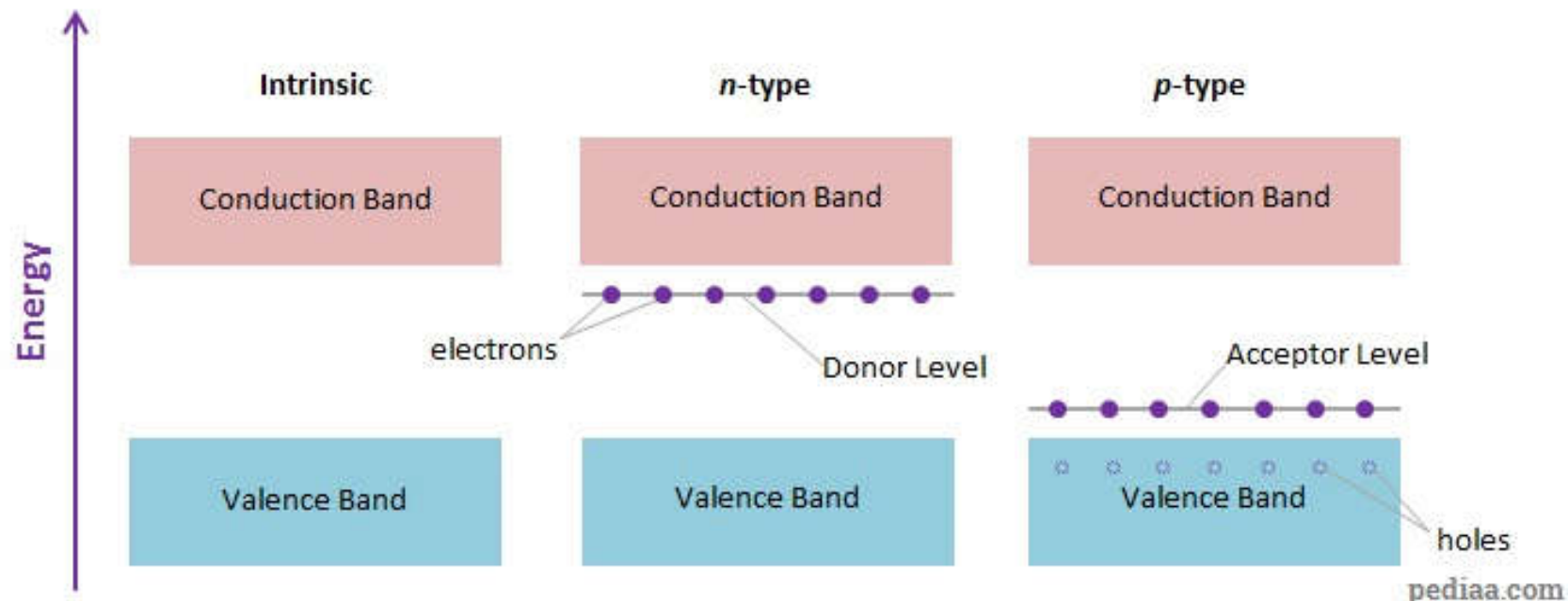
For Si (and Ge):

p dopant: **B, Al, Ga, ...**

n dopant: **P, As, Sb, ...**

These dopants are **shallow level defects**, which can be excited to generated carriers closed to E_c or E_v (~ 0.01 eV), room temperature $k_B T \sim 0.03$ eV

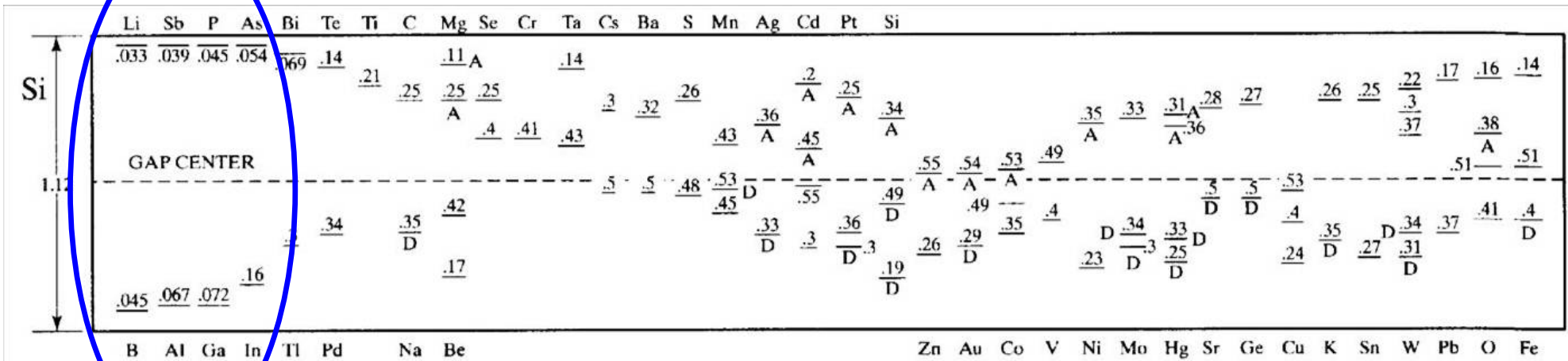
					2
					He
5	6	7	8	9	10
B	C	N	O	F	Ne
13	14	15	16	17	18
Al	Si	P	S	Cl	Ar
31	32	33	34	35	36
Ga	Ge	As	Se	Br	Kr
49	50	51	52	53	54
In	Sn	Sb	Te	I	Xe
81	82	83	84	85	86
Tl	Pb	Bi	Po	At	Rn



Other Defects in Silicon

Many other elements are **deep level defects**, which cannot be excited, making traps for carriers and Si less conductive.

					2
	5	6	7	8	9
	B	C	N	O	F
13	Al	Si	P	S	Cl
31	Ga	Ge	As	Se	Br
49	In	Sn	Sb	Te	I
81	Tl	Pb	Bi	Po	At
					86
					Rn



dopants

deep level defects

Na, K, Au, Cu, Fe, O, ...

Doping in GaAs

For GaAs:

p dopant:

replace Ga: **Mg, Zn, Be**

replace As: **C**

...

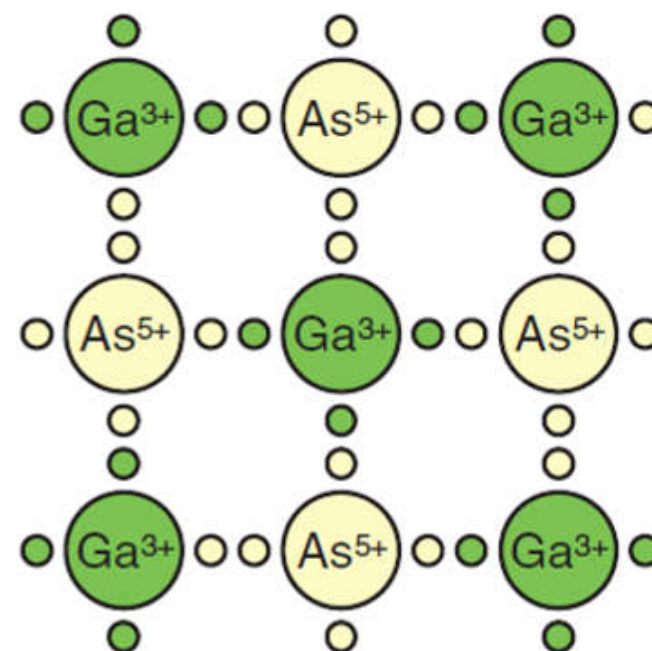
n dopant:

replace As: **Se**

replace Ga: **Si, Ge**

...

					2 He
5 B	6 C	7 N	8 O	9 F	10 Ne
13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn



Extrinsic Semiconductor 掺杂半导体

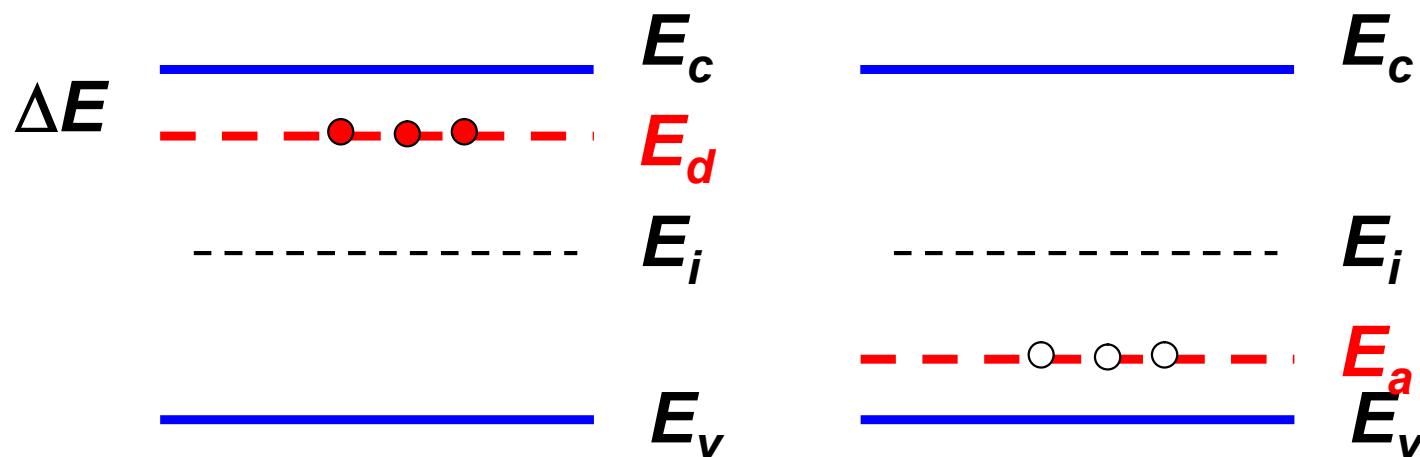
when $T = 0$ K, carriers cannot be excited

$$n_c \rightarrow 0$$

$$p_v \rightarrow 0$$

insulator

electrons and holes are frozen



Extrinsic Semiconductor 掺杂半导体

when $T > 0$ K, carriers can be excited (ionization 电离)

shallow level dopants are easily activated at room temperature $T = 300$ K.

mass action law

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

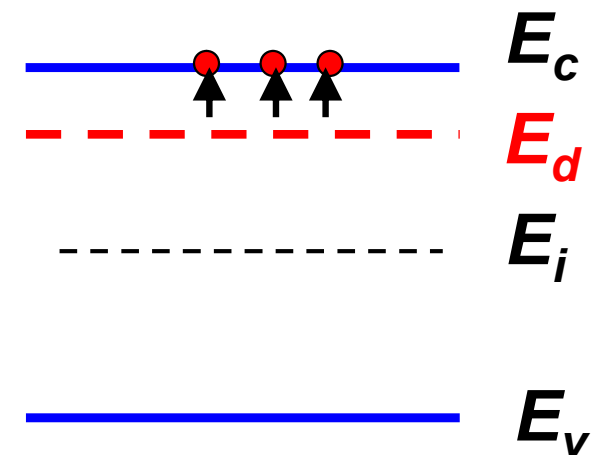
at equilibrium, $n_c p_v$ is a constant

If $N_D \gg n_i$

For n-doping

$$n_c = N_D$$

$$p_v = n_i^2 / n_c$$



N_D - concentration of donor (cm^{-3})

Extrinsic Semiconductor 掺杂半导体

when $T > 0$ K, carriers can be excited (ionization)

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

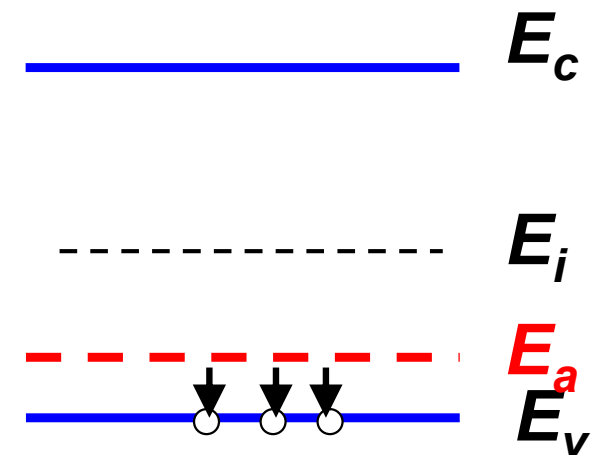
at equilibrium, $n_c p_v$ is a constant

If $N_A \gg n_i$

For n-doping

$$p_v = N_A$$

$$n_c = n_i^2 / p_v$$



N_A - concentration of acceptor (cm^{-3})

Example - Silicon

For intrinsic Si at room temperature ($T = 300$ K)

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

$$n_i \sim 10^{10} \text{ cm}^{-3}$$

$$\sigma \sim 10^{-6} \text{ S/cm}$$

atom density of Si

$$N_{\text{Si}} \sim 10^{22} \text{ cm}^{-3}$$

If we put 1 ppm (10^{-6}) P in Si

$$N_D \sim 10^{16} \text{ cm}^{-3} \gg n_i$$

$$n_c = N_D \sim 10^{16} \text{ cm}^{-3}$$

$$p_v = n_i^2 / n_c \sim 10^4 \text{ cm}^{-3}$$

$$\sigma \sim 10^0 \text{ S/cm}$$

the conductivity is increased by 10^6

the conductivity is related to the doping and weakly dependent on T

Chemical Potential / Fermi Level

For n-doping

$$n_c = N_D$$

$$p_v = n_i^2 / n_c$$

$$n_c \gg p_v$$

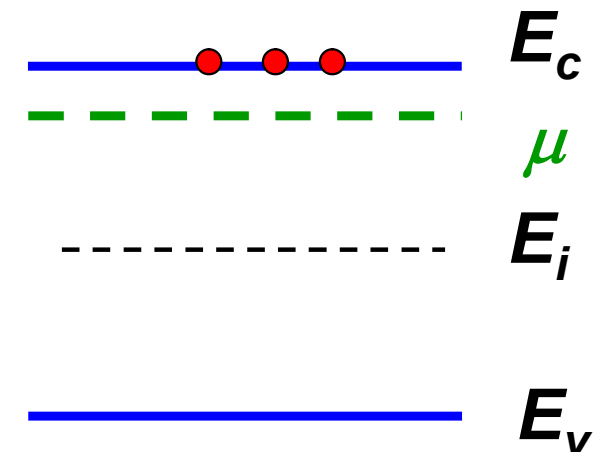
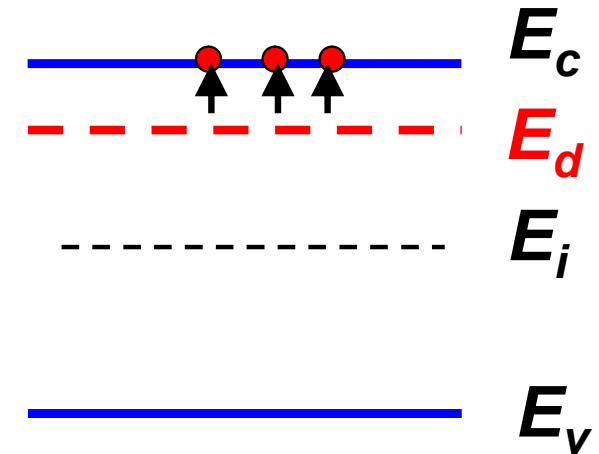
N_D - concentration of donor (cm^{-3})

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

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

→ $E_c - \mu \ll \mu - E_v$

chemical potential / Fermi level
moves closer to E_c



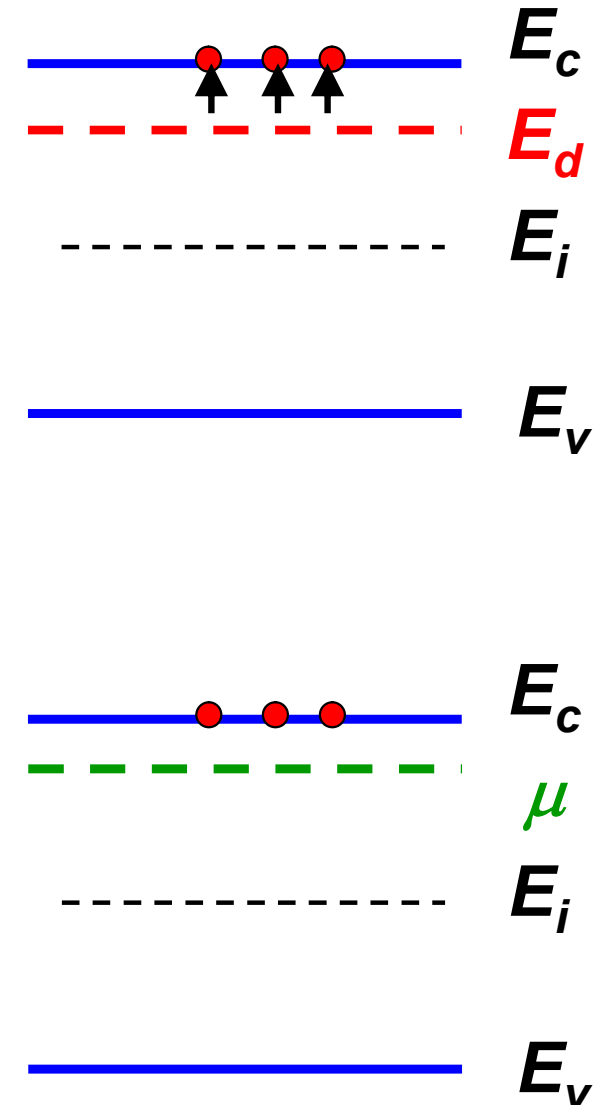
Chemical Potential / Fermi Level

For n-doping

$$n_c = N_D$$

$$p_v = n_i^2 / n_c$$

$$\begin{aligned}\mu &= E_c - k_B T \ln \left(\frac{N_c(T)}{n_c} \right) \\ &= E_i + k_B T \ln \left(\frac{N_D}{n_i} \right) \\ &\approx E_v + \frac{1}{2} E_g + k_B T \ln \left(\frac{N_D}{n_i} \right)\end{aligned}$$



Chemical Potential / Fermi Level

For p-doping

$$p_v = N_A$$

$$n_c = n_i^2 / p_v$$

$$p_v \gg n_c$$

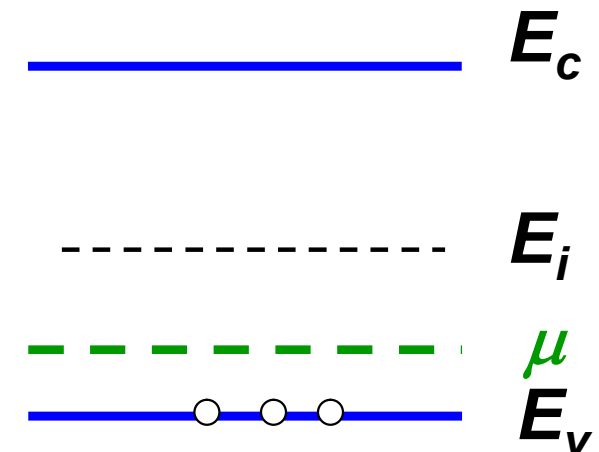
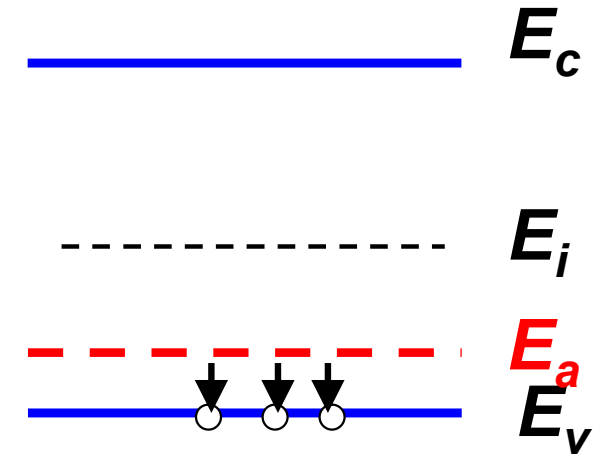
N_A - concentration of acceptor (cm^{-3})

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

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

→ $E_c - \mu \gg \mu - E_v$

chemical potential / Fermi level
moves closer to E_v



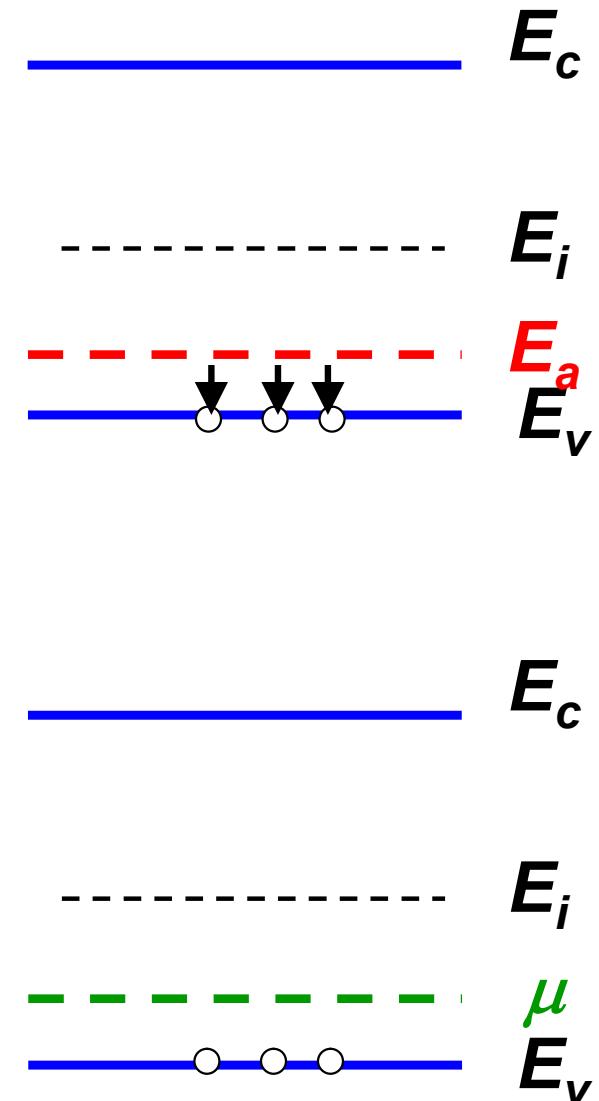
Chemical Potential / Fermi Level

For p-doping

$$p_v = N_A$$

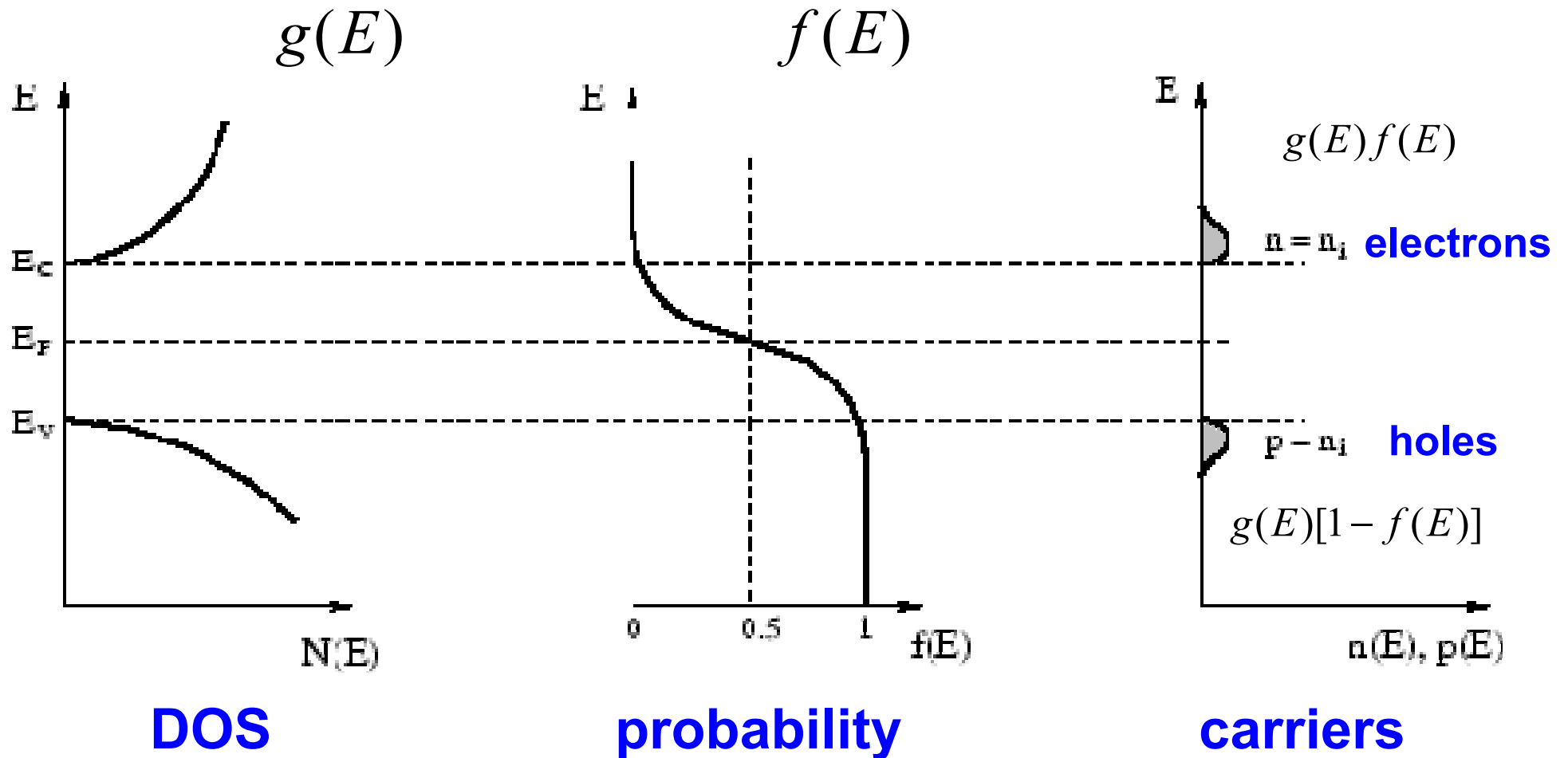
$$n_c = n_i^2 / p_v$$

$$\begin{aligned}\mu &= E_v + k_B T \ln \left(\frac{P_v(T)}{p_v} \right) \\ &= E_i - k_B T \ln \left(\frac{N_A}{n_i} \right) \\ &\approx E_v + \frac{1}{2} E_g - k_B T \ln \left(\frac{N_A}{n_i} \right)\end{aligned}$$



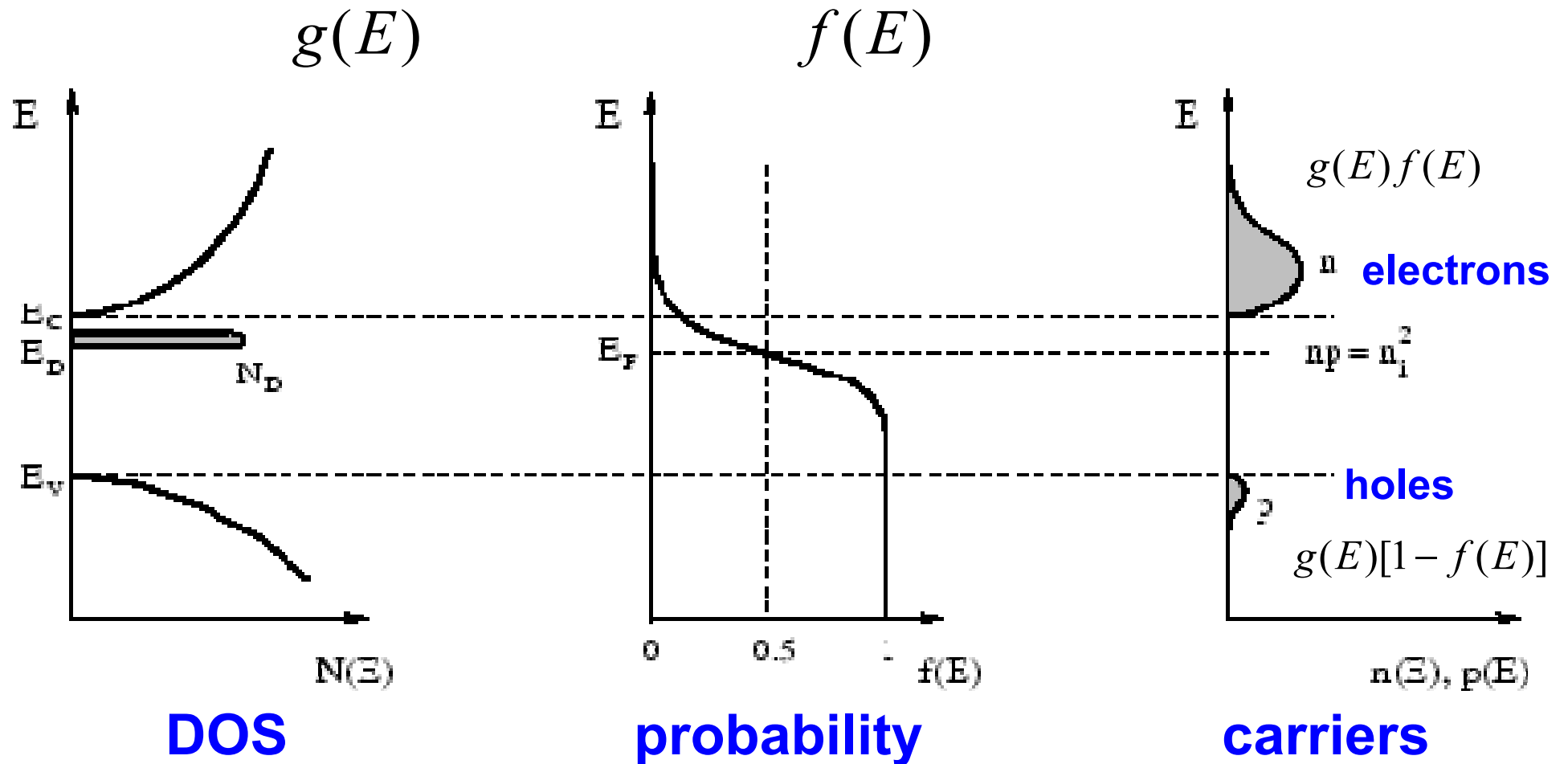
Intrinsic vs. Extrinsic

Intrinsic



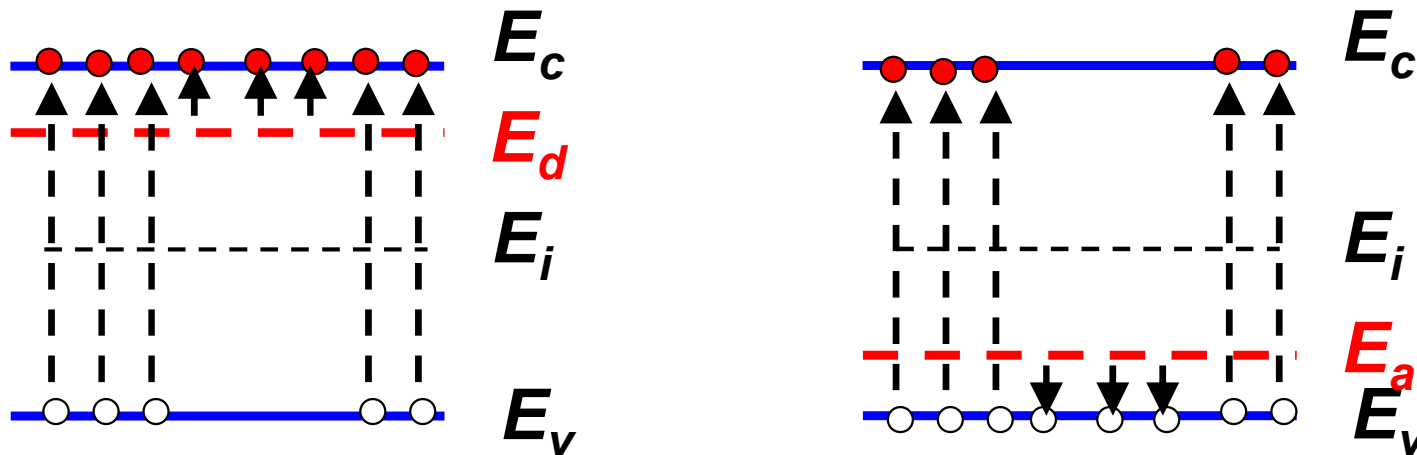
Intrinsic vs. Extrinsic

Extrinsic (n-doping)



At Very High Temperature

when T is very high, more carriers can be excited



$$n_c \approx p_v \approx n_i \gg \text{doping concentration}$$

similar to an intrinsic semiconductor

Extrinsic Semiconductor 掺杂半导体

temperature dependence of carrier concentration

low T , freeze-out

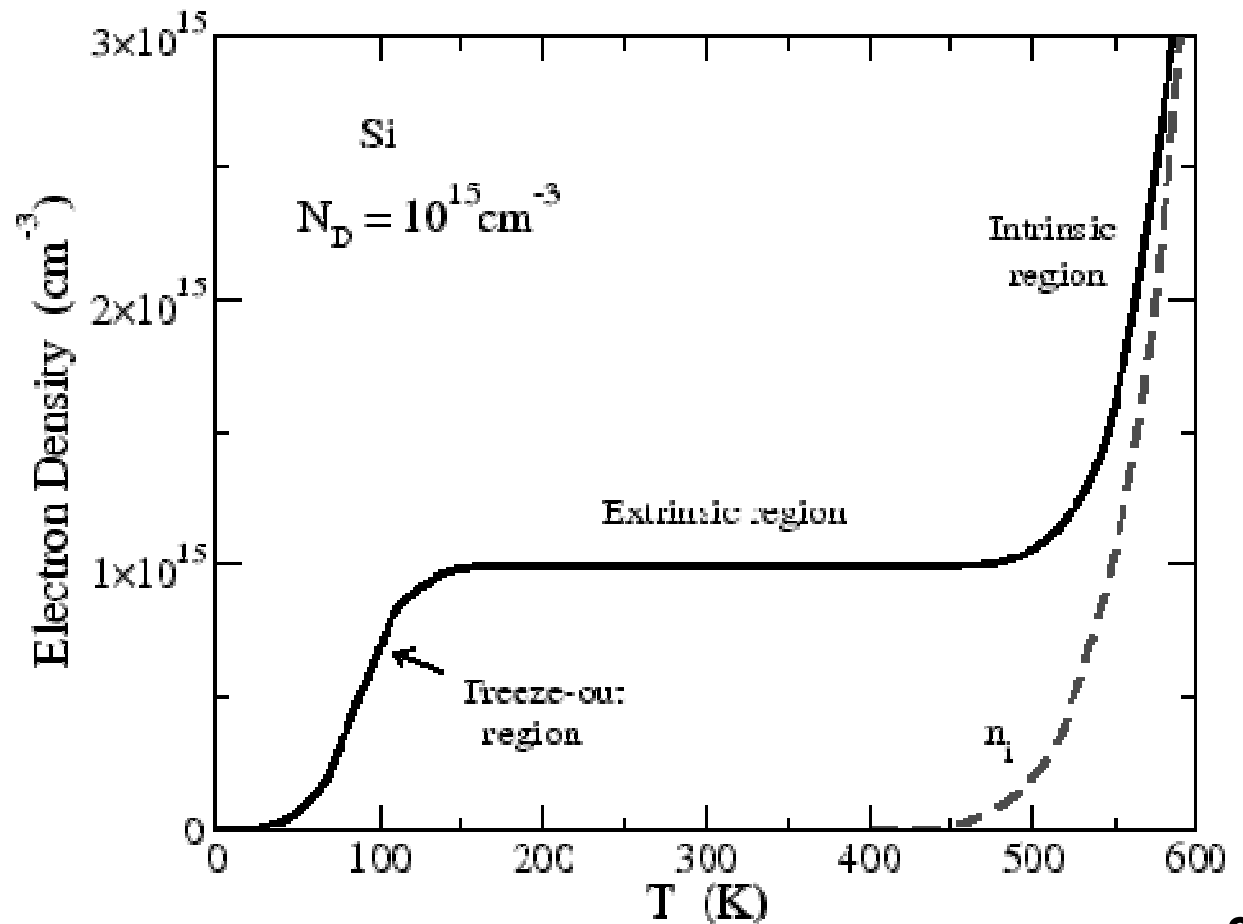
$$n \sim e^{-(E_c - E_D)/k_B T}$$

median T , extrinsic

$$n = N_D$$

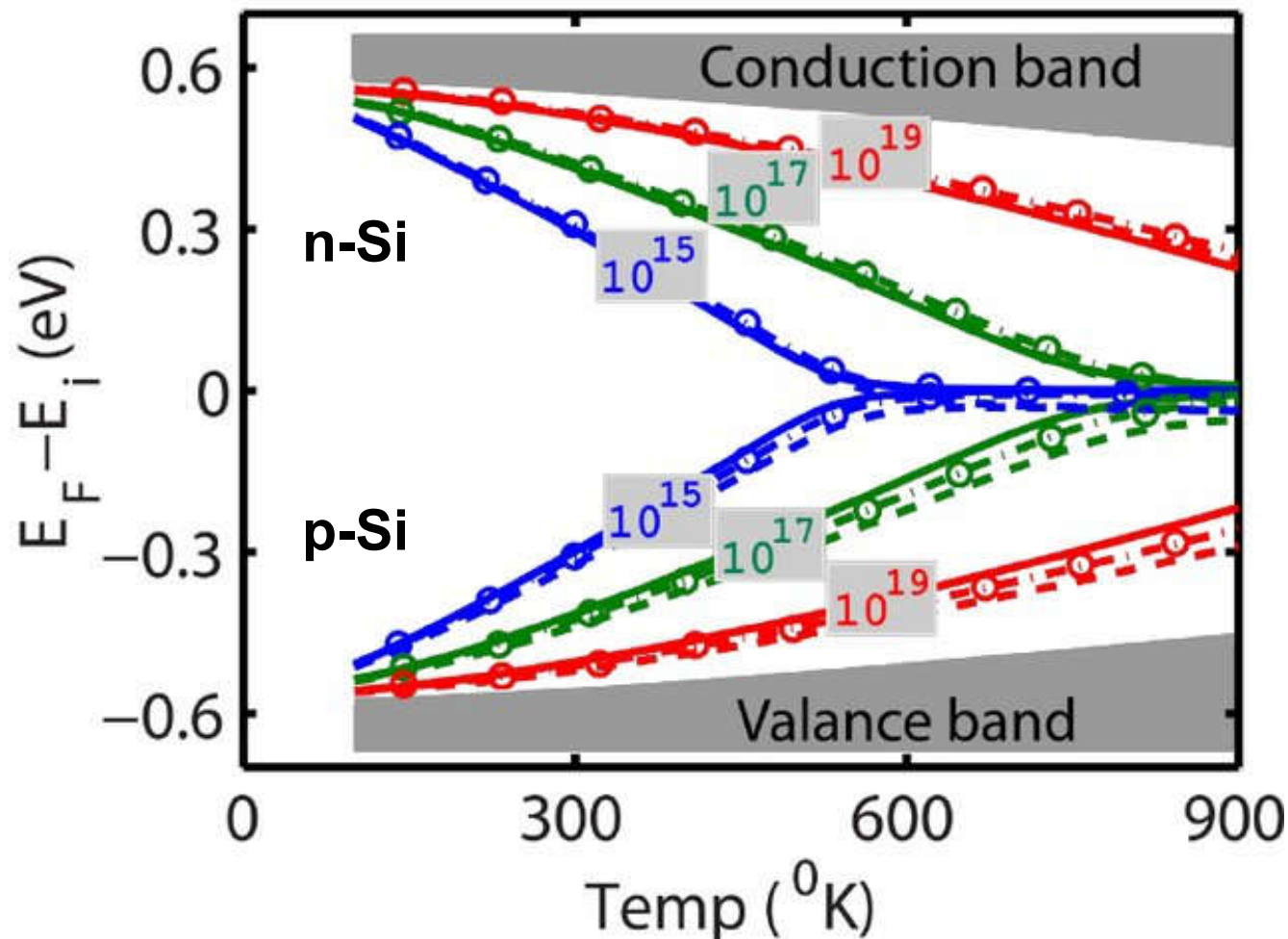
high T , intrinsic

$$n \sim e^{-E_g/2k_B T}$$



Extrinsic Semiconductor 掺杂半导体

temperature dependence of chemical potential



Extrinsic Semiconductor 掺杂半导体

temperature dependence of carrier concentration

low T , freeze-out

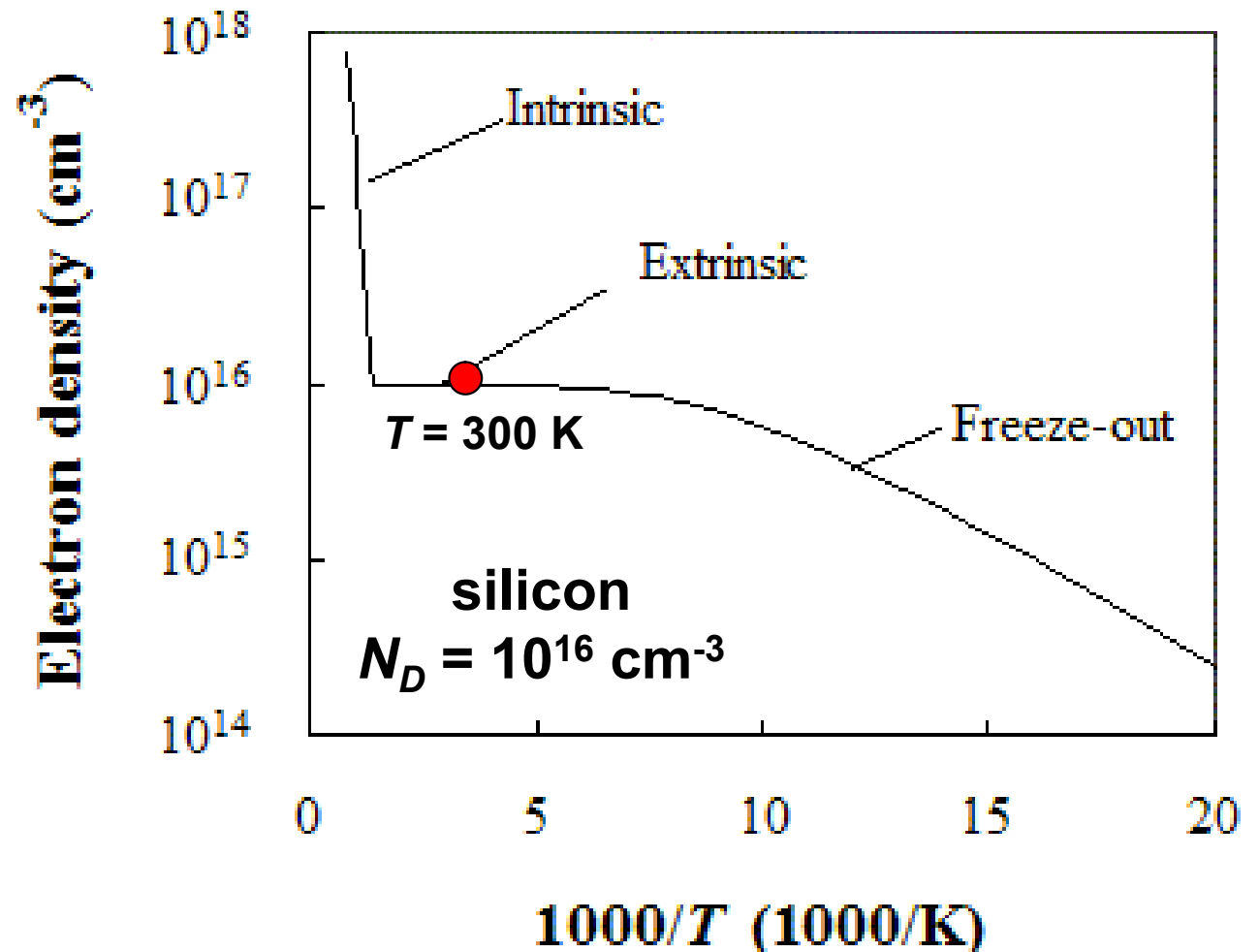
$$n \sim e^{-(E_c - E_D)/k_B T}$$

median T , extrinsic

$$n = N_D$$

high T , intrinsic

$$n \sim e^{-E_g/2k_B T}$$



Extrinsic Semiconductor 掺杂半导体

temperature dependence of mobility μ

at low T

$$\mu \sim T^{3/2}$$

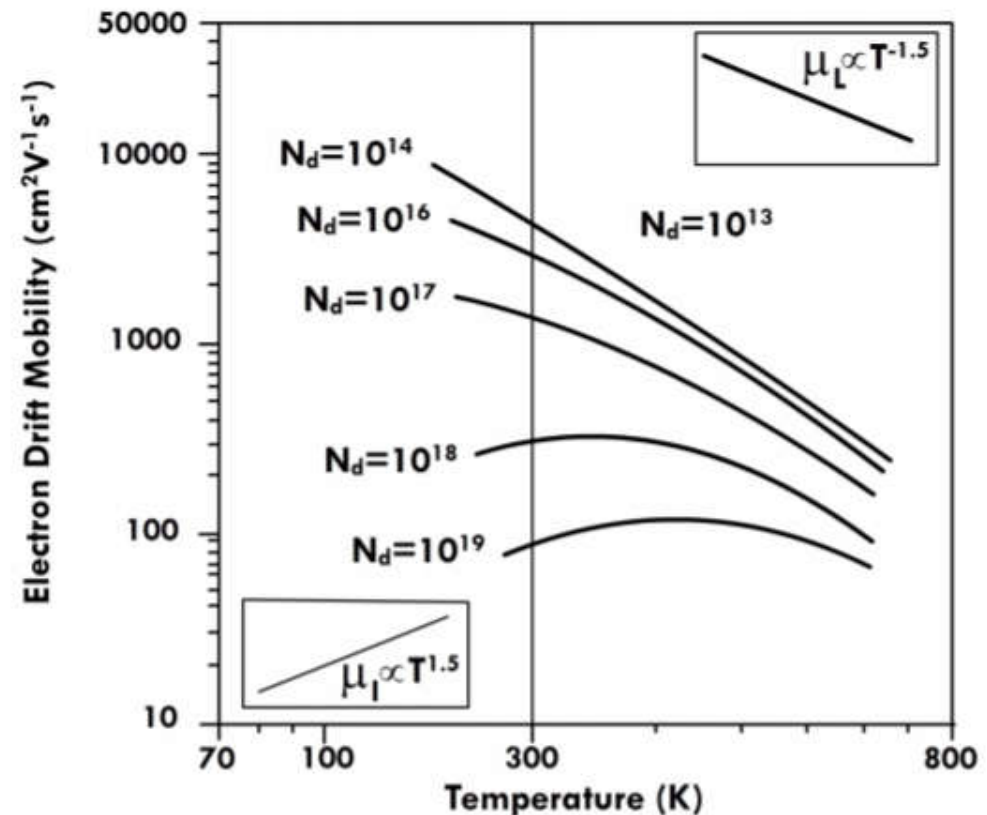
impurity scattering

at high T

$$\mu \sim T^{-3/2}$$

lattice scattering

when doping increases,
mobility decreases, due
to more impurity
scattering

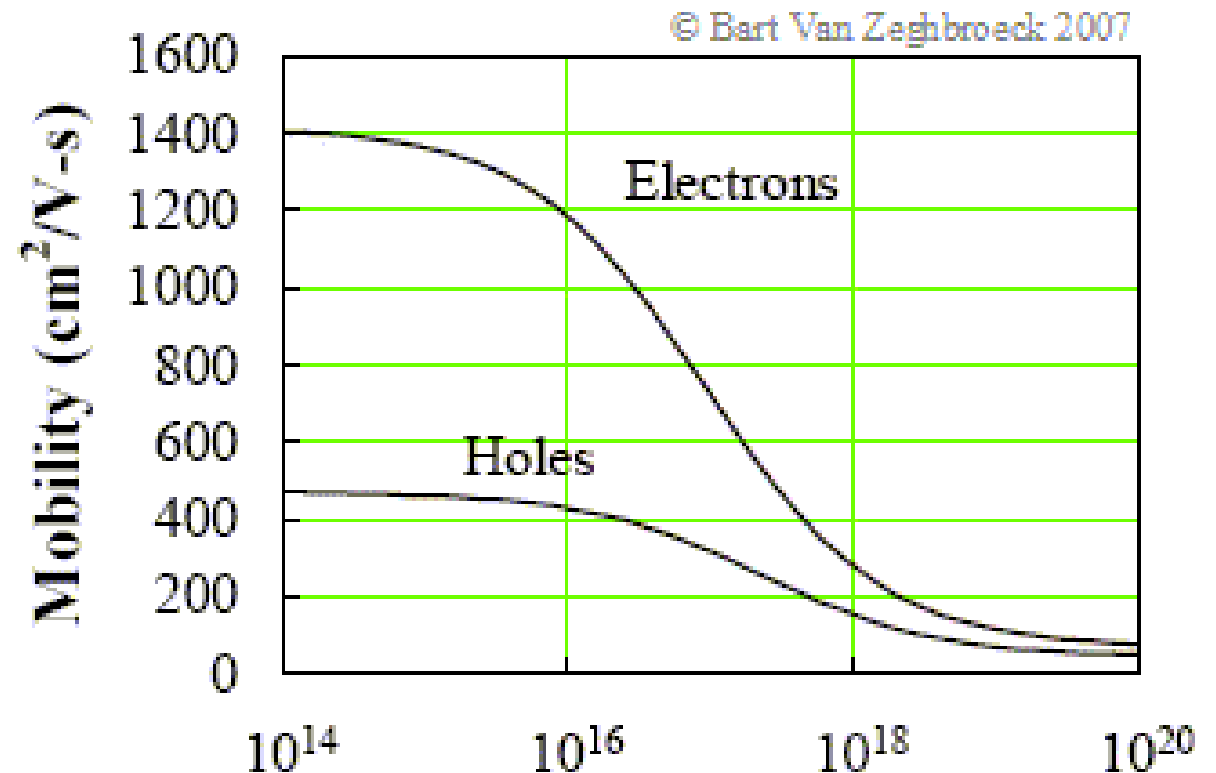


Extrinsic Semiconductor 掺杂半导体

doping dependence of mobility μ

when doping increases,
mobility decreases,
due to more impurity
scattering

silicon, $T = 300\text{ K}$



Q: What happens if there are both donors and acceptors?

doping density = $N_A + N_D$
Doping density (cm^{-3})

Extrinsic Semiconductor 掺杂半导体

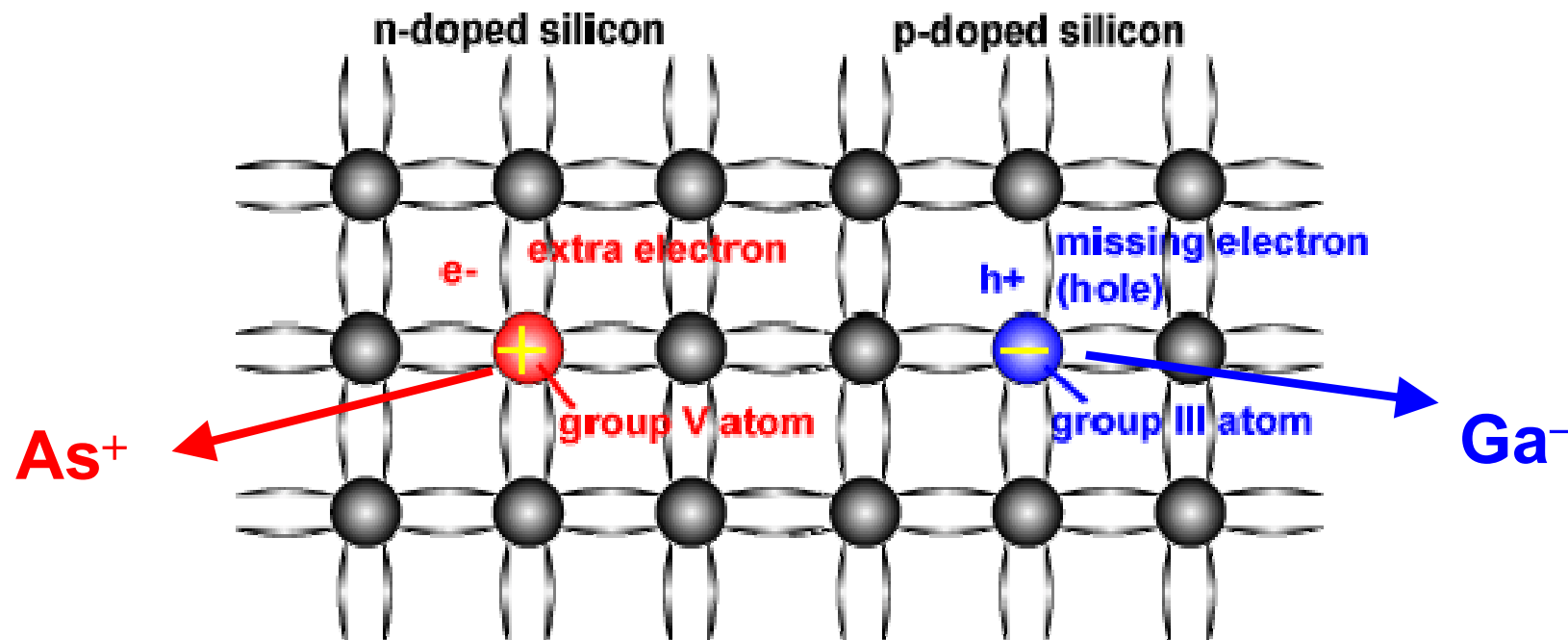
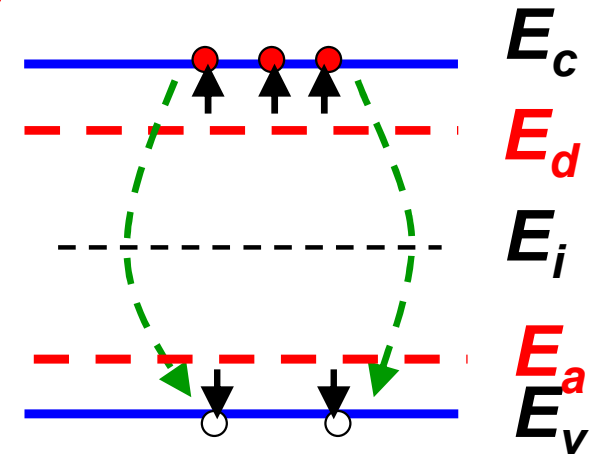
compensated semiconductor (补偿半导体)

contains both donor and acceptor

$$\begin{cases} n_c + N_A = p_v + N_D \\ n_c p_v = n_i^2 \end{cases}$$

charge balance

mass action law



Extrinsic Semiconductor 掺杂半导体

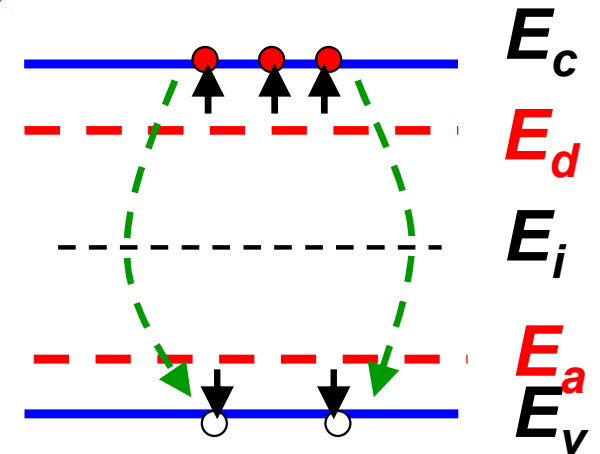
compensated semiconductor (补偿半导体)

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$$\begin{cases} n_c + N_A = p_v + N_D \\ n_c p_v = n_i^2 \end{cases}$$

charge balance

mass action law



if $N_A > N_D$ **→ p-doping**

$$\rightarrow p_v = \frac{N_A - N_D}{2} + \sqrt{\left(\frac{N_A - N_D}{2}\right)^2 + n_i^2}$$

if $N_A - N_D \gg n_i$ **→** $p_v = N_A - N_D$ $n_c = n_i^2 / p_v$

Extrinsic Semiconductor 掺杂半导体

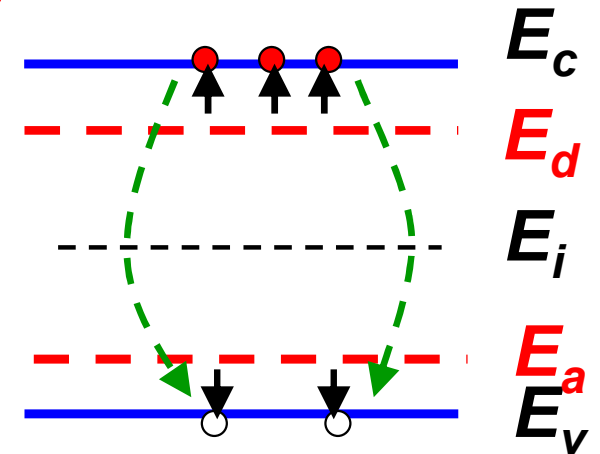
compensated semiconductor (补偿半导体)

contains both donor and acceptor

$$\begin{cases} n_c + N_A = p_v + N_D \\ n_c p_v = n_i^2 \end{cases}$$

charge balance

mass action law



if $N_D > N_A$ \longrightarrow **n-doping**

$$\longrightarrow n_c = \frac{N_D - N_A}{2} + \sqrt{\left(\frac{N_D - N_A}{2}\right)^2 + n_i^2}$$

if $N_D - N_A \gg n_i$ \longrightarrow $n_c = N_D - N_A$ $p_v = n_i^2 / n_c$

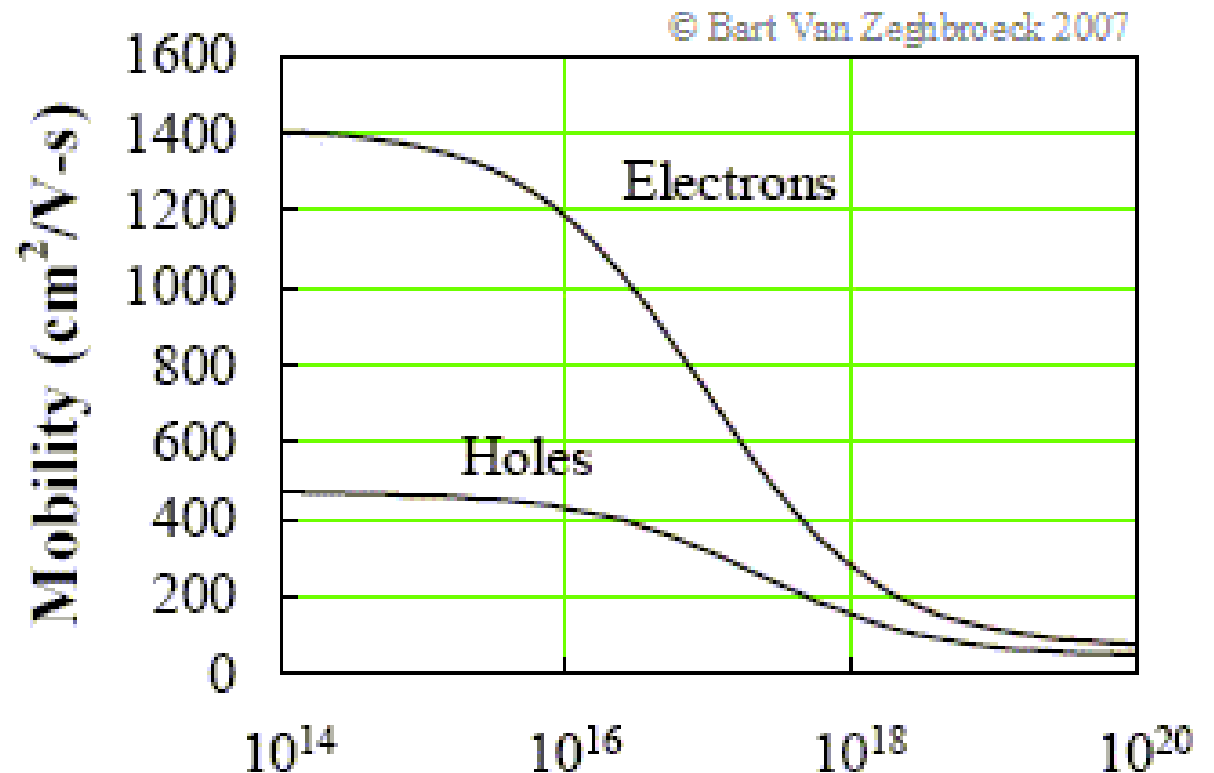
Extrinsic Semiconductor 掺杂半导体

in **compensated semiconductor (补偿半导体)**
contains both donor and acceptor

the mobility μ depends
on $N_A + N_D$

when doping increases,
mobility decreases,
due to more impurity
scattering

silicon, $T = 300\text{ K}$



doping density = $N_A + N_D$

Doping density (cm^{-3})

Mass Action Law - A Little Notion

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

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

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

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

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

Measurement of Doping

■ Hall Effect 霍尔效应

- A current flows through a conductor
- V_H is generated when applying B_z

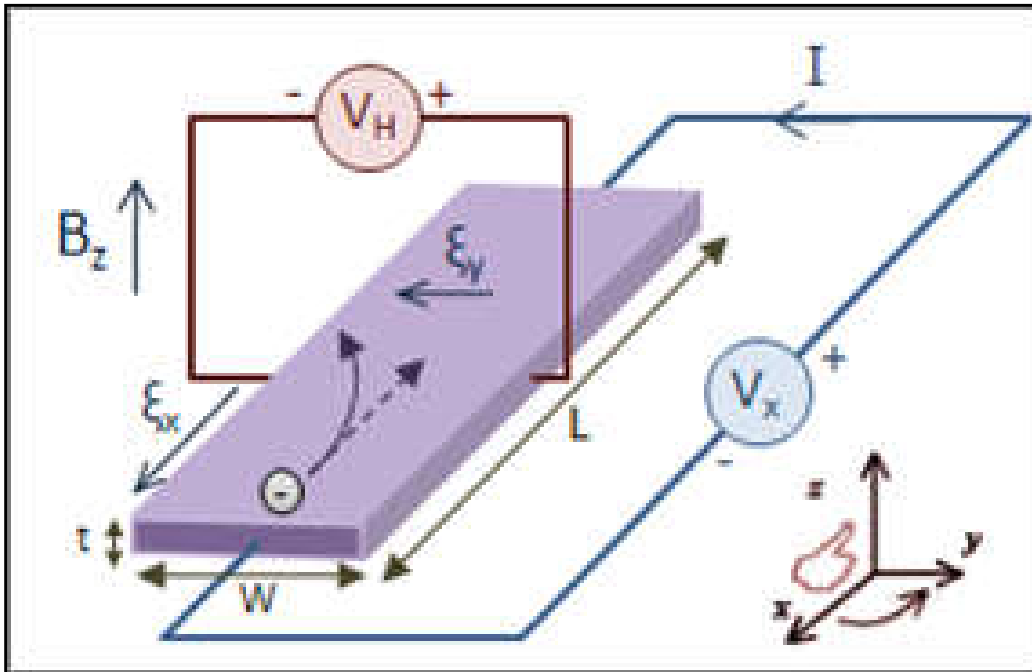
Lorentz Force
at equilibrium

$$eE_y = ev_x B_z$$

$$j_x = nev_x$$

$$E_y = \frac{1}{ne} j_x B_z = R_H j_x B_z$$

R_H - Hall coefficient

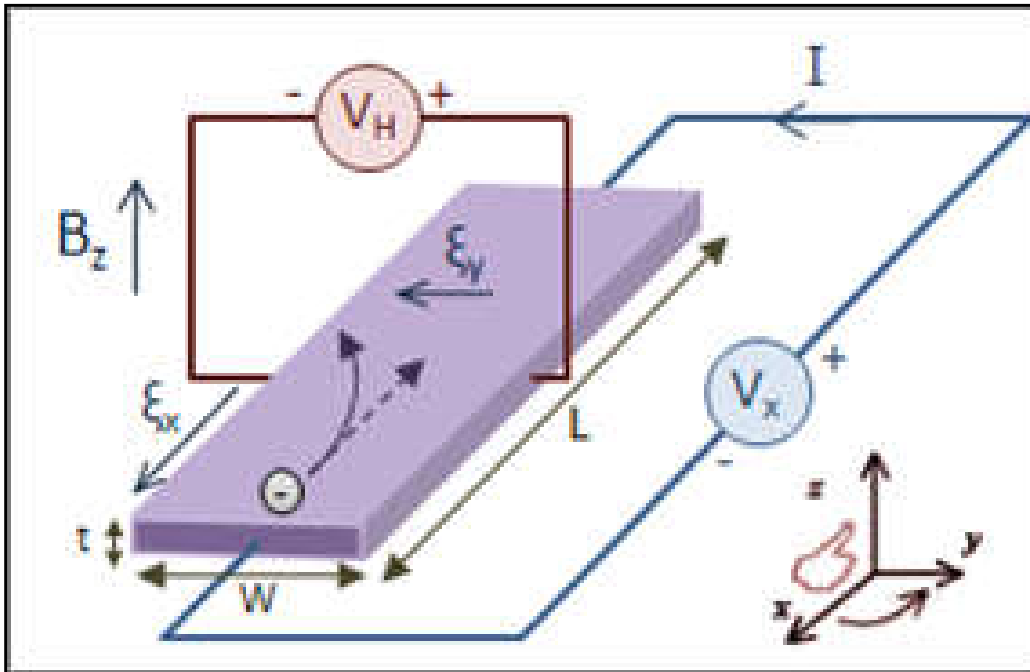


Measurement of Doping

■ Hall Effect 霍尔效应

- A current flows through a conductor
- V_H is generated when applying B_z

$$E_y = \frac{1}{ne} j_x B_z = R_H j_x B_z$$



p-doping

$$R_H = \frac{1}{p_v e}$$

positive

n-doping

$$R_H = -\frac{1}{n_c e}$$

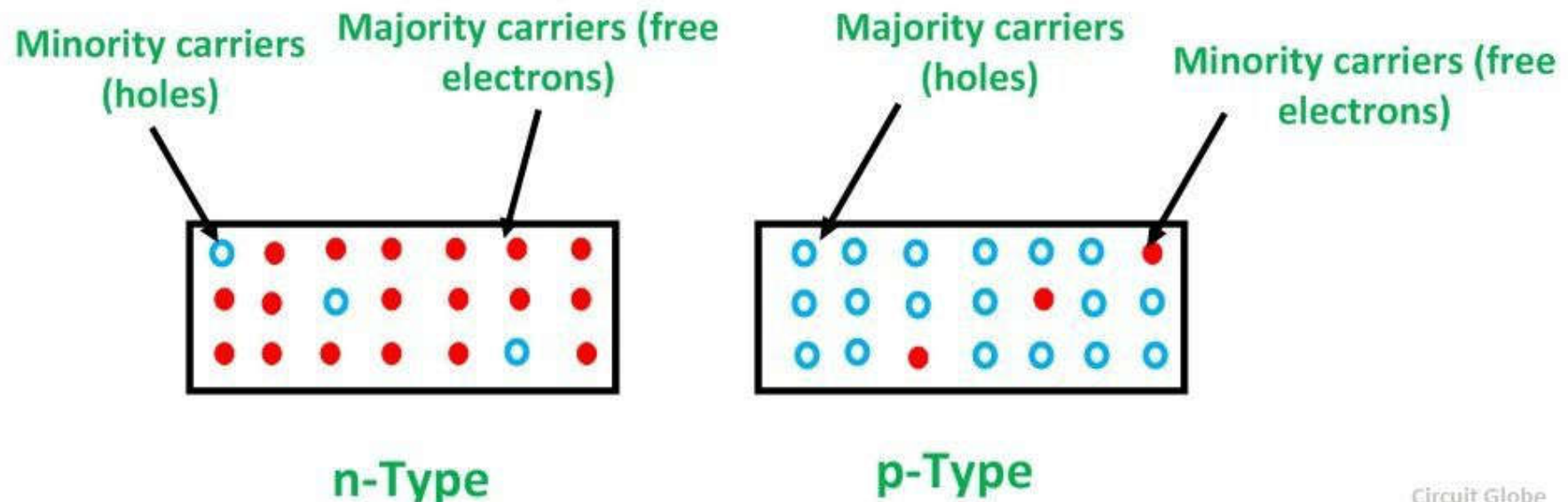
negative

Carrier Behaviors in Semiconductors

- Equilibrium carriers (平衡态载流子)
- Non-equilibrium carriers (非平衡态载流子)
- Current Flow
 - diffusion current
 - drift current
- Generation 产生
- Recombination 复合

Carrier Behaviors in Semiconductors

- Majority carriers (多数载流子)
- Minority carriers (少数载流子)
 - minority carriers are very important, because their amount can be easily changed by current injection, optical absorption, etc.



Equilibrium carriers (平衡态载流子)

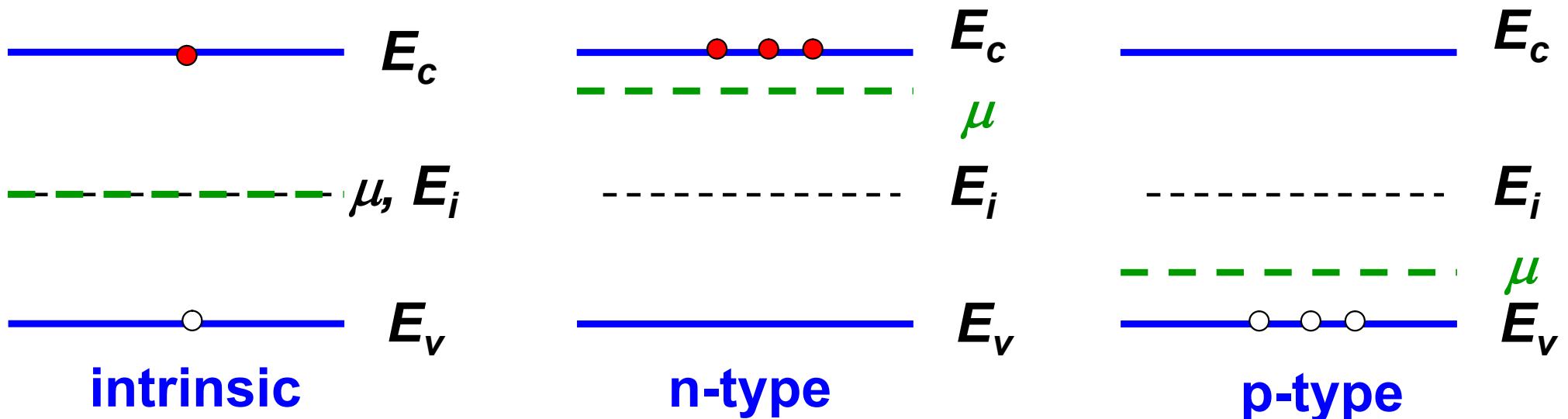
only thermal activation

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

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

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

mass action law



Non-equilibrium carriers (非平衡态载流子)

activation by other energy sources

e.g., photon absorption, current injection, ...

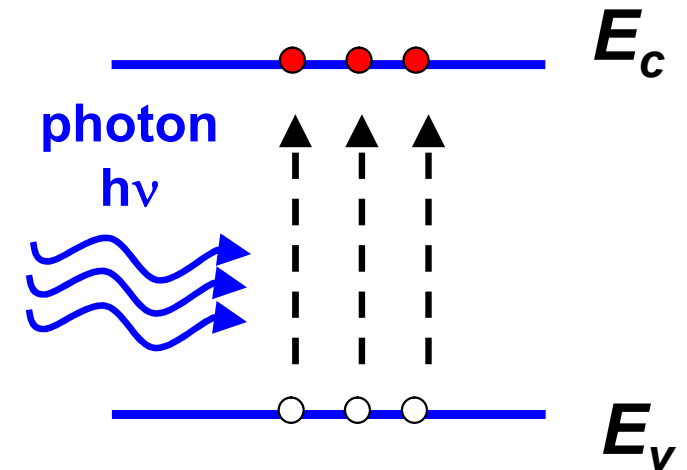
extra more carriers n_c and p_v

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

$$n_c \neq N_c(T)e^{-(E_c-\mu)/k_B T}$$

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

mass action law is not valid



Non-equilibrium carriers (非平衡态载流子)

activation by other energy sources

e.g., photon absorption, current injection, ...

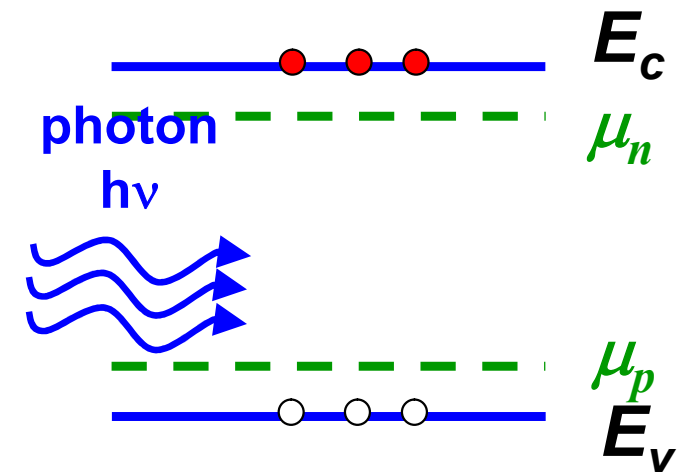
extra more carriers n_c and p_v

rewrite:

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

$$n_c = N_c(T) e^{-(E_c - \mu_n)/k_B T}$$

$$\mu_n \neq \mu_p$$



quasi-Fermi levels (准费米能级)

Current Flow

- **Diffusion current 扩散电流**
 - **caused by concentration gradient**
- **Drift current 迁移电流**
 - **caused by electric field**

Current Flow

- Diffusion current 扩散电流
 - caused by concentration gradient

ink in water



1D

$$j = -qD \frac{\partial n}{\partial x}$$

3D

$$\mathbf{j} = -q\mathbf{D}\nabla n$$

diffusivity 扩散系数

$$D = \mu \frac{kT}{q}$$

n - carrier concentration (#/m³)

D - diffusivity (m²/s) 扩散率

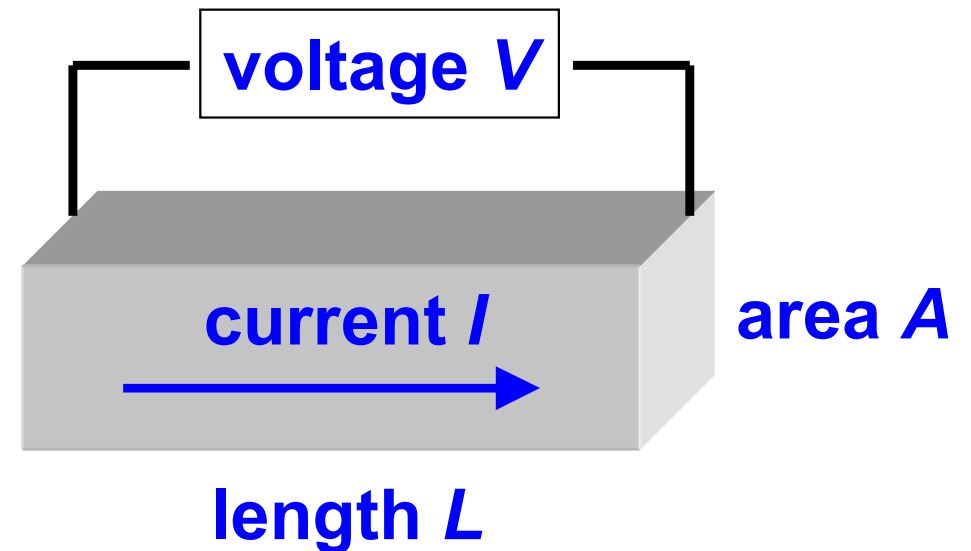
μ - mobility (m²/V/s)

Current Flow

- Drift current 迁移电流
 - caused by electric field

Ohm's Law

$$j = \sigma E = nq\mu E = nqv$$



n - carrier concentration ($\#/m^3$)

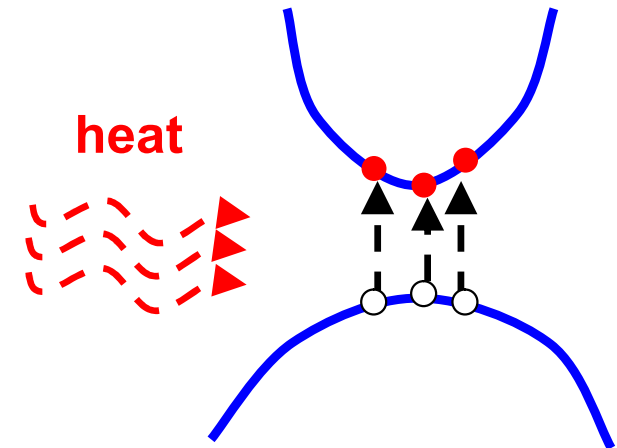
D - diffusivity (m^2/s) 扩散率

μ - mobility ($m^2/V/s$)

Carrier Generation

- Excited by thermal energy

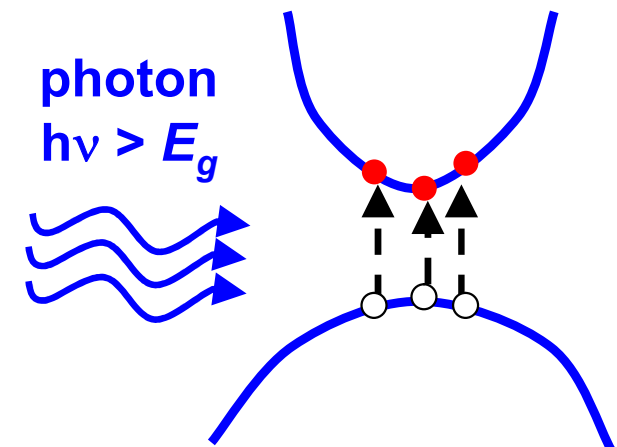
$$n_c p_v = N_v(T) P_v(T) e^{-E_g/k_B T} = n_i^2$$



- Excited by photons

- photodetector
- solar cells
- ...

$$h\nu = e + h$$



- Other sources

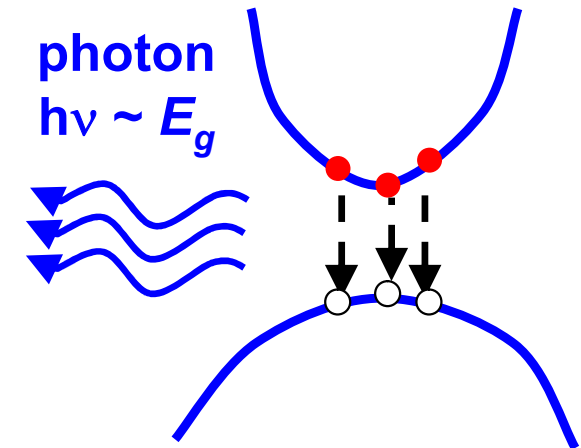
- ...

Carrier Recombination 复合

■ Radiative 辐射

- LED
- laser
- ...

$$e + h = \text{photon}$$

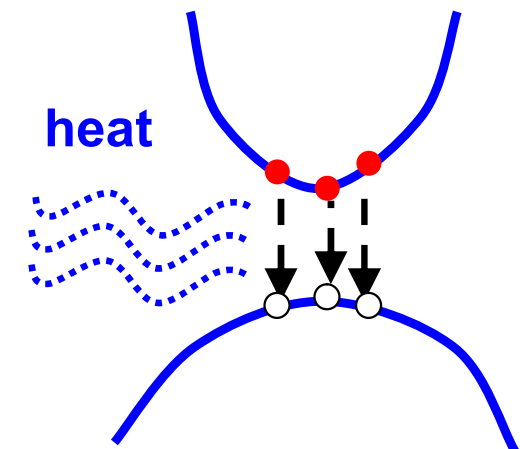


■ Non-radiative recombination

- defects, impurities, surfaces
- lattice (phonons)

$$e + h = \text{phonons}$$

- Auger process
- ...

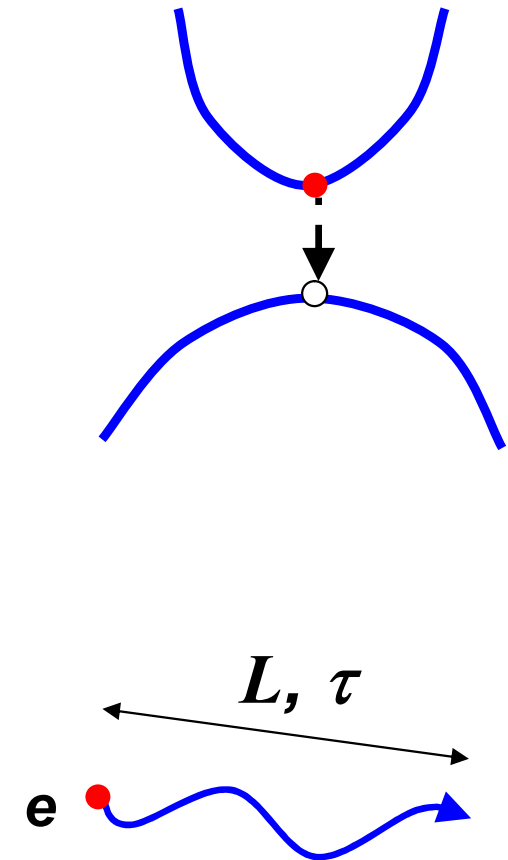


Carrier Recombination 复合

- 载流子寿命 **Carrier lifetime** τ_n and τ_p
 - the averaged time before the non-equilibrium carriers recombine
- 扩散率 **Diffusivity** D_n and D_p
- 扩散长度 **Diffusion length** L_n and L_p
 - the averaged distance carriers move before recombination

$$L = \sqrt{D\tau}$$

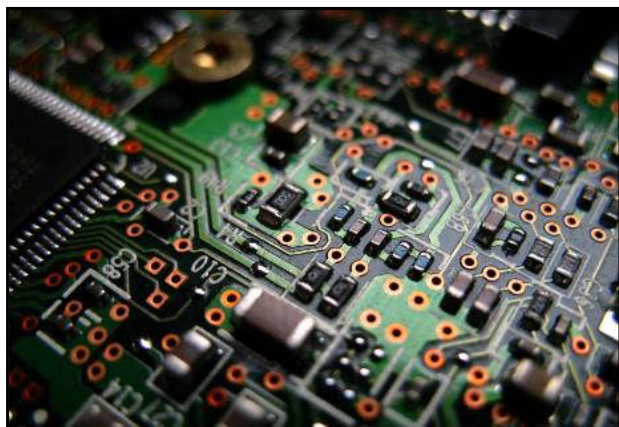
- At non-equilibrium, **minority carrier** diffusion and lifetime are important for device performance



D - diffusivity (m^2/s) 扩散率

Semiconductors - Applications

different carrier behaviors offer different applications



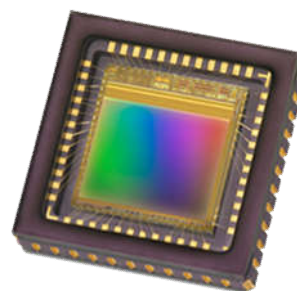
integrated circuits



LEDs



lasers



detectors



solar cells

Thank you for your attention