Fundamentals of Solid State Physics

Semiconductors
- Intrinsic and Extrinsic

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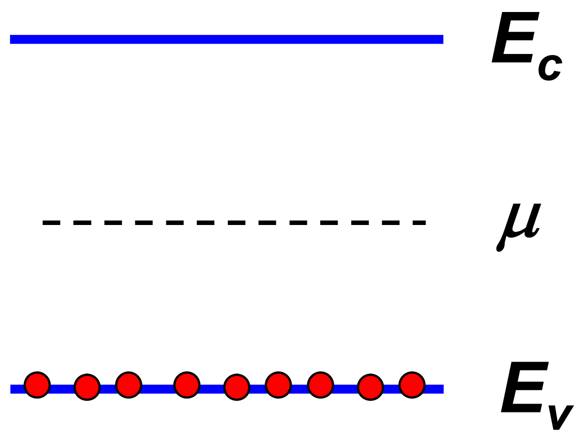
Density of Carriers

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

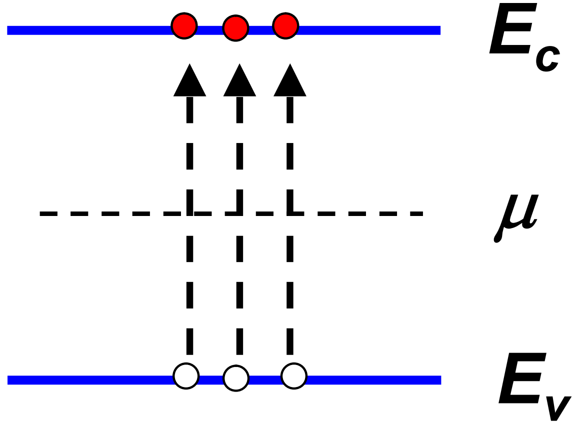
insulator

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

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

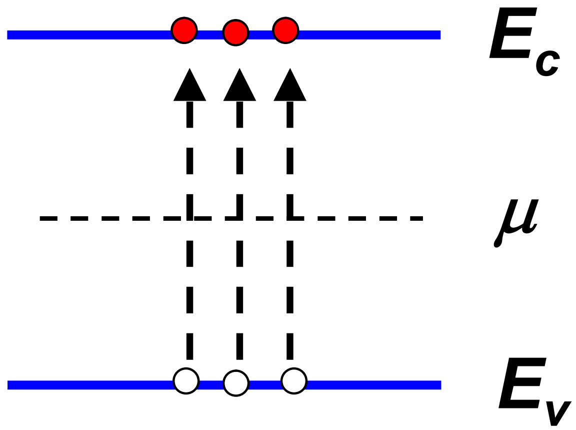
***T* > 0 K**
thermalization 热激发
CB and VB are partly filled
conductor

Density of Carriers

when *T* > 0 K

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

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



→

$$n_c p_v = N_v(T)P_v(T)e^{-(E_c-E_v)/k_BT}$$
$$= N_v(T)P_v(T)e^{-E_g/k_BT}$$

mass action law

at equilibrium, $n_c p_v$ is a constant

Density of Carriers

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

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

effective density of states **(有效态密度)**

no physical meaning, just two constants

For silicon, at room temperature (*T* = 300 K)

$$m_e^* = 1.06 m_0$$

$$m_h^* = 0.58 m_0$$

$$N_c(T) = 2.73\times10^{19}\,\text{cm}^{-3} \qquad P_v(T) = 1.10\times10^{19}\,\text{cm}^{-3}$$

Intrinsic Semiconductor 本征半导体

pure, no impurity, charge balance

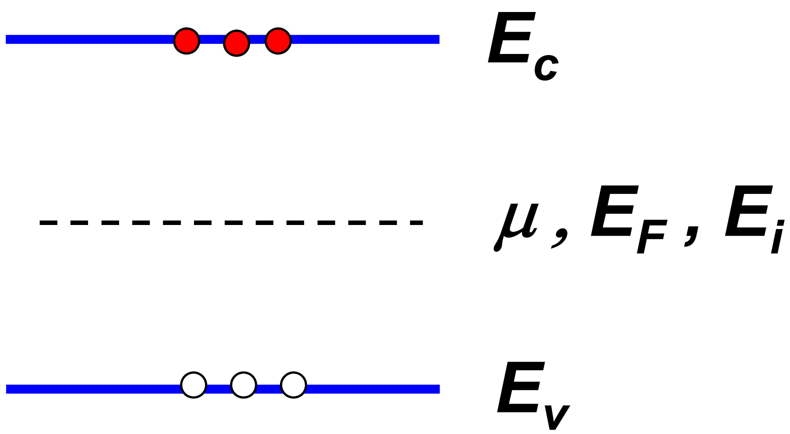
$$n_c = p_v = n_i$$

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

$$\mu = E_F = E_i$$

$$= E_c - k_BT\ln\left(\frac{N_c(T)}{n_i}\right)$$

$$= E_v + k_BT\ln\left(\frac{P_v(T)}{n_i}\right)$$



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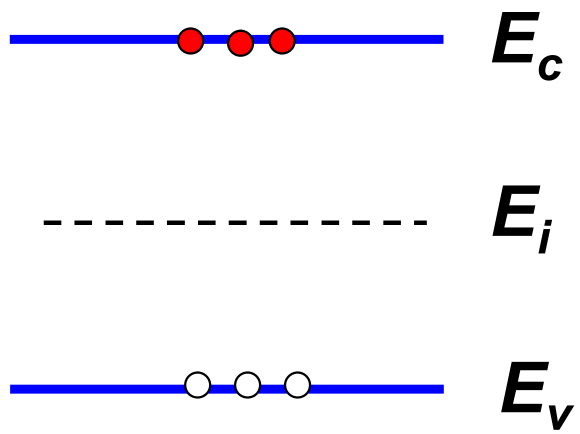
pure, no impurity, charge balance

$$n_c = p_v = n_i$$

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

$$\mu = E_F = E_i$$
$$= E_v + \frac{1}{2}E_g + \frac{3}{4}k_BT\ln\left(\frac{m_h^*}{m_e^*}\right)$$



The chemical potential / Fermi level / Intrinsic level is almost in the middle of the gap

Intrinsic Semiconductor 本征半导体

Example: intrinsic Si at 300 K

$$m_e^* = 1.06 m_0$$

$$m_h^* = 0.58 m_0$$

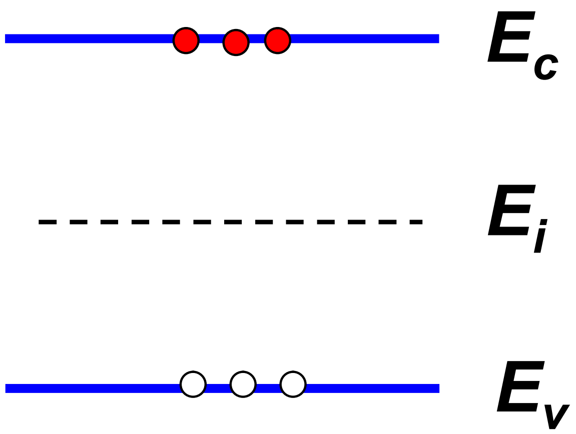
$$N_c(T) = 2.73 \times 10^{19}\ \text{cm}^{-3} \qquad P_v(T) = 1.10 \times 10^{19}\ \text{cm}^{-3}$$

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

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

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

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

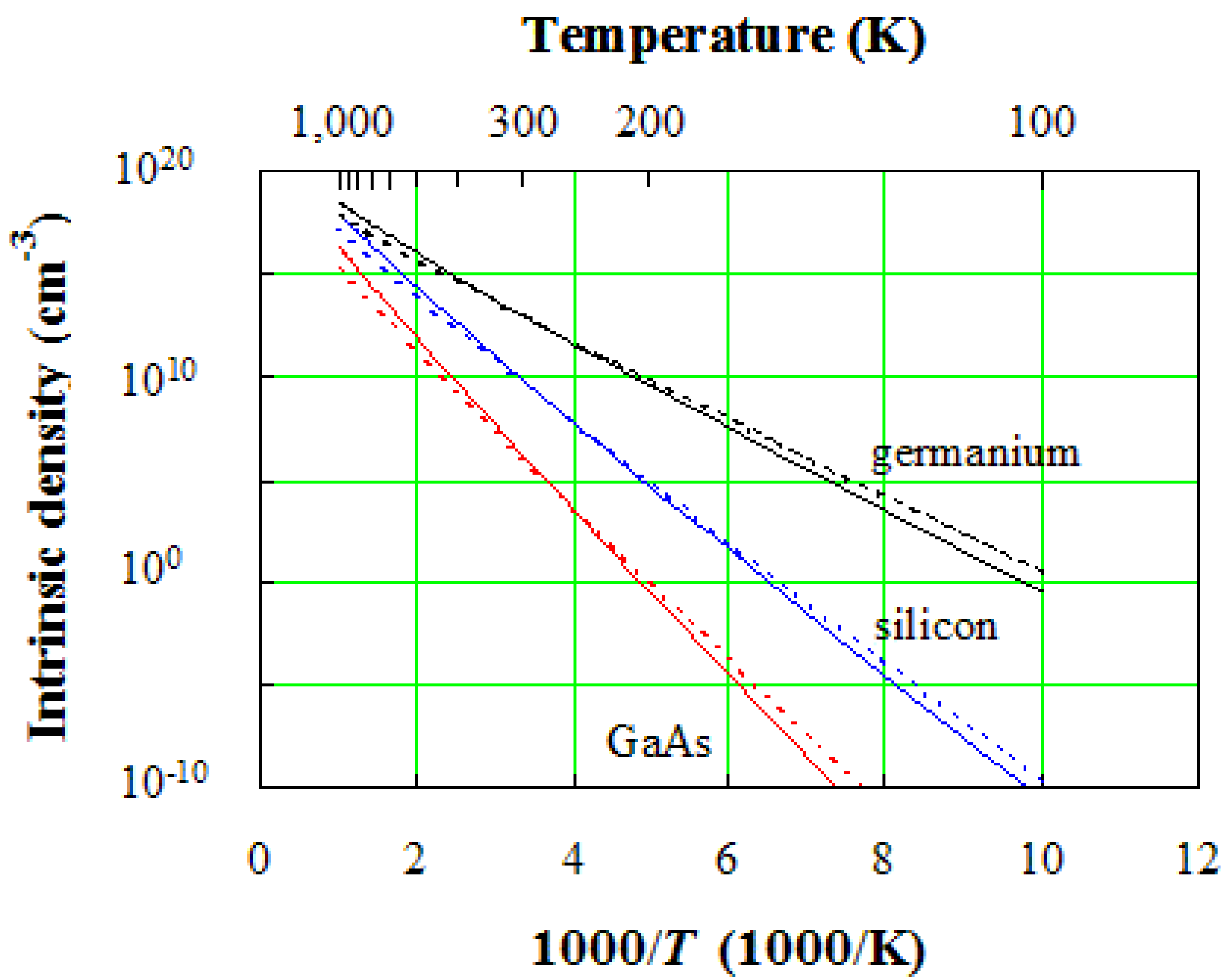


Intrinsic Semiconductor 本征半导体

temperature dependence of carrier concentration

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

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



Intrinsic Semiconductor 本征半导体

temperature dependence of carrier mobility μ

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

at low *T*

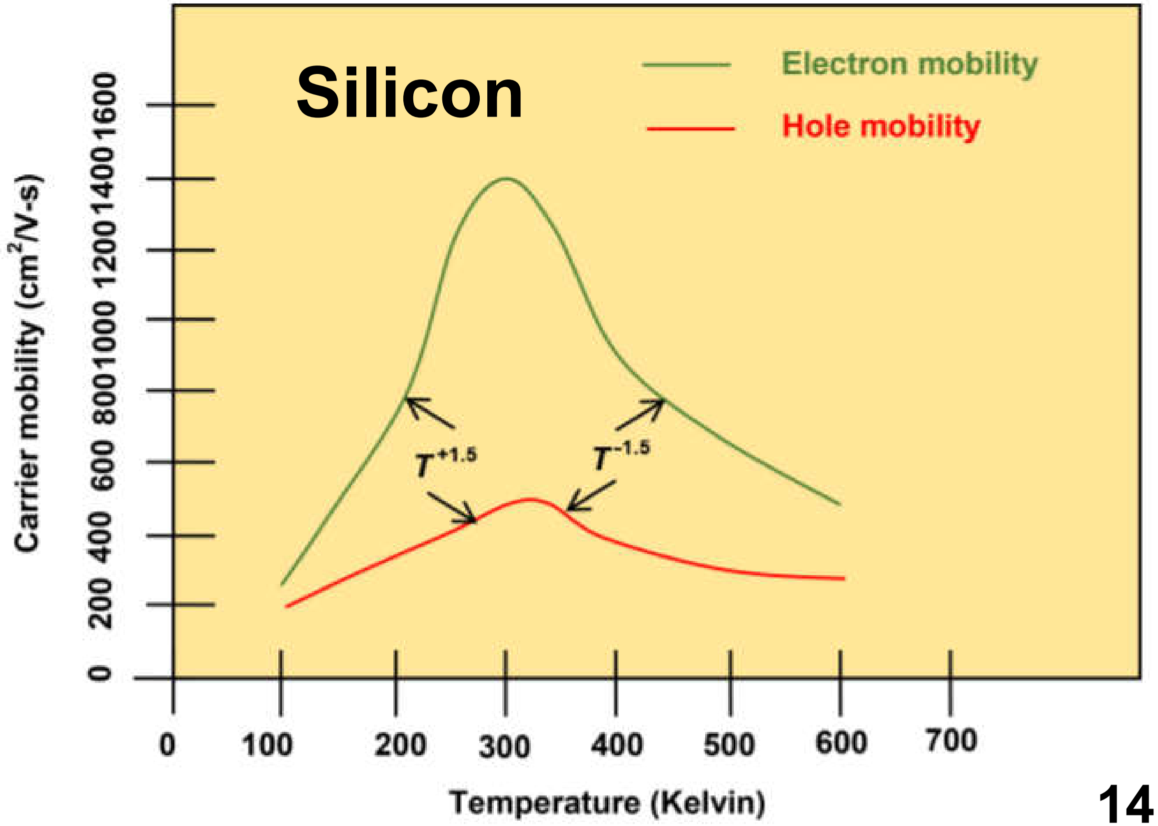
$$\mu \sim T^{3/2}$$

impurity scattering

at high *T*

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

lattice scattering

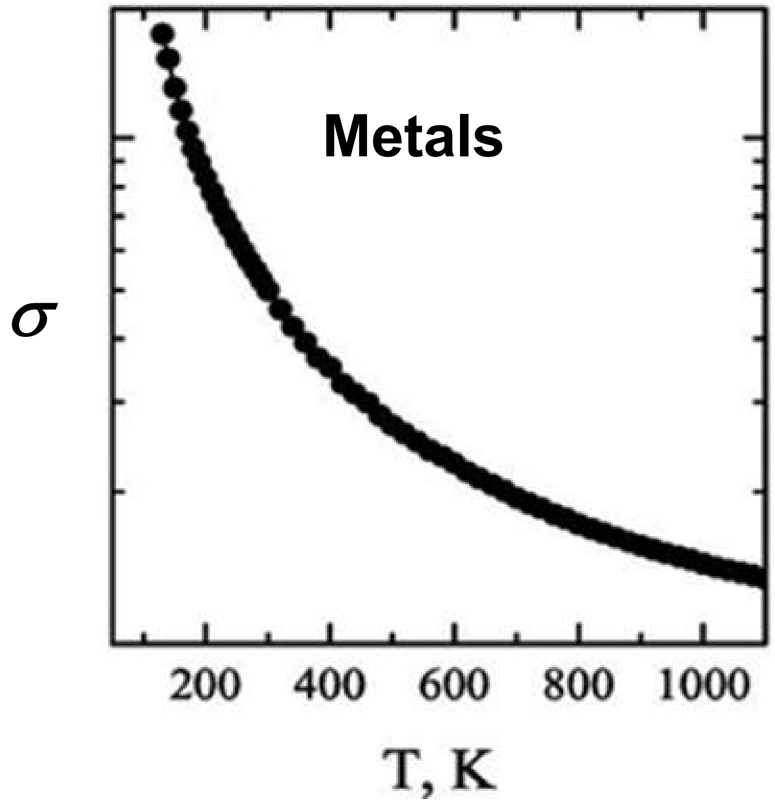


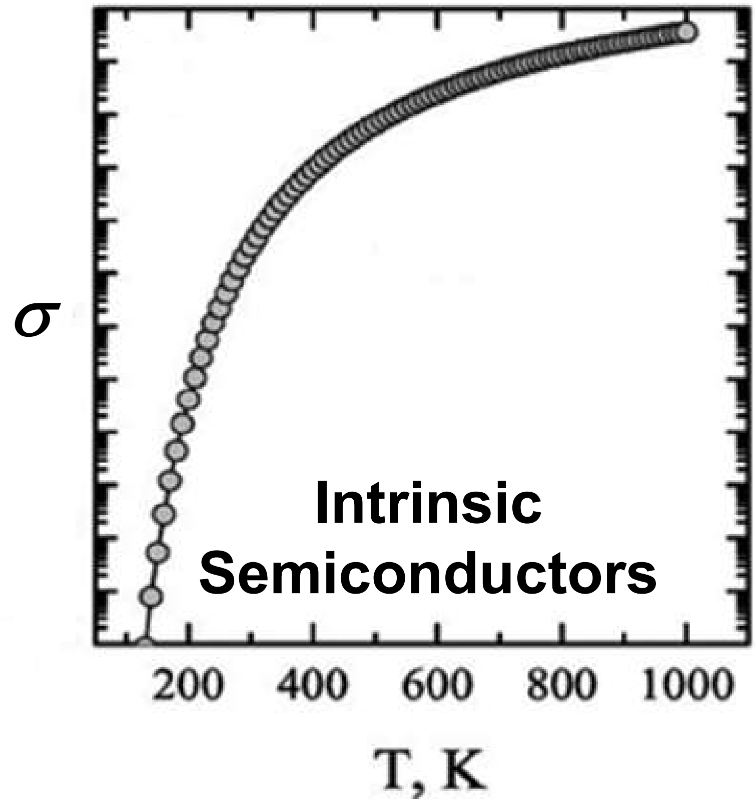
Temperature Dependence of σ

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

	conductivity σ (S/m)
wood	$10^{-14} \sim 10^{-16}$
glass	$10^{-11} \sim 10^{-15}$

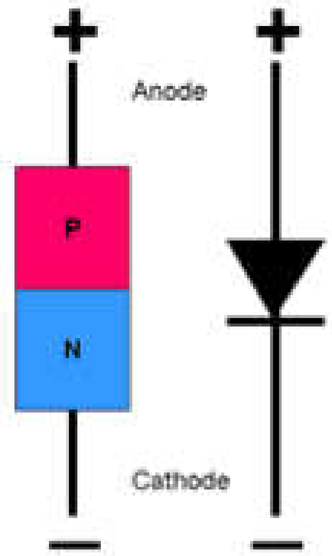
silicon with doping

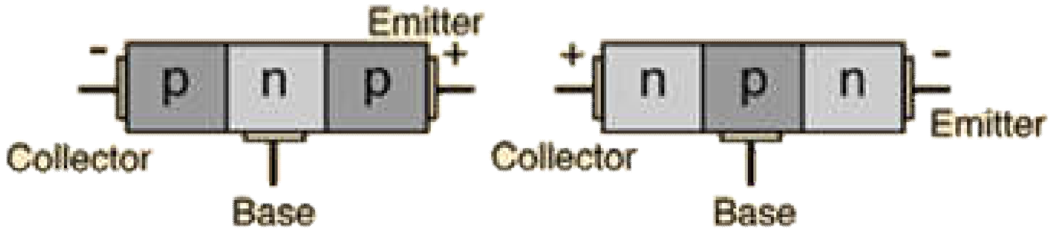
	conductivity σ (S/m)
0	10^{-6}
$1 / 10^{9}$	10^{-1}
$1 / 10^{6}$	10^{2}
$1 / 10^{3}$	10^{5}

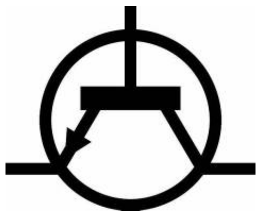
at T = 300 K

Doping Makes Functional Devices

ingots and wafers

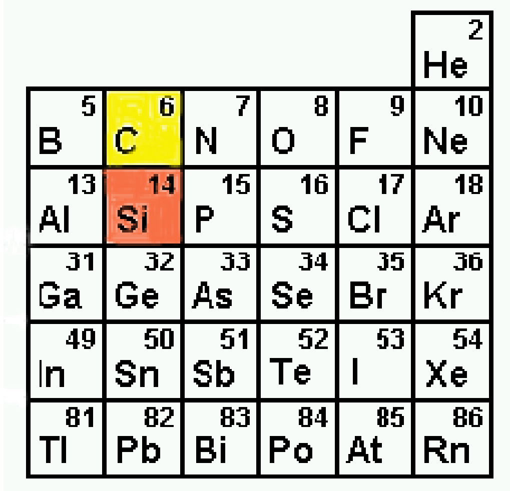


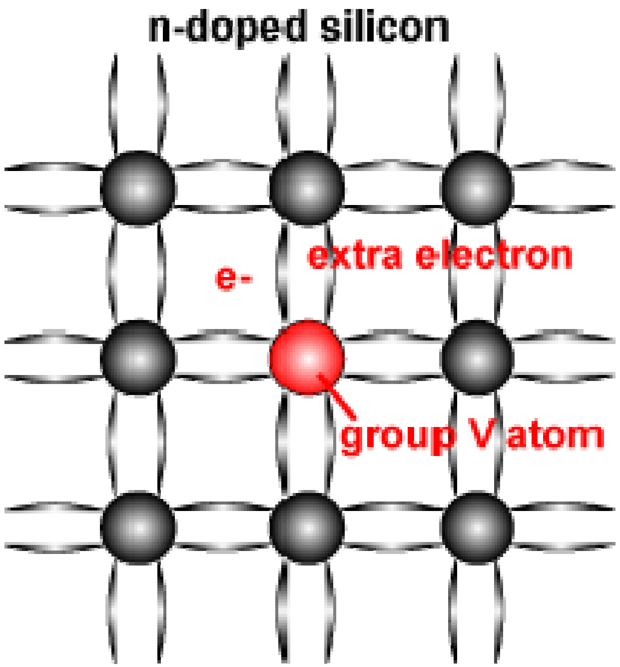


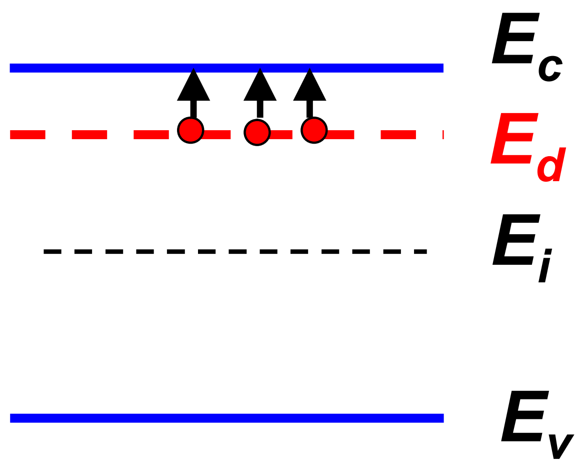


Extrinsic Semiconductor 掺杂半导体

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

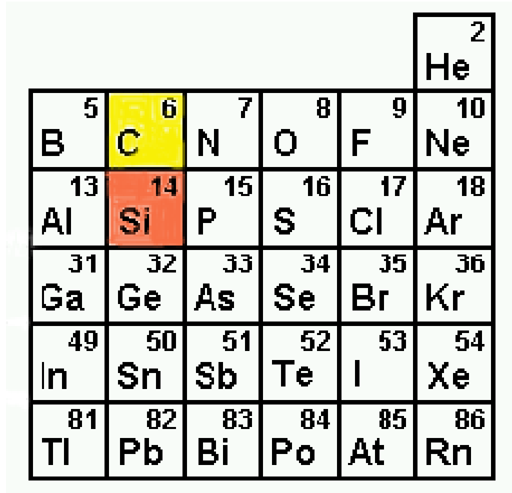


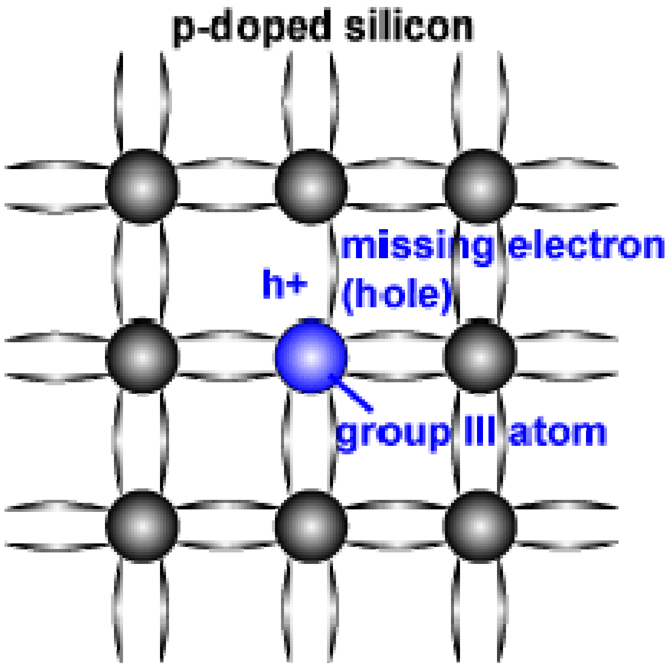


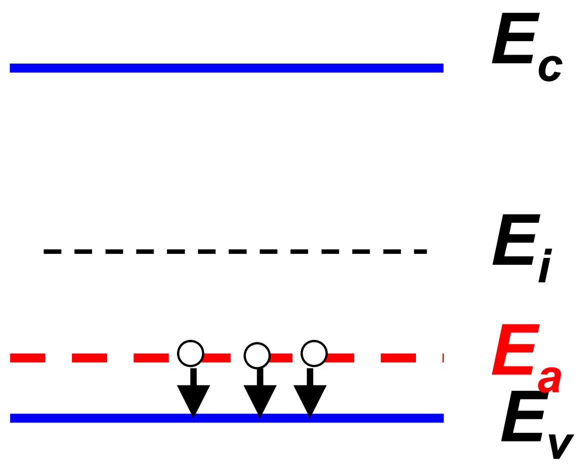


Extrinsic Semiconductor 掺杂半导体

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

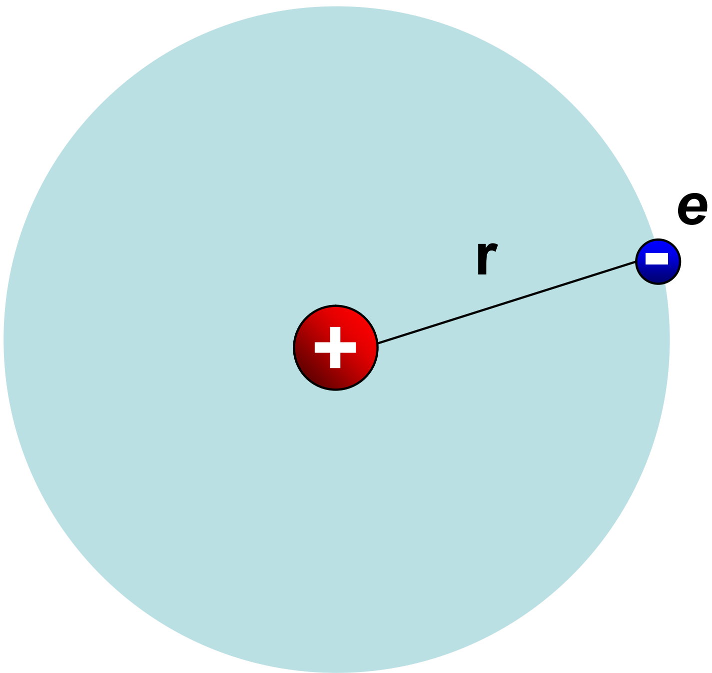






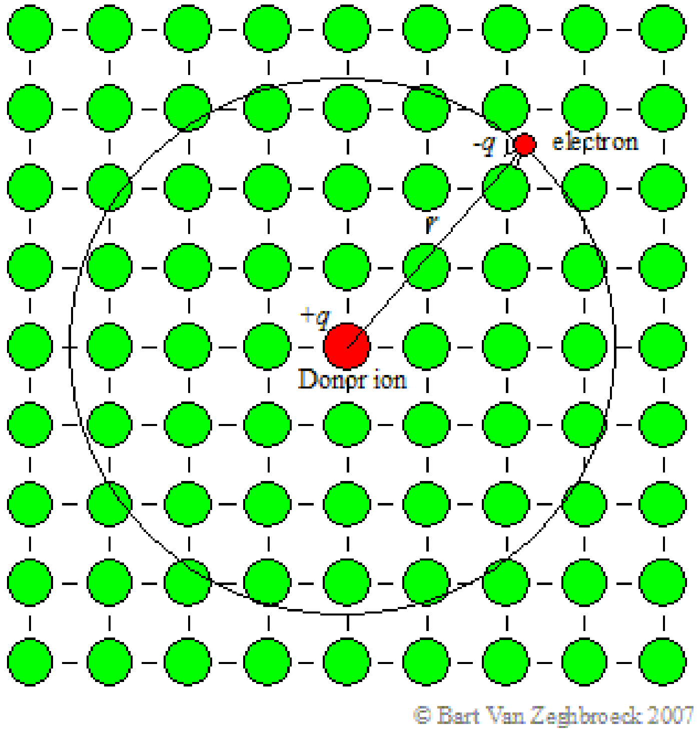
Ionization Energy of Dopants 电离能

Hydrogen Atom



$$E_1 = -\frac{m_0 e^4}{8\varepsilon_0^2 h^2} = -13.6\,\text{eV}$$

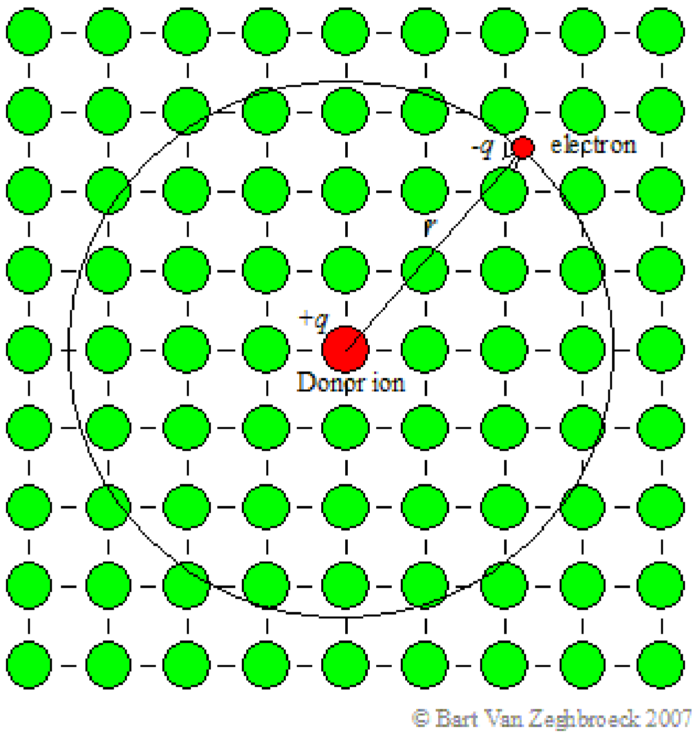
Hydrogen-like Model



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

Ionization Energy of Dopants 电离能

Hydrogen-like Model

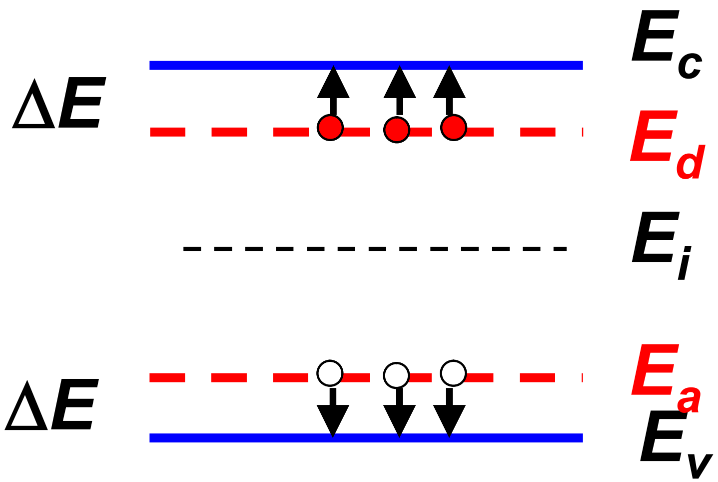


$$\Delta E = 13.6 \frac{m^*}{m_0} \frac{1}{\varepsilon_r^2} \text{eV}$$

m^* - effective mass ~ $0.1m_0$

ε_r - relative dielectric constant ~ 10

→ ΔE ~ 0.01 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 $\mathcal{E}_a - \mathcal{E}_v$)

	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 $\mathcal{E}_c - \mathcal{E}_d$)

	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 ($E_g = \mathcal{E}_c - \mathcal{E}_v$)

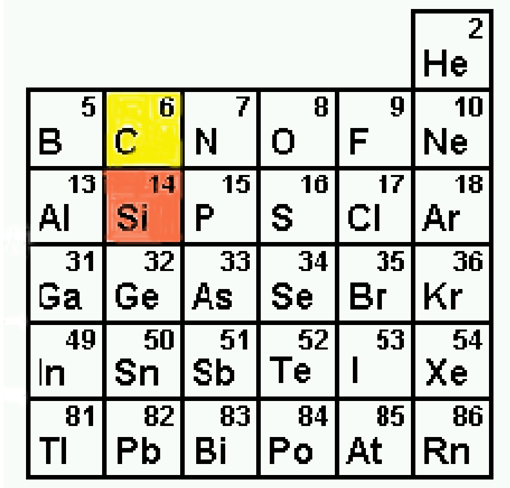
Si	1.12 eV
Ge	0.67 eV

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

Ashcroft & Mermin p.580

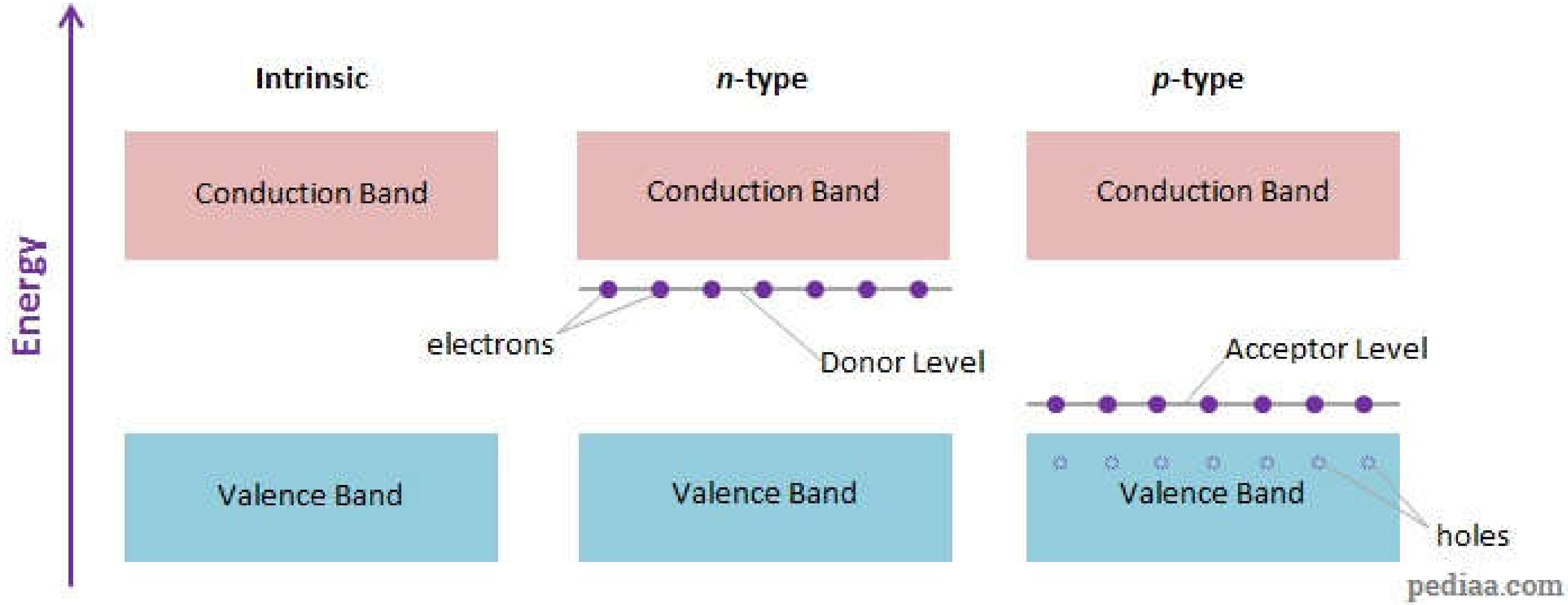
Doping in Silicon

For Si (and Ge):
p dopant: B, Al, Ga, ...
n dopant: P, As, Sb, ...



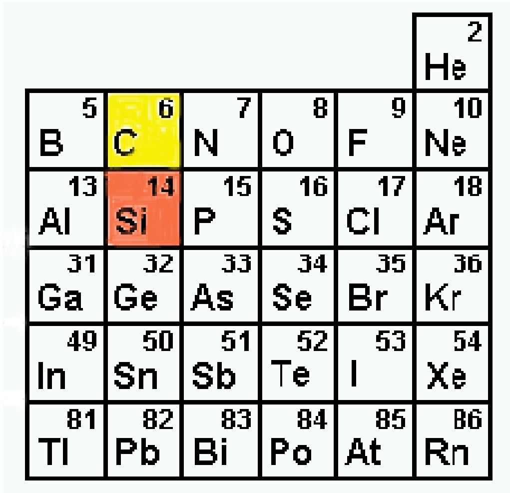
					2 He
5 B	6 C	7 N	8 O	9 F	10 Ne
13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn

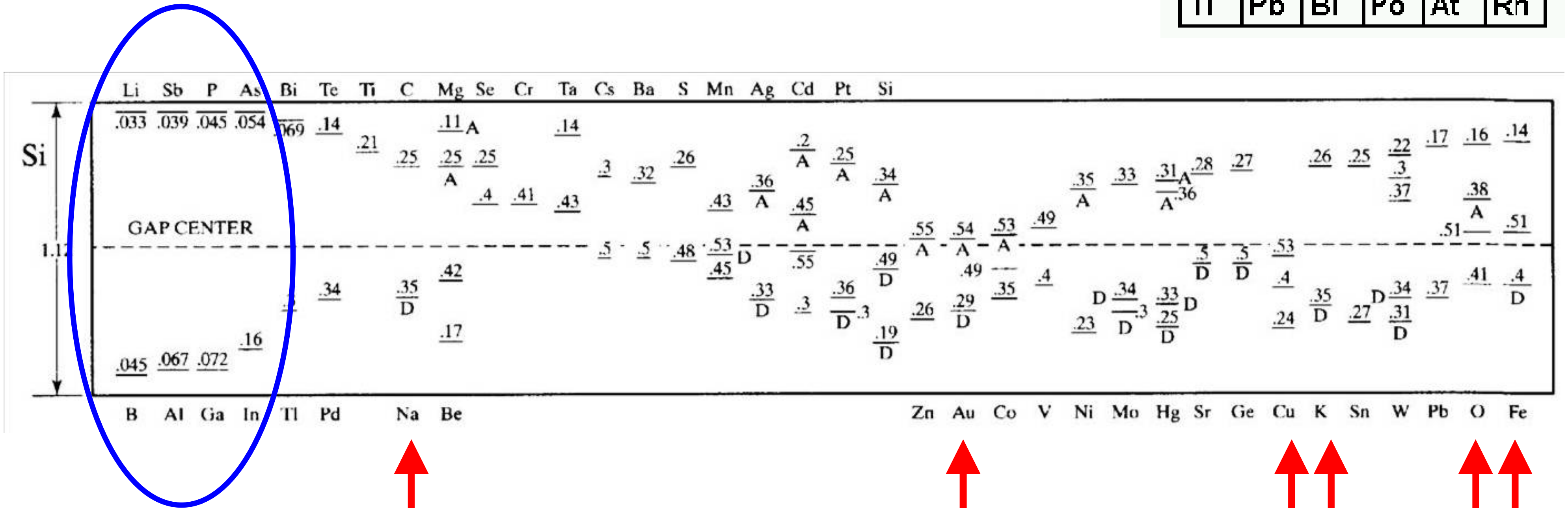
These dopants are shallow level defects, which can be excited to generated carriers closed to E_c or E_v (~ 0.01 eV), room temperature $k_B T$ ~0.03 eV



Other Defects in Silicon

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





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

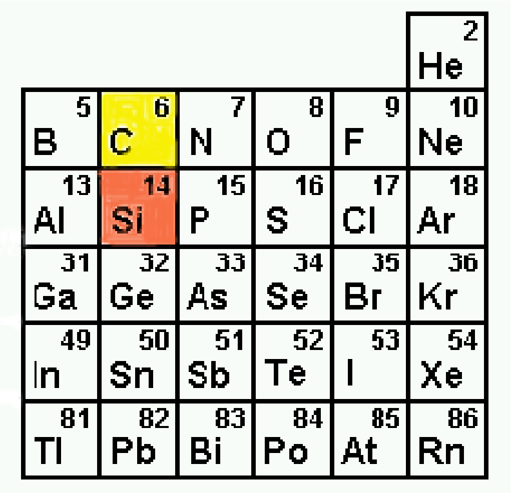
...

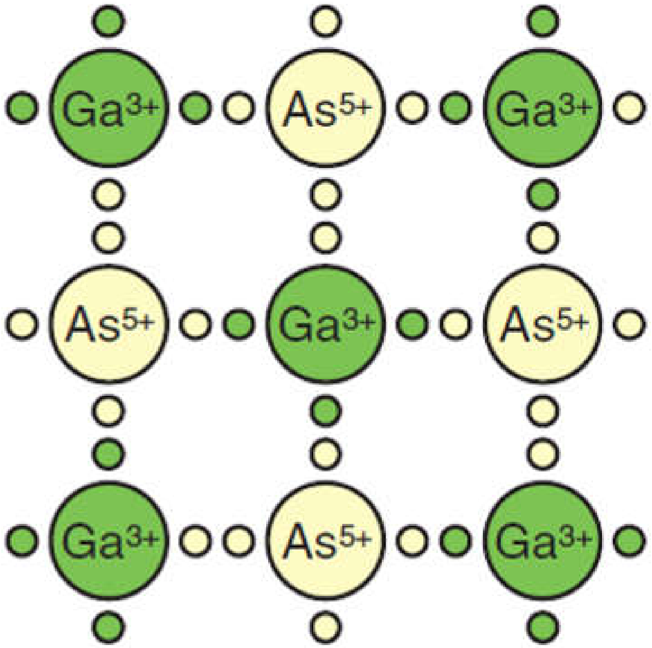
n dopant:

replace As: Se

replace Ga: Si, Ge

...





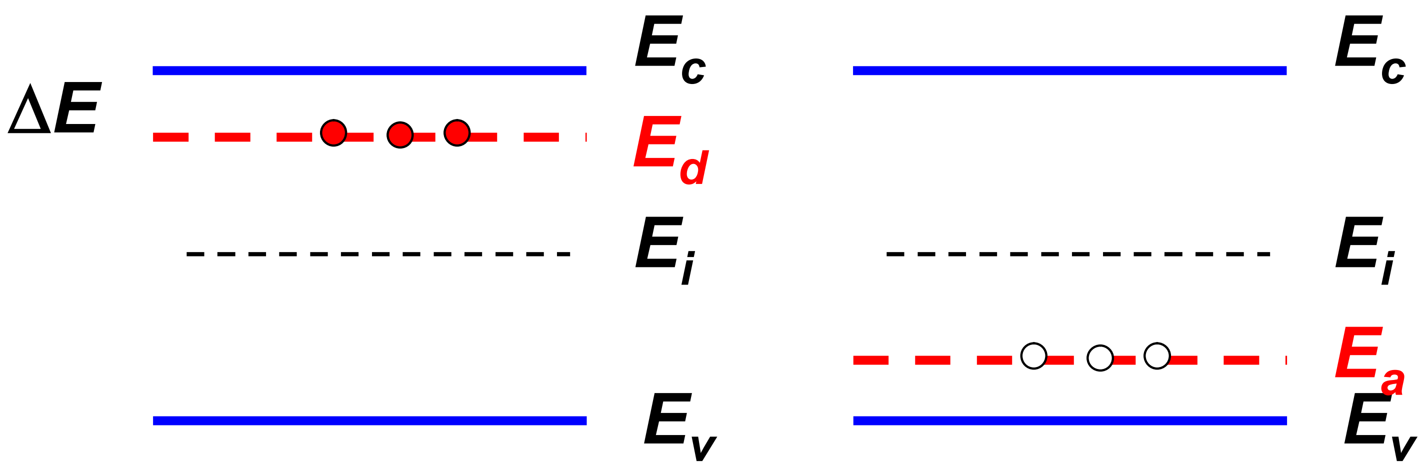
Extrinsic Semiconductor 掺杂半导体

when T = 0 K, carriers cannot be excited

$$n_c \to 0 \qquad p_v \to 0$$

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

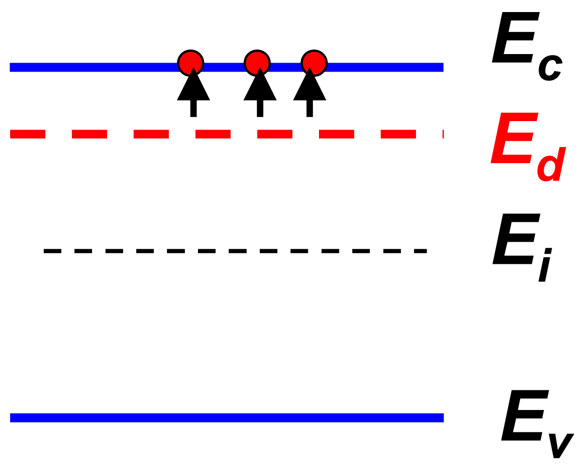
$$n_c p_v = N_v(T) P_v(T) e^{-E_g/k_B T} = n_i^2$$

at equilibrium, $n_c p_v$ is a constant

If $N_D >> n_i$
For n-doping

$$n_c = N_D$$

$$p_v = n_i^2 / n_c$$



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

Example - Silicon

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

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

$$n_i \sim 10^{10}\,\mathrm{cm}^{-3}$$

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

atom density of Si

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

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

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

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

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

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

the conductivity is increased by 10^6

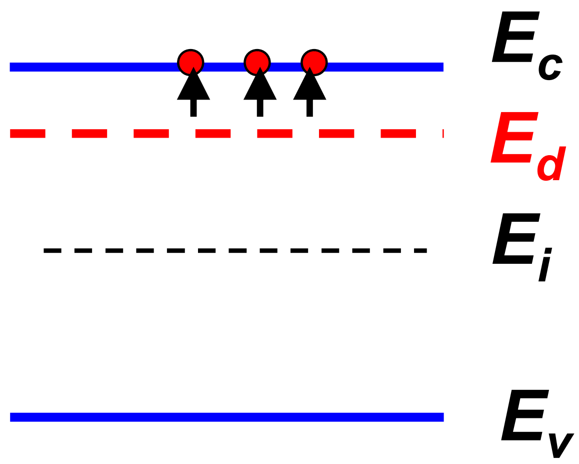
the conductivity is related to the doping and weakly dependent on T

Chemical Potential / Fermi Level

For n-doping

$$n_c = N_D \qquad p_v = n_i^2 / n_c$$

$$n_c \gg p_v$$

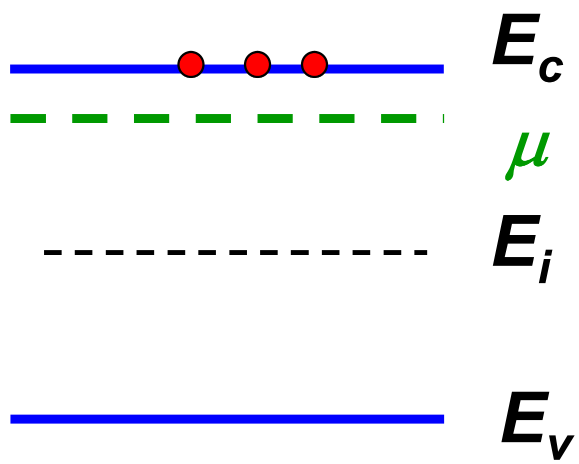


N_D - concentration of donor (cm^{-3})

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

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

→ $$E_c - \mu \ll \mu - E_v$$



chemical potential / Fermi level moves closer to E_c

Chemical Potential / Fermi Level

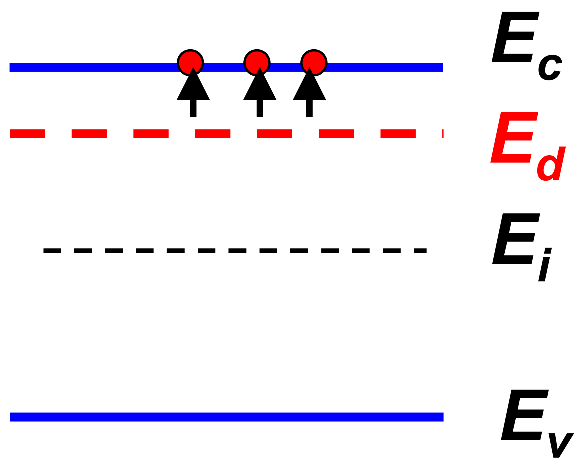
For n-doping

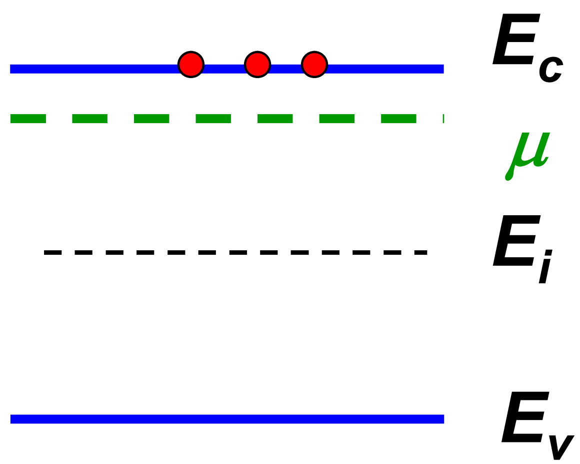
$$n_c = N_D \qquad p_v = n_i^2 / n_c$$

$$\mu = E_c - k_B T \ln\left(\frac{N_c(T)}{n_c}\right)$$

$$= E_i + k_B T \ln\left(\frac{N_D}{n_i}\right)$$

$$\approx E_v + \frac{1}{2}E_g + k_B T \ln\left(\frac{N_D}{n_i}\right)$$





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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

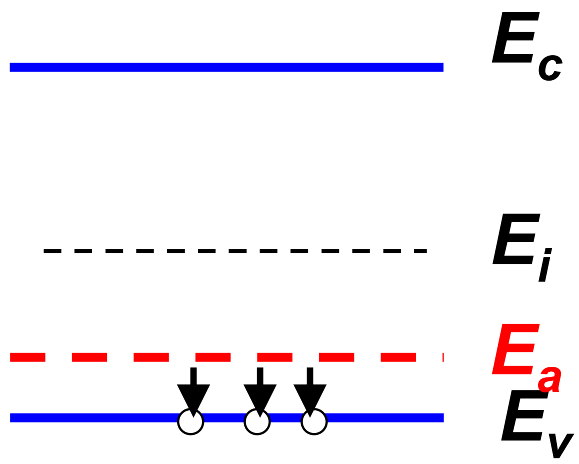
$$n_c p_v = N_v(T) P_v(T) e^{-E_g/k_B T} = n_i^2$$

at equilibrium, $n_c p_v$ is a constant

If $N_A >> n_i$
For p-doping

$$p_v = N_A$$

$$n_c = n_i^2 / p_v$$



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

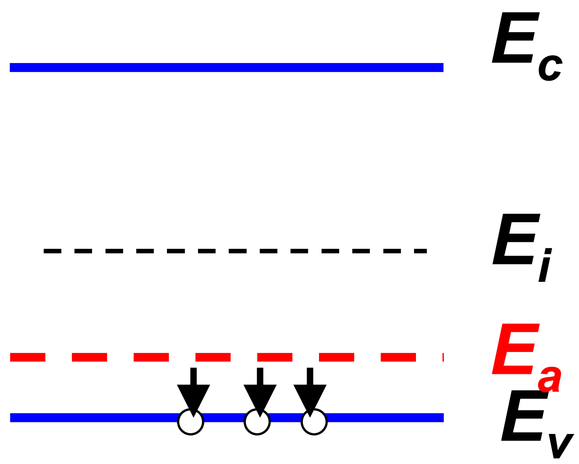
Chemical Potential / Fermi Level

For p-doping

$$p_v = N_A$$

$$n_c = n_i^2 / p_v$$

$$p_v \gg n_c$$

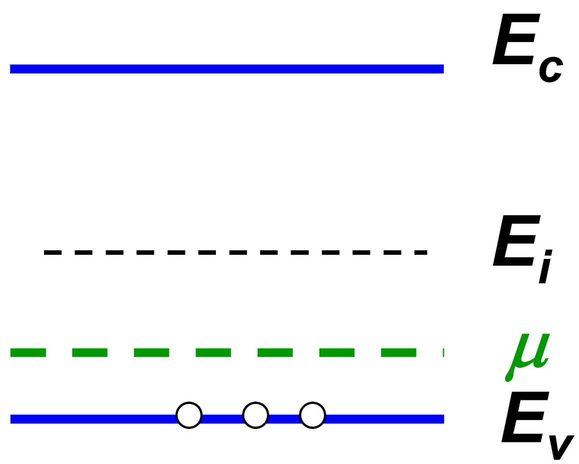


N_A - concentration of acceptor (cm^{-3})

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

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

→ $$E_c - \mu \gg \mu - E_v$$



chemical potential / Fermi level moves closer to E_v

Chemical Potential / Fermi Level

For p-doping

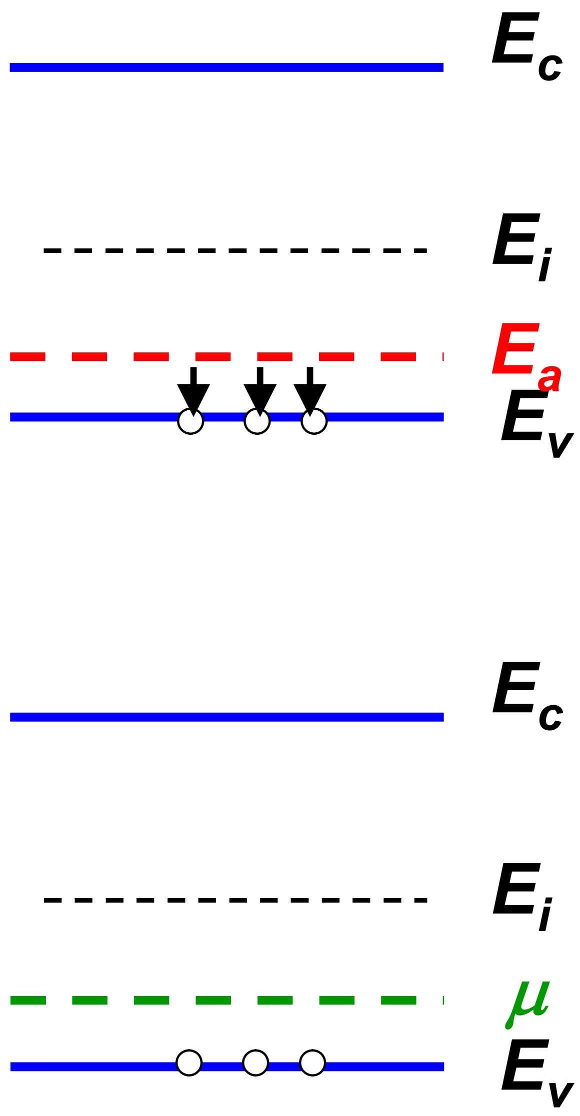
$$p_v = N_A$$

$$n_c = n_i^2 / p_v$$

$$\mu = E_v + k_B T \ln\left(\frac{P_v(T)}{p_v}\right)$$

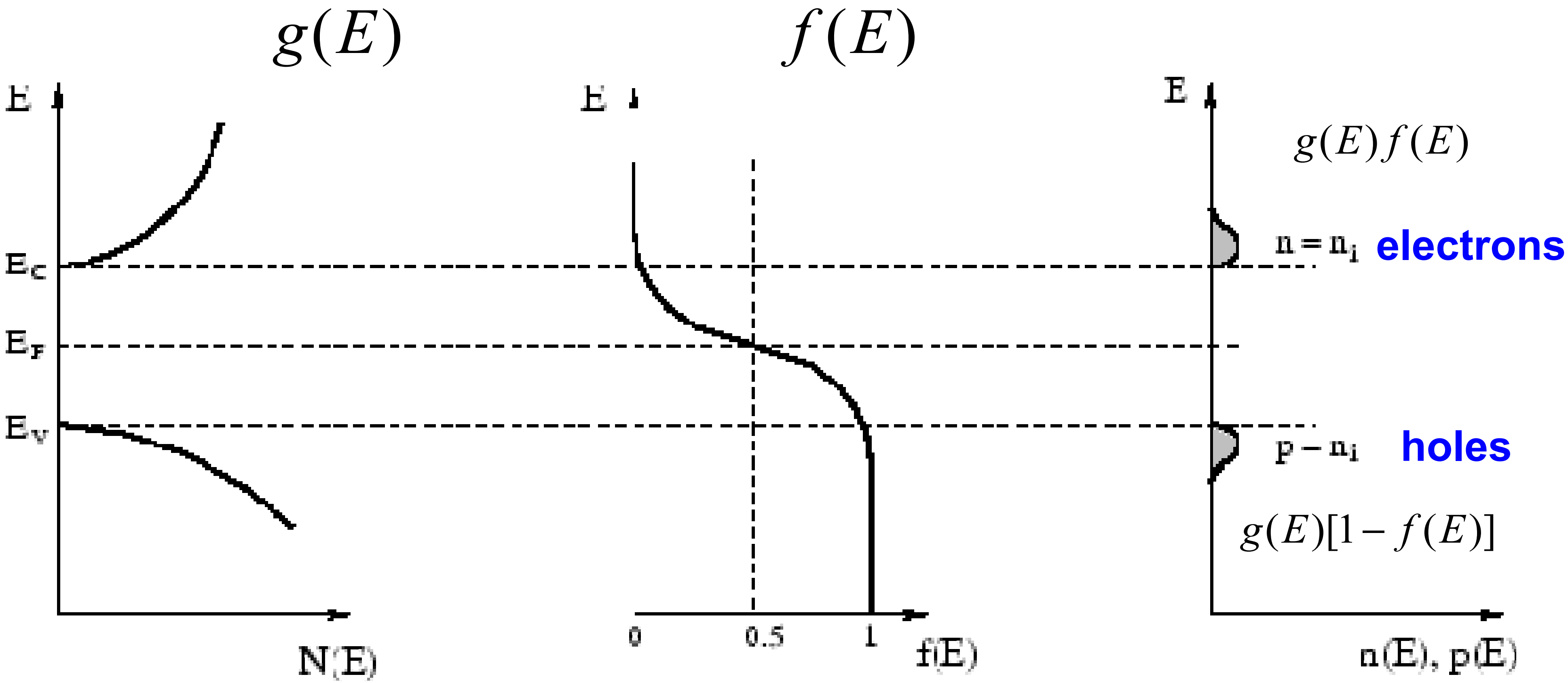
$$= E_i - k_B T \ln\left(\frac{N_A}{n_i}\right)$$

$$\approx E_v + \frac{1}{2}E_g - k_B T \ln\left(\frac{N_A}{n_i}\right)$$



Intrinsic vs. Extrinsic

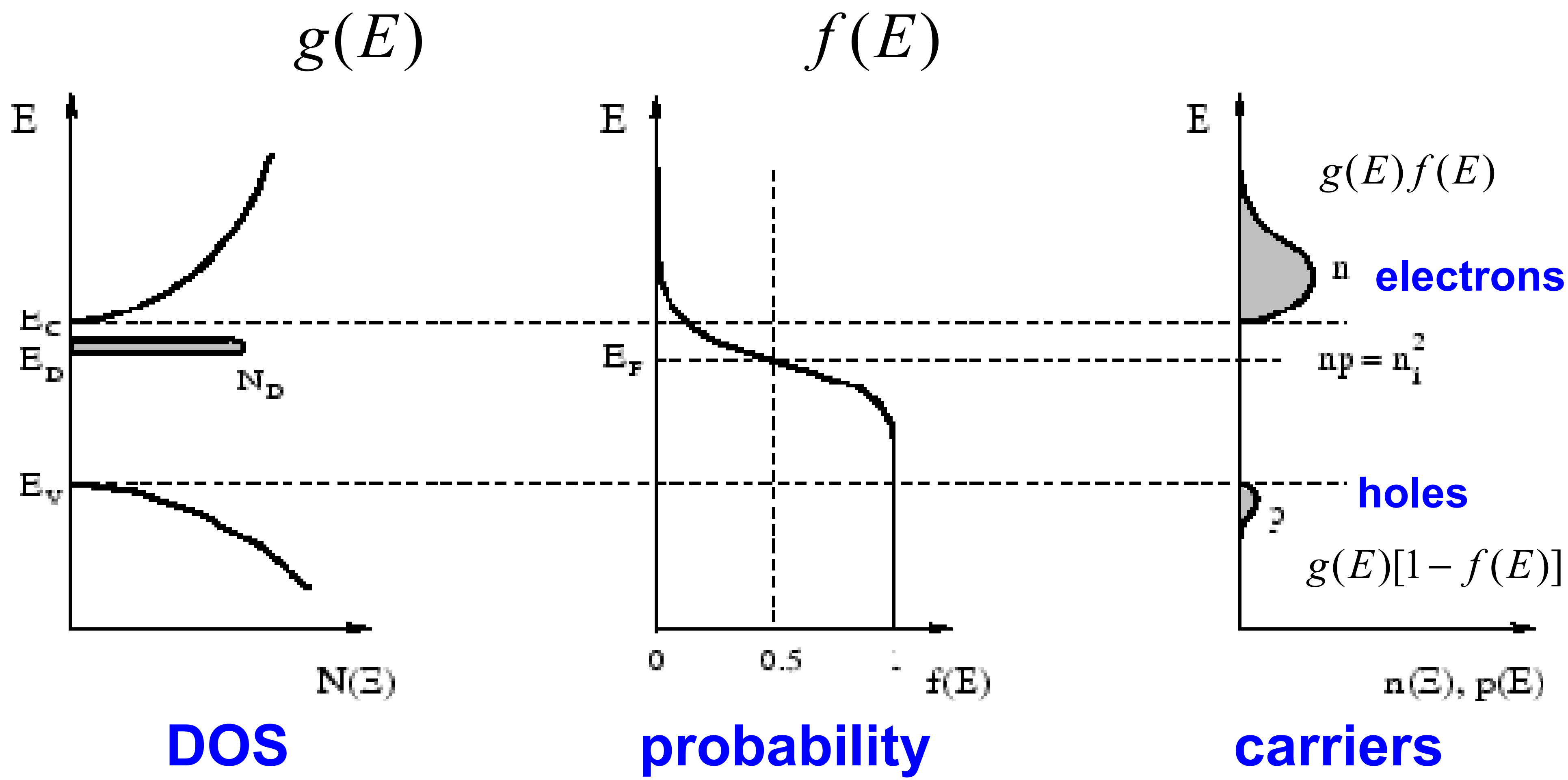
Intrinsic



DOS probability carriers

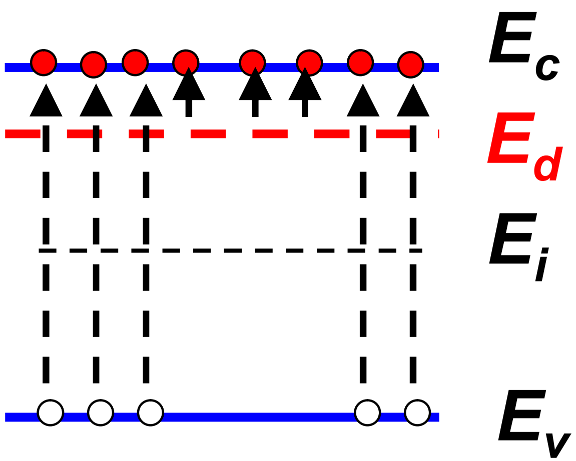
Intrinsic vs. Extrinsic

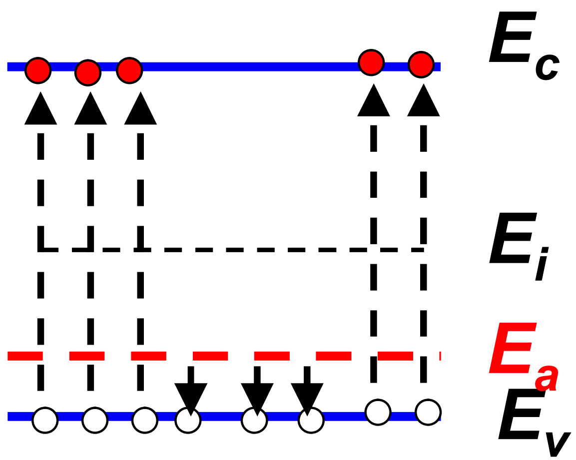
Extrinsic (n-doping)



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

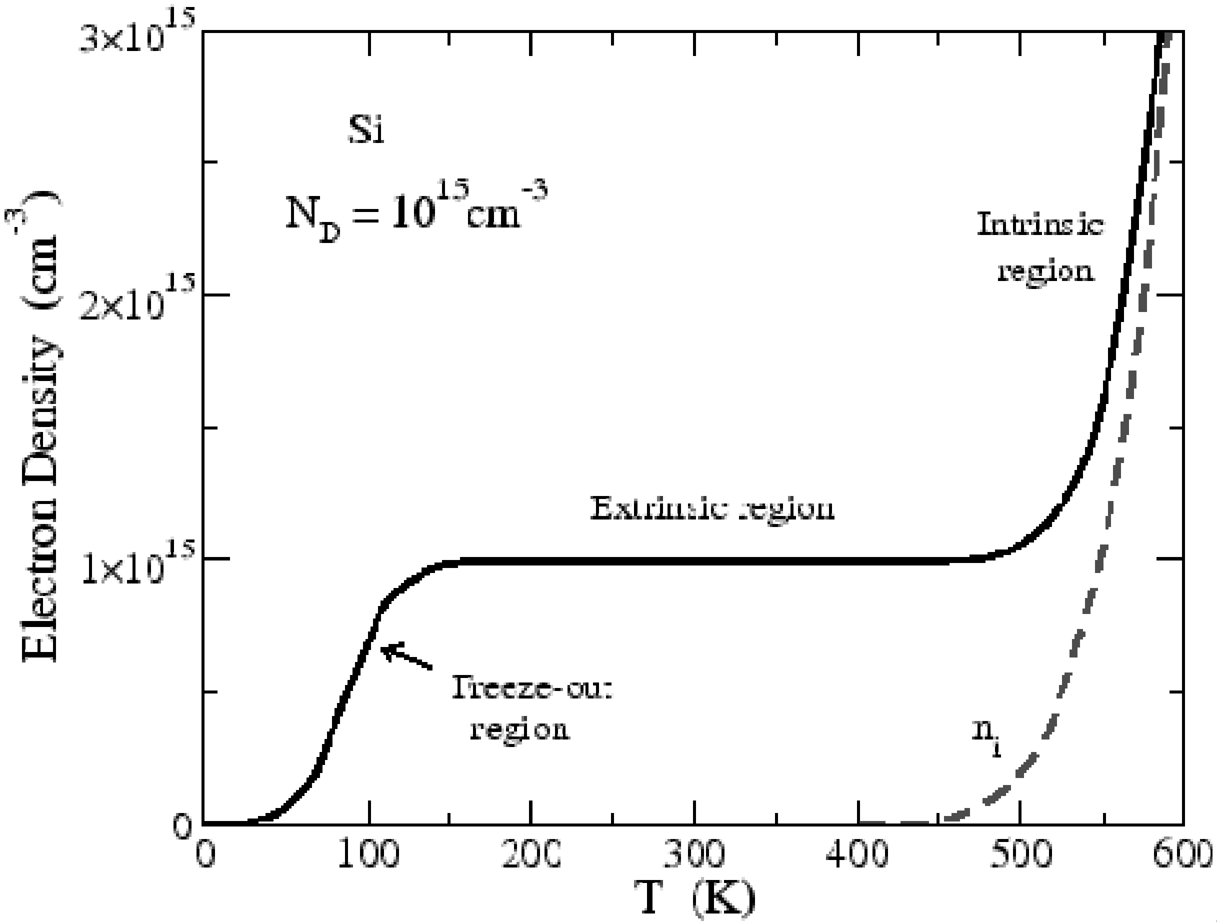
$$n \sim e^{-(E_c - E_D)/k_B T}$$

median *T*, extrinsic

$$n = N_D$$

high *T*, intrinsic

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



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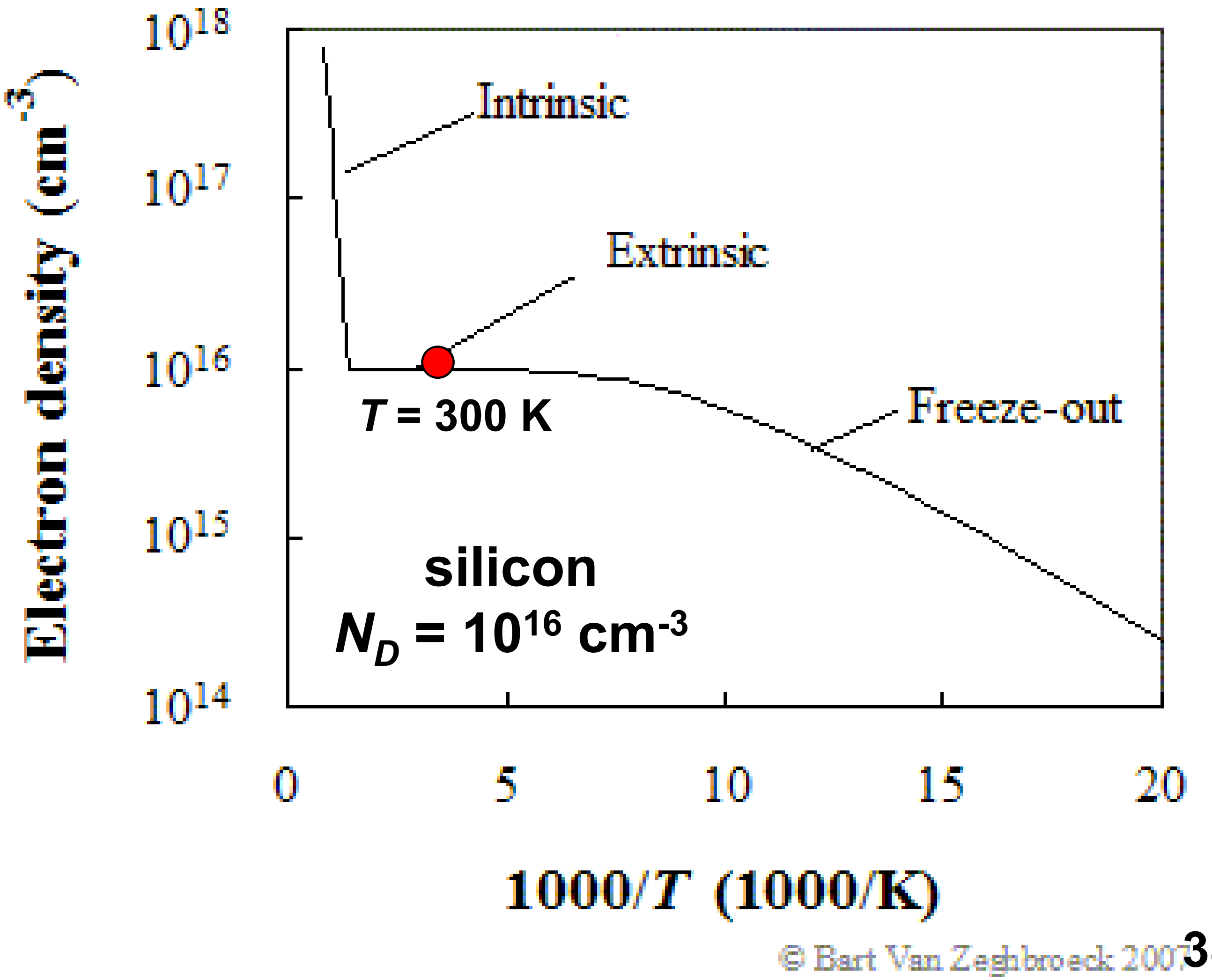
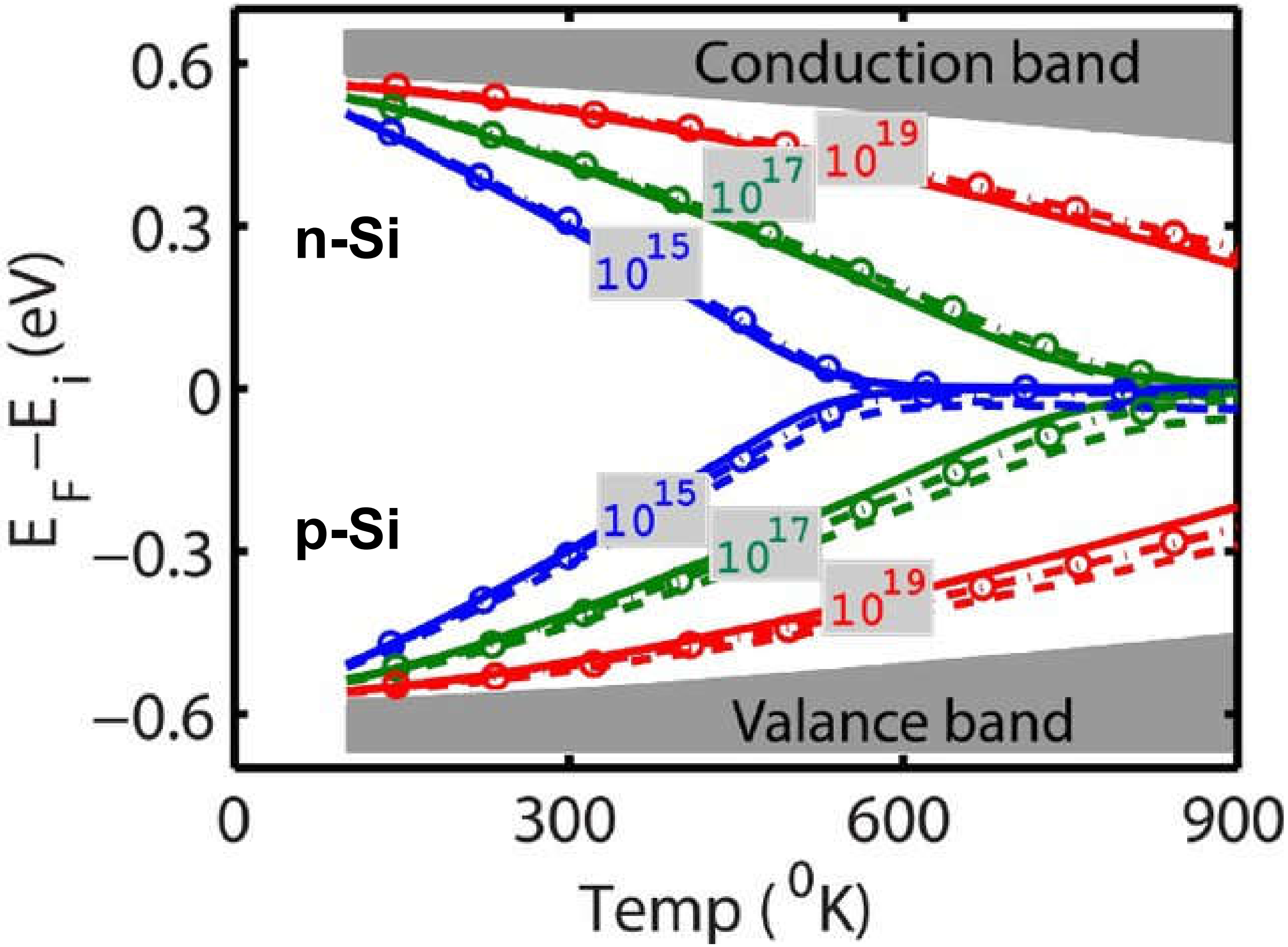


Extrinsic Semiconductor 掺杂半导体

temperature dependence of chemical potential



https://arxiv.org/abs/1110.2405

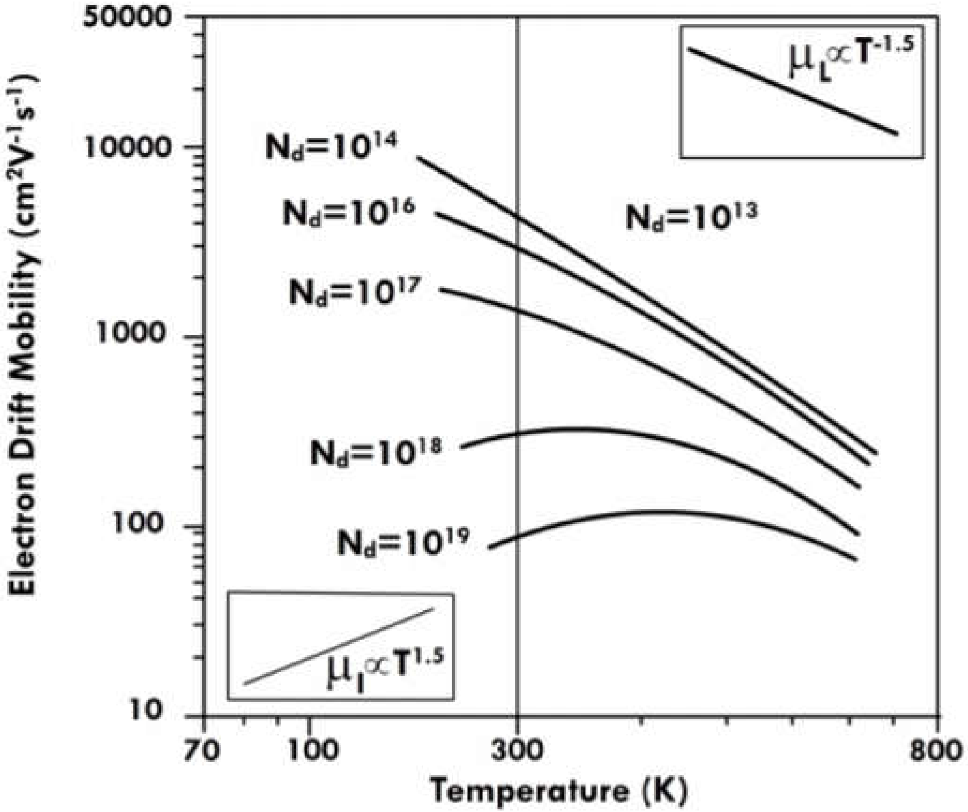
Extrinsic Semiconductor 掺杂半导体

temperature dependence of mobility μ

at low T $\mu \sim T^{3/2}$ **at high T** $\mu \sim T^{-3/2}$

impurity scattering **lattice scattering**

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

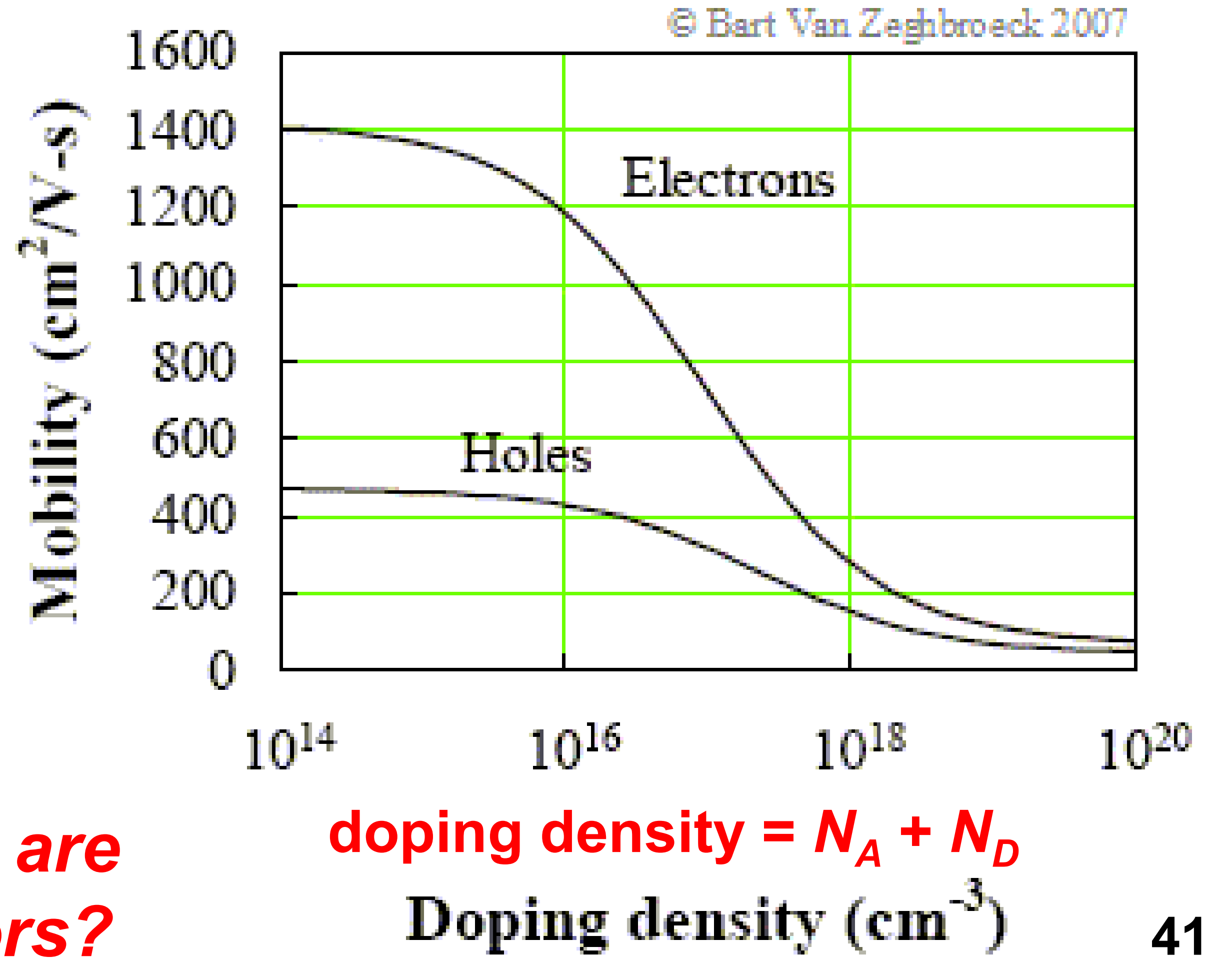


Extrinsic Semiconductor 掺杂半导体

doping dependence of mobility μ

silicon, T = 300 K

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



doping density = $N_A + N_D$

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

Extrinsic Semiconductor 掺杂半导体

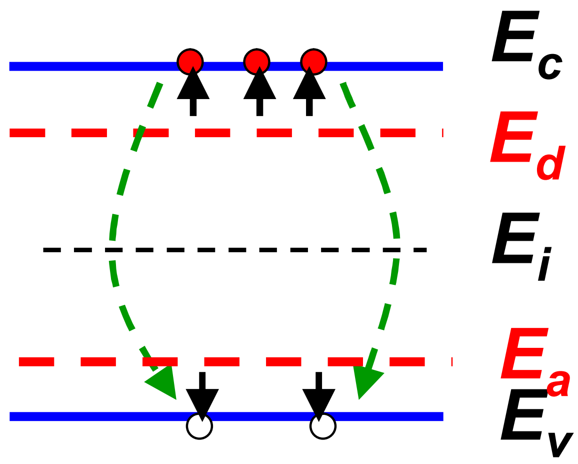
compensated semiconductor (补偿半导体)

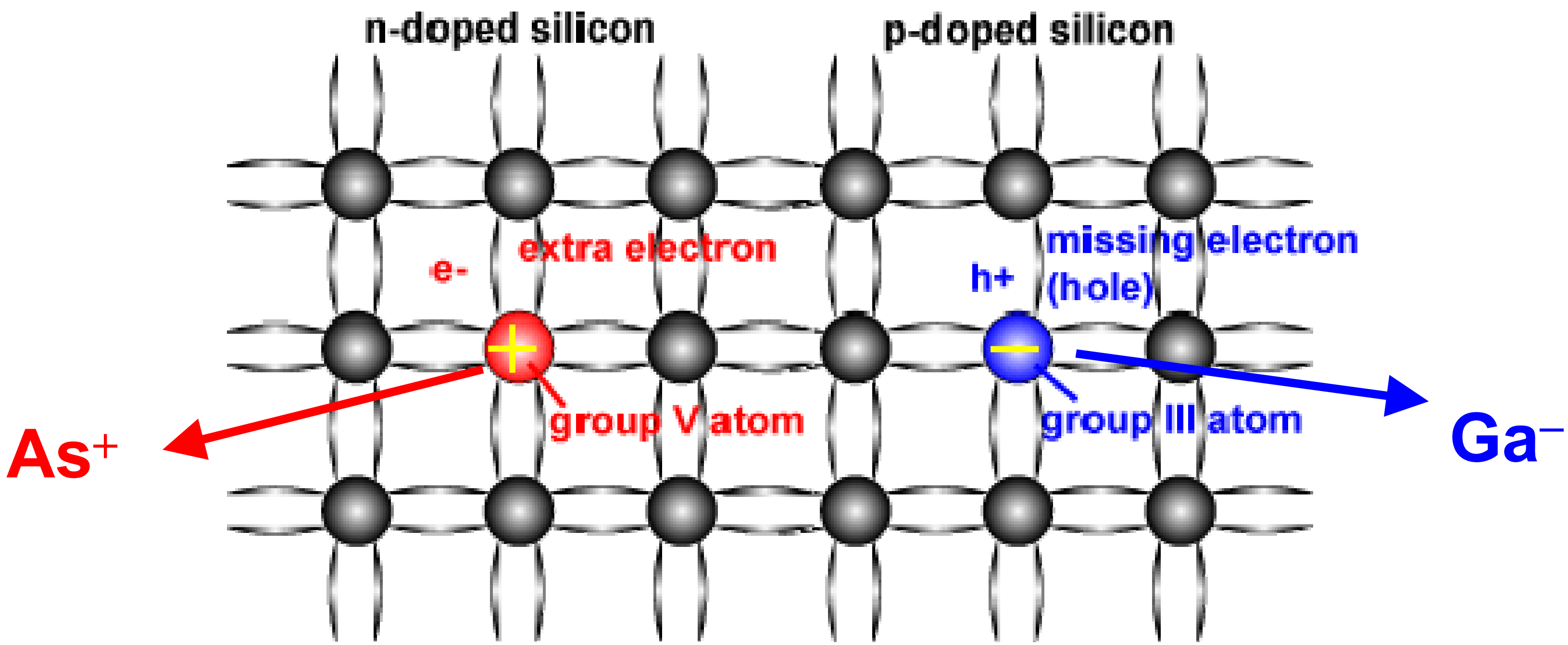
contains both donor and acceptor

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

charge balance

mass action law





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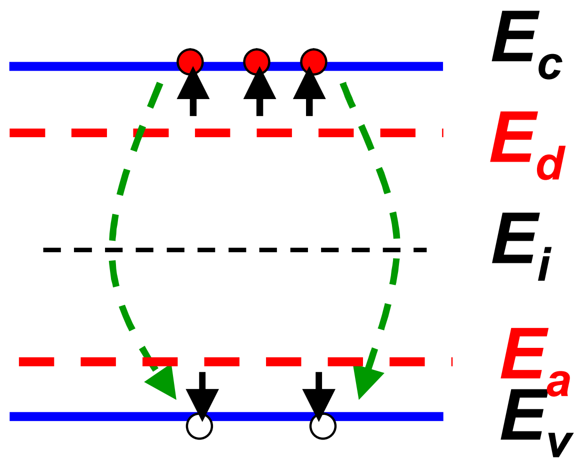
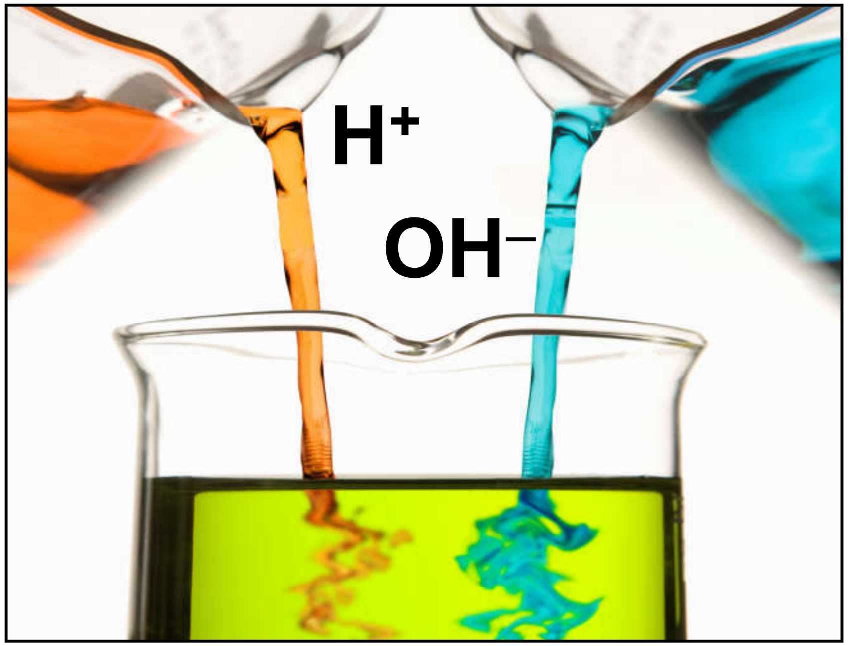


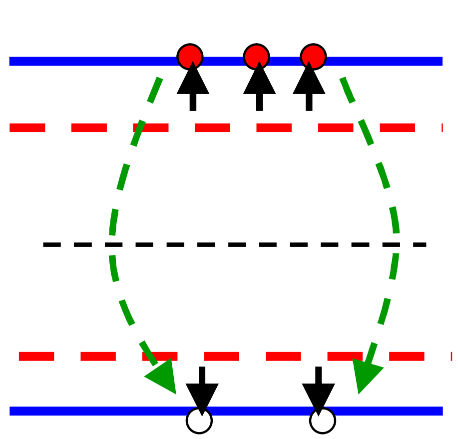


mix acid and base

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 $N_A > N_D$ → **p-doping**

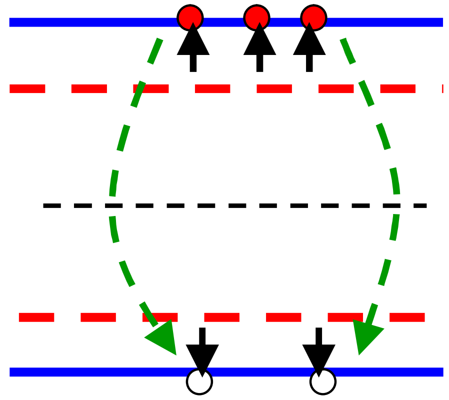
$$\rightarrow \quad p_v = \frac{N_A - N_D}{2} + \sqrt{\left(\frac{N_A - N_D}{2}\right)^2 + n_i^2}$$

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

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 $N_D > N_A$ → **n-doping**

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

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

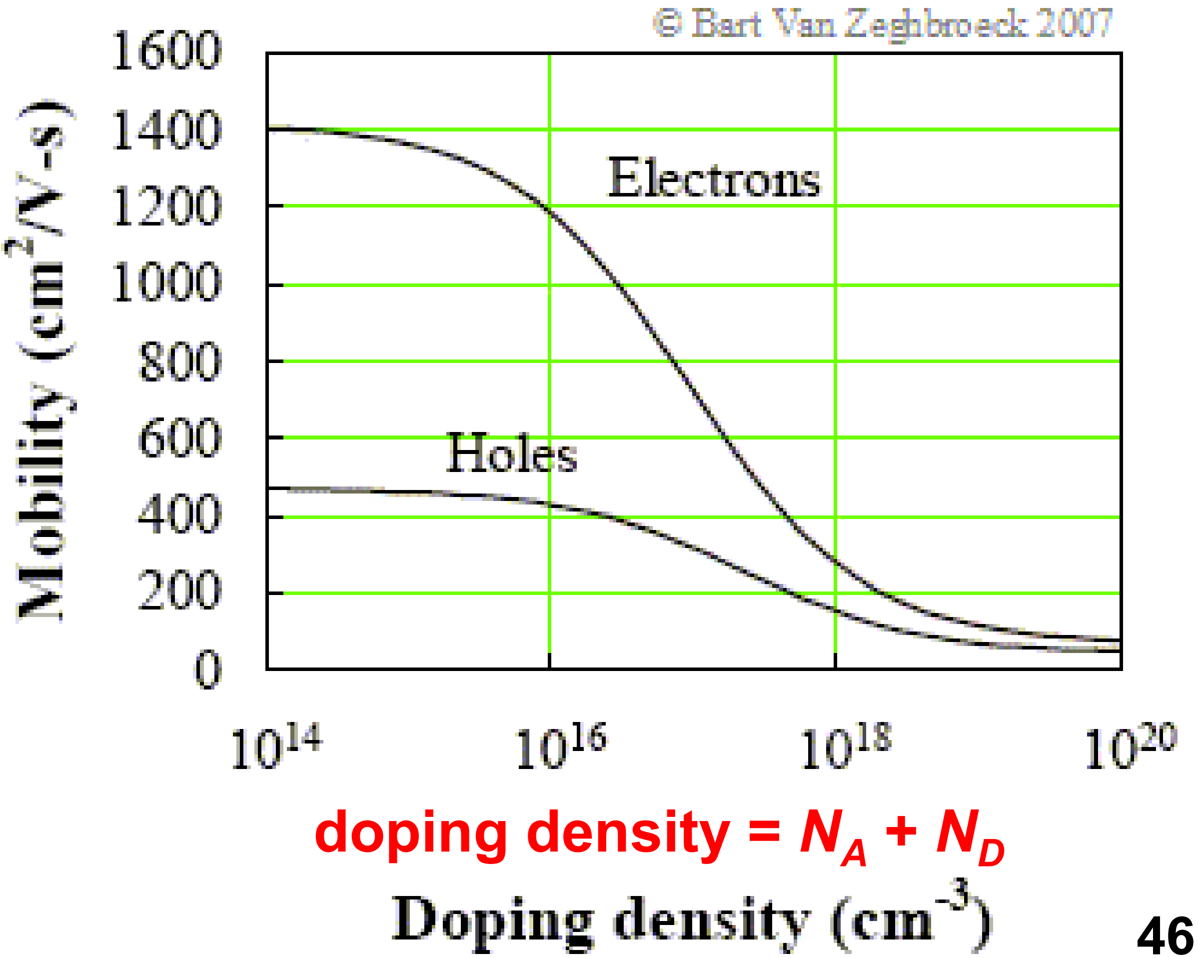
Extrinsic Semiconductor 掺杂半导体

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

the mobility μ depends on all impurities $(N_A + N_D)$

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

silicon, T = 300 K



doping density = $N_A + N_D$

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**

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

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

Thank you for your attention