Semiconductors

Structure

- crystalline
- policrystalline
- amorphous

Chemical composition

- elemental (Si, Ge)
- compounds (GaAs- *III-V*, ZnS *II-VI,* $CuInSe_2$ *I-III-VI*)
- alloys (solid solutions) ($Al_xGa_{1-x}As$, $CuIn_xGa_{1-x}Se_2$)

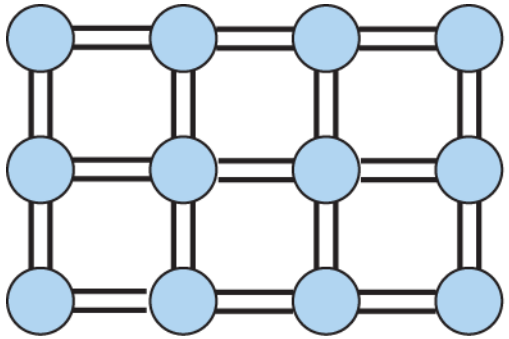
Physical properties

- intrinsic
- doped (Si:P, CdS:In)

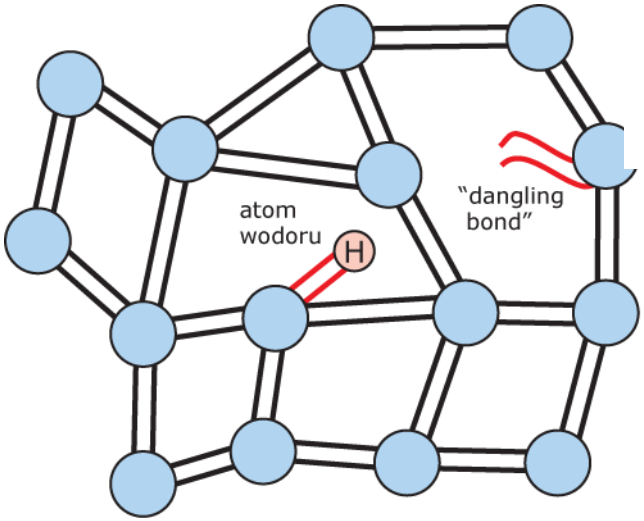
Basic concepts needed to describe photovoltaic device

- conduction and valence band
- direct and indirect bandgap
- free carriers
- doping
- drift velocity, thermal velocity, mobility
- absorption coefficient
- generation, recombination, lifetime
- diffusion current and diffusion length
- pn junction

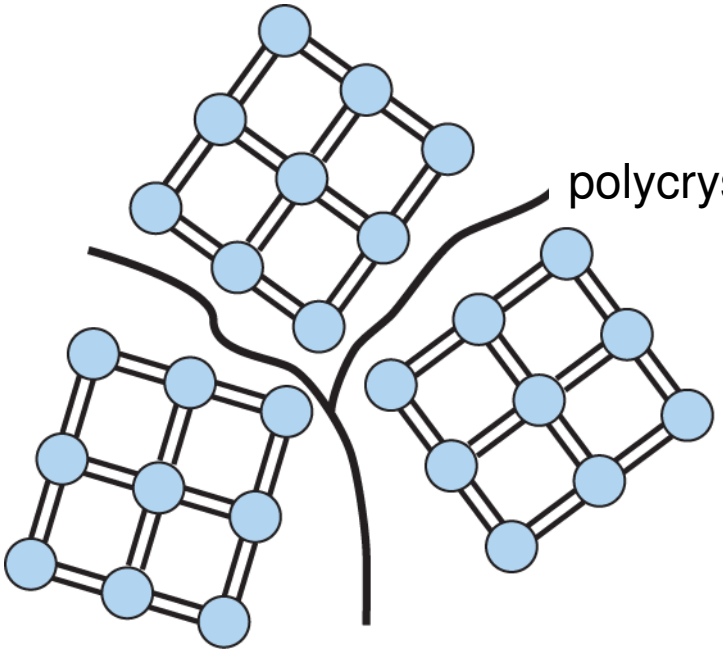
Structure of solids



crystalline



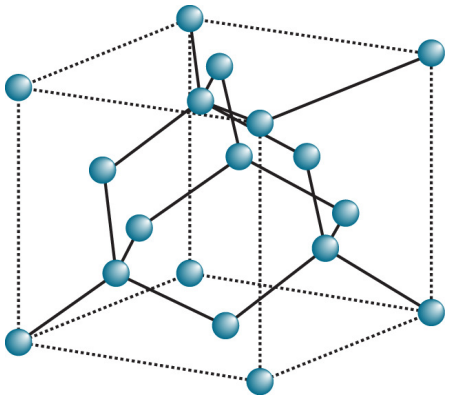
amorphous



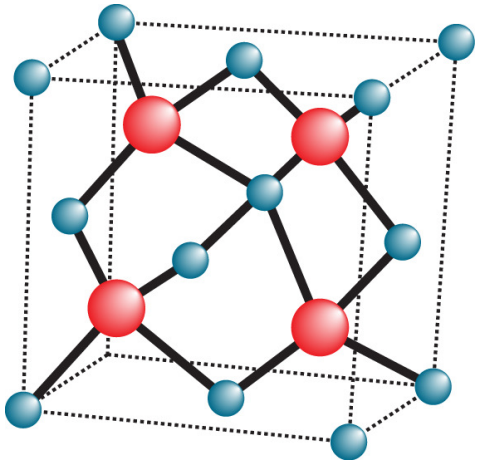
polycrystalline

Crystal structure – unit cell

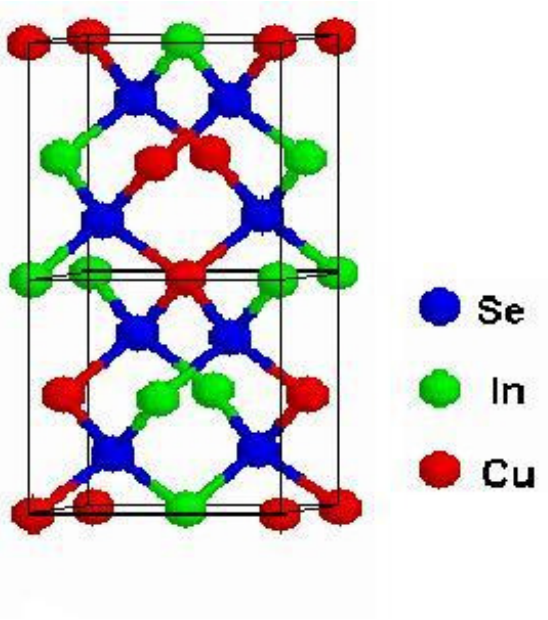
diamond
(Si, Ge)

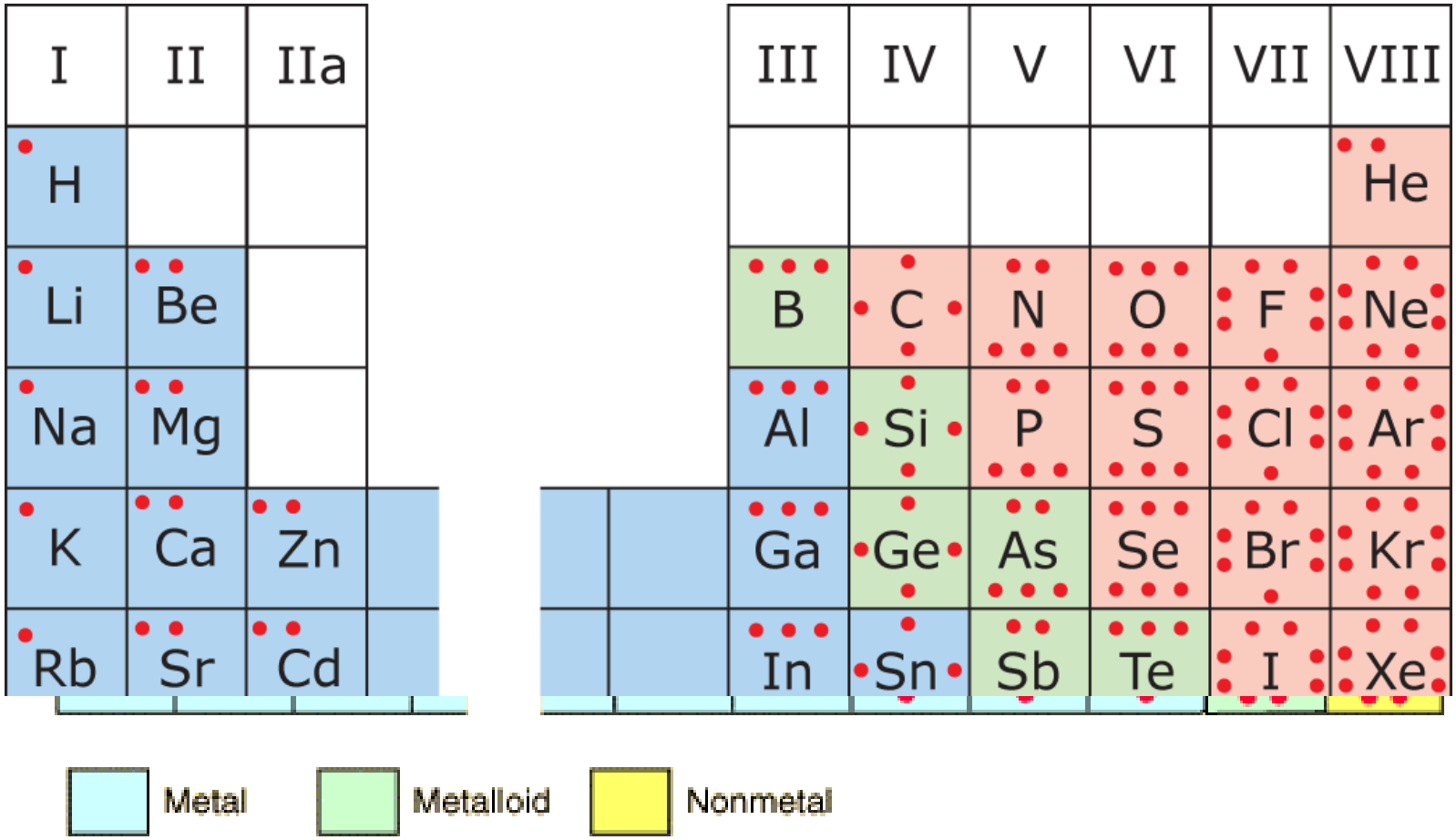


zinc blende
(ZnSe, GaAs)



chalcopyrite
$CuInSe_2$



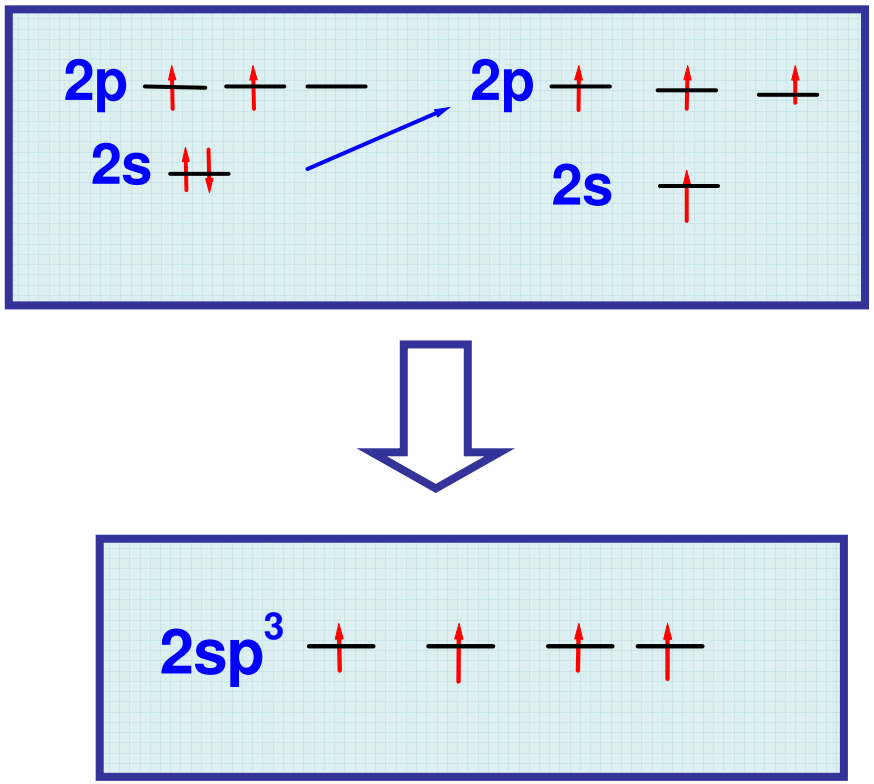


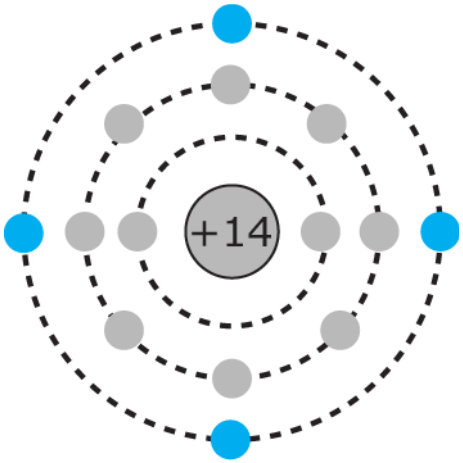
semiconducting compounds: $A^{II}B^{VI}$; $A^{III}B^{V}$; $A^{I}B^{III}C^{VI}_2$

CdTe; GaAs; $CuInSe_2$

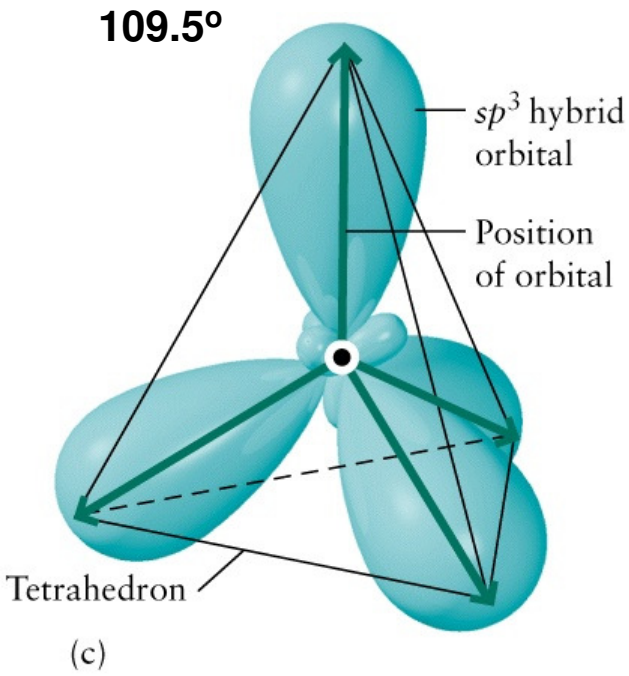
Covalent bonding - sp^3 hybridisation

Example: carbon $2sp^3$ ($Si: 3sp^3$, $Ge: 4sp^3$)

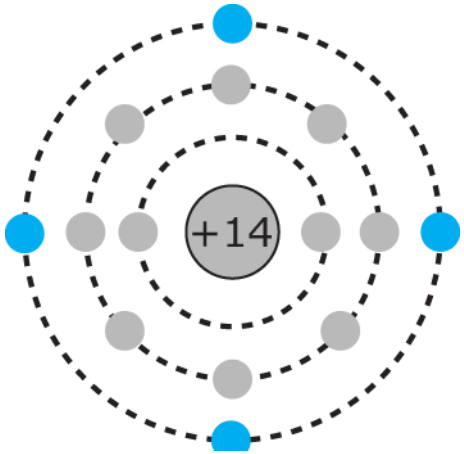


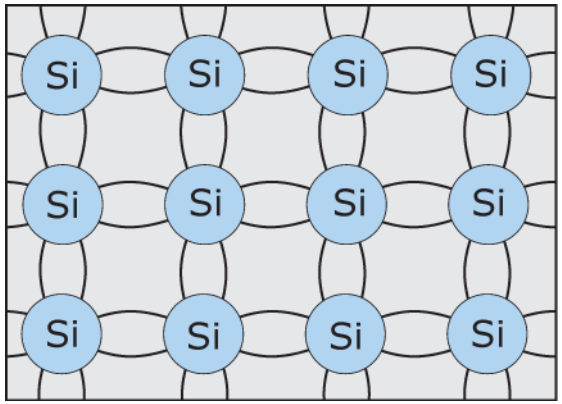


Si -



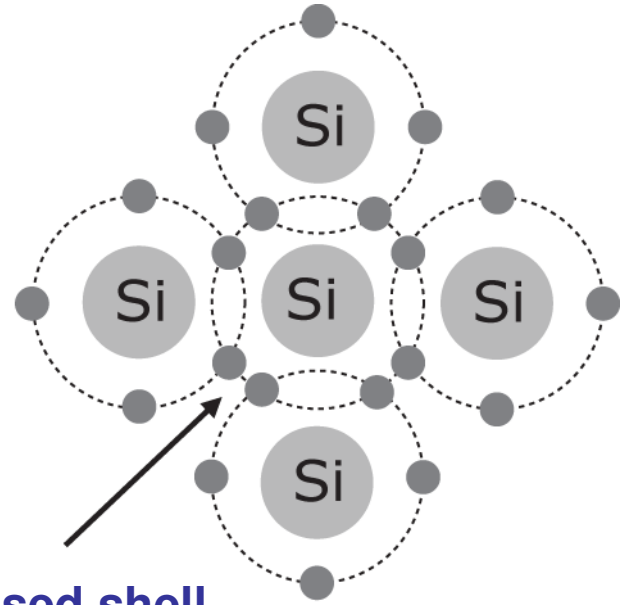
Silicon





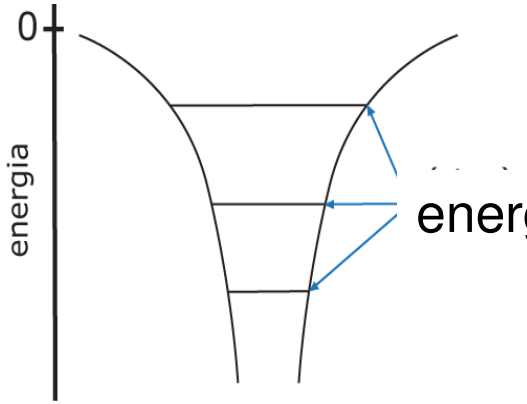
1s –2 electrons
2s – 2 **electrons**
2p – 6 electrons
3s – 2 electrons
3p – 2 electrons

} valence electrons

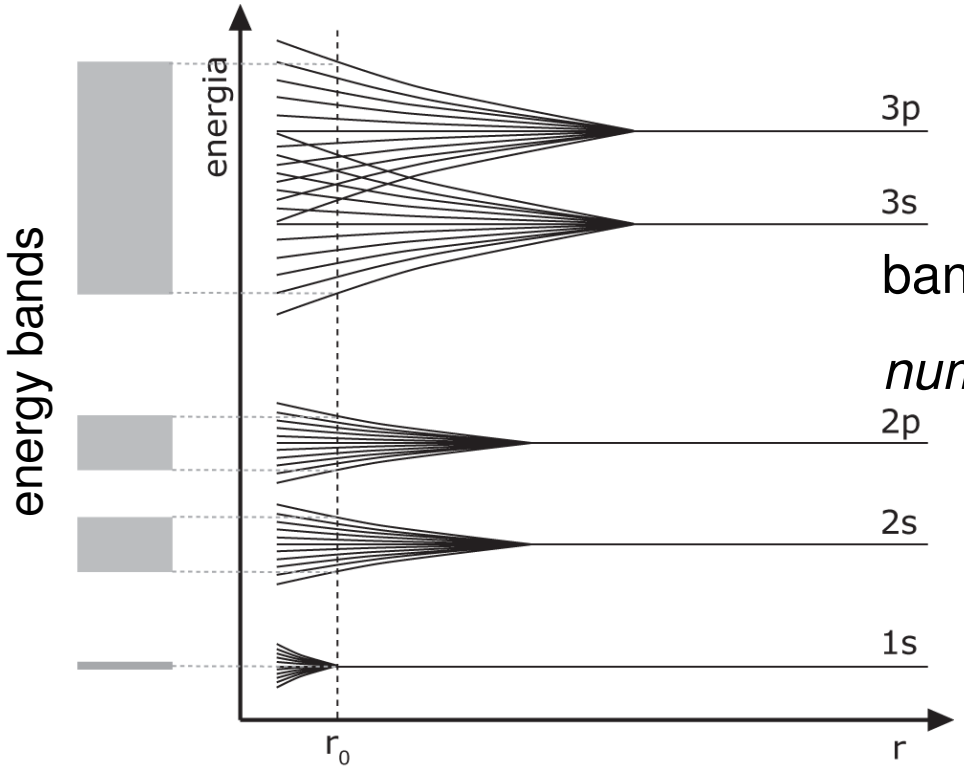


8 electrons: closed shell

Energy bands in solids



energy levels in a single atom (molecule)

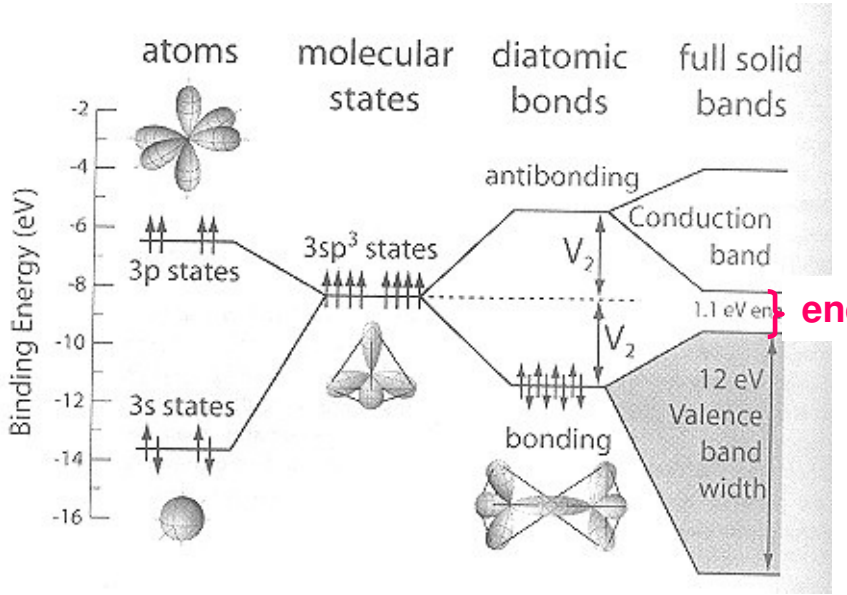


bands: splitting of atomic orbitals

number of levels in a band $(2l+1)*N_{atomów}$

„from bonds to bands”

Si

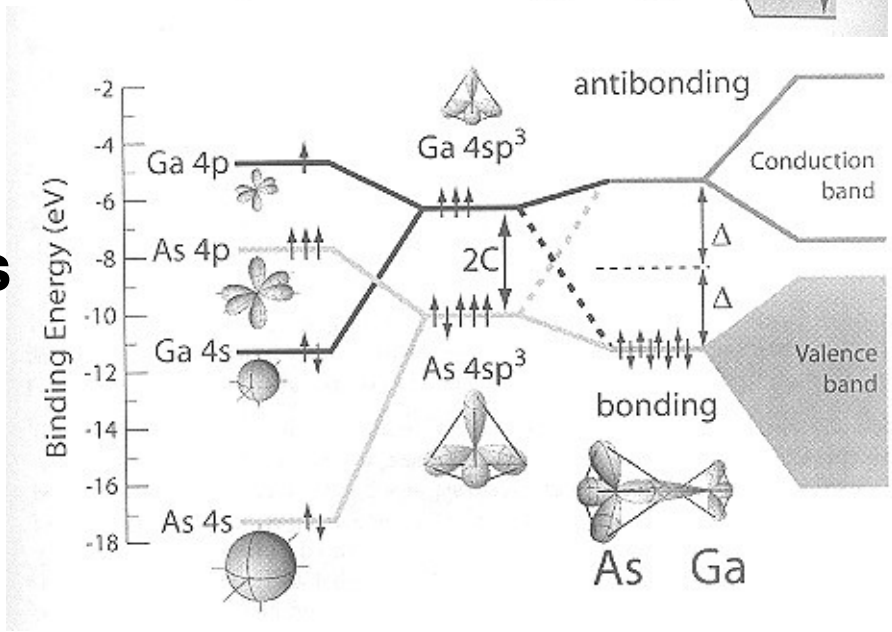


conduction band:
lowest unccupied band

energy gap

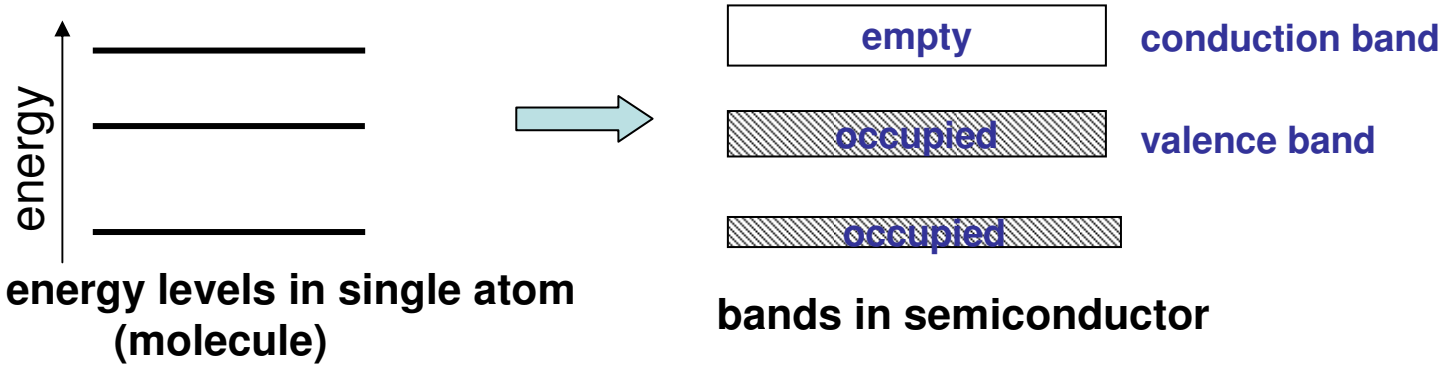
valence band:
highest fully occupied band

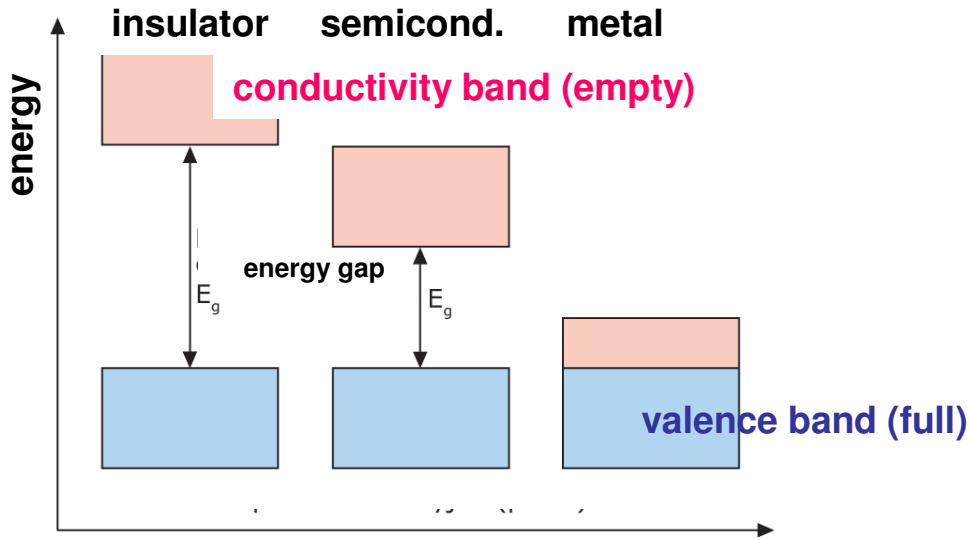
GaAs



covalent semiconductors: 8 electrons in molecular states - closed shell

Insulators, semiconductors, metals

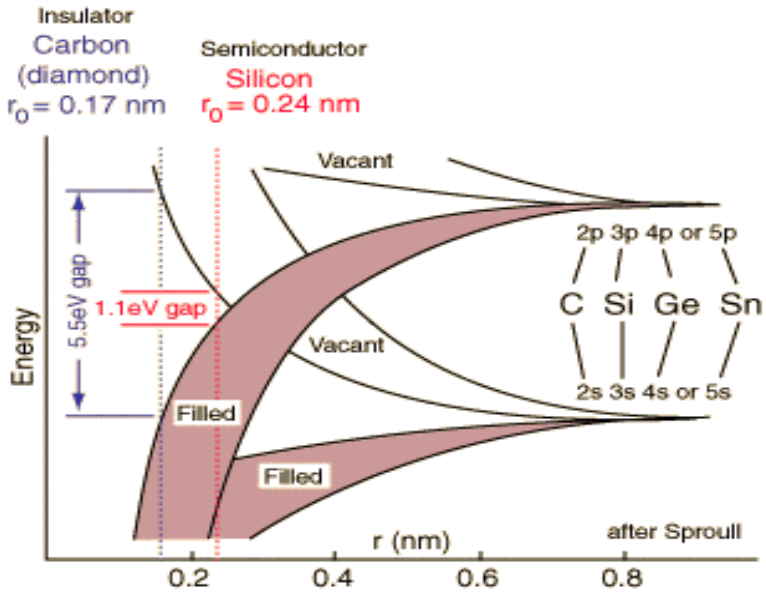




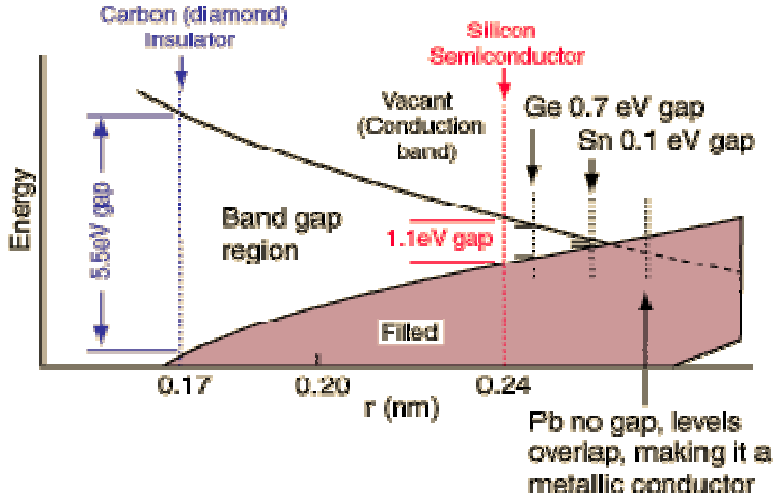
Width of the energy gap depends on the distance between atoms in the lattice!

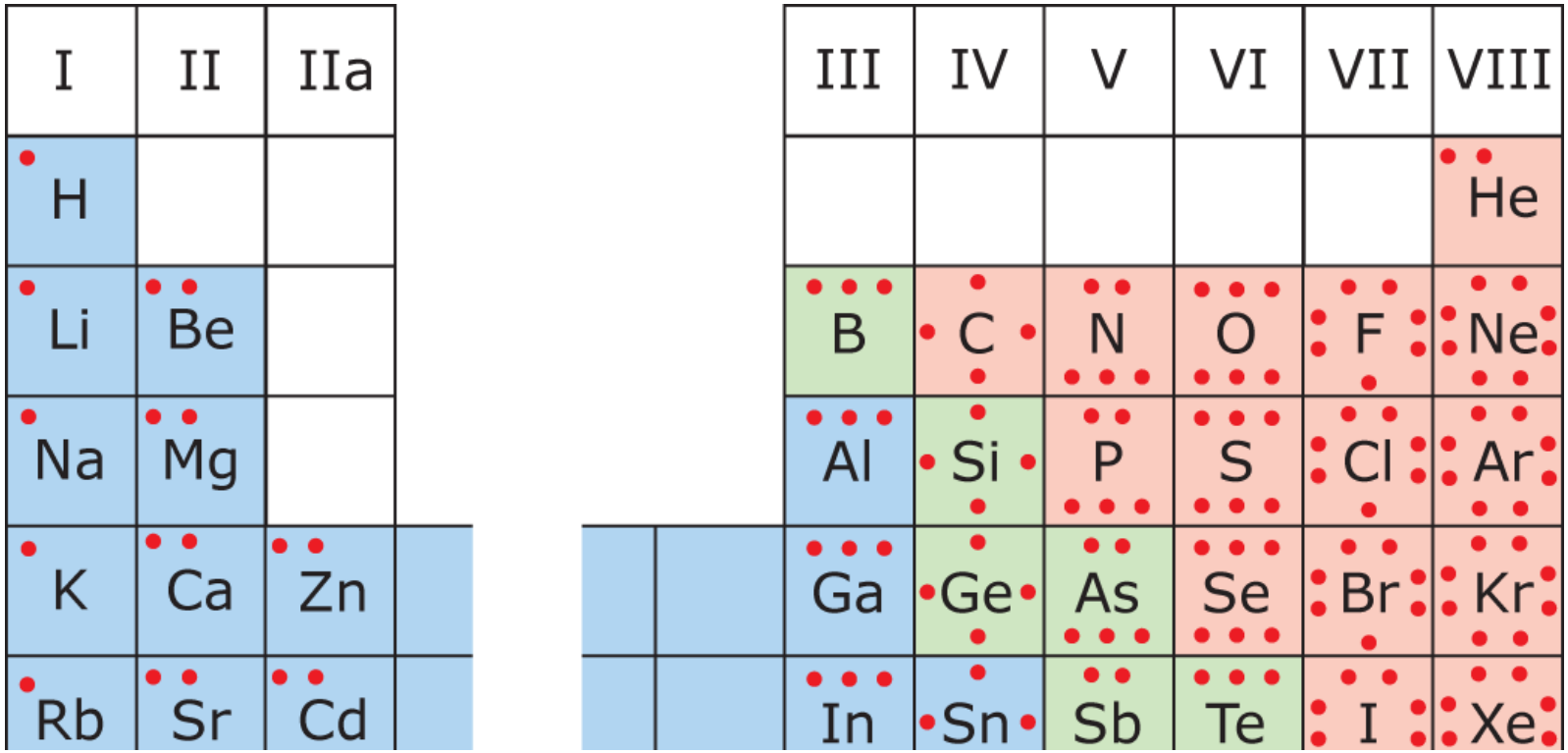
Periodic table environment of semiconductors

B	C_{2p^2}	N
Al	Si_{3p^2}	P
Ga	Ge_{4p^2}	As
In	Sn_{5p^2}	Sb
Tl	Pb_{6p^2}	Bi



distance between atoms





III-V	**E_g [eV]**
GaN	3.4
GaP	2.25
GaAs	1.52
GaSb	0.81
InP	1.42
InAs	0.43
InSb	0.24

II-VI	**E_g [eV]**
ZnS	3.54
ZnSe	2.7
ZnTe	2.25
CdTe	1.56
HgTe	-0.01

Quantum-mechanical description of electrons in periodic lattice

de Broghlie relationship between momentum and wavelength

$$\mathbf{k} \equiv \frac{2\pi}{\lambda}$$

$$\mathbf{p} = \frac{\mathbf{h}}{\lambda} = \frac{\mathbf{hk}}{2\pi} = \hbar\mathbf{k}$$

Wave vector **k** represents momentum of electron

Electron in periodic potential

periodicity in space:

x=x+a

periodicity in momentum:

k=k+2π/a

periodicity in energy

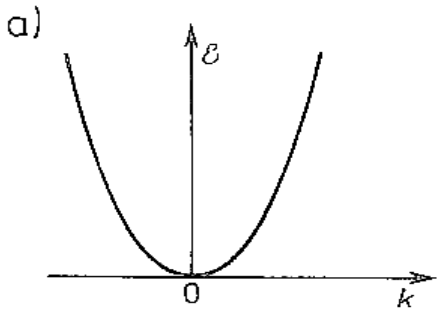
E(k)=E(k+2π/a)

Energy of electron in periodic lattce is a periodic function of momentum

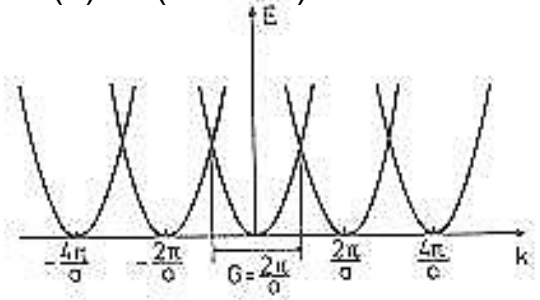
Dependence E(k) = equivalent of E(p)

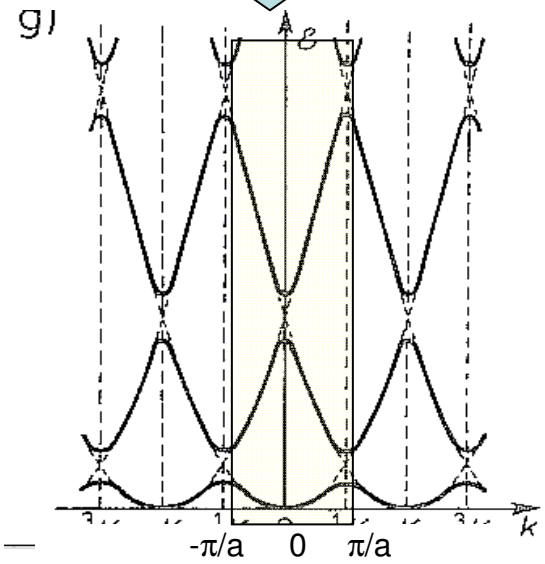
Free electron

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



Electron in periodic lattice
E(k)=E(k+2π/a)





a limited range of momentum (-π/a, π/a) describes fully an electron in crystal lattice

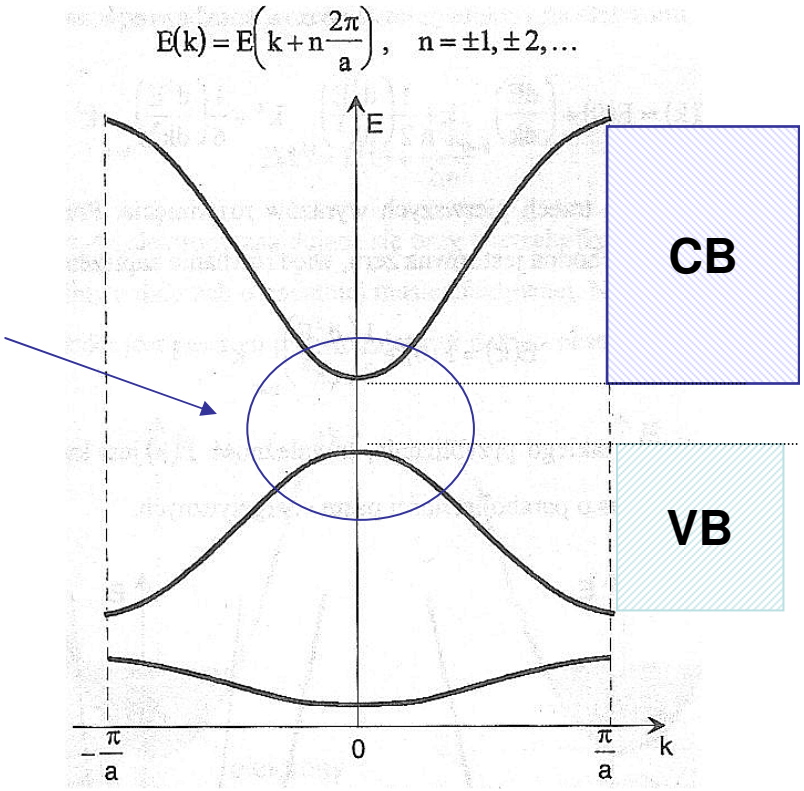
E(k) for electron in periodic lattice

Band structure of semiconductors

free electron in vacuum: $\mathbf{E(p) = \frac{p^2}{2m}}$

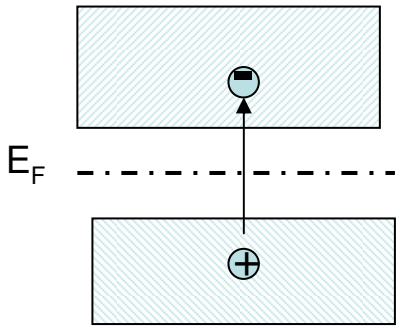
electron in crystal lattice $E = \frac{p^2}{2m^*} = \frac{\hbar^2 k^2}{2m^*}$

m* - effective mass of electron in CB (hole in VB)
(m*≠m, includes interraction of electron (hole) with lattice periodic potential)

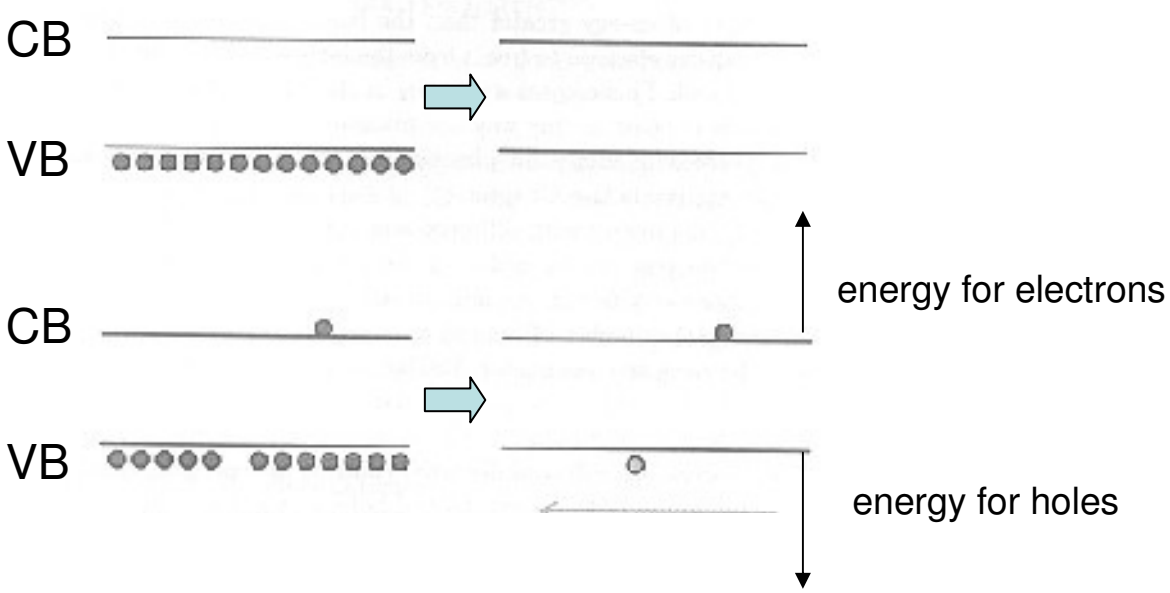


Electrons and holes

thermal generation

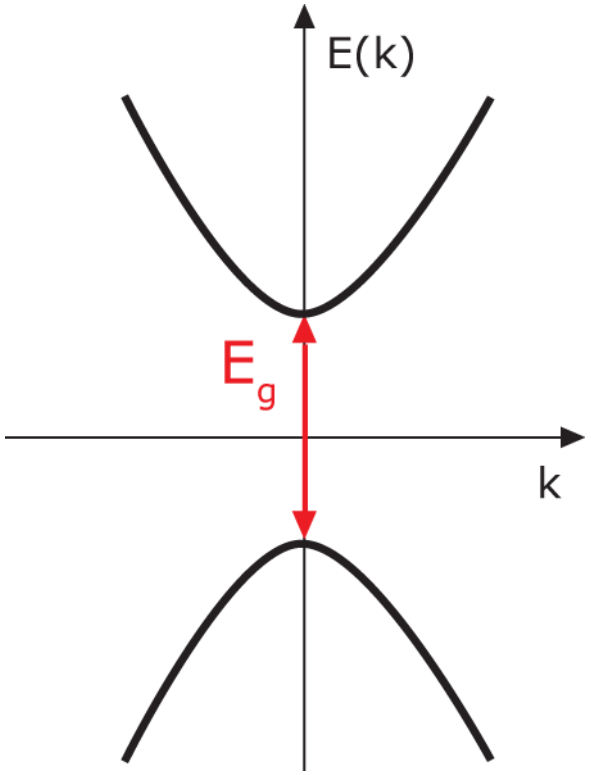


hole – empty place
after excitation of an electron,
quasi-particle with positive charge



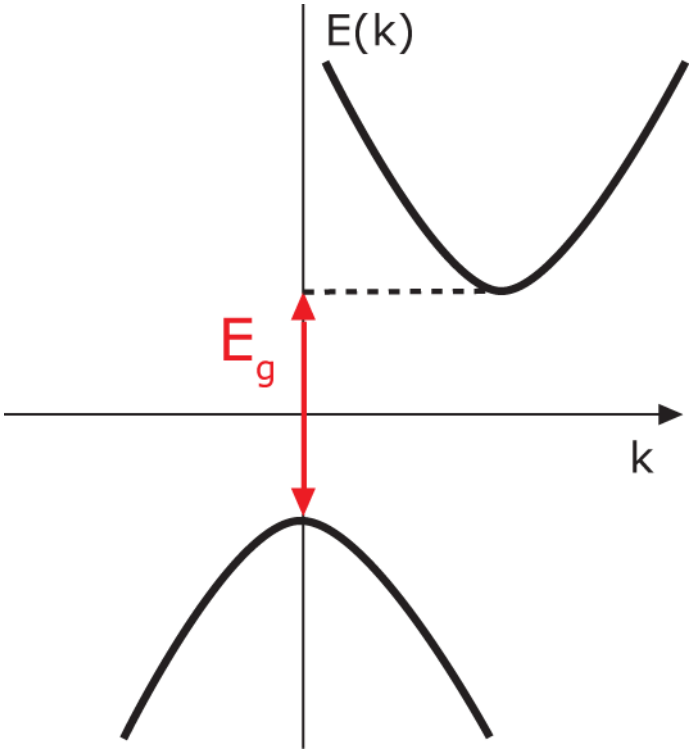
Band structure of semiconductors

direct gap



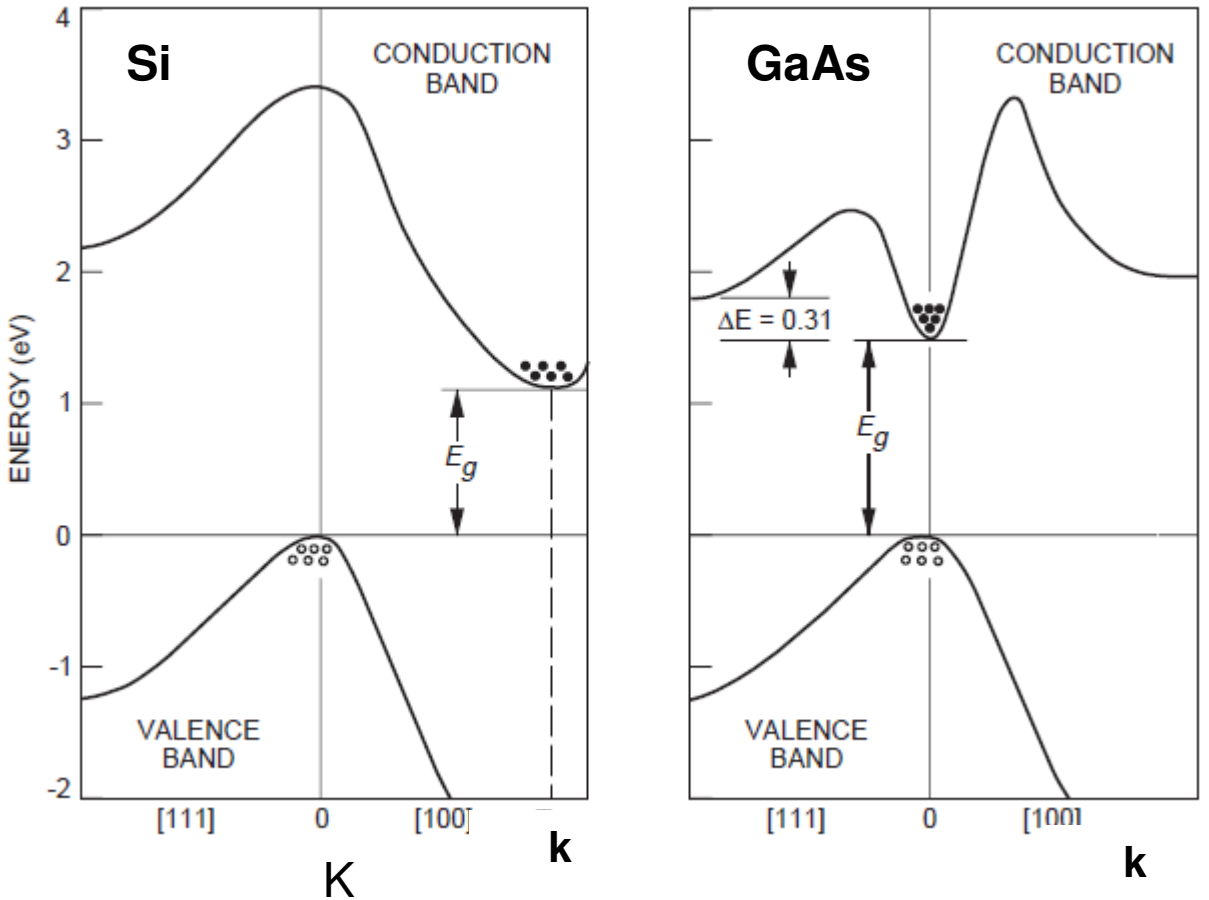
GaAs, CdS, ZnS,
InSb, HgTe, GaN

indirect gap



Si, Ge, GaP, AlAs

Band structure

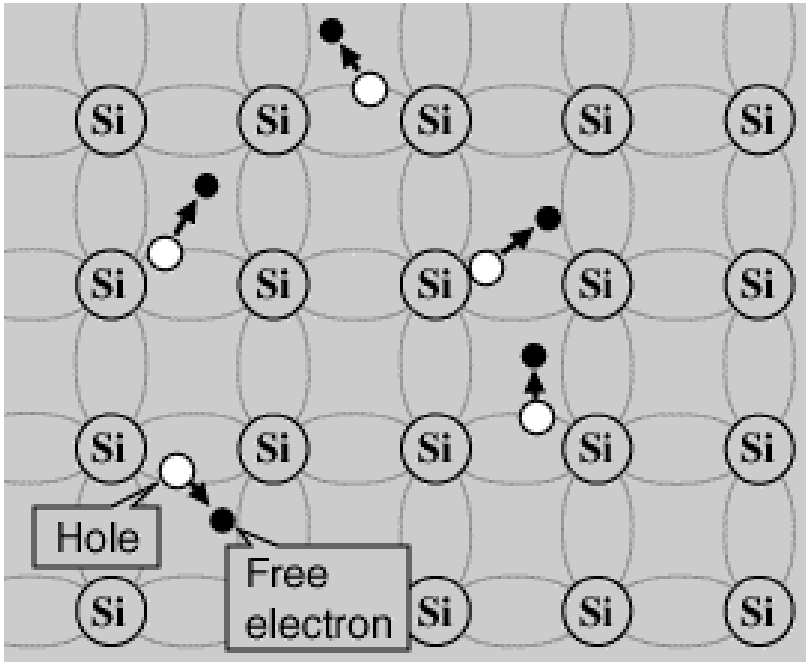


K

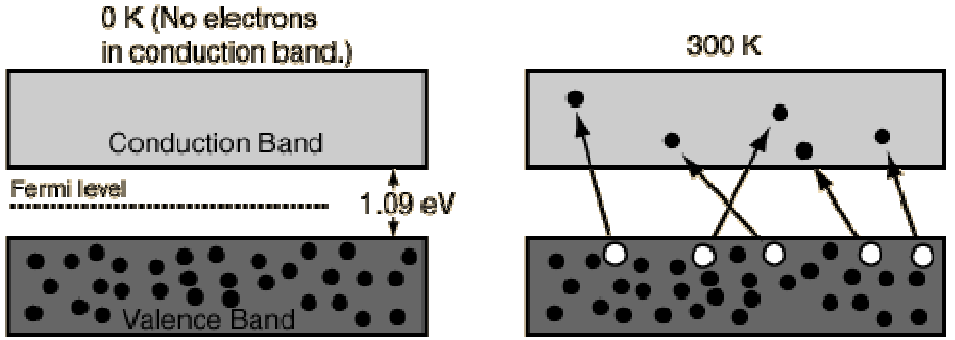
indirect bandgap

direct bandgap

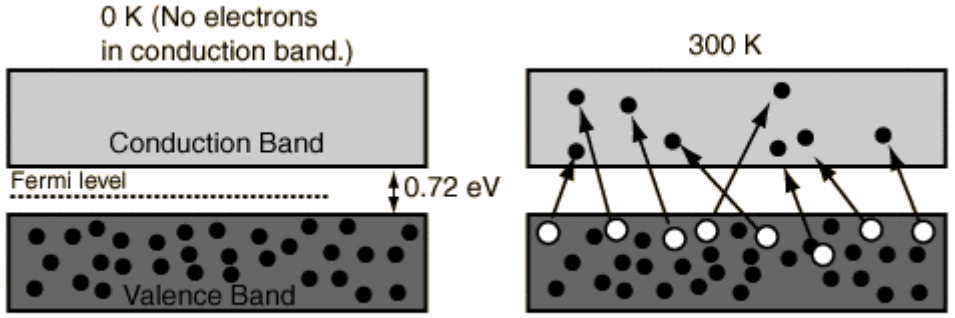
Electrons in the conduction band and holes in the valence band



silicon: E_g=1.09 eV

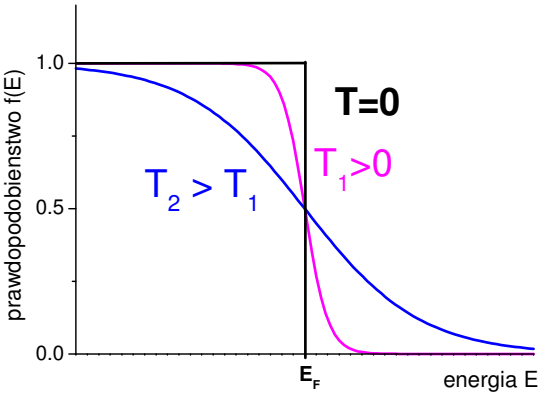


germanium: E_g = 0.72 eV



Concentration of free electrons in CB and holes in VB:

Fermi-Dirac distribution:
probability that electron(hole) will have energy E



$T = 0\,K:$

$f_e(E) = 1$ dla $E < E_F$

$f_e(E) = 0$ dla $E > E_F$

$T > 0\,K$

$$f_e(E) = \frac{1}{1 + \exp\left\{\frac{E - E_F}{k_B T}\right\}}$$

for holes
$f_h = 1 - f_e$

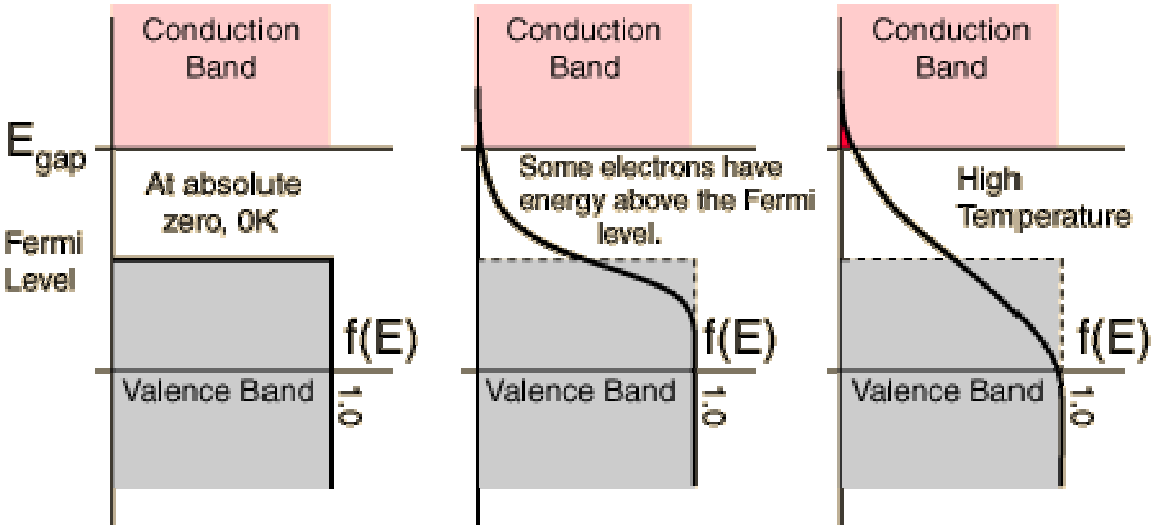
E_F- Fermi-level, $f(E_F) = ½$

---

for electrons: $E - E_F >> k_B T$: $$f_e(E) \approx \exp\left\{\frac{-(E - E_F)}{k_B T}\right\}$$

for holes: $E_F - E >> k_B T$: $$f_e(E) \approx \exp\left\{\frac{-(E_F - E)}{k_B T}\right\}$$

Concentration of free electron and holes



No electrons can be above the valence band at 0K, since none have energy above the Fermi level and there are no available energy states in the band gap.

At high temperatures, some electrons can reach the conduction band and contribute to electric current.

T increases ⇒ probability of thermal excitation increases

⇓

concentration of free electrons and free holes increases

$$n = N_c \exp\left\{\frac{-(E_c - E_F)}{k_B T}\right\}$$

$$p = N_v \exp\left\{\frac{-(E_F - E_v)}{k_B T}\right\}$$

intrinsic semiconductor:

$$E_F - E_V \cong E_c - E_F \cong E_g/2$$

conc. of free electrons in the CB = conc. of free holes in the VB

$$n_i = p_i = (N_C N_V)^{1/2} \exp(-E_g/2k_B T)$$

Effective density of states in the cond. (valence) band N_c, N_v ~10^{19} cm^{-3}

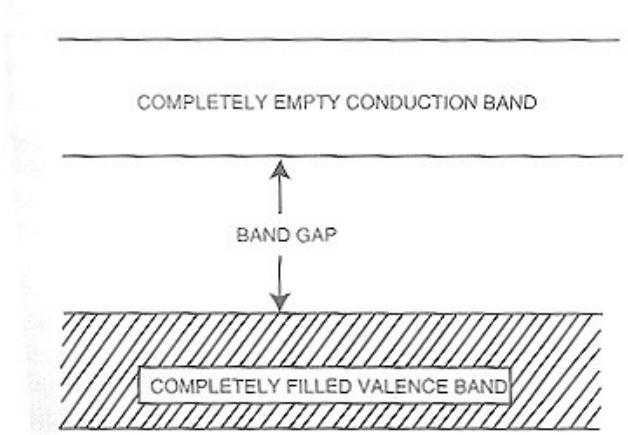
$$k_B T(300\ K) \cong 0.024\ eV$$

E_g	n_i (300 K)	
~0.25 eV	10^{16} cm^{-3}	InSb, PbSe
~1 eV	10^{10} cm^{-3}	Ge, Si, GaAs
~4 eV	$<10^{10}$ cm^{-3}	ZnS, SiC, GaN

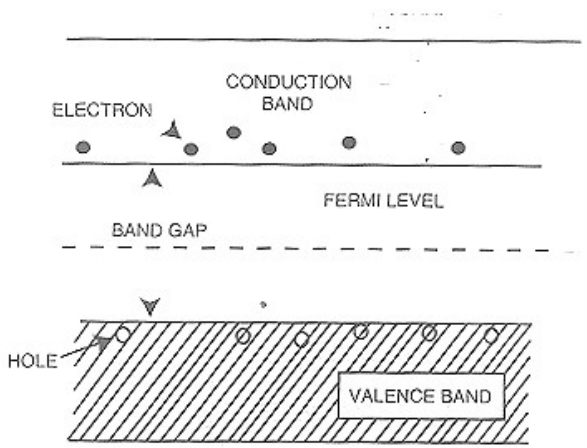
Free electrons and holes

Intrinsic semiconductor

T = 0 K



T > 0 K



Intrinsic free carrier concentration depends on temperature and energy gap

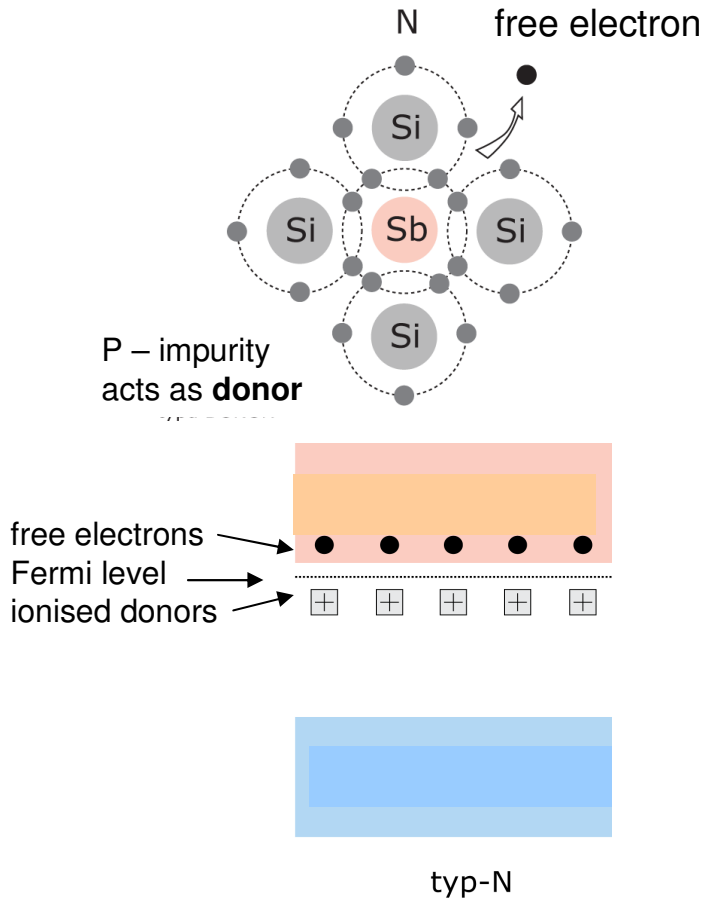
$$n = p = n_i = \sqrt{N_c N_v \exp\left\{\frac{-E_g}{k_B T}\right\}} \approx N_{c,v} \exp\left\{\frac{-E_g}{2k_B T}\right\}$$

$E_g \cong 1$ eV : $n_i \cong 10^{10}$ cm^{-3} *($\sigma = 10^{-5}$- 10^{-3} $\Omega^{-1}m^{-1}$)*

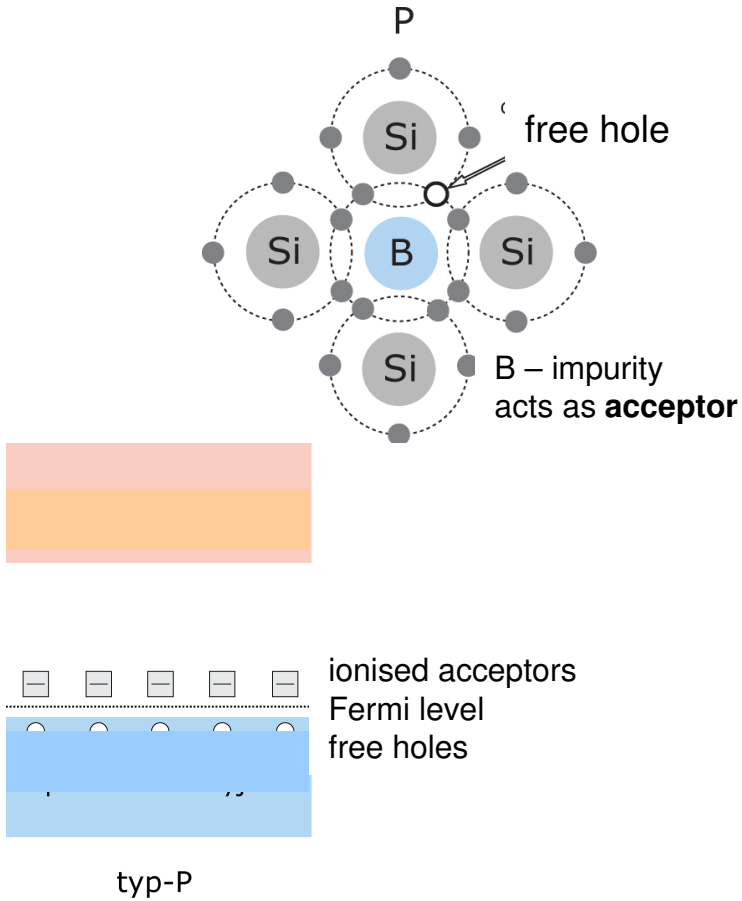
n and p-type doping

Example: Si

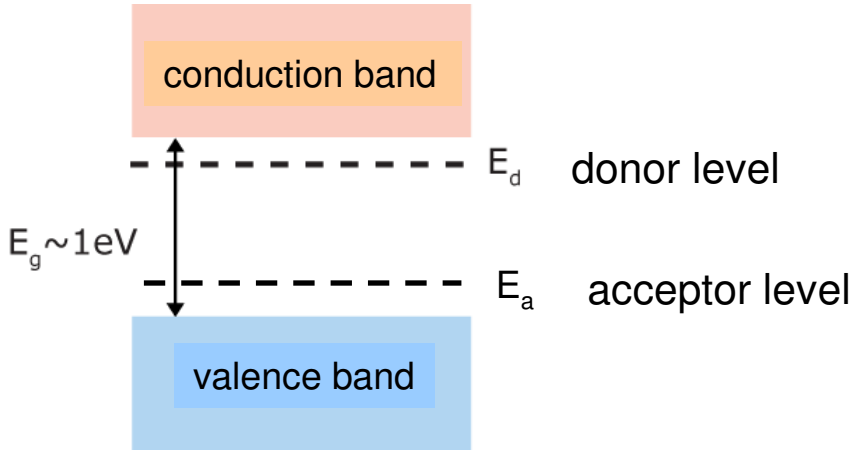
P – donor (5 valence electrons)



B – acceptor (3 valence electrons)



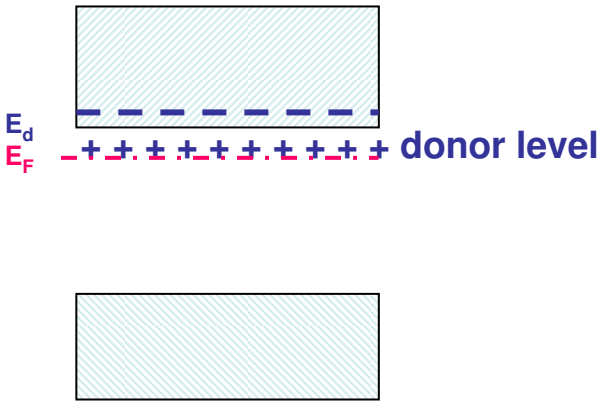
Donors and acceptors



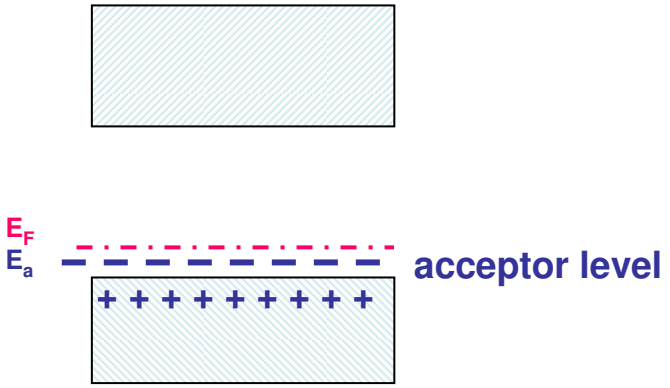
Small ionisation energy of electron or hole from dopant atom is represented by a shallow energy level in the bandgap

E_d and E_a < 100 meV, usually 10-50 meV

n-type doping



p-type doping



$n=N_d$ (all donors ionized at 300 K)

$n=N_c\exp\{-(E_c-E_F)/k_BT\}$

majority carriers

minority carriers

$p=N_a$ (all acceptors ionized)

$p=N_V\exp\{-(E_F-E_V)/k_BT\}$

E_F close to CB

$p=n_i^2/N_d << n$

E_F close to VB

$n=n_i^2/N_a << p$

1 per million atom replaced by a dopant

concentration of majority carriers 10^{16} cm^{-3} >> n_i

concentration of minority carriers 10^4 cm^{-3} << n_i

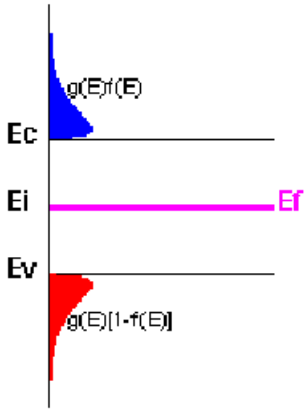
Free carriers in perfect lattice, $F_{ext}=0$

free electron (hole) moves with k=const

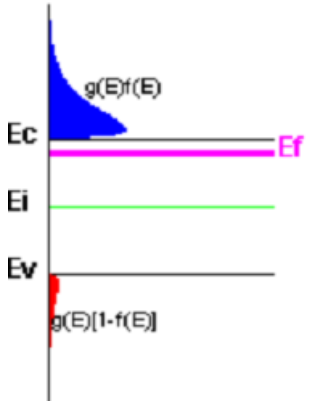
$$v = \frac{\hbar k}{m^*} = \text{const}\ (\text{near the band minimum or maximum}$$

energy distribution of free carriers in the bands

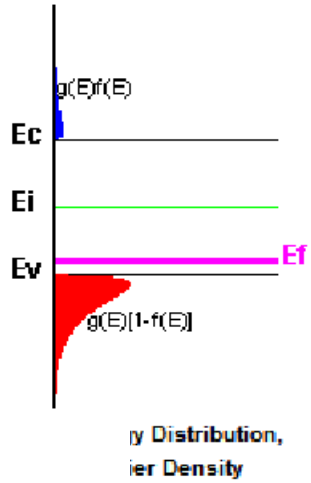
intrinsic semiconductor



n-doped semiconductor



p-doped semiconductor



y Distribution,
ier Density

$E_{av}=3/2\ k_BT$ average energy of free carrier

average thermal velocity of free carrier

$$v_{th} = \sqrt{\frac{3k_BT}{m^*}} \approx 10^5 \text{ m/s at } 300\text{ K}$$