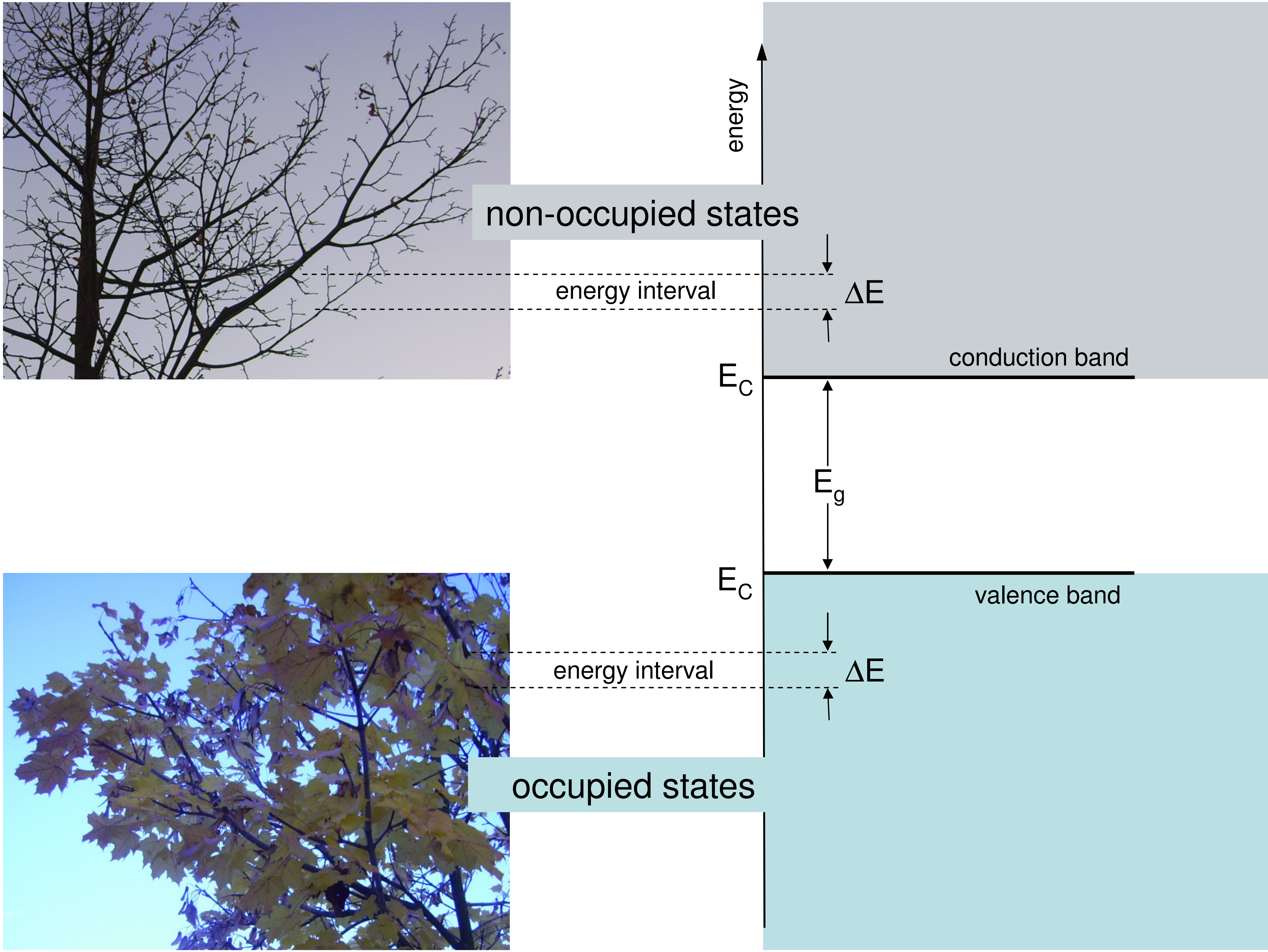
Photovoltaik 3

Electrons and Holes in Semiconductors

Resources:
Peter Würfel, Physik der Solarzellen
Jenny Nelson, The Physics of Solar Cells
Thomas Dittrich, lecture notes

1. Free electron and hole densities
2. Intrinsic carrier concentration
3. Doping of semiconductors
4. Equilibrium and excess charge carriers



energy

non-occupied states

energy interval

ΔE

conduction band

E_C

E_g

E_C

valence band

energy interval

ΔE

occupied states

Density of free electrons and holes

$$dn, dp \quad \propto \quad dE$$

$$dn \quad \propto \quad D_e(E)$$

$$dp \quad \propto \quad D_h(E)$$

$$dn \quad \propto \quad f_e(E) = f(E)$$

$$dp \quad \propto \quad f_h(E) = 1 - f(E)$$

E	energy
dE	energy interval
$D_{e,h}$	density of electron states
f	occupation probability for an electron
E_A	width of the conduction and valence bands

$$dn = D_e(E) \cdot f(E) \cdot dE$$

$$n = \int_{E_C}^{E_C + E_A} D_e(E) \cdot f(E) \cdot dE$$

$$dp = D_h(E) \cdot [1 - f(E)] \cdot dE$$

$$p = \int_{E_V - E_A}^{E_V} D_h(E) \cdot [1 - f(E)] \cdot dE$$

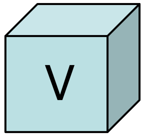
Density of states

number of states per volume and energy interval

$$D(E) \equiv \frac{1}{V} \cdot \frac{dN(E)}{dE}$$

Delocalization

Free charge carriers do not belong to a chemical bond.
Free charge carriers in an ideal semiconductor are delocalized.
One free charge carrier is delocalized over the whole volume.



$$(\Delta x)^3 = V$$

Δx – volume of one delocalized state
One delocalized state occupies the whole volume.

Delocalization and Heisenberg uncertainty principle

Heisenberg uncertainty principle
Δp momentum of an electron in a state
h = 6.626 10^{-34} Js

$$\Delta x \cdot \Delta p = h$$

phase space volume per state

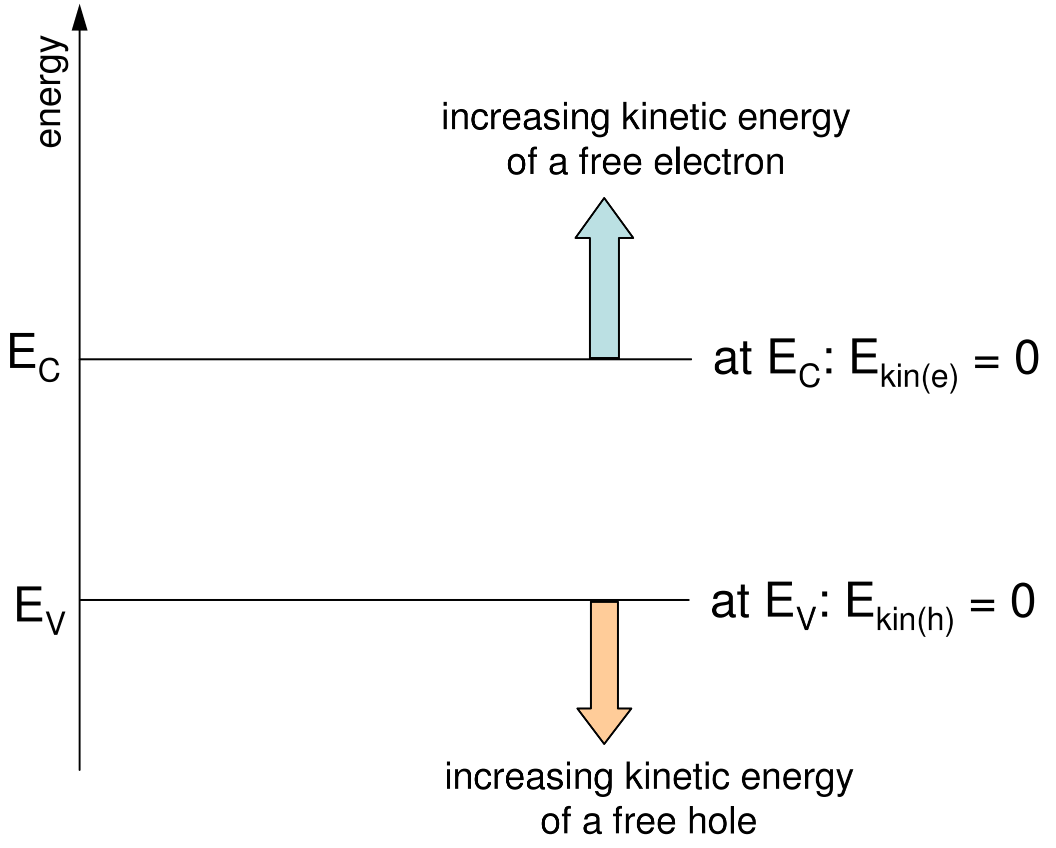
$$(\Delta x)^3 \cdot (\Delta p)^3 = h^3$$

volume in momentum space which
can be occupied by one state

$$(\Delta p)^3 = \frac{h^3}{V}$$

keep in mind: p means here momentum

Kinetic energy of free electrons and holes

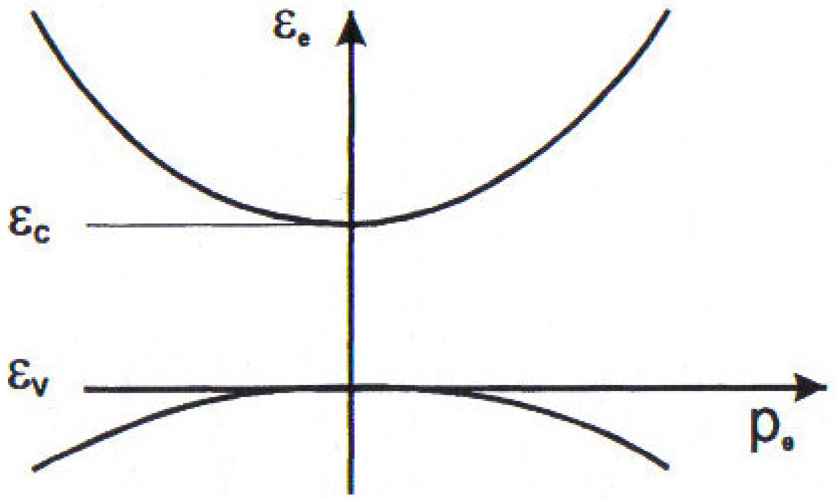


$$E_{kin} = \frac{p^2}{2 \cdot m}$$

p momentum
m mass

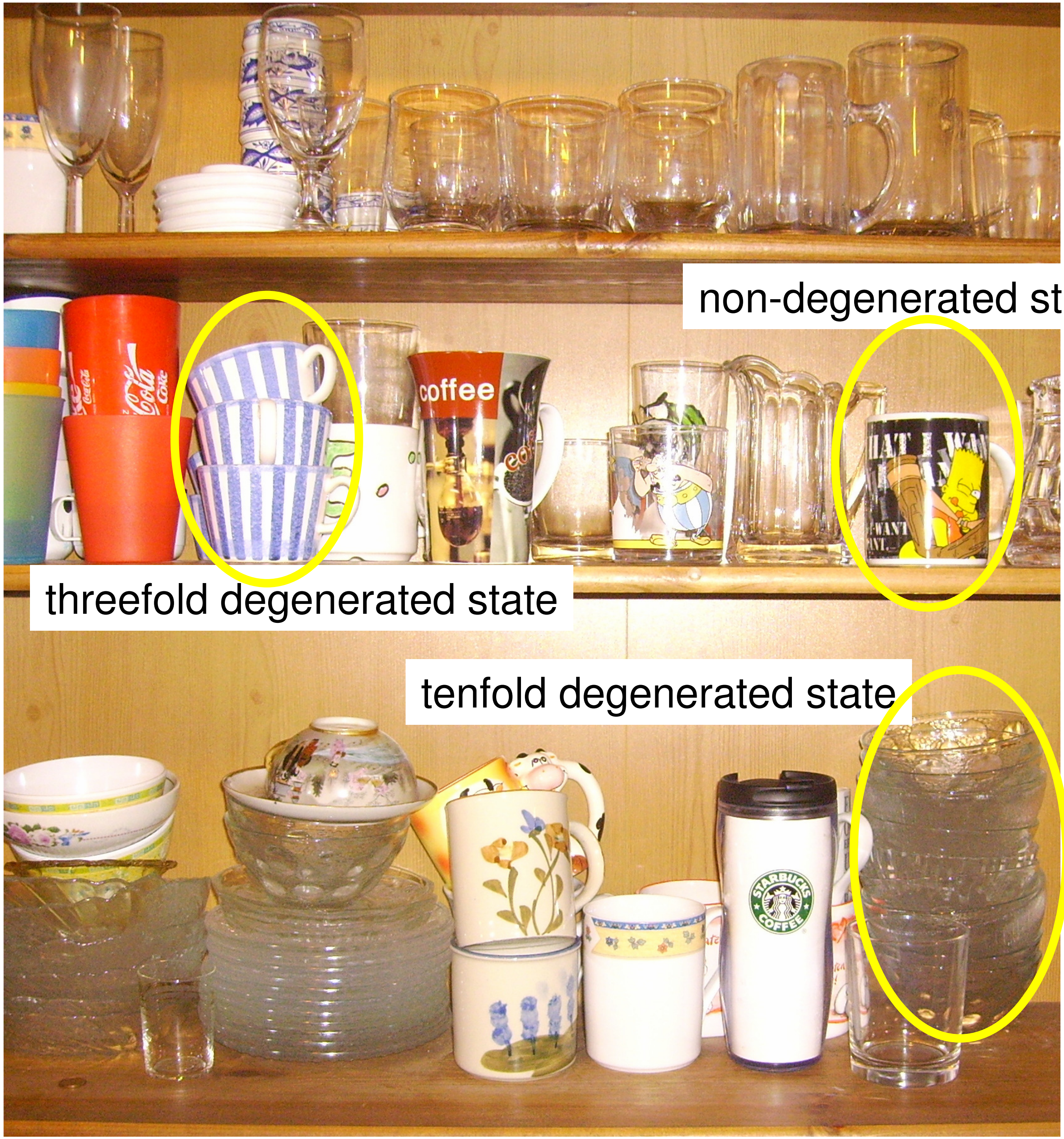
keep in mind: p means here momentum

Effective mass



$$\frac{1}{m_e^*} = \frac{\partial^2 \varepsilon_e}{\partial p_e^{\;2}}$$

Degeneration of states



non-degenerated state

threefold degenerated state

tenfold degenerated state

states in a cupboard: one place can be occupied by more than one cup or glass

degeneration: one state can be occupied by more than one particle

twofold degeneration of electron states due to spin-up and spin-down

From the number of states as a function of momentum to the density of states as a function of energy

for states with p’ ≤ p

$N(\lvert p \rvert) \quad \propto \quad \frac{4\pi}{3} \cdot \lvert p \rvert^3$	volume of a sphere with radius |p| in momentum space
$N(\lvert p \rvert) \quad \propto \quad 2$	spin degeneration
$N(\lvert p \rvert) \quad \propto \quad \frac{1}{(\Delta p)^3}$	inverse volume of one state in momentum space

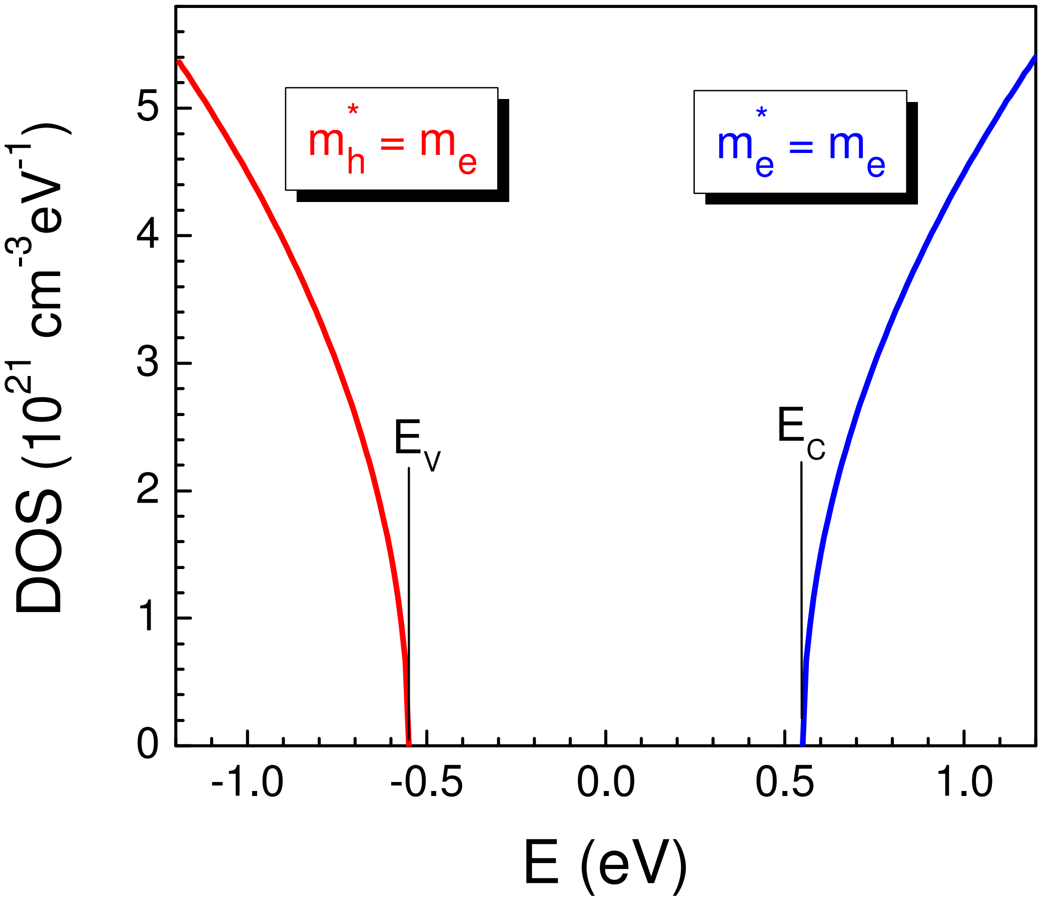
$N(\lvert p \rvert) = \frac{8\pi}{3 \cdot h^3} \cdot V \cdot \lvert p \rvert^3$ substitution: $p_{(e)} = \sqrt{(E - E_C) \cdot 2 \cdot m_e^*}$ $N_e(E) = \frac{8\pi}{3 \cdot h^3} \cdot V \cdot \left(2 \cdot m_e^*\right)^{3/2} \cdot (E - E_C)^{3/2}$ $D_e(E) = \ldots$

$$D_e(E) = 4\pi \cdot \left(\frac{2 \cdot m_e^*}{h^2} \right)^{3/2} \cdot (E - E_C)^{1/2}$$

$$D_h(E) = 4\pi \cdot \left(\frac{2 \cdot m_h^*}{h^2} \right)^{3/2} \cdot (E_V - E)^{1/2}$$

keep in mind: p means here momentum

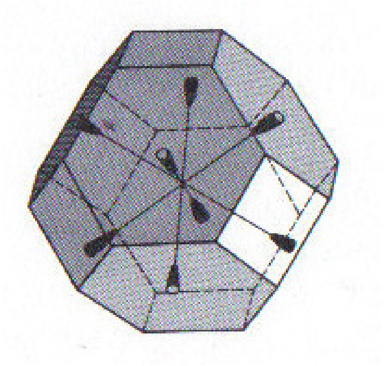
Order of DOS in conduction and valence bands



	$\frac{m_e^*}{m_e}$	$\frac{m_h^*}{m_e}$
Si	1.08	0.55
Ge	0.88	0.29
GaAs	0.067	0.47

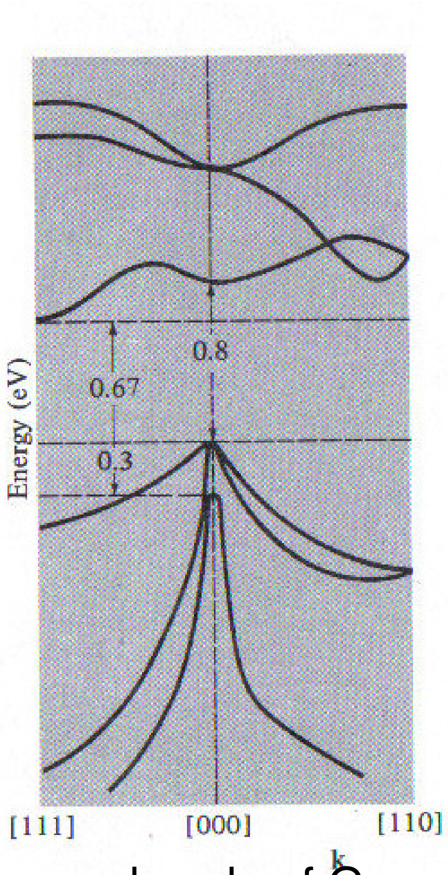
$$D(E) = \frac{6.7 \cdot 10^{21}}{cm^3 \cdot eV} \cdot \left(\frac{m_e^*}{m_e} \right)^{3/2} \cdot (E - E_C)^{1/2}$$

Band structure of Germanium



-Constant-energy surface near the conduction band minimum

-Representation by four ellipsoids

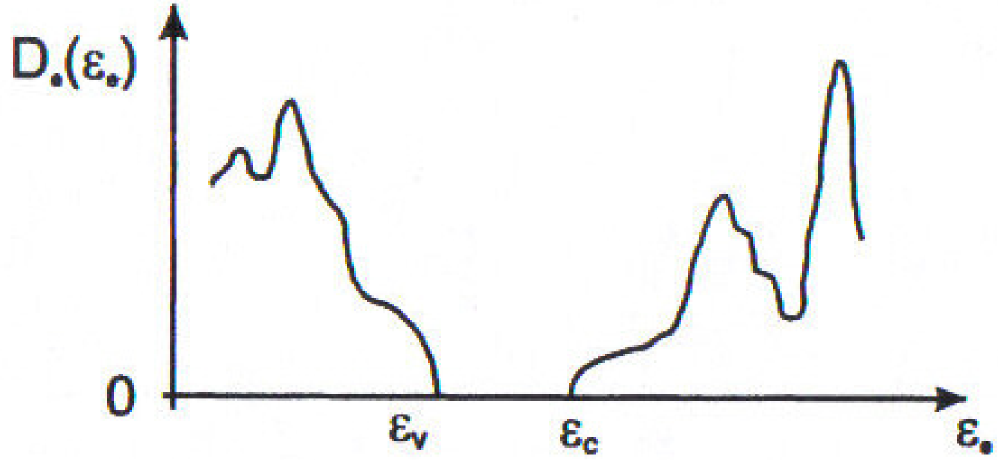


Energy bands of Ge along [111]

-Heavy and light holes

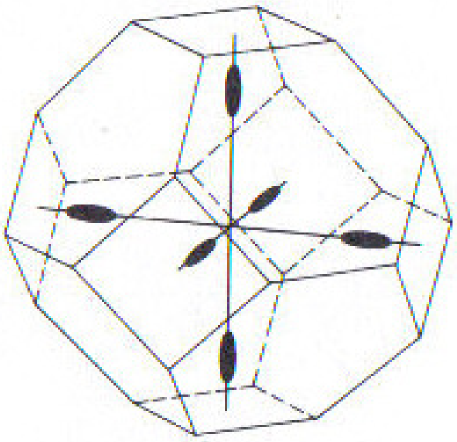
-For large k deviations from parabolic approximation

Density of States of Germanium

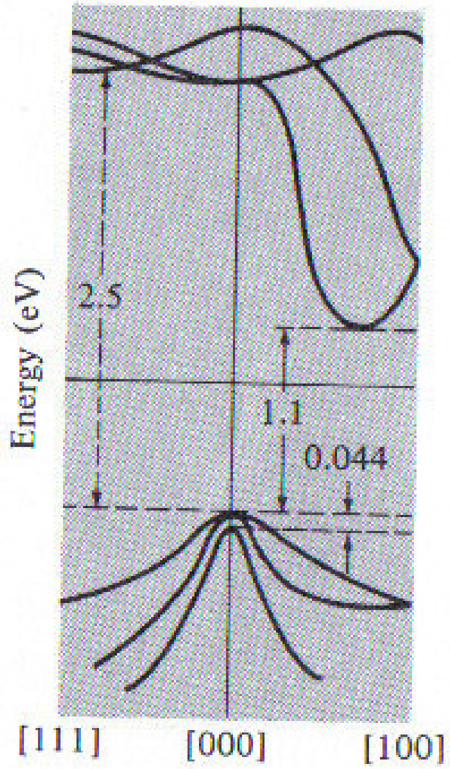


Zustandsdichte für Elektronen im Leitungs- und Valenzband des Halbleiters Germanium

Band structure of Silicon
Indirect semiconductor



Constant energy surface
near conduction band minimum



Energy bands in silicon

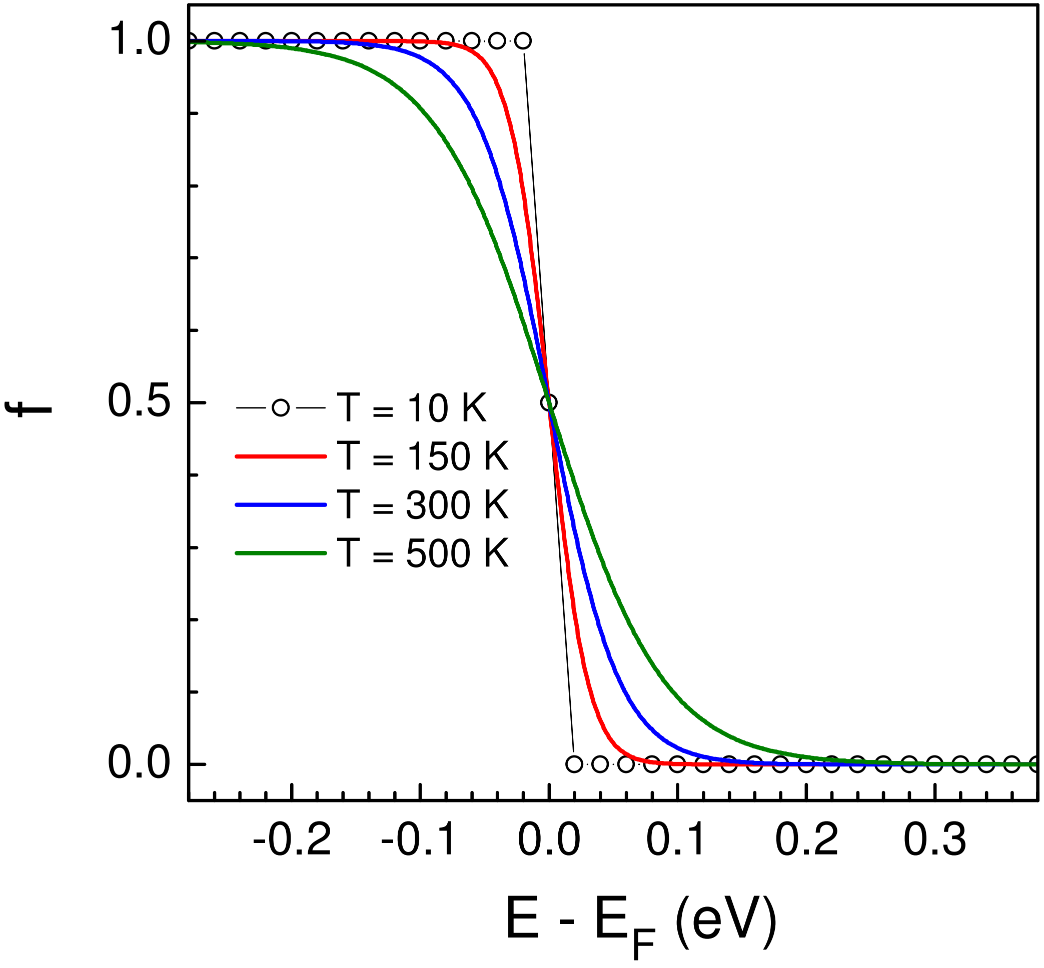
From Ashcroft Merwin, Solid state phyisics

Fermi-Dirac statistics

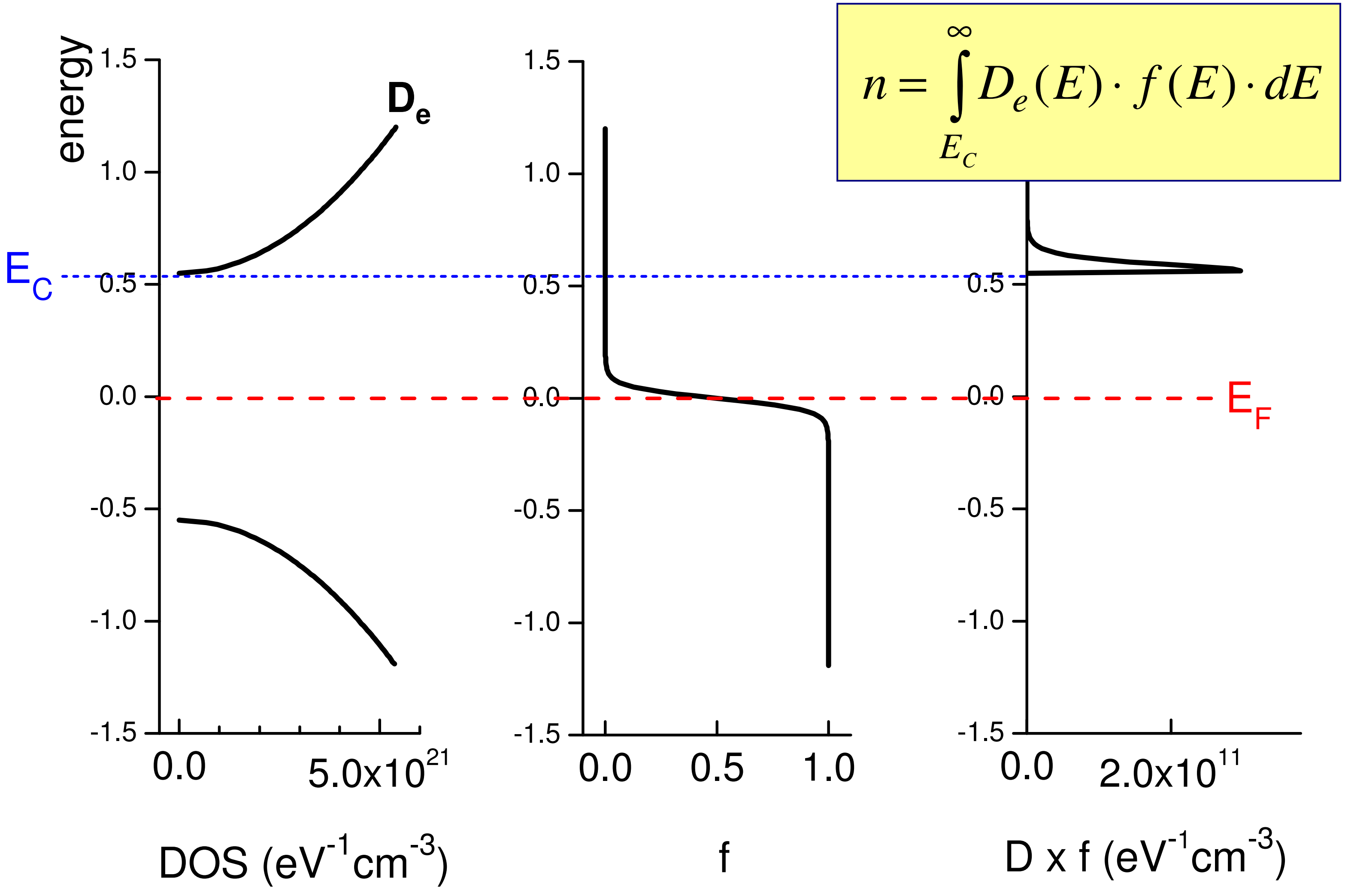
$$f(E) = \frac{1}{\exp\left(\frac{E - E_F}{k_B \cdot T}\right) + 1}$$

E_F – Fermi-energy

distribution function following
from the nature of the electron

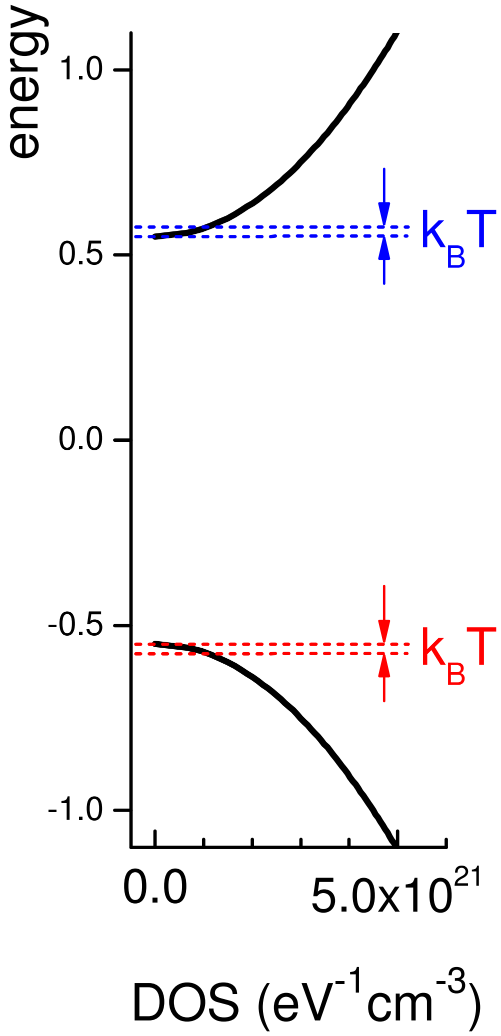


The product of $D_e(E)$ and $f(E)$



$$n = \int_{E_C}^{\infty} D_e(E) \cdot f(E) \cdot dE$$

The effective DOS



$$N_C = \int_{E_C}^{E_C + k_B \cdot T} D_e(E) \cdot dE$$

$$N_V = \int_{E_V - k_B \cdot T}^{E_V} D_h(E) \cdot dE$$

$$N_{C(V)} = 2 \cdot \left(2\pi \cdot k_B \cdot T \cdot \frac{m^*_{e(h)}}{h^2} \right)^{3/2}$$

	$N_C (cm^{-3})$	$N_V (cm^{-3})$
Si	$2.4 \cdot 10^{19}$	$1 \cdot 10^{19}$
Ge	$1 \cdot 10^{19}$	$6 \cdot 10^{18}$
GaAs	$5 \cdot 10^{17}$	$7 \cdot 10^{18}$

Densities of free charge carriers

$$n = N_C \cdot \exp\left(-\frac{E_C - E_{Fn}}{k_B \cdot T} \right)$$

$$p = N_V \cdot \exp\left(-\frac{E_{Fp} - E_V}{k_B \cdot T} \right)$$

Boltzmann statistics

Effective density of states

$$N_C = 2\cdot\left(2\pi\cdot k_B\cdot T\cdot\frac{m_e^*}{h^2}\right)^{3/2}$$

$$N_C = 2.5\left(\frac{m_e^*}{m_e}\right)^{3/2}\left(\frac{T}{300K}\right)^{3/2}\times10^{19}\,\mathrm{cm}^{-3}$$

$$N_C = 2\cdot\left(2\pi\cdot k_B\cdot T\cdot\frac{m_h^*}{h^2}\right)^{3/2}$$

$$N_V = 2.5\left(\frac{m_h^*}{m_e}\right)^{3/2}\left(\frac{T}{300K}\right)^{3/2}\times10^{19}\,\mathrm{cm}^{-3}$$

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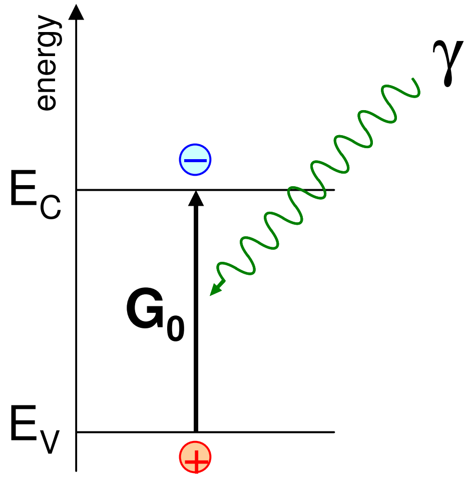
Re-absorption of black body irradiation

semiconductor emits black body irradiation
semiconductor absorbs its own black body irradiation for hν ≥ E_g



$$\gamma \rightarrow e^{-} + h^{+}$$

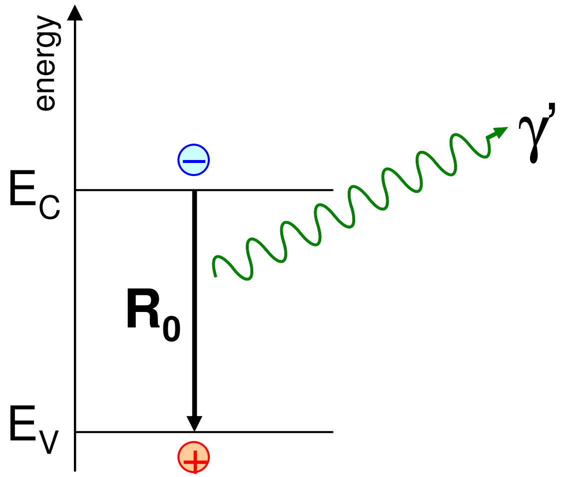
G_0 thermal generation rate of free charge carriers

Recombination of free charge carriers

free carrier concentrations can not increase infinitely

↓

limitation by recombination



$$e^- + h^+ \quad \rightarrow \quad \gamma'$$

R_0 recombination rate

$$R_0 = B \cdot n_0 \cdot p_0$$

R_0 is proportional to n_0 and p_0
B recombination rate constant

Thermal equilibrium

$$\boxed{G_0 = R_0}$$

⇓

$$n_0 \cdot p_0 = \frac{G_0}{B} = const$$

$$n_0 \cdot p_0 = N_C \cdot N_V \cdot \exp\left(- \frac{E_C - E_{Fn} + E_{Fp} - E_V}{k_B \cdot T} \right)$$

$$n_0 \cdot p_0 = N_C \cdot N_V \cdot \exp\left(- \frac{E_g}{k_B \cdot T} \right) \cdot \exp\left(- \frac{E_{Fp} - E_{Fn}}{k_B \cdot T} \right)$$

E_{Fn} and E_{Fp} can change with the free carrier concentration

$$\Rightarrow \boxed{E_{Fn} = E_{Fp}}$$

Intrinsic carrier concentration

in thermal equilibrium $n_0 \cdot p_0 = const \equiv n_i^2$

n_i intrinsic carrier concentration

$$\boxed{n_i = \sqrt{n_0 \cdot p_0}}$$

Intrinsic carrier concentration

in thermal equilibrium

$$n_i = \sqrt{n_0 \cdot p_0}$$

from Boltzmann statistics

$$n_0 = N_C \cdot \exp\left(-\frac{E_C - E_F}{k_B \cdot T}\right)$$

$$p_0 = N_V \cdot \exp\left(-\frac{E_F - E_V}{k_B \cdot T}\right)$$

Intrinsic carrier concentration

in thermal equilibrium

$$n_i = \sqrt{n_0 \cdot p_0}$$

Boltzmann statistics

$$n_0 = N_C \cdot \exp\left(-\frac{E_C - E_F}{k_B \cdot T}\right)$$

$$p_0 = N_V \cdot \exp\left(-\frac{E_F - E_V}{k_B \cdot T}\right)$$

$$n_i = \sqrt{N_V \cdot N_C} \cdot \exp\left(-\frac{E_g}{2 \cdot k_B \cdot T}\right)$$

intrinsic semiconductor

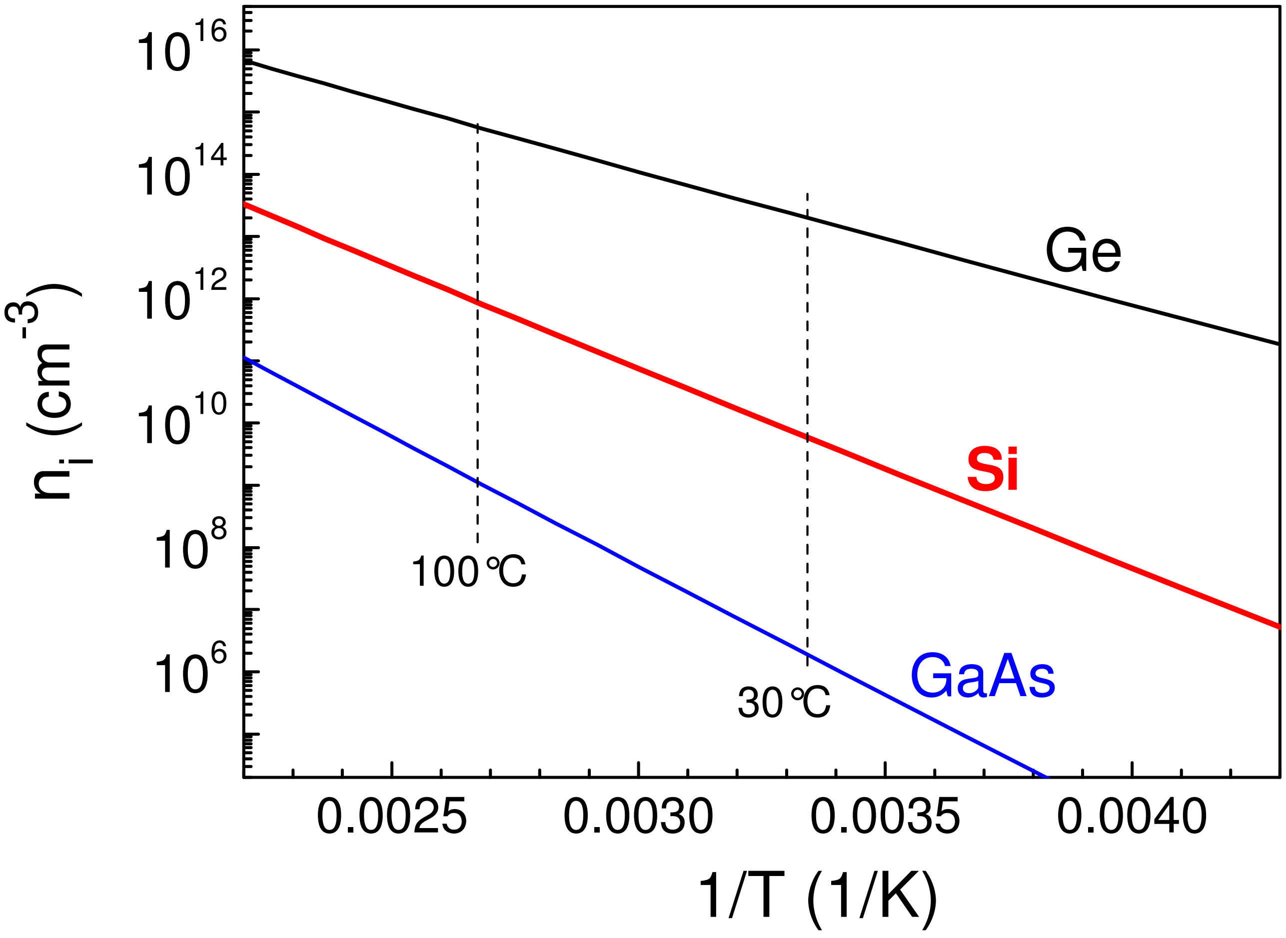
$$n_i = n_0 = p_0$$

intrinsic Fermi-level

$$E_F = E_i = \frac{E_C + E_V}{2} + \frac{3}{4} \cdot k_B \cdot T \cdot \ln \frac{m_h^*}{m_e^*}$$

*

Temperature dependence of the intrinsic carrier concentration



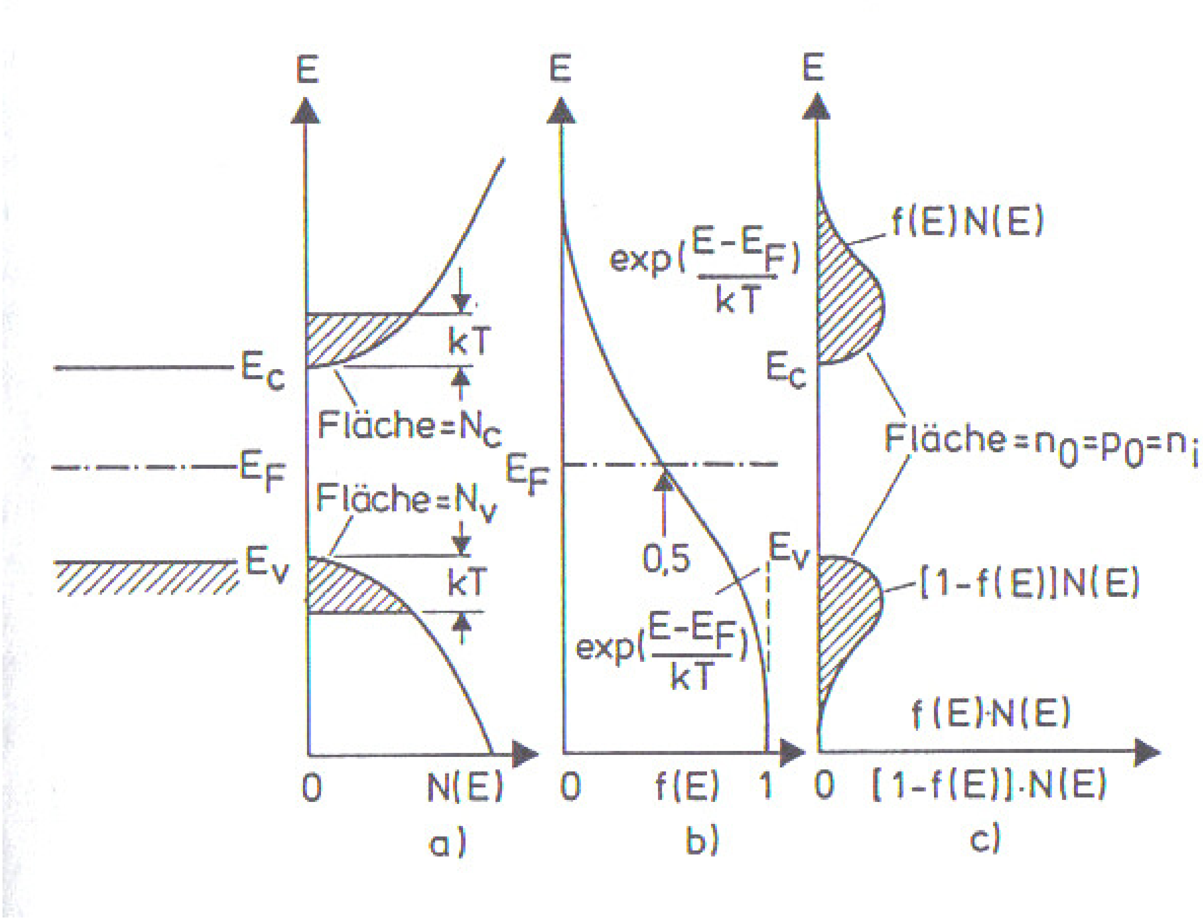
Intrinsic carrier concentrations at room temperature

$n_i(Si) \approx 10^{10}\ cm^{-3}$

$n_i(GaAs) \approx 10^{6}\ cm^{-3}$

$n_i(Ge) \approx 10^{13}\ cm^{-3}$

Intrinsic semiconductor



1. Free electron and hole densities
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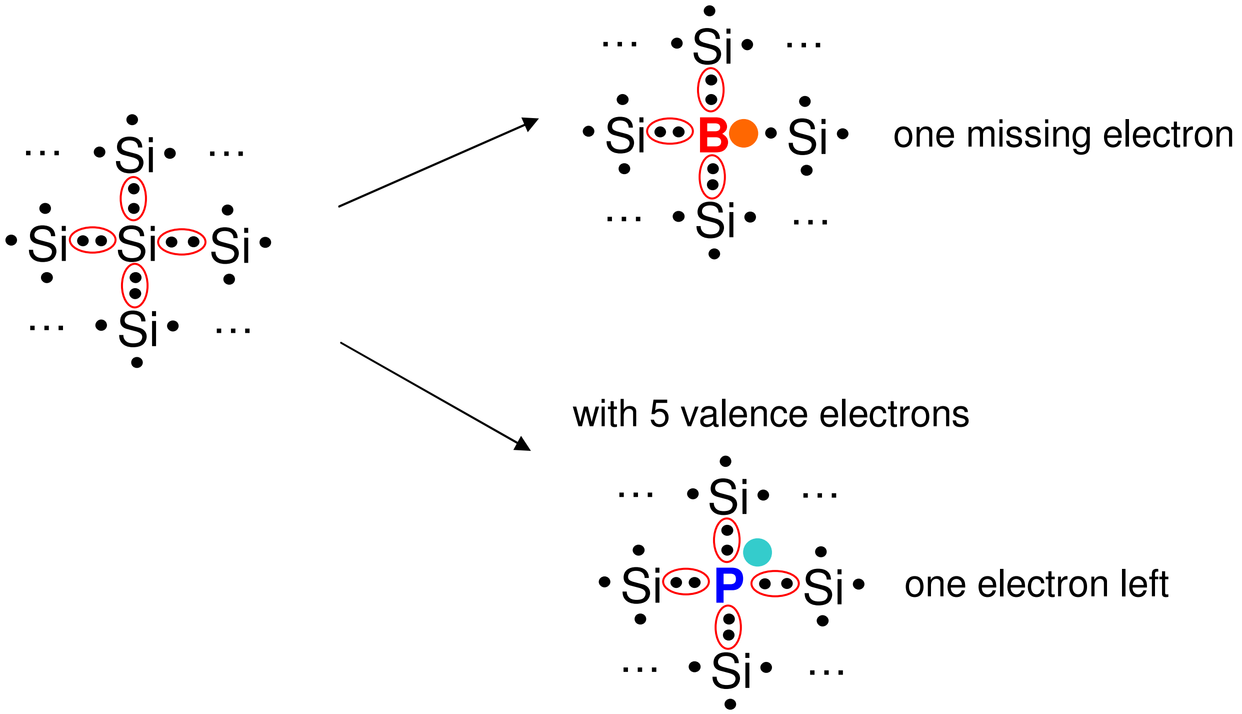
Impurity in a crystal lattice



with 3 valence electrons

one missing electron

with 5 valence electrons

one electron left

There are impurities which can be incorporated into the lattice replacing a host atom. importance of valence

Doping of semiconductors

Incorporation of impurity atoms into the crystal lattice of the semiconductor.

Impurity atoms have different valence in comparison to the atoms of the host lattice.

n-type doping

The impurity atom has more valence electrons than needed for bonding.
Impurity atom giving an electron is named donor.
Un-bonded electron can be into the conduction band.

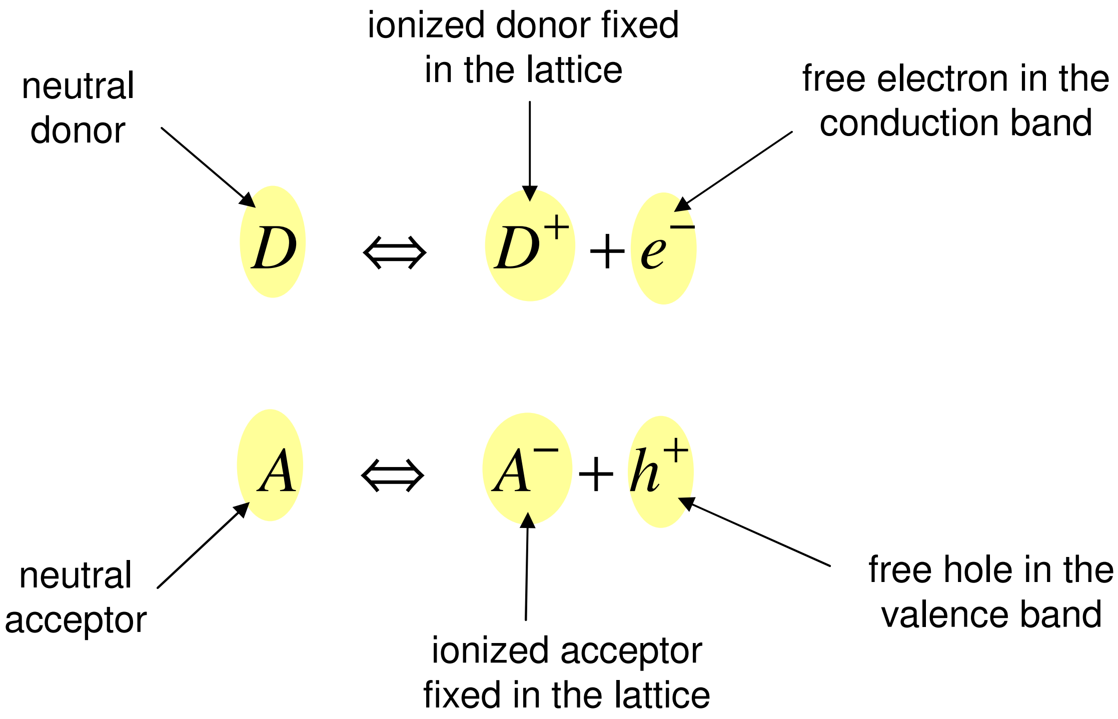
creation of a mobile electron in the conduction band

p-type doping

The impurity atom has less valence electrons than needed for bonding.
Impurity atom taking an electron is named acceptor.
Electron needed for bonding can be taken from the valence band.

creation of a mobile hole in the valence band

Free charge carriers and fixed ionized impurity



neutral donor

ionized donor fixed in the lattice

free electron in the conduction band

$$D \Leftrightarrow D^{+} + e^{-}$$

$$A \Leftrightarrow A^{-} + h^{+}$$

neutral acceptor

ionized acceptor fixed in the lattice

free hole in the valence band

charge neutrality:

n-type $N_D{}^{+} = n_0$

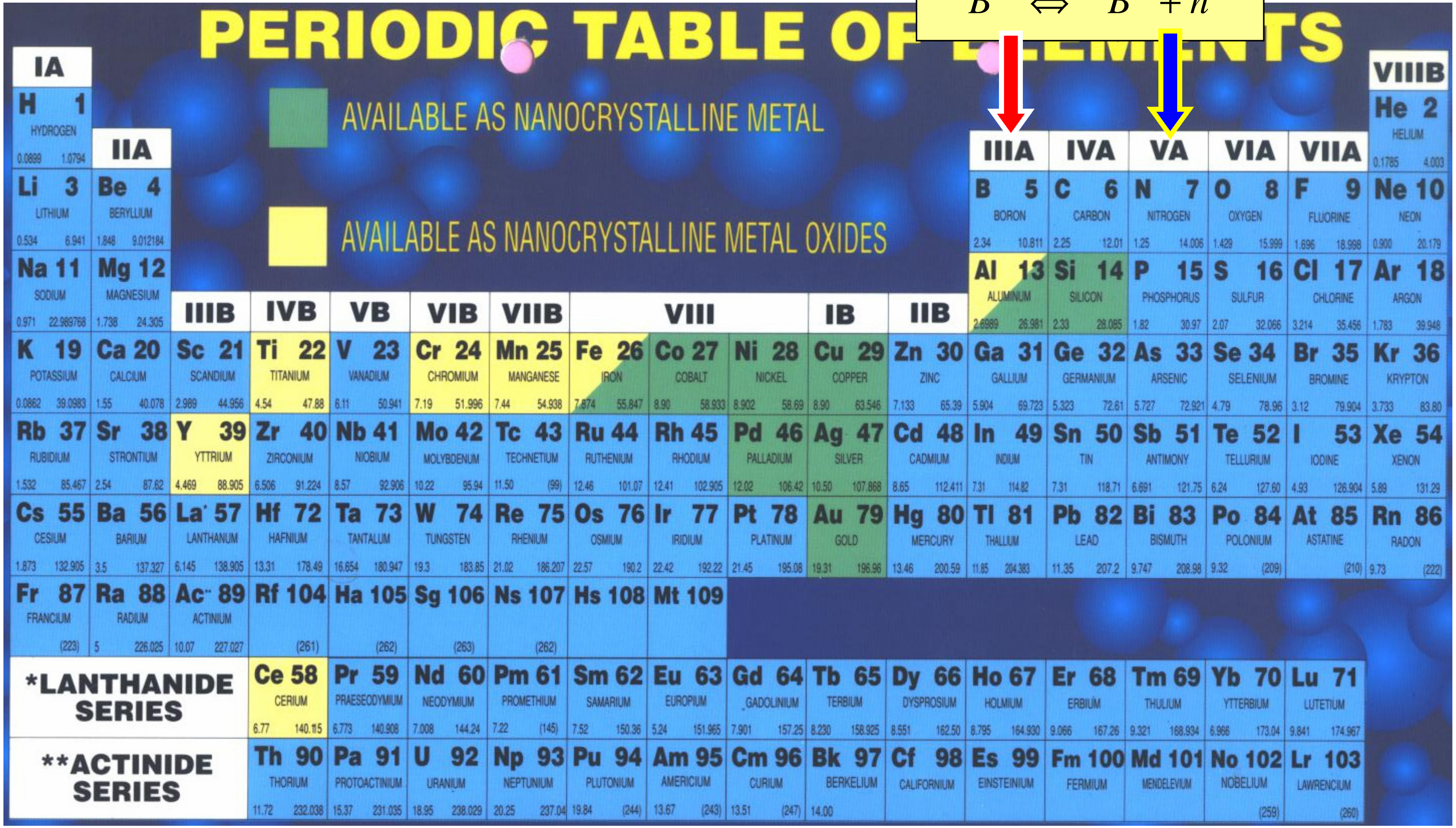
p-type $N_A{}^{-} = p_0$

Doping of Si

donors: P, As,…
acceptors: B, Al,…

$$P \Leftrightarrow P^+ + e^-$$

$$B \Leftrightarrow B^- + h^+$$



PERIODIC TABLE OF ELEMENTS

🟩 AVAILABLE AS NANOCRYSTALLINE METAL

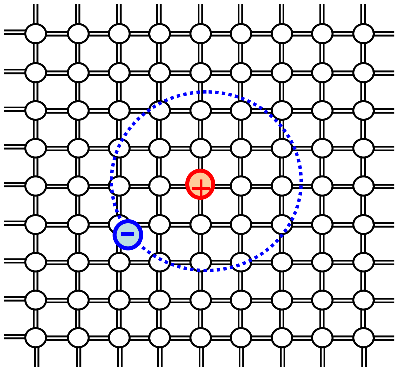
🟨 AVAILABLE AS NANOCRYSTALLINE METAL OXIDES

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIB
H 1 HYDROGEN 0.0899 1.0794																	He 2 HELIUM 0.1785 4.003
Li 3 LITHIUM 0.534 6.941	Be 4 BERYLLIUM 1.848 9.012184											B 5 BORON 2.34 10.811	C 6 CARBON 2.25 12.01	N 7 NITROGEN 1.25 14.006	O 8 OXYGEN 1.429 15.999	F 9 FLUORINE 1.696 18.998	Ne 10 NEON 0.900 20.179
Na 11 SODIUM 0.971 22.989768	Mg 12 MAGNESIUM 1.738 24.305											Al 13 ALUMINUM 2.6989 26.981	Si 14 SILICON 2.33 28.085	P 15 PHOSPHORUS 1.82 30.97	S 16 SULFUR 2.07 32.066	Cl 17 CHLORINE 3.214 35.456	Ar 18 ARGON 1.783 39.948
K 19 POTASSIUM 0.0862 39.0983	Ca 20 CALCIUM 1.55 40.078	Sc 21 SCANDIUM 2.989 44.956	Ti 22 TITANIUM 4.54 47.88	V 23 VANADIUM 6.11 50.941	Cr 24 CHROMIUM 7.19 51.996	Mn 25 MANGANESE 7.44 54.938	Fe 26 IRON 7.874 55.847	Co 27 COBALT 8.90 58.933	Ni 28 NICKEL 8.902 58.69	Cu 29 COPPER 8.90 63.546	Zn 30 ZINC 7.133 65.39	Ga 31 GALLIUM 5.904 69.723	Ge 32 GERMANIUM 5.323 72.61	As 33 ARSENIC 5.727 72.921	Se 34 SELENIUM 4.79 78.96	Br 35 BROMINE 3.12 79.904	Kr 36 KRYPTON 3.733 83.80
Rb 37 RUBIDIUM 1.532 85.467	Sr 38 STRONTIUM 2.54 87.62	Y 39 YTTRIUM 4.469 88.905	Zr 40 ZIRCONIUM 6.506 91.224	Nb 41 NIOBIUM 8.57 92.906	Mo 42 MOLYBDENUM 10.22 95.94	Tc 43 TECHNETIUM 11.50 (99)	Ru 44 RUTHENIUM 12.46 101.07	Rh 45 RHODIUM 12.41 102.905	Pd 46 PALLADIUM 12.02 106.42	Ag 47 SILVER 10.50 107.868	Cd 48 CADMIUM 8.65 112.411	In 49 INDIUM 7.31 114.82	Sn 50 TIN 7.31 118.71	Sb 51 ANTIMONY 6.691 121.75	Te 52 TELLURIUM 6.24 127.60	I 53 IODINE 4.93 126.904	Xe 54 XENON 5.89 131.29
Cs 55 CESIUM 1.873 132.905	Ba 56 BARIUM 3.5 137.327	La* 57 LANTHANUM 6.145 138.905	Hf 72 HAFNIUM 13.31 178.49	Ta 73 TANTALUM 16.654 180.947	W 74 TUNGSTEN 19.3 183.85	Re 75 RHENIUM 21.02 186.207	Os 76 OSMIUM 22.57 190.2	Ir 77 IRIDIUM 22.42 192.22	Pt 78 PLATINUM 21.45 195.08	Au 79 GOLD 19.31 196.96	Hg 80 MERCURY 13.46 200.59	Tl 81 THALLIUM 11.85 204.383	Pb 82 LEAD 11.35 207.2	Bi 83 BISMUTH 9.747 208.98	Po 84 POLONIUM 9.32 (209)	At 85 ASTATINE (210)	Rn 86 RADON 9.73 (222)
Fr 87 FRANCIUM (223)	Ra 88 RADIUM 5 226.025	Ac** 89 ACTINIUM 10.07 227.027	Rf 104 (261)	Ha 105 (262)	Sg 106 (263)	Ns 107 (262)	Hs 108	Mt 109									

*LANTHANIDE SERIES													
Ce 58 CERIUM 6.77 140.115	Pr 59 PRAESEODYMIUM 6.773 140.908	Nd 60 NEODYMIUM 7.008 144.24	Pm 61 PROMETHIUM 7.22 (145)	Sm 62 SAMARIUM 7.52 150.36	Eu 63 EUROPIUM 5.24 151.965	Gd 64 GADOLINIUM 7.901 157.25	Tb 65 TERBIUM 8.230 158.925	Dy 66 DYSPROSIUM 8.551 162.50	Ho 67 HOLMIUM 8.795 164.930	Er 68 ERBIUM 9.066 167.26	Tm 69 THULIUM 9.321 168.934	Yb 70 YTTERBIUM 6.966 173.04	Lu 71 LUTETIUM 9.841 174.967

**ACTINIDE SERIES													
Th 90 THORIUM 11.72 232.038	Pa 91 PROTOACTINIUM 15.37 231.035	U 92 URANIUM 18.95 238.029	Np 93 NEPTUNIUM 20.25 237.04	Pu 94 PLUTONIUM 19.84 (244)	Am 95 AMERICIUM 13.67 (243)	Cm 96 CURIUM 13.51 (247)	Bk 97 BERKELIUM 14.00	Cf 98 CALIFORNIUM	Es 99 EINSTEINIUM	Fm 100 FERMIUM	Md 101 MENDELEVIUM	No 102 NOBELIUM (259)	Lr 103 LAWRENCIUM (260)

Hydrogen model of doping



ionization energy

$$E_{ion} \propto \frac{m^*}{\varepsilon^2}$$

Bohr-radius

$$a_0 \propto \frac{\varepsilon}{m^*}$$

$$E_{ion}(H-atom) = 13.56\,eV$$

$$a_0(H-atom) = 0.051\,nm$$

ε_{Si}=11.9

estimation of the ionization or binding energy

$$E_{ion} = E_{ion}(H-atom)\cdot\frac{m^*_{e(Si,GaAs,...)}}{m_e}\cdot\frac{\varepsilon^2_{vac}}{\varepsilon^2_{Si,GaAs,...}}$$

E_{ion} = 6 meV (GaAs) … ≈ 50 meV (Si)

⇓

all impurities are ionized at room temperature

$$N_D \approx N_D^{\;+} = n_0$$

$$N_A \approx N_A^{\;-} = p_0$$

Energy levels of some impurities in Si

donors

	$E_C - E_D\ (eV)$
Sb	0.039
P	0.044
As	0.049
Bi	0.069

acceptors

	$E_V + E_A\ (eV)$
B	0.046
Al	0.057
Ga	0.065
In	0.16

Minority and majority charge carriers

majority charge carriers:

- electrons in n-type
- hole in p-type

minority carriers:

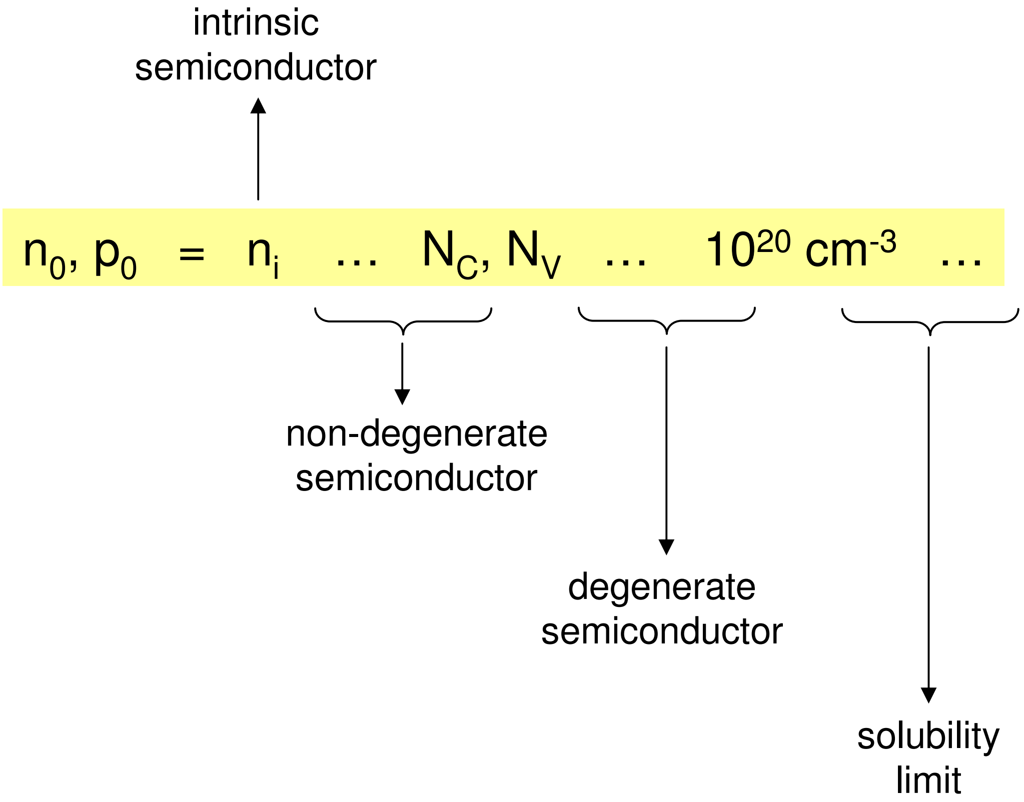
- holes in n-type
- electrons in p-type

$$n_i^2 = n_0 \cdot p_0$$

Example: p-Si, $N_A = 10^{16}$ cm^{-3}

n_i(Si) ≈ 10^{10} cm^{-3}
majority: $p_0 = 10^{16}$ cm^{-3}
minority: $n_0 = 10^4$ cm^{-3}

Doping range of semiconductors



intrinsic semiconductor

$n_0, p_0 \;=\; n_i \;\; \ldots \;\; N_C, N_V \;\; \ldots \;\; 10^{20}\ \mathrm{cm}^{-3} \;\; \ldots$

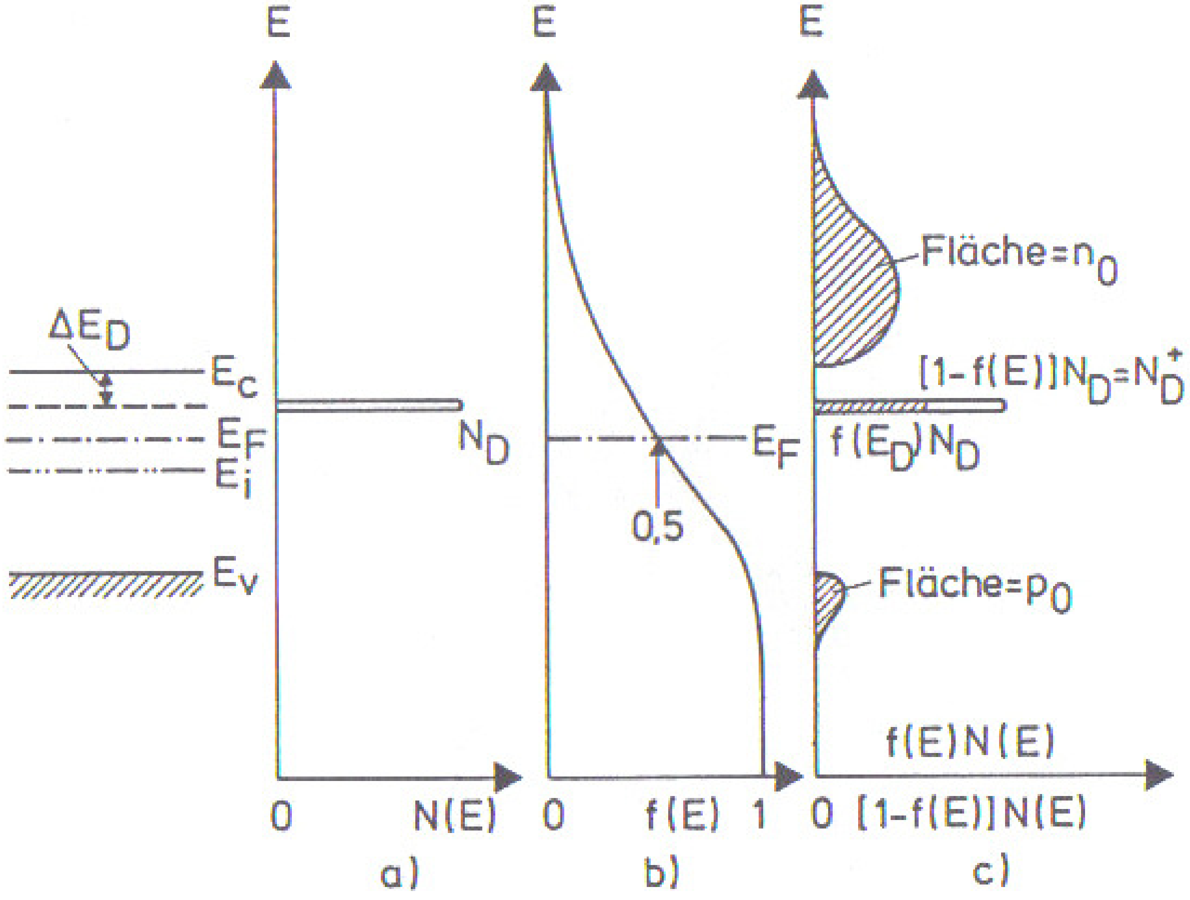
non-degenerate semiconductor

degenerate semiconductor

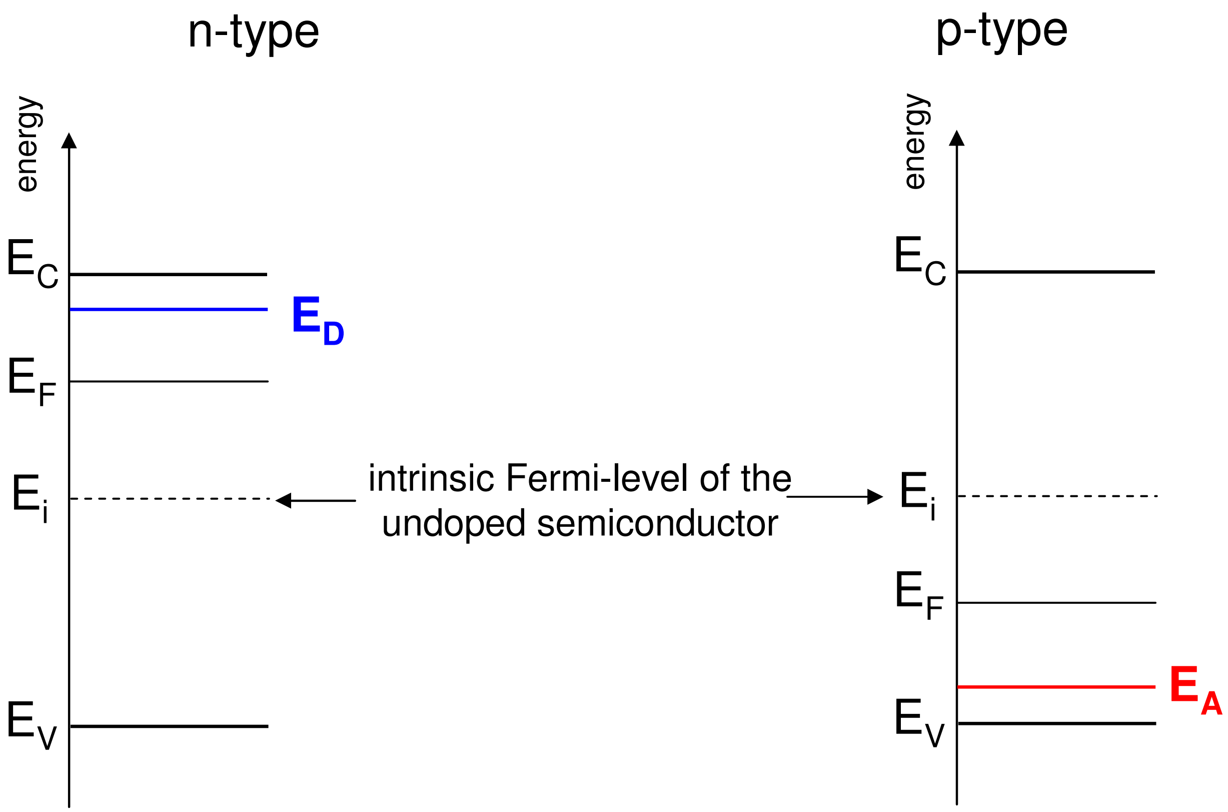
solubility limit

for Si from minority to majority: ≈ 20 orders of magnitude
huge change of conductivity (about 10 orders of magnitude for majority carriers)

Doped semiconductor



Energetic levels in doped semiconductors



$$E_F = E_C - k_B \cdot T \ln\left(\frac{N_C}{n_0}\right)$$

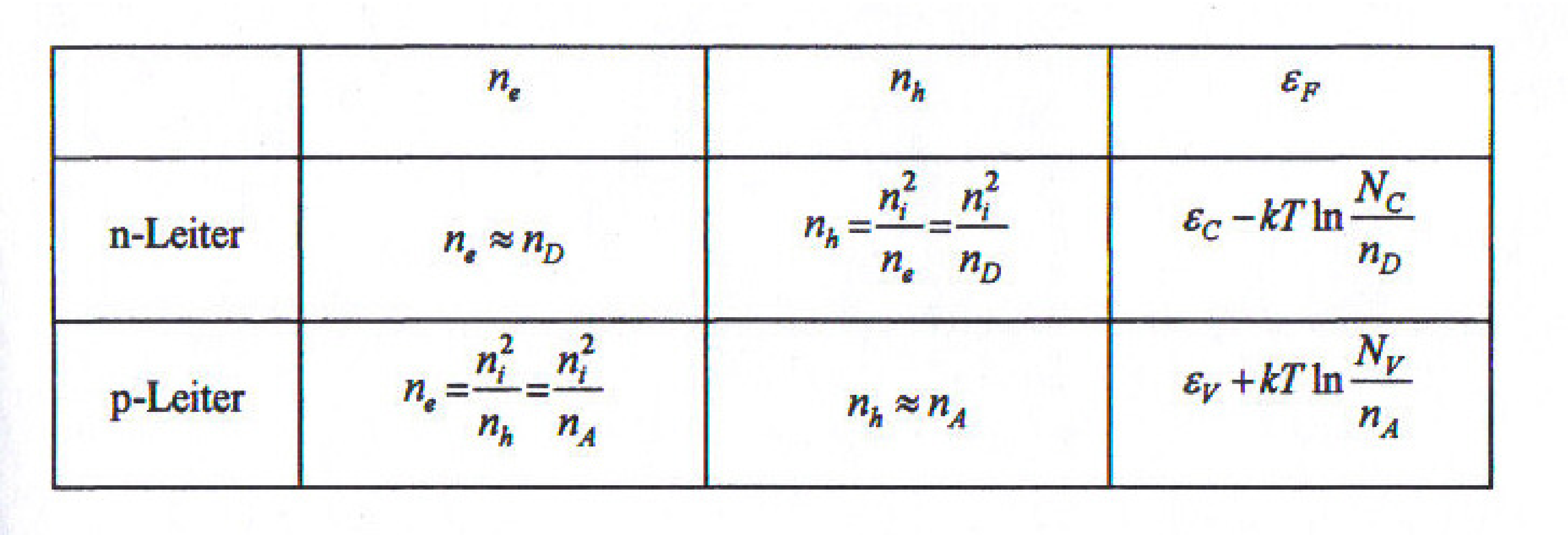
for: $n_i << n_0 < N_C$

$$E_F = E_V + k_B \cdot T \ln\left(\frac{N_V}{p_0}\right)$$

for: $n_i << p_0 < N_V$

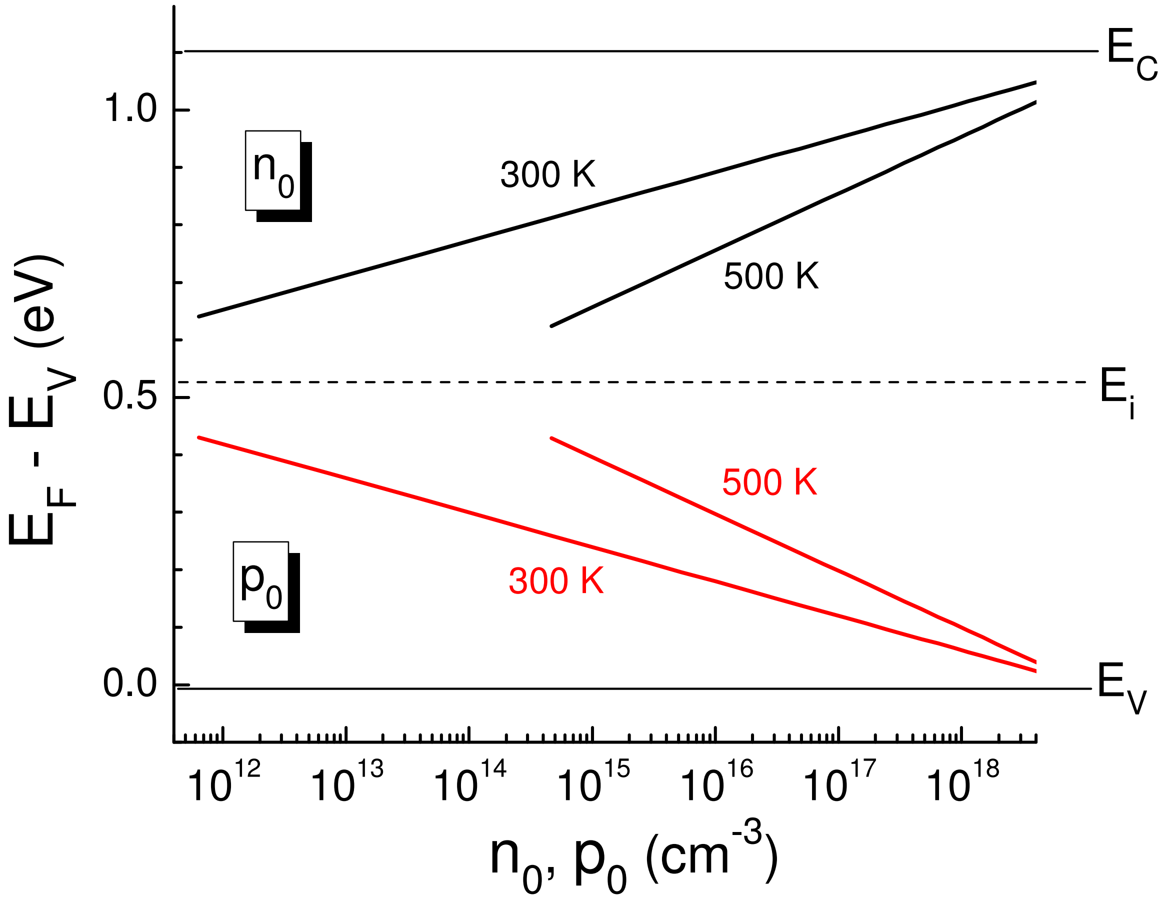
*

Formulaes for the doped semiconductor



	n_e	n_h	ε_F
n-Leiter	$n_e \approx n_D$	$n_h = \frac{n_i^2}{n_e} = \frac{n_i^2}{n_D}$	$\varepsilon_C - kT \ln \frac{N_C}{n_D}$
p-Leiter	$n_e = \frac{n_i^2}{n_h} = \frac{n_i^2}{n_A}$	$n_h \approx n_A$	$\varepsilon_V + kT \ln \frac{N_V}{n_A}$

Doping dependence of the Fermi-level



(temperature dependence of E_g has not been considered)

1. Free electron and hole densities
2. Intrinsic carrier concentration
3. Doping of semiconductors
4. Equilibrium and excess charge carriers

Quasi-Fermi-levels under illumination

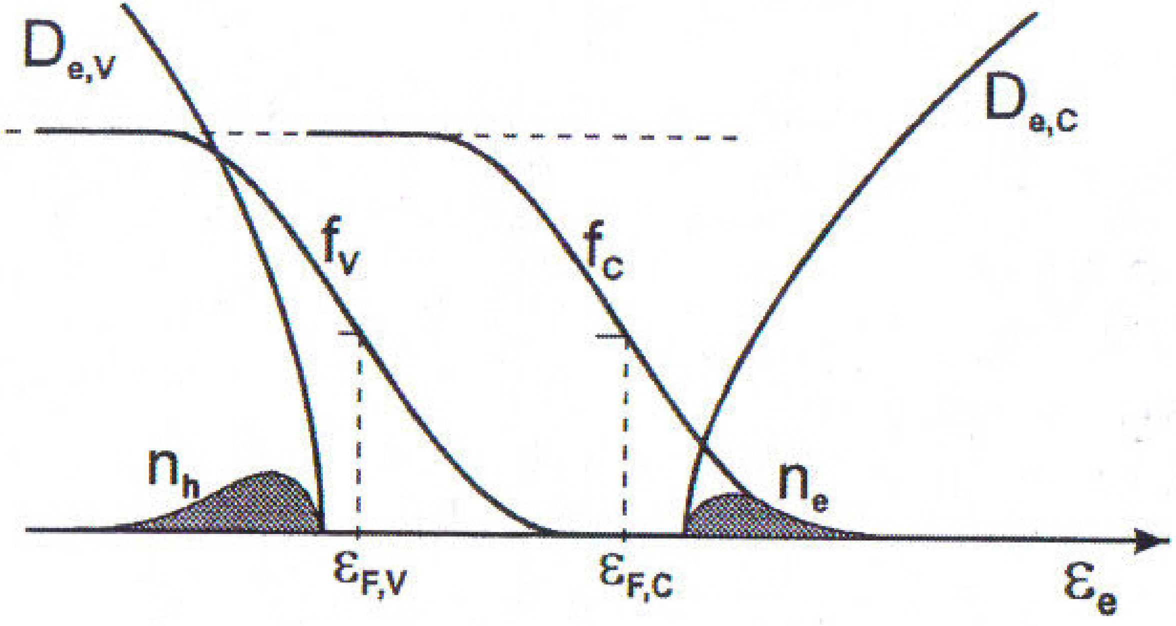


Abb. 3.12 Im belichteten Halbleiter wird die Besetzung von Leitungsband *C* und Valenzband *V* von verschiedenen Fermi-Verteilungen f_C und f_V geregelt.

thermal equilibrium

$$E_F = E_{Fo} = E_{Fn} = E_{Fp}$$

$$n_i^2 = n_0 \cdot p_0$$

$$E_{Fo} = E_C - k_B \cdot T \cdot \ln\left(\frac{N_C}{n_0}\right)$$

$$= E_V + k_B \cdot T \cdot \ln\left(\frac{N_V}{p_0}\right)$$

under illumination
(or non-equilibrium)

$$\boxed{E_{Fn} \neq E_{Fp}}$$

$$n = n_0 + \Delta n$$

$$p = p_0 + \Delta p$$

$$n_0 \cdot p_0 > n_i^2$$

equilibrium charge carriers

excess charge carriers

$$E_{Fn} = E_C - k_B \cdot T \cdot \ln\left(\frac{N_C}{n_0 + \Delta n}\right)$$

$$E_{Fp} = E_V + k_B \cdot T \cdot \ln\left(\frac{N_V}{p_0 + \Delta p}\right)$$

separation into quasi Fermi-levels in non-equilibrium

Ideal charge-selective contact

$$q \cdot V_{OC} = E_{Fn} - E_{Fp}$$

no losses of potential energy at contacts

$$\begin{aligned} E_{Fn} - E_{Fp} &= E_C - E_V - k_B \cdot T \cdot \ln\left(\frac{N_C}{n_0 + \Delta n} \cdot \frac{N_V}{p_0 + \Delta p} \right) \\ &= k_B \cdot T \cdot \ln\left(\frac{N_C \cdot N_V}{n_0 \cdot p_0} \right) - k_B \cdot T \cdot \ln\left(\frac{N_C}{n_0 + \Delta n} \cdot \frac{N_V}{p_0 + \Delta p} \right) \\ &= k_B \cdot T \cdot \ln\left(\frac{n_0 + \Delta n}{n_0} \cdot \frac{p_0 + \Delta p}{p_0} \right) \end{aligned}$$

Origin of V_{OC}

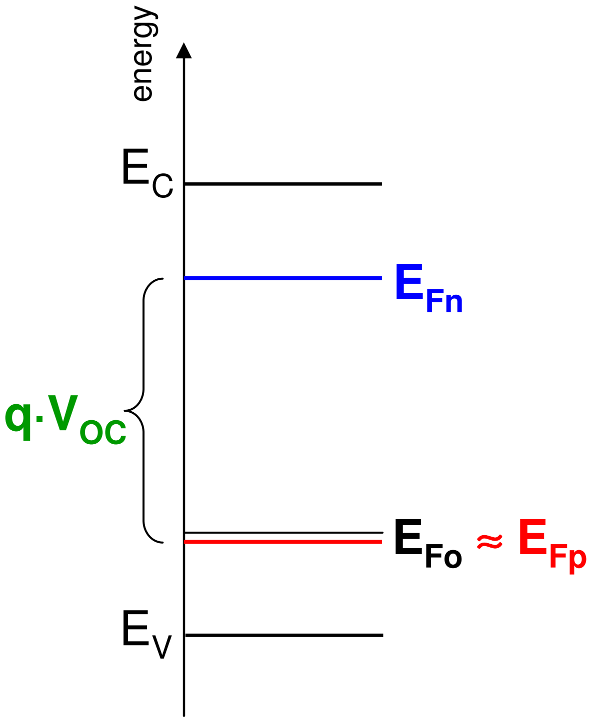
$$V_{OC} = \frac{k_B \cdot T}{q} \cdot \ln\left(\frac{n_0 + \Delta n}{n_0} \cdot \frac{p_0 + \Delta p}{p_0}\right)$$

$$V_{OC} = \frac{k_B \cdot T}{q} \cdot \ln\left(\frac{\Delta n}{n_0}\right)$$

example: p-type Si

$$n_0 + \Delta n \approx \Delta n$$

$$p_0 + \Delta p \approx p_0$$



Concentration ratio of photo generated and minority charge carriers determines V_{OC}.

Example: p-Si under illumination

typical doping range of the base: $p_0 = 10^{16}$ cm^{-3}

$n_0 = 10^4$ cm^{-3}

typical concentration of photo generated charge carriers

$\Delta n = \Delta p = 10^{15}$ cm^{-3}

$$E_{F0} = E_V + 0.179\,eV$$

$$E_{Fn} = E_C - 0.26\,eV = E_g + E_V - 0.26\,eV = E_V + 0.857\,eV$$

$$E_{Fp} = E_V + 0.177\,eV$$

$$E_{F0} - E_{Fp} = 0.002\,eV$$

$$E_{Fn} - E_{F0} = 0.680\,eV$$

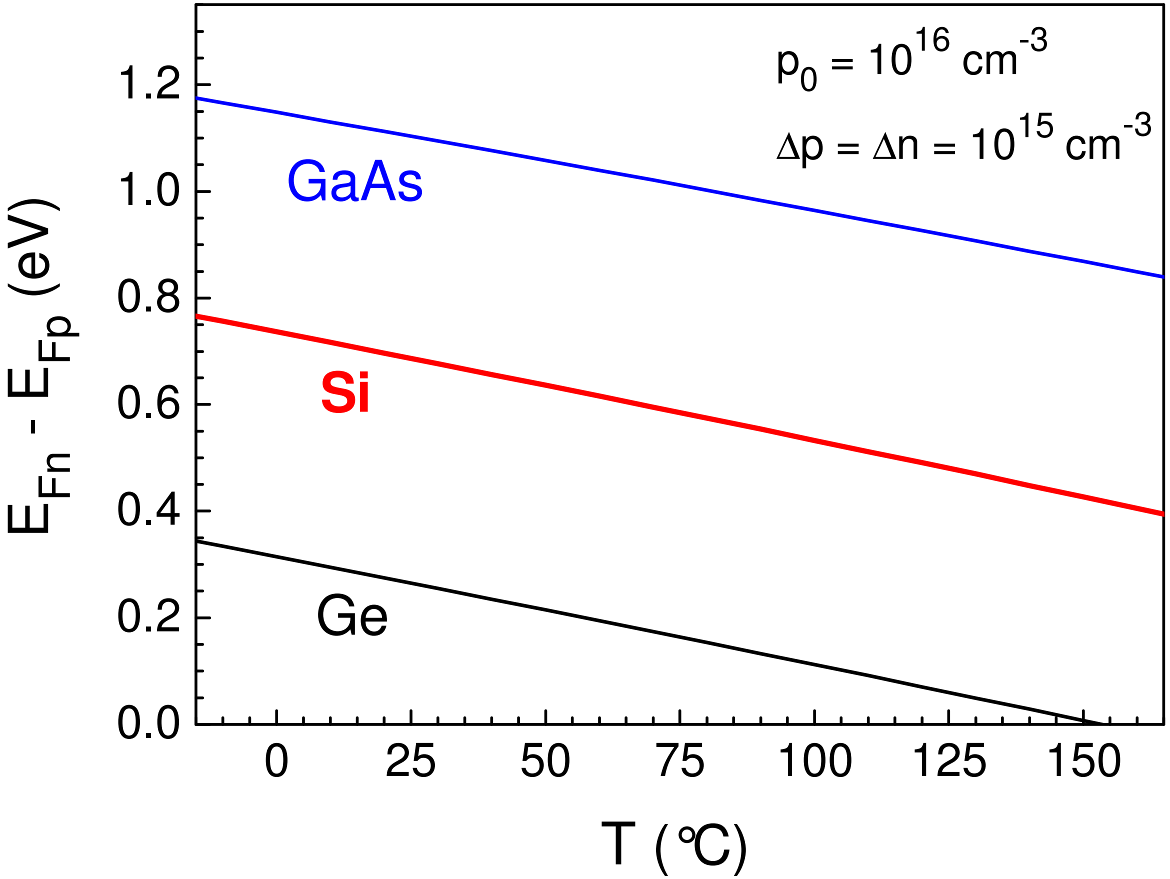
$$E_{Fn} - E_{Fp} = 0.678\,eV$$

$$E_{F0} - E_{Fp} << E_{Fn} - E_{F0}$$

Temperature dependent separation of quasi Fermi-levels

$$n_i^{\,2} = N_V \cdot N_C \cdot \exp\left(-\frac{E_g}{kT}\right)$$

$$E_{Fn} - E_{Fp} = kT \cdot \ln\left(\frac{(n_0 + \Delta n)\cdot(p_0 + \Delta p)}{n_i^{\,2}}\right)$$



Strong temperature dependence of n_i is the reason for the decrease of V_{OC} with increasing temperature.