Lecture 7 – 30/10/2024

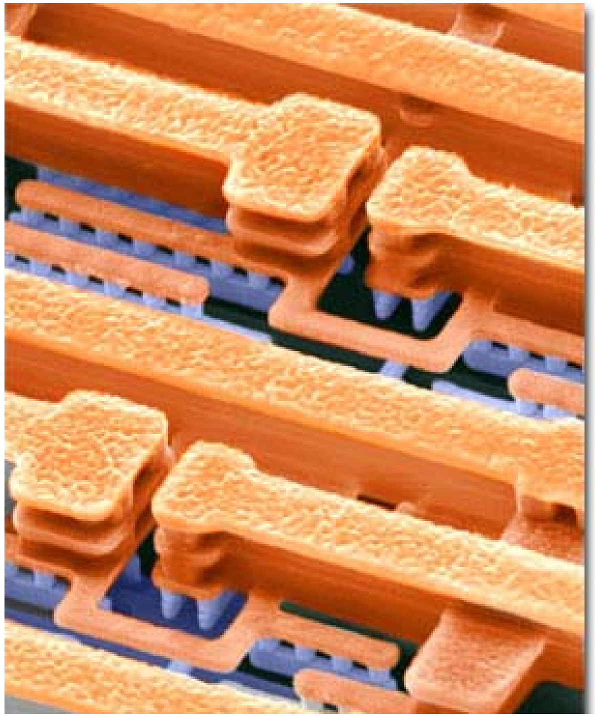
Rather technical but also full of physics!
$\Rightarrow$ Essential to gain a proper microscopic understanding of semiconductors

Carrier transport

- Mobility at low and high electric field

Out of equilibrium semiconductors

- Continuity equations
- Band-to-band recombinations
- Single-level recombinations



Summary Lecture 6

Fermi level calculation

Remember…

$$n = N_c e^{(E_F - E_c)/k_B T}$$

$$p = N_v e^{(E_v - E_F)/k_B T}$$

$$\boxed{E_F = E_c - k_B T \ln\frac{N_c}{n} = E_v + k_B T \ln\frac{N_v}{p}}$$

Non-degenerate semiconductor

n (*or* p) << N_c (*or* N_v) $\Rightarrow$ E_F lies in the bandgap

n (*or* p) > N_c (*or* N_v) $\Rightarrow$ the Fermi level lies within the CB (or VB)

Degenerate semiconductor = Highly doped (Boltzmann approx. not valid anymore)

Non-degenerate semiconductors

$$\boxed{np = N_c N_v e^{-\frac{E_c - E_v}{k_B T}}}$$

Mass action law

$$n = p = n_i = \sqrt{N_c N_v e^{-\frac{E_g}{2k_B T}}}$$

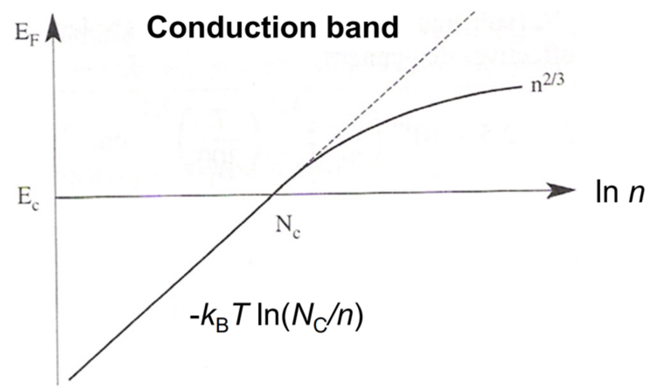
$$E_F = \left(\frac{E_v + E_c}{2}\right) + \frac{k_B T}{2}\ln\left(\frac{N_v}{N_c}\right)$$

Degenerate semiconductors $np \neq n_i^2$

Boltzmann approx. no longer valid, Fermi-Dirac distr. ≈ step function

$$n = \frac{1}{3\pi^2}\left(\frac{2m^*}{\hbar^2}\right)^{3/2}(E_F - E_c)^{3/2}$$

Indep. of *T* !



Summary Lecture 6

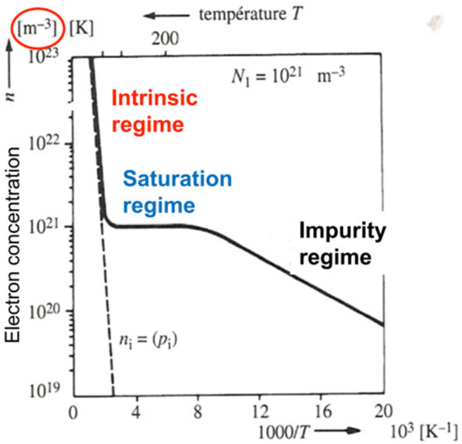
Occupancy of donor/acceptor levels

$$N_D = N_D^0 + N_D^+$$

$$N_D^+ = N_D \frac{1}{1 + 2e^{(E_F - E_c + E_D)/k_B T}}$$

$$\boxed{n + N_A^- = p + N_D^+}$$ Charge neutrality condition

Occupancy of donor/acceptor levels (Illustration with donors)



Low T: Charge neutrality with p = 0 $\Rightarrow$ $n = N_D^+$

Intermediate T: Fully ionized donors but no transition from VB to CB (p = 0) $\Rightarrow$ $n = N_D$ Indep. of T !

In practice, the minority carrier concentration is ≠ 0 so that (sl. 16 Lect. 6) $\Rightarrow$ $n = N_D + p$

High T: High thermal energy so intrinsic behavior dominates $\Rightarrow$ $n_i >> N_D$, $n = p = n_i$

Carrier transport: impact of an electric field

$$F = qE = m^* \frac{dv_i(t)}{dt}$$

$$< v > = v_d = \mu E$$

$$\boxed{\mu = \frac{q\tau_c}{m^*}}$$ Mobility

Carrier transport

Carrier mobility at low electric field

Coulomb interaction most effective when v_{th} is low, hence explaining why it dominates @ low T(K)

Hyperbolic trajectories (straight line far away from ionized impurities)

Interaction probability $\propto N_{D,A}$

$$\tau_c = \frac{1}{\left[v \cdot \left(N_{D,A}\right)^{1/3}\right]}$$

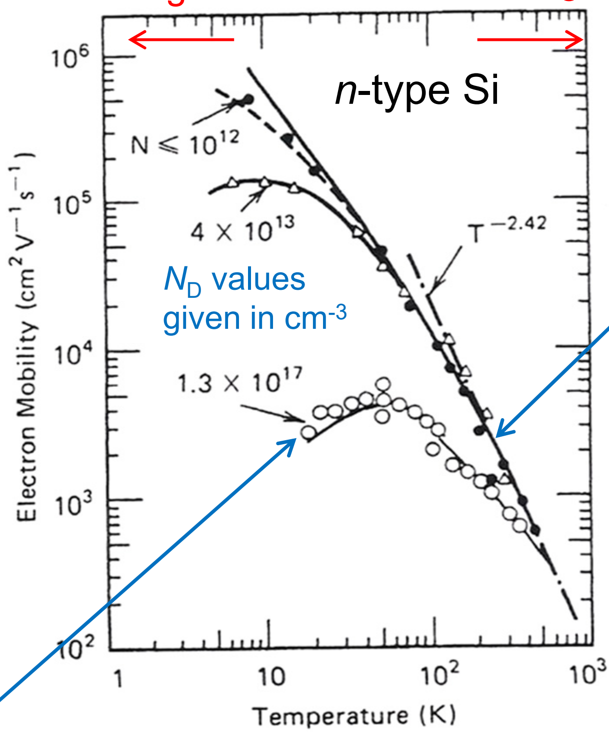
$$\mu_{N_{D,A}} \propto m_{eff}^{-1/2} N_{D,A}^{-1} T^{3/2}$$

Ionized impurities (Coulomb interaction) = *f*(v_{th}, $N_{D,A}$)

Mobility vs doping

Extrinsic regime

Intrinsic regime



Scattering due to interactions with the lattice (mainly LA and LO phonons, interband scattering, …)

$$\mu_{LA} = cst \cdot m_{eff}^{-5/2} T^{-3/2}$$

Dominating term in purely covalent crystals (Si, Ge,…)

$$\mu_{LO} = cst \cdot T^{-2}$$

$$\boxed{1/\mu_{tot} = 1/\mu_{latt} + 1/\mu_{ions} + \dots \quad \text{Matthiessen rule}}$$

Mobility at high electric field

"Hot" electrons

Overview

At low electric field, the electrons can be considered as being in **thermal equilibrium with the lattice.** Then, the electron velocity is proportional to the electric field

$v_d = \mu E$ (microscopic equivalent of Ohm's law)

At high electric field, the velocity due to the field is no longer negligible compared to the thermal velocity. One can then introduce an **effective temperature** such that

$$1/2\, m^* v_e^2 = 3/2\, k_B T_e$$

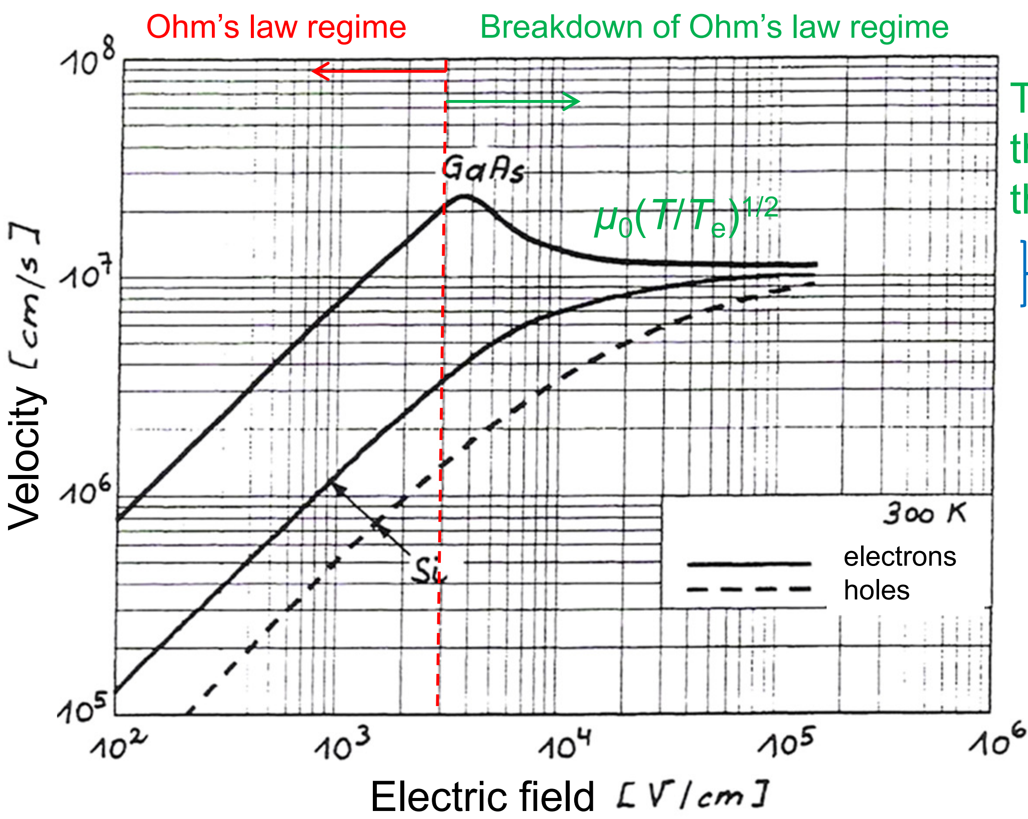
with $T_e > T$. Considering as a first approximation that the mean free path does not change then the mobility writes

$$\mu = q\tau_e/m^* = (q/m^*)(\lambda_e/v_e) = (q/m^*)\,(\tau_c/\tau_c)\,(\lambda_e/v_e) = \mu_0\,(v/\lambda)\,(\lambda_e/v_e) = \mu_0 (T/T_e)^{1/2}$$

This term is accounting for the breakdown of Ohm's law (T_e increases together with E as can be inferred from slide 8)

where μ_0 is the mobility at low field and T is the lattice temperature

Saturation velocity



The larger the electric field E, the larger T_e until reaching the saturation velocity

Saturation velocity

Saturation velocity

In the saturation regime, the energy increase stored by the electron and due to the high electric field is released by emitting an optical phonon of energy E_{ph}

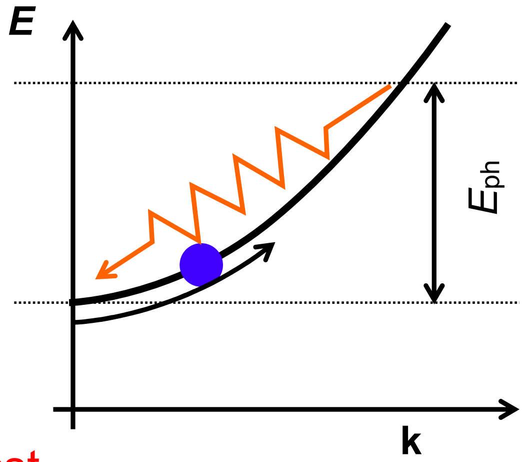
$$qE_{sat} \times v_{sat}\tau_{op} = E_{ph}$$ **Work**

Electric field at saturation

On the other hand $v_{sat} = \mu_{sat}E_{sat} = (q\tau_{op}/m^*)E_{sat}$

Carrier mobility at saturation

Finally $\boxed{v_{sat} = (E_{ph}/m^*)^{1/2}}$



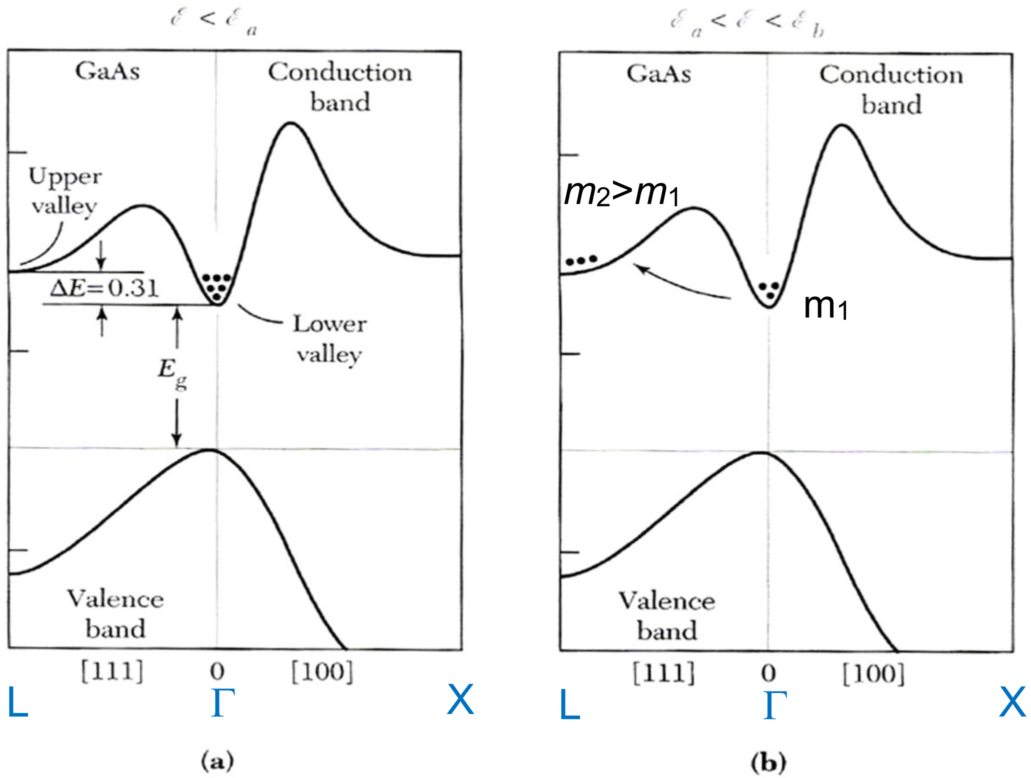
$$\hbar \frac{d}{dt}\mathbf{k} = \mathbf{F}_{ext}$$

Treatment valid because $\lambda \approx \tau_c \cdot v_{th} \approx \tau_{op} \cdot v_{sat}$ Mean free path $\equiv$ cst

Side note: The energy relaxation process of hot electrons at saturation is ensured by the emission of an optical phonon, mostly LO ones, since the emission rate of such phonons is very high. The corresponding electron-phonon matrix element (due to Frölich interaction) leads to a relaxation time due to scattering by LO phonons that is less than 1ps, a value which is significantly shorter than the radiative lifetime of photons of the same energy (on the order of 1 μs as will be computed in Lecture 14).

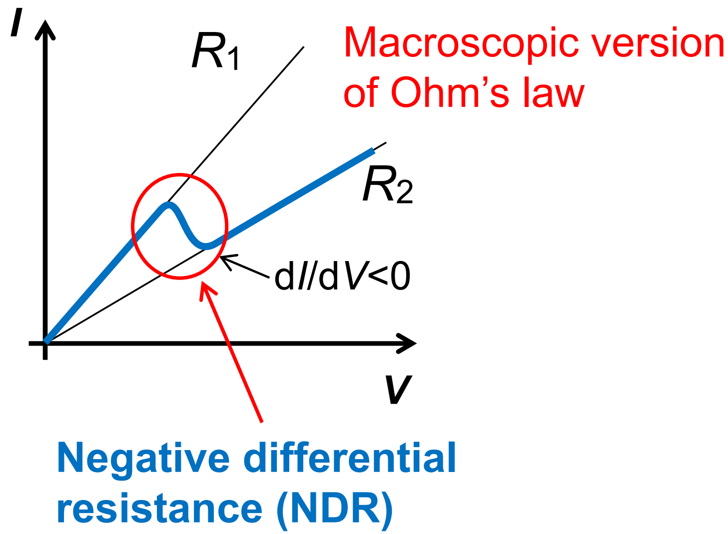
Saturation velocity	Si	GaAs
Experiments	1×10^7 cm s^{-1}	1.2×10^7 cm s^{-1}
Calculations	2×10^7 cm s^{-1}	3×10^7 cm s^{-1}

Transfer toward upper minima in the CB (case of GaAs)



$m_2 > m_1 \Rightarrow \mu_2 < \mu_1$

$\Rightarrow R_2 > R_1$



Effect at play in Gunn diodes to generate microwaves (1963)

Out of equilibrium semiconductors

Continuity equations

We go **beyond thermal equilibrium** for which $np = n_i^2$ (mass action law) by considering the **impact of excess carriers** injected by electrical or optical means.

$$\boxed{\frac{\partial n}{\partial t} = G - R + \left(\frac{1}{q}\right)\nabla \cdot \mathbf{J}_\mathbf{n}}$$

Continuity equation for electrons

where $n(\mathbf{r},t)$ is the electron density in the differential volume element dV, G and R are the electron generation and recombination rates, respectively, and the divergence of $\mathbf{J}_\mathbf{n}/q$ is the difference between the inward and outward flux of electrons in the volume dV.

Sum of the drift and diffusion currents

$\propto \mathbf{E}$ Fick's law

$$\boxed{\frac{\partial p}{\partial t} = G - R - \left(\frac{1}{q}\right)\nabla \cdot \mathbf{J}_\mathbf{p}}$$

Continuity equation for holes

The generation rate G can be both of thermal (G_{th}) and light-induced origin (G_L). Electrons and holes being created simultaneously, their generation rates are identical.

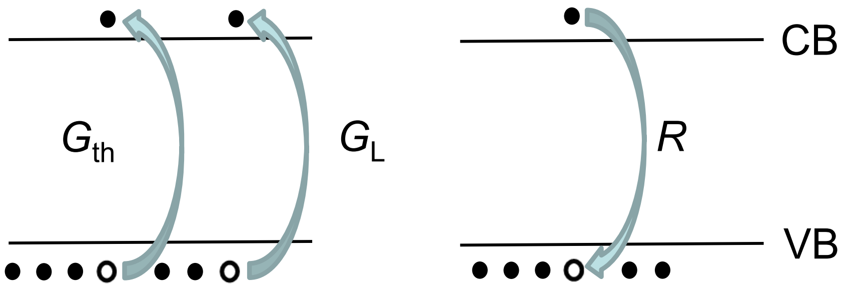
Continuity equations

In the dark and under thermal equilibrium, we verify: $G_{th} = R$

The recombination rate depends on $n(\mathbf{r},t)$ and $p(\mathbf{r},t)$. Hence, for a direct band-to-band recombination process we get:

$\boxed{R = Bnp}$ (mass action law)

where the bimolecular recombination coefficient B is semiconductor-dependent



Whenever possible, we will use the subscript "0" to define thermal equilibrium. Therefore, we get:

$G_{th} = Bn_0p_0$

Continuity equations

Out of equilibrium, we have $R - G_{th} = B(np\text{-}n_0p_0)$

In a p-type semiconductor for small deviations from thermal equilibrium such that $p \approx p_0$, we obtain

$$R - G_{th} \approx Bp_0(n\text{-}n_0)=(n\text{-}n_0)/\tau_n$$

where $\boxed{\tau_n = 1/(Bp_0)}$ is the **lifetime of electrons**.

Similarly, for an n-type semiconductor, we obtain

$$R - G_{th} \approx Bn_0(p\text{-}p_0)=(p\text{-}p_0)/\tau_p$$

where $\boxed{\tau_p = 1/(Bn_0)}$ is the **lifetime of holes**.

The expressions given for τ_n and τ_p are valid for direct band-to-band recombinations. For indirect recombinations through single levels, more complex expressions are at play. However, under weak injection, the general shape for $R - G_{th}$ remains valid so that continuity equations can be used whatever the recombination mechanism that is involved.

Theoretical framework when describing the *p-n* junction

Continuity equations

Under weak injection, we have

For a *p*-type semiconductor,

$$\boxed{\frac{\partial n}{\partial t} = \left(\frac{1}{q}\right)\nabla\cdot\mathbf{J_n} - \frac{(n-n_0)}{\tau_n} + G_\mathrm{L}, \quad \text{and} \quad \frac{\partial p}{\partial t} = \frac{\partial n}{\partial t}}$$

For an *n*-type semiconductor,

$$\boxed{\frac{\partial p}{\partial t} = -\left(\frac{1}{q}\right)\nabla\cdot\mathbf{J_p} - \frac{(p-p_0)}{\tau_p} + G_\mathrm{L}, \quad \text{and} \quad \frac{\partial n}{\partial t} = \frac{\partial p}{\partial t}}$$

Let us note that this is the **minority carrier concentration** that **determines** the **variation of global concentrations over time**, which is expected for processes governed by a mass action law.

Band-to-band recombinations

Band-to-band recombination processes dominate in direct band gap semiconductors for weak to moderate doping or injection levels ($\leq 10^{18}$ cm^{-3}).

Example: Case of a p-type semiconductor ($p_0 >> n_0$) under weak injection ($\Delta p = \Delta n << p_0$). At thermal equilibrium, we have:

$R_{eq} = G_{th} = Bn_0 p_0$

For a system driven out of equilibrium, R will increase vs its R_{eq} value whereas to 1st order G_{th} will remain constant (G_{th} is determined by the energy distribution of free carriers, which does not depend on injection if it remains weak):

$$\boxed{R - G_{th} = B(n_0 + \Delta n)\cdot(p_0 + \Delta p) - Bn_0 p_0 \approx Bp_0 \cdot \Delta n \approx \frac{\Delta n}{\tau_n}.}$$

The proportionality constant between (R-G_{th}) and Δn is taken equal to $1/\tau_n$, i.e., as before we have:

$$\tau_n = \frac{1}{Bp_0} \text{ for electrons in a } p\text{-type semiconductor}$$

and similarly,

$$\tau_p = \frac{1}{Bn_0} \text{ for holes in an } n\text{-type semiconductor}$$

For radiative recombinations, *B* can be computed exactly

⇒ *To be seen at the very end of this semester (Lecture 14)!*

Band-to-band recombinations

For high free carrier concentrations (> 10^{18} cm^{-3}), a novel band-to-band recombination process appears: the **Auger process** (also called the Auger-Meitner process).

Specificities of the Auger-Meitner process:

- Three-body process
- Non-radiative recombination process
- Interband energy given to the 3rd particle through an exchange of kinetic energy
- Probability of the process $\propto n^2p$ *or* p^2n

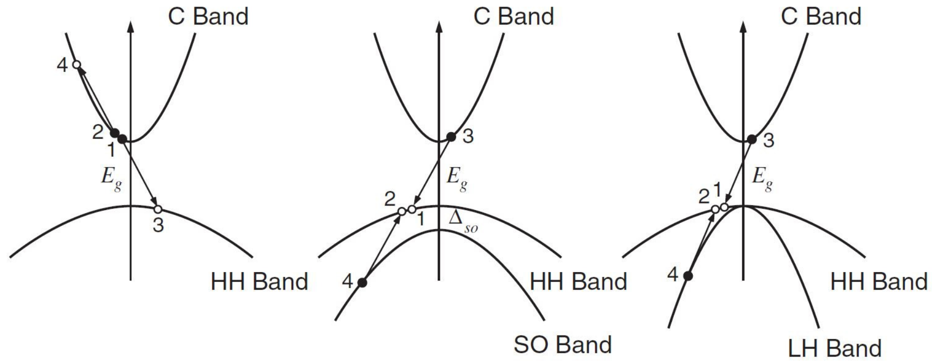
$$\tau_{n,\text{Auger}} \approx \frac{1}{\left[C\cdot\left(p_0+\Delta n\right)^2\right]},\ \text{high injection } n \approx \Delta n$$

$$\tau_{p,\text{Auger}} \approx \frac{1}{\left[C\cdot\left(n_0+\Delta p\right)^2\right]},\ \text{high injection } p \approx \Delta p$$

Auger coefficient

Not to be confused with the conduction band minimum!

- Coefficient C strongly temperature-dependent, ↑ with a dependence $\exp[-E_C/k_BT]$ where $E_C \propto E_g$



Single-level recombinations

Single-level recombination processes dominate in indirect band gap semiconductors (e.g., in Si or Ge) owing to the very long (interband) radiative lifetime

Definition of emission and capture rates

For the sake of simplicity, we consider a single intermediate level, which can trap electrons.

Level characteristics:

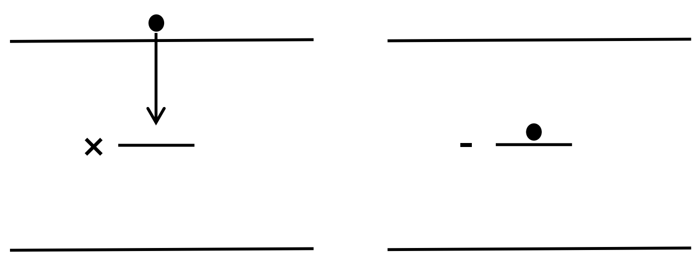
- Two charge states: neutral state (empty acceptor) N_t^x and negative state (acceptor with a trapped electron) N_t^-
- 4 types of transition can be at play

a. Capture of an electron of the conduction band

Capture rate (mass action law)

Electron capture coefficient

$$\boxed{r_{c,n} = \beta_n n N_t^x = v_{th}\sigma_n n N_t^x}$$



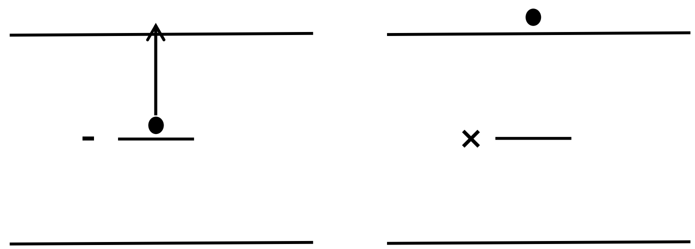
$\beta_n = v_{th}\sigma_n$ where σ_n is the **electron capture cross section** (at least on the order of 10^{-16} cm^2, which is the cross section of an atom)

Single-level recombinations

b. Emission of an electron toward the conduction band

Emission rate

$$\boxed{r_{e,n} = e_n N_t^-}$$

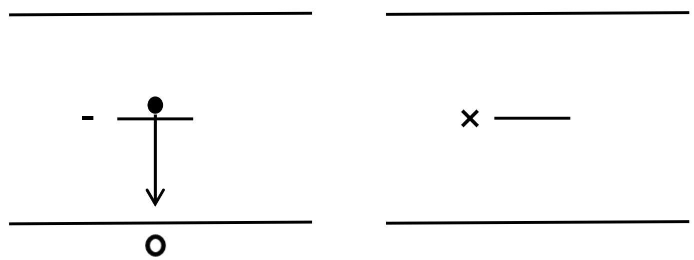


The emission rate is $\propto N_t^-$ and e_n is the **emission probability**

c. Capture of a hole from the valence band (≡ emission of an electron toward the valence band)

Capture rate

$$\boxed{r_{c,p} = \beta_p p N_t^- = v_{th} \sigma_p p N_t^-}$$



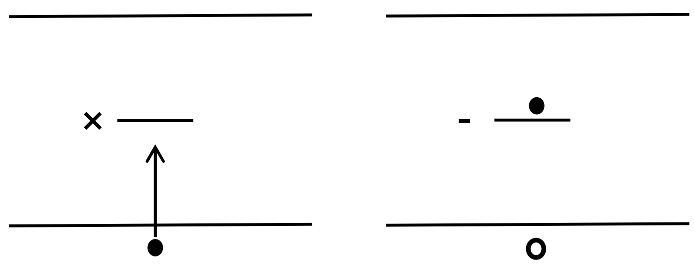
σ_p is the **hole capture cross section**

Single-level recombinations

d. Emission of a hole toward the valence band (≡ capture of an electron of the valence band by the intermediate level)

Emission rate

$$\boxed{r_{e,p} = e_p N_t^x}$$



The emission rate is $\propto N_t^x$, which depicts centers that can emit a hole (≡ capture of an electron)

Determination of emission probabilities

At thermal equilibrium, we have an equality between emission and capture processes

$r_{c,n} = r_{e,n}$ and $r_{c,p} = r_{e,p}$

$v_{th}\sigma_n n N_t^x = e_n N_t^-$ and $v_{th}\sigma_p p N_t^- = e_p N_t^x$

with $N_t^- = N_t f$ and $N_t^x = N_t(1-f)$ where N_t is the total concentration of acceptor levels and f is Fermi-Dirac distribution

Within Boltzmann approximation for which, $n = n_i \exp\left[\left(E_F - E_{F_i}\right)/k_B T\right]$ and $p = n_i \exp\left[\left(E_{F_i} - E_F\right)/k_B T\right]$,we can show that:

Intrinsic Fermi level

$$\boxed{\begin{aligned} e_n &= v_{th}\sigma_n n_i \exp\left[\left(E_t - E_{F_i}\right)/k_B T\right] = v_{th}\sigma_n n_t \\ e_p &= v_{th}\sigma_p n_i \exp\left[\left(E_{F_i} - E_t\right)/k_B T\right] = v_{th}\sigma_p p_t \end{aligned}}$$

where n_t and p_t are the electron and hole concentrations if $E_F = E_t$

Single-level recombinations

Determination of the recombination rate under injection

Under injection, we assume that injection probabilities remain constant. Let us consider G_L the electron-hole pairs generated per cm^3 per second under illumination. The time-dependence of n and p is given by:

$$\frac{dn}{dt} = G_L + r_{e,n} - r_{c,n}$$

$$\frac{dp}{dt} = G_L + r_{e,p} - r_{c,p}$$

Uniform excitation

No drift and diffusion current

Here, we neglect the band-to-band recombination terms vs emission and capture rates through traps. The net recombination rates through the traps (capture - emission) are then given by:

$$R_n = r_{c,n} - r_{e,n} = v_{th}\sigma_n\left(nN_t^x - n_t N_t^-\right)$$

$$R_p = r_{c,p} - r_{e,p} = v_{th}\sigma_p\left(pN_t^- - p_t N_t^x\right)$$

$\neq$ thermal equilibrium

In the steady-state, we fulfill $R_n = R_p$. Note however that n, p, N_t^- and N_t^x will all depend on the injection level and as such they cannot be expressed anymore as a function of E_F. However, for the sake of simplification we will express N_t^- and N_t^x as a function of n and p.

Single-level recombinations

Using:

$$N_\mathrm{t}^x + N_\mathrm{t}^- = N_\mathrm{t}$$

and

$$\sigma_n\left(nN_\mathrm{t}^x - n_\mathrm{t}N_\mathrm{t}^-\right) = \sigma_p\left(pN_\mathrm{t}^- - n_\mathrm{t}N_\mathrm{t}^x\right)$$ because R_n = R_p (= R) To be shown in the exercises!

we obtain:

$$\boxed{R = \sigma_n\sigma_p v_\mathrm{th} N_\mathrm{t} \frac{np - n_\mathrm{t}p_\mathrm{t}}{\sigma_n\left(n + n_\mathrm{t}\right) + \sigma_p\left(p + p_\mathrm{t}\right)}}$$

The **recombination rate** is **proportional to** the **product of capture cross sections** and the **total number of traps N_t**. The **maximum value of R** will be reached by **levels located close to the mid gap** (very small n_t and p_t values vs n and p).

The theory describing recombinations occurring through single-levels located in the band gap is due to Shockley, Read and Hall and is often called SRH mechanism.

W. Shockley and W. T. Read, Phys. Rev. **87**, 835 (1952); R. N. Hall, Phys. Rev. **87**, 387 (1952)

> 5300 citations > 2200 citations

Single-level recombinations

Two specific cases

- p-type semiconductor, weak injection: $p = p_0 + \Delta p \approx p_0$, $n = n_0 + \Delta n \approx \Delta n$

$$\boxed{R = \sigma_n v_{\text{th}} N_{\text{t}} \Delta n = \frac{\Delta n}{\tau_n} \text{ with } \tau_n = \frac{1}{\sigma_n v_{\text{th}} N_{\text{t}}}}$$

The lifetime of electrons will only depend on N_t and their capture cross section

- n-type semiconductor, weak injection: $n = n_0 + \Delta n \approx n_0$, $p = p_0 + \Delta p \approx \Delta p$

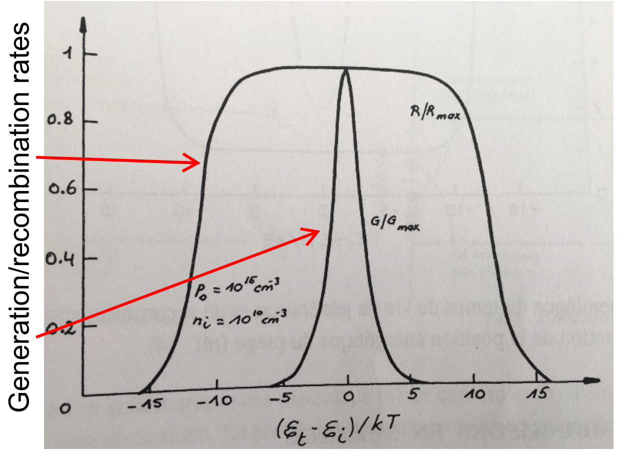
$$\boxed{R = \sigma_p v_{\text{th}} N_{\text{t}} \Delta p = \frac{\Delta p}{\tau_p} \text{ with } \tau_p = \frac{1}{\sigma_p v_{\text{th}} N_{\text{t}}}}$$

Based on the relationship $n_t p_t = n_i^2$ and the main result of previous slide, we get:

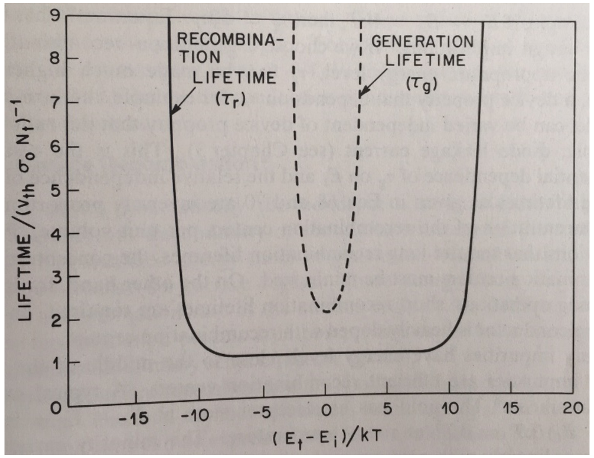
$$\boxed{R = \frac{np - n_{\text{i}}^2}{(n + n_{\text{t}})\tau_p + (p + p_{\text{t}})\tau_n}}$$

The net recombination rate *R* goes through a maximum close to the middle of the band gap

Single-level recombinations



Variation of the *net recombination rate* and the *net generation rate* normalized to their maximum value obtained when $E_t = E_{Fi}$. The net generation rate increases rapidly when E_t gets close to E_{Fi} unlike the net recombination rate that remains constant over a broad energy range.



Recombination lifetime and generation lifetime versus energy level of the recombination center/trap.

⇒ Determination of R and G and τ_r and τ_g to be done in the exercises!