ECE 536 – Integrated Optics and Optoelectronics Lecture 3 – January 25, 2022

Spring 2022

Tu-Th 11:00am-12:20pm Prof. Umberto Ravaioli ECE Department, University of Illinois

Lecture 3 Outline

- Some more pointers on what to review in semiconductor electronics
- Generation and Recombination
 - Band-to-band (radiative)
 - Shockley-Read-Hall (non-radiative)
 - Auger (non-radiative)

Density of states

Consider a system using the parabolic band model with spherical symmetry: The number of states below an energy E is formed by an eighth sphere in k-space:

$$N(E) = \frac{2}{\pi^{3}} \int_{V} d^{3}k = \frac{2}{\pi^{3}} \left(\frac{1}{8} \cdot \frac{4}{3} \pi k^{3} \right) = \frac{1}{3\pi^{2}} k^{3}$$
Using $E = E_{C} + \frac{\hbar^{2} k^{2}}{2m_{e}^{*}} \implies k = \left(\frac{2m_{e}^{*}}{\hbar^{2}} \right)^{1/2} \left(E - E_{C} \right)^{1/2}$

$$N(E) = \frac{1}{3\pi^{2}} \left(\frac{2m_{e}^{*}}{\hbar^{2}} \right)^{3/2} \left(E - E_{C} \right)^{3/2}$$

$$N(E) = \frac{1}{3\pi^{2}} \left(\frac{2m_{e}^{*}}{\hbar^{2}} \right)^{3/2} \left(E - E_{C} \right)^{3/2}$$

$$(- *)^{3/2}$$

$$\rho_e(E) = \frac{dN(E)}{dE} = \frac{3}{2} \cdot \frac{1}{3\pi^2} \left(\frac{2m_e^*}{\hbar^2}\right)^{3/2} \left(E - E_C\right)^{1/2} = \frac{1}{2\pi^2} \left(\frac{2m_e^*}{\hbar^2}\right)^{3/2} \left(E - E_C\right)^{1/2} \text{ for } E > E_C$$

Similarly for holes:

$$\rho_h(E) = \frac{dN(E)}{dE} = \frac{1}{2\pi^2} \left(\frac{2m_h^*}{\hbar^2}\right)^{3/2} \left(E_V - E\right)^{1/2} \text{ for } E < E_V$$

Density of states

From the previous slides:

$$n = \int_{-\infty}^{\infty} f_n(E)\rho_e(E)dE = \int_{-\infty}^{\infty} \frac{1}{1 + e^{(E-F_n)/k_B T}} \frac{1}{2\pi^2} \left(\frac{2m_e^*}{\hbar^2}\right)^{3/2} \left(F_n - E_C\right)^{1/2} dE$$
$$p = \int_{-\infty}^{\infty} f_p(E)\rho_h(E)dE = \int_{-\infty}^{\infty} \frac{1}{1 + e^{(F_p - E)/k_B T}} \frac{1}{2\pi^2} \left(\frac{2m_h^*}{\hbar^2}\right)^{3/2} \left(E_V - F_p\right)^{1/2} dE$$

Using the Fermi-Dirac integral:

$$F_{j}(\eta) = \frac{1}{\Gamma(j+1)} \int_{0}^{\infty} \frac{x^{j} dx}{1+e^{(x-\eta)}}$$

$$n = N_{C} F_{1/2} \left(\frac{F_{n} - E_{C}}{k_{B}T}\right) \text{ where } N_{C} = 2 \left(\frac{m_{e}^{*} k_{B}T}{2\pi\hbar^{2}}\right)^{3/2} = 2.51 \times 10^{19} \left(\frac{m_{e}^{*}}{m_{o}} \frac{T}{300}\right)^{3/2} cm^{-3}$$

$$p = N_{V} F_{1/2} \left(\frac{E_{V} - F_{p}}{k_{B}T}\right) \text{ where } N_{V} = 2 \left(\frac{m_{h}^{*} k_{B}T}{2\pi\hbar^{2}}\right)^{3/2} = 2.51 \times 10^{19} \left(\frac{m_{h}^{*}}{m_{o}} \frac{T}{300}\right)^{3/2} cm^{-3}$$

Approximation of Fermi-Dirac Integral

The Fermi-Dirac integral is defined as:

$$F_j(\eta) = \frac{1}{\Gamma(j+1)} \int_0^\infty \frac{x^j dx}{1 + e^{(x-\eta)}}$$

An approximate analytical form is given by:

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$$F_j(\eta) = \frac{1}{e^{-\eta} + C_j(\eta)}$$

For $j = \frac{1}{2}$, the expression for C giving an error of less than $\frac{5}{0.5\%}$ is: $C_{1/2}(\eta) = \frac{3(\pi/2)^{1/2}}{\left[\eta + 2.13 + (|\eta - 2.13|^{12/5} + 9.6)^{5/12}\right]^{3/2}}$

Approximation of Fermi-Dirac Integral

Another approximation of the Fermi-Dirac integral valid for $|\eta| \gg 1$ and j = 1/2 is:

 $F_{1/2}(\eta) \sim e^{\eta} \qquad \text{for } \eta \ll -1$ $\sim \frac{4}{3} \left(\frac{\eta^3}{\pi}\right)^{1/2} \qquad \text{for } \eta \gg 1$



Approximate Inverse (Nilsson, 1973)

$$\eta = \frac{\ln(u)}{1 - u} + v - \frac{v}{1 + (0.24 + 1.08v)^2}$$
$$u = F_{1/2}(\eta) \qquad v = \left(3\sqrt{\pi} \cdot u / 4\right)^{2/3}$$

Consider a bulk semiconductor in equilibrium

Charge Neutrality: $n_o + N_A^- = p_o + N_D^+$

 N_A^- is the ionized acceptor concentration and N_D^+ is the ionized donor concentration

In the simplified model, $N_D^+ \sim N_D$ but more specifically: $N_A^- = (\text{Density of Acceptors}) \times (\text{Probability State is Filled})$ $= N_A \times \frac{1}{1 + g_A e^{(E_A - E_F)/k_B T}} = \frac{N_A}{1 + g_A e^{(E_A - E_F)/k_B T}}$

 g_A is the ground state degeracy factor for acceptors

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 g_A is the ground state degeracy factor for acceptors

For common semiconductors $g_A = 4$: 2 spin states, 2 degenerate bands (lh, hh) Similarly for donors:

 $N_D^+ = (\text{Density of Donors}) \times (\text{Probability State is Empty})$



 g_D is the donor ground state degeneracy, and $g_D = 2$ (2 spin states)

Using the expressions for N_A^- and N_D^+ with charge neutrality the Fermi Energy can be determined.



W. Shockley, Electrons and Holes in Semiconductors, D. Van Nostrand, Princeton, N.J., 1950.

Assuming a nondegenerate case:

$$n_{o} = n_{i}e^{(E_{F} - E_{i})/k_{B}T} = N_{C}e^{(E_{F} - E_{C})/k_{B}T}$$
$$p_{o} = n_{i}e^{(E_{i} - E_{F})/k_{B}T} = N_{V}e^{(E_{V} - E_{F})/k_{B}T}$$

In equilibrium, by multiplying these expressions it can be seen:

$$n_{o}p_{o} = n_{i}e^{(E_{F}-E_{i})/k_{B}T}n_{i}e^{(E_{i}-E_{F})/k_{B}T} = n_{i}^{2}$$
$$= N_{C}e^{(E_{F}-E_{C})/k_{B}T}N_{V}e^{(E_{V}-E_{F})/k_{B}T} = N_{C}N_{V}e^{-E_{g}/k_{B}T}$$

For n-type material, $N_D^+ - N_A^- \gg n_i$

$$n_o \simeq N_D^+ - N_A^-$$
 and $p_o = n_i^2 / (N_D^+ - N_A^-)$

For p-type material, $N_A^- - N_D^+ \gg n_i$

$$p_o \simeq N_A^- - N_D^+$$
 and $n_o = n_i^2 / (N_A^- - N_D^+)$

The expression for the intrinsic energy can be shown to be:

$$E_{i} = \frac{E_{c} + E_{v}}{2} + \frac{3k_{B}T}{4} \ln\left(\frac{m_{h}^{*}}{m_{e}^{*}}\right)$$

Light Hole Effects

Total hole concentration: $p = p_{hh} + p_{lh}$ $p_{hh} = N_V^{hh} F_{1/2} \left(\frac{E_v - E_F}{k_B T} \right)$ where $N_V^{hh} = 2 \left(\frac{m_{hh}^* k_B T}{2\pi \hbar^2} \right)$

and

$$p_{lh} = N_V^{lh} F_{1/2} \left(\frac{E_v - E_F}{k_B T} \right) \text{ where } N_V^{lh} = 2 \left(\frac{m_{lh}^* k_B T}{2\pi\hbar^2} \right)$$

Generation-Recombination

- The standard description of Generation-Recombination in semiconductors is phenomenological.
- More advanced treatment comes from quantum mechanics in the time-dependent perturbation theory framework, based on the Fermi's golden rule.
- Generation-recombination transitions can be classified as:
 - Radiative (creation or annihilation of photons)
 - Non-radiative (no photons involved; may involve phonons or energy exchange with other particle)

Correction: Errata in Book

- Pg. 41, top of page, between equations 2.3.3 and 2.3.4
- Current Text is: " $0 = Bn_o p_o = e_r$ "
- Should Be: " $0 = Bn_o p_o e_r$ "

The consequence of this is that $Bn_op_o = e_r$ in equilibrium where there is no optical generation or electrical injection of carriers.

Errata

• Equation 3.6.15 should be:

$$a_m^{(0)}(t=0) = 0$$
 not $a_m^{(0)}(t) = 0$

Band-to-Band Recombination



Band-to-Band Generation



$$G_n = G_p = e_r$$

Net Recombination Rate $E_{\rm c}$ $E_{\rm c}$ $E_{\rm v}$ $E_{\rm v}$ net recombination rate $R = R_n - G_n = R_p - G_p = B \cdot np - e_r$

in equilibrium

$$0 = B \cdot n_0 p_0 - e_r$$

$$n_0 p_0 = n_i^2$$

$$B \cdot n_0 p_0 = e_r \longrightarrow R = B(np - n_0 p_0)$$

Deviation from Equilibrium



Deviation from Equilibrium

Low-level injection conditions

$$\delta n, \delta p \ll (n_o + p_o)$$

Electrons and holes generated in pairs

$$\delta n = \delta p$$



Nonradiative G-R Processes

Shockley-Read-Hall G-R

Band-to-band G-R is an "intrinsic" process which already exists when the semiconductor is in pure form. Realistic materials contain impurities/dopants/defects and are therefore "extrinsic".

Energy levels within the gap are efficient recombination centers, particularly in the vicinity of the mid-gap.

Such deep levels, or "traps" promote non radiative processes, so it is important to understand their behavior for photonic applications.



From Langer & Heinrich, 1414-1417

Simple model for trap mediated G-R

$R = \sigma v_{th} N_t \delta n$ $\uparrow \uparrow \uparrow$ excess carrier concentration trap/defect density electron thermal velocity trap capture cross-section

SRH – Electron Capture



 $E_{\rm v}$

probability of occupied trap



SRH – Electron Emission



SRH – Hole Capture



SRH – Hole Emission



Relationship between Emission and Capture Coefficients

In thermal equilibrium there should be no net Generation-Recombination of electrons and holes

$$R_{n} - G_{n} = R_{p} - G_{p} = 0$$

$$c_{n}nN_{t}(1 - f_{t}) - e_{n}N_{t} \cdot f_{t} = c_{p}pN_{t} \cdot f_{t} - e_{p}N_{t} \cdot (1 - f_{t}) = 0$$

$$c_{n}nN_{t} - c_{n}nN_{t}f_{t} - e_{n}N_{t} \cdot f_{t} = -e_{p}N_{t} + c_{p}pN_{t} \cdot f_{t} + e_{p}N_{t}f_{t}$$

$$c_{n}nN_{t} + e_{p}N_{t} = c_{n}nN_{t}f_{t} + e_{n}N_{t} \cdot f_{t} + c_{p}pN_{t} \cdot f_{t} + e_{p}N_{t}f_{t}$$

$$= (c_{n}nN_{t} + e_{n}N_{t} + c_{p}pN_{t} + e_{p}N_{t})f_{t}$$

Relationship between Emission and Capture Coefficients

We determine an expression for f_t

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$$c_{n}nN_{t} + e_{p}N_{t} = (c_{n}nN_{t} + e_{n}N_{t} + c_{p}pN_{t} + e_{p}N_{t})f_{t}$$

$$\int_{t}^{t} = \frac{(c_{n}n + e_{p})N_{t}}{(c_{n}nN_{t} + e_{n}N_{t} + c_{p}pN_{t} + e_{p}N_{t})} = \frac{c_{n}n + e_{p}}{(c_{n}n + e_{n} + c_{p}p + e_{p})}$$

Get the net Generation-Recombination rate

$$f_{t} = \frac{c_{n}n + e_{p}}{(c_{n}n + e_{n} + c_{p}p + e_{p})}$$

$$R_{p} - G_{p} = c_{p}pN_{t} \cdot f_{t} - e_{p}N_{t} \cdot (1 - f_{t}) = \frac{c_{p}pc_{n}n - e_{p}e_{n}}{c_{n}n + e_{n} + c_{p}p + e_{p}}N_{t}$$

$$R_{n} - G_{n} = R_{p} - G_{p} = \frac{np - n_{i}^{2}}{\tau_{p}(n + n_{1}) + \tau_{n}(p + p_{1})}$$
Electron Lifetime: $\tau_{n} = \frac{1}{c_{n}N_{t}}$
Hole Lifetime: $\tau_{p} = \frac{1}{c_{p}N_{t}}$

$$n_{1} = \frac{e_{n}}{c_{n}}$$

$$p_{1} = \frac{e_{p}}{c_{p}}$$

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The auxiliary parameters can be expressed as

$$n_{1} = \frac{e_{n}}{c_{n}}$$

$$n_{1} = N_{C}(T) \exp\left(\frac{E_{T} - E_{C}}{k_{B}T}\right)$$

$$n_{1} = n_{i} \exp\left(\frac{E_{T} - E_{i}}{k_{B}T}\right)$$

$$\tau_n = \frac{1}{\sigma N_t v_{th,n}}$$

$$v_{th} = \sqrt{\frac{3k_BT}{m^*}}$$

$$p_1 = \frac{e_p}{c_p}$$
$$p_1 = N_V(T) \exp\left(\frac{E_V - E_T}{k_B T}\right)$$

$$p_1 = n_i(T) \exp\left(\frac{E_i - E_T}{k_B T}\right)$$



SRH with Low-Level Injection $R_n - G_n = R_p - G_p = \frac{np - n_i^2}{\tau_p (n + n_1) + \tau_n (p + p_1)}$



$$np - n_i^2 = (n_o + \delta n)(p_o + \delta p) - n_i^2$$
$$= n_o p_o + n_o \delta p + p_o \delta n + \delta n \delta p - n_i^2$$

SRH with Low-Level Injection

$$np - n_i^2 = (n_o + \delta n)(p_o + \delta p) - n_i^2$$
$$= n_o p_o + n_o \delta p + p_o \delta n + \delta n \delta p - n_i^2$$

$$R = R_n - G_n = \frac{n_o \delta p + p_o \delta n + \delta p \delta n}{\tau_p (n + n_1) + \tau_n (p + p_1)}$$

$$=\frac{\left(n_{o}+p_{o}\right)\delta n}{\tau_{p}\left(n+n_{1}\right)+\tau_{n}\left(p+p_{1}\right)}=\frac{\delta n}{\tau_{o}}$$

$$\tau_{o} = \frac{\tau_{p} (n + n_{1}) + \tau_{n} (p + p_{1})}{(n_{o} + p_{o})}$$

$$R = \frac{\delta n}{\tau_o}$$

Semiconductor surfaces may be responsible for substantial non-radiative recombination.

Surfaces are interruptions of the periodic crystal so the band structure is modified locally, including electronic states inside the gap.

Because surface atoms lack some neighbors, there are partially filled electron orbitals or **dangling bonds** which may be acceptor or donor like.

Surface reconstruction may also occur with structure different from the bulk. Theoretical prediction is difficult.

Consider a p-type semiconductor illuminated to cause uniform steady-state generation rate G. The continuity equation electrons is 1D is



The current density is caused by electrons flowing to the surface. In the bulk, there is no space dependence so the continuity equation is simply G = R at steady-state. The excess carrier in the bulk is simply $\delta n_{\infty} = G\tau_n$.

Assuming a diffusion current for the electrons

$$J_n = eD_n \frac{\partial}{\partial x} \delta n(x,t)$$

we have the continuity equation

$$\frac{\partial}{\partial t}\delta n(x,t) = G - \frac{\delta n(x,t)}{\tau_n} + D_n \frac{\partial^2}{\partial x^2} \delta n(x,t)$$

At the semiconductor surface, carriers recombine rapidly due to surface states



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At the semiconductor surface, carriers recombine rapidly due to the surface states. The current boundary condition at the surface is

$$eD_n \frac{\partial}{\partial x} \delta n(x,t) \Big|_{x=0} = eS_n \delta n(x,t) \Big|_{x=0}$$

where *S* is the surface recombination velocity. At the semiconductor surface, carriers recombine rapidly due to surface states.

The steady-state solution for the carrier density is

$$n(x) = n_o + \delta n(x) = n_o + \delta n_{\infty} \left[1 - \frac{\tau_n S \exp(-x/L_n)}{L_n + \tau_n S} \right]$$



Surface recombination leads to reduced luminescence efficiency and also to heating of the surface, which are unwanted effects for electroluminescent devices.

Semiconductor	Surface recombination velocity
GaAs	$S = 10^6 \text{ cm/s}$
GaN	$S = 5 \times 10^4 \text{ cm/s}$
InP	$S = 10^3 \text{ cm/s}$
Si	$S = 10^1 \text{ cm/s}$

Auger non-radiative processes

Auger Processes

Auger processes involve three particles.

For instance, in Auger recombination, the energy which becomes available through electron-hole recombination ($\approx E_g$) is dissipated by the excitation of a free electron high into the conduction band, or by a hole deeply excited into the valence band.

The highly excited carriers lose subsequently the energy by multiple phonon emission until reaching the band edge.







Auger – Hole Capture (k-space) С С 1 ' Η 2' Η H L $\stackrel{2}{\sim}$ s S S(d) CHHH process (c) CHLH process (b) CHSH process C = Conduction bandH = Heavy-hole bandL = Light-hole bandS = Spin-orbit split-off band



Auger Processes

During Auger recombination energy and momentum must be conserved. Because of the different band details, the two Auger coefficients are generally different. The highly excited carriers lose subsequently the energy by multiple phonon emission until reaching the band edge.

$$R_n = C_n n^2 p$$

more likely to occur in n-type

$$R_p = C_p n p^2$$

more likely to occur in p-type

In thermal equilibrium Auger G-R processes balance:

$$R_{n} - G_{n} = C_{n} n_{o}^{2} p_{o} - e_{n} n_{o} = 0$$
$$R_{p} - G_{p} = C_{p} n_{o} p_{o}^{2} - e_{p} p_{o} = 0$$

$$e_n = C_n n_o p_o = C_n n_i^2$$
$$e_p = C_p n_o p_o = C_p n_i^2$$

Total net Auger recombination rate

$$R = R_{n} - G_{n} + R_{p} - G_{p} = \left(C_{n}n + C_{p}p\right)\left(np - n_{i}^{2}\right)$$

High-excitation limit

When density of excited carriers is much higher than at equilibrium, the Auger rate equations reduce to

$$R = \left(C_n n + C_p p\right) \left(np - n_i^2\right) \approx \left(C_n + C_p\right) n^3 = Cn^3$$

Typical values of the Auger coefficient C for III-V semiconductors are in the range $10^{-29} - 10^{-28}$ cm⁶/s.

- Auger recombination reduces luminescence efficiency at high excitation intensity or at high carrier injection, due to the cubic dependence on concentration.
- At lower carrier concentrations, Auger recombination rate is low and practically negligible.

The Auger-droop controversy in LED

The mechanism causing nitride LED to lose efficiency at high power (*efficiency droop*) was identified as Auger recombination in 2007 by Lumileds Co. However, this started a controversy since another cause, leakage of carriers out of the quantum well structure, was proposed as the responsible mechanism.

Various experimental ("Direct Measurement of Auger Electrons ...", Phys Rev Lett 110, 177406, 2013) and theoretical ("Ultrafast Hot Carrier Dynamics in GaN and Its Impact on the Efficiency Droop" Nano Letters, 2017, 17, 8, p. 5013) papers have since supported one hypothesis or the other.

IEEE Spectrum has chronicled for years the debate. The initial paper "The LED's Dark Secret" (2009) is still interesting reading.

Radiative vs. non-radiative recombination

Even though non-radiative recombination can be reduced, it cannot be eliminated completely.

Additionally, all real crystals will always have native defects which may introduce deep levels acting as traps.

From thermodynamics considerations, if the energy to generate a defect is E_a , the associate probability is given by the Boltzmann factor $\exp(-E_a/k_BT)$.

Estimate of point defect concentration

Assume a crystal with lattice constant $a_o = 5.6$ Å and eight atoms per cubic cell. If the energy needed to move a lattice atom into interstitial position is 1.0eV, estimate the density of interstitial defects at room temperature.

$$N_{a} = \frac{8}{\left(5.6 \times 10^{-8}\right)^{3}} = 4.5 \times 10^{22} \text{ atoms/cm}^{-3}$$
$$N_{def} = N_{a} \exp\left(-\frac{1.0}{E_{a}} - \frac{0.0256}{k_{B}T}\right) \approx 4.9 \times 10^{-5} \text{ cm}^{-3}$$

Radiative vs. non-radiative recombination

Chemical purity is always an issue. The purest III-V semiconductors will still have impurity concentrations on the order of 10^{12} cm⁻³.

Nonetheless, the internal luminescence efficiency has grown from a fraction of 1% up to 90%+ today, because of improved crystal quality and reduced defect/impurity concentrations.

Internal quantum efficiency of a semiconductor with non-radiative recombination centers

when
$$n \gg (n_o + p_o)$$
:
 $(n \approx \delta n)$

$$R = An + Bn^2 + Cn^3 = \frac{n}{\tau(n)}$$

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intrinsic quantum efficiency



Deep Levels

Deep levels can be caused by *native defects* (vacancies, interstitials), unwanted impurities, dislocations, impurity-defect complexes, and combinations of different defects.

Experimental analysis is often complicated by the fact that deep-levels may also be associated with radiative transitions.

For instance, Ga vacancies are common point defects in GaN, which luminesce with peak in the yellow band.



Stimulated Emission

An incoming photon interacts with an electron causing it to drop to a lower energy level. The energy transfers to the EM field, generating a new photon with phase, frequency, polarization, and direction of travel which are the same as those of the incident photon.

In contrast, spontaneous emission occurs randomly without particular correlation with the ambient EM field.



Stimulated Emission

 $R = v_g g(n) S$

where:

S is the photon density (units cm^{-3})

 v_g is the group velocity (units cm/s):

$$v_g = \frac{c}{n_g}$$

g(n) is the optical gain (units cm⁻¹) n_g is the group index $v_g g(n)$ is the "rate of growth"

Impact Ionization

It is essentially the reverse of an Auger recombination process, but the rate depends upon current densities as opposed to carrier concentrations.

Detailed theoretical analysis is quite difficult because of the need for a full band structure and it has been addressed with Monte Carlo simulation in some materials. Physics of threshold remains fuzzy.

Models are typically semi-empirical with calibration from measurements.





Net Generation-Recombination rate



Empirical form of ionization coefficients. Both measure the number of generated electron-hole pairs per unit distance.

$$\alpha_n(E) = \alpha_n^{\infty} e^{-(E_{nc}/E)^{\gamma}}$$

$$\beta_p(E) = \beta_p^{\infty} e^{-(E_{pc}/E)^{\gamma}}$$

$$E_{nc} \text{ and } E_{pc} \text{ are critical fields}$$

$$1 \le \gamma \le 2$$

Reading Assignments

Continue with Chapter 2 of the book by Chuang.