Radiative and non-radiative recombination

There are two recombination that can occur in a semiconductor:

1. radiative recombination
2. non-radiative recombination

In the light emitting devices the radiative process are preferred. We can never reduce the non-radiative recombination but we can minimize it.

1 Radiative electron-hole recombination

Under the equilibrium then the law of mass action states that the product of electron and hole concentration, under a given temperature, is constant

\[ n_0 p_0 = n_i^2 \]  \hspace{1cm} (1)

\( n_0 \)-equilibrium electron concentration
\( p_0 \)-equilibrium hole concentration
\( n_i \)-intrinsic carrier concentration

Total carrier concentration is given by sum of equilibrium and excess carrier concentration.

\[ n = n_0 + \Delta n \quad \text{and} \quad p = p_0 + \Delta p \]  \hspace{1cm} (2)

The recombination rate is proportional to the product to the electron and hole concentration, that is \( R \propto np \). The recombination rate per unit time per unit volume can then be written

\[ R = \frac{dn}{dt} = \frac{dp}{dt} = Bnp \]  \hspace{1cm} (3)

This is the bimolecular rate equation, and \( B \) is a constant called bimolecular recombination coefficient, where the typical value is \( 10^{-11} \text{ to } 10^{-9} \text{ cm}^3/\text{s} \) for III-V semiconductors.

2 Radiative recombination for low-level exciton

Electrons and holes are generated and anhilated (by recombination) in pairs, the steady state hole and electron excess concentration are equal, i.e. \( \Delta n(t) = \Delta p(t) \), And from equation 3 we will get

\[ R = B[n_0 + \Delta n(t)][p_0 + \Delta p(t)] \]  \hspace{1cm} (4)

For the case of low-level excitation, the photo-generated carrier concentration is much smaller than majority carrier concentration, \( \Delta n << (n_0 + p_0) \), and we also have that \( \Delta n(t) = \Delta p(t) \) we will then get from equation 4

\[ R = Bn_i^2 + B(n_0 + p_0)\Delta n(t) = R_0 + R_{excess} \]  \hspace{1cm} (5)

The time dependent carrier concentration calculated from the rate equation is

\[ \frac{dn(t)}{dt} = G - R = (G_0 + G_{excess}) - (R_0 + R_{excess}) \]  \hspace{1cm} (6)

Semiconductor has been illuminated with the light and excess carriers are generated, \( G_0 = R_0 \)
\[ \frac{d}{dt} \Delta n(t) = -B(n_0 + p_0)\Delta n(t) \]  
(7)

and the solution will be

\[ \Delta n(t) = \Delta n_0 e^{-B(n_0 + p_0)t} \]  
(8)

and after rewriting we get

\[ \Delta n(t) = \Delta n_0 e^{-t/\tau} \]  
(9)

where \( \tau \) is the carrier lifetime \( \tau = [B(n_0 + p_0)]^{-1} \).

In the case for low-level excitation the photo generated carrier concentration is much smaller than the majority carrier concentration. However the photogenerated carrier concentration is much larger than the minority carrier concentration.

3 Radiative recombination for high-level excitation

For high-level excitation, the photogenerated carrier concentration is larger than equilibrium carrier concentration, i.e. \( \Delta n \gg (n_0 + p_0) \). Bimolecular rate equation is then given by

\[ \frac{d}{dt} \Delta n(t) = -B\Delta n^2 \]  
(10)

and then we get

\[ \Delta n(t) = \frac{1}{Bt + \Delta n_0^{-1}} \]  
(11)

The time constant here will be

\[ \tau(t) = t + \frac{1}{B\Delta n_0} \]  
(12)

Minority carrier lifetime increases with time. For sufficiently long times, low-level excitation conditions will be reached and \( \tau \) will approach the low-level value.

4 Non-radiative recombination in the bulk

During the non-radiative recombination, the electron energy is converted to vibrational energy of lattice atoms, i.e. phonons. Thus the electron energy is converted to heat.

Most common cause for non-radiative recombination events are defects in the crystal structure. This effects include unwanted foreign atoms, native defects, dislocations. All such defects have energy level structure that are different from substantial semiconductor atoms. And it’s quite common for such defects to form one or several energy levels within the forbidden gap of the semiconductor.

Energy levels within the gap of the semiconductors are efficient recombination centers, in particular if the energy level is close to the middle of the gap.

Trap-assisted recombination occurs when an electron falls into a "trap", this is an energy level within the bandgap caused by the presence of a foreign atom or a structural defect. Once the trap is filled it cannot accept another electron. The electron occupying the trap, in a second step, falls into an empty valence band state, thereby completing the recombination process.

The non-radiative recombination rate through a deep level with trap energy \( E_T \) and concentration \( N_T \)

\[ R_{SR} = \frac{p_0 \Delta n + n_0 \Delta p + \Delta n \Delta p}{(N_T v_p \sigma_p)^{-1}(n_0 + n_1 + \Delta n) + (N_T v_n \sigma_n)^{-1}(p_0 + p_1 + \Delta p)} \]  
(13)
\( \Delta n = \Delta p \)

- \( v_n \) and \( v_p \) - electron and hole velocities
- \( \sigma_n \) and \( \sigma_p \) - capture cross section of the traps
- \( n_1 \) and \( p_1 \) - electron and hole concentrations if the Fermi energy is located at the trap levels:

\[
\begin{align*}
n_1 &= n_i \exp \left( \frac{E_T - E_{Fi}}{k_B T} \right) \\
p_1 &= n_i \exp \left( \frac{E_{Fi} - E_T}{k_B T} \right)
\end{align*}
\] (14)

- \( E_{Fi} \) - Fermi level in the intrinsic semiconductors.

Non radiative lifetime of excess electrons can be deduced from \( R_{SR} = \Delta n/\tau \), which will give

\[
\frac{1}{\tau} = \frac{n_0 + n_1 + \Delta n}{(N_T v_p \sigma_p)^{-1}(n_0 + n_1 + \Delta n) + (N_T v_n \sigma_n)^{-1}(p_0 + p_1 + \Delta p)}
\] (15)

If we assume p-type semiconductor, i.e. the holes are in majority \( p_0 >> n_0 \) and \( p_0 >> p_1 \), and we assume small deviation from equilibrium, i.e. \( \Delta n << p_0 \) then minority carrier lifetime is given by

\[
\frac{1}{\tau} = \frac{1}{\tau_{n0}} = N_T v_n \sigma_n
\] (16)

If the electrons were majority carriers, the lifetime would be

\[
\frac{1}{\tau} = \frac{1}{\tau_{p0}} = N_T v_p \sigma_p
\] (17)

Results shows that Shocckley -Read recombination rate is limited by the rate of the capture of minority carriers, since the capture of majority carriers is much more likely event than the capture of minority carriers. From equation 15 we will get

\[
\tau = \tau_{n0} \frac{p_0 + p_1}{p_0 + n_0 + \tau_{p0} \frac{n_0 + n_1 + \Delta n}{p_0 + n_0}} \approx \tau_{n0} \frac{p_0 + p_1}{p_0 + n_0}
\] (18)

For small deviations from equilibrium, i.e \( \Delta n << p_0 \), which will give

\[
\tau = \tau_{n0} \left( 1 + \frac{p_0 + p_1}{p_0 + n_0} \right)
\] (19)

The lifetime does not change for small deviations from equilibrium in an extrinsic semiconductor.

We assume that the trap captures electrons and holes at the same rate, i.e. \( v_n \sigma_n = v_p \sigma_p \) and \( \tau_{n0} = \tau_{p0} \), and we get from equation 19

\[
\tau = \tau_{n0} \left( 1 + \frac{p_0 + p_1}{p_0 + n_0} \right)
\] (20)

For special case of intrinsic material, i.e. \( n_0 = p_0 = n_i \) the equation becomes

\[
\tau_i = \tau_{n0} \left( 1 + \frac{p_1 + n_1}{2n_i} \right) = \tau_{n0} \left[ 1 + \cosh \left( \frac{E_T - E_{Fi}}{k_B T} \right) \right]
\] (21)

- \( E_{Fi} \) - the Fermi level typical close to the middle of gap.

The non-radiative life time is minimized, if \( E_T - E_{Fi} \) is zero, when the traplevel is at or close to the midgap energy. For such midgap levels the lifetime is given by \( \tau = 2\tau_{n0} \). This shows that deep levels are effective recombination centers if they are near in the middle of the gap.

Another non-radiative recombination is Auger recombination, it is given off in the form of kinetic energy to another electron.

The energy that becomes available through electron-hole recombination (\( E_g \)) 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 carrier will subsequently lose energy by multiple phonon emission until they are close to the band edge.

Recombination rate due to the Auger process

\[ R_{\text{Auger}} = C_p n p^2 \]  \hspace{1cm} (22)

and

\[ R_{\text{Auger}} = C_n n^2 p \]  \hspace{1cm} (23)

Auger recombination reduces the luminescence efficiency in semiconductors only at very high excitation intensity or at very high carrier injection currents. At lower carrier concentrations, the Auger recombination rate is very small and can be neglected.

5 Non-radiative recombination at surfaces

Atoms at the surface cannot have the same bonding structure as bulk atoms due to the lack of neighboring atoms. Thus some of the valence orbitals do not form a chemical bond. These partially filled electron orbitals, or dangling bonds, are electronic states that can be located in the forbidden gap of the semiconductor where they act as recombination center.

Surface recombination leads to a reduced luminescence efficiency and also to a heating of the surface due to non-radiative recombination at the surface. Both effects are unwanted in electro luminescent devices.

Surface recombination can occur only when both type of carrier are present. It is important in the design of LEDs that the carrier-injected active region, in which both type of carriers are presented, be far removed from any surface. This can be archived by carrier injection under a contact that is much smaller than the semiconductor die.

6 Competition between radiative and non-radiative recombination

Just as for surface recombination, non-radiative bulk recombination and Auger recombination can never be totally avoided. Any semiconductor crystal will have some native defects.

It is also difficult to fabricate materials with impurity levels lower than the parts per billion range (ppb). Thus even the purest semiconductors contain impurities in the \(10^{12} \text{cm}^{-3}\).

The total probability of recombination is given by the sum of the radiative and non-radiative probabilities

\[ \tau^{-1} = \tau_r^{-1} + \tau_{nr}^{-1} \]  \hspace{1cm} (24)

where \(\tau_r\) and \(\tau_{nr}\) are radiative and non-radiative lifetime.

The relative probability of radiative recombination is given by radiative probability over the total probability of recombination. Thus the probability of radiative recombination or internal quantum efficiency is given by

\[ \eta_{\text{int}} = \frac{\tau_r^{-1}}{\tau_r^{-1} + \tau_{nr}^{-1}} \]  \hspace{1cm} (25)

The internal quantum efficiency gives the ratio of the number of light quanta emitted inside the semiconductor to the number of charge quanta undergoing recombination. Not all photons emitted internally may escape from the semiconductor due to the light escape problem, reabsorption in the substrate, or after reabsorption mechanism.