5.1.2 Recombination and Luminescence

High Injection Approximations for Recombination Rates

Luminescence is the word for *light emission* after some energy was deposited in the material.

- **Photoluminescence** describes light emission stimulated by exposing the material to *light* – by necessity with a higher energy than the energy of the luminescence light. Photoluminescence is also called **fluorescence** if the emission happens less than about **1 μs** after the excitation, and **phosphorescence** if it takes long times – up to hours and days – for the emission.
- **Cathodoluminescence** describes excitation by energy-rich *electrons*, **chemoluminescence** provides the necessary energy by *chemical reactions*.
- Here we are interested in **electroluminescence**, in particular in **injection luminescence.**

Injection luminescence occurs if *surplus* carriers are injected into a semiconductor which then recombine via a *radiative channel*.

- This implies *non-equilibrium*, i.e. $n_e \cdot n_h > n_i^2$ and *net recombination rates U* given by the basic equation from the Shockley-Read-Hall theory for direct semiconductors:

$$U = R - G_{therm} = r \cdot (n_e \cdot n_h - n_i^2) = r \cdot n_i^2 \cdot \left(\exp \frac{E_F{}^e - E_F{}^h}{kT} - 1 \right)$$

- Some, but not necessarily all of the recombination events described by U produce light, and these *radiative recombination channels* are of particular interest for optoelectronics.

Since optoelectronic devices usually are made to produce *plenty* of light, the deviation of the carrier densities from equilibrium must be large to obtain large values of U.

- If we write the densities, as before, as $n_{e,h} = n_{e,h}(equ) + \Delta n_{e,h}$, we now may use *the simplest possible approximation* called **high injection approximation**:

$$\Delta n_{e,h} \gg n_{min}(equ)$$

- i.e. the minority carrier density is far *above* equilibrium.
- That is different from the approximation made before, where we assumed that $\Delta n_{e,h}$ was small.

The surplus carriers contained in $\Delta n_{e,h}$ are always *injected* into the volume under consideration (called **recombination zone** or **recombination volume**), usually by forward currents across a junction. They always must come in equal numbers, i.e. in pairs to maintain charge neutrality; otherwise large electrical fields would be generated that would restore neutrality. We thus have

$$\Delta n_e = \Delta n_h$$

- The recombination volume usually is the space charge region of a junction or an other volume designed to have *low carrier densities* in equilibrium. Since the equilibrium density of both carrier types in the **SCR** is automatically very low, we may easily reach the high injection case. For a bulk piece of a (doped) semiconductor this is much more difficult – you would have to illuminate with extremely high intensity to increase the minority carrier density by some factor.

The surplus density of carriers decays with a characteristic lifetime τ which is given by the individual life times of all recombination channels open to the carriers. Since $R \gg G_{therm}$ for the high injection case, we have in analogy to the approximation made for (small) deviations from equilibrium:

$$U = R - G_{therm} \approx R = \frac{n}{\tau}$$

- We call this approximation (where we neglect G) "**high-injection**" approximation or the *high injection case* because the high density of surplus carriers is usually provided by injecting them over a forwardly biased junction into the region of interest.
- Note that while the rate equations are formally the same for high or low injection (or everything in between), τ is not a constant but may depend on the degree of injection (as we will see).

Now we have to look at all the possibilities for recombination – called **recombination channels** – that are open for carriers as possible ways back to equilibrium. Recombination channels generating light we will call **radiative channels**.

The **band-band recombination channel** (with which we started above, using the full Shockley-Read-Hall equations) can now be extremely simplified:

$$R_{b\text{-}b} = v \cdot \sigma \cdot n^2$$

- or, considering that $v \cdot \sigma$ may no longer be totally correct as the proportionality factor,

$$R_{b\text{-}b} = B_{b\text{-}b} \cdot n^2$$

- and the index "**b-b**" denotes band-band recombination. The proportionality constant **B** is occasionally called a **recombination coefficient**.

If we use the same approximations for the recombination channel via deep levels, we obtain a rather simple relation, too, for the recombination rate R_{dl}

$$R_{dl} = B_{dl} \cdot n$$

- With B_{dl} = recombination coefficient for this case.

Recombination via band-band transitions and via deep levels was all we considered so far. What kind of *other* recombination channels are available, especially for direct semiconductors and the high injection case?

- There are several, some very special and specific and only relevant for certain materials and/or doping. In this subchapter we will look at the most important ones.

Before we do that, however, we will give some thought to the *equilibrium case*.

- In *thermal equilibrium*, we still have generation and recombination described by the equilibrium rates G_{therm} and R_{therm} and $U_{therm} = G_{therm} - R_{therm} = 0$.
- Now a *tough question* comes up: If recombination occurs via band-band recombination and results in the emission of a photon, does this mean that our piece of semiconductor, just lying there, would emit photons and thus *glow in the dark*?
- Obviously that can not be. Energy would be transported out of the semiconductor which means it would become cooler just lying there, a clear violation of the "second law". On the other hand, a single recombination event "does not know" if it belongs to equilibrium or non-equilibrium, so radiation must be produced, even in equilibrium. We seem to have a *paradox*.

The apparent paradox becomes solved as soon as we consider that any piece of a material "glows" in the dark (or in the bright) because it emits and absorbs radiation leading to an equilibrium distribution of radiation intensity versus wave length – the famous "**black body**" **radiation** of **Max Planck**.

- Recombination events in equilibrium do produce light – but the photons mostly will become reabsorbed and, in general, will not leave the material. The small amount that does escape to the environment must be exactly balanced by electromagnetic radiation absorbed from the environment.
- This topic will be considered in more detail in an advanced module.

Additional Recombination Channels

So far we considered only band-band recombination and recombination via deep levels. There are, however, more recombination channels, some of which are particular to compound semiconductors.

But first we look at universal mechanisms occurring in all semiconductors. They are:

- **Auger** recombination. In this case the energy of the recombination event is transferred to another electron in the conduction band, which then looses its surplus energy by "thermalization", i.e. by transferring it to the phonons of the lattice. This means that *no light is produced*.
- Donor–acceptor recombination or recombination via "**shallow levels**". This includes transitions from a donor level to an acceptor level or to the valence band, and transitions form the conduction band to an acceptor level.
- **Mixed forms**: From a donor level via a deep level to the valence band, etc.

Now for *material specific* recombination channels. The most important one with direct technical uses is recombination via "**localized excitons**".

- **Excitons** are something like hydrogen atoms (or, even closer in similarity, positronium = atom consisting of electron and positron) – except that a *hole* and not a proton is the partner of the electron. They are thus electron–hole pairs bound by electrostatic interaction. They can form in any semiconductor, are mobile and do not live very long at room temperature because their binding energy is very small. They decompose ("get ionized") into a free electron and a free hole.
- If you wonder why they do not simply recombine, think about it. They can't possibly have the same wave vector (how would they "circle" each other then?) and thus need a third partner for the recombination process to occur.
- On occasion, however, they might become *trapped* at certain lattice defects and then recombine, *emitting light*. **GaP**, though an indirect semiconductor, can be made to emit light by enforcing this mechanism.
- We will come back to excitons later; more about them can be found in an advanced module.

The picture below illustrates these points.
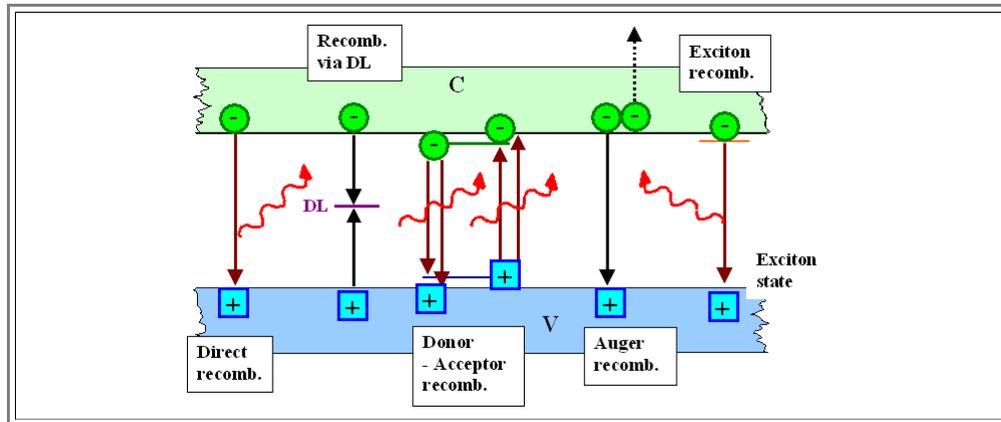
The picture is far too simple and we will have to consider some of the processes in more detail later (especially recombination via excitons). Here we look at Auger recombination and donor–acceptor recombination.

- Even without going into details, it is rather clear that (radiative) donor–acceptor recombination in all **3** variants (note that two of the four arrows shown in the drawing above refer to equivalent processes) is not all that different from direct (and radiative) band–band recombination. Especially for relatively high doping densities, when the individual energy levels from the doping atoms overlap forming a small band in the band gap, we might simply add the dopant states to the states in the conduction or valence band, respectively.
- We then can treat donor-acceptor recombination as subsets of the band-band recombination, possibly adjusting the recombination coefficient B_{b-b} somewhat.

This leaves us with **Auger recombination**. This is an important recombination process that cannot be avoided *and that always reduces the quantum yield of radiation production*.

- It has not been covered in the treatment of Shockley-Read-Hall recombination before, and we will not attempt a formal treatment here. It is, however, simple to understand in the context of the high-injection approximation used for optoelectronics.
- Since you need *three* carriers at the *same time* at the *same place* (the e^- and h^+ that recombine plus a third carrier to remove the energy), the Auger recombination rate, R_A, is proportional to the third power of the carrier density n:

$$R_A = B_A \cdot n^3$$

- This means that for large carrier densities n (always way above equilibrium), and therefore large doping, Auger recombination sooner or later will be the dominating process, limiting the yield of radiative transitions.

Total Recombination and Quantum Yield

All recombination processes will occur independently and the total recombination rate will be determined by the combination of all channels.

- The situation is totally analogous to the flow of current through several resistors switched in parallel. The individual recombination rates R_i add up (like the currents) and for the total recombination rate we have

$$R_{total} = \sum_i R_i = \sum_i \frac{n}{\tau_i} = n \cdot \sum_i \frac{1}{\tau_i}$$

- The total recombination time τ_{total} is thus defined by

$$\frac{1}{\tau_{total}} = \frac{1}{\tau_{b\text{-}b}} + \frac{1}{\tau_{dl}} + \frac{1}{\tau_A} + \frac{1}{\tau_{exciton}} + ...$$

● Since we are only interested in radiative and non-radiative channels, we may write this as

$$\frac{1}{\tau_{total}} = \frac{1}{\tau_{rad}} + \frac{1}{\tau_{non\text{-}rad}}$$

$$R_{total} = R_{rad} + R_{non\text{-}rad} = \frac{n}{\tau_{rad}} + \frac{n}{\tau_{non\text{-}rad}}$$

The quantum efficiency η_{qu} introduced before now can be calculated. It is given by the fraction of R_{rad} relative to R_{total}, or

$$\eta_{qu} = \frac{R_{rad}}{R_{total}} = \frac{1/\tau_{rad}}{1/\tau_{rad} + 1/\tau_{non\text{-}rad}}$$

● Obviously, the result is

$$\eta_{qu} = \frac{1}{1 + \dfrac{\tau_{rad}}{\tau_{non\text{-}rad}}}$$

That is easy enough, but now need some numbers for the recombination coefficients in order to get some feeling for what is going on in different semiconductors.

● It should be clear that the B_i defined above are related to quantities like the thermal velocity, the capture cross sections, the density of deep (and shallow) levels, and so on – they depend to some extent on the particular circumstances of the semiconductor considered. e.g. doping, cleanliness, defect density, etc.

● It should also be clear the B_i are not absolute constants for a given materials but only useful as long as the approximations used are holding. in other words, there are no universal numbers for a certain semiconductor. We only can give typical numbers.

● With this disclaimers in mind, we use the following values (if two numbers are included, they come from different sources). Yellow denotes the indirect semiconductors and the **GaP** value is for the very unlikely direct recombination without excitons.

(T = 300K)	Si		Ge		GaAs		InP		GaP	
	B	τ [µs]	B	τ [µs]	B	τ [µs]	B	τ [µs]	B	τ [µs]
B_{dl} [s^{-1}]	$1 \cdot 10^5$				$1 \cdot 10^8$					
$B_{b\text{-}b}$ [cm^{3}s^{-1}]	$1 \cdot 10^{-14}$ $1.8 \cdot 10^{-15}$	5,500	$5.3 \cdot 10^{-14}$	200	$3 \cdot 10^{-10}$ $7.2 \cdot 10^{-10}$	0.015	$1.26 \cdot 10^{-9}$	0.008	$5.4 \cdot 10^5$	2,000
B_A [cm^{6}s^{-1}]	$2 \cdot 10^{-32}$				$1 \cdot 10^{-27}$					

Now we can construct a *recombination rate vs. surplus carrier density diagram* as follows:
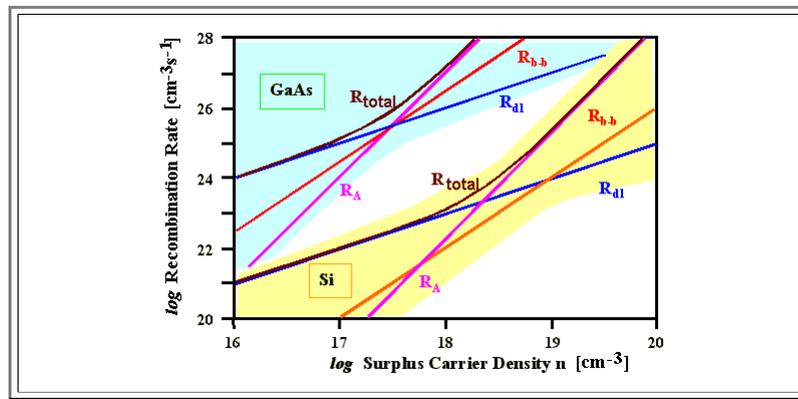
We can see a few interesting points:

- The recombination rate in **Si** is generally much smaller than in **GaAs** – a direct effect of the much larger lifetimes.

- Direct recombination in **Si** is not strictly forbidden – rather, it is just unlikely. At a typical carrier density of **10^{18} cm^{-3}** we have about **10^{22}** photons generated in **Si** per **s** and **cm^3** compared to about **$3 \cdot 10^{26}$** in **GaAs**.

- $R_{b\text{-}b}$ in **GaAs** is similar to the recombination rates of the Auger and deep level channels at densities around **$4 \cdot 10^{17}$ cm^{-3}**, whereas in **Si**, for most densities $R_{b\text{-}b}$ is much smaller than the other recombination rates.

- Although for large carrier densities the Auger recombination process always dominates, it may still be useful to increase **n**: While the quantum efficiency goes *down*, the amount of light produced still *increases* with **n.**

- For very large carrier densities (say **10^{19} cm^{-3}** and beyond as occasionally encountered in power circuits), even **Si** may produce some visible light.

The **GaAs** curves now provide a first answer to our second question about the quantum efficiency.

- For **$n = 10^{16}$ cm^{-3}**, we have about **$4 \cdot 10^{22}$** radiative recombination events per **s** and **cm^3** out of a total of about **10^{24}** per **s** and **cm^3**, which gives a quantum efficiency of **4 %.**

- At the high density end, around **$n = 10^{19}$ cm^{-3}**, the situation is similar, the quantum efficiency is in the few percent range.

- The highest quantum efficiency is around **30 %** for densities around **$n = 5 \cdot 10^{17}$ cm^{-3}**.

Of course, given the values of the recombination coefficients, we could calculate the quantum efficiency precisely, but that would not be very helpful because real devices are more sophisticated than the simple forwardly biased junction implicitly assumed in this consideration.

- This means that we now must look more closely at the important compound semiconductors, especially on how they are doped and what typical differences to **Si** occur.

- We will, however, first do a little exercise for injection across a straight **p-n** junction in order to get acquainted with some real numbers for carrier densities produceable by injection.

Exercise 5.1.2-1
Calculate carrier densities from the forward current of junctions.