

More to Recombination

Some General Remarks

Advanced

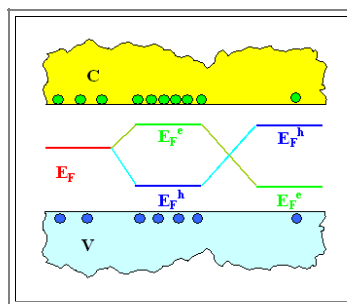
- In the treatment given [so far](#), we looked at the *direct* recombination in direct semiconductors (producing light), and the recombination via *deep levels* in indirect semiconductors.
- The theory behind it all was the [Shockley-Read-Hall \(SRH\) theory](#). What is left to do is:
 - Expand the **SRH** model.
 - Discuss recombination mechanisms not intrinsically contained in the **SRH** model - for example "[Auger](#)" recombination with a conduction band electron as a third partner, or recombination via "[excitons](#)". Whatever it is, it will become important later, as you can glimpse by activating the links.
- Lets start by looking a bit more closely at the results we already obtained from the **SRH** theory. The final formula for *net* recombination via deep levels was

$$R = U_{DL} = \frac{v \cdot \sigma^e \cdot N_{DL} \cdot (n^e \cdot n^h - n_i^2)}{n^e + n^h + 2n_i \cdot \cosh \frac{E_{DL} - E_{MB}}{kT}}$$

- With R = net recombination rate under non-equilibrium conditions, N_{DL} = concentration of deep levels, E_{MB} = mid-band level, v = (group) velocity of the electrons (and holes), and σ^e = scattering cross section of the electron (or hole).
- That we are considering *non-equilibrium* is evident from the term $n^e \cdot n^h - n_i^2$ which would be zero for equilibrium, according to the [mass action law](#).
- So far we considered non-equilibrium situations where $n^e \cdot n^h > n_i^2$, and then the recombination rate must be larger than in equilibrium; $R > 0$, which is born out by the equation above.
- Now just for the hell of it, lets reverse the situation and assume that $n^e \cdot n^h < n_i^2$, i.e. that we have *not enough carriers of both kinds* around.
- As we will see later, this is a [rather common situation](#) in reversely biased **pn-junctions**. Lets see what kind of information we can draw from our equation above. It will lead us to the concept of the "*generation lifetime*"

Generation Lifetime

- The condition $n^e \cdot n^h < n_i^2$ implies that the [quasi Fermi energy](#) for electrons is lower than that for holes, i.e. $E_F^e < E_F^h$. Lets see what that implies in a little picture



- On the left we have equilibrium, with a somewhat higher density of electrons than holes - the material is (barely) **n**-type. In the middle we have the typical situation for non-equilibrium with excess carriers of both types (e.g. because we generate electron - hole pairs by illumination and draw a photo-current). The population density of both carrier types is *increased*; $E_F^e > E_F^h$.
- On the right we have the hypothetical situation that $E_F^e < E_F^h$, the population density is now *decreased* for both carrier types.
- This means that $n^e \cdot n^h < n_i^2$, and in a first approximation we may simply replace $(n^e \cdot n^h - n_i^2)$ by $-n_i^2$. This yields

$$U_{DL} = \frac{v \cdot \sigma^e \cdot N_{DL} \cdot (-n_i)}{2 \cosh[(E_{DL} - E_{MB})/kT]}$$

The first essential result is that U_{DL} is now *negative*.

Since U_{DL} was the difference between recombination and generation, we now have a **net generation** rate of **carriers** with a rate U_{DL} as given above.

We may thus equate U_{DL} with G_{net} , the (net) generation rate: $U_{DL} = G_{net}$

Now we use a little trick and simply define a *generation life time* τ_G by

$$U_{DL} = G_{net} := \frac{n_i}{\tau_G}$$

Insertion and comparison gives us for τ_G

$$\tau_G = \frac{2 \cosh \frac{E_{DL} - E_{MB}}{kT}}{v \cdot \sigma^e \cdot N_{DL}}$$

We could have used this trick before, too, for a relatively general definition of the *recombination* life time τ_R . Let's see how it goes.

We start with the equation for small deviations of the carrier concentrations from the equilibrium values for U_{DL} which we can identify as the net recombination rate R_{net} in this case

$$U = R_{net} = v \cdot \sigma^e \cdot N_{DL} \cdot \frac{[n^e(equ) + \Delta n] \cdot [n^h(equ) + \Delta n] - n_i^2}{n^e(equ) + n^h(equ) + 2 \Delta n + 2 n_i \cdot \cosh[(E_{DL} - E_{MB})/kT]}$$

With $\Delta n \ll n^e, n^h$, and $n^e(equ) \cdot n^h(equ) = n_i^2$, we can simplify this equation to

$$R_{net} = \frac{v \cdot \sigma^e \cdot N_{DL} \cdot \Delta n}{1 + [2 n_i / (n^e(equ) + n^h(equ))] \cdot \cosh[(E_{DL} - E_{MB})/kT]}$$

Again we define τ_R by $R_{net} := \Delta n / \tau_R$, which gives us as a relatively general formula.

$$\tau_R = \frac{1}{v \cdot \sigma^e \cdot N} \cdot \left(1 + \left(\frac{2 n_i}{n^e(equ)} + n^h(equ) \cdot \cosh \frac{E_{DL} - E_{MB}}{kT} \right) \right)$$

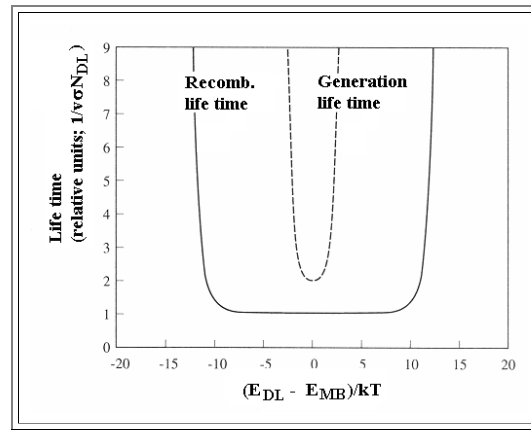
We see immediately that for *doped* semiconductors, i.e. $n^e(equ)$ or $n^h(equ) \gg n_i$, we get the old result

$$\tau_R = \frac{1}{v \cdot \sigma^e \cdot N_{DL}}$$

It is interesting to note that the dependence of the two life times τ_R and τ_G on the exact position on the deep level in the band gap is *not symmetric*.

τ_G is much more sensitive to the exact position, as is shown in the picture containing both general functions (still containing the *cosh* term).

- As we must expect, $\tau_G = 2\tau_R$ if the deep level is exactly in midband position. For deviation from the middle position, the generation life time can be much larger then the corresponding recombination life time.



Surface Recombination

In real life, deep levels are not always distributed homogeneously in the bulk, but may only exist at internal or external surfaces (i.e. grain boundaries, interfaces, or simply the surface of the semiconductor. We will only use the word "surface" from now on which stands for all kinds of interfaces.

- In this case we have to introduce an **area density** or **surface density** of deep levels, N_{DL}^S , and our recombination (or generation) rates are now confined to the interface in question, denoted by R^S or G^S , respectively.

If we add possible surface states to the general mechanism of the **SRH** theory, we obtain for U^S , *the net recombination (or generation) rate at the surface* (be happy that we do not *deduce* this formula!):

$$U^S = R_{net}^S = \frac{v \cdot \sigma^e \cdot \sigma^h \cdot N_{DL}^S \cdot (n^{e,s} \cdot n^{h,s} - n_i^2)}{\sigma^e \cdot \left(n^{e,s} + n_i \cdot \exp \left(\frac{E_{DL} - E_{MB}}{kT} \right) \right) + \sigma^h \cdot \left(n^{h,s} + n_i \cdot \exp \left(\frac{E_{DL} - E_{MB}}{kT} \right) \right)}$$

- With the scattering cross sections separately given for electrons and holes, and with the $n^{e/h,s}$ denoting the *volume concentrations at the surface(?)*

What is the $n^{e/h,s}$, *the volume concentration of the carriers at the surface*

- First, it is a *surface concentration*, i.e. measured in *particles per cm²* or just *cm⁻²*
- Second, it is what you would have on a slice cutting through the volume of a crystal. In other words, *we have* for a lattice constant *a*, which is the smallest meaningful thickness of a slice in a crystal

$$n^{e/h,s} = n^{e/h} \cdot a$$

However, it would be too simple minded to just take the bulk values of $n^{e/h}$! In general, there will be some band-bending near the surface, induced by the same deep levels (called "**surface states**" in this case, that give rise to the surface recombination. Look at the [consideration of a simple junction](#) to see how it works.

- So you first must determine the volume concentration at the surface *under the prevailing conditions* and then convert it to surface concentrations..

OK, now we know what the symbols in the formula mean, but what can we do with it?

- Well, lets make some approximations to see what happens. First, as always, we consider the simple case of small deviations from the equilibrium values of $n^{e/h,s}$, ie. $n^{e/h,s} = n^{e/h,s}(\text{equ}) + \Delta n^S$ and $\Delta n^S \ll n^{e/h,s}$; moreover, we assume that $\sigma^e = \sigma^h = \sigma$.

- We now are [familiar with this approach](#), and obtain

$$U = R_{net} = \frac{v \cdot \sigma \cdot N_{DL}^S \cdot \Delta n^S}{1 + 2n_i / [n^{e,s}(\text{equ}) + n^{h,s}(\text{equ})] \cdot \cosh[(E_{DL} - E_{MB})/kT]} \quad := S_r \cdot \Delta n^S$$

- This looks [rather familiar](#)

Again the recombination rate at the surface is proportional to the excess carrier density (at the surface), and we define

- $U = R_{\text{net}} := S_r \cdot \Delta n^s$, and the quantity S_r *is for surfaces* what the recombination time τ_r (or to be more precise: $1/\tau_r$) is for the bulk.
- Since now n^s is a surface concentration (yes! it is confusing), S_r must have the dimension **cm/s**, it is therefore called the **surface recombination velocity**.
- As before, noting that $n_i/(n^e, s(\text{equ}) + n^h, s) \ll 1$ under normal conditions, we may simplify to

$$S_r \approx v \cdot \sigma$$

If we again play the game [from above](#), switching recombination into generation, we obtain the **surface generation velocity** S_g

$$S_g = \frac{v \cdot \sigma \cdot N_{\text{DL}}^s}{\cosh \frac{E_{\text{DL}} - E_{\text{MB}}}{kT}}$$

Ok - you get the drift. But what does it signify?

- Well, we have seen that it is [fairly easy](#) to "kill" the (bulk) life time by minute contaminations of some contaminants in the bulk of the crystal. *It is even easier to kill the surface recombination velocity, i.e. make it very large.*
- And while a short volume life time is usually (but not always) *pretty* bad for devices, a large surface (or really interface) recombination or generation velocity is *very* bad *for sure*.
- This is one reason why the **Si/SiO₂** interface has been such a tremendous success story: Its interface recombination velocity can be exceedingly small, say **0,1 cm/s**. But just getting some process parameters wrong *a little bit* while making the oxide, may change that dramatically - you may have surface recombination velocities several orders of magnitude larger.
- Unfortunately, many interfaces have recombination velocities far larger, even in the best cases! "**Passivation**" of the interface or surface states, usually including some heating in hydrogen atmosphere *and* some black magic, is an overwhelmingly important part of semiconductor technology. There is a [special module](#) devoted to some of these topics.

Other Channels of Recombination

So far we have covered direct recombination and recombination via deep levels. Each mechanism is called a **recombination channel** for obvious reasons, but there are more than just the two channels considered so far.

- Some more mechanisms will be covered in [other parts](#) of the Hyperscript, here we just give an overview.

Important at high doping levels is the [Auger recombination](#).

- In this case, the energy (and momentum) of the recombining electron - hole pair is transferred to a second electron in the conduction band.
- This is a recombination channel that always allows recombination in indirect semiconductors and thus puts an absolute limit to the life time. It is clear that the probability of such an event requires that *three* mobile particles - two electrons and one hole - are about at the *same place in space*; its probability thus can be expected to increase with increasing carrier density.

Another mechanism is [recombination via shallow states](#), especially via the energy level of the dopant atoms. This includes transitions from a donor level to an acceptor level or to the valence band, and transitions from the conduction band to an acceptor level.

- This mechanism is especially active at low temperatures (when there are free state at that levels). It is not very different from band-band recombination for direct semiconductors and can be treated as a subset of his case.

Finally, there is recombination via [excitons](#). This is a very important mechanism for some semiconductors, in particular **GaP**, because it allows an indirect semiconductor to behave like a direct one, i.e. to emit light as a result of excitonic recombination.

- What is an exciton? And how does it achieve the remarkable feat mentioned above. Well, activate the link above (getting ahead of yourself in the lecture course) and find out.

Several Recombination Channels in Parallel

- What happens if the carriers have several possibilities for recombinations; i.e. several recombination channels exist in parallel?
 - For example, if Auger recombination is comparable in likelihood to direct recombination - what will happen?
- Again, this is covered in some detail in [chapter 5](#), here we only note the important principle:
 - The various processes are independent of each other, i.e. the channels are switched "in parallel".
 - The total recombination R_{total} and the effective recombination time τ_{total} are simply given by.

$$R_{\text{total}} = R_1 + R_2 + R_3 + \dots$$

$$\frac{1}{\tau_{\text{total}}} = \frac{1}{\tau_1} + \frac{1}{\tau_2} + \frac{1}{\tau_3} + \dots$$

Appendix : Changing from Volume to Surface Concentration

- Changing from volume to **surface concentration** might be a bit confusing, especially for mathematicians.
 - If you imagine a distribution of (mathematical) points in space with an average density of n^V , and then ask how large is the density of points n^S on an arbitrary (mathematical) plane stretching through the volume, the answer is $n^S = 0$, because mathematical points are infinitely small and mathematical planes infinitely thin - you never will cut a point with a plane this way.
 - Our "points", however, are atoms - they are not infinitely small. Our planes are not infinitely thin either, their minimal useful thickness corresponds to the size of an atom, or to a lattice constant.
- So in computing a **surface density of atoms**, you can do two things:
 - You actually count the atoms lying on the chosen plane of the crystal (making sure you know if you want your density for a **lattice plane** or for **crystallographically equivalent sheets of atoms in a crystal** (This is **not** the same: the density of atoms on a **{110} atomic layer** of a **fcc** crystal is only $\frac{1}{2}$ of that of a **{110} lattice plane**; if you don't see it, **make a drawing!**).
 - You just take the atoms contained in a sheet with thickness **a**. Its volume thus is **A · a** for an area of **A cm²**. Since a volume of **1 cm³** contains n^V particles, a volume of **A · a** contains $n^V \cdot A \cdot a$ particles; the surface density n^S thus is

$$n^S = \frac{n^V \cdot A \cdot a}{A} = n^V \cdot a$$