Chapter VII: High Non-Equilibrium Perturbations (Carrier Generation and Recombination)

VII.1 Introduction

When a semiconductor is subjected to external excitations such as light or high-energy particles, it can be driven out of equilibrium. This results in the generation of excess carriers, altering the balance of electrons and holes.

The creation of a free carrier corresponds to a transition either **between energy bands** (valence band – conduction band) or **between a discrete energy level and a band**:

- **Electron transition from the valence band (VB) to the conduction band (CB)**, creating an electron–hole pair.
- **Electron transition from a donor level E_D** (located in the bandgap) to the CB, leaving behind a fixed positive charge (ionized atom) and a free electron in the CB.
- **Electron transition from the VB to an acceptor level E_A** in the bandgap, leaving a fixed negative charge and a hole in the VB.

Understanding how these carriers are generated and how they recombine is essential for analyzing the behavior of optoelectronic devices such as solar cells, LEDs, and photodetectors.

VII.2 Carrier generation

Carrier generation is the process by which electron-hole pairs are created in a semiconductor.

This can occur due to:

- Photons (light).
- Ionizing particles (ionizing radiation).

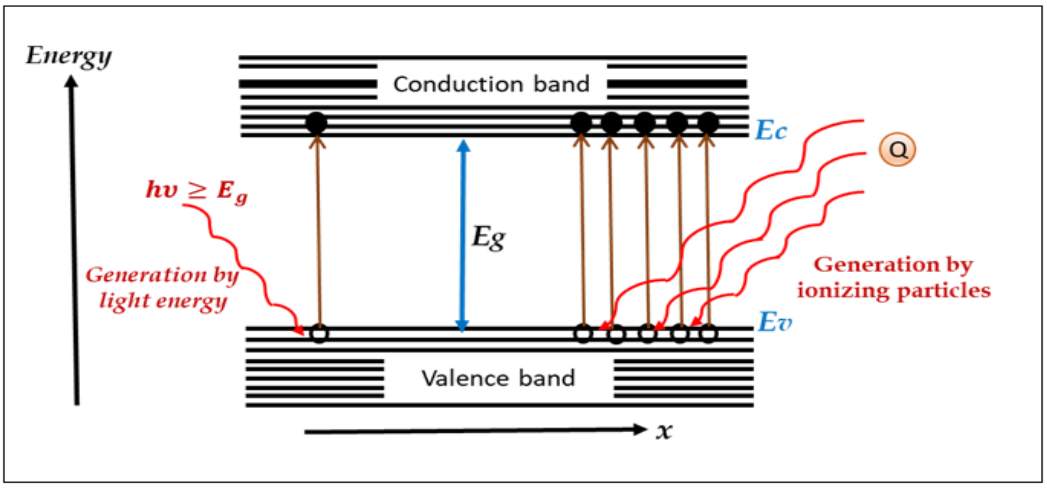

Figure VII.1 Carrier generation caused by light absorption and ionization from high-energy particle beams (VB → CB)

VII.2.1 Generation due to light absorption (photons)

When photons with energy greater than or equal to the bandgap energy **(Eg)** strike a semiconductor, they can excite an electron from the valence band to the conduction band. This process generates an electron-hole pair:

Photon energy: $h\upsilon = h\frac{c}{\lambda} \geq E_g$

- **λ (µm)** is the wavelength;
- **c** = 3×10^8 m/s, is the speed of light;
- $\boldsymbol{\upsilon}$ is the photon frequency;
- ***h*:** Planck's constant.

This is the fundamental mechanism in photodiodes and solar cells. The generation rate depends on the intensity, wavelength, and absorption coefficient of the material.

The following figure illustrates the creation of an electron-hole pair by a photon (excited by illumination):

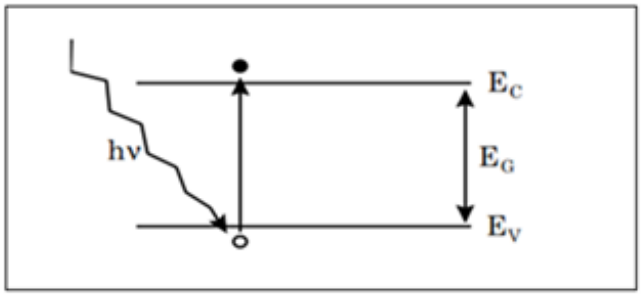

Figure VII.2 Generation of an electron-hole pair by photon absorption

Light absorption in a semiconductor follows the **Beer-Lambert Law**. This law tells us that as light travels through a material, its intensity decreases exponentially:

$$I(x) = I_0 . e^{-\propto x} \iff \Phi(x) = \Phi_0 . e^{-\propto x}$$

Where:

- I(x) and Φ(x) represent the light's **intensity** and **photon flux** at a certain distance x into the material;
- I_0 and Φ_0 are the initial intensity and photon flux right at the surface (x = 0)
- α is the absorption coefficient (m^{-1}). A larger α means the light is absorbed more quickly.

For a photon to create an electron-hole pair, its energy must be greater than the semiconductor's band gap (**Eg**). When this condition is met, the material absorbs the light very strongly, and the absorption coefficient α is very high (in the range of 10^5 à 10^8 m^{-1}).

The absorption of these photons directly leads to the creation of charge carriers (electrons and holes). The **rate of carrier generation** is a measure of how many new carriers are created per unit of time and volume. This rate is directly related to how many photons are being absorbed at a given point in the material.

$$G_{n,p}(x) = \Phi_0 \propto . e^{-\propto x} = \propto \Phi(x)$$

VII.2.2 Generation due to charged high-energy particles (radiation)

In addition to light, high-energy ionizing radiation—such as alpha particles, beta particles, X-rays, or gamma rays—can generate electron-hole pairs in semiconductors.

These particles interact with the atoms in the crystal lattice, transferring energy that ionizes the material and creates charge carriers.

The radiation involved in such processes typically has **energies ranging from a few keV up to 10 MeV**. When this energy is deposited in the semiconductor, it produces a large number of electron-hole pairs. However, the **energy required to generate one pair :** $h\upsilon \geq E_g$, because additional energy is dissipated through lattice vibrations (phonons) and other non-ionizing interactions.

- The **number of carriers generated** over a differential distance dx can be expressed as:

$$dN = \frac{dE}{E_{pair}} \qquad G_{n,p} = \Phi \frac{1}{E_{pair}} \left(\frac{dE}{dx}\right)$$

Where:

- **Φ(x)** is the **radiation flux** at position xxx,
- **dE** is the **energy lost** by the particle over the distance **dx** within the semiconductor.

This generation mechanism is especially relevant in radiation sensors and particle detectors. Since the amount of energy deposited can be significant, **multiple electron-hole pairs** are often created along the path of the incident particle. The resulting high concentration of excess carriers can strongly disturb the equilibrium conditions, which is why this phenomenon is classified under large perturbations.

However, it is important to note that ionizing radiation may also introduce **defect states** or **deep traps** in the material's bandgap, which can accelerate recombination or degrade device performance over time.

VII.3 Quasi-Fermi levels

In thermal equilibrium, the distribution of electrons and holes in a semiconductor is governed by a single Fermi level, which reflects the probability that an energy state is

occupied by an electron. However, when the semiconductor is subjected to external excitation—such as illumination or carrier injection—the system moves out of equilibrium.

For instance, when an **n-type semiconductor** is illuminated, **additional electron-hole pairs are generated**, increasing both the electron and hole concentrations. Under these nonequilibrium conditions, the equilibrium Fermi level no longer accurately describes the carrier distributions. Instead, we define two separate energy levels:

- E_{Fn}: the **quasi-Fermi level for electrons**,
- E_{Fp}: the **quasi-Fermi level for holes**.

These two levels are collectively called **quasi-Fermi levels**, and they quantify the individual distributions of electrons and holes under nonequilibrium.

The **occupancy probability** of a state at energy **E** becomes:

$$f_n(E) = \frac{1}{1 + e^{\frac{E - E_F}{KT}}}$$

$$f_p(E) = 1 - f_n(E) = \frac{1}{1 + e^{\frac{E_F - E}{KT}}}$$

From this, the carrier concentrations are determined by:

$$n = n_i \mathrm{e}^{\frac{E_{Fn} - E_{Fi}}{KT}} \qquad p = n_i \mathrm{e}^{-\frac{E_{Fp} - E_{Fi}}{KT}}$$

The product np becomes:

$$np = {n_i}^2 \mathrm{e}^{\frac{E_{Fn} - E_{Fp}}{KT}}$$

which shows that $\boldsymbol{np > {n_i}^2}$ under nonequilibrium, due to the shift of the quasi-Fermi levels.

Example:

Consider a silicon bar at 300 K, with:

- ni = 1,5×10^{10} cm^{-3} (intrinsic carrier concentration),
- Donor doping giving n_0 = 10^{14} cm^{-3},
- Then p_0 = ni^2/n_0 = 2,25×10^6 cm^{-3}.

Suppose light generates Electron-hole pairs with a concentration of: $\delta_n = \delta_p = 2\times10^{13}$ cm^{-3}.

The position of the Fermi level at equilibrium relative to the intrinsic Fermi level (which is approximately at the middle of the bandgap).

$$E_F - E_{Fi} = KTln\left(\frac{n_0}{n_i}\right) = 1.38 \times 10^{-23} \times 300 \times ln\left(\frac{10^{14}}{1.5\times10^{10}}\right) = 4.6 \times 10^{-20}\ J = 0.228\ eV$$

Under nonequilibrium conditions, the carrier concentrations become:

$n = n_0 + \delta n = 1.2 \times 10^{14}\ cm^{-3}\ (\approx n_0)$ p= $p_0 + \delta p = 0.2 \times 10^{14}\ cm^{-3}\ (\approx \delta p)$

The separation between the quasi-Fermi levels and the intrinsic Fermi level:

$$E_{Fn} - E_{Fi} = KTln\left(\frac{n}{n_i}\right) = 1.38 \times 10^{-23} \times 300 \times ln\left(\frac{1.2 \times 10^{14}}{1.5 \times 10^{10}}\right) = 0.233\ eV$$

$$E_{Fp} - E_{Fi} = -KTln\left(\frac{p}{n_i}\right) = -1.38 \times 10^{-23} \times 300 \times ln\left(\frac{0.2 \times 10^{14}}{1.5 \times 10^{10}}\right) = -0.186\ eV$$

The separation between the quasi-Fermi levels (E_{Fn} , E_{Fp} and the intrinsic Fermi level (E_{Fi}) indicates the extent of the deviation from equilibrium.

Band diagram interpretation:

A graphical representation would show the conduction and valence bands with the quasi-Fermi levels E_{Fn} and E_{Fp} separated—visually demonstrating the nonequilibrium state:

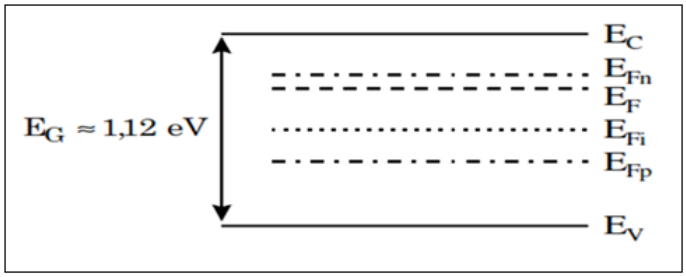

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Figure VII. 3 Band diagram

VII.4 Recombination and carrier lifetime

When a semiconductor is illuminated, **electron-hole pairs are generated** through the absorption of photons. Under thermal equilibrium, the carrier concentrations satisfy the relation:

$$n_0 p_0 = n_i^2$$

However, under **nonequilibrium conditions**, incident photons are absorbed by **valence electrons**, giving them enough energy to break their covalent bonds and transition to the **conduction band**, thereby creating free electrons and holes.

Yet, this generation process **cannot increase indefinitely**. It is inherently limited by an **opposing process known as recombination**, where electrons and holes annihilate each other. Recombination restores the system toward equilibrium by reducing the excess carrier concentration.

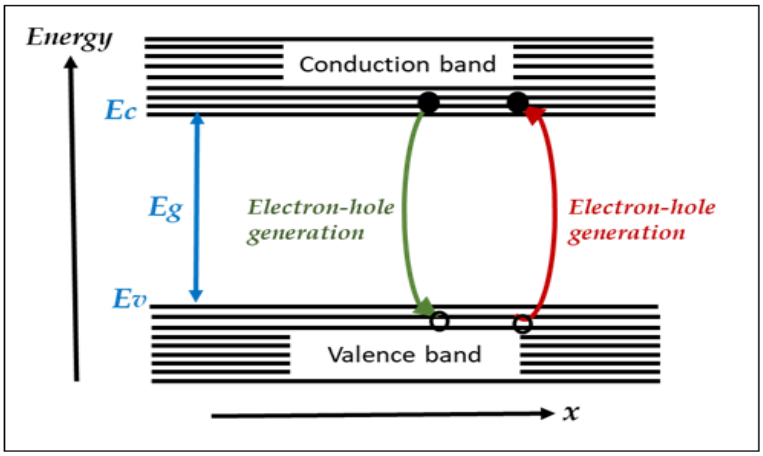

Figure VII. 4 Generation and recombination of electron-hole pairs

The **recombination rate** represents the number of electrons (or holes) recombining per unit volume and per unit time. In the case of **direct recombination**, where electrons from the conduction band directly recombine with holes in the valence band (common in direct bandgap semiconductors like GaAs), the rate can be expressed as:

$$R = \beta.(np - n_i^2)$$

Where:

- R is the recombination rate (cm $^{-3}$/s);
- β is the direct recombination coefficient;
- n and p are the electron and hole concentrations under nonequilibrium;
- $\mathbf{n_i}$ is the intrinsic carrier concentration.

The recombination rate depends on how far the system has been perturbed from equilibrium:

- At equilibrium, $np = n_i^2$, so: $R = 0$;
- When $np > n_i^2$, recombination becomes active to reduce the excess carriers.

➢ VII.4.1 Lifetime expression * Time-dependent expressions

The recombination process is described qua.ntitatively by the **recombination rate**, which represents the number of carriers (electrons or holes) that recombine per unit volume and per unit time. This rate is defined separately for electrons and holes but is equal in steady-state conditions since each recombination event involves both an electron and a hole. The recombination rate depends on how far the system is from equilibrium, as well as on material properties and recombination mechanisms.

$$R_n = -\frac{dn(t)}{dt} = \frac{\Delta n}{\tau_n} = \frac{n-n_0}{\tau_n} \quad , \qquad R_p = -\frac{dp(t)}{dt} = \frac{\Delta p}{\tau_p} = \frac{p-p_0}{\tau_p}$$

- R_n is the electron recombination rate;
- R_p is the hole recombination rate.

- These expressions are used in the case of **small perturbations from equilibrium**, where the excess carrier concentrations $\Delta n \ll n_0, \Delta p \ll p_0$

- They describe the **temporal evolution of excess carriers**, such as after a short optical pulse. The decay of carriers follows an exponential form:
- $\Delta n(t) = \Delta n(0).e^{-t/\tau_n}$
- Commonly used in **transient photoconductivity experiments** and when analyzing the **response time of optoelectronic devices**.

VII.4.2 Direct Recombination Expression (in Direct Bandgap Semiconductors)

$$R = \beta.n.p$$

With corresponding carrier lifetimes:

$\tau_n = \frac{1}{\beta.p_0}$, $\tau_p = \frac{1}{\beta.n_0}$

- These expressions are used in **direct bandgap semiconductors** (e.g., GaAs, InP), where electrons and holes **recombine directly** and emit photons (radiative recombination).
- Used to model the **steady-state recombination rate**, without focusing on time evolution.
- Essential for evaluating **quantum efficiency** in LEDs and semiconductor lasers, where recombination is rapid and proportional to *np.*

VII.4.3 Shockley – Read – Hall (SRH) Recombination – indirect recombination

$$R_{SRH} = \frac{np - n_i^2}{\tau_p(n + n_1) + \tau_n(p + p_1)}$$

- ***n1*** is the **effective electron concentration** when the trap level is at thermal equilibrium with the conduction band.

$$n_1 = N_c e^{-\frac{E_T - E_C}{KT}}$$

- ***p1*** is the **effective hole concentration** when the trap level is at thermal equilibrium with the valence band.

$$p_1 = N_v e^{-\frac{E_V - E_T}{KT}}$$

Where:

- E_T : energy level of the trap (recombination center),
- E_C, E_V : energies of the conduction and valence bands,
- N_c, N_v : effective density of states in the conduction and valence bands,
- K : Boltzmann's constant,
- T : temperature (in kelvins).

When the trap is exactly at **midgap**, we get:

$$n_1 = p_1 = n_i$$

- This expression is used in **indirect bandgap materials** like **silicon**, where recombination occurs via **trap levels (defects or impurities)** in the bandgap.
- Describes **non-radiative recombination**, which dominates at low injection levels or in defective materials.
- Widely used in **silicon-based photodetectors, solar cells**, and when evaluating **crystalline quality**.

This table summarizes the main mathematical expressions used to describe carrier recombination in semiconductors. Each model applies to different physical contexts and material types, from time-dependent excess carrier decay to steady-state and defect-assisted recombination. It also highlights typical use cases for each expression.

Table VII.1 Comparison of recombination rate models in semiconductors.

Expression	*Context*	*Material type*	*Use case*
$R_n = -\frac{dn}{dt}$	Time-dependent, small signal	All	Transients, carrier lifetime measurements
$R = \beta np$	Steady-state, direct recombination	Direct bandgap (GaAs)	LEDs, lasers, radiative recombination
R_{SRH}	Trap-assisted recombination	Indirect bandgap (Si)	Defect analysis, solar cells, non-radiative losses

VII.4.4 Surface recombination

At the surface of a semiconductor, unsatisfied chemical bonds create states in the bandgap that can act as recombination centers. The surface recombination rate depends on the surface recombination velocity S and the excess carrier concentration:

$$R_s = S.\Delta n$$

Minimizing surface recombination is critical in high-efficiency devices. Techniques such as surface passivation are employed to reduce S.

VII.5. Photoconductivity

Photoconductivity refers to the increase in a semiconductor's electrical conductivity when it is exposed to light.

Let us consider a **silicon bar** connected to a **voltage source** and a **load resistor**.

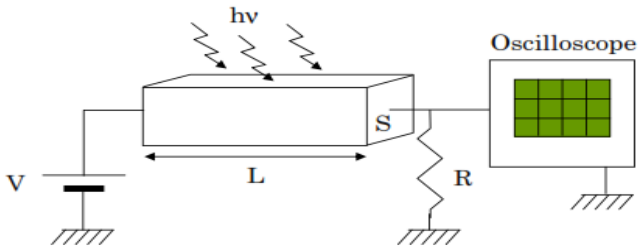

Figure VII. 5. Flux(Eclairement) permanent (régime stationnaire) de photons

When the semiconductor is subjected to a **steady (continuous) photon flux**, photons are absorbed and generate **electron-hole pairs**, which increases the number of free carriers in the conduction and valence bands.

This increase in carrier concentration leads to a corresponding increase in the material's conductivity, described by:

$$\sigma = q(n\mu_n + p\mu_p)$$

Where :

- σ is the electrical conductivity;
- q is the elementary charge;
- n and p are the concentrations of electrons and holes (including both equilibrium and excess carriers);
- μn and μ_p are the respective mobilities.

The **change in conductivity due to illumination** is:

$$\Delta\sigma = q(\Delta n\mu_n + \Delta p\mu_p)$$

In most low-level injection cases where $\Delta n = \Delta p$, this simplifies to:

$$\Delta\sigma = q\Delta n(\mu_n + \mu_p)$$

This change in conductivity results in a measurable **photocurrent** through the external resistor, and this photocurrent is **directly proportional to the light intensity** under steady-state conditions.

- **At thermal equilibrium**

$$\frac{dn(t)}{dt} = G_n - R_n = 0$$

$$R_n = G_n = R_p = G_p = \frac{dn_0}{\tau_n} = \frac{dp_0}{\tau_p}$$

and the carrier concentrations remain constant:

$$n_0 p_0 = n_i^2$$

Photoconductivity forms the basis of **many optoelectronic applications**, such as **photodetectors, optical switches, and ambient light sensors**, by converting optical signals into electrical responses.

VII.6. Luminescence

Luminescence is the emission of light resulting from a material returning to equilibrium after having been excited. It occurs when **electron-hole pairs recombine**, and the **energy released during this process is emitted as a photon**.*

This phenomenon can be observed in various forms, depending on the **excitation mechanism**:

- **Photoluminescence (PL)**

Photoluminescence occurs when a material is excited by **incoming photons**. The absorbed photon energy promotes electrons to the conduction band, creating electron-hole pairs. After excitation stops, **light is emitted** at a different frequency as the system relaxes back toward equilibrium.

- If the **emission time** is **short** (on the order of milliseconds), the material is referred to as **fluorescent**.
- If the **emission is delayed** (lasting seconds or even minutes), the material exhibits **phosphorescence**.

Photoluminescence is widely used in **material characterization** (e.g., bandgap measurement, defect analysis).

- **Electroluminescence (EL)**

In electroluminescence, electron-hole pairs are generated by **carrier injection**—typically by applying a voltage across a **p-n junction**. When the injected electrons and holes recombine, **photons are emitted**.

This process forms the operating principle behind **light-emitting diodes (LEDs)** and **laser diodes**.

- **Cathodoluminescence (EL)**

This type of luminescence is triggered by an **electron beam** that excites the material. It is used in specialized applications such as **electron microscopy** and **display technologies**.

Note:

The **wavelength (or color) of the emitted light** corresponds approximately to the material's bandgap energy:

$$h\upsilon = E_g$$

Luminescence is both a **diagnostic tool** in semiconductor physics and a **functional principle** in a wide range of optoelectronic devices.