Chapter 6
Lecture Notes
Semiconductors in Nonequilibrium Conditions

Excess electrons in the conduction band and excess holes in the valence band may exist in addition to the thermal-equilibrium concentrations if an external excitation is applied to the semiconductor. The creation of excess electrons and holes means that the semiconductor is no longer in thermal equilibrium.

Carrier generation and recombination

**Generation** ⇒ process whereby electrons and holes are created

**Recombination** ⇒ process whereby electrons and holes are coincided and lost.

A sudden change in temperature or optical excitation can generate excess electrons and holes creating a nonequilibrium condition.
Injection ⇒ A process of introducing excess carriers in semiconductors.

Generation and recombination are two types:

(i) Direct band-to-band generation and recombination and

(ii) the recombination through allowed energy states within the bandgap, referred to as traps or recombination centers.
Direct band-to-band generation and recombination

Thermal equilibrium:

The random generation-recombination of electrons-holes occur continuously due to the thermal excitation.

In direct band-to-band generation-recombination, the electrons and holes are created-annihilated in pairs:

\[ G_{n0} = G_{p0} \quad R_{n0} = R_{p0} \]

At thermal equilibrium, the concentrations of electrons and holes are independent of time; therefore, the generation and recombination rates are equal, so we have,

\[ G_{n0} = G_{p0} = R_{n0} = R_{p0} \]
# Excess carrier generation and recombination

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Nonequilibrium Excess Carriers

When excess electrons and holes are created,

\[ n(t) = n_0 + \delta n(t), \quad p(t) = p_0 + \delta p(t) \quad \text{and} \quad np \neq n_i^2 \]

The excess electrons and holes are created in pairs,

\[ g'_n = g'_p \quad \text{and} \quad \delta n(t) = \delta p(t) \]

The excess electrons and holes recombine in pairs,

\[ R'_n = R'_p \]

The excess carrier will decay over time and the decay rate depends on the concentration of excess carrier.

\[ \frac{dn(t)}{dt} \propto [n_i^2 - n(t)p(t)] \quad \text{or}, \quad \frac{dn(t)}{dt} = \alpha_r [n_i^2 - n(t)p(t)] \]

\( \alpha_r \) is the constant of proportionality for recombination.
Nonequilibrium Excess Carriers

\[
\frac{dn(t)}{dt} = \alpha_r \left[ n_i^2 - n(t)p(t) \right]
\]

\[
n(t) = n_0 + \delta n(t), \quad p(t) = p_0 + \delta p(t) \quad \text{and} \quad \delta n(t) = \delta p(t)
\]

\[
\frac{d\delta n(t)}{dt} = -\alpha_r \delta n(t) [(n_0 + p_0) + \delta n(t)]
\]

**For low-level injection condition:** \((p_0 + n_0) >> \delta n(t)\)

For p-type material, \(p_0 >> n_0\)

Thus,

\[
\frac{d\delta n(t)}{dt} = -\alpha_r \delta n(t)p_0
\]

The solution is,

\[
\delta n(t) = \delta n(0)e^{-\alpha_r p_0 t} = \delta n(0)e^{-t/\tau_{n_0}}
\]

where \(\tau_{n_0}\) is the excess minority carrier lifetime for electron and \(\tau_{n_0} = 1/(\alpha_r p_0)\)
\[
\frac{d\delta n(t)}{dt} = -\alpha_r \delta n(t)[(n_0 + p_0) + \delta n(t)]
\]

\[
R'_n = -\frac{d\delta n(t)}{dt} = \alpha_r \delta n(t)[(n_0 + p_0) + \delta n(t)] = \frac{\delta n}{\tau_0}
\]

\[
\tau_0 = \frac{1}{\alpha_r (p_0 + n_0 + \delta n)}
\]

For high-level injection condition:

\[(p_0 + n_0) \langle \delta n(t) \rangle\]

Examples
The recombination rate for electrons in p-type material,

\[ R'_n = -\frac{d\delta n(t)}{dt} = \alpha_r \delta n(t) \tau_{n0} = \frac{\delta n(t)}{\tau_{n0}} \]

The excess electrons and holes recombine in pairs, (in p-type material)

\[ R'_n = R'_p = \frac{\delta n(t)}{\tau_{n0}} \]

The recombination rate is a positive quantity.

And, for n-type

\[ R'_n = R'_p = \frac{\delta p(t)}{\tau_{p0}} \]

where \( \tau_{p0} \) is the minority carrier lifetime of holes.

The excess recombination rate is determined by the excess minority carrier lifetime.
Continuity equations:

The continuity equation describes the behavior of excess carriers with time and in space in the presence of electric fields and density gradients.

\[
\frac{\partial p}{\partial t} \bigg|_{x \to x + \Delta x} = \lim_{\Delta x \to 0} \frac{F_p^+(x) - F_p^+(x + \Delta x)}{\Delta x} + g_p - R_p
\]

F = F^+ represents hole particle flux (\# / cm^2 –s)
Continuity equations

\[ \frac{\partial p}{\partial t} = -\frac{\partial F_p^+}{\partial x} + g_p - R_p \]

The hole flux, \( F_p^+ = \frac{J_p}{e} \) The unit of hole flux is holes/cm²-s

\[ \frac{\partial p}{\partial t} = -\frac{1}{e} \frac{\partial J_p}{\partial x} + g_p - R_p \]

Similarly for electrons,

\[ \frac{\partial n}{\partial t} = \frac{1}{e} \frac{\partial J_n}{\partial x} + g_n - R_n \]

These are the continuity equations for holes and electrons respectively
Recall: In one dimension, the electron and hole current densities due to the drift and diffusion are given by:

\[ J_p = e\mu_p pE - eD_p \frac{\partial p}{\partial x} \]
\[ J_n = e\mu_n nE + eD_n \frac{\partial n}{\partial x} \]

Substitute these in the continuity equations:

\[ \frac{\partial p}{\partial t} = D_p \frac{\partial^2 p}{\partial x^2} - \mu_p \frac{\partial (pE)}{\partial x} + g_p - R_p \]
\[ \frac{\partial n}{\partial t} = D_n \frac{\partial^2 n}{\partial x^2} + \mu_n \frac{\partial (nE)}{\partial x} + g_n - R_n \]

Or,

\[ \frac{\partial n}{\partial t} = D_n \frac{\partial^2 n}{\partial x^2} + \mu_n \left( E \frac{\partial n}{\partial x} + n \frac{\partial E}{\partial x} \right) + g_n - R_n \]

\[ \frac{\partial p}{\partial t} = D_p \frac{\partial^2 p}{\partial x^2} - \mu_p \left( E \frac{\partial p}{\partial x} + p \frac{\partial E}{\partial x} \right) + g_p - R_p \]
The thermal-equilibrium concentrations, $n_0$ and $p_0$, are not functions of time. For the special case of homogeneous semiconductor, $n_0$ and $p_0$ are also independent of the space coordinates. So the continuity may then be written in the form of:

\[
\frac{\partial \delta n}{\partial t} = D_n \frac{\partial^2 \delta n}{\partial x^2} + \mu_n \left( E \frac{\partial \delta n}{\partial x} + n \frac{\partial E}{\partial x} \right) + g_n - R_n
\]

\[
\frac{\partial \delta p}{\partial t} = D_p \frac{\partial^2 \delta p}{\partial x^2} - \mu_p \left( E \frac{\partial \delta p}{\partial x} + p \frac{\partial E}{\partial x} \right) + g_p - R_n
\]

Time–dependent diffusion equations
Ambipolar transport equation

Under applied external electric field, the excess electrons and holes created by any mean say, light illumination, tend to drift in the opposite directions. Separation of these charged particles induces an internal electric field opposite to the applied external electric field. This induced internal electric field attract the electrons and holes move toward each other, holding the pulses of excess electrons and holes together. So, the electric field appears in the time-dependent diffusion equations is composed of the external and the induced internal electric fields. Electrons and holes drift or diffuse together with a single effective mobility or diffusion coefficient. This phenomena is called ambipolar transport.

\[ \frac{e(\delta p - \delta n)}{\varepsilon_s} = \frac{\partial E_{\text{int}}}{\partial x} ; \quad |E_{\text{int}}| \ll |E_{\text{app}}| \]  

The effect of internal field

As the electrons and holes are diffusing and drifting together:

\[ g_n = g_p = g \quad \text{and} \quad R_n = R_p = R \]
\[
\frac{\partial \delta n}{\partial t} = D_n \frac{\partial^2 \delta n}{\partial x^2} + \mu_n \left( E \frac{\partial \delta n}{\partial x} + n \frac{\partial E}{\partial x} \right) + g - R
\]

\[
\frac{\partial \delta n}{\partial t} = D_p \frac{\partial^2 \delta n}{\partial x^2} - \mu_p \left( E \frac{\partial \delta n}{\partial x} + p \frac{\partial E}{\partial x} \right) + g - R
\]

Eliminating \( \frac{\partial E}{\partial x} \)

\[
\frac{\partial \delta n}{\partial t} = D' \frac{\partial^2 \delta n}{\partial x^2} + \mu'E \frac{\partial \delta n}{\partial x} + g - R
\]

\[
D' = \frac{D_n D_p (n + p)}{D_n n + D_p p}
\]

\[
\mu' = \frac{\mu_n \mu_p (p - n)}{\mu_n n + \mu_p p}
\]

Assumption: Charge neutrality (quasi-neutrality) \( \delta n \approx \delta p \)

\( D' \) is the ambipolar diffusion coefficient

\( \mu' \) is called the ambipolar mobility
Ambipolar transport equation

For p-type semiconductors \( D' \approx D_n \) and \( \mu' \approx \mu_n \)

For n-type semiconductors \( D' \approx D_p \) and \( \mu' \approx -\mu_p \)

For p-type semiconductors

\[
\frac{\partial \delta n}{\partial t} = D_n \frac{\partial^2 \delta n}{\partial x^2} + \mu_n E \frac{\partial \delta n}{\partial x} + g - \frac{\delta n}{\tau_{n0}}
\]

And for n-type semiconductors

\[
\frac{\partial \delta p}{\partial t} = D_p \frac{\partial^2 \delta p}{\partial x^2} - \mu_p E \frac{\partial \delta p}{\partial x} + g - \frac{\delta p}{\tau_{p0}}
\]
Applications of ambipolar transport equation

(1) Steady state: \( \frac{\partial(\delta n)}{\partial t} = \frac{\partial(\delta p)}{\partial t} = 0 \)

(2) Uniform distribution of excess Carriers: \( D_p \frac{\partial^2 (\delta n)}{\partial x^2} = 0, \quad D_n \frac{\partial^2 (\delta n)}{\partial x^2} = 0, \quad \frac{\partial \delta n}{\partial x} = \frac{\partial \delta p}{\partial x} = 0 \)

(3) Zero Electric Field: \( E \frac{\partial (\delta n)}{\partial x} = E \frac{\partial (\delta p)}{\partial x} = 0 \)

(4) No excess carrier generation: \( g' = 0 \)

(5) No excess carrier recombination: \( R' = \frac{\delta n}{\tau_{n0}} = \frac{\delta p}{\tau_{p0}} = 0 \)

(6) Infinite carrier lifetimes, \( \tau_{p0} = \tau_{n0} = \infty, \quad R' = \frac{\delta n}{\tau_{n0}} = \frac{\delta p}{\tau_{p0}} = 0 \)
**Indirect recombination:**

In real semiconductors, there are some crystal defects and these defects create discrete electronic energy states within the forbidden energy band.

**Recombination through the defect (trap) states is called indirect recombination**

The carrier lifetime due to the recombination through the defect energy state is determined by the **Shockley-Read-Hall** theory of recombination.

**Shockley-Read-Hall recombination:**

Shockley-Read-Hall theory of recombination assumes that a single trap center exists at an energy $E_t$ within the bandgap.
The trap center here is acceptor-like. It is negatively charged when it contains an electron and is neutral when it does not contain an electron.

There are four basic processes:

1. **Electron capture**: An electron is captured at the energy level $E_c$.
2. **Electron emission**: An electron is emitted from the energy level $E_v$.
3. **Hole capture**: A hole is captured at the energy level $E_c$.
4. **Hole emission**: A hole is emitted at the energy level $E_v$.

The four basic trapping and emission processes for the case of an acceptor-type trap.
Capture rate $\propto$ (free carrier concentration $\times$ (concentration of empty defects states)

Emission rate $\propto$ (trapped carrier concentration $\times$ (concentration of empty conduction or valence band states)

Emission rate $\propto$ (concentration of trapped carriers)

The electron capture rate (process 1),

$$R_{cn} = C_n n [1 - f_F(E_t)] N_t$$

The electron emission rate (process 2),

$$R_{en} = E_n N_t f_E(E_t)$$

The relationship between the capture $C_n$ and emission coefficients $E_n$ can be determined by the principle of detailed balance.

**Principle of Detailed Balance:** Under equilibrium conditions each fundamental process and its inverse must self-balance independent of any other process that may be occurring inside the material.

Under thermal equilibrium, $R_{cn} = R_{en}$, which gives a relation between $C_n$ and $E_n$. 
In nonequilibrium, the net rate at which electrons are captured from the conduction band is given by,

\[ R'_n = R_{cn} - R_{en} \]

Under steady state condition, there is no change of trap carrier concentration.

Thus

\[ R'_n = R'_p = \frac{C_n C_p N_t (np - n_i^2)}{C_n (n + n') + C_p (p + p')} \]

Where,

\[ n' = N_c \exp \left[ -\frac{(E_c - E_t)}{kT} \right] \quad \text{and} \quad p' = N_v \exp \left[ -\frac{(E_t - E_v)}{kT} \right] \]

The trap level energy is near the midgap so that \( n' \) and \( p' \) are not too different from the intrinsic carrier concentration \( n_i \). \n
\[ n' = p' = n_i \]

At thermal equilibrium, \( np = n_0 p_0 = n_i^2 \) so that \( R'_n = R'_p = 0 \)
\[
R' = \frac{C_n C_p N_t (np - n_i^2)}{C_n (n + n') + C_p (p + p')} \approx \frac{(np - n_i^2)}{\tau_{p0}(n + n_i) + \tau_{n0}(p + n_i)}
\]

\[
= \frac{(n_0 + \delta n)(p_0 + \delta n) - n_i^2}{\tau_{p0}(n_0 + \delta n + n_i) + \tau_{n0}(p_0 + \delta n + n_i)}
\]

\[
R' = \frac{(n_0 + p_0)\delta n + (\delta n)^2}{\tau_{p0}(n_0 + \delta n + n_i) + \tau_{n0}(p_0 + \delta n + n_i)}
\]

\[
\tau_{n0} = \frac{1}{C_n N_t}
\]

\[
\tau_{p0} = \frac{1}{C_p N_t}
\]

**Limits of extrinsic doping and low injection:**

**For p-type semiconductors**
\[
R_n' = \frac{\delta n}{\tau_{n0}}
\]

**For n-type semiconductors**
\[
R_p' = \frac{\delta p}{\tau_{p0}}
\]

For high level injection,
\[
R_p' = R_n' = \frac{\delta p}{\tau_{p0} + \tau_{n0}}
\]
**Example** A step illumination is applied uniformly to an n-type semiconductor at time $t = 0$ and switched off at time $t = t_{off}$ ($t_{off} >> \tau_{p0}$). No applied bias.

(1) Find the expression of the hole concentration and

(2) Sketch hole concentration vs time for $0 < t < \infty$.

(3) Also find the expression of the conductivity for $0 < t < \infty$.

\[ \frac{\partial \delta p}{\partial t} = D_p \frac{\partial^2 \delta p}{\partial x^2} - \mu_p E \frac{\partial \delta p}{\partial x} + g' - \frac{\delta p}{\tau_{p0}} \]
Example 6.2:

A semiconductor has the following properties:
The semiconductor is a homogeneous, p-type material in thermal equilibrium for \( t \leq 0 \). At \( t = 0 \), an external source is turned on which produces excess carriers uniformly at rate of \( g' = 10^{20} \text{cm}^{-3} \text{s}^{-1} \). At, \( t = 2 \times 10^{-6} \text{s} \) the external source is turned off.

(1) Derive the expression for the excess-electron concentration as a function of time for \( 0 \leq t \leq \infty \).

(2) Determine the value of excess electron concentration at (i) \( t = 0 \),
(ii) \( t = 2 \times 10^{-6} \text{s} \), (iii) \( t = 3 \times 10^{-6} \text{s} \) and (iv) \( t = \infty \).

(3) Plot the excess electron concentration as a function of time.

\[
D_n = 25 \text{cm}^2 / \text{s} \quad \tau_{n0} = 10^{-6} \text{s} \\
D_p = 10 \text{cm}^2 / \text{s} \quad \tau_{p0} = 10^{-7} \text{s}
\]
Example: A continuous illumination is applied to an $n$-type semiconductor at time $x = 0$ and no carrier generation for $x > 0$. That means $g' = 0$ for $x > 0$.
Determine the steady state excess concentrations for holes for $x > 0$ and the hole diffusion current.

**Numerical:** Consider $p$ type Silicon at $T = 300$ K. Assume that $\tau_{n0} = 5 \times 10^{-7}$ s, $D_n = 25 \text{ cm}^2/\text{s}$ and $\delta n(0) = 10^{15} \text{ cm}^{-3}$. Determine excess hole concentration profile.

\[
\frac{\partial \delta p}{\partial t} = D_p \frac{\partial^2 \delta p}{\partial x^2} - \mu_p E \frac{\partial \delta p}{\partial x} + g' - \frac{\delta p}{\tau_{p0}}
\]

\[
0 = D_p \frac{\partial^2 \delta p}{\partial x^2} - \frac{\delta p}{\tau_{p0}}
\]

\[
\delta p(x) = A e^{-\frac{x}{L_p}} + B e^{-\frac{-x}{L_p}}
\]
\[ \delta p(x) = Ae^{\frac{x}{L_p}} + Be^{\frac{-x}{L_p}} \]

Steady-state generation rate at \( x = 0 \).

Steady-state electron and hole concentrations for the case when excess electrons and holes are generated at \( x = 0 \).
Dielectric relaxation time constant:

If an amount of net charge is injected suddenly in a semiconductor, the free charge carriers of opposite sign try to balance the injected charge and establish charge neutrality. How fast the charge neutrality can be achieved is determined by the dielectric relaxation time constant, \( \tau_d \). This phenomenon is called dielectric relaxation. The excess net charge decays exponentially,

\[
\nabla \cdot E = \frac{\rho}{\varepsilon} \quad , \quad J = \sigma E \quad , \quad \nabla \cdot J = -\frac{\partial \rho}{\partial t}
\]

\[
\frac{d\rho}{dt} + \left(\frac{\sigma}{\varepsilon}\right)\rho = 0
\]

\[
\rho(t) = \rho(0) e^{-t/\tau_d} \quad \text{where} \quad \tau_d = \frac{\varepsilon}{\sigma}
\]

Example 6.6
(a) Find the dielectric relaxation time constant if the resistivity of the sample is \( 10^{14} \) \( \Omega \)-cm and relative permittivity is 6.3.

(b) Find the dielectric relaxation time constant of an n-type Silicon with \( N_d = 10^{16} \) cm\(^{-3} \).
Surface Effects

Steady-state excess hole concentration versus distance from a semiconductor surface.

\[ 0 = D_p \frac{\partial^2 \delta p}{\partial x^2} + g' - \frac{\delta p}{\tau_{p0}} \]

\[ \delta p(x) = g' \tau_p + A e^{\frac{x}{L_p}} + B e^{\frac{-x}{L_p}} \]

\[ \frac{\delta p_B}{\delta p_S} = \frac{\tau_{pB}}{\tau_{pS}} \]
\[ 0 = D_p \frac{\partial^2 \delta p}{\partial x^2} + g' - \frac{\partial p}{\tau_{p0}} \]

As \( x \to \infty \quad Ae_{L_p}^{x} \to \infty \quad ; \quad Be_{L_p}^{x} \to 0 \quad \therefore B \neq 0, \text{but} \quad \Rightarrow A = 0 \]

\[ \delta p(x \to \infty) = g'\tau_p \quad ; \delta p(x \to 0) = g'\tau_p + B \]
Time and Spatial Dependence of Excess Carrier Concentration

Example: A finite number of carriers is generated instantaneously at time $t = 0$ and $x = 0$, but $g' = 0$ for $t > 0$. Assume an n-type semiconductor with a constant applied electric field $E_0$, which is applied in the $+x$ direction. Determine the excess carrier concentration as a function of $x$ and $t$.

The ambipolar equation for $t > 0$ and $x > 0$,

$$\frac{\partial \delta p}{\partial t} = D_p \frac{\partial^2 \delta p}{\partial x^2} - \mu_p E_0 \frac{\partial \delta p}{\partial x} - \frac{\delta p}{\tau_{p0}}$$

The solution of the above equation,

$$\delta p(x, t) = \frac{e^{-t/\tau_{p0}}}{(4\pi D_p t)^{1/2}} \exp \left[ -\frac{(x - \mu_p E_0 t)^2}{4D_p t} \right]$$
Excess-hole concentration versus distance at various times for zero applied electric field.
Quasi-Fermi level:

If excess carriers are created in a semiconductor, the Fermi energy is strictly no longer defined. Under nonequilibrium condition, we can assign individual Fermi level for electrons and holes. These are called quasi-Fermi levels and the total electron or hole concentration can be determined using these quasi-Fermi levels. We can write,

\[ n_0 + \delta n = n_i \exp\left(\frac{E_{Fn} - E_{Fi}}{kT}\right) \]

\[ p_0 + \delta p = n_i \exp\left(\frac{E_{Fi} - E_{Fp}}{kT}\right) \]
Example Given: n-type semiconductor at 300K. \( n_0 = 10^{15} \text{ cm}^{-3} \), \( p_0 = 10^5 \text{ cm}^{-3} \), \( n_i = 10^{10} \text{ cm}^{-3} \), \( \delta n = \delta p = 10^{13} \text{ cm}^{-3} \). Calculate (a) the Fermi energy level and (b) the quasi Fermi energy levels.