Homework:

1. Without violating the physics laws, please describe the “ideal” solar energy converting system in your mind.
What we learnt last lecture:

**Semiconductor in Equilibrium**: Fermi Level, Fermi Dirac Statistics, Boltzmann Approximation, Electron and Hole Density, Doping, n-type Semiconductor, p-type Semiconductor

\[
p = N_V \exp \left( \frac{E_V - E_F}{k_B T} \right) \quad n = N_C \exp \left( \frac{E_F - E_C}{k_B T} \right)
\]

**Semiconductor under Bias**: Quasi Fermi Level

\[
n = n_i \exp \left( \frac{E_{Fn} - E_i}{k_B T_n} \right)
\]

\[
p = n_i \exp \left( \frac{E_i - E_{Fp}}{k_B T_p} \right)
\]
Lecture 4

Generation and Recombination

References:
The output of a solar cell (photocurrent) is determined by a balance between photogeneration, charge recombination and current generation.

Two simple principles:
(1) the number of carriers of each type must be conserved;
(2) the electrostatic potential due to the carrier charges obeys Poisson’s equation.
Semiconductor Transport Equation

For a semiconductor containing electrons and holes, conservation of electron number requires that

\[
\frac{\partial n}{\partial t} = \frac{1}{q} \nabla \cdot J_n + G_n - U_n
\]

\[
\frac{\partial p}{\partial t} = -\frac{1}{q} \nabla \cdot J_p + G_p - U_p
\]

\(G\) is the volume rate of generation of electrons/holes, \(U\) is the volume rate of recombination. (Continuity Equation)

\[
\nabla^2 \phi = \frac{q}{\varepsilon_s} \left( -\rho_{fixed} + n - p \right)
\]
1D Continuity Equation

\[ \frac{\partial n}{\partial t} = \frac{1}{q} \frac{\partial J_n}{\partial x} + G_n - U_n \]

To solve the continuity equation, we need to know the forms of \( G_n \) and \( U_n \).
Generation and Recombination

**Generation:** An electronic *excitation* event increasing the number of free carrier available to carry charge. Requires an input of energy provided by the vibrational energy of the lattice (phonons), light (photons) or the kinetic energy of another carrier. For solar cell, the most important generation is **photogeneration**, i.e. by the absorption of a photon.

![Diagram of generation and recombination](Image)

**Recombination:** An electronic *relaxation* event reducing the number of free carrier. Releases energy taken by the same mechanisms to those of generation. For every generation process there is an equivalent recombination process.
Only the excess recombination and generation rates are considered in the continuity equation, thermal generation is not included explicitly as a contribution to $G$. For band to band generation and recombination processes,

$$G_n^{\text{th}} = U_n^{\text{th}}$$
$$G_p^{\text{th}} = U_p^{\text{th}}$$

In thermal equilibrium,

$$U_n = U_p = U$$
$$G_n = G_p = G$$
What happens under illumination?

(1) As photon energy $< E_g$, photons are absorbed to increase the kinetic energy of mobile carriers or to generate phonons.

(2) At high carrier density the absorbed photons can promote electrons between localized states.

(3) As photon energy is near to $E_g$, band to band and localized state to band transitions are dominant.

(4) The photon may be scattered by interfaces and by inhomogeneities in non-uniform media.
Optical Processes in Two-Level System

Consider the interaction of a steady state light field with a two-level system. Assume the two energy levels are in quasi thermal equilibrium with quasi Fermi levels of $E_{Fp}$ and $E_{Fn}$.

Absorption of a photon to promote an electron

Relaxation of an electron with spontaneous photon emission

Photogeneration: The generation of mobile electrons and holes through the absorption of light in the semiconductor. It is the most important process in photovoltaic devices.

Absorption of a photon to result in relaxation and stimulated photon emission
Light Absorption

Macroscopic absorption coefficient ($\alpha$): the sum of the absorption cross section per unit volume of material for the various optical processes. It describes how the light intensity is attenuated on passing through the material.

$$\frac{dI(x)}{dx} = -\alpha I(x)$$

For a material of non-uniform $\alpha$ the intensity at a depth $x$, is given by

$$I(x) = I(0) \exp \left[ -\int_0^x \alpha(E, x') dx' \right]$$

$I(0)$ is the intensity just inside the interface. For uniform $\alpha$, that is the simple Beer-Lambert law.

$$I(x) = I(0) \exp(-\alpha x)$$
Photogeneration

Assume all photons absorbed are to generate free carriers, the spectral photogeneration rate, per unit volume, at a depth $x$ below the surface is

$$g(E,x) = [1 - R(E)] \alpha(E) b_s(E) \exp\left[-\int_0^x \alpha(E,x')dx'\right]$$

In the case of absorption by excitons or sensitizers, the optical generation rate is

$$g(E,x) = [1 - R(E)] \eta_{diss}(E) \alpha(E) b_s(E) \exp\left[-\int_0^x \alpha(E,x')dx'\right]$$
Photogeneration and Thermalization

Photogeneration does not depend on the energy of the absorbed photon, except that the energy exceed the band gap. Higher energy photons generate carriers with higher kinetic energy. But that energy is quickly lost and only $E_g$ of potential energy remains to be collected.

The important quantity is the number of excitation events and not the amount of energy absorbed. It is the essential difference between photovoltaic and solar thermal action.
Photogeneration and **Thermalization**

The photogenerated carriers lose any extra kinetic energy by thermalization or cooling. Microscopically, they undergo repeated collisions with the lattice, giving up some of their kinetic energy to produce a phonon while they decay into a lower energy state, until they are in thermal equilibrium with the ambient. Phonons are the means by which energy is carried away to the outside world.

Absorption of Semiconductors

Because of the requirement of phonon participation in order to satisfy the conservation of momentum, the absorption coefficient of an “indirect” gap semiconductor is normally small. The probability of finding a phonon of energy $E_p$ is given by Bose-Einstein statistics:

$$f_p = \frac{1}{\exp\left(\frac{E_p}{k_B T}\right) - 1}$$

In amorphous material, the lack of long-range order means that crystal momentum need not be conserved in an optical transition. The band gap is always “direct”. e.g. the absorption coefficient is larger in amorphous than in crystalline silicon.
Absorption of Semiconductors

The absorption coefficient for a direct band gap semiconductor,\[
\alpha(E) = \alpha_0 \left( E - E_g \right)^{1/2}
\]
\(\alpha_0\) is a material dependent constant. For indirect band gap semiconductor, \[
\alpha(E) = \alpha_0 \left( E - E_g \right)^2
\]

**Absorption length**: the distance light of a particular wavelength must travel before intensity is attenuated by a factor \(e\) (~63%).

**Reflectivity** has not been treated explicitly above. For typical semiconductor, \(R(E)\) is ~30-40% at visible wavelength, which can be reduced by using anti-reflection coating or surface texturing.
Absorption edge for the direct band gap semiconductors GaAs is sharper than for the indirect band gap materials, silicon and germanium.
a, Multiphoton absorption. b, Free-carrier absorption. c, Impact ionization. d, Carrier distribution before scattering. e, Carrier–carrier scattering. f, Carrier–phonon scattering. g, Radiative recombination. h, Auger recombination. i, Diffusion of excited carriers. j, Thermal diffusion. k, Ablation. l, Resolidification or condensation.
Recombination

**Recombination:** the loss of mobile electrons or holes by certain removal mechanisms. For a photovoltaic device, several different recombination mechanisms may be dominant at the same time.

Unavoidable recombination process: Spontaneous emission (or Radiative recombination) and Stimulated emission (Auger recombination).

Avoidable recombination process: Trap state mediated non-radiative recombination.
Radiative Recombination

In a non-degenerate semiconductor, as $E-\Delta\mu>>k_B T$, to a good approximation the radiative recombination rate is

$$U_{rad} = B_{rad}(np - n_i^2)$$

Where the radiative recombination coefficient (carrier density independent)

$$B_{rad} = \frac{1}{n_i^2} \frac{2\pi}{h^3 c^2} \int_0^\infty n_s^2 \alpha(E) \exp\left(-\frac{E}{k_B T}\right) E^2 dE$$

As $B_{rad}$ is larger for materials with high $\alpha(E)$, radiative recombination is more important in direct band gap materials. In addition, radiative recombination from either band to impurity states inside the band gap can be dominant over band to band events.

Radiative recombination of an electron via localized states
Radiative Recombination

For doped materials, the radiative recombination rate is proportional to the excess minority carrier density.

\[ U_{rad} = \frac{n - n_0}{\tau_{n,rad}} \quad \text{(for p-type material)} \quad \tau_{n,rad} = \frac{1}{B_{rad} N_a} \]

\[ U_{rad} = \frac{p - p_0}{\tau_{p,rad}} \quad \text{(for n-type material)} \quad \tau_{p,rad} = \frac{1}{B_{rad} N_d} \]

\( \tau \) is the minority carrier radiative lifetime, which can be measured from time-resolved fluorescence spectrum. \( N_a \) and \( N_d \) are the doping densities of p- and n-type materials, respectively.

Radiative recombination is unimportant for practical cells at operating point. But in the limit of perfect of perfect material it is the mechanism which limits efficiency.
Auger Recombination

For band-to-band Auger recombination, an electron and two holes or a hole and two electrons are involved.

\[ U_{\text{Aug}} = A_p \left( n^2 p - n_0^2 p_0 \right) \]
\[ U_{\text{Aug}} = A_n \left( n p^2 - n_0 p_0^2 \right) \]

Auger process are most important where carrier densities are high. e.g. in low band gap and doped materials, or at high temperature.
Auger Recombination

The rate dependence on doping density is strong. For a doped material, the minority carrier lifetime for band-to-band Auger recombination:

\[ \tau_{n,\text{Aug}} = \frac{1}{A_n N_a^2} \]

\[ \tau_{p,\text{Aug}} = \frac{1}{A_p N_d^2} \]

Auger events conserve **momentum and energy**. So Auger recombination can occur in indirect band gap material, unlike the radiative recombination is suppressed. It is therefore much **more important in indirect** than direct band gap materials. It is the dominant loss mechanism in very pure Si and Ge.
Shockley Read Hall Recombination

**Shockley Read Hall (SRH) recombination:** Trap assisted recombination. 
*By far the most important recombination processes in real semiconductors.*

![Diagram of Shockley Read Hall Recombination]

Localized states serving mainly to capture and release one type of carrier are usually called **traps**. Those capturing both types of carriers are called **recombination centers**.

Recombination centers usually lie deeper into the band gap than traps.
Shockley Read Hall Recombination

Consider a semiconductor containing a density $N_t$ trap states at an energy $E$ in the band gap. Empty traps can capture electrons from the CB, and filled traps can capture holes from the VB. The rates at which electrons and holes are captured are

$$U_{nc} = B_n n N_t (1 - f_t) \quad B_n = \nu_n \sigma_n \quad \tau_{n,SRH} = 1/B_n N_t$$

$$U_{pc} = B_p p N_t f_t \quad B_p = \nu_p \sigma_p \quad \tau_{p,SRH} = 1/B_p N_t$$

$\nu$ is the mean thermal velocity and $\sigma$ the capture cross section of the trap for electrons and holes. By considering equilibrium state, the rates at which electrons and holes are released are

$$G_{nc} = B_n n_t N_t f_t$$

$$G_{pc} = B_p p_t N_t (1 - f_t)$$

$n_t$ and $p_t$ are the electron/hole densities when the electron/hole Fermi levels are equal to the trap level.

In the steady state, the net rate of electron capture ($U_{nc} - G_{nc}$) by the traps must be equal to the net rate of hole capture ($U_{pc} - G_{pc}$), where $f_t$ can be calculated.
Shockley Read Hall Recombination

The net recombination rate \( (U_{nc}-G_{nc}) \) or \( (U_{pc}-G_{pc}) \) for trap-assisted (SRH) recombination is given by:

\[
U_{SRH} = \frac{np-n_i^2}{\tau_{n,SRH}(p+p_t)+\tau_{p,SRH}(n+n_t)}
\]

For doped semiconductors, for p-type material, \( p>>n \), provided that \( \tau_n N_a \gg \tau_p n_t \) and \( N_a \gg p_t \), \( U_{SRH} \) simplifies and becomes proportional to the excess minority carrier density,

\[
U_{SRH} \approx \frac{n-n_0}{\tau_{n,SRH}} \quad (p \gg n)
\]

\[
U_{SRH} \approx \frac{p-p_0}{\tau_{p,SRH}} \quad (n \gg p)
\]

Similarly for n-type material.
Surface and Grain Boundary Recombination

If a surface contains a density \( N_s \) traps per unit area, within a very thin layer \( \delta_x \) around the surface, the surface recombination flux will be

\[
U \delta x = \frac{n_s p_s - n_i^2}{\frac{1}{S_n} (p_s + p_t) + \frac{1}{S_p} (n_s + n_t)}
\]

per unit area, where \( n_s/p_s \) are electron/hole densities at the surface. \( S_n/S_p \) are the surface recombination velocity for electrons/holes.

In doped material, the recombination flux simplifies. The leakage of minority carriers to the surface results in a surface recombination current.

\[
U \delta x \approx S_n (n_s - n_0)
\]

\[
U \delta x \approx S_p (n_s - n_0)
\]
Traps vs. Recombination Centers

When a carrier is captured by a trap, it may then be released or it may be annihilated by the capture of the opposite type of carrier. When the time for electron release by thermal activation

$$\frac{1}{\tau_{esc}} = B_n n_i \exp\left( \frac{E_t - E_i}{k_B T} \right)$$

is much shorter than the time for capture of a hole

$$\frac{1}{\tau_{cp}} = B_p p$$

the state can be considered an electron trap rather than a recombination center. This may happen if the state is close in energy to the CB edge, or if the cross section for electron capture is much larger than for hole capture.

Traps serve to slow down the transport of carrier but they do not remove them.
Transport Equation

Now we could solve continuity equation and Poisson’s equation

\[
\frac{\partial n}{\partial t} = \frac{1}{q} \frac{\partial J_n}{\partial x} + G_n - U_n
\]

\[
\frac{\partial p}{\partial t} = -\frac{1}{q} \frac{\partial J_p}{\partial x} + G_p - U_p
\]

\[
\nabla^2 \phi = \frac{q}{\varepsilon_s} \left( -\rho_{\text{fixed}} + n - p \right)
\]

If we know \(a(E,x), R(E),\) and \(b_s(E)\) for \(G(x)\) and provide the sum of all the recombination processes--radiative \((B_{\text{rad}})\), Auger (Auger coefficient), and trap assisted--as a function of \(n, p, \phi\) and \(x\).
Steady State Transport

Since solar cells operate in the steady state we are usually interested in the case where

\[ \frac{\partial n}{\partial t} = \frac{\partial p}{\partial t} = 0 \]

and

\[ 0 = \frac{1}{q} \frac{\partial J_n}{\partial x} + G_n - U_n \]

\[ 0 = -\frac{1}{q} \frac{\partial J_p}{\partial x} + G_p - U_p \]

In the steady state, the electron and hole densities in each band and in localized states must be constant. This means that the generation and capture terms for the exchange of carriers *between band and trap states* much cancel out, and so trapping can be left out of the continuity equation. As a consequence, the generation and recombination processes are all effectively band-to-band: \( G_n = G_p \) and \( U_n = U_p \).
Photon recycling: The above assumed that the density of photons at a point is determined solely by the absorption within the material. As the density of photons resulting from radiative recombination is not negligible, a further continuity equation is required for photons.

**Transport in 1D Crystal**

As

\[ J_n(x) = qD_n \frac{dn}{dx} + q\mu_n Fn \]

For a 1D crystalline material in the steady state, the transport equation

\[
D_n \frac{d^2 n}{dx^2} + \mu_n F \frac{dn}{dx} + \mu_n n \frac{dF}{dx} - U + G = 0
\]

\[
D_p \frac{d^2 p}{dx^2} + \mu_p F \frac{dp}{dx} + \mu_p p \frac{dF}{dx} - U + G = 0
\]
Transport in 1D Crystal

For a doped material,

1. as one carrier type greatly exceeds the other, the recombination rate

\[ U \approx \left( n - n_0 \right) / \tau_n \]

2. as electric field \( F \) is zero or constant,

the transport equation for minority carriers

\[
\frac{d^2 n}{dx^2} + \frac{qF}{k_B T} \frac{dn}{dx} - \frac{n - n_0}{L_n^2} + \frac{G(x)}{D_n} = 0 \quad \text{(electrons in the p region)}
\]

\[
\frac{d^2 p}{dx^2} + \frac{qF}{k_B T} \frac{dp}{dx} - \frac{p - p_0}{L_p^2} + \frac{G(x)}{D_p} = 0 \quad \text{(holes in the n region)}
\]

Where we used the Einstein relation \( \mu = qD / k_B T \), and

\[
L_n = \sqrt{\tau_n D_n}
\]

\[
L_p = \sqrt{\tau_p D_p}
\]
Summary

- **Photo absorption** and **photogeneration** in direct and indirect band gap materials.

- **Recombination**: Radiative, Auger, trap assisted recombination in the bulk or at the surface.

- **Continuity equation**

\[
\frac{\partial n}{\partial t} = \frac{1}{q} \frac{\partial J_n}{\partial x} + G_n - U_n
\]