ME 432 Fundamentals of Modern Photovoltaics

Discussion 12: Carrier Thermalization

21 September 2020
Summary: Light Absorption & Thermalization

Let’s consider the optimal band gap solar cell:

\[ \eta_{\text{total}} = \eta_{\text{absorption}} \times \eta_{\text{excitation}} \times \eta_{\text{transport}} \times \eta_{\text{separation}} \times \eta_{\text{collection}} \]

So how does the energy loss break down for this optimal band gap system?

- Absorption: 18% of incoming energy is not absorbed
- Thermalization: 47% of the incoming energy is lost as heat
- Transport, Separation, Collection: 2% of the incoming energy must be lost through recombination (thermodynamics … we haven’t gotten there yet)
- Leaving us with 33%

\( E_{\text{gap}} \sim 1.2-1.3 \text{ eV} \)
Learning Objectives: Carrier Excitation & Thermalization

1. **Describe what phonons are.**
2. Calculate the fraction of incident solar energy lost to “thermalization.”
3. Considering the effects of light absorption and thermalization, plot efficiency vs. bandgap, and denote specific materials on the figure (homework).
4. What is meant by direct and indirect semiconductor? What are the implications of direct and indirect absorption for PV cells?
5. Explain, using $E$ vs. $k$ diagrams, why direct absorbers are more efficient absorbers of sunlight.
6. Describe some implications of the use of direct vs. indirect semiconductors on solar cells.
What are phonons?

- Phonons are the quanta of crystal lattice vibrations (particle picture)
- A particular crystalline solid possesses a characteristic set of normal vibrational modes: phonons of different wavelengths and directions (wave picture)
What are phonons?

• At any finite temperature $T>0K$, there is an equilibrium population of phonons living in a crystal
• As temperature increases, the phonon population increases
• As the crystal vibrates, it is dissipating heat to the environment
• Whereas we said that photons (light waves) have large energy and small momentum, phonons are the opposite: small energies, large momentum
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Thermalization: Our Second Big Source of Loss in a PV cell
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1. A photon of energy larger than the band gap strikes an electron in a semiconductor.

$E_{ph} > E_g$
Conduction band

Valence band

2. Absorption of the photon results in promotion of the electron from the valence band to the conduction band, creating two free carriers (a hole in the valence band and an electron in the conduction band)

Thermalization: Our Second Big Source of Loss in a PV cell
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3. Thermalization: Within picoseconds, the crystal vibrations result in the scattering of the free carrier electron and hole to the conduction and valence band edges.

Consequently, for the photon of energy $E_{ph}$ provided by the sun:

a. only $E_g$ ends up stored in the semiconductor
b. $E_{ph} - E_g$ is dissipated as heat to the environment
Question: Why does the hole go “up” during thermalization?
Answer: A hole going “up” in the valence band corresponds exactly to an electron going “down” in the valence band, and hence represents an energy loss.
• In a semiconductor of band gap $E_g$, for every photon of energy $E_{ph}$ that is absorbed, thanks to thermalization losses:
  – only a fraction ($E_g / E_{ph}$) of the photon’s energy is stored in the semiconductor and can be converted to useful energy (electricity)
  – the rest of the photon’s energy is dissipated to the environment through lattice vibrations

• To minimize thermalization losses, we want to use as large gap a semiconductor as possible
Timescale of Thermalization

Key concept: There is virtually nothing we can do about it. Thermalization happens too fast.

Fig. 4. Energy relaxation of carriers after a short, high-intensity laser pulse at $t = 0$.

M.A. Green, Physica E 14, 65 (2002)
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Theoretical Efficiency vs. Band Gap

- The figure below shows that maximum theoretical efficiency of a solar cell as a function of its band gap.
- You will calculate this as part of your homework assignment.

For small band gaps, efficiency is limited by thermalization losses.

For large band gaps, efficiency is limited by losses due to non-absorption of the solar spectrum.

The tradeoff between thermalization and non-absorption losses results in the optimal band gap of a semiconductor of approximately 1.2 eV, and a maximum theoretical efficiency of close to 30%.
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Due to the absorption that takes place, the intensity of a light wave propagating through a material decays exponentially as it travels.

The parameter $\alpha$ describes how quickly the exponential decay occurs. $\alpha$ is known as the absorption coefficient, and is a material property that also depends on the wavelength.
Optical Absorption in Semiconductors

After: http://pveducation.org/pvcdrom/pn-junction/absorption-coefficient

Steep Absorption Edge: “Direct Semiconductors”

Shallow Absorption Edge: “Indirect Semiconductors”
**Direct vs. Indirect Semiconductors**

- Depending on how sharp the transition in the absorption coefficient is, we categorize our semiconductors into two categories:
  - **Direct** semiconductors: sharp onset of absorption
  - **Indirect** semiconductors: shallow onset of absorption
- Whether a semiconductor is direct or indirect has serious implications for how thick a solar cell made from that semiconductor must be
  - Example: photovoltaics made of indirect semiconductors like silicon must be quite thick (100’s of µm) to absorb sufficient quantities of the solar spectrum
  - On the other hand, direct gap semiconductors (GaAs, CdTe, etc) will generally absorb 99% of an incident AM1.5 spectrum within a few µm.
  - Typical silicon solar cell thickness: 300µm, typical CdTe solar cell thickness: 2 µm.
Silicon: Not a Great Absorber

Cross-section of solar cell:

300 µm Si absorber layer

Image Credit: Q-Cells
Silicon : Not a Great Absorber

cross-section of solar cell:

300 µm Si absorber layer

$e^- - h^+$

Image Credit: Q-Cells
Silicon: Not a Great Absorber

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Cross-section of solar cell:

Image Credit: Q-Cells
Silicon: Not a Great Absorber

Key concept: The thicker the absorber layer is, the farther the electron and hole have to travel before they reach the top/bottom metal contacts and can be extracted into an external circuit. The thicker the absorber layer is, the more opportunity that something will go wrong (recombination) before the electron and hole can be extracted.
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What determines whether a semiconductor is a direct or indirect absorber?

• To answer this question, we need to become familiar with something called “E vs. k” diagrams, or “electronic band structure diagrams”
• These are simply diagrams showing the available states for electrons to occupy – now including energy and momentum
• E stands for “energy” of the electron and k stands for “crystal momentum” of the electron
• Let’s look at a few examples
• P.S. Congratulations. This is as deep into quantum mechanics as we are going to get in the class. If you’ve made it this far, you’re good to go!
Electronic Band Structure of Silicon

- Valence Band (filled)
- Conduction Band (empty)
- $E_{\text{gap}}$
Electronic Band Structure of Silicon

- Valence band maximum (VBM)
- Conduction band minimum (CBM)

Based on the plot, the energy difference between the VBM and the CBM is around 1.1 eV.

This number does, indeed, correspond to the band gap of Silicon.

Notice that the VBM and the CBM occur at different values of $\vec{k}$.

Because of this, silicon is known as an indirect gap semiconductor.
Electronic Band Structure of GaAs

Conduction Band (empty)

Valence Band (filled)

$E_{\text{gap}}$
Based on the plot, the energy difference between the VBM and the CBM is around 1.4 eV. This number does, indeed, correspond to the band gap of GaAs. Notice that, unlike Si, the VBM and the CBM occur at the same value of \( \vec{k} \). Because of this, GaAs is known as a \textbf{direct} gap semiconductor.
Electronic Band Structure of Ge

- Conduction band minimum (CBM)
- Valence band maximum (VBM)
- Ge is an indirect gap semiconductor

$E_{\text{gap}} = 0.66 \text{ eV}$
Electronic Band Structure of InP

InP is a direct gap semiconductor.
What are these E vs. k diagrams?

• every single point corresponds to an electronic state ($\psi$) that can be occupied by two electrons
• each electronic state ($\psi$) is differentiated from the others by two parameters: k,n
• “k” is the k-vector, “n” is the number of the band, counting up from the bottom
• An electron occupying the state $\psi_{n,k}$ has an energy E
• There is also a charge distribution associated with each state $\psi_{n,k}$
Example: Electronic States in Silicon

The total charge distribution associated with all of the electronic states $\psi$ below the VBM calculated via DFT (density functional theory)
Direct vs. Indirect Semiconductors

generally, semiconductors are classified into two categories:

examples: InP, GaAs  Si, Ge
So why does the absorption coefficient $\alpha$ vary so much for a direct or indirect absorber?

- We’ve talked about two types of particles that can scatter electrons:

<table>
<thead>
<tr>
<th>Photons</th>
<th>Phonons</th>
</tr>
</thead>
<tbody>
<tr>
<td>quanta of electromagnetic radiation</td>
<td>quanta of crystal vibrations</td>
</tr>
<tr>
<td>Have high energy $E$</td>
<td>Have low energy $E$</td>
</tr>
<tr>
<td>Have small momentum $k$</td>
<td>Have large momentum $k$</td>
</tr>
</tbody>
</table>

- During a scattering process, both energy and momentum must be conserved
- Thus, light absorption in a direct semiconductor requires only photons
- And, light absorption in an indirect semiconductor requires a photon and a phonon, and is statistically less likely to occur
So why does the absorption coefficient $\alpha$ vary so much for a direct or indirect absorber?

A direct transition requires only a change in energy $\Delta E$, and a photon is sufficient to do the job.

An indirect transition requires a change in energy $\Delta E$ and momentum $\Delta k$, and thus a photon and a phonon must be involved.
So why does the absorption coefficient $\alpha$ vary so much for a direct or indirect absorber?

- Now we know why direct gap semiconductors are much better absorbers of light. Only a photon is needed to provide the $\Delta E$ for the transition from the VBM to the CBM to take place. For any photon with energy exceeding the gap, absorption can place very efficiently ($\alpha$ is large).
- On the other hand, indirect semiconductors need a photon to provide the $\Delta E$ and a phonon to provide the $\Delta k$ for a transition from the VBM to the CBM to occur. Since the process requires two particles, it is much less likely to occur. Absorption may or may not take place, even for photons with energy exceeding the gap ($\alpha$ is small).
- Thus, solar cells made from indirect semiconductors need to be thicker because we need to provide more opportunities for the transition to take place.
- Question. For which type of semiconductor – direct or indirect – is absorption more temperature dependent? Why?
Temperature Dependence of Absorption Coefficient in Indirect Semiconductors

After Grosso and Pastori-Parravicini, Solid State Physics

Answer. Absorption in indirect semiconductors is temperature-dependent, because phonons are needed and phonon population depends on temperature.
Example: Silicon

Show where absorption occurs due to indirect transitions; show where absorption occurs due to direct transitions.

http://www.ioffe.ru/SVA/NSM/Semicond/Si/Figs/145.gif
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Implications - Summary

• Direct gap materials can be thinner and still absorb most of the incident light. They are good candidates for thin films. Because crystalline Silicon has an indirect gap, the absorbing layer needs to be thicker (e.g. 300 µm thick Si wafers)

• Radiative recombination is $10^3$-$10^4$ times faster in direct gap materials than indirect. (However, it is typically non-radiative, rather than radiative, recombination that is limits real device performance)

• Absorption coefficient $\alpha(\lambda)$ is more strongly dependent on temperature for indirect gap semiconductors (since phonon population is strongly dependent on temperature)

• Thermalization happens ... whether direct or indirect. Since it takes place through the emission (rather than absorption) of phonons, direct/indirect doesn’t matter.