Lecture 13
Solar Cells
Schroder: Chapter 4.4

Announcements

Homework 3/6:
• Is online now.
• Due Monday May 14th at 10:00am.
• I will return it the following Monday (21st May).

Homework 4/6:
• Will be online 14th May.
• Due Monday May 21st at 10:00am.
• I will return it the following Monday (28th May).
Lecture 13

• Motivation for Solar Energy.
• Basics of Solar Power Conversion
• Carrier Generation.
• Carrier Extraction.
• Device Characterization.
• Solar Cell Devices.
• Advanced Topics.

The Need for Solar
Global Power Demands

- Current global power demand ~16 TW.
- Projected to be ~30 TW by 2050.
- How are we going to supply this power?
- Fossil fuels have been very useful getting us where we are, but are unlikely to be a long term solution.

Sustainable Power Sources

- Potential Global Capacity:
  - Wind: 2-4 TW
  - Biomass: 5-7 TW
  - Tidal: 2 TW
  - Geothermal: 10 TW
  - Hydro: 5 TW
  - Solar: $10^5$ TW
How About Photosynthesis?

- The easiest way to capture solar energy is via plants.
- Grow them, harvest them, burn them.

• This would only be ~0.3% efficient (photon energy in / usable energy out).

Silicon Solar Cells

• Nowadays we can do significantly better than nature:

• Typical silicon solar cells are approximately 25% efficient.
Installed Capacity is High

- Installation rate has consistently beaten expectations.

Driven by Cost

- The cost of solar power is dropping.
- $0.30 / Watt in 2015.
- Driven by research into renewables over the past few decades.
Solar Farms Now Economic

• Dubai (2016):

• Morocco (2017):

What About Storage?

• Storage remains more expensive than solar production.
• But this is partially because it has not been industrially scaled.
• Tesla Gigafactory (near Reno NV):
What About Storage?

- Tesla sells commercial batteries for home storage / going off-grid.
- But they are targeting utility-scale storage.
- Installed “Mega Battery” in Hornsdale Australia.
  - 129 Mwh capacity.

Basics of Solar Power Conversion
Photoelectric Effect

- The photoelectric effect was first experimentally discovered in 1839 by Becquerel.
- He found that if you shine light on one of these electrodes, you could generate a voltage.

\[ E = hf \]

- Metals have a property called work function \( \phi \) (units of energy).
- If \( E > \phi \), electrons can be emitted.
Work Function

- Consider the band picture of a metal:

\[ E = 0 \]

Vacuum Energy

Electrons above here are free

\[ h\nu > \phi \]

<table>
<thead>
<tr>
<th>Metal</th>
<th>( \phi ) (eV)</th>
<th>( \lambda ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>4.26-4.74</td>
<td>262-291</td>
</tr>
<tr>
<td>Au</td>
<td>5.10-5.47</td>
<td>226-243</td>
</tr>
<tr>
<td>Al</td>
<td>4.06-4.26</td>
<td>291-305</td>
</tr>
<tr>
<td>Ca</td>
<td>2.87</td>
<td>432</td>
</tr>
<tr>
<td>Cu</td>
<td>4.53-5.10</td>
<td>243-274</td>
</tr>
<tr>
<td>Pd</td>
<td>4.25</td>
<td>292</td>
</tr>
</tbody>
</table>

Solar Spectrum

- What light do we receive from the sun?
Illuminating Semiconductors

- Consider the band picture:

\[ E_{CBM} \] \[ E_{VBM} \]

\[ \text{Conduction Band Minimum} \]
\[ \text{Valence Band Maximum} \]

\[ h_\nu > E_G \]

\[ E_G = E_{CBM} - E_{VBM} \]

- Carriers are excited across the band gap:

\[ E_G \]

Carrier Generation
Charge Generation

- Charge generation in semiconductors is a complex topic (beyond the scope of this lecture).
- We can broadly describe the absorption properties via quantum efficiency:
- External Quantum Efficiency (EQE):
  \[ EQE = \frac{\text{Carriers Created}}{\text{Photons Incident}} \]
- Internal Quantum Efficiency (IQE):
  \[ IQE = \frac{\text{Carriers Created}}{\text{Photons Absorbed}} \]

Charge Generation

- Absorption if characterized through optical spectroscopy.
  - Direct band gap semiconductors e.g. GaAs, CdTe, just require photon.
  - Indirect band gap semiconductors e.g. Si, CIGS, also require a phonon for absorption to occur.

Excitons

- In some materials (e.g. Si, GaAs, perovskites) free carriers are generated directly in material.

- However often free carrier pairs are not generated directly.
- Instead what is termed an exciton is created.
  - A quasi-particle that exists only in solids.
  - Electron and hole remain bound.
  - They are better described by a single wavefunction.
Excitons

- The physical description is as follows:
  - Light generates an electron and a hole.
  - They separate (conservation of momentum).
  - Positively charged hole distorts electrons in the lattice.
  - This provides screening/repulsion to free electron.
  - Equilibrium occurs with a binding energy ($E_B$).
- Thermal energy ($k_B T$) required to collapse charges.

Thermalization

- To excite carriers in a semiconductor, the energy of incoming photons needs to be equal to, or in excess of, the band gap.

- What happens to this excess energy?
Thermalization

• The behaviour of carriers depends on the material properties.

• But generally carriers “thermalize” very quickly (~ps) in solar materials.

• Scattering events:
  • Ionized Impurity.
  • Phonons.
  • Band-to-band impact ionization.

So energy above the band gap is normally wasted.

• Every photon above band gap will provide same energy as one at band-gap.
Extracting Carriers

- Creating charge carriers is not enough – we need to be able to extract them before they recombine.
Extracting Carriers

• The average time carriers live for is parameterised by the lifetime $\tau$.
• In reality, there are several processes, each of which depend on the carrier density in a different way:

Monomolecular

Bimolecular

Auger

The rate of change of total carrier density ($n$ is holes and electrons) can be described by:

$$\frac{dn}{dt} = nk_1 + n^2k_2 + n^3k_3$$
Extracting Carriers

• Carriers also need to be able to make it to the electrodes before they recombine (i.e. in time $\tau$):

\[ \begin{align*}
\text{Cathode} & \quad \text{Anode} \\
 & \quad V
\end{align*} \]

Extracting Carriers

• To determine how far carriers can move before recombination we need to know their “velocity”.

• In reality, we use velocity normalised for electric field strength, i.e. mobility:

\[ \mu = \frac{v}{E} \]

Charge carrier mobility

Electric field strength

Carrier velocity
Extracting Carriers

- With a knowledge of carrier lifetime and mobility we can evaluate the **diffusion length**:

\[ L = \frac{k_B T}{e \mu \tau} \]

- This quantifies the average distance that carrier can travel before they recombine.
- Informs on how thick we can make our cells.

Example

- Diffusion length in silicon with phosphorus concentration:

Del Alamo and Swanson, Sol. State. Electron. 30 (1987) 1127
Device Characterization

IV Characteristics

- A solar cell is just a diode.
- The circuit is typically modelled by the following circuit:

\[ I_{ph} - R_S - R_{SH} - R_L \]

\[ V \]

Photogenerated Current

Series Resistor

Cell

Load Resistor

Shunt Resistor

Applied Bias

Graph:

- Dark
- Light

\[ J (\text{mA/cm}^2) \]

\[ V (\text{V}) \]
IV Characteristics

- The IV characteristics are described as follows:

\[ I = I_{ph} - I_0 \left[ \exp \left( \frac{eV + IR_S}{nk_BT} \right) - 1 \right] - \frac{V + IR_S}{R_{SH}} \]

- An ideal solar cell would have:
  - \( R_{SH} = \infty \)
  - \( R_S = 0 \)

- Giving:

\[ I = I_{ph} - I_0 \left[ \exp \left( \frac{eV}{nk_BT} \right) - 1 \right] \]
Short-Circuit Current

- The short-circuit current is defined as the current that flows when $V = 0$, and is labelled $I_{SC}$.

$$J_{SC} = eG(L_e + L_h)$$

$G =$ Carrier generation rate

$L_e =$ Electron diffusion length

$L_h =$ Hole diffusion length

- The short-circuit current is dependent on how quickly we generate carriers in the cell, and how well we can extract them.

- It can be approximated by:

- The short circuit current is a property of the solar cell material and design.
Short-Circuit Current

\[ I = I_{ph} - I_0 \left[ \exp \left( \frac{eV + IR_S}{nk_BT} \right) - 1 \right] - \frac{V + IR_S}{R_{SH}} \]

- If \( V = 0 \), we label the current \( I_{sc} \):
  \[ I_{sc} = I_{ph} - I_0 \left[ \exp \left( \frac{I_{sc}R_S}{nk_BT} \right) - 1 \right] - \frac{IR_S}{R_{SH}} \]

- If we can approximate series resistance \( R_S = 0 \):
  \[ I_{sc} = I_{ph} \]

- I.e. the short circuit current for an ideal solar cell is just the photo-generated current

Open-Circuit Voltage

- The voltage that occurs when the current from the solar cell is zero.

\[ V_{OC} \]

The open circuit voltage \( V_{OC} \) is the maximum voltage from a solar cell and occurs when the net current through the device is zero.

http://www.pveducation.org/pvcdrom/open-circuit-voltage
Open-Circuit Voltage

• The open circuit voltage is again due to the material properties and device design.

\[ I = I_{ph} - I_0 \left[ \exp \left( \frac{eV + IR_S}{nk_BT} \right) - 1 \right] - \frac{V + IR_S}{R_{SH}} \]

• The open circuit voltage \((V_{oc})\) can be found by setting \(I = 0\):

\[ 0 = I_{ph} - I_0 \left[ \exp \left( \frac{eV_{oc}}{nk_BT} \right) - 1 \right] - \frac{V_{oc}}{R_{SH}} \]

\[ \frac{V_{oc}}{R_{SH}} = I_{ph} - I_0 \left[ \exp \left( \frac{eV_{oc}}{nk_BT} \right) - 1 \right] \]

Open-Circuit Voltage

\[ \frac{V_{oc}}{R_{SH}} = I_{ph} - I_0 \left[ \exp \left( \frac{eV_{oc}}{nk_BT} \right) - 1 \right] \]

• If we have infinite shunt resistance \((R_{SH} = \infty)\):

\[ 0 = I_{ph} - I_0 \left[ \exp \left( \frac{eV_{oc}}{nk_BT} \right) - 1 \right] \]

\[ I_{ph} = I_0 \left[ \exp \left( \frac{eV_{oc}}{nk_BT} \right) - 1 \right] \]

\[ \frac{I_{ph}}{I_0} + 1 = \exp \left( \frac{eV_{oc}}{nk_BT} \right) \]

\[ V_{oc} = \frac{nk_BT}{e} \ln \left( \frac{I_{ph}}{I_0} + 1 \right) \]
Fill Factor

- The solar cell is operated when the power \((IV)\) is a maximum.
- We define this as the maximum power point \((I_{mp} \text{ and } V_{mp} \text{ respectively})\).

\[
\frac{d(IV)}{dV} = 0
\]

- In the case that \(R_S = 0\) and \(R_{SH} = \infty\), this can be shown to be:

\[
V_{mp} = V_{oc} - \frac{n k_B T}{e} \ln \left[ \frac{e V_{mp}}{n k_B T} + 1 \right]
\]
Fill Factor

- The so-called fill-factor ($FF$) is a parameter used in the determination of solar cell efficiency:

$$FF = \frac{V_{mp}I_{mp}}{V_{oc}I_{sc}}$$

- Typically this is evaluated numerically from measured data:

It can also be interpreted visually as the "squareness" of the current-voltage characteristics.
Solar Cell Efficiency

• Despite being difficult to evaluate from first-principles, $FF$, $V_{oc}$ and $J_{sc}$ are all reasonably easy to evaluate from real solar cell data.

• With a knowledge of the incident optical power density $P$, we can then evaluate the efficiency of the solar cell:

\[
\eta = \frac{V_{oc}J_{sc}FF}{P}
\]

• The power density depends on location, but typically we consider “1 sun” as $P = 100 \text{ mW/cm}^2$.

Solar Cell Devices
**PN-Junctions**

- Even with long diffusion lengths, charge extraction in solar cells is not efficient.

- The in-built electric field of a pn junction aids separation of charges.

- This is the strategy taken by silicon solar cells.

**Organic Semiconductors**

- Organic Semiconductors are of interest because they can be processed cheaply and over large areas.
Organic Semiconductors

- However they have very short carrier diffusion lengths ($L \sim 10$ nm) so pn junctions have to be designed in different ways.
- A so-called bulk heterojunction involves inter-penetrating p and n networks, with separation length scales of $\sim 10$nm.
- Understanding and controlling morphology is crucial in the field.

Charge Blocking Layers

- Selectivity of contacts can be improved by using hole-blocking layers or electron-blocking layers.
- Ensures correct carriers exit through the correct contact.
- Basically these layers act as “carrier filters.”
Dye-Sensitized Solar Cells

- Essentially a combination of electrical and electrochemical reactions.
- A highly absorbing dye on an electron-conducting oxide (e.g. TiO$_2$) scaffold absorbs light.
- Electron is transported via TiO$_2$ to electrode.
- The hole is transferred to an electrolyte solution.
- Undergoes redox reaction and transported to other electrode.

Hybrid Halide Perovskites

Remarkable Properties

- Low effective mass: ($m_e^* \sim m_h^* \sim 0.1m_e$).\textsuperscript{[1]}
- High in-grain structural order.\textsuperscript{[2]}
- Small Urbach tail energy ($\sim 15$ meV).\textsuperscript{[3]}
- Low density of trap states ($\sim 10^{10}$ cm$^{-3}$).\textsuperscript{[3]}
- Moderate measured carrier mobilities ($\sim 100$ cm$^2$/Vs).\textsuperscript{[4]}
- High calculated mobilities ($\sim 10^3$ cm$^2$/Vs).\textsuperscript{[5]}

\textsuperscript{[1]} Miyata et al. Nat. Phys. 11 (2015) 582
\textsuperscript{[2]} Etgar et al. JACS 134 (2012) 17396
\textsuperscript{[4]} Semonin et al. JPCL 7 (2016) 3510
\textsuperscript{[5]} Wang et al. PCCP 18 (2016) 22188
Other Technologies

- Copper indium gallium selenide (CIGS).

- Cadmium Telluride (CdTe).

Current Records

https://www.nrel.gov/pv/assets/images/efficiency-chart.png
Advanced Topics

Multi-Junction Solar Cells

- Layer multiple solar cells on top of each other.
- Each layer overlaps with different region of solar spectrum.
- Avoids losing energy of high-energy photons.
Solar Concentrators

• Using a lenses / mirrors to focus more light onto your solar cell.

• Basically the same as making a bigger cell, without paying for it.

Photon Recycling

• This is the observation that in some systems (GaAs and perovskites) photons emitted via radiative recombination (bimolecular) are not always lost.
Singlet Fission

- As the name implies, this is the strange observation that you can create two photons from one.
- This requires a particular energetic alignment, and has only been observed in organic semiconductors:

\[
\frac{|\uparrow - \downarrow|}{\sqrt{2}} \geq \frac{E_G}{2}
\]

- Potentially create a larger current (2×) from higher energy photons.
- Possible for ICE > 100%.

Rashba Effect

- This is the observation that in some semiconductors (e.g. perovskites) the band gap can be direct and indirect under different circumstances.
- This allows for fast (direct) absorption, and slow (indirect), emission of light.
- Can lead to very long carrier lifetimes.
Next Time...

• MOS Capacitors

\[ C_{\text{flatband}} \]

\[ C_{\text{ox}} \]

\[ V \]

\[ C_{\text{inv}} \]

ECE / ChE 613 – Electronic Materials Characterization
Spring 2018 - John Labram