Light Absorption, Charge Excitation and Transport

Lecture 3 – 2.626
Tonio Buonassisi
Semiconductor Fundamentals

I can explain a semiconductor bandgap to a layperson

Counts

T  F
Light Absorption
Photons – Quanta of Light

Quantum theory describes the frequency dependence of photon energy.

**Particle-wave duality:**
Photons have discrete quanta of energy.
Photons have momentum.
Light can be polarized.
Light can be diffracted.

Relevant Equations:

\[ E_{ph} = h\nu = \frac{hc}{\lambda} \]

\[ p_{ph} = \hbar k = \frac{h}{\lambda} \]
Photons – Transmission Through a Medium

Simple Derivation of Beer-Lambert’s Law:

\[
\frac{dI_z}{I_z} = -\sigma \cdot N \cdot d\bar{z}
\]

\[
\ln(I_z) = -(\sigma \cdot N \cdot \bar{z}) + C
\]

\[
\ln(I_0) - \ln(I_l) = -(\sigma \cdot N \cdot 0) + C + (\sigma \cdot N \cdot l) + C = \sigma \cdot N \cdot l
\]

\[
I = I_o \cdot e^{-\sigma \cdot l \cdot N} = I_o \cdot e^{-\alpha \cdot l}
\]
Photons – Transmission Through a Medium

\[ I = I_o \cdot e^{-\alpha \cdot l} \]

\( \alpha \) is a function of the wavelength of light, and property of the medium.
Photons – Interactions with Matter

Semi-classical (Bohr) model of the atom

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Photons – Interactions with Matter

Quantum model of the atom

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http://static.howstuffworks.com/gif/atom-quantum.jpg
http://media-2.web.britannica.com/eb-media/06/96906-004-FB4A8411.gif
High-Energy Photon-Matter Interactions

- At high energies (> 1keV), photons interact primarily with core electrons and nucleons.

\[
\begin{align*}
\tau & = \text{photoelectric interaction} \\
\sigma_{\text{coh}} & = \text{coherent scattering (Raleigh)} \\
\sigma_{\text{incoh}} & = \text{incoherent scattering (Compton)} \\
\kappa_n & = \text{pair formation from interaction with nuclear particle} \\
\kappa_e & = \text{pair formation from interaction with electron}
\end{align*}
\]

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http://xdb.lbl.gov/Section3/Image_Sec3/Sec3135.gif
http://xdb.lbl.gov/Section3/Image_Sec3/Sec3150.gif
Low-Energy Photon-Matter Interactions

- At low energies (~1 eV) typical for visible light, photons interact primarily with valence electrons.

http://www.humboldt.edu/~ccat/solarcooking/parabolic/parabolic_solar_cooker_pg_3.html.htm

Courtesy of Humboldt Campus Center for Appropriate Technology. Used with permission.
Absorption Coefficient ($\alpha$) for different materials

\[ I = I_0 \cdot e^{-\alpha l} \]

Absorption Coefficient of Semiconductor Materials

- GaAs
- InP
- Germanium
- Crystalline Silicon
- Amorphous Silicon

 Courtesy of Christiana Honsberg and Stuart Bowden. Used with permission.
Absorption Coefficient ($\alpha$) for different materials

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Sharp absorption onset.

Broad absorption onset.

(6.2 eV)  (0.62 eV)

wavelength, (nm)

Courtesy of Christiana Honsberg and Stuart Bowden. Used with permission.
Bandgap
Bandgap: Basic Description

Bonds: why stuff is tough.

Excited electrons: why materials conduct

- The “bandgap energy” can most simply be understood, as the finite amount of energy needed to excite a highly localized electron into a delocalized, excited state in a semiconductor.
An atom in isolation has discrete electron energy levels.

As atoms move closer together, as in a crystal, electron wavefunctions overlap. Electrons are Fermions, meaning two particles cannot occupy the same state. Discrete atomic electron energy levels split, forming bands.

The gap between bands, denoting an energy range in which no stable orbitals exist, is the “bandgap”.

Image removed due to copyright restrictions. Please see any diagram of discrete vs. continuous energy levels, such as http://www.webexhibits.org/causesofcolor/images/content/20.jpg
Bandgap: Physicist’s Description

\[ \psi_{nk}(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} u_{nk}(\mathbf{r}). \]

- The wavefunction of an electron in a crystal is described by the product of a periodic function (as follows from a periodic crystal lattice) with a plane wave envelope function (describing electron localization).

For introductory reading, see C. Kittel, “Introduction to Solid State Physics”
Bandgap: Physicist’s Description

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Electron isopotential surface in silicon

For real systems, use (a) symmetry + group theory or (b) pseudopotentials + computer modeling to solve for electron wavefunctions. For many crystal structures, strong directional dependence of the wavefunction.

http://www.pwscf.org/

For advanced reading, see P. Yu and M. Cardona, “Fundamentals of Semiconductors”
Classes of Materials, based on Bandgap

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http://upload.wikimedia.org/wikipedia/commons/3/3f/BandGap-Comparison-withfermi-E.PNG
**Bandgap: Physicist’s Description**

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Bandgap: Physicist’s Description

The directional dependence of the electron wavefunction in a crystalline solid gives rise to “energy band diagrams”, which are largely dictated by crystal symmetry and atomic potential.

Different methods (Free Electron and Empirical Pseudopotential) for calculating the Band Structure of Germanium

A comparison of the band structure of Ge as calculated by (a) the tight-binding, (b) the empirical pseudopotential, and (c) the nearly free electron methods.

P. Yu and M. Cardona, “Fundamentals of Semiconductors”  
Figure by MIT OpenCourseWare.
Charge Excitation in a Semiconductor

Let’s take a closer look at how charge is excited in a semiconductor.

Figure by MIT OpenCourseWare.

P. Yu and M. Cardona, “Fundamentals of Semiconductors”
Charge Excitation in a Semiconductor

Here’s the bandgap, which we recognize.

Figure by MIT OpenCourseWare.

P. Yu and M. Cardona, “Fundamentals of Semiconductors”
Charge Excitation in a Semiconductor

The red arrow indicates the excitation of charge at low photon energies, near the absorption edge (the lowest photon energy, at which the material begins to absorb photons).

P. Yu and M. Cardona, “Fundamentals of Semiconductors”
Charge Excitation in a Semiconductor

Note the change in direction (momentum) $\rightarrow$ a phonon is required to assist this transition! Complex interactions (photon + phonon acting on an electron approximately instantaneously) are rare, thus this transition is of relatively low probability.

Figure by MIT OpenCourseWare.

P. Yu and M. Cardona, “Fundamentals of Semiconductors”
Charge Excitation in a Semiconductor

This red arrow denotes the direct transition (no phonon required). Because it is only a two-body interaction, this transition is much more likely to occur.

P. Yu and M. Cardona, “Fundamentals of Semiconductors”
Absorption Coefficient ($\alpha$) for different materials

\[ I = I_0 \cdot e^{-\alpha \cdot l} \]

Absorption Coefficient of Semiconductor Materials

- GaAs
- InP
- Germanium
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- Amorphous Silicon

Direct transition
Indirect Transition

Courtesy of Christiana Honsberg and Stuart Bowden. Used with permission.
<table>
<thead>
<tr>
<th>Direct Bandgap Material</th>
<th>Indirect Bandgap Material</th>
</tr>
</thead>
</table>

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M.A. Green, *Solar Cells.*
Absorption Coefficient ($\alpha$) for different materials

$I = I_o \cdot e^{-\alpha \cdot l}$
Absorption Coefficient ($\alpha$) for different materials

$$I = I_0 \cdot e^{-\alpha \cdot l}$$

Absorption Coefficient of Semiconductor Materials

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Direct transition

Indirect Transition

(6.2 eV) (0.62 eV)

wavelength (nm)

Courtesy of Christiana Honsberg and Stuart Bowden. Used with permission.
Thickness estimate for solar cell materials

Based on these absorption coefficients, estimate a reasonable thickness for a GaAs solar cell, and a Si solar cell, such that 90% of the light at 800 nm is absorbed.
Charge Transport in Semiconductors

The “curvature” of a band (in E vs. k) is a function of carrier mobility (i.e., drift velocity of carriers under an applied field). Mobility is an intrinsic property of a semiconducting material. Mobility can be reduced by adding dopants, but it can rarely be enhanced without fundamentally altering the material structure or composition.

For introductory reading, see C. Kittel, “Introduction to Solid State Physics”
Light Absorption and Charge Transport in Organic Materials
Why most polymers and organic solids are insulators

- \( sp^3 \) hybridized orbitals form sigma bonds.
- The electrons are highly localized.

Courtesy of Ilan Gur. Used with permission.
Why conjugated molecules can be semiconductors

- $p$ orbitals form $\pi$ bonds.
- $\pi$ electrons are more delocalized than $\sigma$ electrons.

Courtesy of Ilan Gur. Used with permission.
Chemical structure of common conjugated polymers

PA: polyacetylene
(1st conducting polymer)

PPV: poly(phenylene-vinylene)
(used in 1st polymer LED)

PT: polythiophene
(widely used in transistors)

PPP: poly(para-phenylene)
(large bandgap)

Courtesy of Ilan Gur. Used with permission.
Bonding and antibonding orbitals

For a $\sigma$ bond, the energy gap is 6-12 eV.

For a $\pi$ bond, the energy gap is 1-3 eV.

Courtesy of Ilan Gur. Used with permission.
Band structure of conjugated polymers

Each $p$ electron is the unit cell results in one $\pi$ band.

Empty $\pi^*$ bands

Full $\pi$ bands

The band gaps of conjugated polymers are in the range of 1 to 3 eV.

Courtesy of Ilan Gur. Used with permission.
Tuning the bandgap of conjugated polymers

Courtesy of Ilan Gur. Used with permission.

Slide from Ilan Gur, UC Berkeley
Light Absorption, Charge Transport in Nanomaterials
Light Absorption in Nanomaterials

In nanomaterials, particle size can be comparable to the electron wavefunction in at least one dimension, resulting in “quantum confinement”.

Courtesy of A. Paul Alivisatos. Used with permission.
Light Absorption in Nanomaterials

Quantum confinement (function of particle size, shape) changes light absorption characteristics drastically, for the same material. Below, nanoparticles of the same material in suspension, with drastically different absorption characteristics.

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Bandgap vs. Length and Diameter


Courtesy of A. Paul Alivisatos. Used with permission.
Charge Transport in Nanoparticle Composites (Distributed Heterojunctions)

Many possible mechanisms of charge transport in nanoparticle composite materials (dispersive hopping, conductive percolation...)

The charge transport method dictates carrier mobility, and ultimately, device performance.

Figure by MIT OpenCourseWare.
Percolation

• 1 % PCBM quenches the photoluminescence.

• 18 % PCBM is needed to provide a continuous pathway for electrons to travel to the electrode.

Sean Shaheen