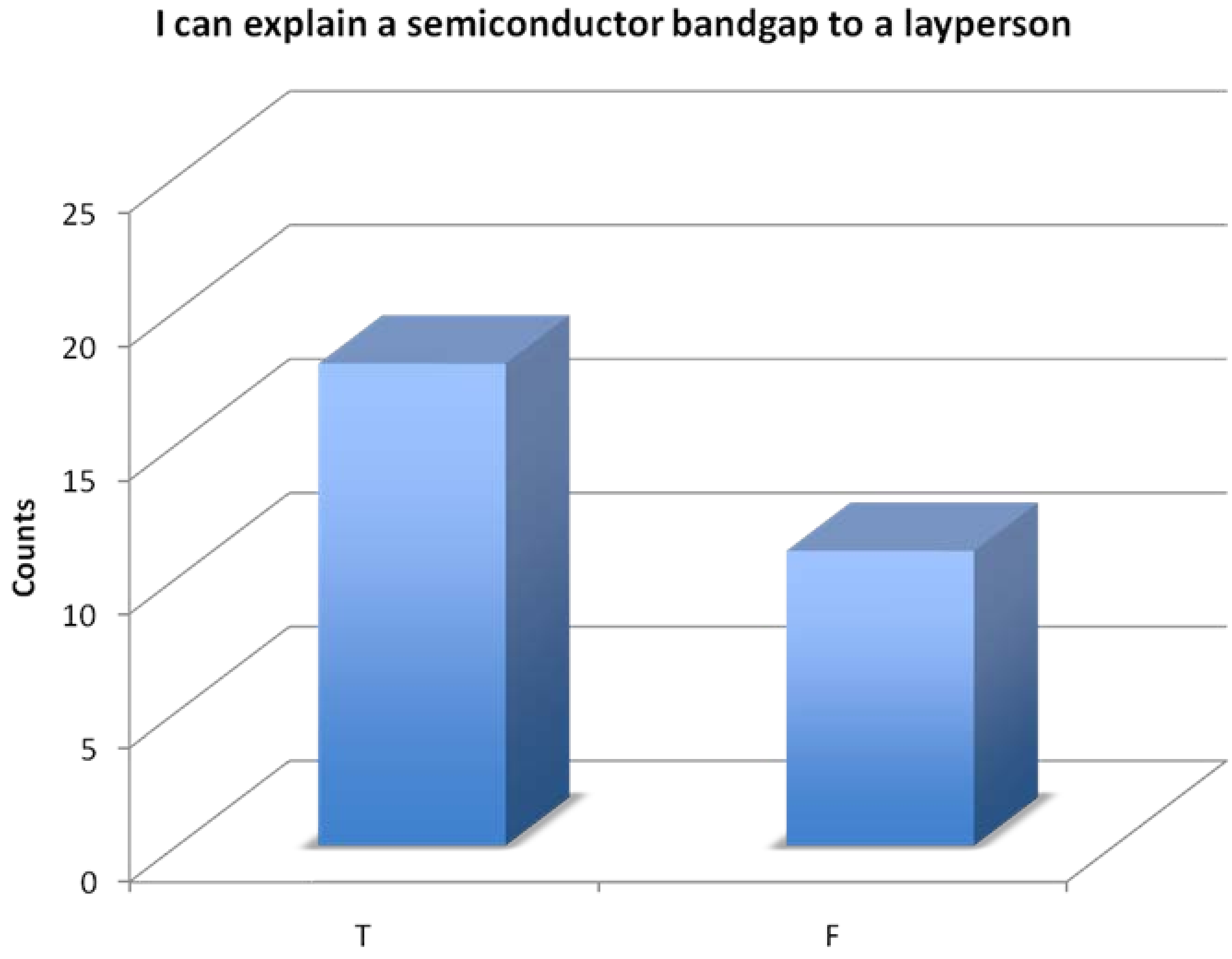
2.626 Fundamentals of Photovoltaics
Fall 2008

Light Absorption, Charge Excitation and Transport

Lecture 3 – 2.626

Tonio Buonassisi

Semiconductor Fundamentals



Light Absorption

Photons – Quanta of Light

Quantum theory describes the frequency dependence of photon energy.

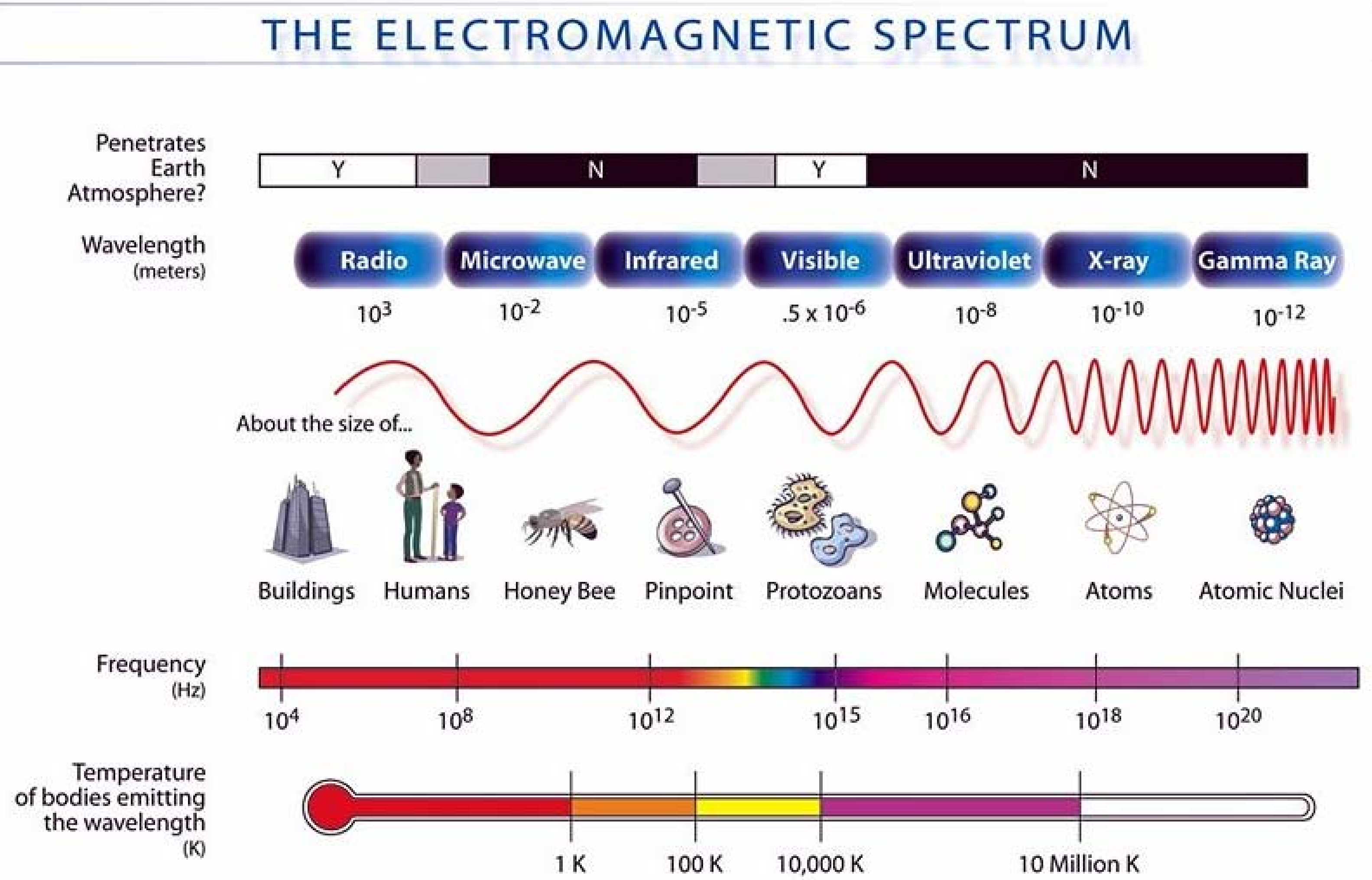
Particle-wave duality:

Photons have discrete quanta of energy.
Photons have momentum.
Light can be polarized.
Light can be diffracted.

Relevant Equations:

$$E_{\mathrm{ph}} = h\nu = \frac{hc}{\lambda}$$

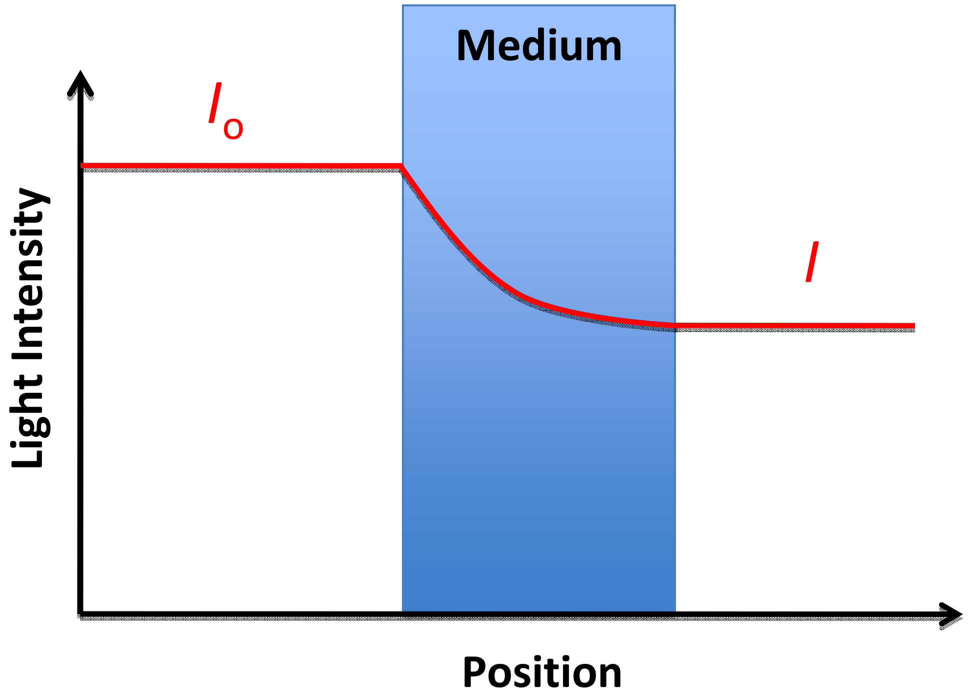
$$p_{\mathrm{ph}} = \hbar k = \frac{h}{\lambda}$$



Courtesy NASA.

http://www.als.lbl.gov/als/quickguide/vugraph.html

Photons – Transmission Through a Medium



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

Simple Derivation of Beer-Lambert's Law:

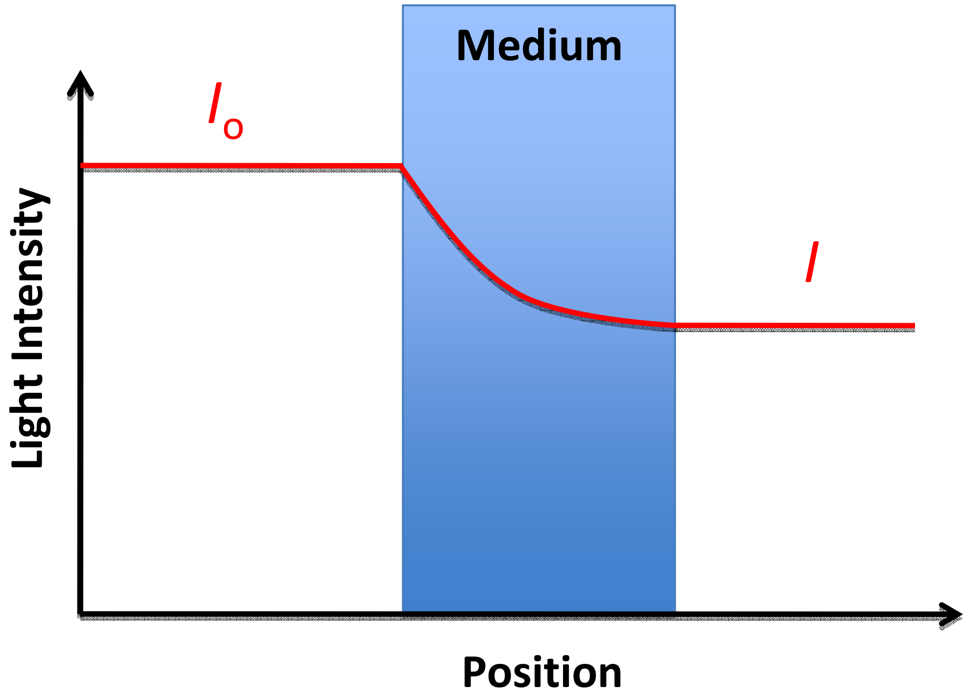
$$\frac{dI_z}{I_z} = -\sigma \cdot N \cdot dz$$

$$\ln(I_z) = -(\sigma \cdot N \cdot z) + C$$

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

$$I = I_o \cdot e^{-\sigma \cdot l \cdot N} = I_o \cdot e^{-\alpha \cdot l}$$

Photons – Transmission Through a Medium

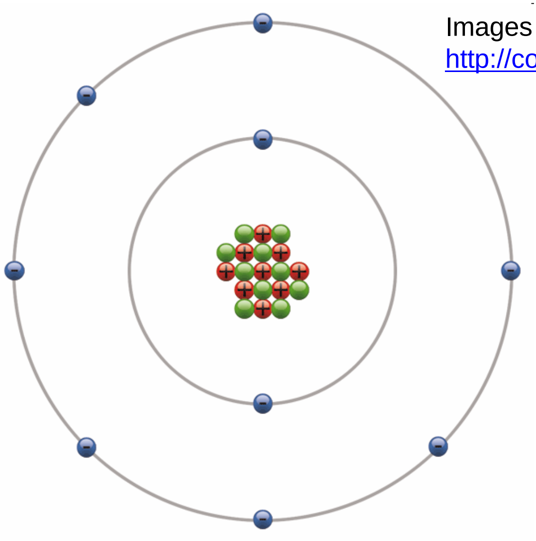


$$I = I_o \cdot e^{-\alpha \cdot l}$$

α 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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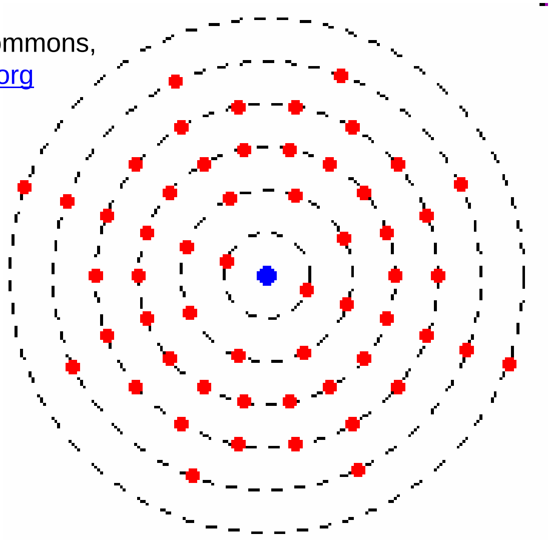

Image removed due to copyright restrictions. Please see http://static.howstuffworks.com/gif/atom-h-he-li-na.gif

Photons – Interactions with Matter

Quantum model of the atom

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.

Lead

Carbon

core electrons

core electrons

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http://xdb.lbl.gov/Section3/Image_Sec3/Sec3135.gif

http://xdb.lbl.gov/Section3/Image_Sec3/Sec3150.gif

http://xdb.lbl.gov/Section3/Sec_3-1.html

τ = photoelectric interaction

σ_{coh} = coherent scattering (Raleigh)

σ_{incoh} = incoherent scattering (Compton)

κ_n = pair formation from interaction with nuclear particle

κ_e = pair formation from interaction with electron

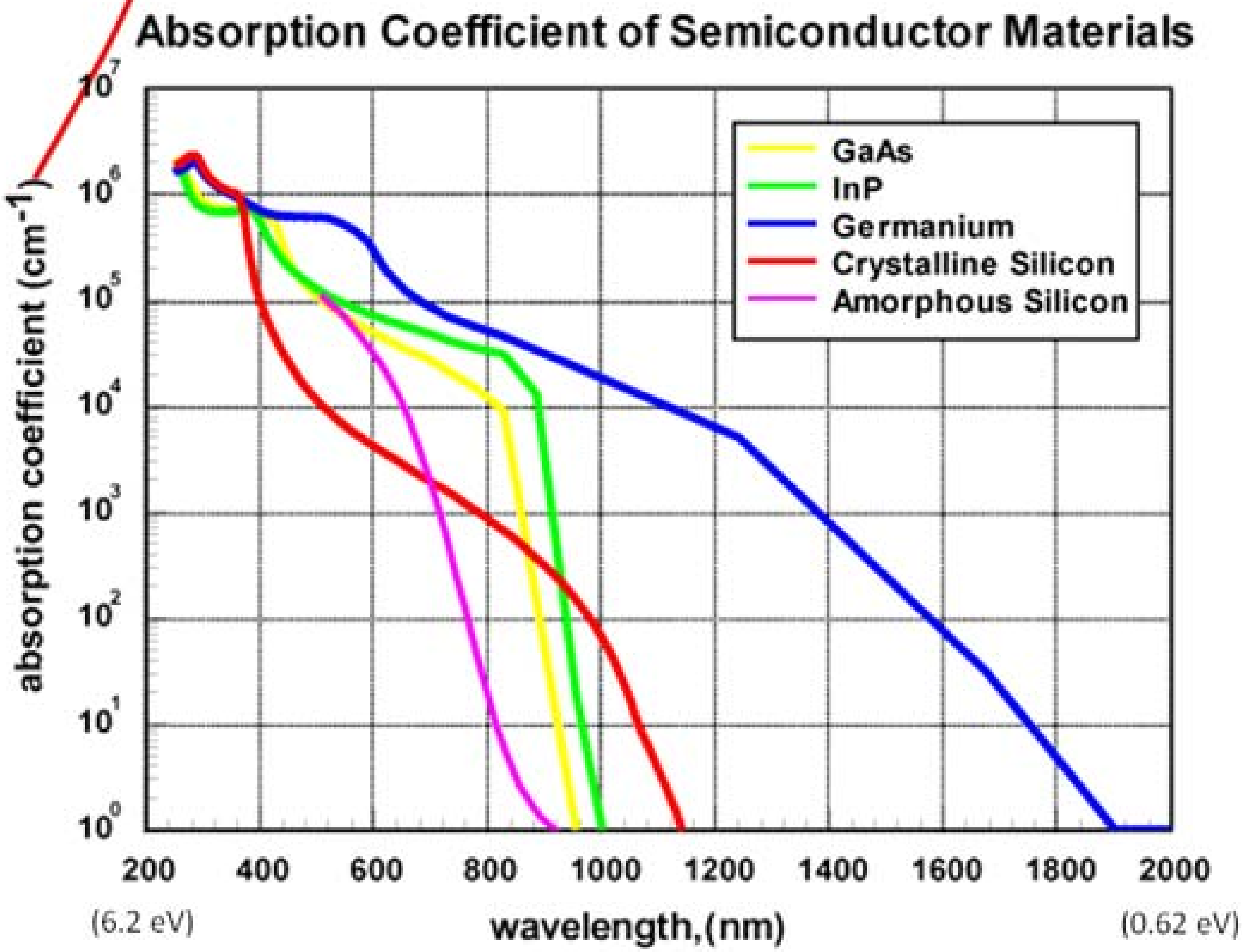
Low-Energy Photon-Matter Interactions

- 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

Absorption Coefficient (α) for different materials

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



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Absorption Coefficient (α) for different materials

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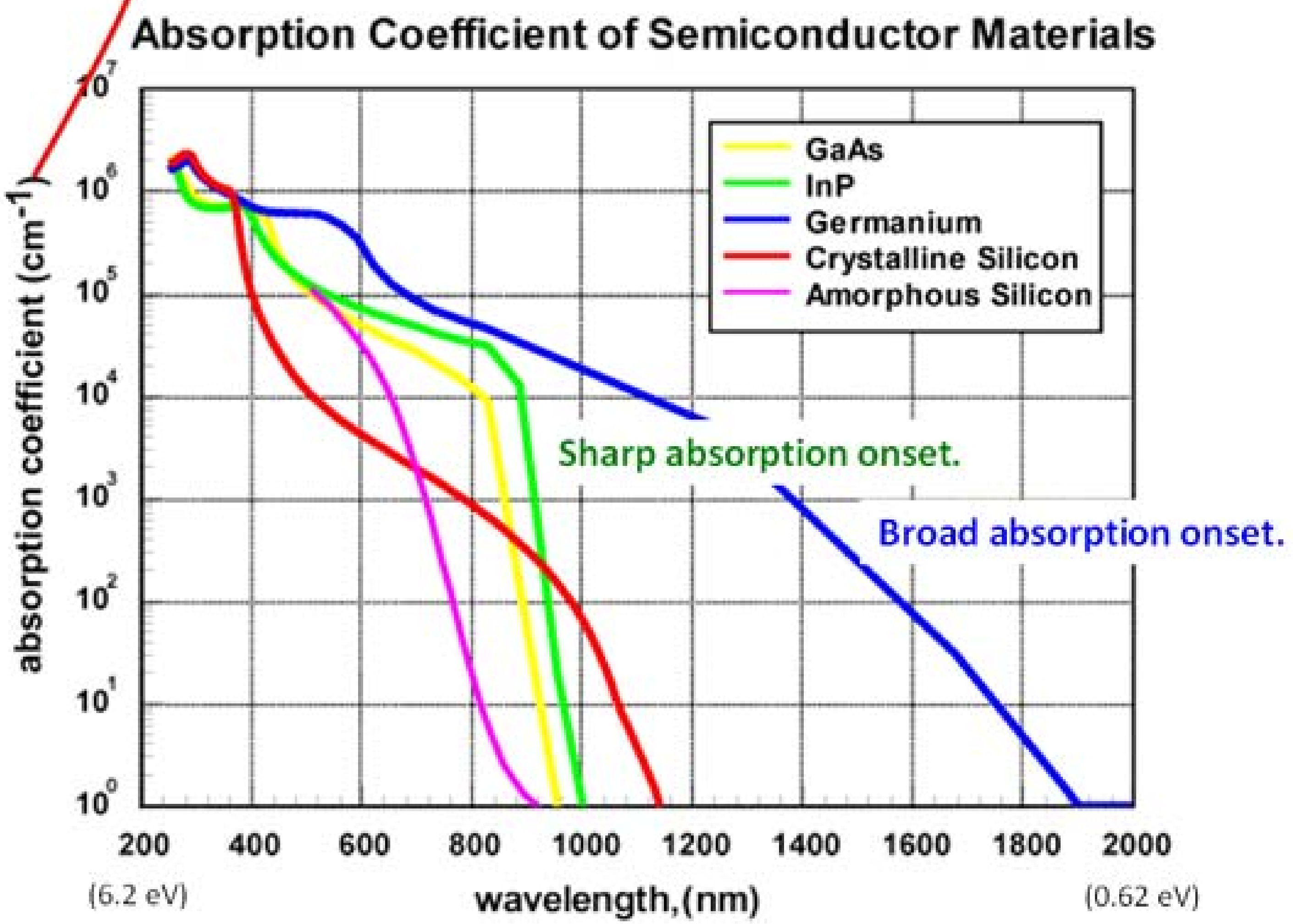
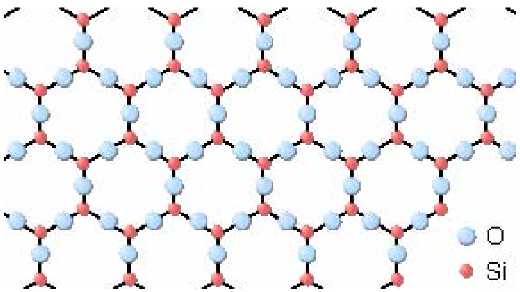
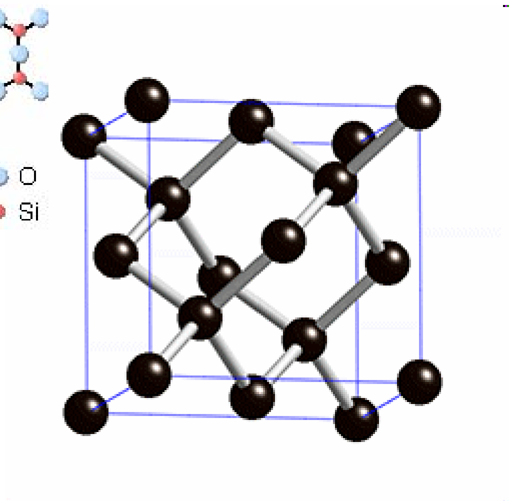


Bandgap

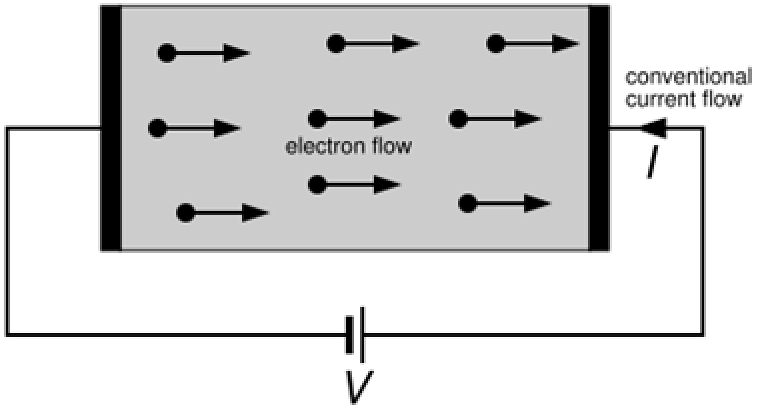
Bandgap: Basic Description

Bonds: why stuff is tough.





Excited electrons: why materials conduct



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- 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.

Bandgap: Chemist's Description

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
http://commons.wikimedia.org/wiki/File:Electronic_structure_of_materials.jpg

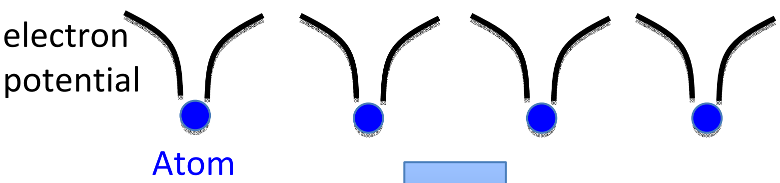
- An atom in isolation has discrete electron energy levels.
- As atoms move closer together, as in a crystal, electron wavefunctions overlap. Electrons are Fermions, meaning two particles cannot occupy the same state. Discrete atomic electron energy levels split, forming bands.
- The gap between bands, denoting an energy range in which no stable orbitals exist, is the "bandgap".

Bandgap: Physicist's Description

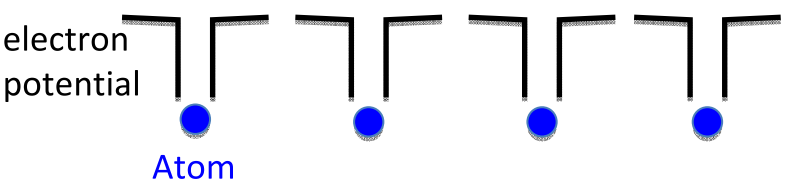
$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}).$$

- 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).

Schematic of a repeating Coulomb potential in a crystal



Kronig-Penney idealization of a repeating Coulomb potential in a crystal (easier to solve numerically)



Solve Schrödinger's equation → two possible solutions:
(1)Electron wavefunction centered on atoms (bound state)
(2)Electron wavefunction centered between atoms (excited state).

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.

Image removed due to copyright restrictions. Please see http://en.wikipedia.org/wiki/Image:BlochWave_in_Silicon.png

http://www.pwscf.org/

For advanced reading, see P. Yu and M. Cardona, "Fundamentals of Semiconductors"

Classes of Materials, based on Bandgap

http://upload.wikimedia.org/wikipedia/commons/3/3f/BandGap-Comparison-withfermi-E.PNG

Bandgap: Physicist's Description

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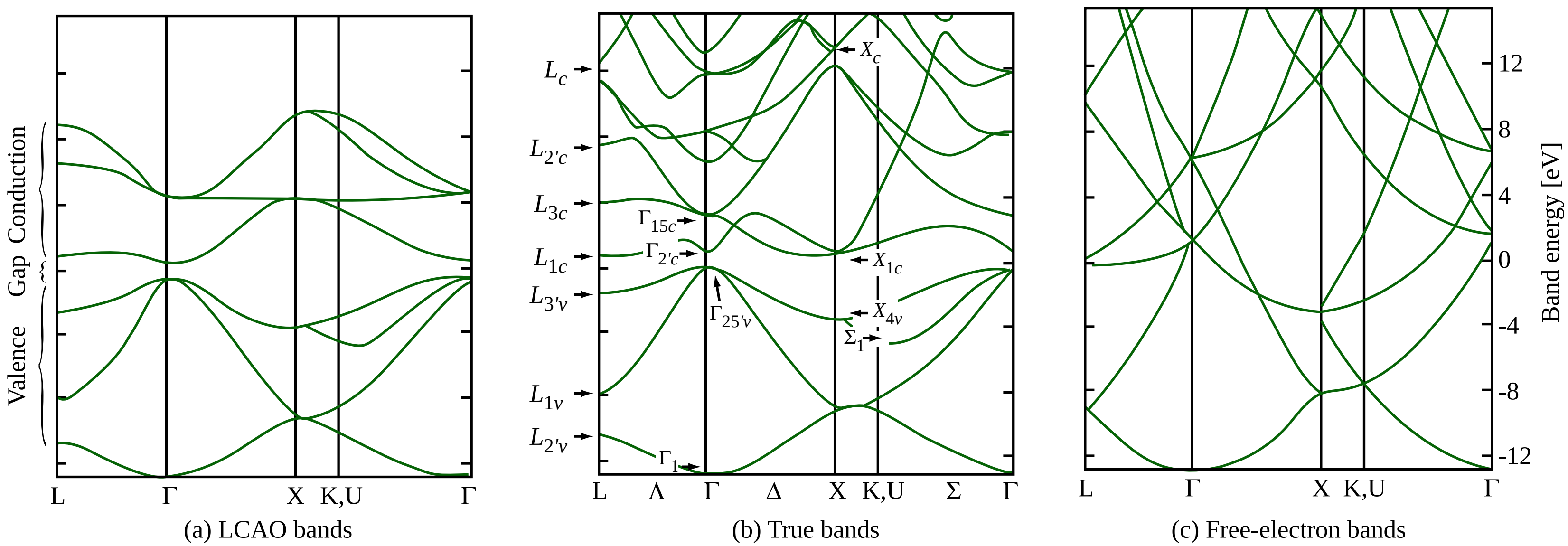
Bandgap: Physicist's Description

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



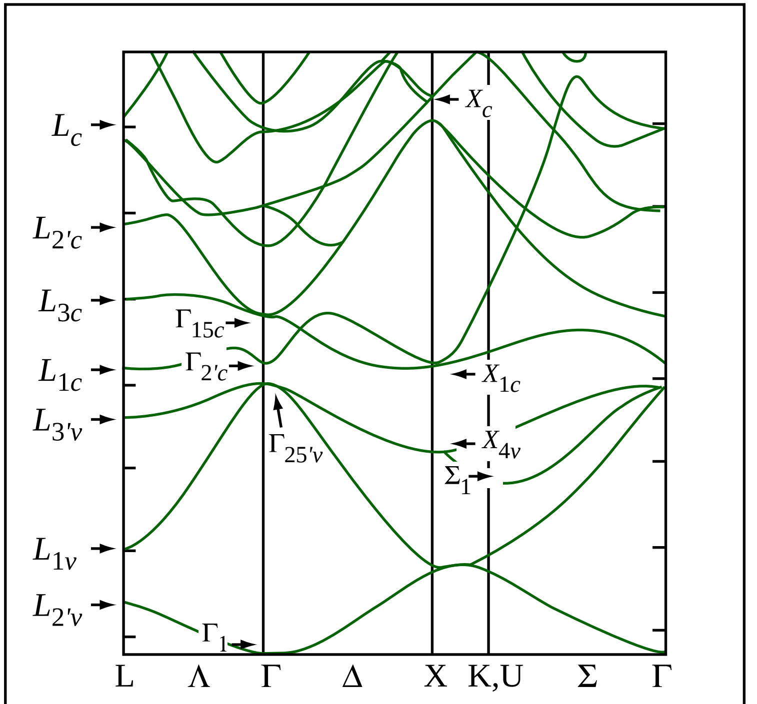
A comparison of the band structure of Ge as calculated by (a) the tight-binding, (b) the empirical pseudopotential, and (c) the nearly free electron methods.

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.



(b) True bands

Figure by MIT OpenCourseWare.

P. Yu and M. Cardona, "Fundamentals of Semiconductors"

Charge Excitation in a Semiconductor

Here's the bandgap, which we recognize.

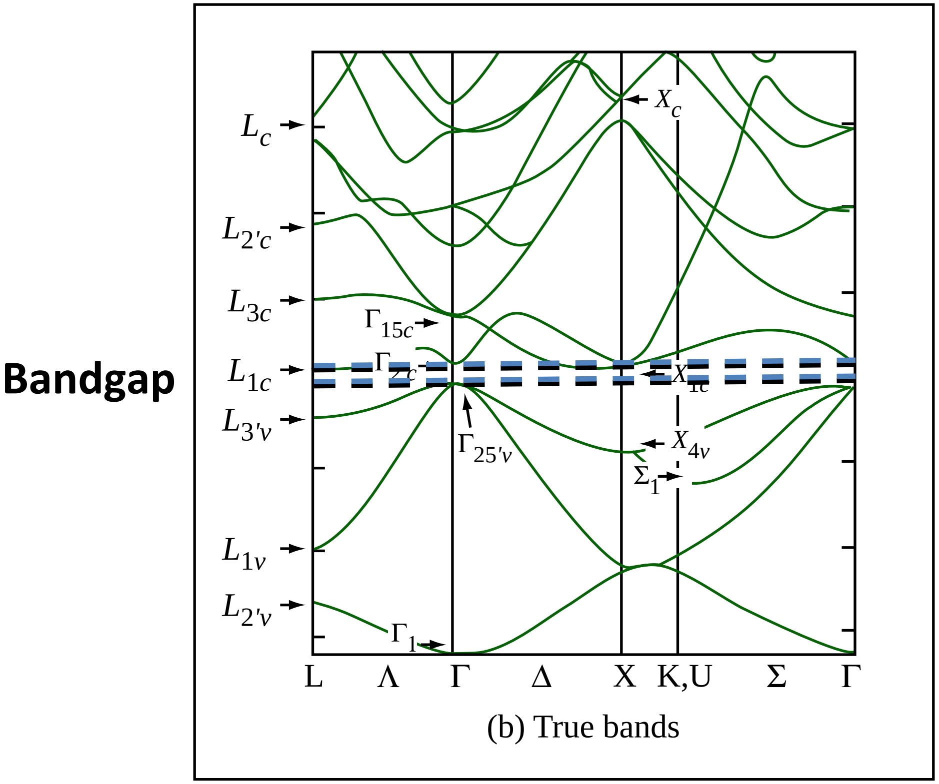
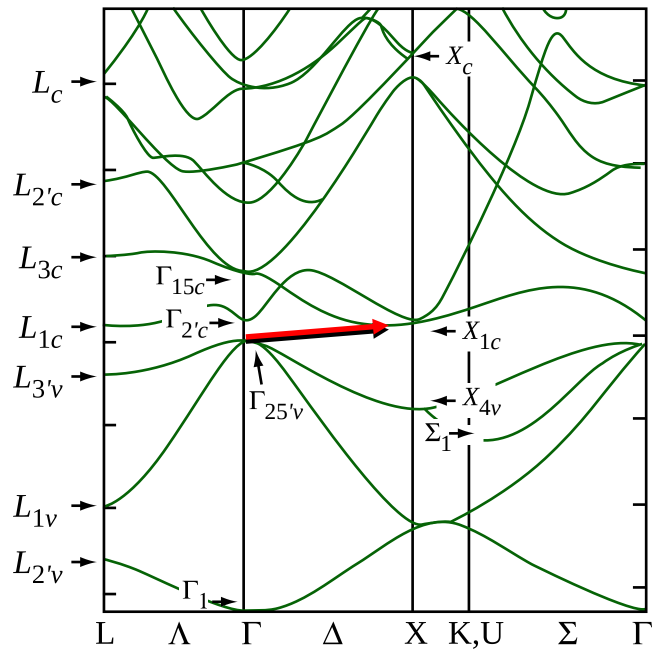


Figure by MIT OpenCourseWare.

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).



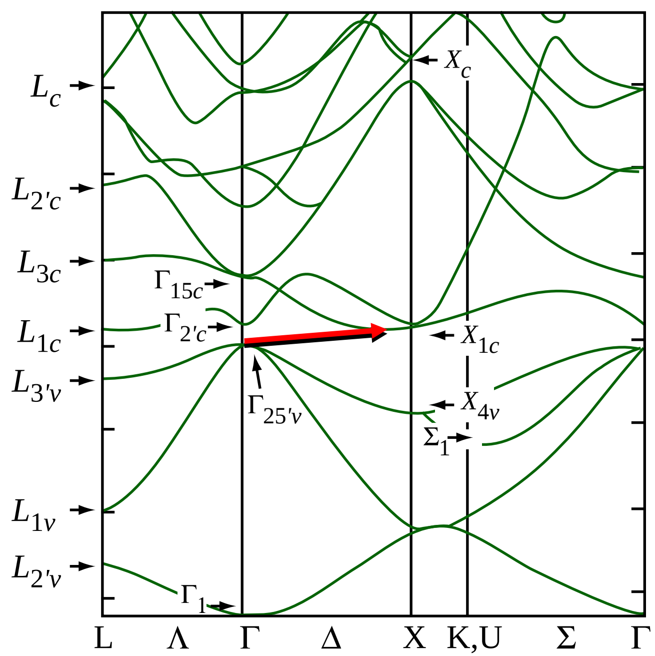
(b) True bands

Figure by MIT OpenCourseWare.

P. Yu and M. Cardona, “Fundamentals of Semiconductors”

Charge Excitation in a Semiconductor

Note the change in direction (momentum) → 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.



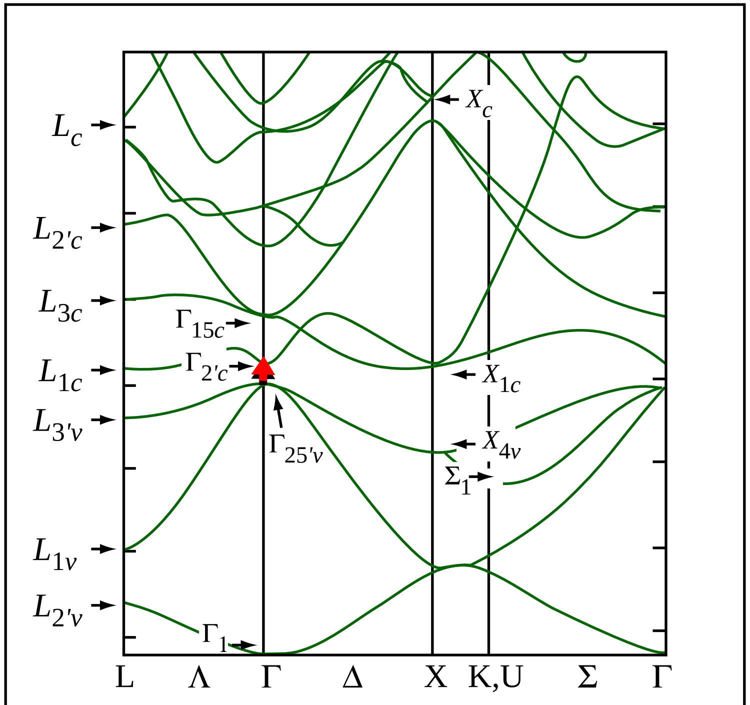
(b) True bands

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.



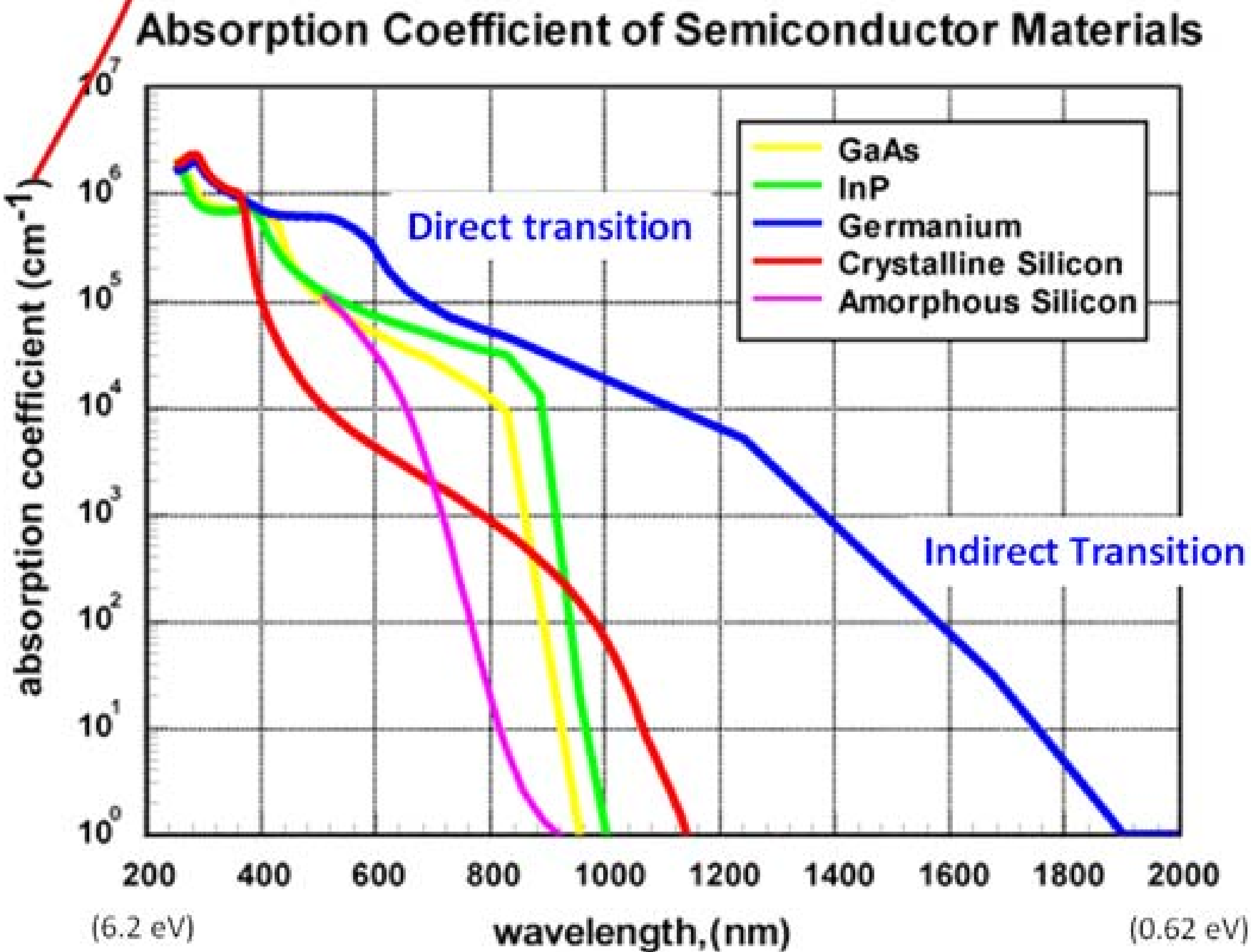
(b) True bands

Figure by MIT OpenCourseWare.

P. Yu and M. Cardona, "Fundamentals of Semiconductors"

Absorption Coefficient (α) for different materials

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



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Direct and Indirect Bandgap Materials

Direct Bandgap Material

Images removed due to copyright restrictions. Please see Fig. 2.8 and 2.9 in Green, M. A. *Solar Cells: Operating Principles, Technology, and System Applications*. Englewood Cliffs, NJ: Prentice-Hall, 1982.

http://en.wikipedia.org/wiki/File:Direct.svg

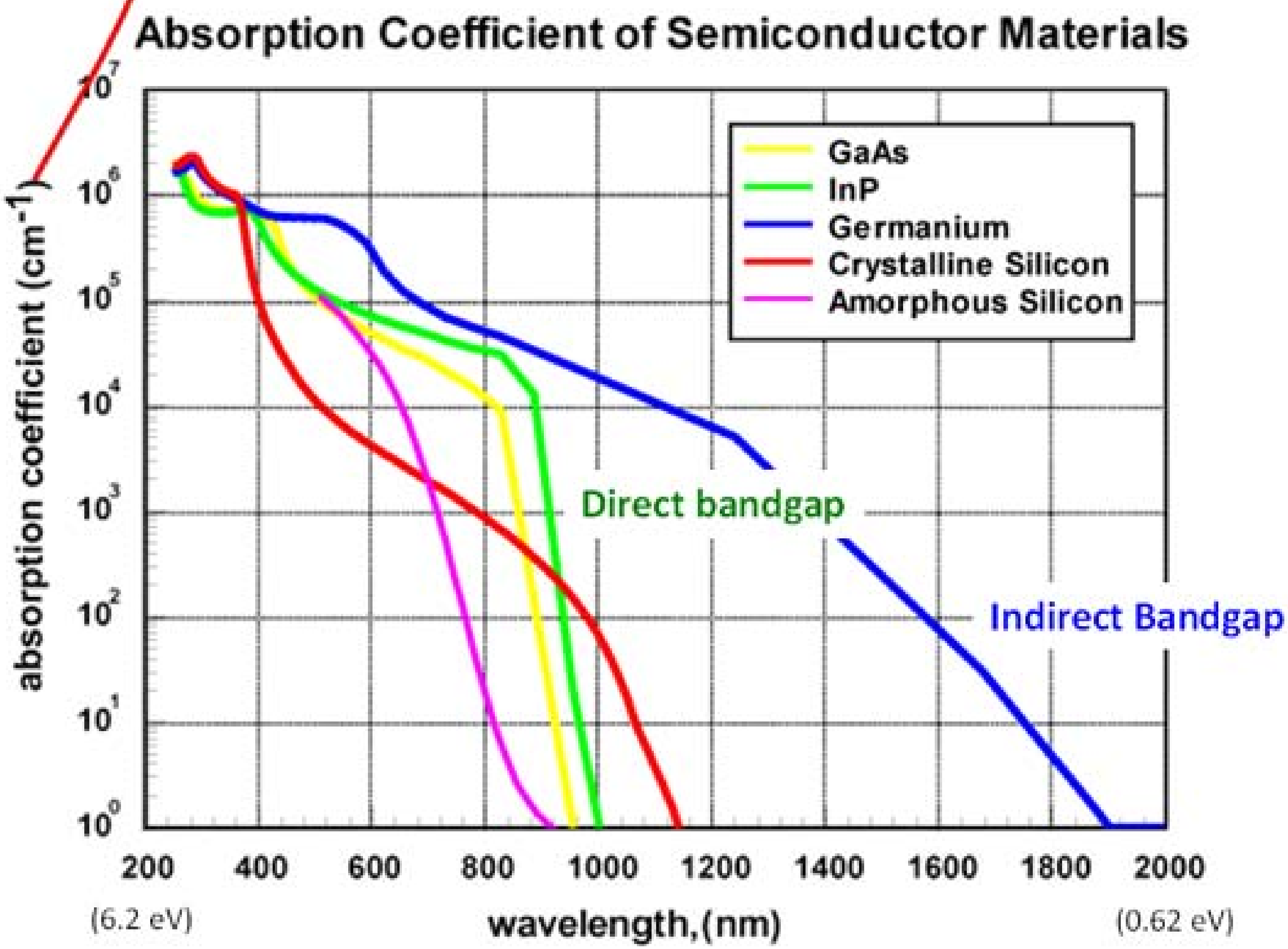
http://en.wikipedia.org/wiki/File:Indirect_Bandgap.svg

Indirect Bandgap Material

M.A. Green, *Solar Cells.*

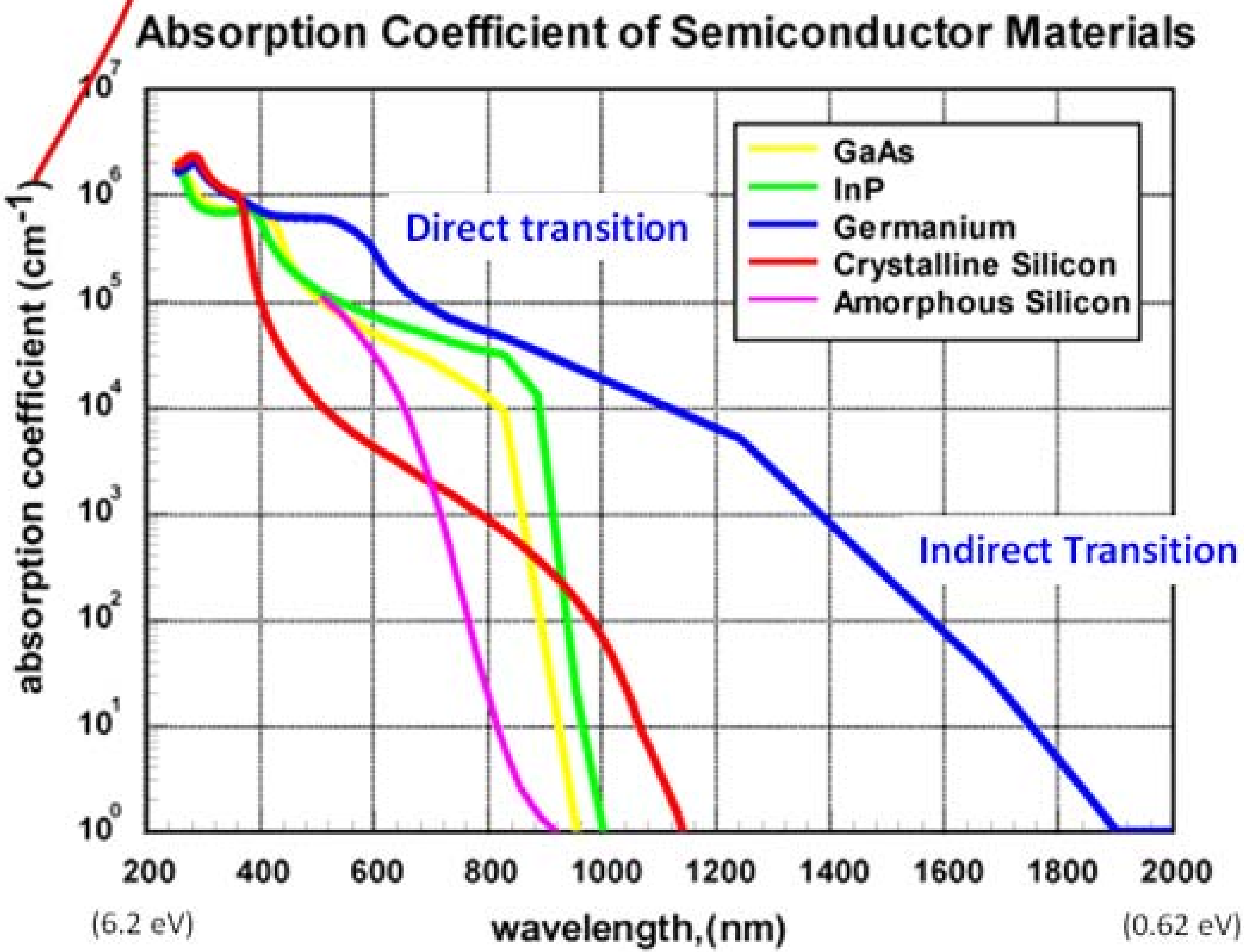
Absorption Coefficient (α) for different materials

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



Absorption Coefficient (α) for different materials

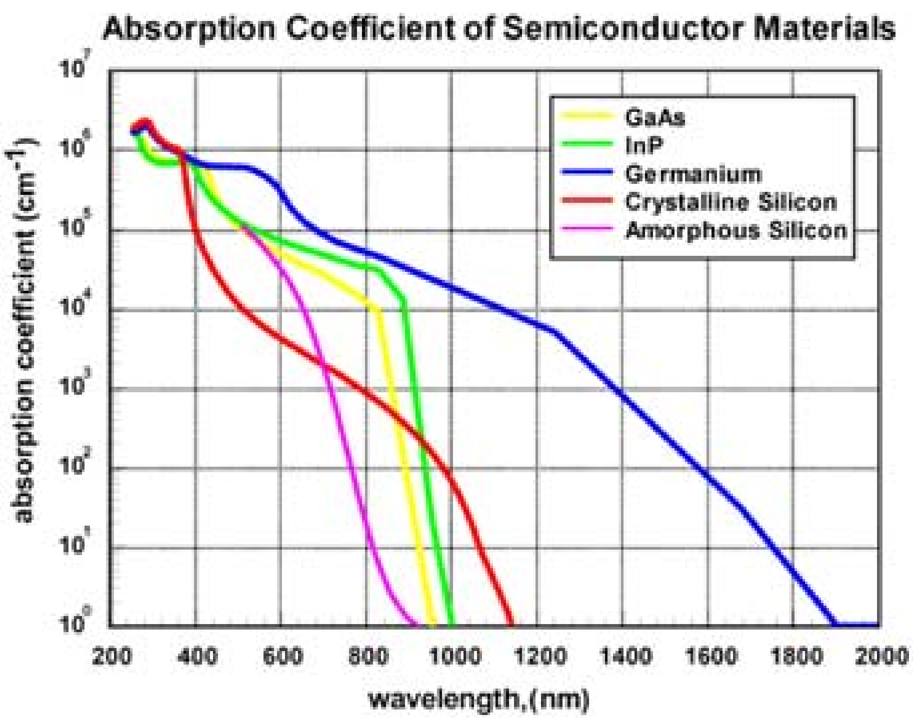
$$I = I_o \cdot e^{-\alpha \cdot l}$$

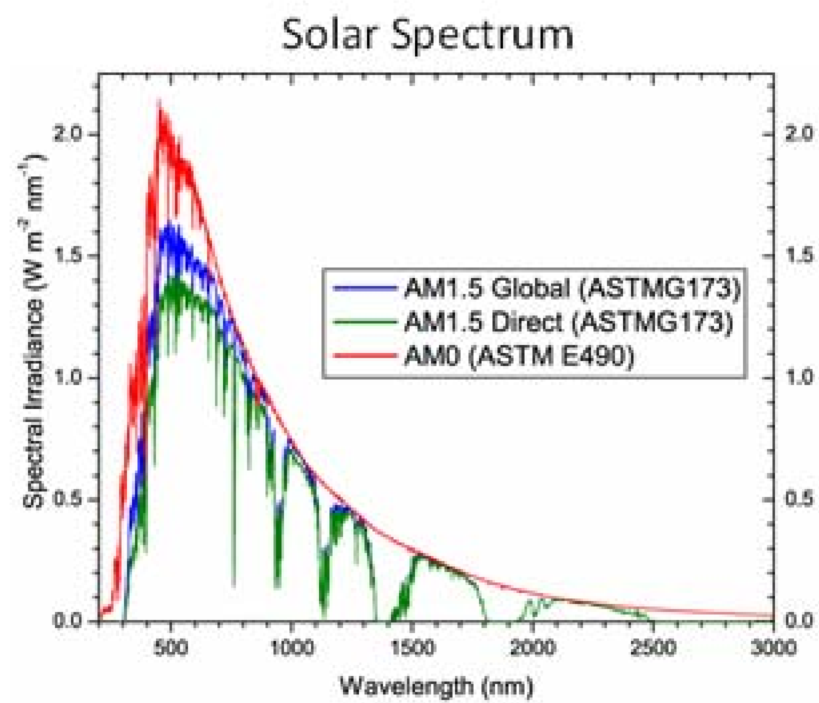


Thickness estimate for solar cell materials

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.

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





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.

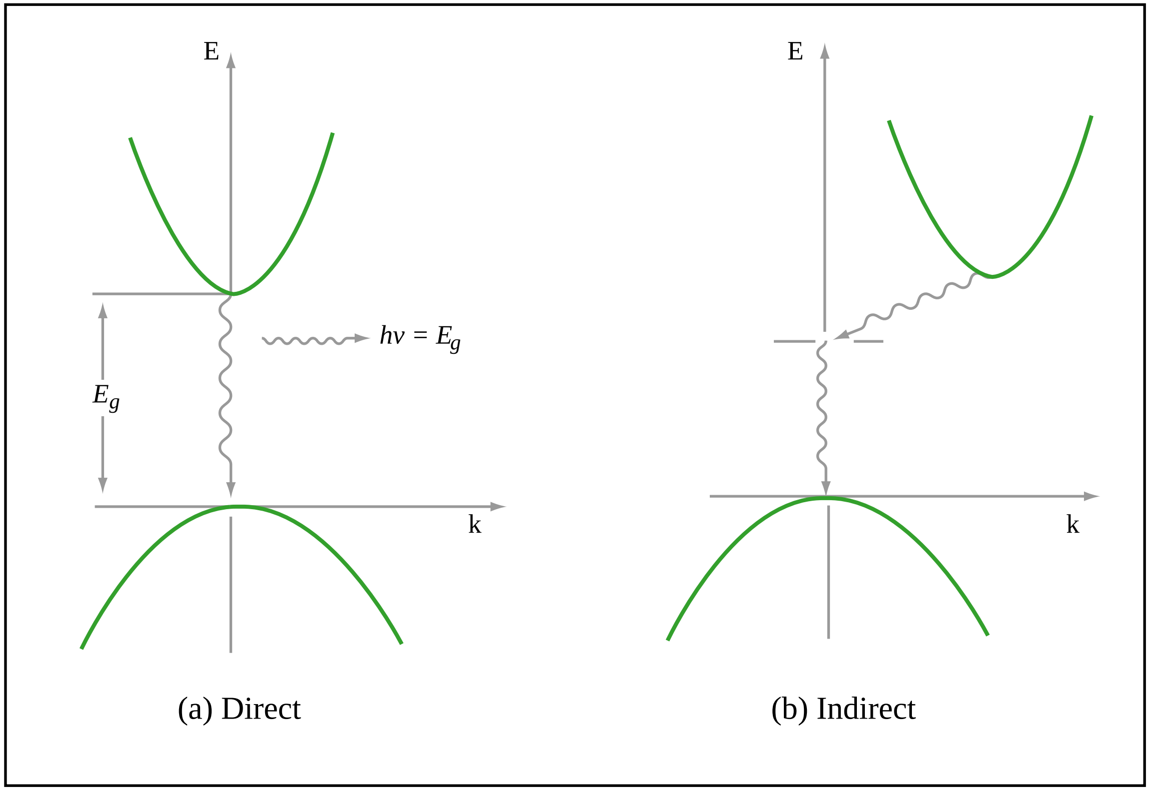
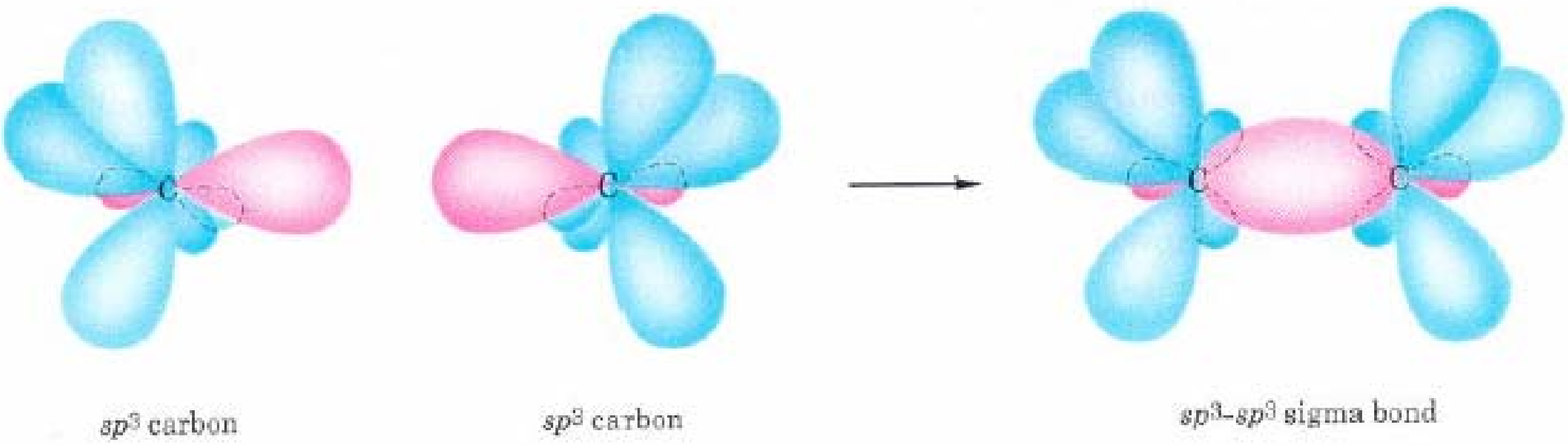


Figure by MIT OpenCourseWare.

For introductory reading, see C. Kittel, "Introduction to Solid State Physics"

Light Absorption and Charge Transport in Organic Materials

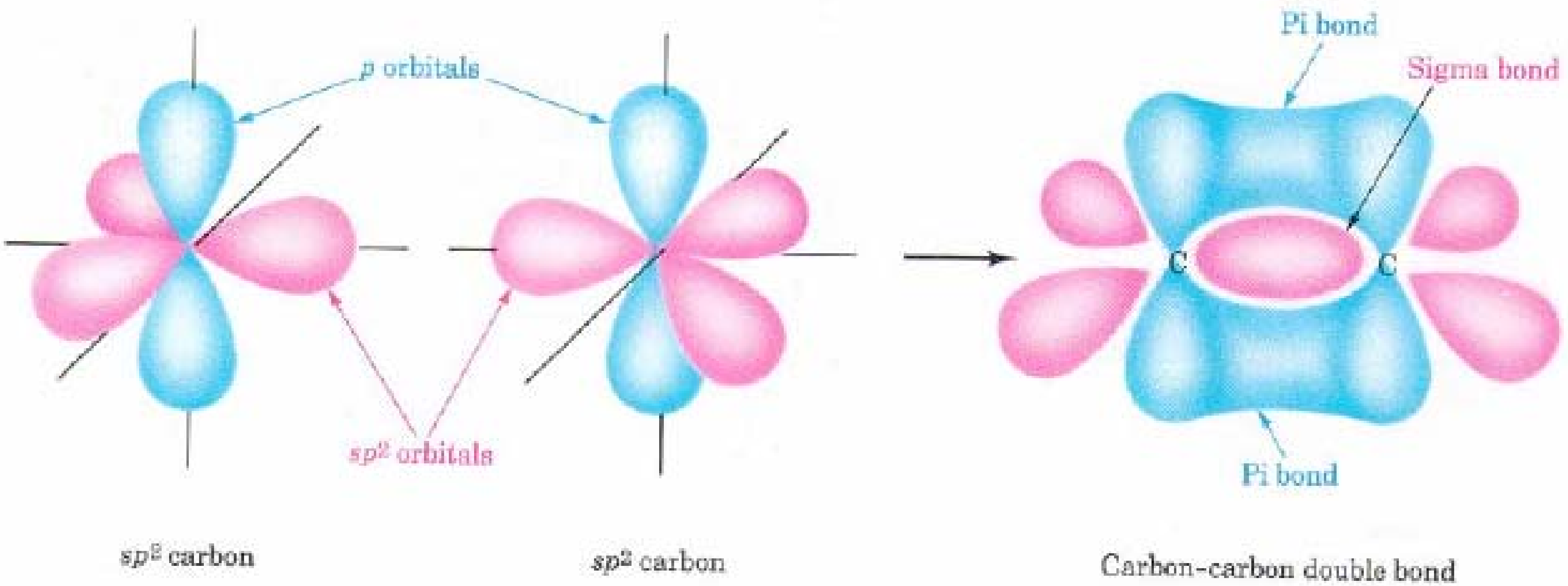
Why most polymers and organic solids are insulators



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

Slide from Ilan Gur, UC Berkeley

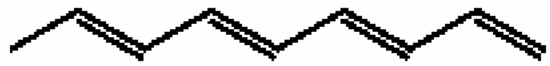
Why conjugated molecules can be semiconductors



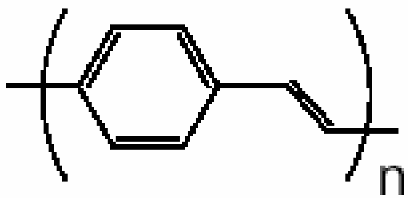
- p orbitals form π bonds.
- π electrons are more delocalized than σ electrons.

Slide from Ilan Gur, UC Berkeley

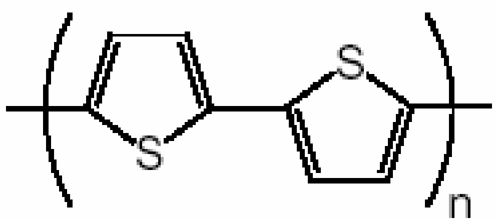
Chemical structure of common conjugated polymers



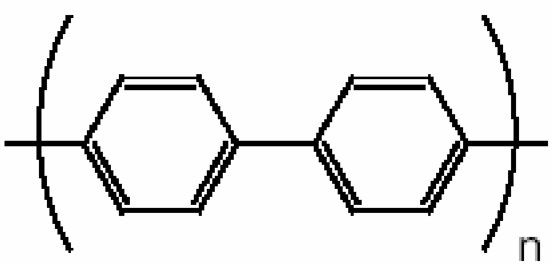
PA: polyacetylene
(1st conducting polymer)



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



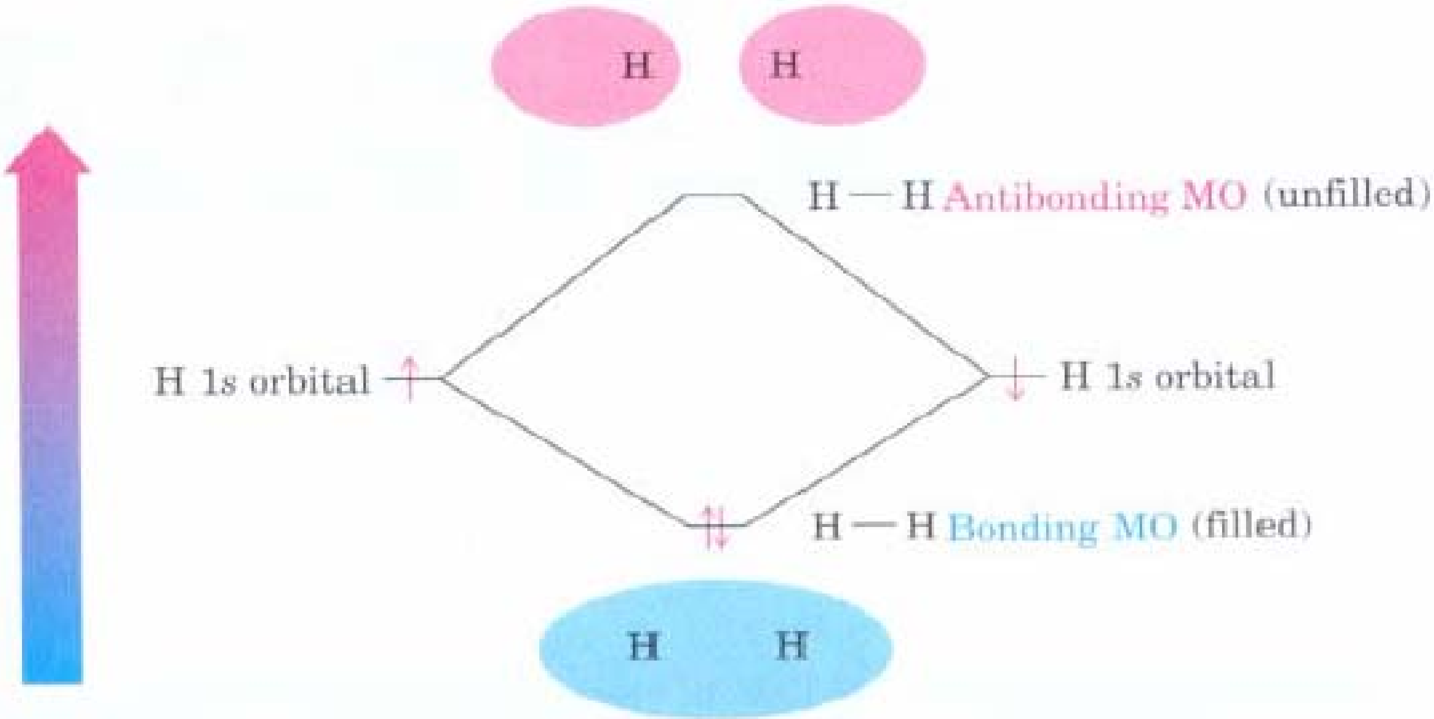
PT: polythiophene
(widely used in transistors)



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

Slide from Ilan Gur, UC Berkeley

Bonding and antibonding orbitals

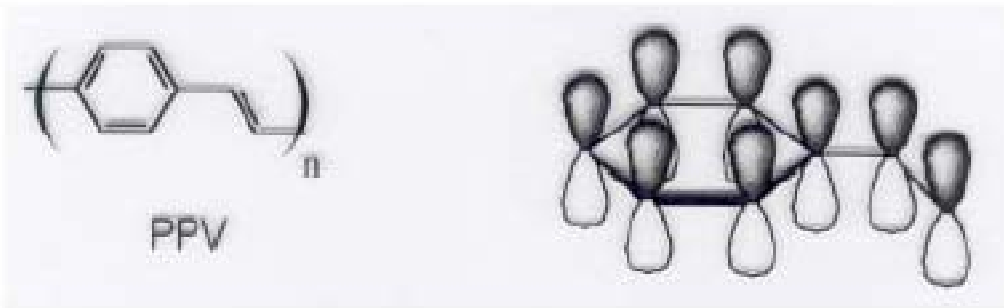


For a α bond, the energy gap is 6-12 eV.

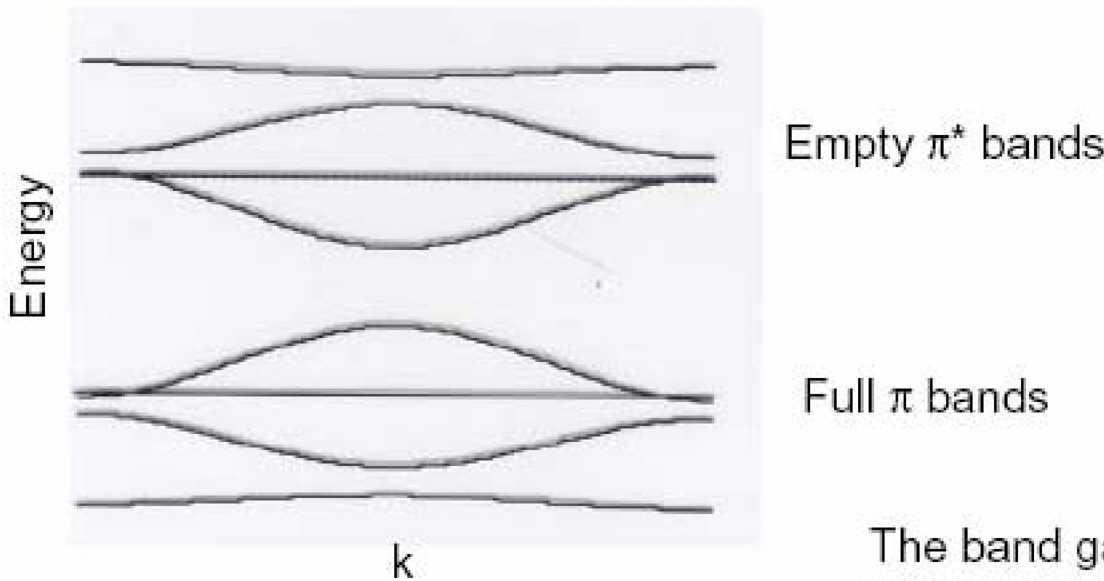
For a π bond, the energy gap is 1-3 eV.

Slide from Ilan Gur, UC Berkeley

Band structure of conjugated polymers



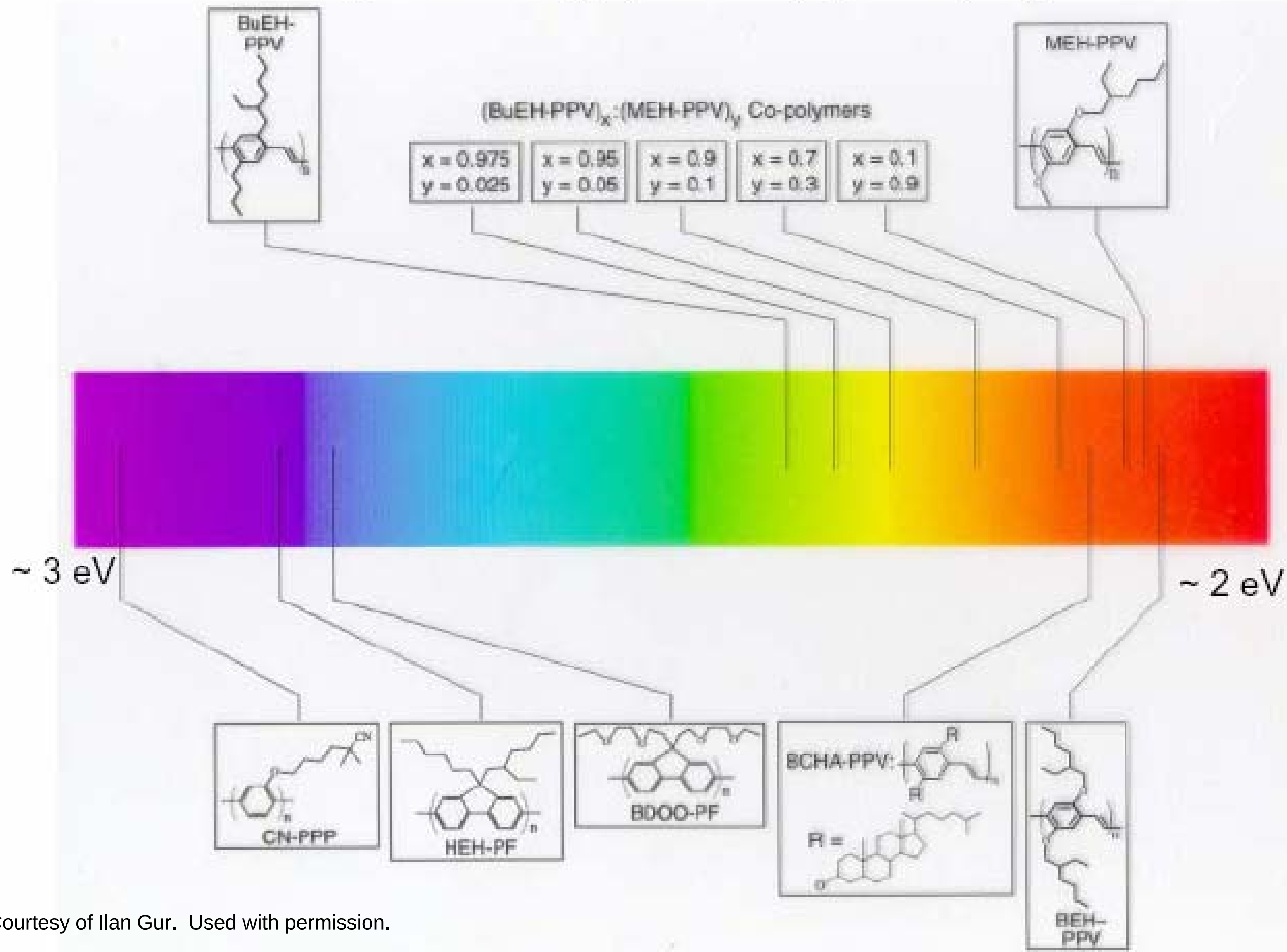
Each p electron is the unit cell results in one π band.



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

Slide from Ilan Gur, UC Berkeley

Tuning the bandgap of conjugated polymers



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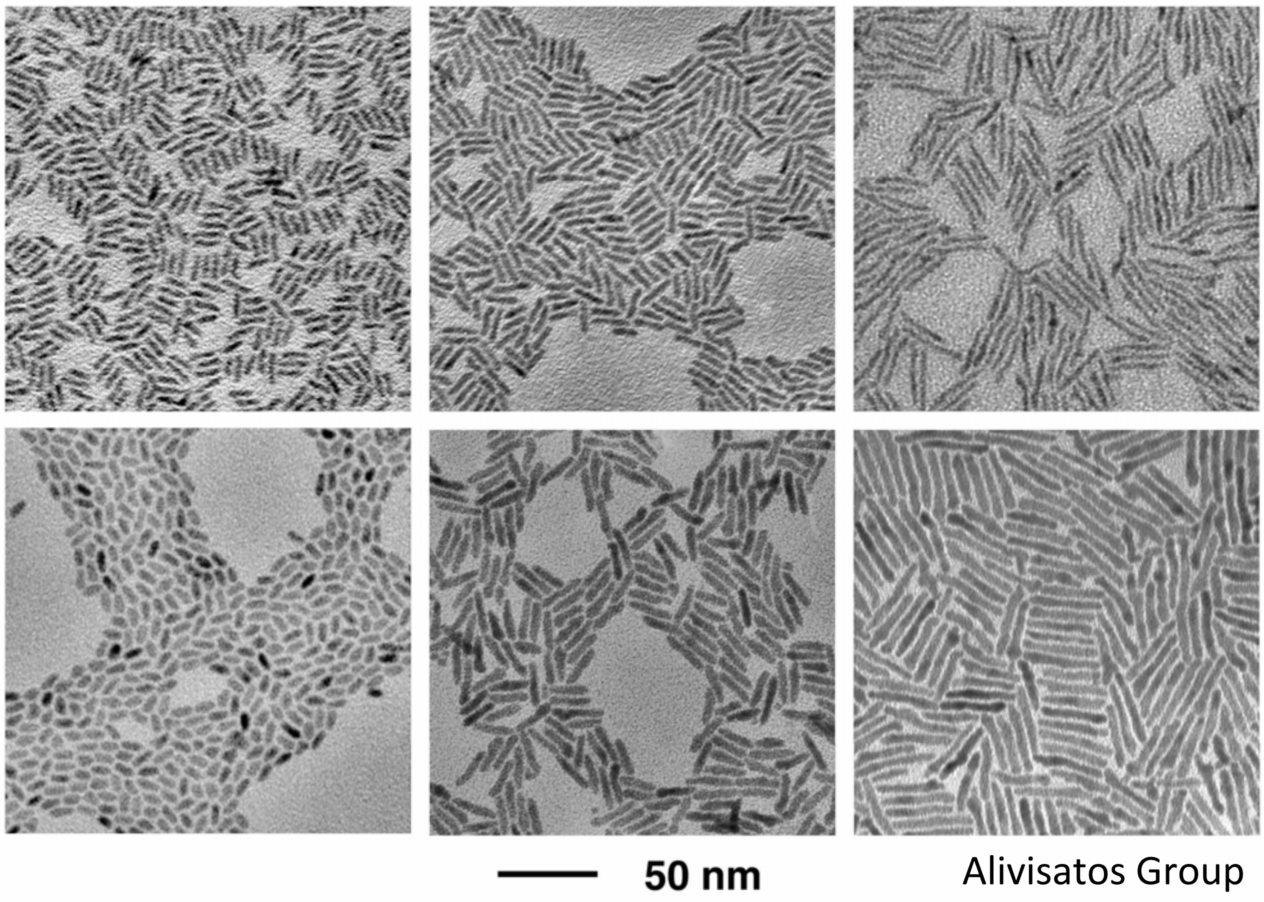
Light Absorption, Charge Transport in Nanomaterials

Light Absorption in Nanomaterials

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

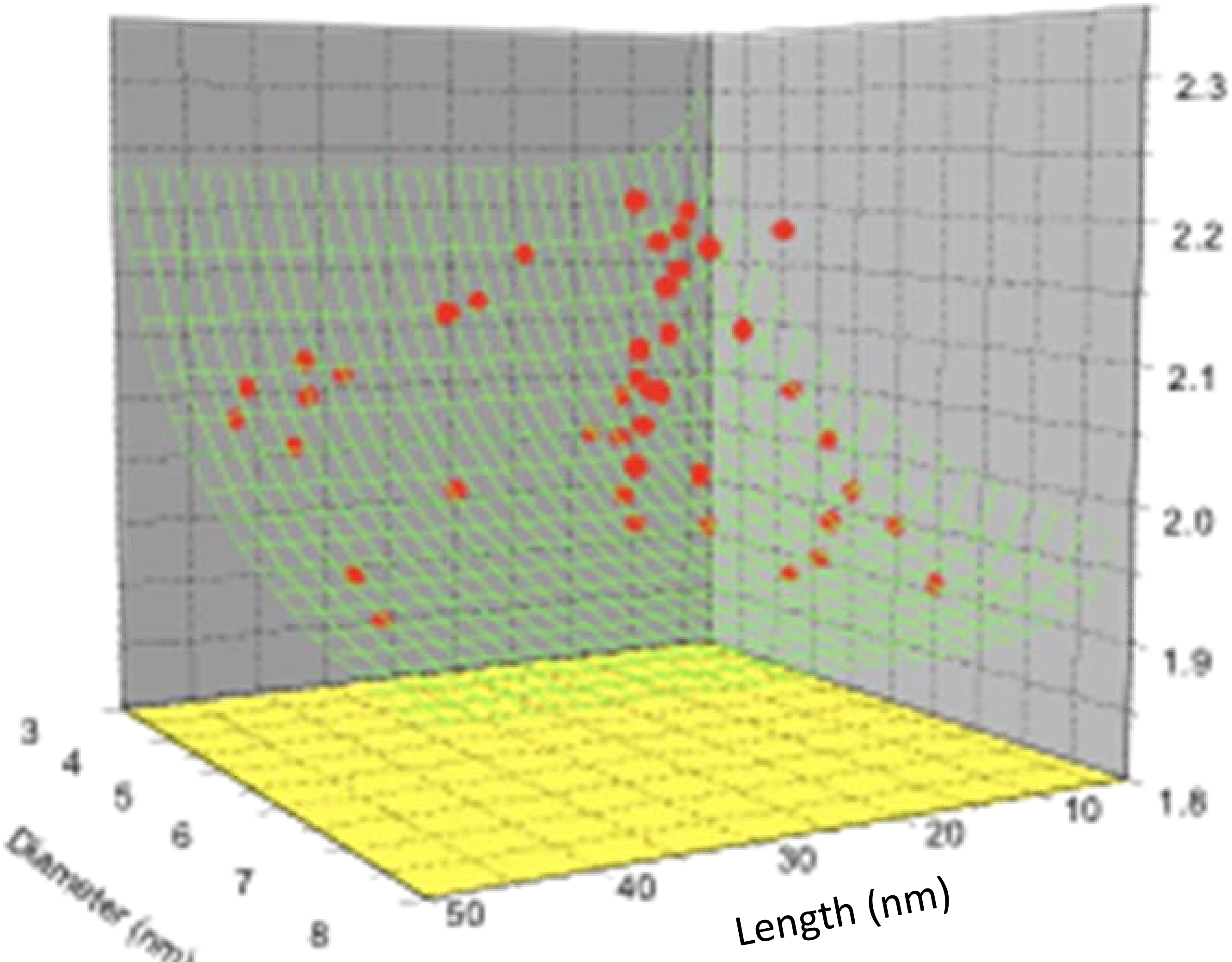


Light Absorption in Nanomaterials

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.

http://jessy.baker.googlepages.com/ucberkeley

Bandgap vs. Length and Diameter



Li, L. S., J. T. Hu, W. D. Yang and A. P. Alivisatos (2001). "Band gap variation of size- and shape-controlled colloidal CdSe quantum rods." Nano Letters **1**(7): 349-351.

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.

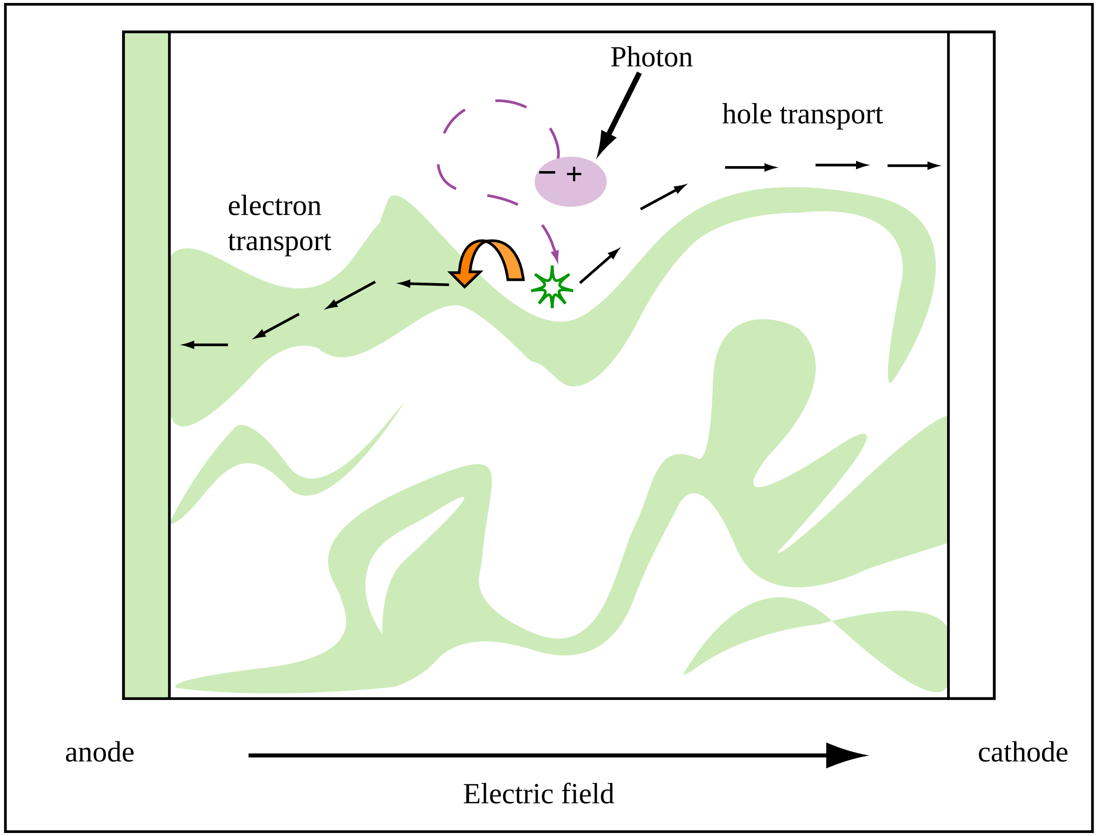
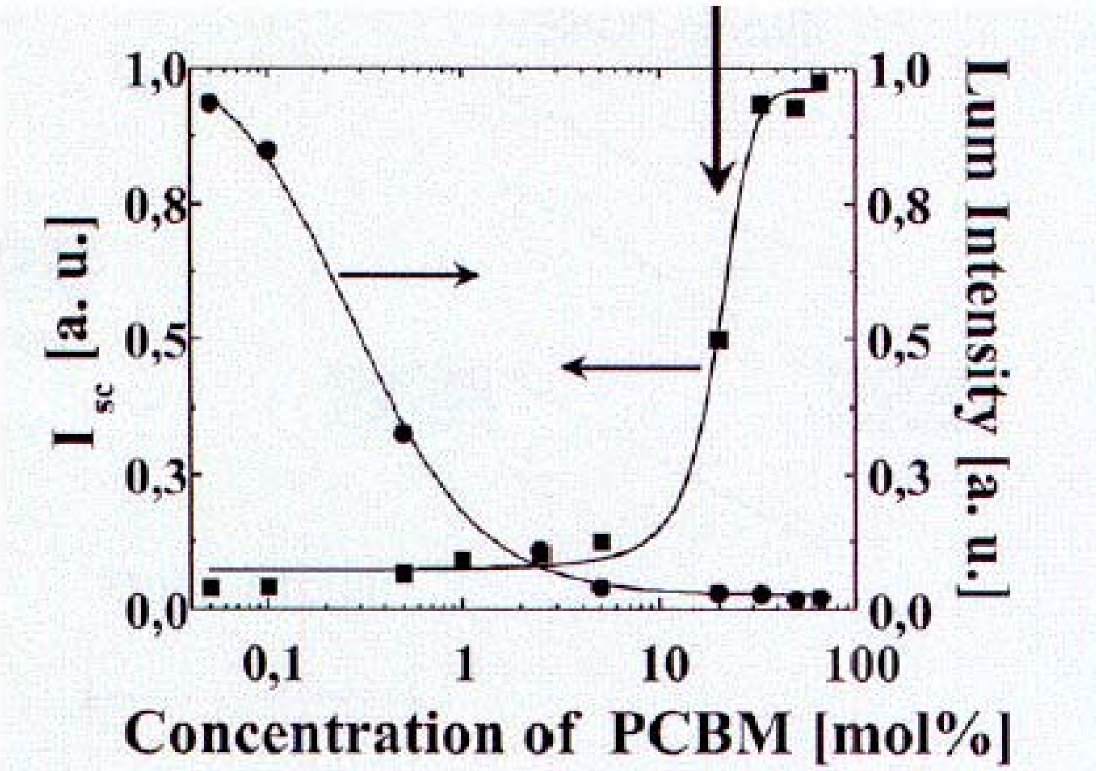


Figure by MIT OpenCourseWare.

Percolation



- 1 % PCBM quenches the photoluminescence.

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

Sean Shaheen