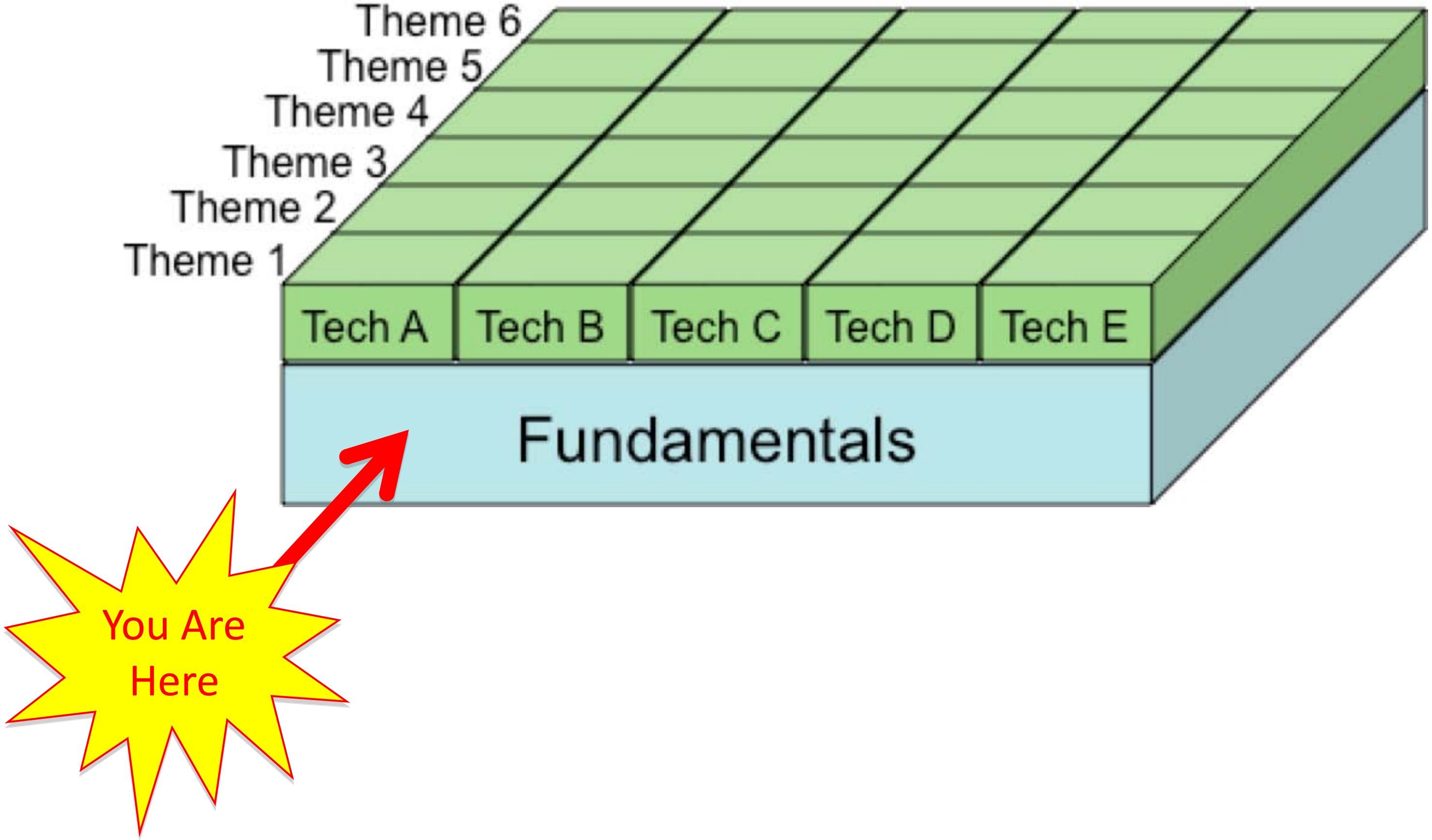
Charge Excitation

Lecture 4 – 9/20/2011

MIT Fundamentals of Photovoltaics
2.626/2.627 – Fall 2011

Prof. Tonio Buonassisi

2.626/2.627 Roadmap



2.626/2.627: Fundamentals

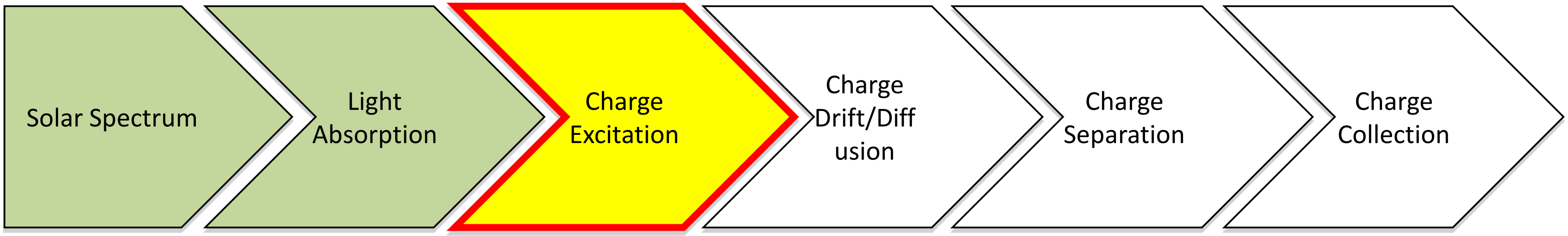
Every photovoltaic device must obey:

$$\text{Conversion Efficiency } (\eta) \equiv \frac{\text{Output Energy}}{\text{Input Energy}}$$

For most solar cells, this breaks down into:

Inputs

Outputs



Solar Spectrum

Light Absorption

Charge Excitation

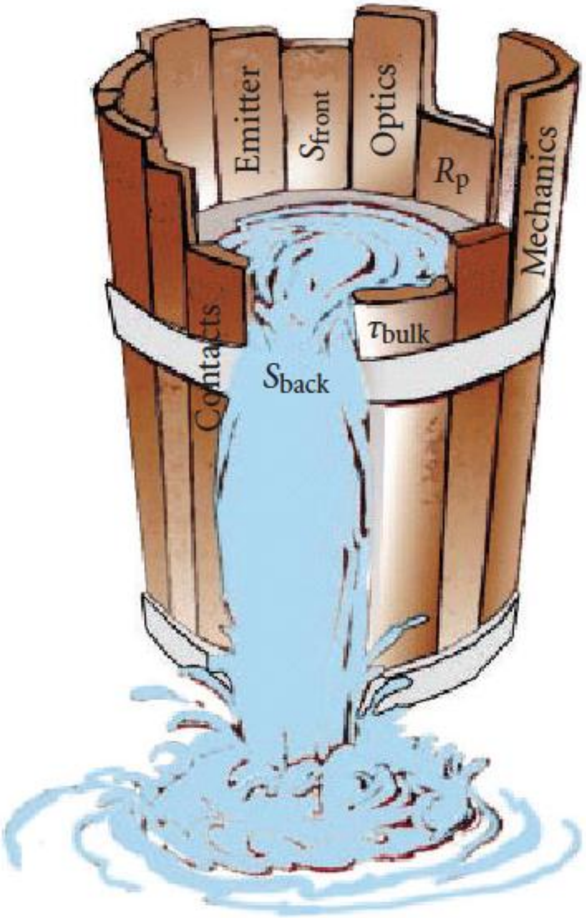
Charge Drift/Diffusion

Charge Separation

Charge Collection

$$\eta_{\text{total}} = \eta_{\text{absorption}} \times \eta_{\text{excitation}} \times \eta_{\text{drift/diffusion}} \times \eta_{\text{separation}} \times \eta_{\text{collection}}$$

Liebig's Law of the Minimum



S. Glunz, *Advances in Optoelectronics* 97370 (2007)

Image by S. W. Glunz. License: CC-BY. Source: "High-Efficiency Crystalline Silicon Solar Cells." *Advances in OptoElectronics* (2007).

$$\eta_{\text{total}} = \eta_{\text{absorption}} \times \eta_{\text{excitation}} \times \eta_{\text{drift/diffusion}} \times \eta_{\text{separation}} \times \eta_{\text{collection}}$$

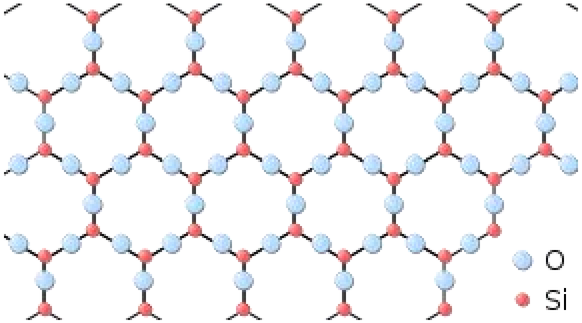
Learning Objectives: Solar Resource

1. **Describe phenomenologically how a "band gap" forms**
2. Describe optical absorption in semiconductors as transitions of charge carriers on an energy band diagram.
3. Calculate the fraction of photons lost (not absorbed) by a semiconductor material with a given band gap, thickness, and reflectivity.
4. Calculate fraction of incident solar energy lost to "thermalization."
5. Plot efficiency vs. bandgap, and denote specific materials.

Bandgap: Basic Description

Bonds: why stuff is tough.

Excited electrons: why materials conduct



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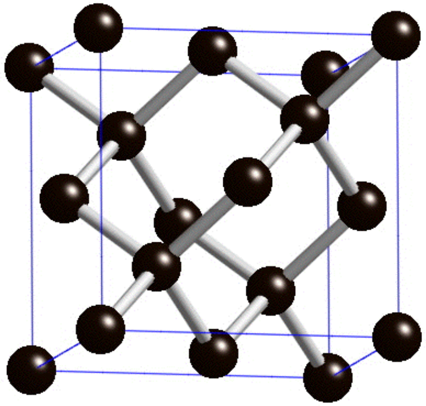

Courtesy of Harry Bhadeshia.
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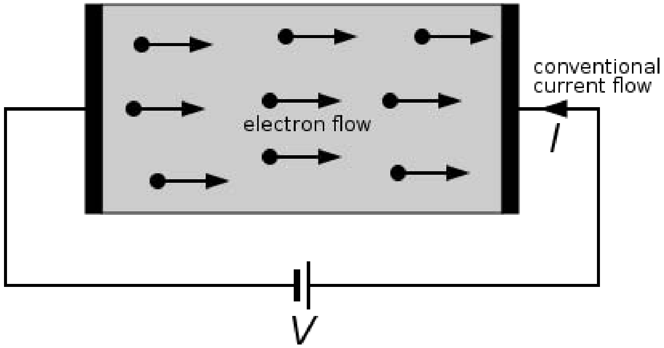

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- The “bandgap energy” can most simply be understood, as the finite amount of energy needed to excite a highly localized electron into a delocalized, excited state in a semiconductor.

Bandgap: Chemist's Description

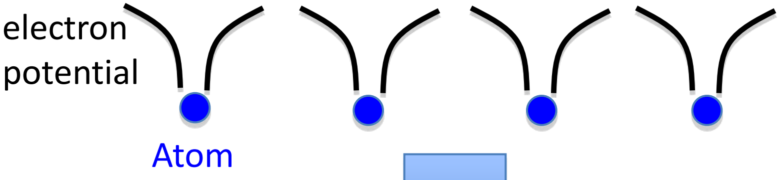
- An atom in isolation has discrete electron energy levels.
- As atoms move closer together, as in a crystal, electron wavefunctions overlap. Electrons are Fermions, meaning two particles cannot occupy the same state. Discrete atomic electron energy levels split, forming bands.
- The gap between bands,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

Bandgap: Physicist's Description

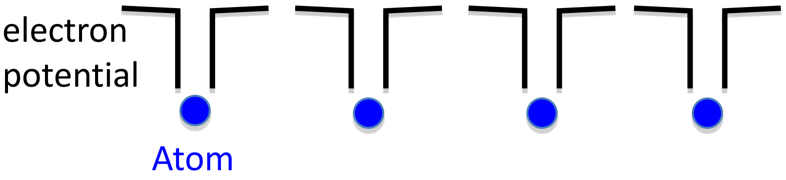
$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}).$$

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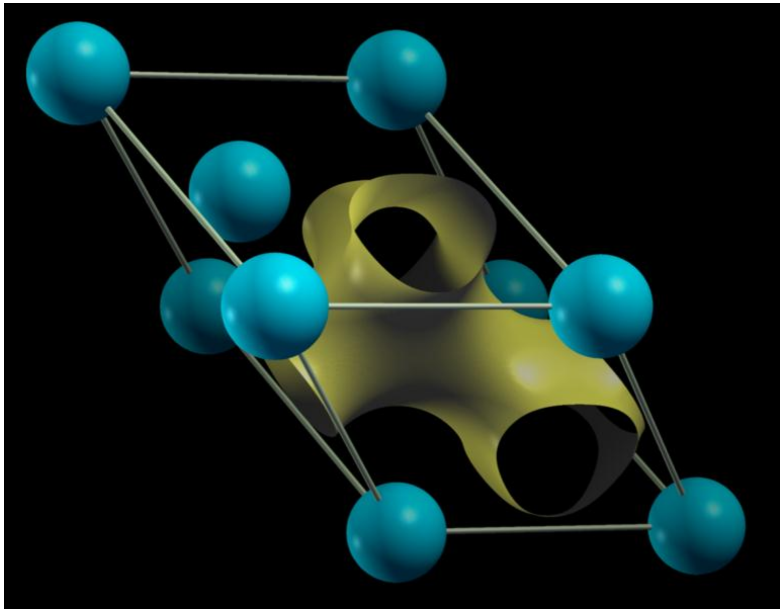
For real systems, use (a) symmetry + group theory or (b) pseudopotentials + computer modeling to solve for electron wavefunctions. For many crystal structures, strong directional dependence of the wavefunction.

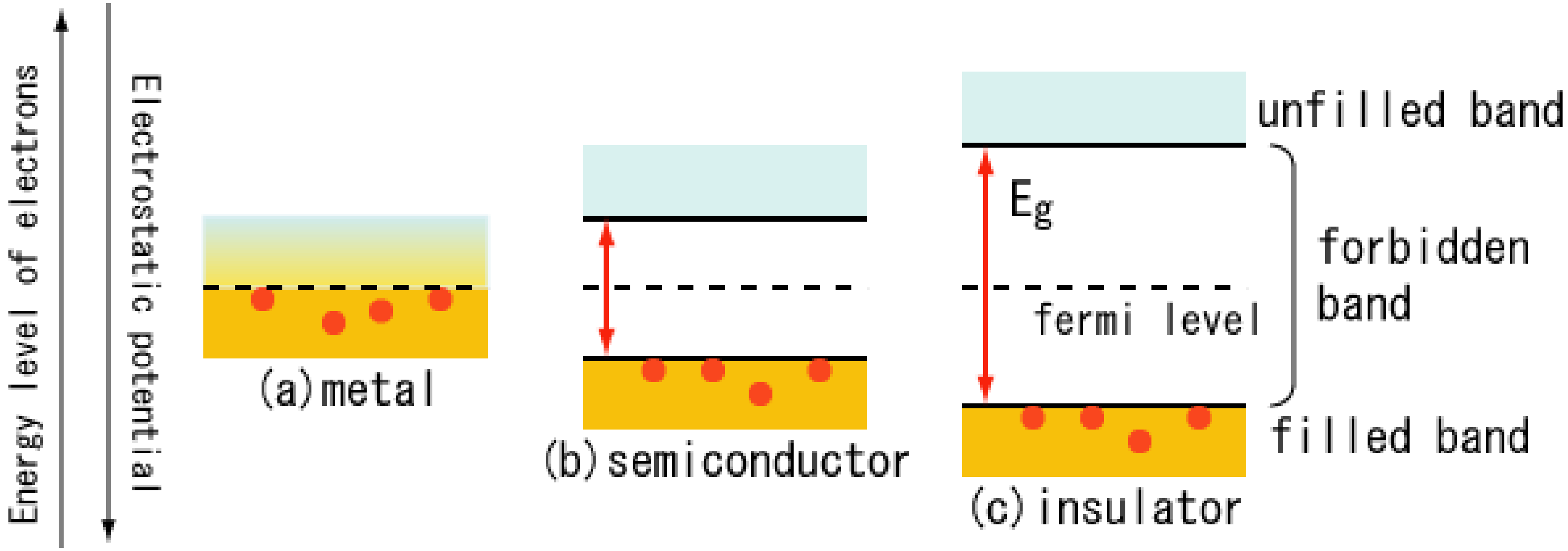
Electron isopotential surface in silicon



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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Learning Objectives: Solar Resource

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Photons – Quanta of Light

- Quantum theory describes the frequency dependence of photon energy.

Relevant Equations:

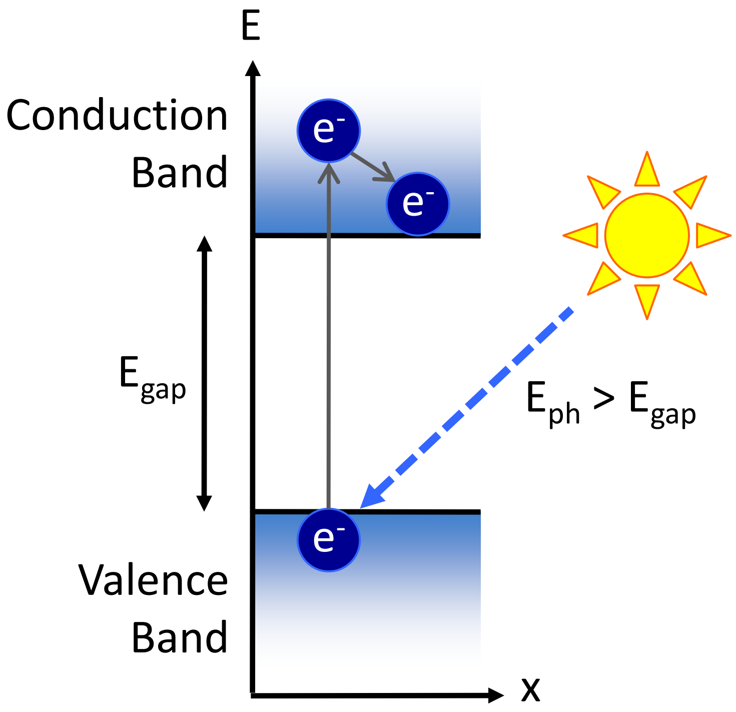
$$E_{\mathrm{ph}} = h\nu = \frac{hc}{\lambda}$$

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

Particle-wave duality:

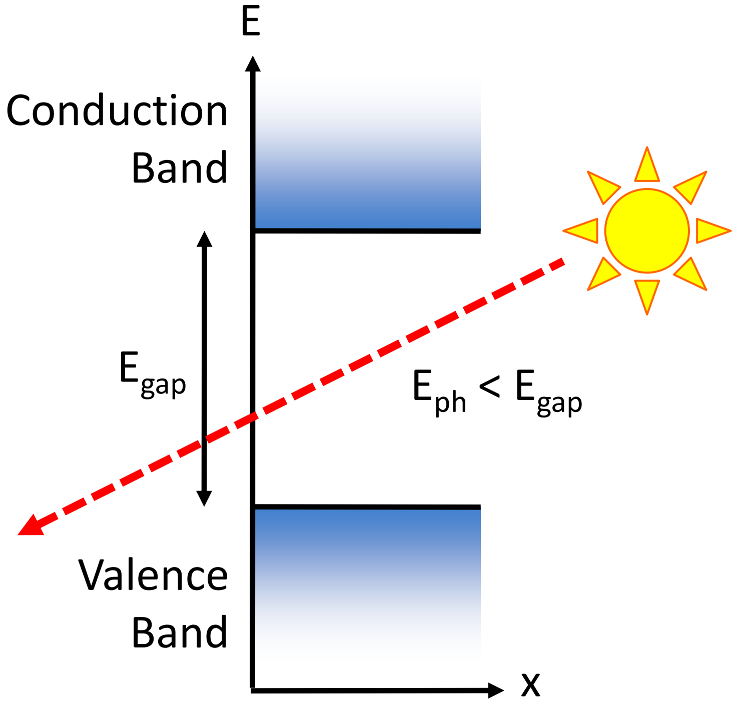
Photons have discrete quanta of energy.
Photons have momentum.
Light can be polarized.
Light can be diffracted.
Light waves can destructively and constructively interfere.

Charge Promotion in Semiconductors



At photon energies above the band gap
(*i.e.*, shorter photon wavelengths),
light is absorbed by the semiconductor
and charge is promoted into the conduction band

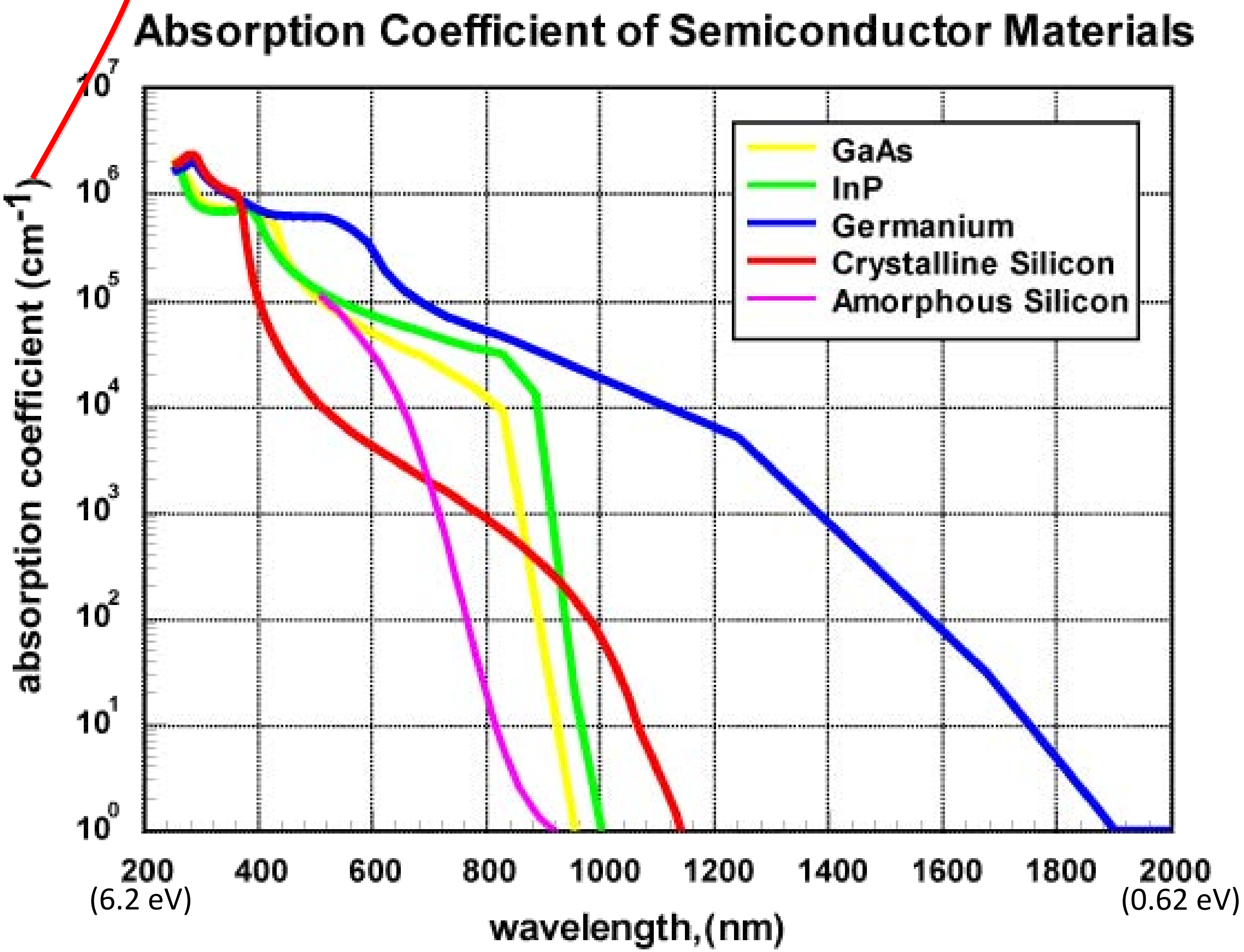
Charge Promotion in Semiconductors



At photon energies less than the band gap (*i.e.*, longer photon wavelengths), incident light is not efficiently absorbed.

Absorption Coefficient (α) for different materials

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

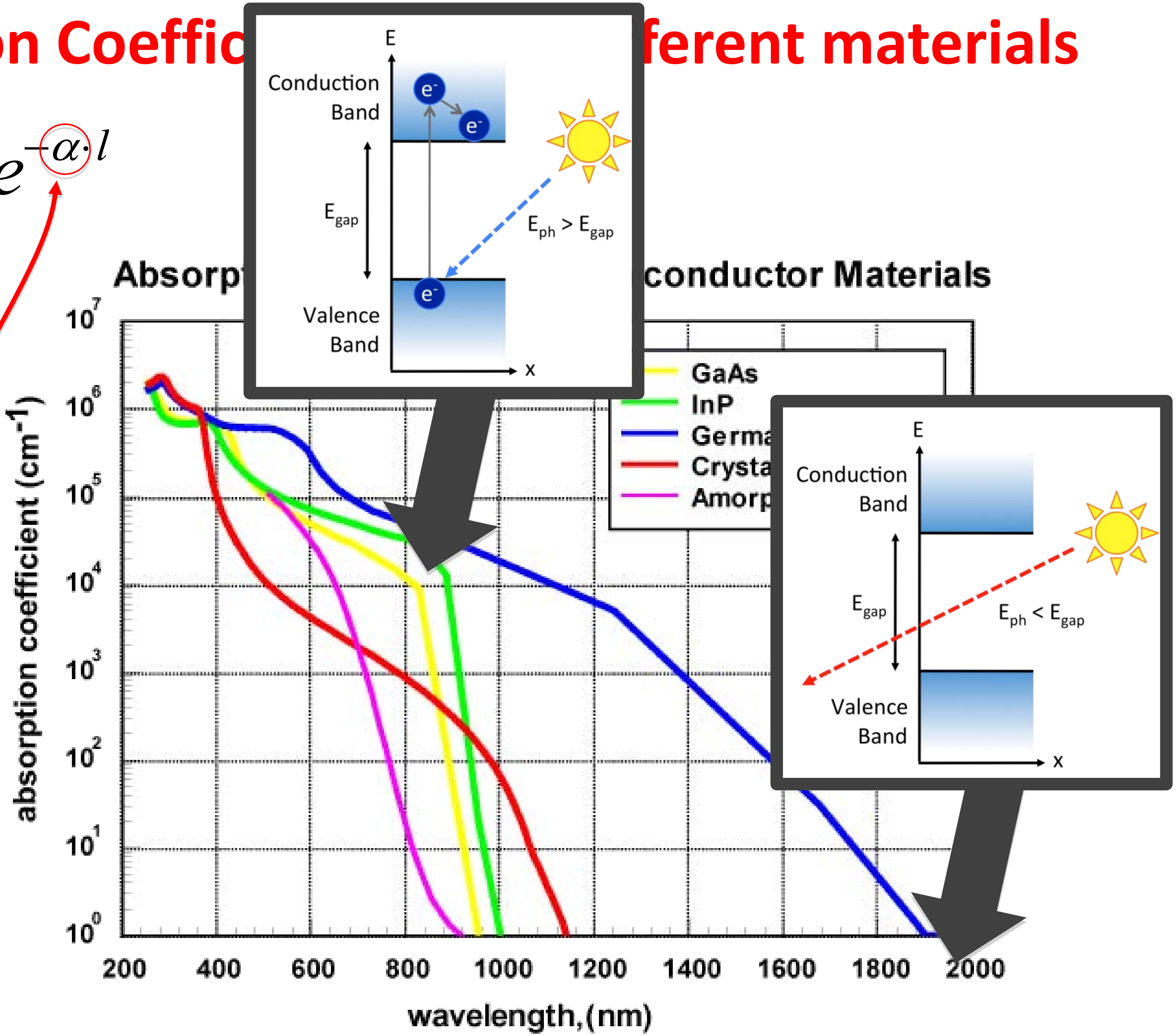


Courtesy of PVCDROM. Used with permission.

Buonassisi (MIT) 2011

Absorption Coeffic ferent materials

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



(6.2 eV)

(0.62 eV)

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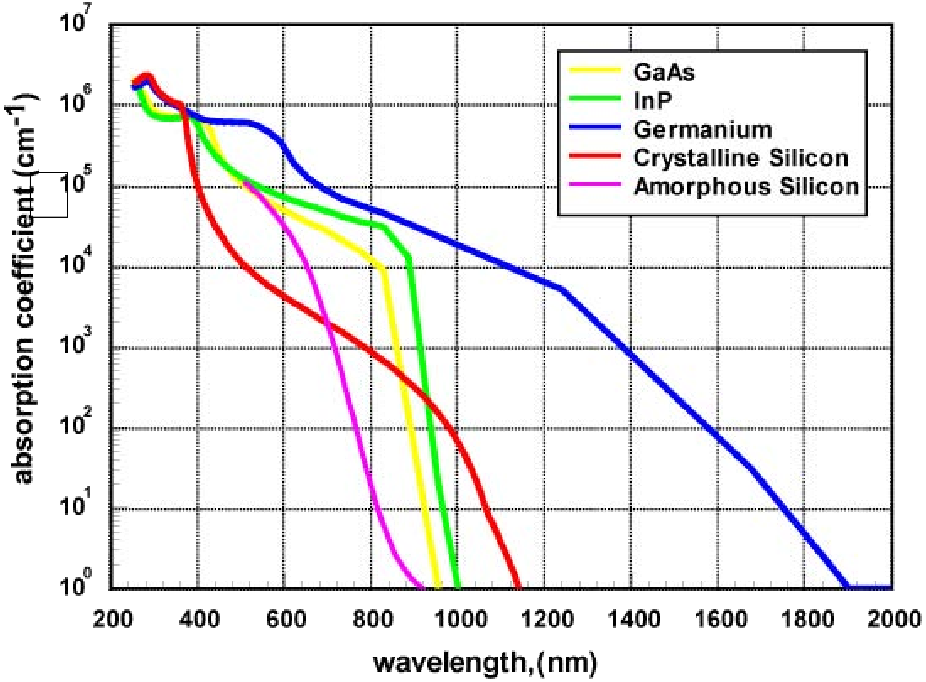
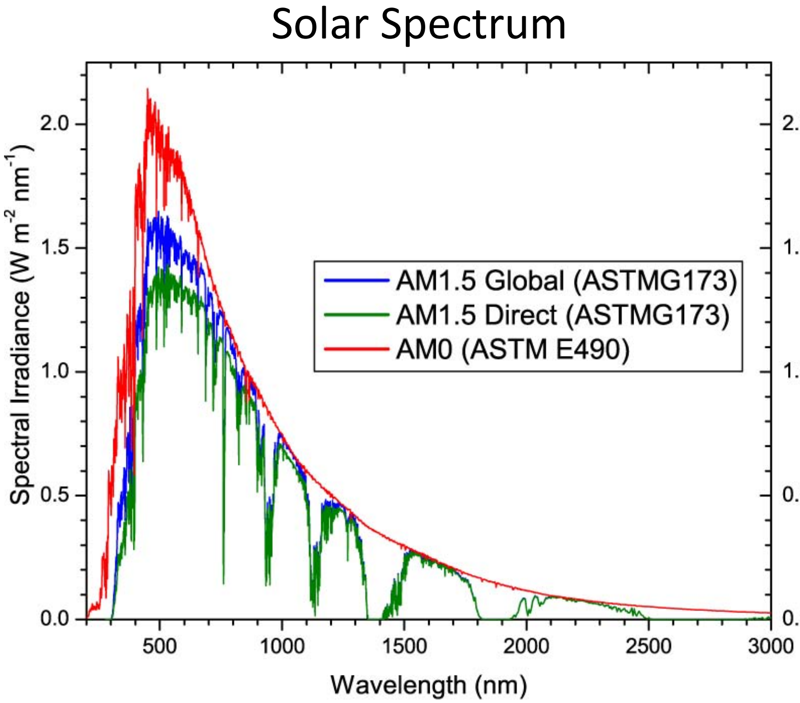
Thickness estimate for solar cell materials

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.

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





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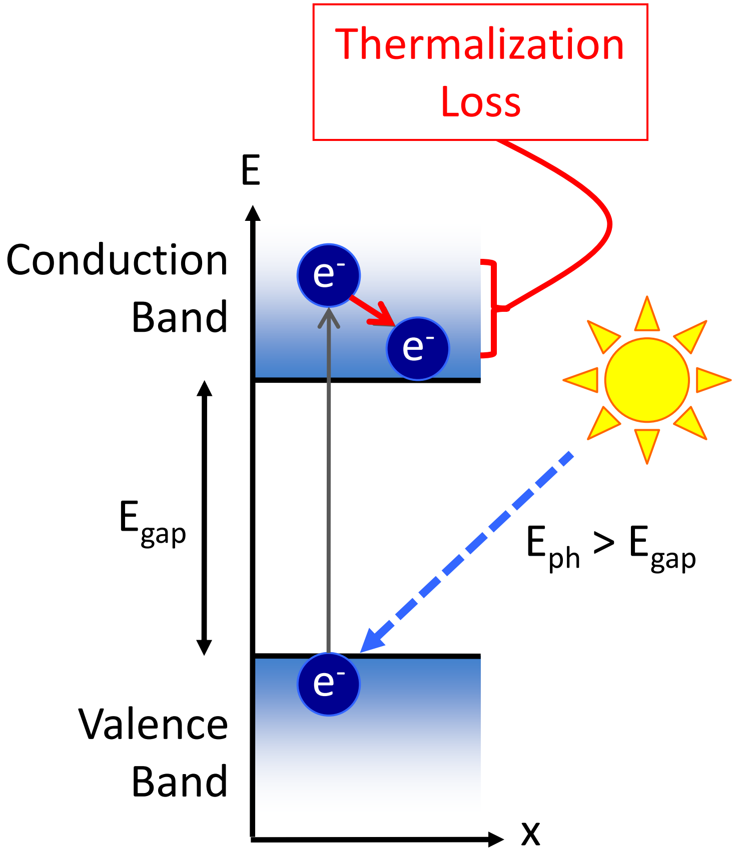
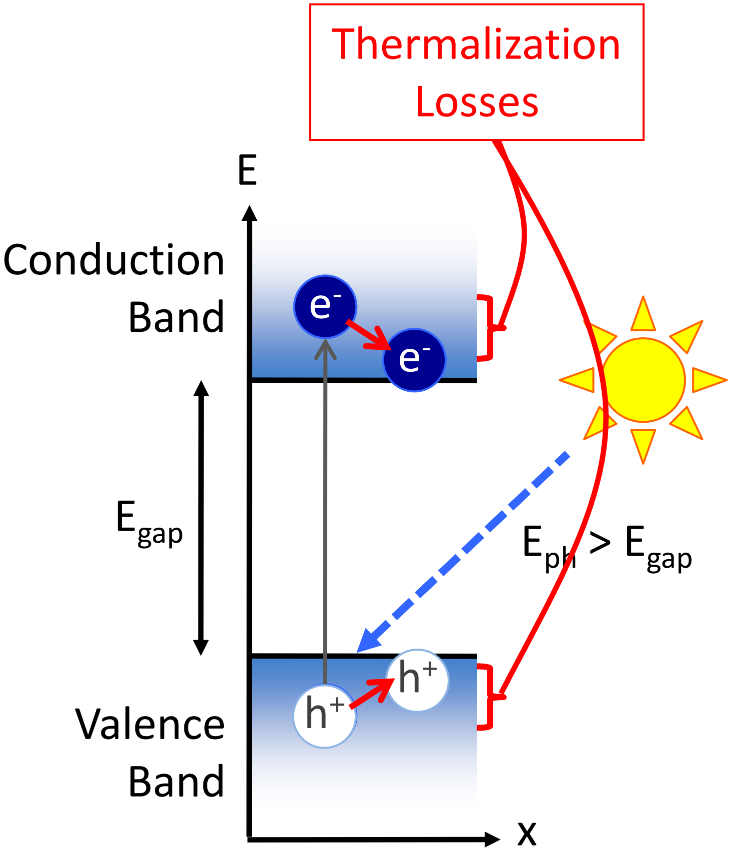
Thermalization



At photon energies above the band gap
(*i.e.*, shorter photon wavelengths),
light is absorbed by the semiconductor
and charge is promoted into the conduction band

Photon energy in excess of the bandgap
is lost due to "thermalization."

Thermalization



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Time Scale of Thermalization

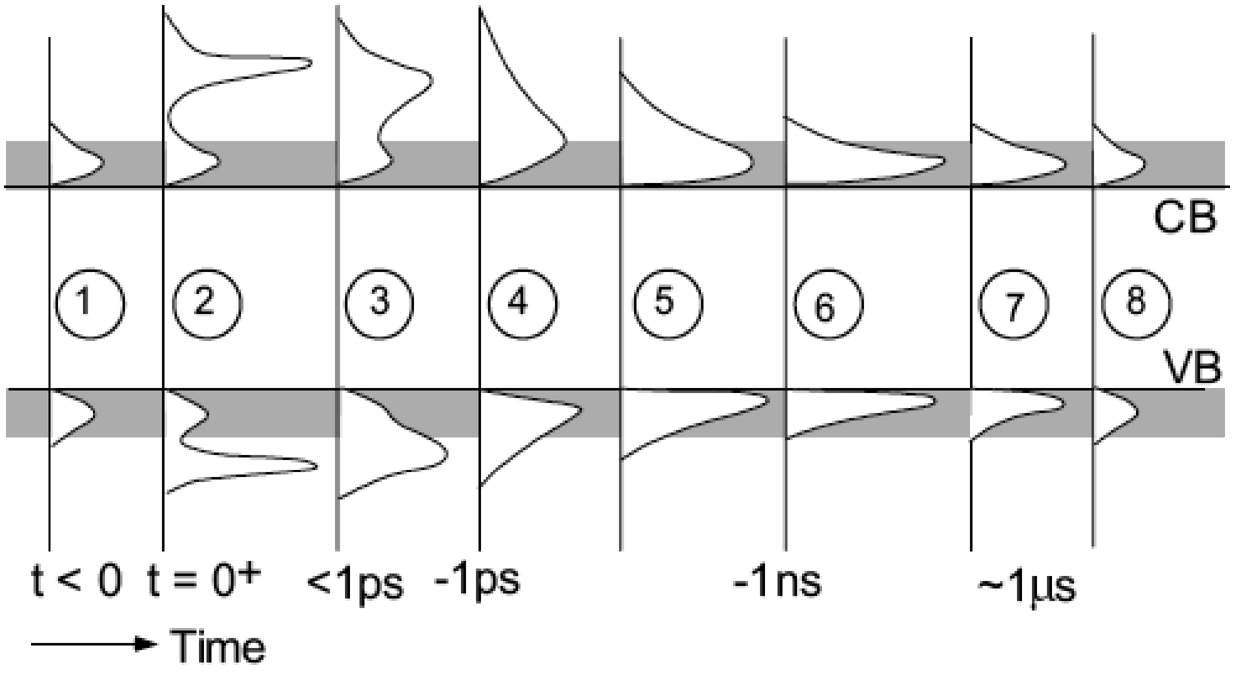

Fig. 4. Energy relaxation of carriers after a short, high-intensity laser pulse at $t = 0$.

Courtesy of Elsevier, Inc., http://www.sciencedirect.com. Used with permission.

M.A. Green, *Physica E* **14**, 65 (2002)

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Energy Losses: First Approx.

Thermalization Losses

(band gap too small)

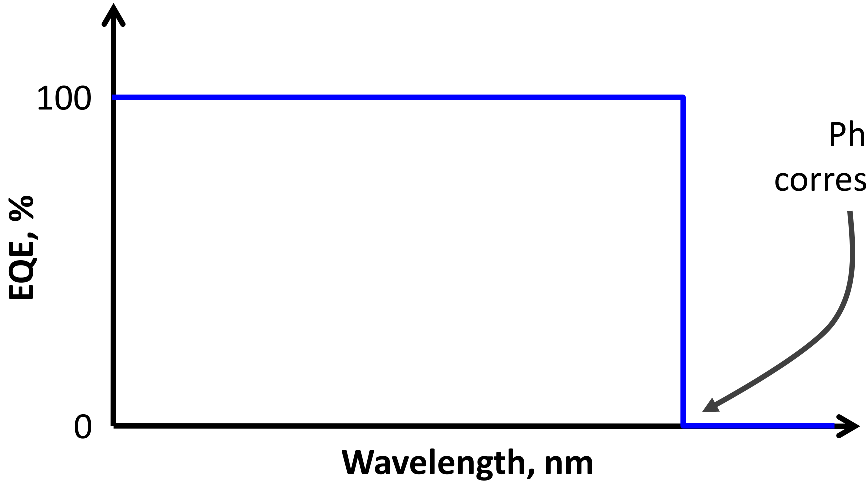
Non-Absorption Losses

(band gap too large)

Approximating Non-Absorption Losses

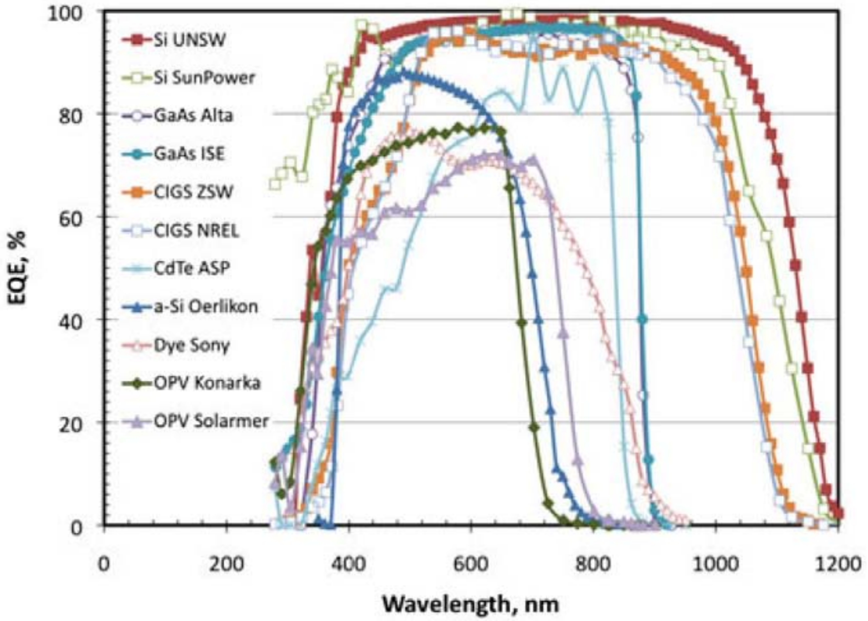
Approximation

EQE = **External Quantum Efficiency**, *i.e.*, the efficiency at which free charge carriers are generated by incident photons on the device.



Photon wavelength corresponding to $E_{ph} = E_{gap}$

Reality

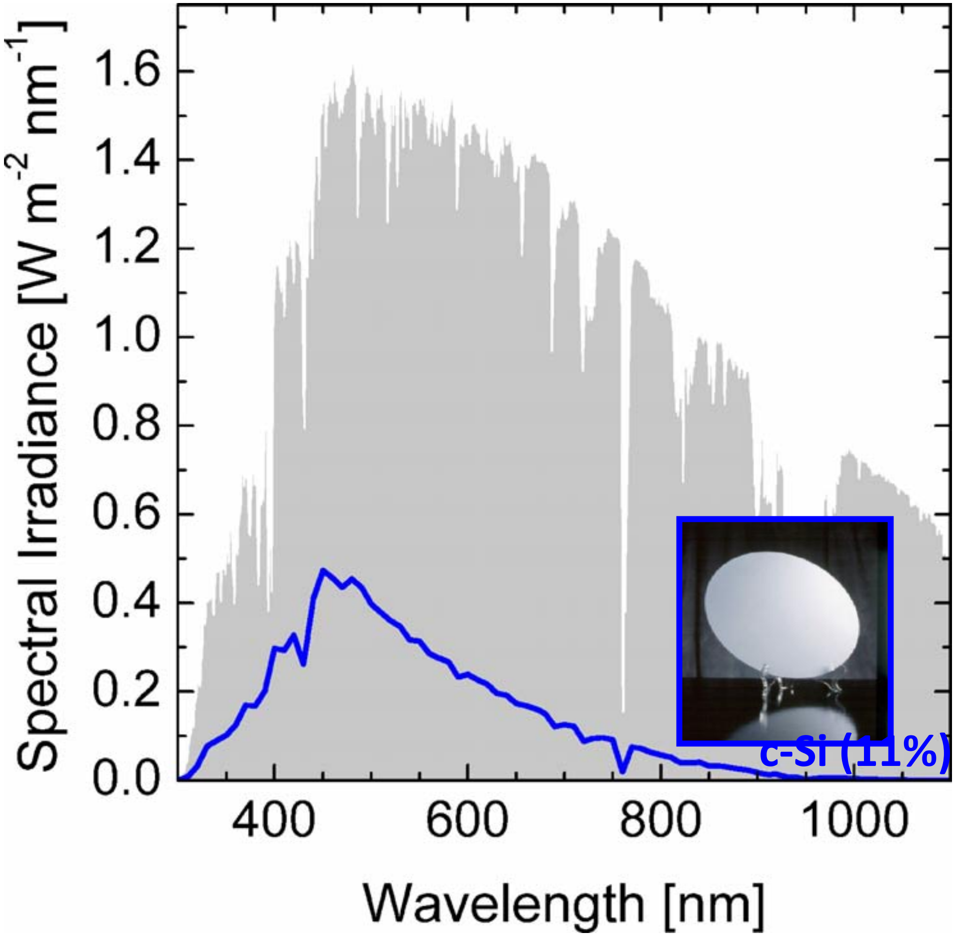


M.A. Green, "Radiative efficiency of state-of-the-art photovoltaic cells," *Progress in Photovoltaics* (DOI: 10.1002/pip1147), 2011.

Approximating Non-Absorption Losses

Reality

Solar Capture: 1 µm Absorber, Single Pass



Approximating Thermalization Losses

Approximation

$$\text{If } E_{\text{ph}} > E_{\text{gap}},\ \text{then}$$

$$E_{\text{ph}} \approx E_{\text{gap}} + E_{\text{thermalization}}$$

Reality

- For high-energy photons (E_{ph} > ~3 x E_{g}), electron-electron interactions can exist, including multiple carrier (exciton) generation.
- For really high-energy photons (keV–GeV range), core electron interactions, e^{-}-p^{+} pair formation, occur.

Representation of Maximum Power: Single Junction

Energy Losses: First Approximation

Balance between Thermalization and Non-Absorption Losses

Please see lecture video for relevant graphs and explanation.

Advanced Concept:
Tandem Cells (Multijunction Devices)

Exceeding the S.-Q. Limit

Maximum Power: Multi-Junction

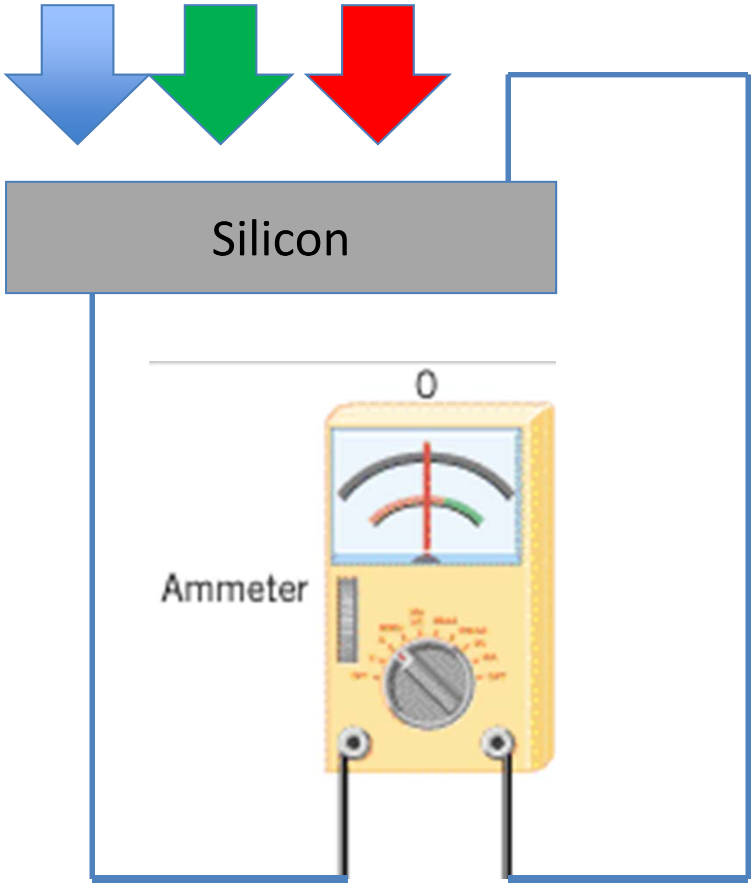
Spectral Splitters

Please see lecture video for relevant graphs and explanation.

Photocurrent Generation

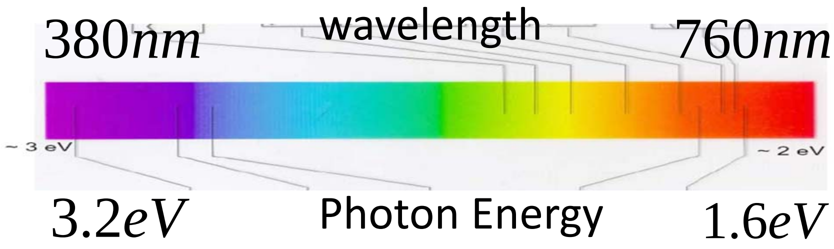
Experimental observations

Experiment 1



LIGHT

Color- Wavelength- Photon Energy

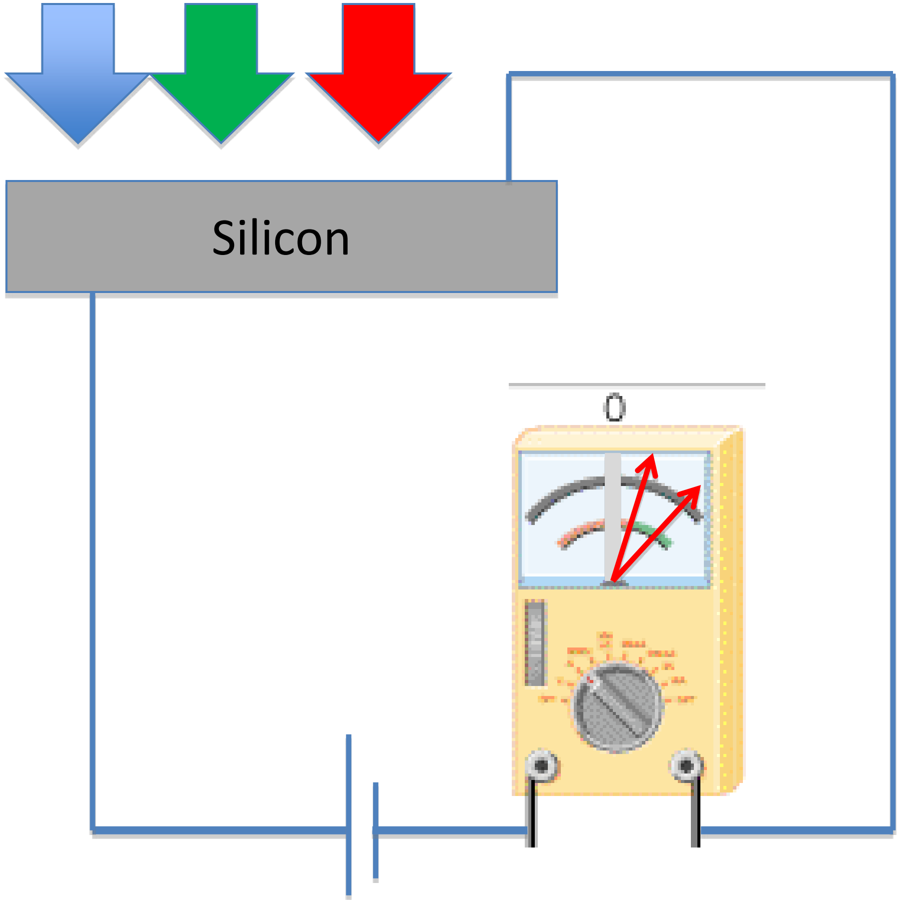


Courtesy of Ilan Gur. Used with permission.

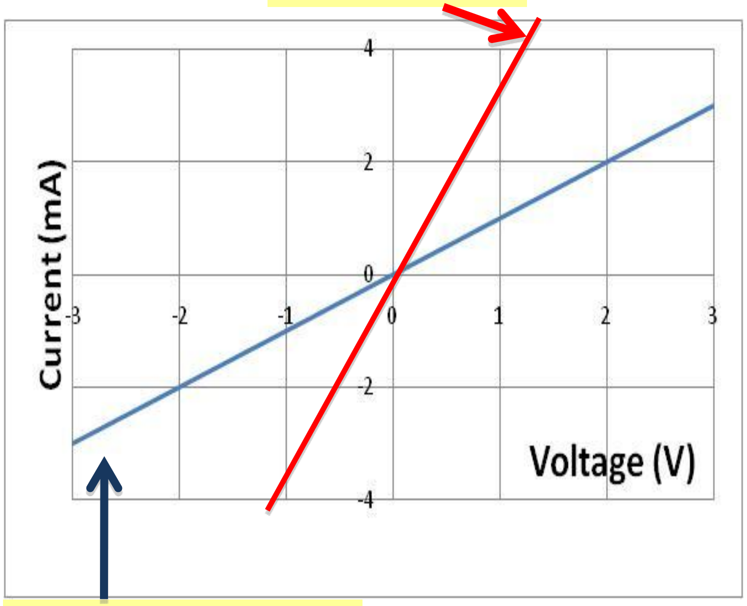
$$E_{\mathrm{ph}}(eV) = \frac{1.24}{\lambda(\mu m)}$$

No Current Observed under light, regardless its color (wavelength)

Experiment 2



Under light

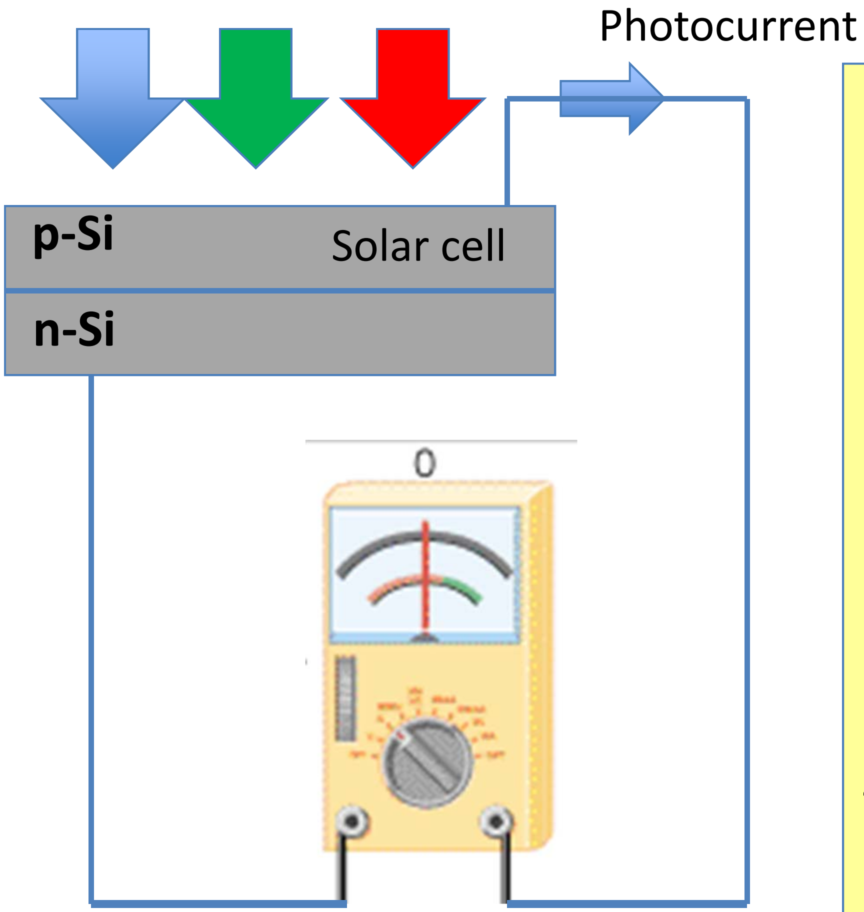


Under darkness

Small Current under darkness , larger current under light

Conclusion: The electric field of the battery is necessary to generate the photocurrent

Experiment 4



Observations:

1. No need for a battery to detect a photocurrent

2. The photocurrent is generated if

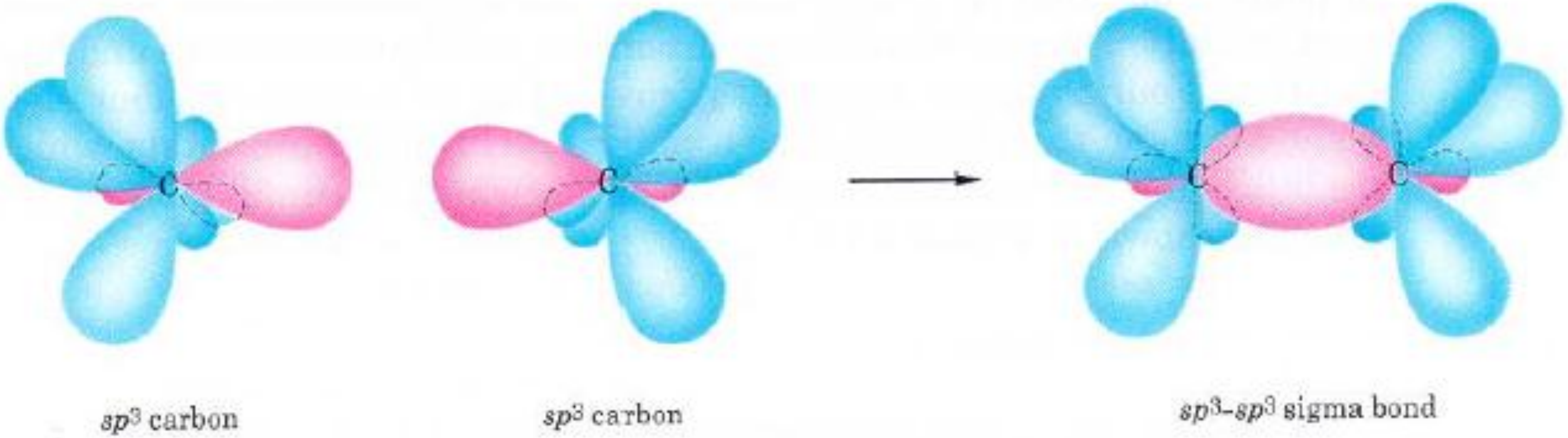
$$\lambda < \lambda_{\min}$$

3. λ_{min} depends on the material.

4. The photocurrent depends on the " Quality" of the material: (Purity , Defects , Cristallinity: monocrystalline, polycrystalline or amorphous)

Light Absorption in Organic Materials

Why most polymers and organic solids are insulators



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

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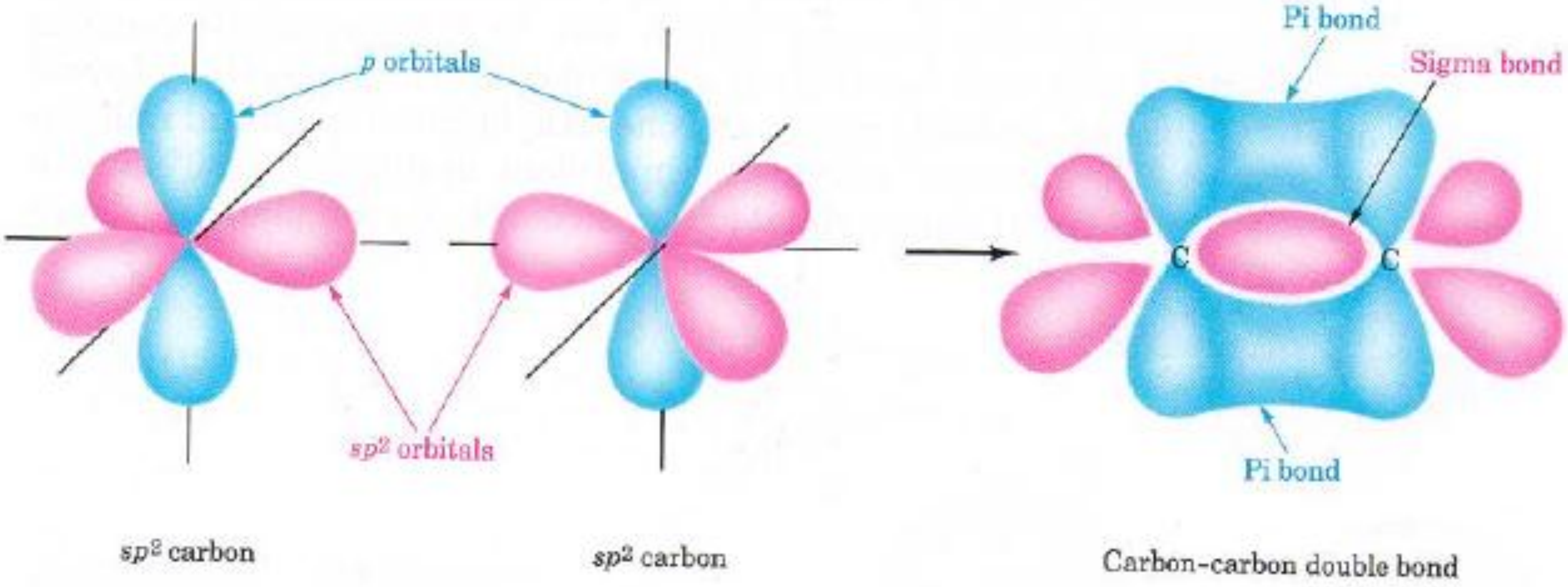
Why conjugated molecules can be semiconductors



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

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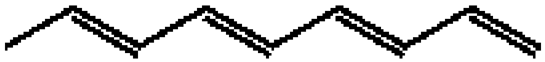
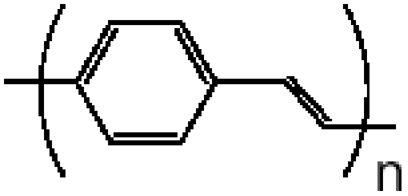
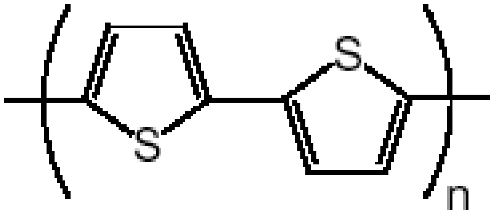
Chemical structure of common conjugated polymers



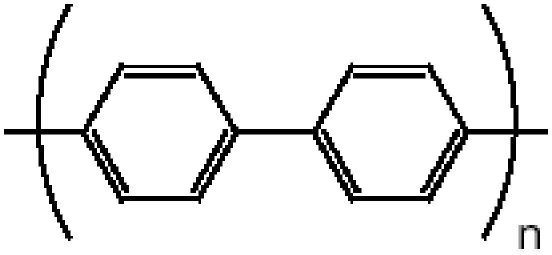
PA: polyacetylene
(1st conducting polymer)



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



PT: polythiophene
(widely used in transistors)



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

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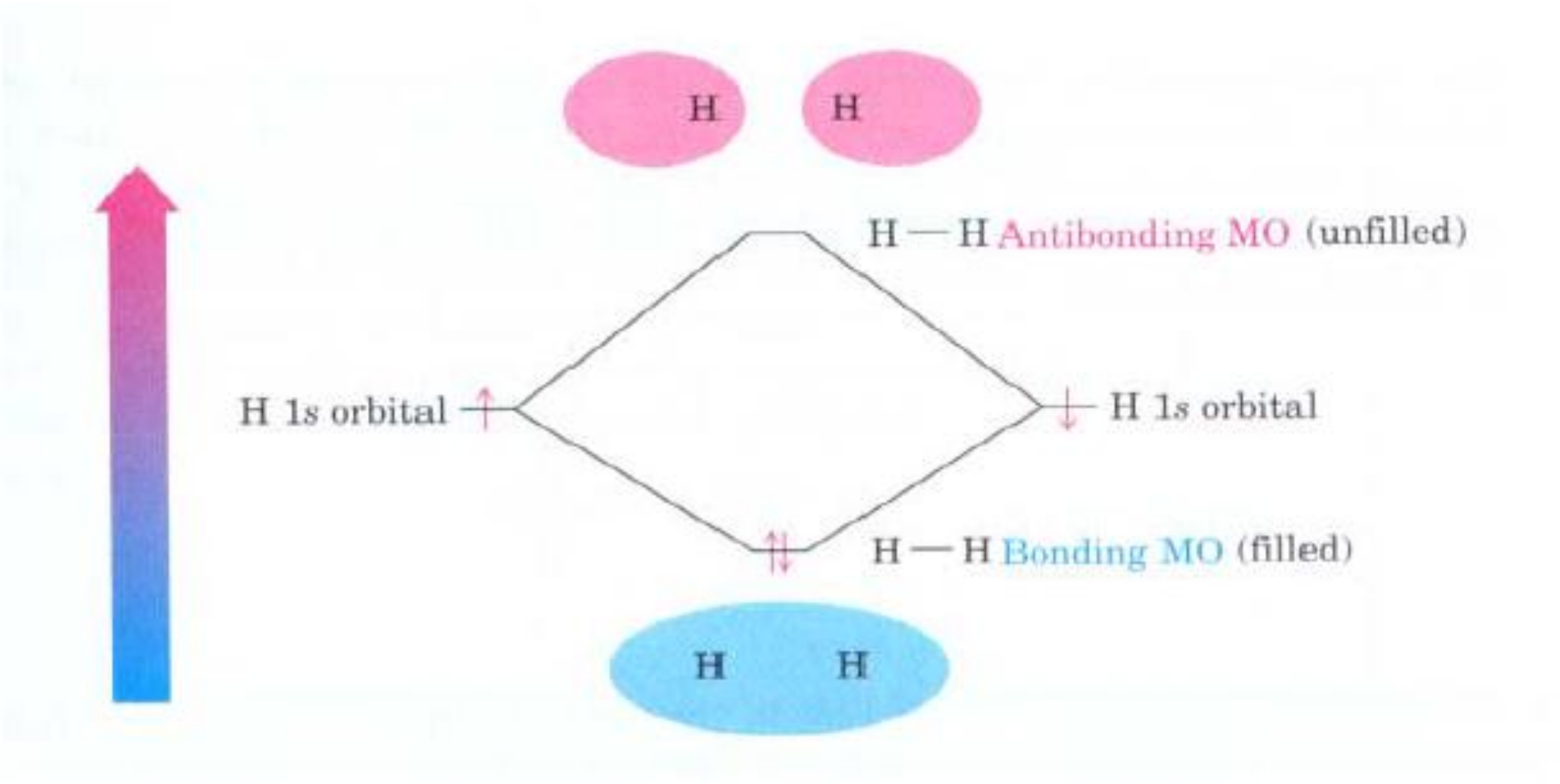
Bonding and antibonding orbitals



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

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

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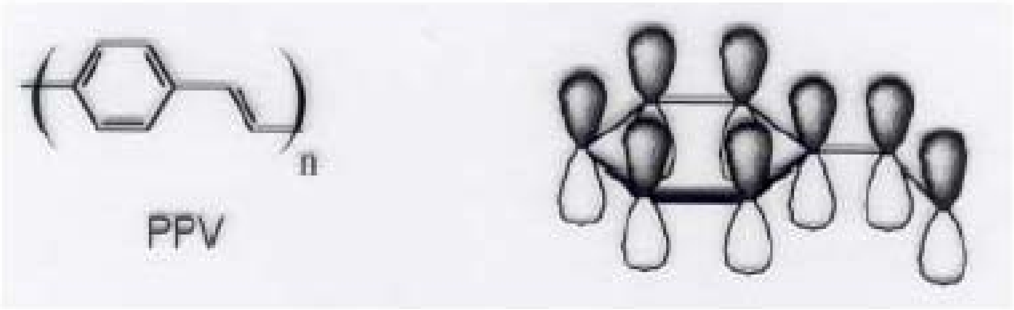
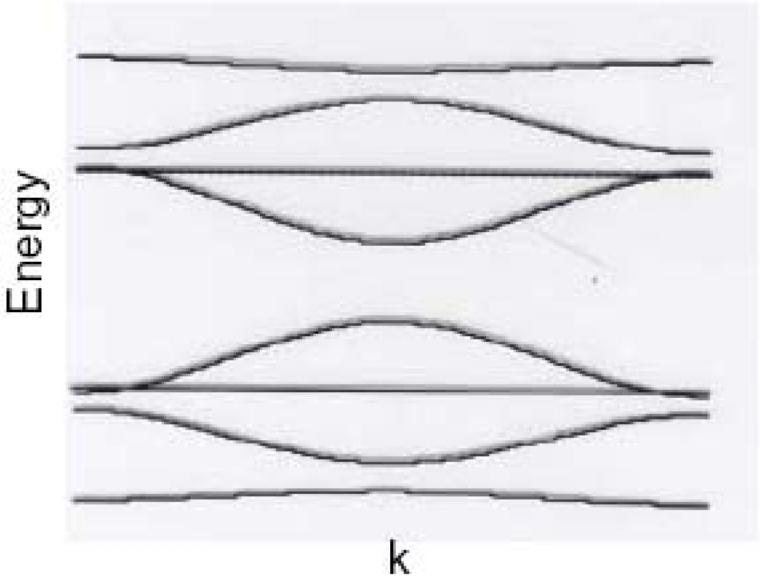
Band structure of conjugated polymers



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



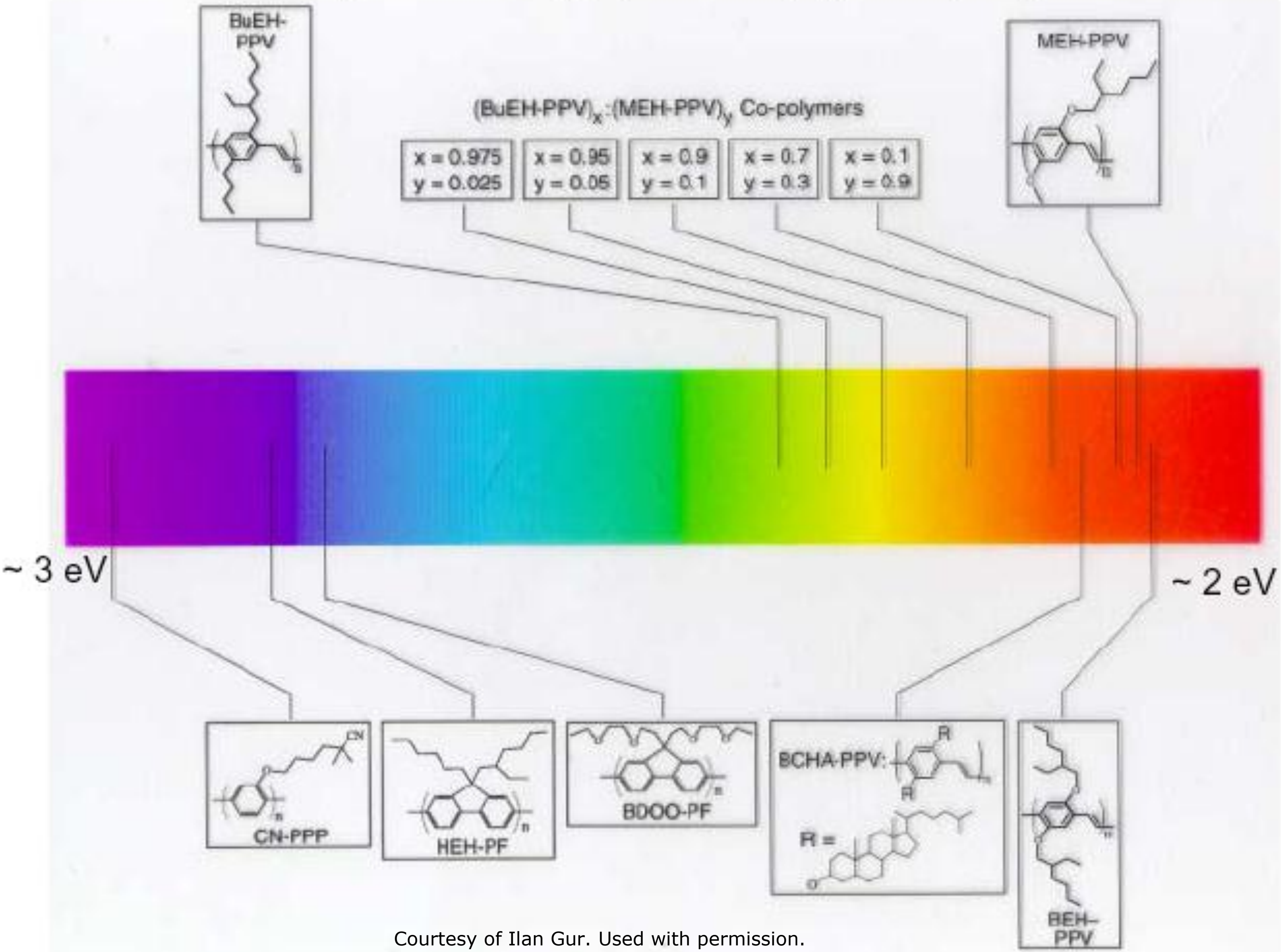
Empty π* bands

Full π 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



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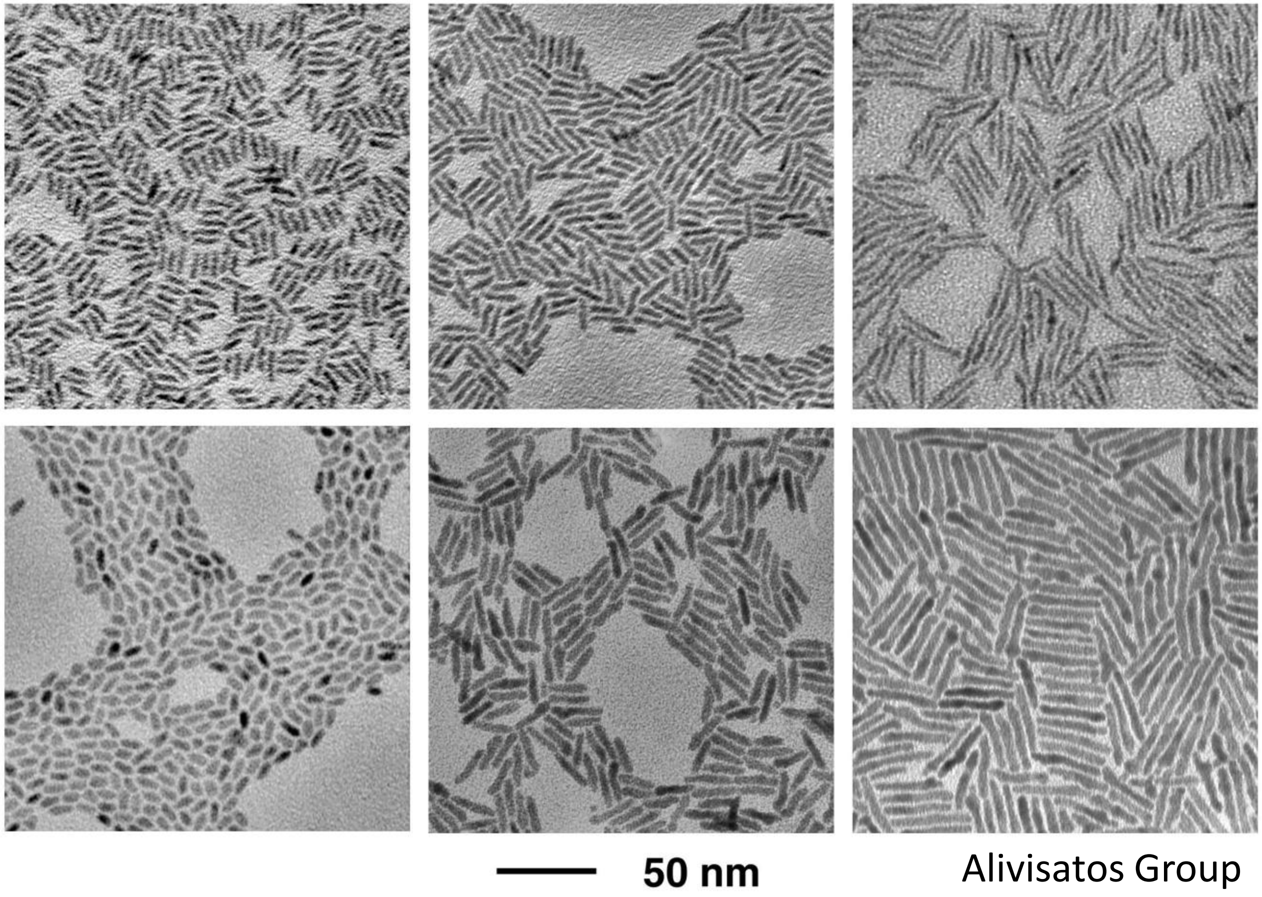
Light Absorption in Nanomaterials

Light Absorption in Nanomaterials

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



Alivisatos Group

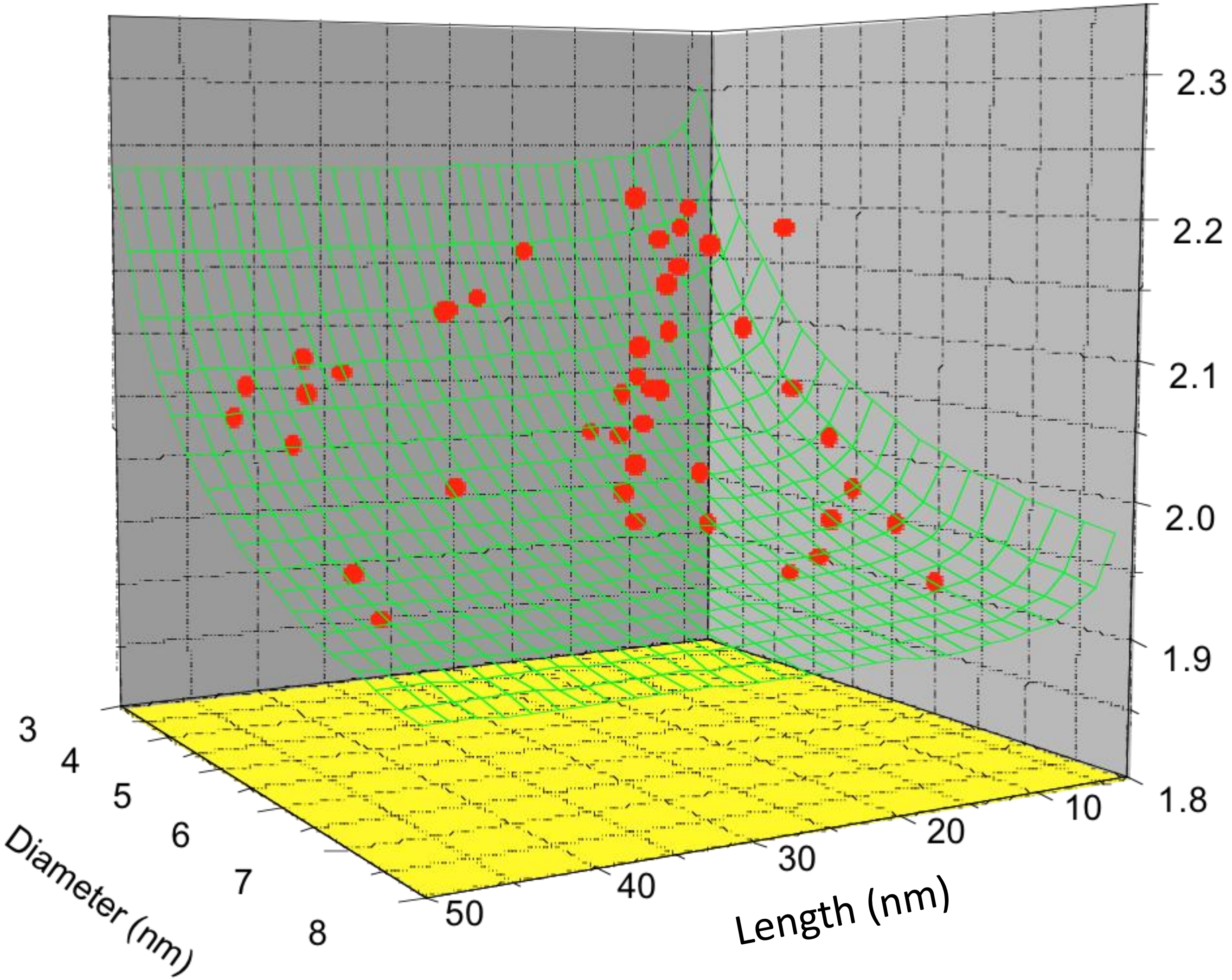
Courtesy of A. Paul Alivisatos. Used with permission.

Light Absorption in Nanomaterials

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

Image removed due to copyright restrictions.

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." <u>Nano Letters</u> **1**(7): 349-351.

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2.627 / 2.626 Fundamentals of Photovoltaics
Fall 2013