2.626 Fundamentals of Photovoltaics
Fall 2008

Light Absorption, Charge Excitation and Transport

Lecture 4 – 2.626

Tonio Buonassisi

Concept Quiz: Summary

Problem 1: ***Great!***

Identify which unit denotes "power", and which denotes "energy": kWh, kW.

Problem 2: ***So-so…***

For a solar system rated at 2 kW_{peak} (the peak power), provide an estimate of kW_{ave} (the average power) this system will produce in Boston. (Full credit for answers accurate to within a factor of two).

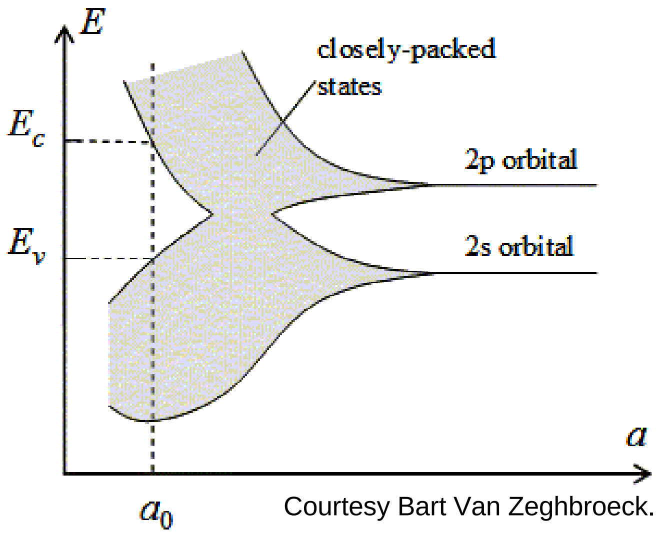
Quick Outline of Today's Lecture

Last class, we discussed *light absorption*, *charge excitation*, and *charge carrier mobility* in semiconductors, organic molecules, and nanoparticles.

This class, we discuss *free carrier concentrations*, *conductivity*, and *recombination*.

Review: Bandgap

Arises due to interfering atomic electron orbitals.



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http://ece-www.colorado.edu/~bart/book/book/chapter2/ch2_3.htm

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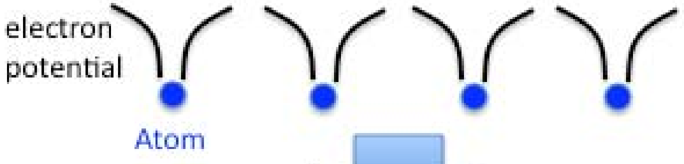
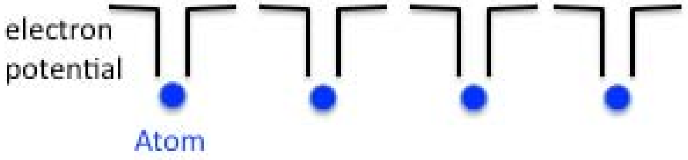
Created by repeating crystal potential.

Schematic of a repeating Coulomb potential in a crystal



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



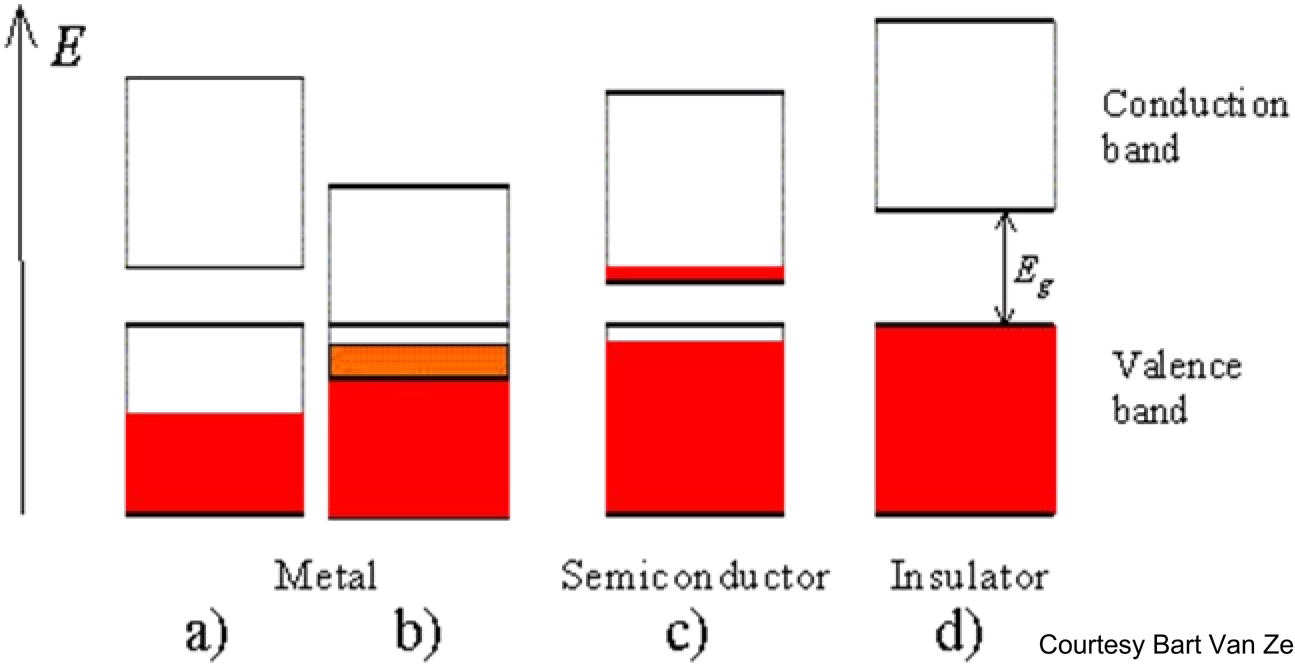
$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}).$$

Solve Schrödinger's equation → two possible solutions:

(1) Electron wavefunction centered on atoms (bound state)

(2) Electron wavefunction centered between atoms (excited state).

Classes of Materials, based on Bandgap



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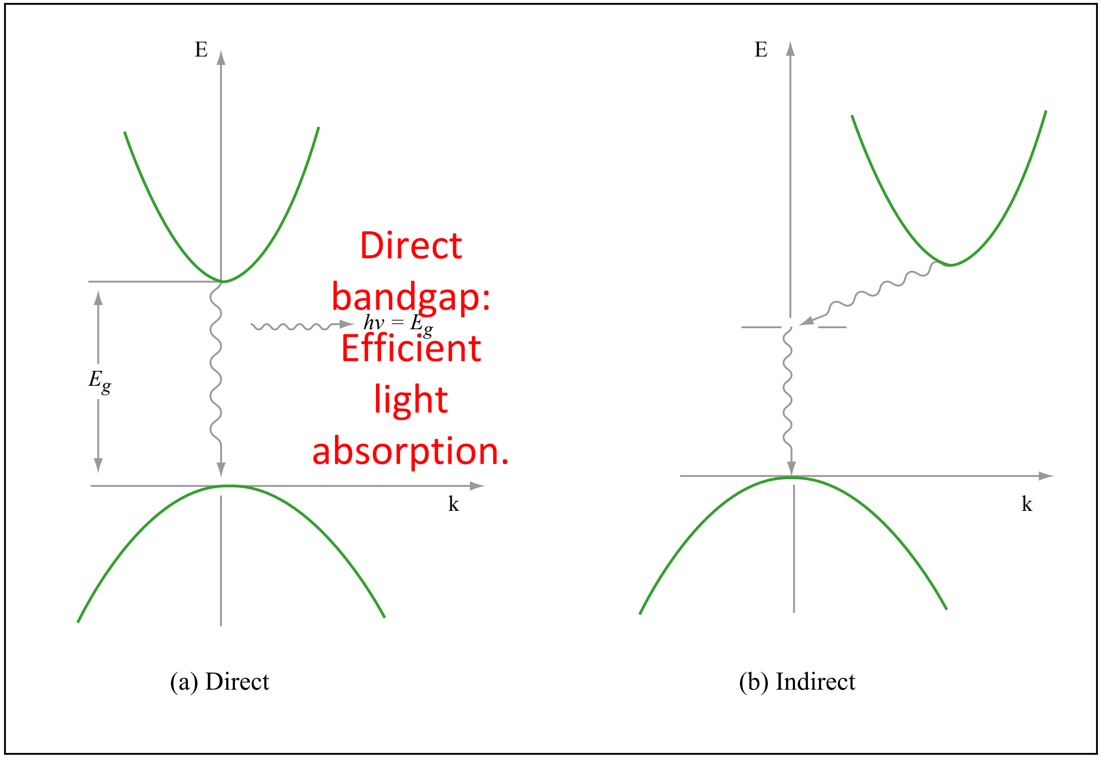
Review: Optical Absorption in Semiconductor

Material properties described by the **energy band diagram**:

1. Absorption of light.



(a) Direct

(b) Indirect

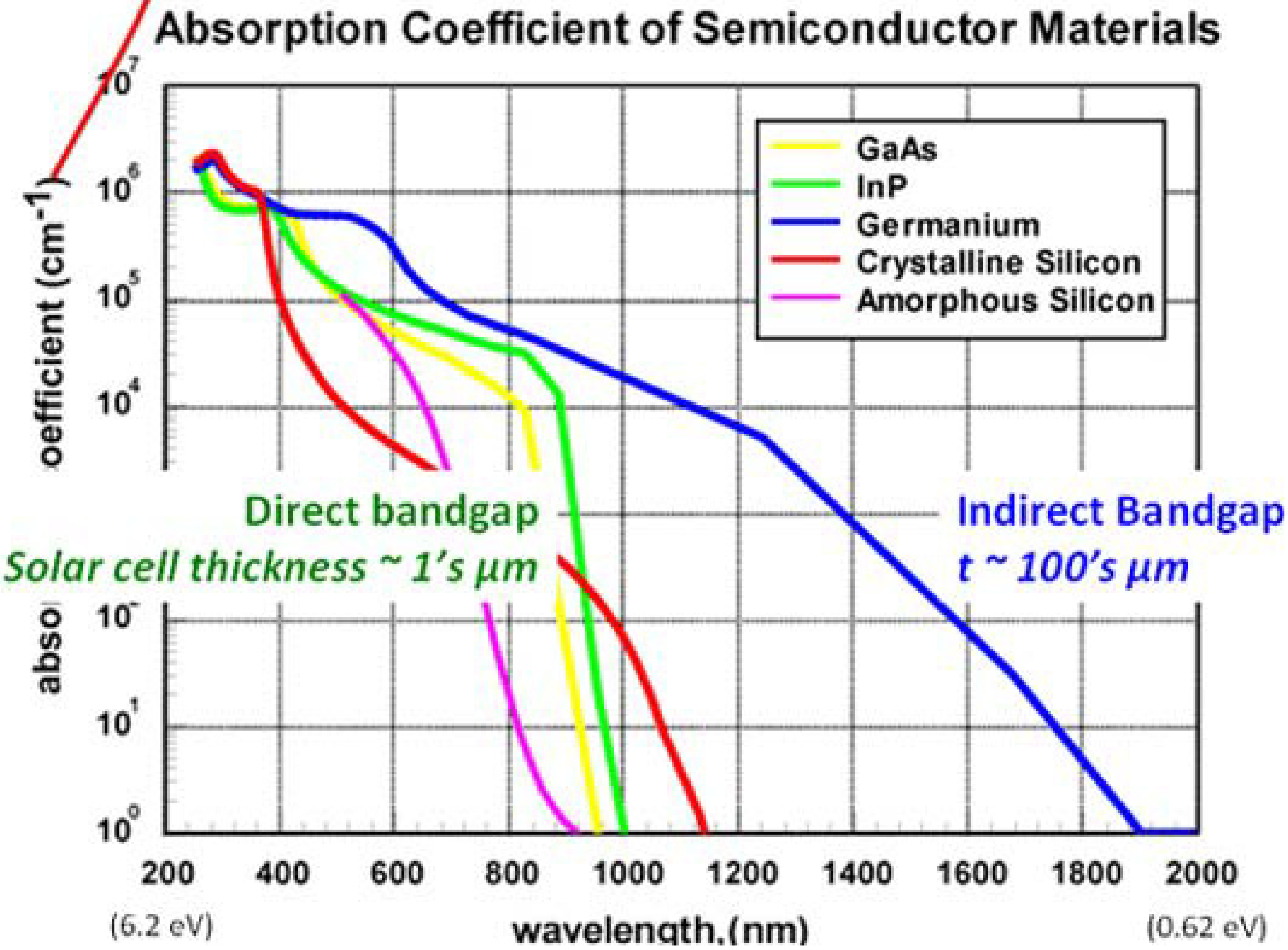
Direct bandgap: Efficient light absorption.

Indirect bandgap: phonon-assisted transition. Less efficient light absorption.

Figure by MIT OpenCourseWare.

Absorption Coefficient (α) for different materials

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



Direct bandgap

Solar cell thickness ~ 1's µm

Indirect Bandgap

t ~ 100's µm

Courtesy Christiana Honsberg and Stuart Bowden. Used with permission.

Review: Carrier Mobility

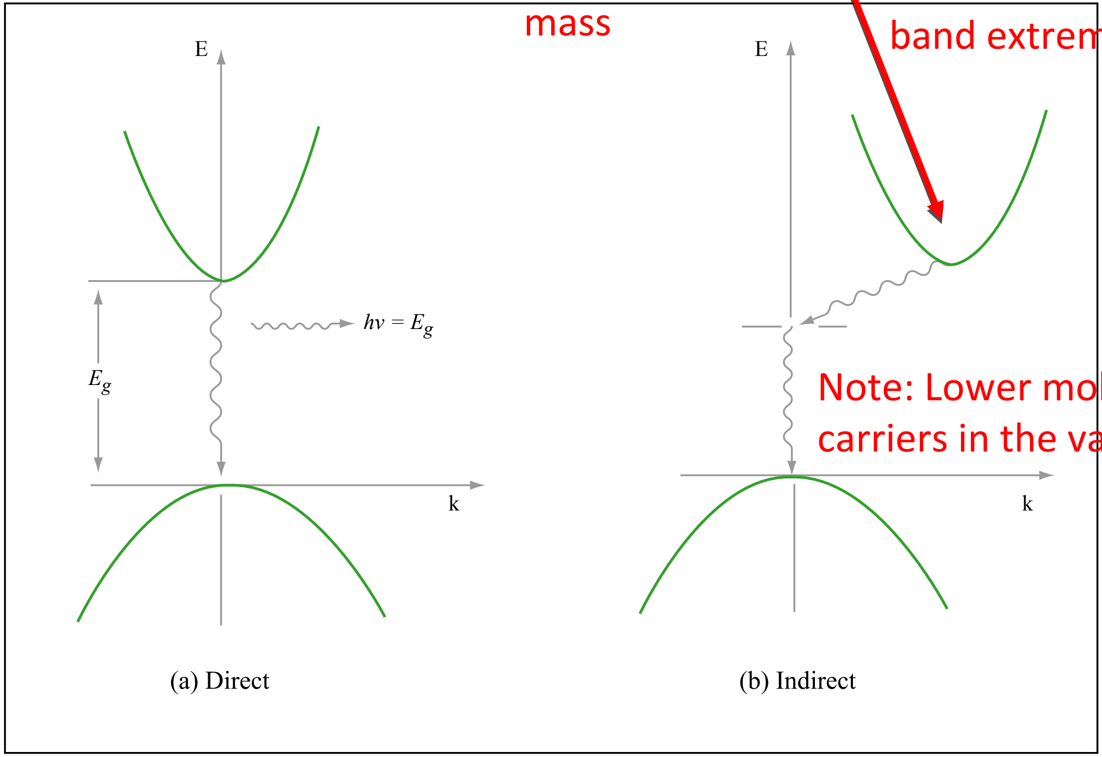
$$\mu = \frac{q}{m \cdot v_{\mathrm{m}}} \qquad \frac{1}{\boxed{m^*}} = \frac{1}{\hbar^2}\boxed{\frac{d^2E}{dk^2}}$$

Effective mass

Curvature at band extremum

Material properties described by the **energy band diagram**:

1. Absorption of light.
2. Carrier mobility.



(a) Direct

(b) Indirect

Note: Lower mobility for carriers in the valence band!

Figure by MIT OpenCourseWare.

μ = mobility
q = charge
v_{m} = momentum transfer collision frequency
m = mass
*m** = effective mass
h = Planck's constant

Question: Carriers in *which band* generally have higher mobility?

Review: Carrier Mobility

$$\mu = \frac{q}{m \cdot v_{\mathrm{m}}}$$

$$\frac{1}{\boxed{m^*}} = \frac{1}{\hbar^2}\boxed{\frac{d^2E}{dk^2}}$$

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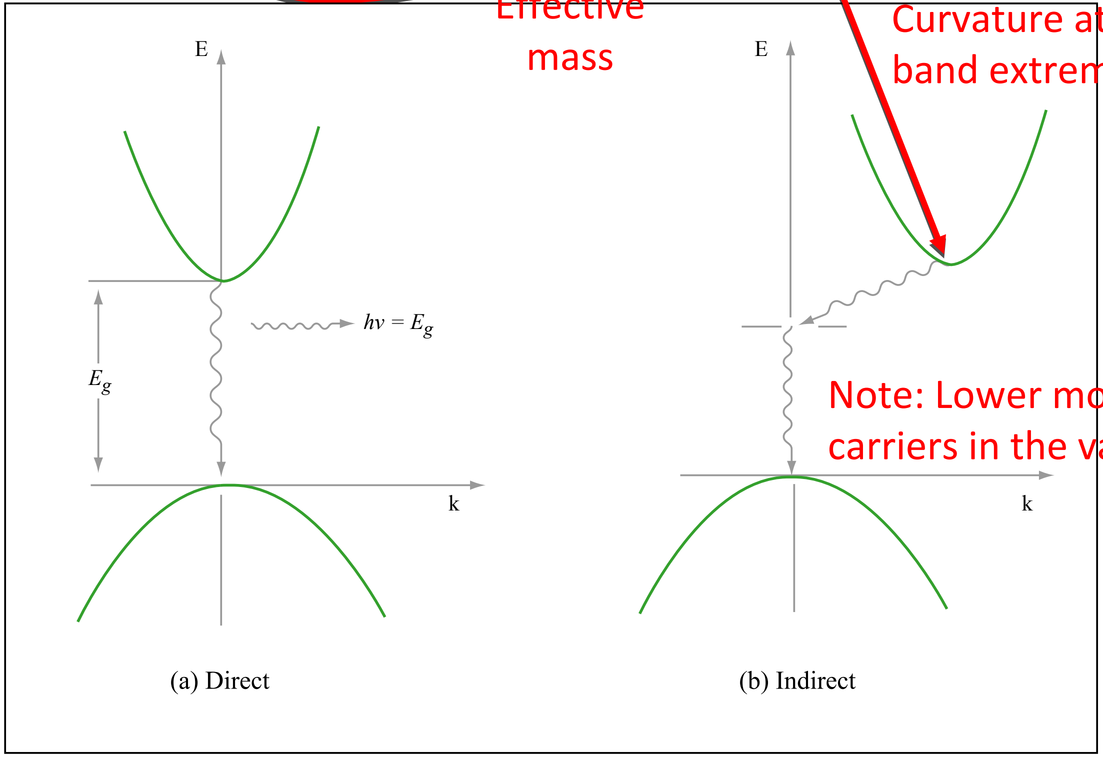

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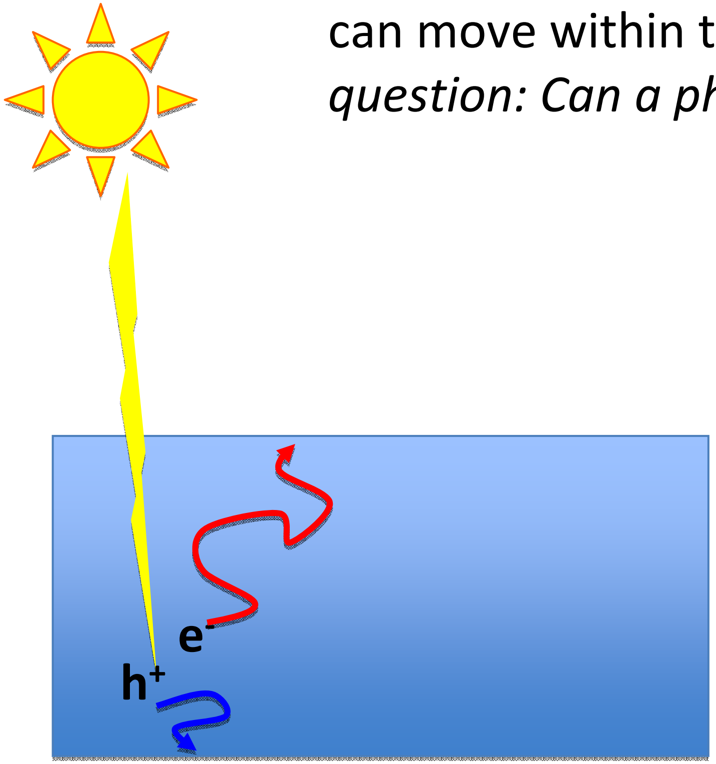
Carrier Mobility, Diffusion Length, and Lifetime



Once we know the mobility, we can calculate how far a carrier can move within the crystal… *(and answer the all-important question: Can a photoexcited carrier make it out of the device?)*

Relationship between mobility and diffusivity:

$$\mu = \frac{q}{kT} D$$

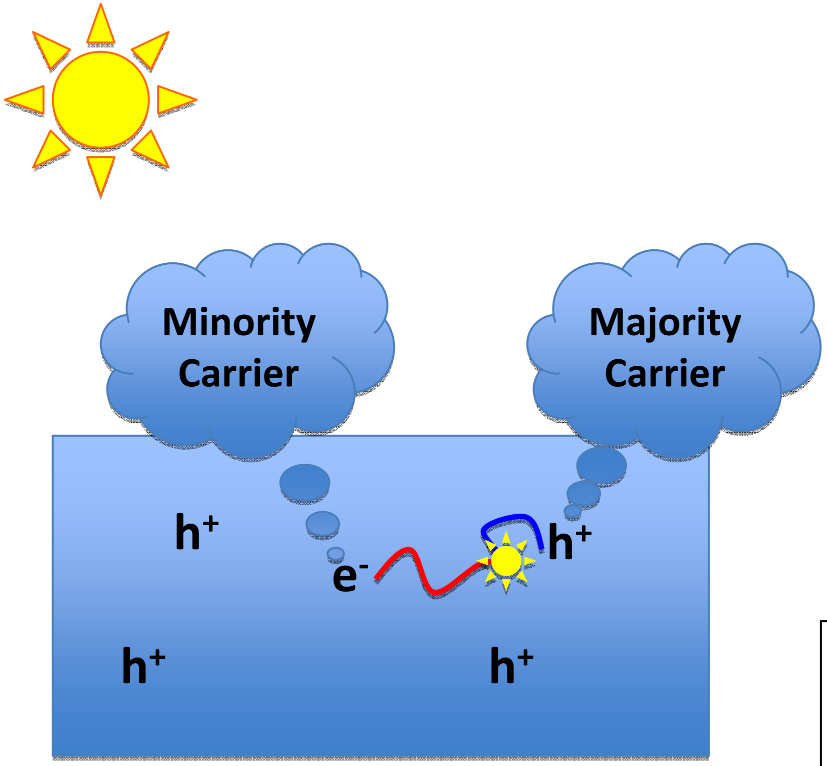
D = diffusivity
μ = mobility

Relationship between diffusivity and diffusion length:

$$L_{\mathrm{diff}} = \sqrt{D \cdot \tau}$$

L_{diff} = diffusion length
τ = carrier lifetime

Carrier Lifetime and Recombination



Bulk Minority Carrier Lifetime:

$$\tau = \frac{\Delta n}{R}$$

Δn = Excess minority carrier concentration

R = Recombination rate

First approximation of minority carrier lifetime, for low injection (e.g., illumination) conditions.

Order of Magnitude:

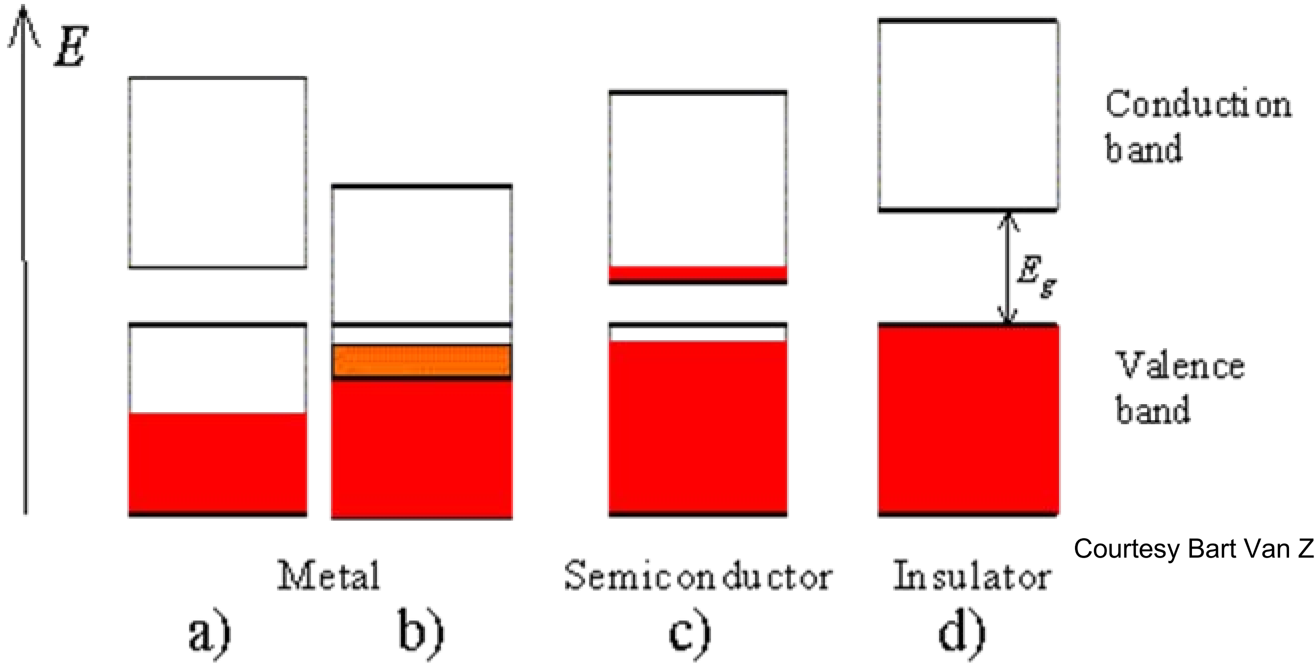
For an indirect bandgap material, τ is typically on the order of a few μs to a few ms.

For a direct bandgap material, τ is typically on the order of 10’s of ns to 1 μs.

Conductivity

Question: Which electrons in a material contribute to conductivity?

Classes of Materials, based on Bandgap



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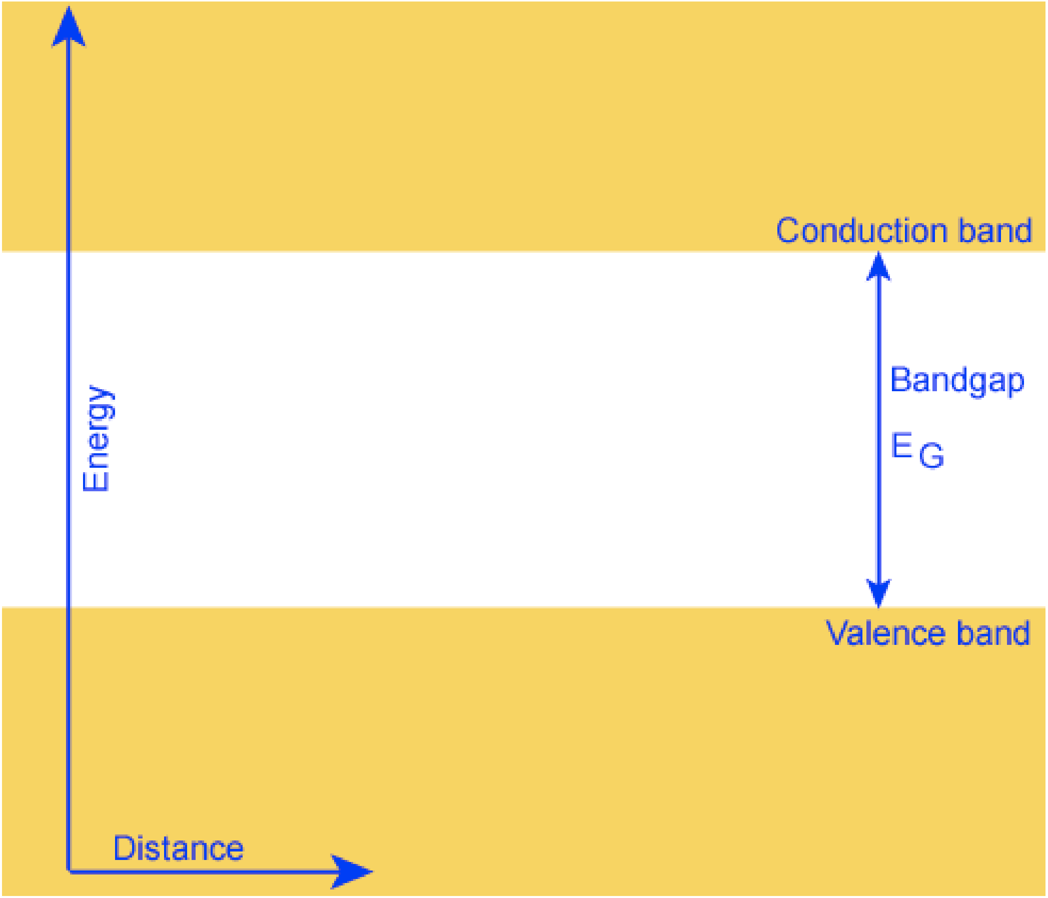
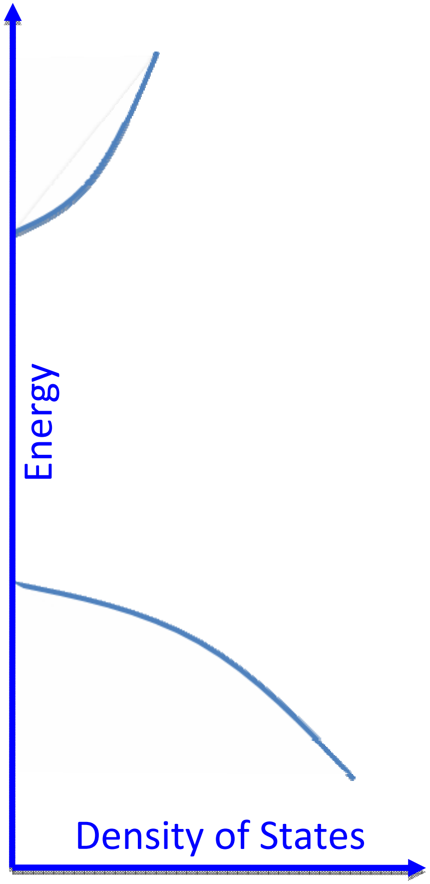
Conductivity

Band Diagram (E vs. x)



Density of States



http://pvcdrom.pveducation.org/

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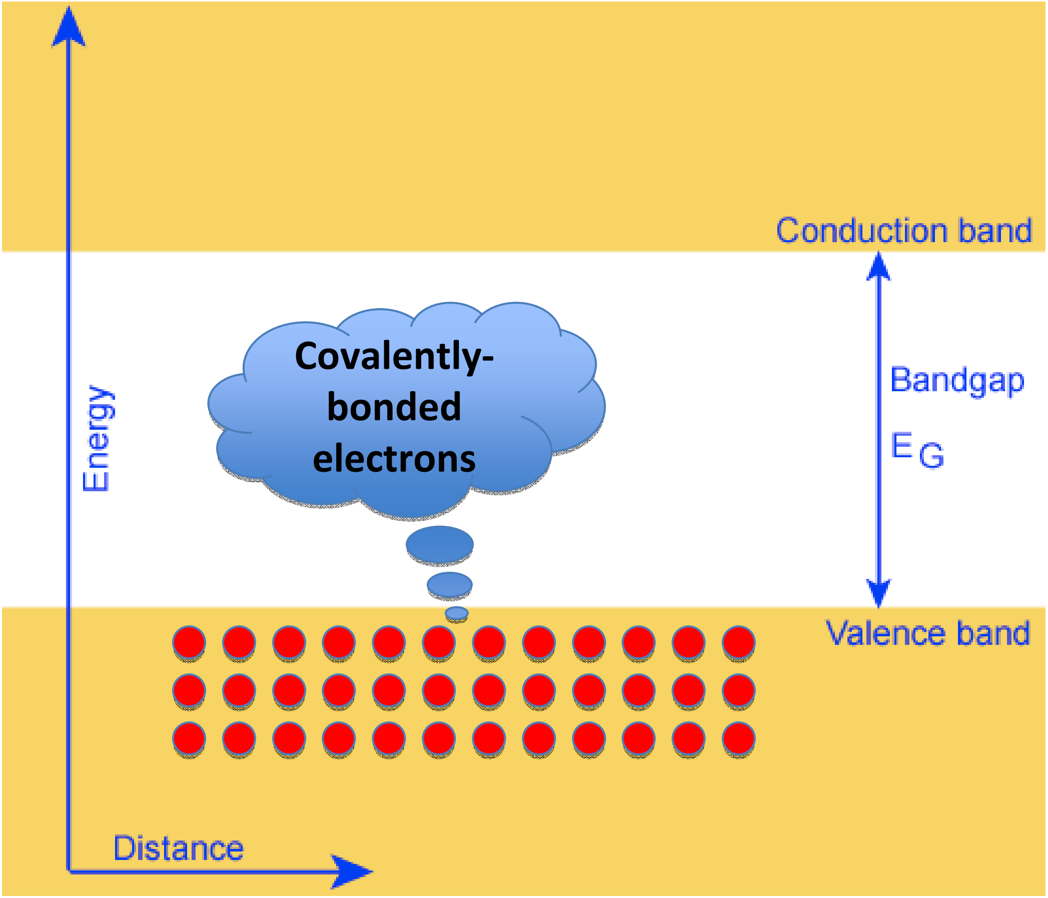
Conductivity: Dependence on Temperature

At absolute zero, no conductivity (perfect insulator).

Band Diagram (E vs. x)



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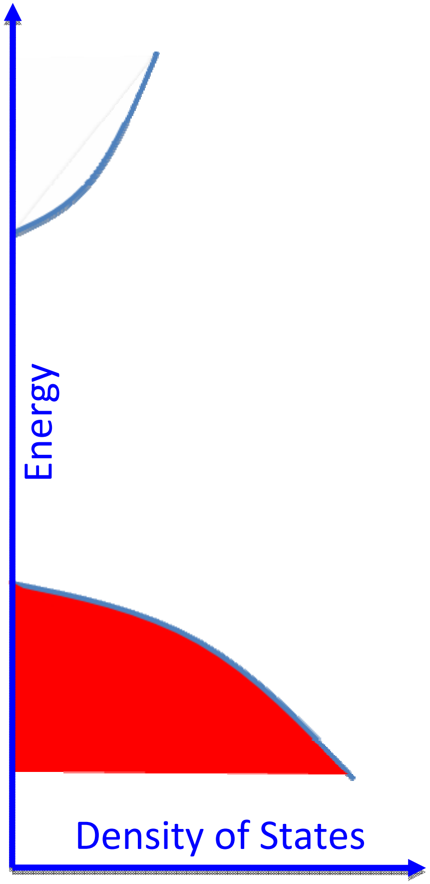

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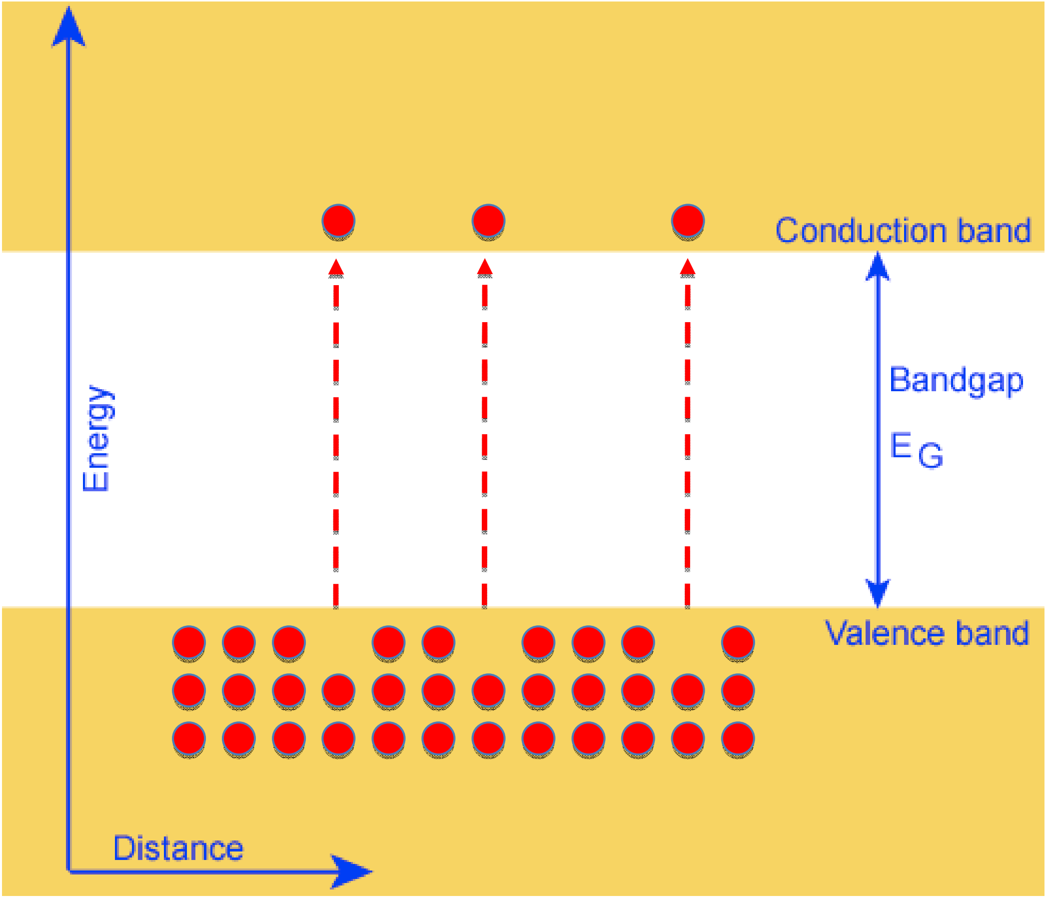
Conductivity: Dependence on Temperature

At T > 0 K, some carriers are thermally excited across the bandgap.

Band Diagram (E vs. x)



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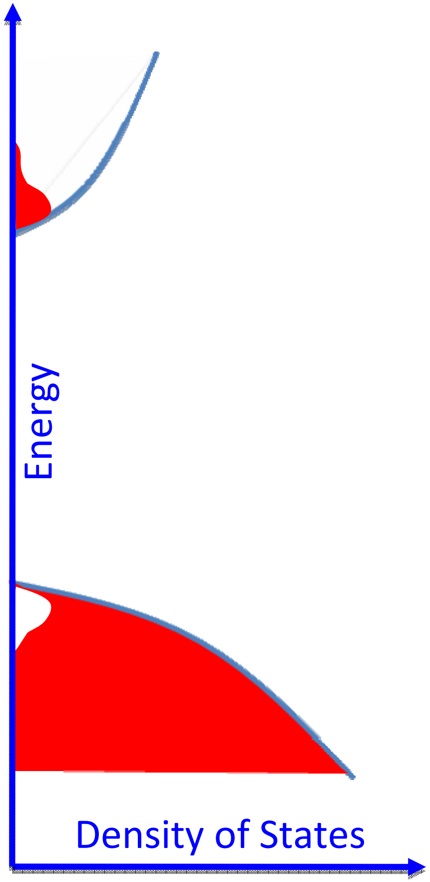

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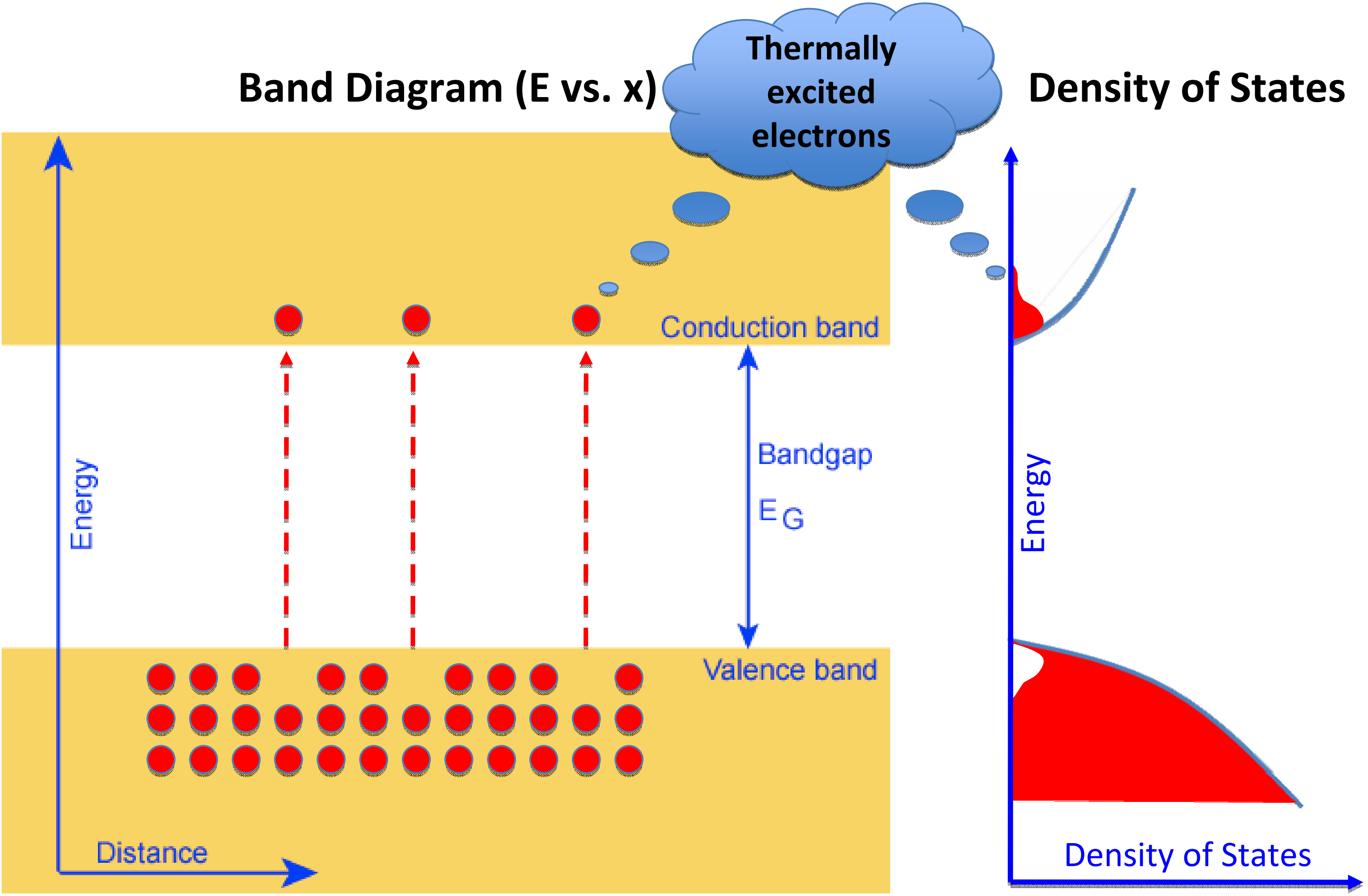

Band Diagram (E vs. x)

Thermally excited electrons

Density of States

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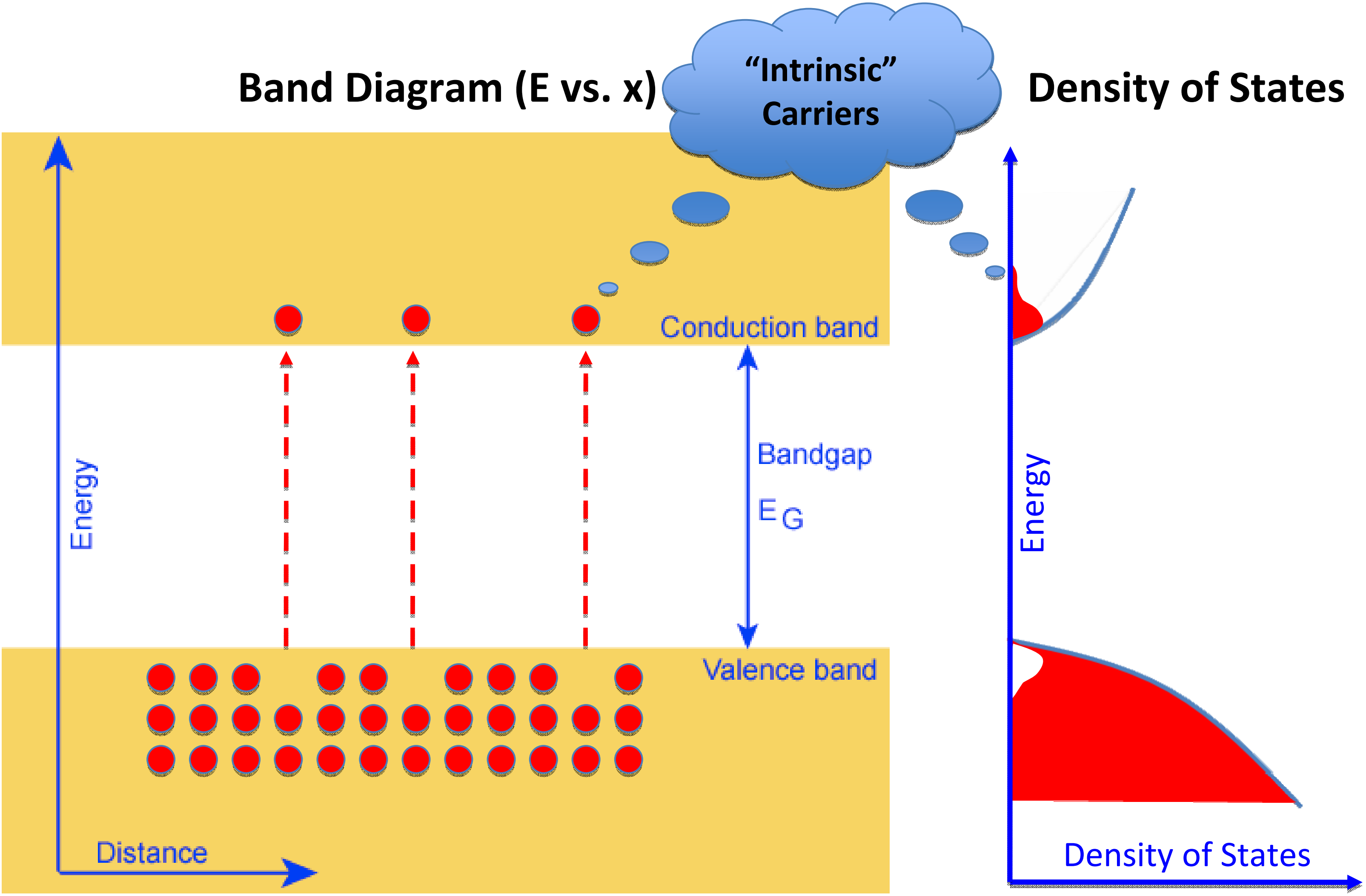

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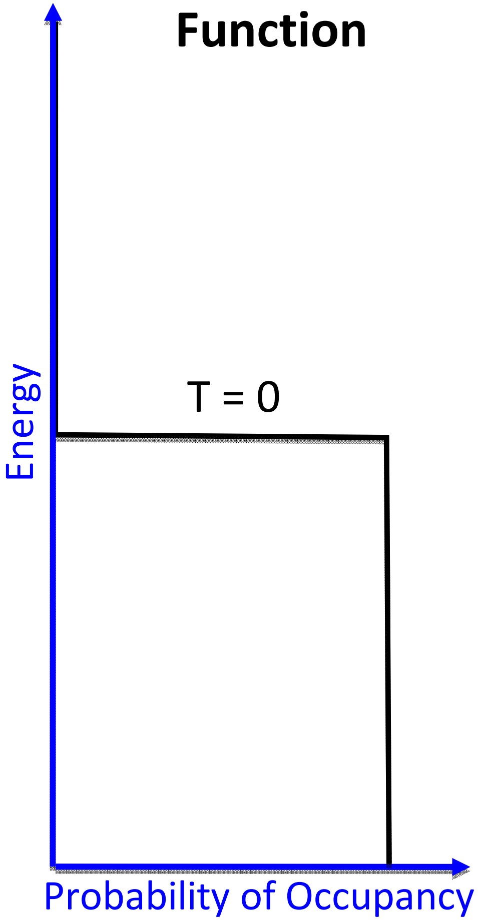
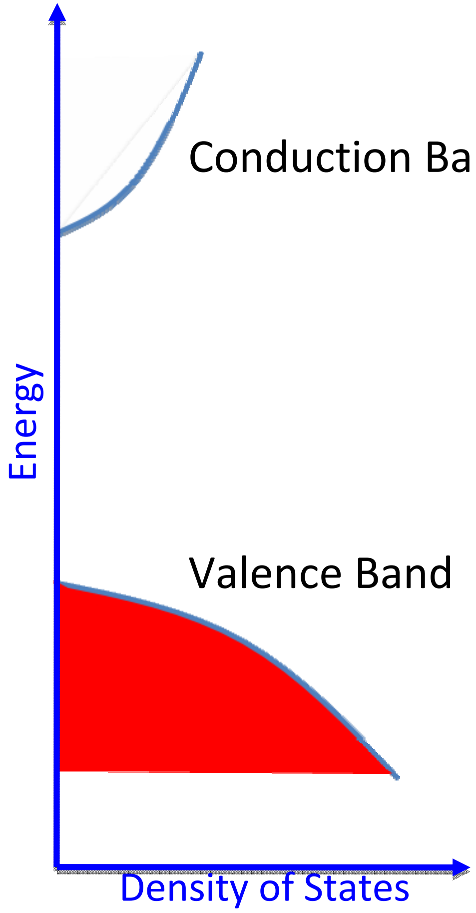


Probability Distribution Function

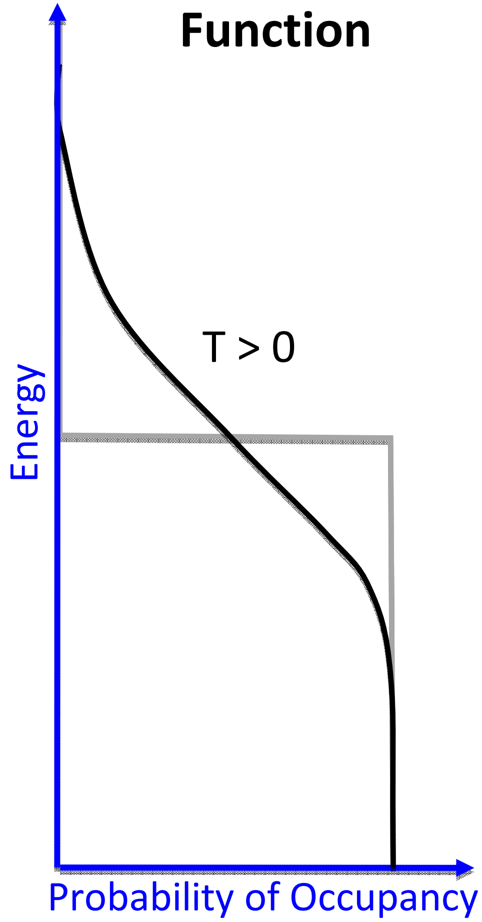


Density of States

Conductivity: Dependence on Temperature

At a finite temperature, finite conductivity (current can flow).

Probability Distribution Function



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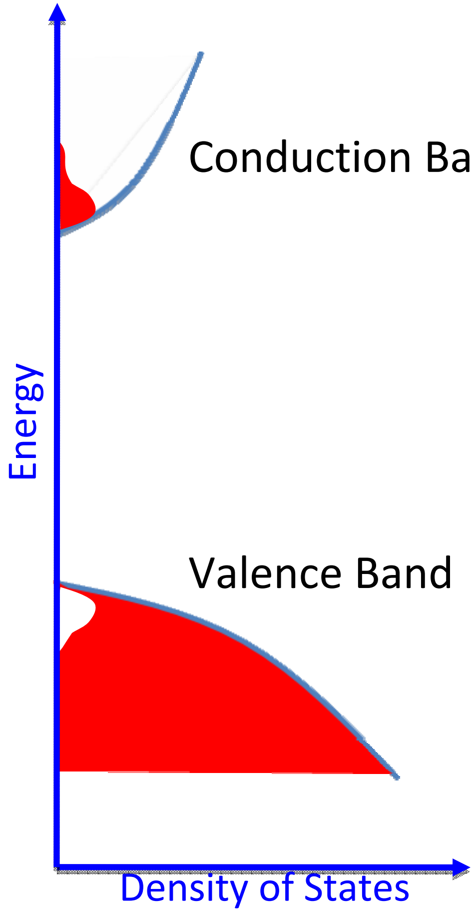

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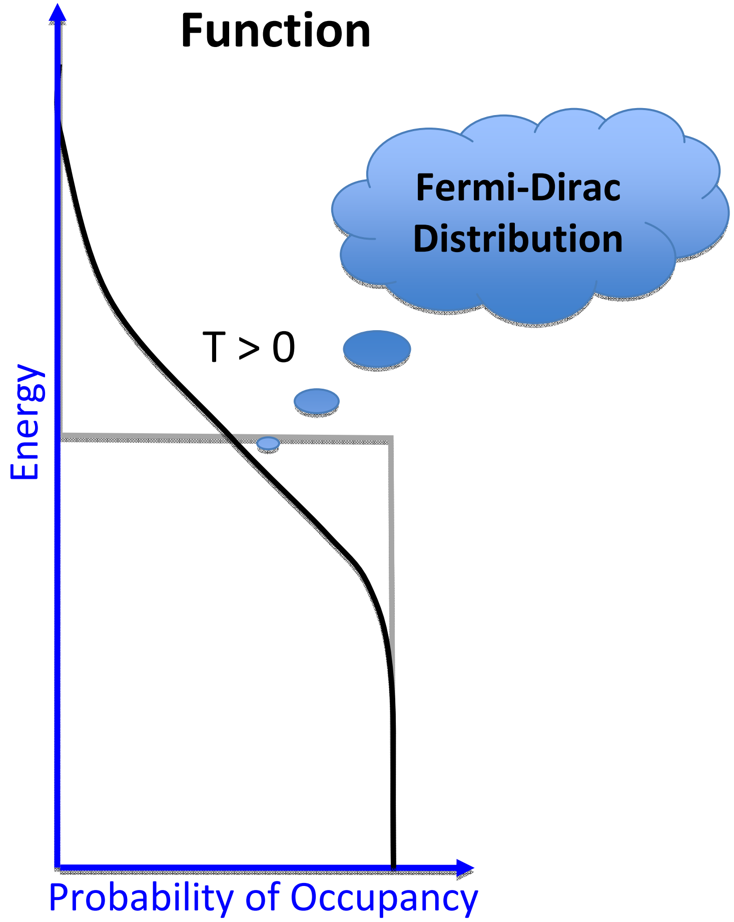

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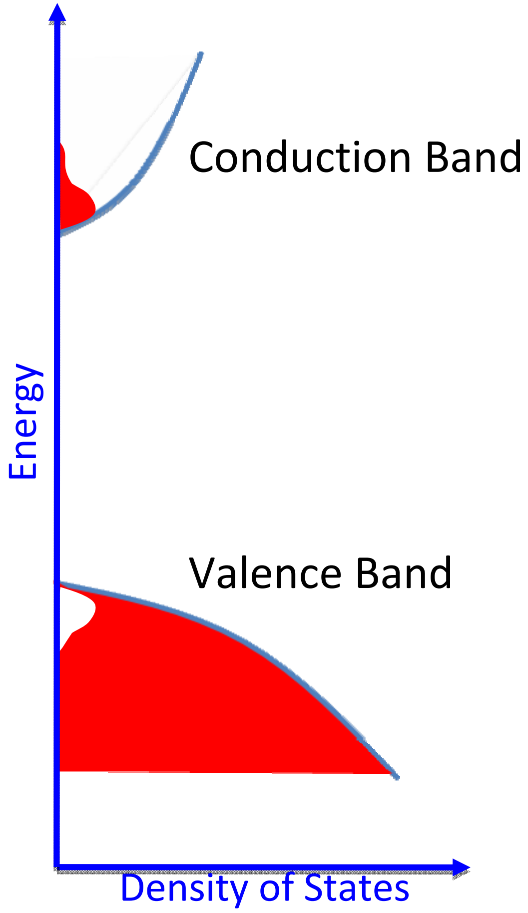

Fermi-Dirac Distribution

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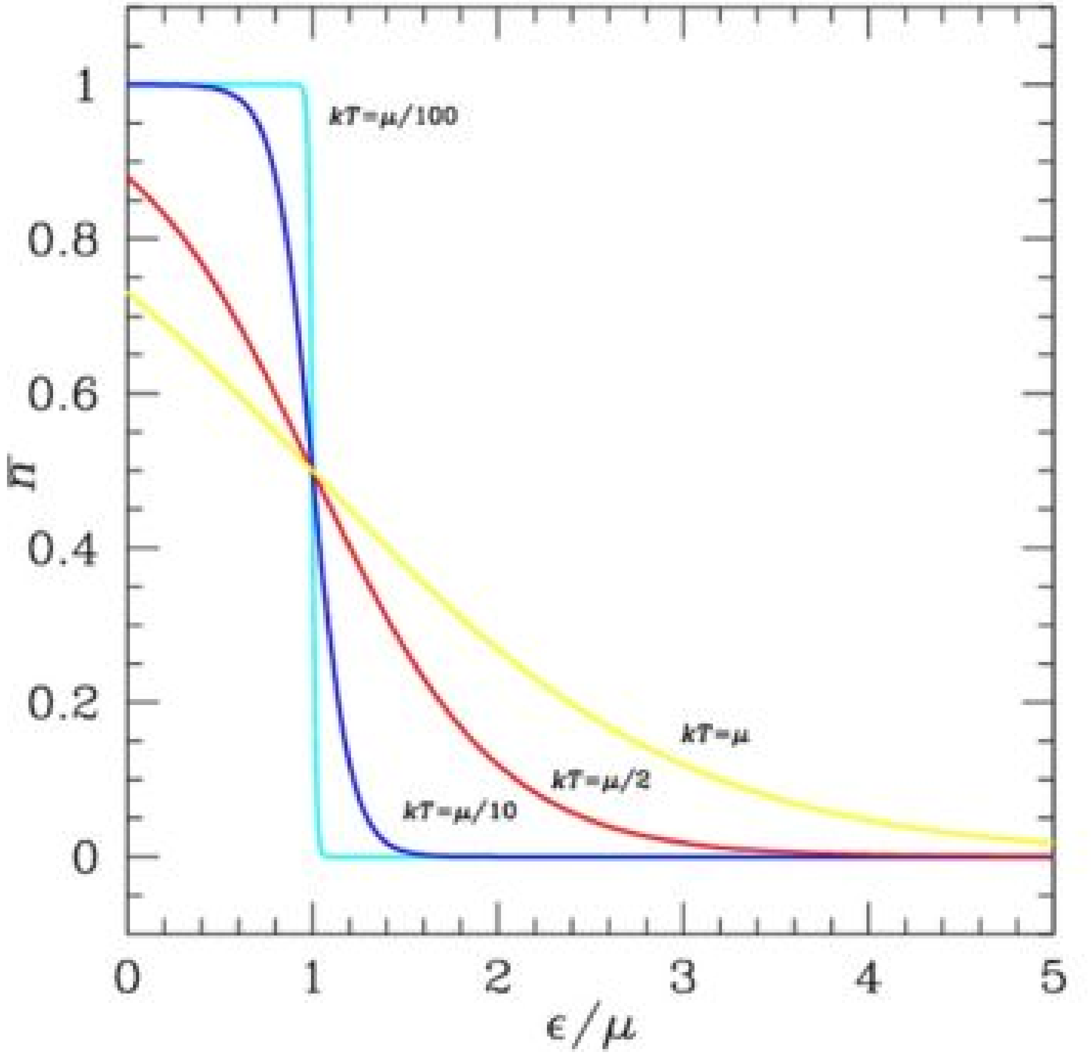

http://www.answers.com/topic/semiconductor

$\bar{n}$ = probability of occupancy

E = Particle energy

μ = Fermi energy (chemical potential)

kT = Thermal Energy (Boltzmann's constant x temperature)

To reduce noise in a Si CCD camera, should you increase or decrease temperature?

Lower Temperature = Lower Intrinsic Carrier Concentration

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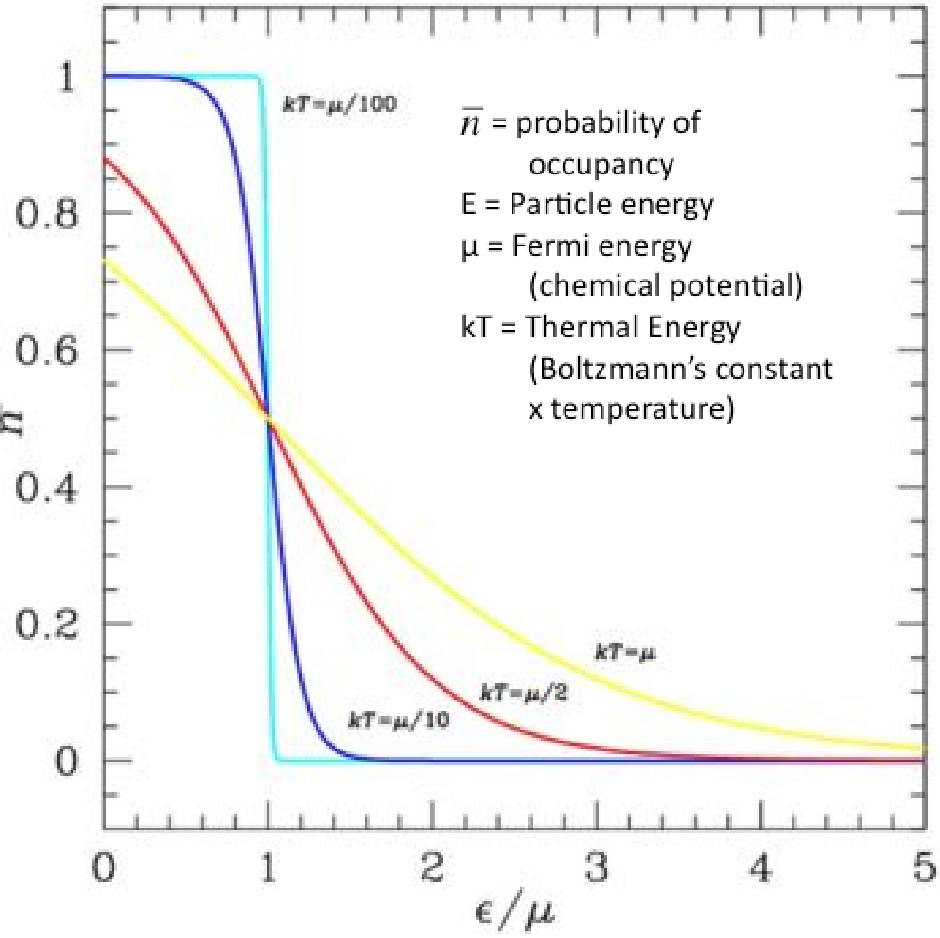

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CCD inside a LN dewar

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http://msowww.anu.edu.au/observing/detectors/wfi.php

Temperature Dependence of Intrinsic Carrier Concentration

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Temperature Dependence of Intrinsic Carrier Concentration

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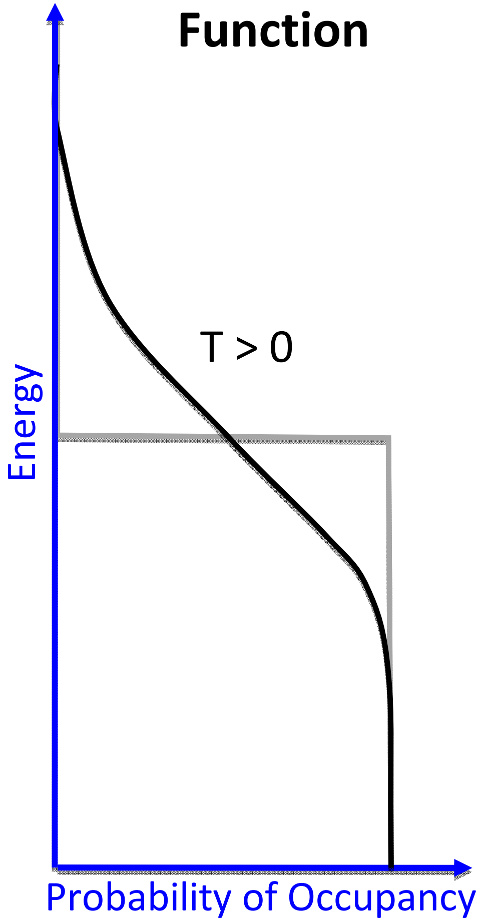
http://www.tf.uni-kiel.de/matwis/amat/semi_en/kap_2/illustr/n_intrin_arrhenius.gif

Question: Transistors made from which semiconductor material experience greater electronic noise at room temperature: Germanium or Silicon?

Intrinsic Conductivity: Dependence on Bandgap

At a finite temperature, finite conductivity (current can flow).

Probability Distribution Function



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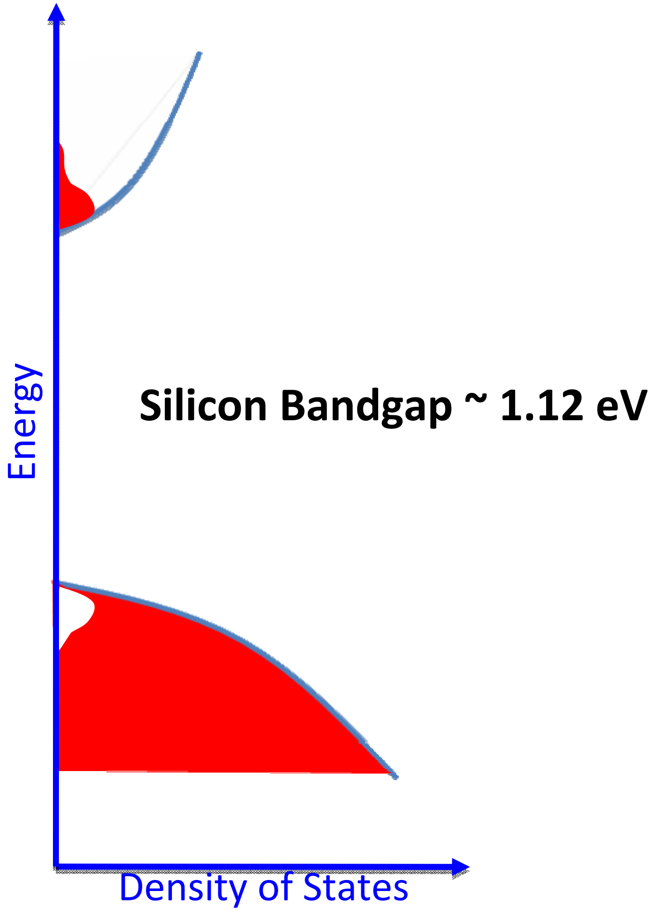
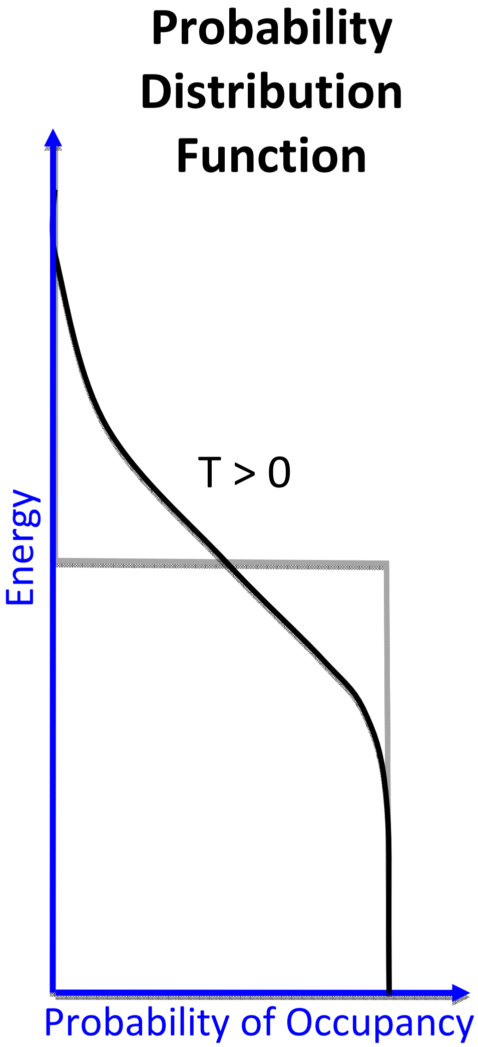
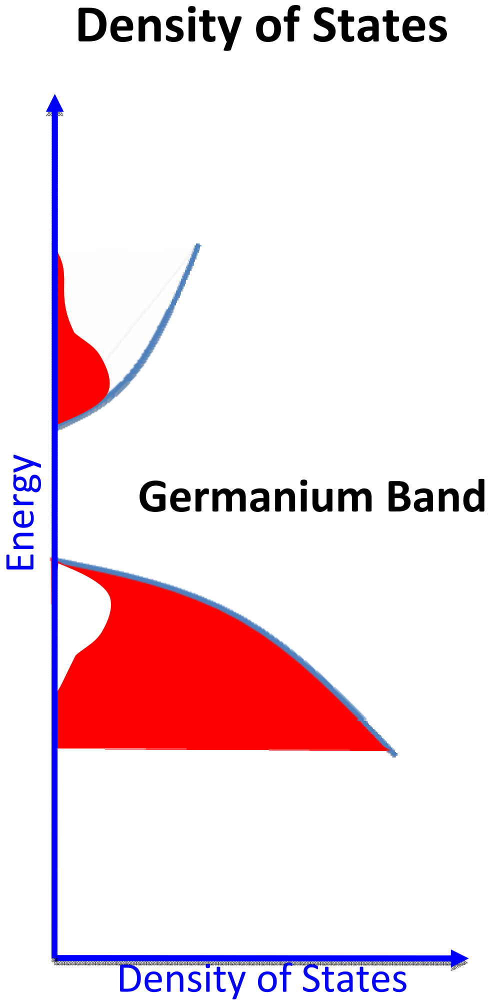


Silicon Bandgap ~ 1.12 eV

Intrinsic Conductivity: Dependence on Bandgap

At a finite temperature, finite conductivity (current can flow).





Germanium Bandgap ~ 0.67eV

Intrinsic Conductivity: Dependence on Bandgap

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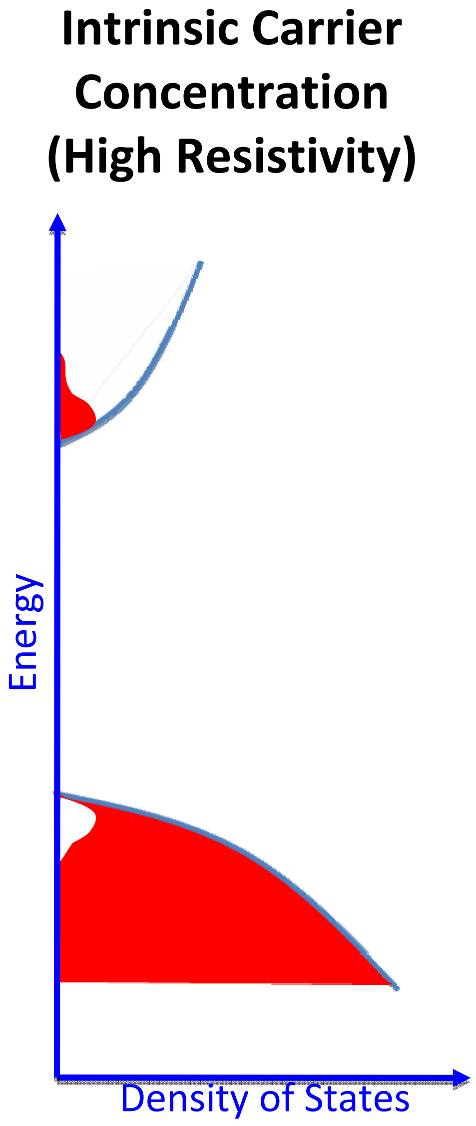
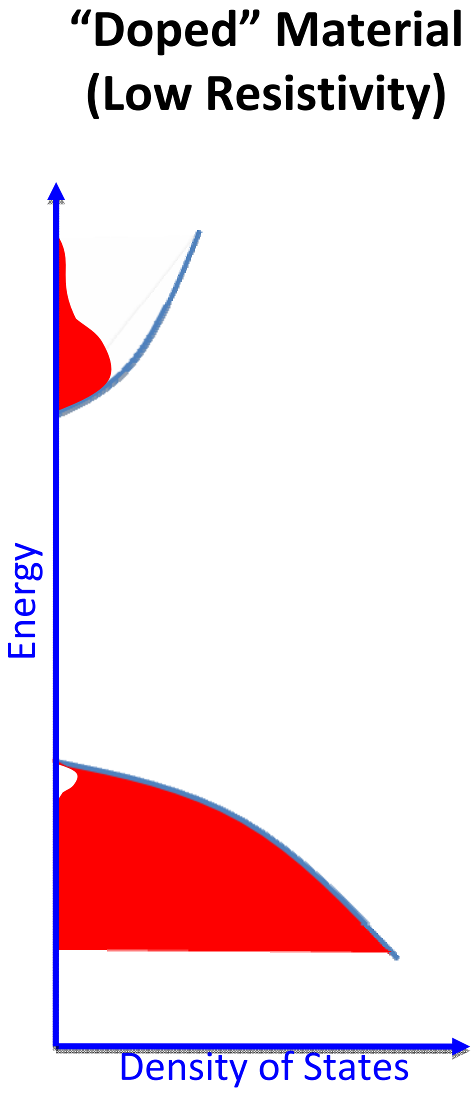
Intentional Modification of Conductivity

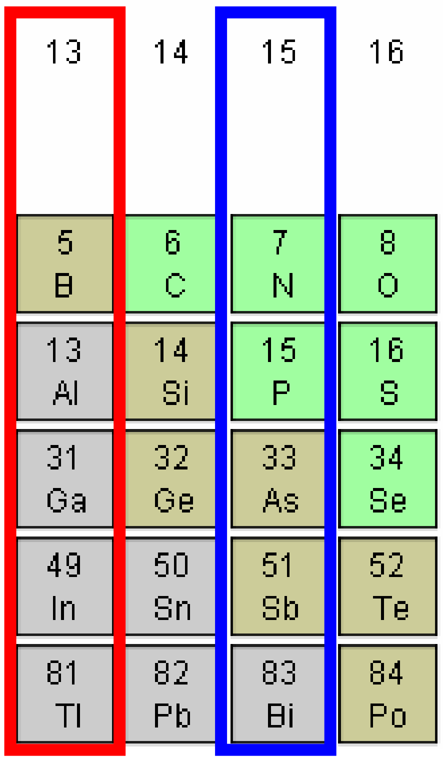
Increasing Conductivity



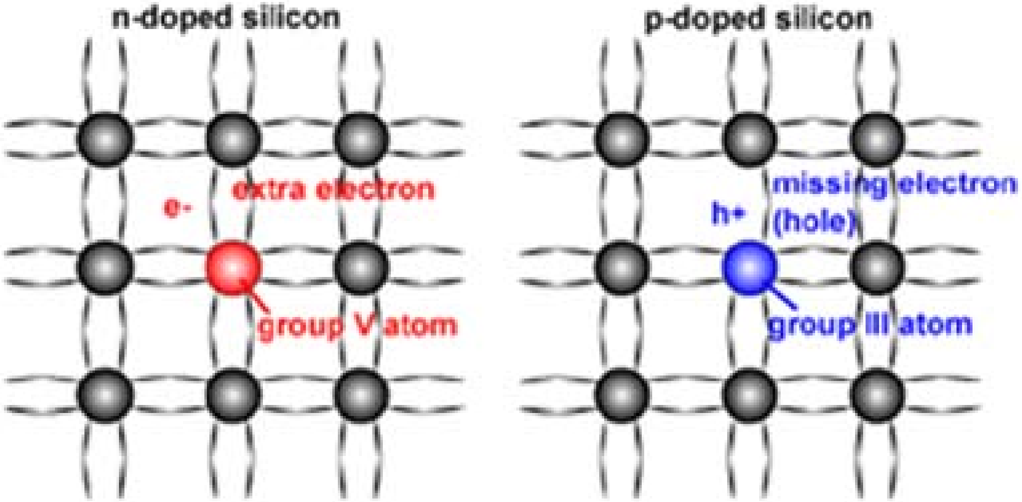


Dopant Atoms

Periodic Table



13	14	15	16
5 B	6 C	7 N	8 O
13 Al	14 Si	15 P	16 S
31 Ga	32 Ge	33 As	34 Se
49 In	50 Sn	51 Sb	52 Te
81 Tl	82 Pb	83 Bi	84 Po



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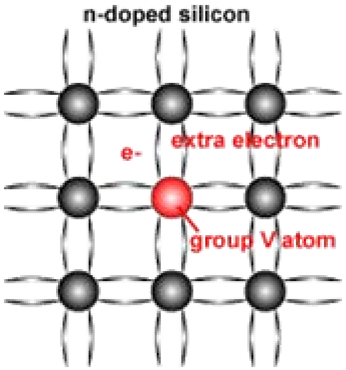
Carrier Binding Energy to Shallow Dopant Atoms



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Carrier binding energy to a shallow (hydrogenic) dopant atom:

$$E = E_{\mathrm{H}} \frac{m^*}{m_{\mathrm{e}}} \frac{1}{\varepsilon^2} = (13.6\ \mathrm{eV}) \cdot \frac{m^*}{m_{\mathrm{e}}} \frac{1}{\varepsilon^2}$$

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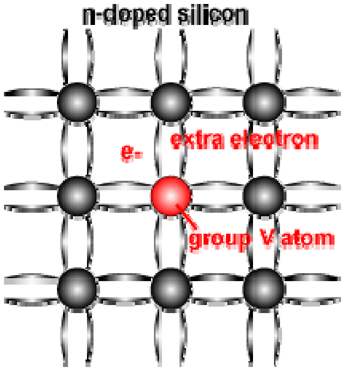

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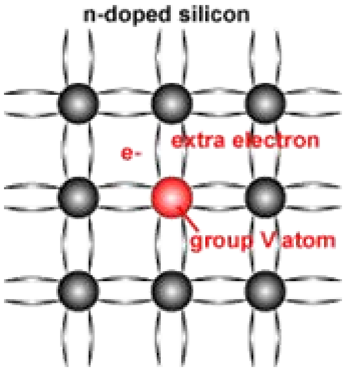
Effective mass correction

Electron screening

Carrier Binding Energy to Shallow Dopant Atoms



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Order of Magnitude Calculation

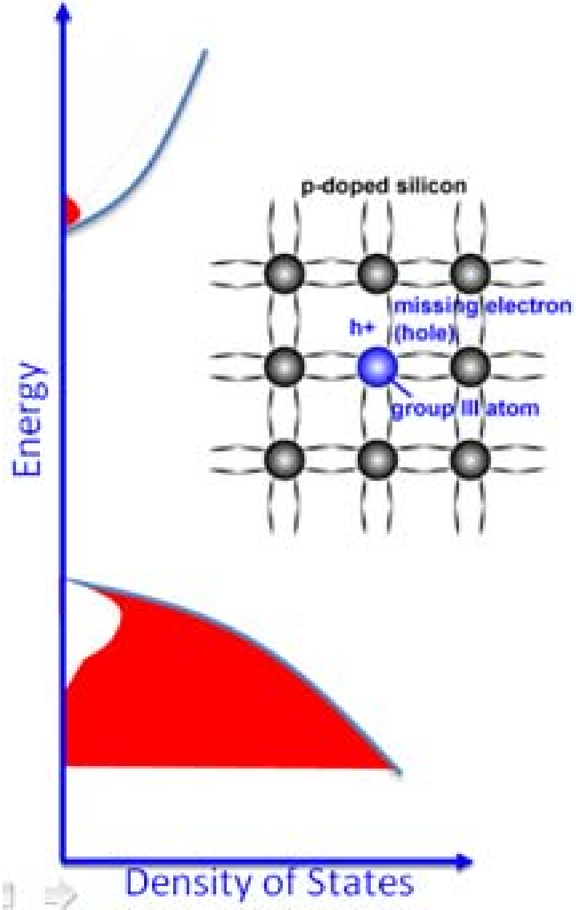
Si(ε=11.7): $E_{\text{donor}} \approx$ 33 meV; $E_{\text{acceptor}} \approx$ 75 meV

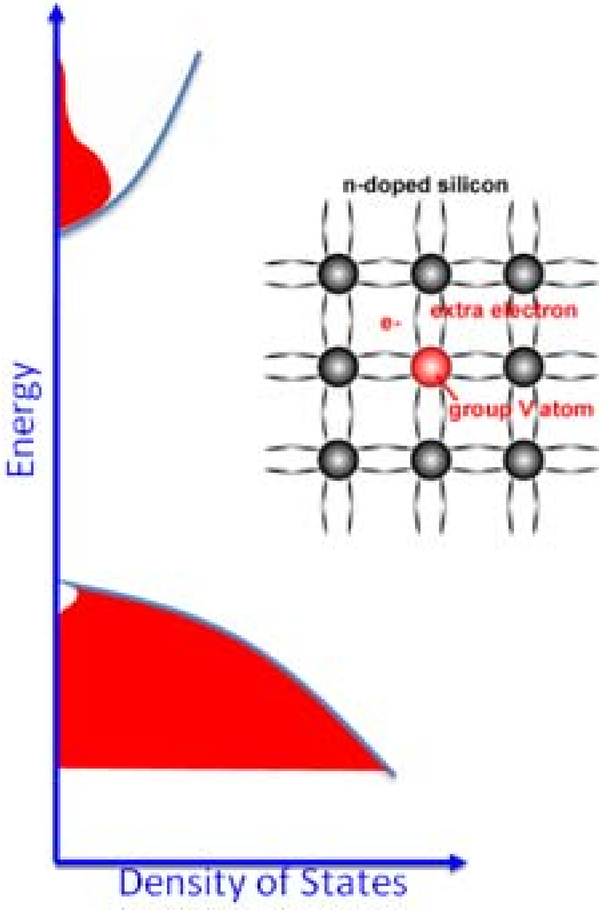
GaAs(ε=13.2): $E_{\text{donor}} \approx$ 6 meV; $E_{\text{acceptor}} \approx$ 28 meV

kT at room temperature ≈ 26 meV

→ *most shallow dopants should be ionized at room temperature!*

Dopant Atoms


p-type material


n-type material

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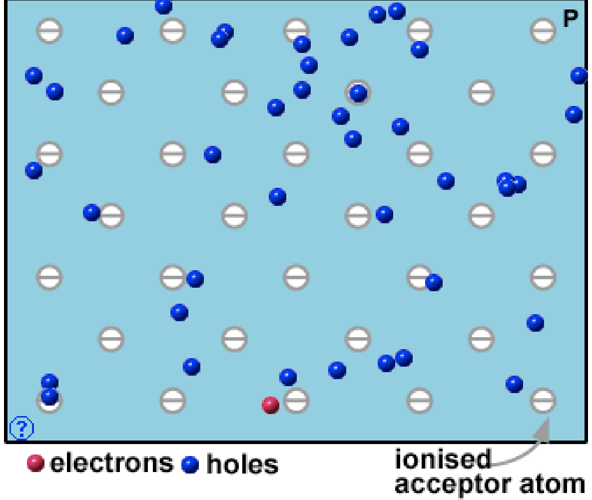

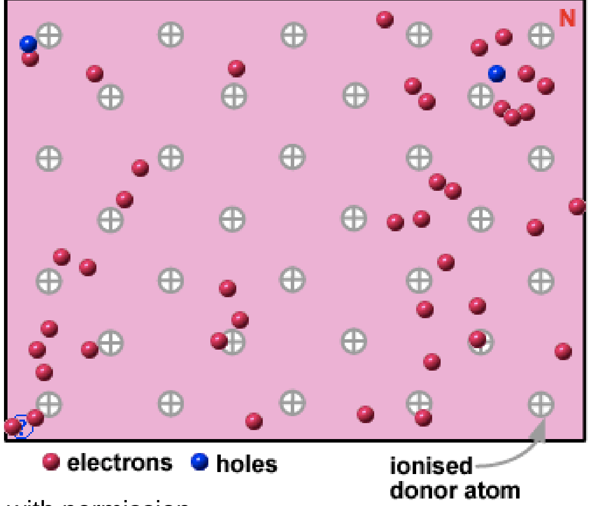

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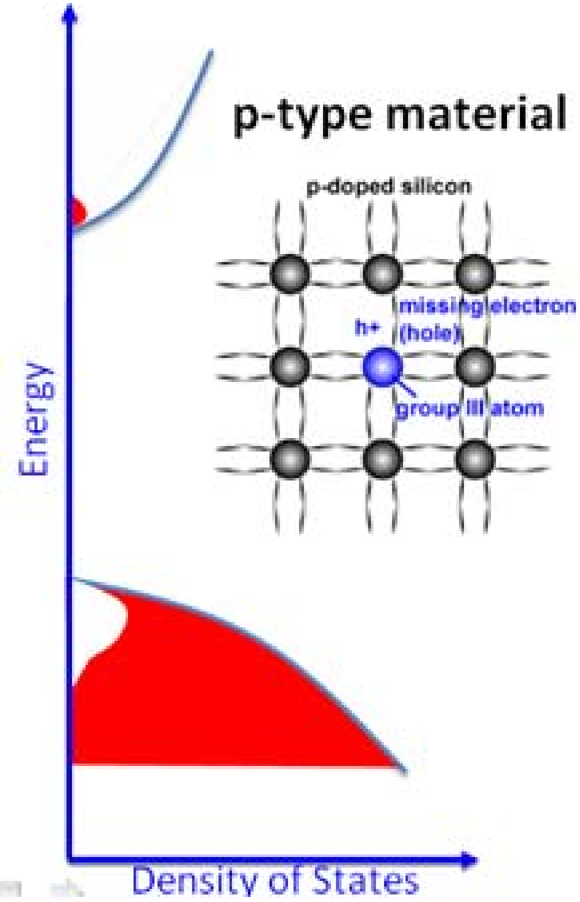

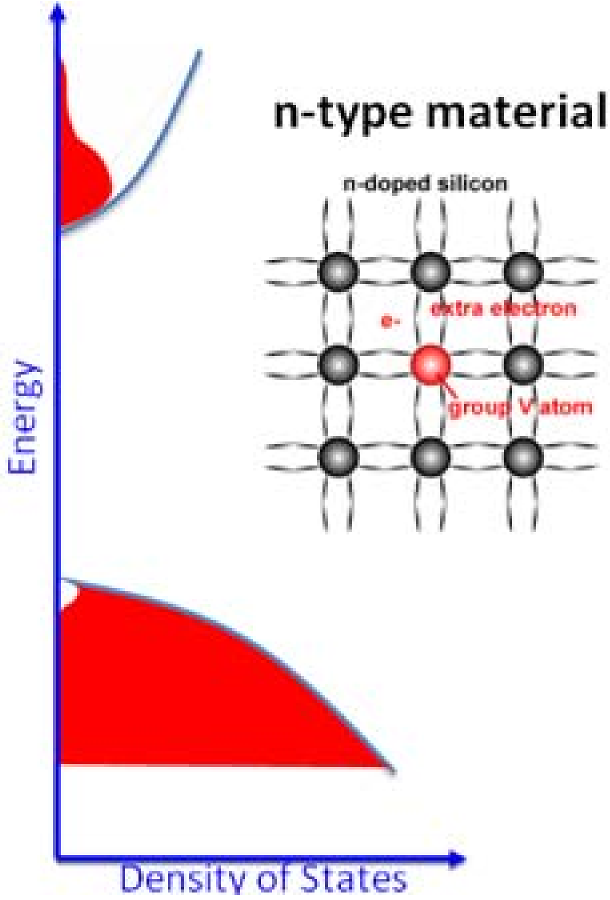

Resistivity as a Function of Dopant Concentration

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Resistivity as a Function of Dopant Concentration

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This degree of control (many orders of magnitude!) over the fundamental electrical properties of the material, is what makes semiconductors so versatile.

Resistivity of Polymers can also be Tailored

Comparison of conjugated polymers to other materials

Courtesy of Ilan Gur. Used with permission.

Stretch-aligning polyacetylene and removing chemical defects has increased the conductivity to 10^5 $\text{Ohm}^{-1}\text{cm}^{-1}$. Further improvements are expected.

Slide from Ilan Gur, UC Berkeley

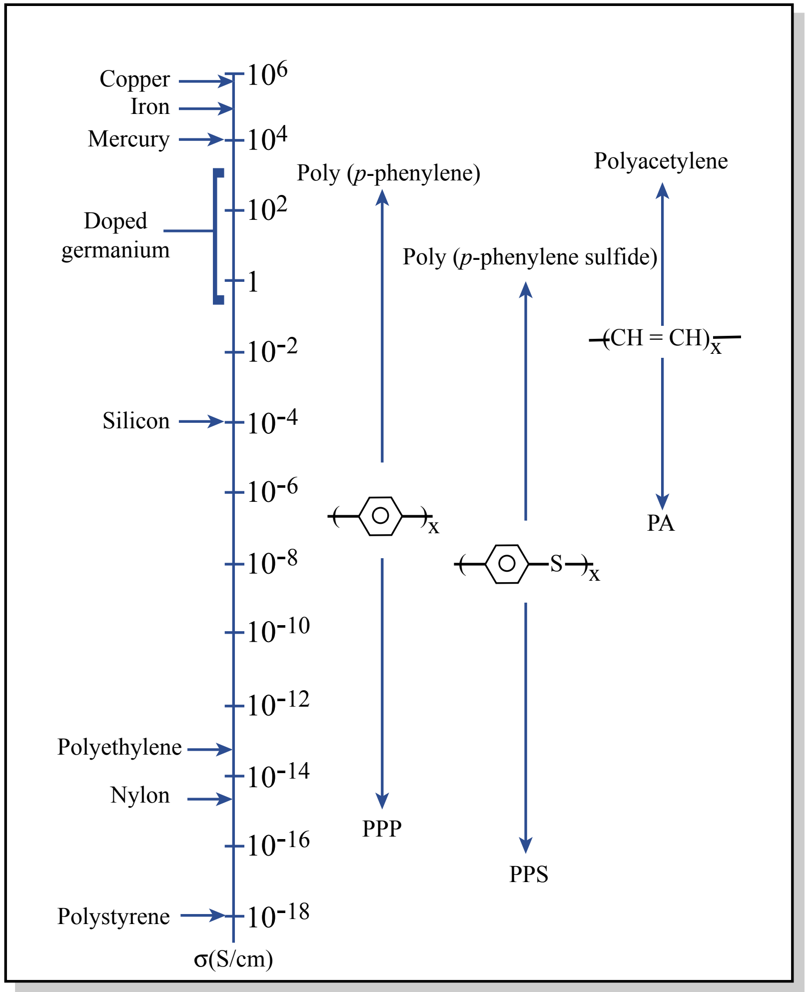
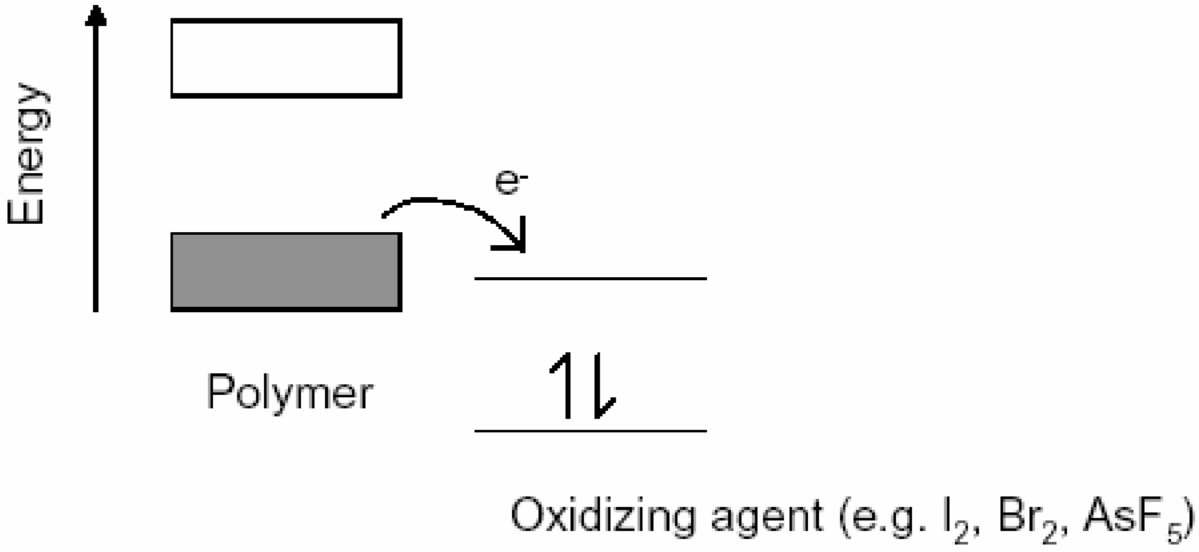


Figure by MIT OpenCourseWare.

P-type Doping of Polymers

Doping conjugated polymers

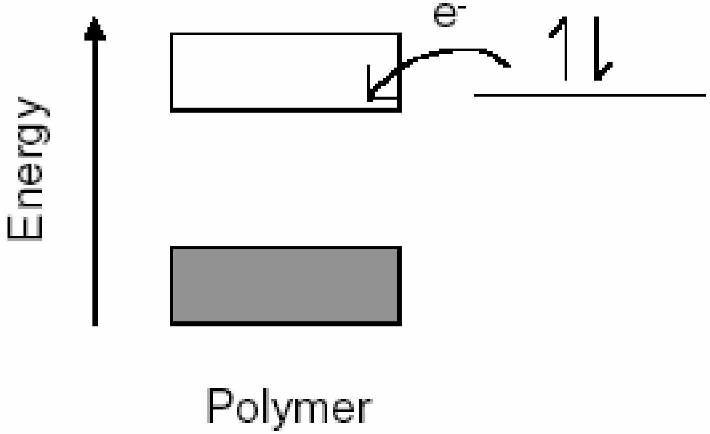


Oxidizing agents act as p-type dopants, i.e. they generate holes in the polymer.

Courtesy of Ilan Gur. Used with permission.

N-type Doping of Polymers

n-type doping



Courtesy of Ilan Gur. Used with permission.

Reducing agents such as calcium and lithium can introduce electrons into the conduction band of a conjugated polymer.

Resistivity of Polymers can also be Tailored

Electrical conductivity of *trans*-$(CH)_x$ as a function of (AsF_5) dopant concentration

Polyacetylene is a semiconductor, but when it is heavily doped, it undergoes an insulator-to -metal transition.

For comparison, the conductivity of copper is 10^6 $(\text{Ohm-cm})^{-1}$.

In 2000, Heeger, MacDiarmid and Shirakawa won the Nobel Prize in Chemistry for this experiment and their development of the science and technology of conjugated polymers.

Image removed due to copyright restrictions. Please see Fig. 1 in Chiang, C. K, et al. “Electrical Conductivity of Doped Polyacetylene.” *Physical Review Letters* 39 (1977): 1098.

Courtesy of Ilan Gur. Used with permission.

Heeger, MacDiarmid, Shirakawa et al., *Phys. Rev. Lett.*, **39** (1977) p. 1098.

Mobility and Carrier Concentration in Semiconductor

Increased concentration of ionized dopant atoms increases conductivity, but can reduce carrier mobility (due to scattering).

Mobility and Carrier Concentration in Polymer

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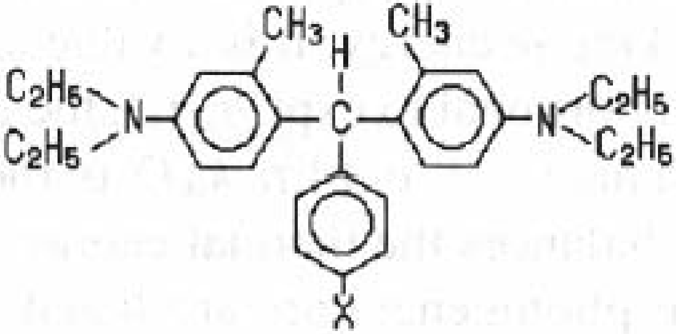
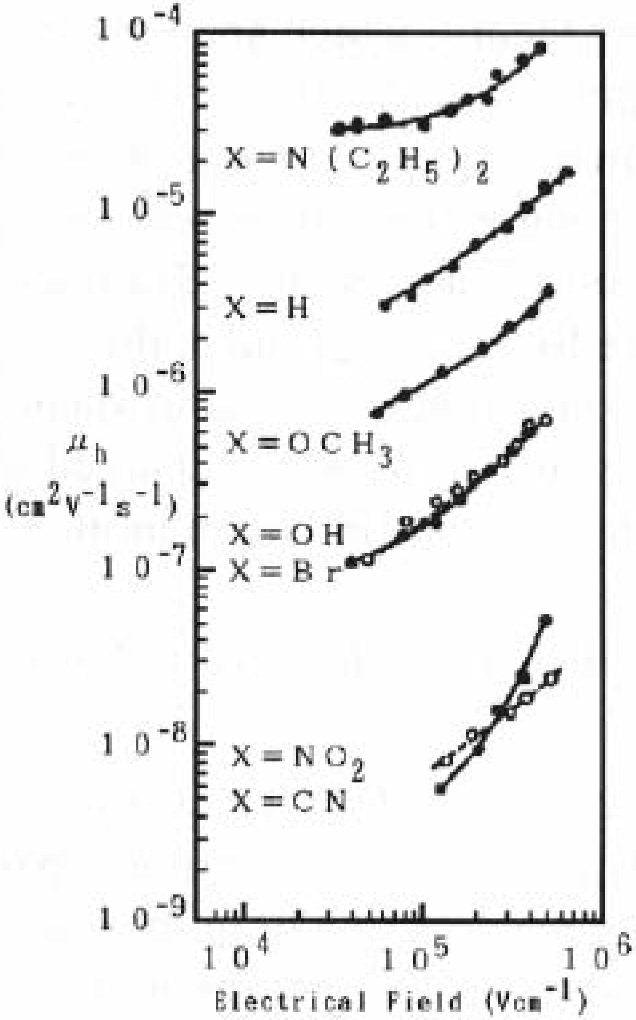
Effect of substituent on the **hole** mobility



All samples consisted of 40 % by weight of the molecule shown above blended into polycarbonate.

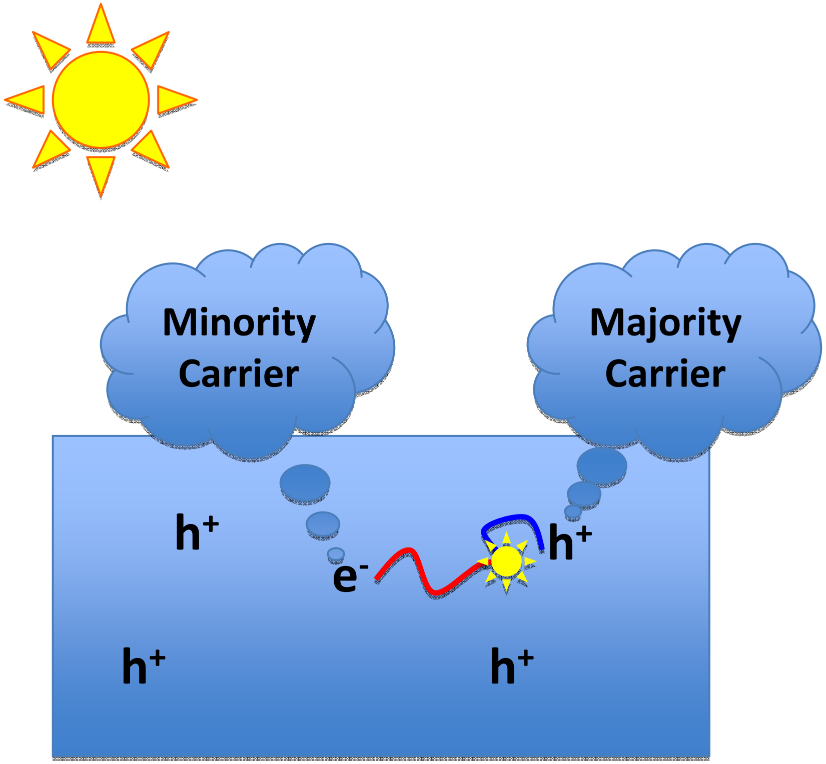


Slide from Ilan Gur, UC Berkeley

Mobility and Carrier Concentration in Semiconductor

Increased concentration of ionized dopant atoms increases conductivity, but can reduce carrier mobility (due to scattering).

Carrier Lifetime and Recombination



Bulk Minority Carrier Lifetime:

$$\tau = \frac{\Delta n}{R}$$

Δn = Excess minority carrier concentration

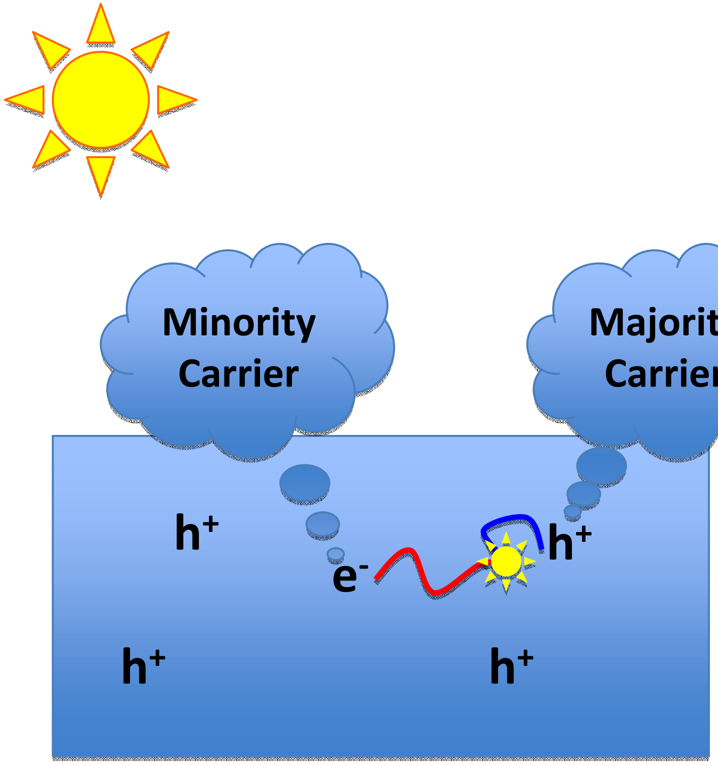
R = Recombination rate

First approximation of minority carrier lifetime, for low injection (e.g., illumination) conditions.

More Detailed Calculation:

$$\frac{1}{\tau_{\text{bulk}}} = \frac{1}{\tau_{\text{band}}}$$

Carrier Lifetime and Recombination



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$$\tau = \frac{\Delta n}{R}$$

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First approximation of minority carrier lifetime, for low injection (e.g., illumination) conditions.

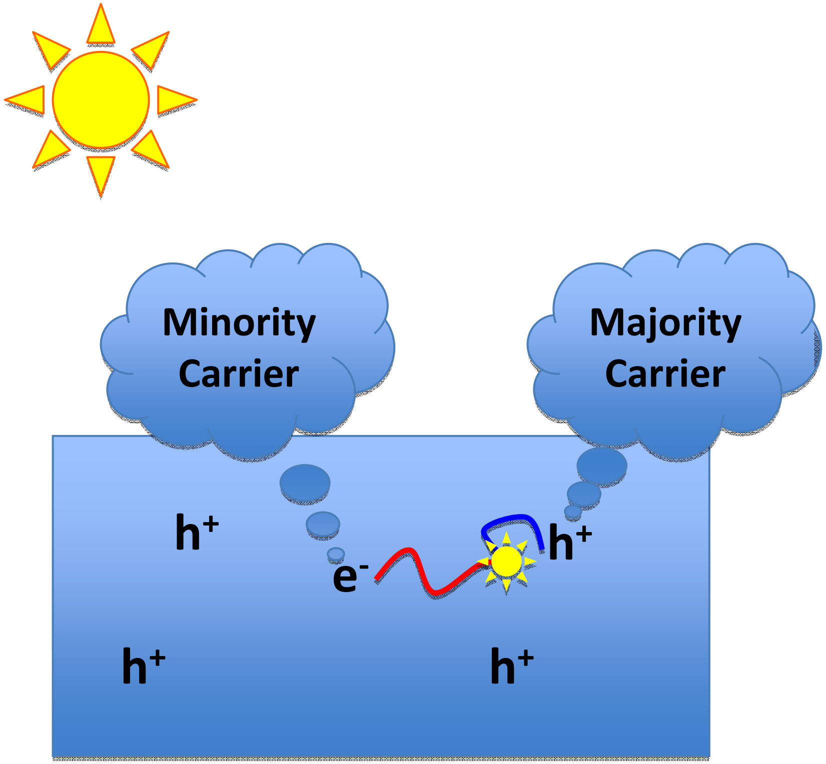
More Detailed Calculation:

$$\frac{1}{\tau_{\text{bulk}}} = \frac{1}{\tau_{\text{band}}} + \frac{1}{\tau_{\text{Auger}}}$$

Dominant under very high injection conditions

$$\tau_{\text{Auger}} = \frac{1}{CN_{\text{A}}}$$

Carrier Lifetime and Recombination



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First approximation of minority carrier lifetime, for low injection (e.g., illumination) conditions.

More Detailed Calculation:

$$\frac{1}{\tau_{\text{bulk}}} = \frac{1}{\tau_{\text{band}}} + \frac{1}{\tau_{\text{Auger}}} + \frac{1}{\tau_{\text{SRH}}}$$

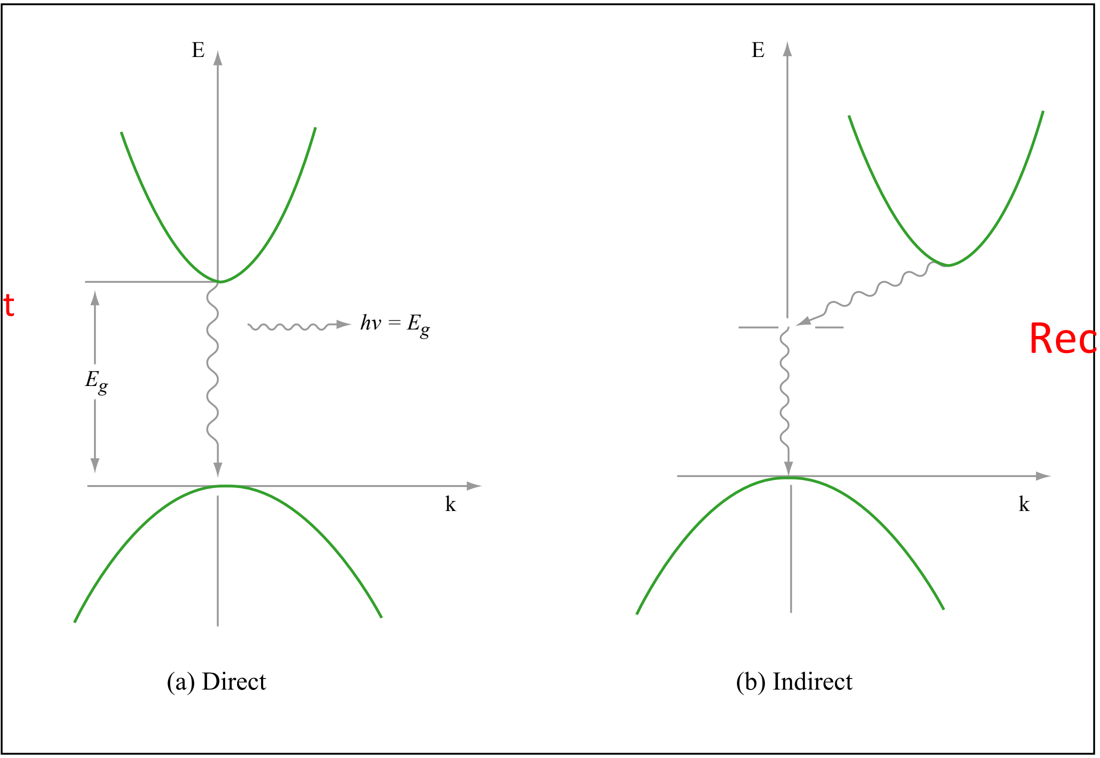
Defect-mediated recombination

Defects and Carrier Recombination

Direct Bandgap Semiconductor

Indirect Bandgap Semiconductor

Recombination efficient
(no phonon required)
τ ~ ns to μs



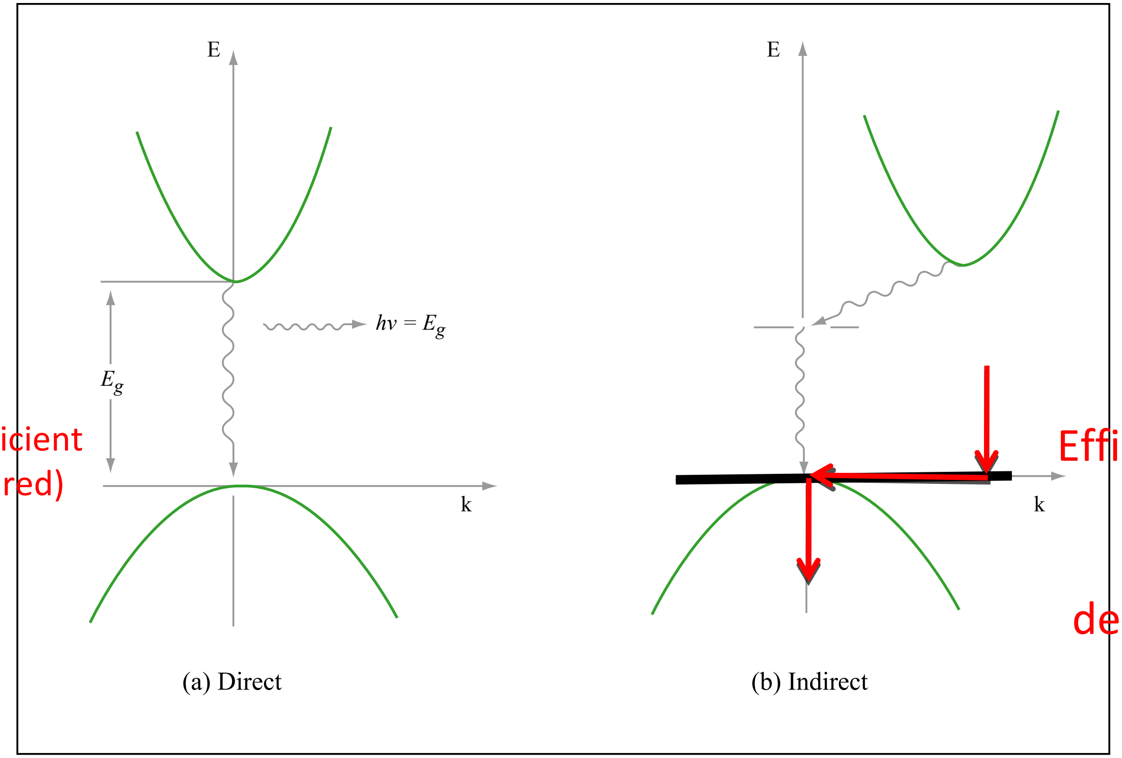
Recombination inefficient
(phonon required)
τ ~ ms

Figure by MIT OpenCourseWare.

Defects and Carrier Recombination

Direct Bandgap Semiconductor

Indirect Bandgap Semiconductor



(a) Direct

(b) Indirect

Recombination efficient
(no phonon required)
τ ~ ns to μs

Efficient recombination
via defect level!
τ < μs with high
defect concentrations

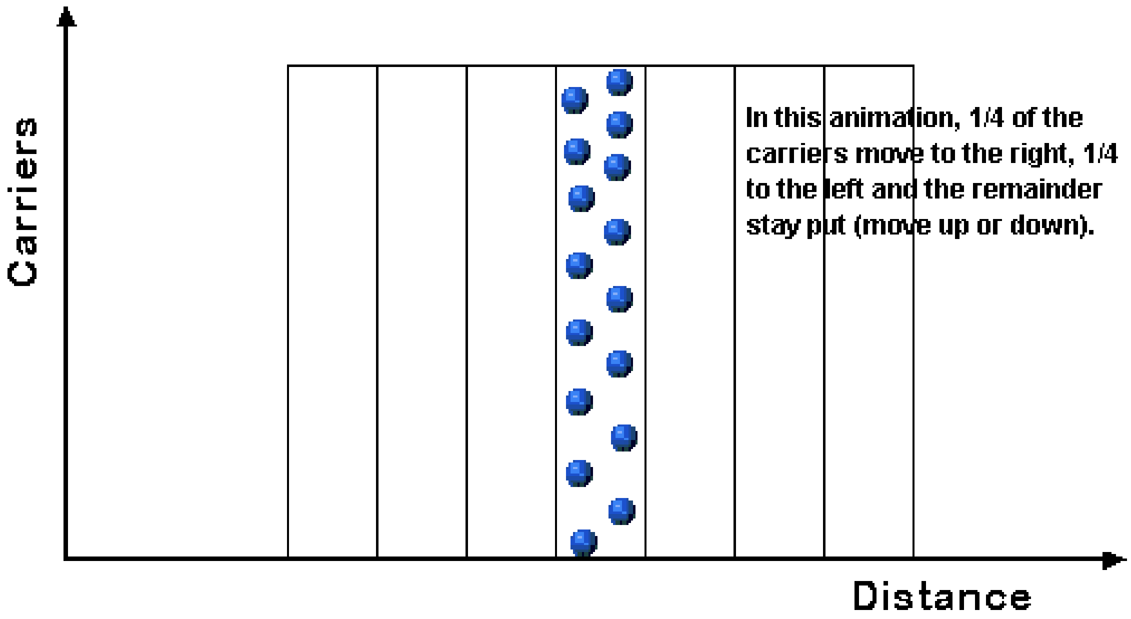
Figure by MIT OpenCourseWare.

Carrier Motion

Under equilibrium conditions in a homogeneous material: Individual carriers constantly experience Brownian motion, but the <u>net</u> charge flow is zero.

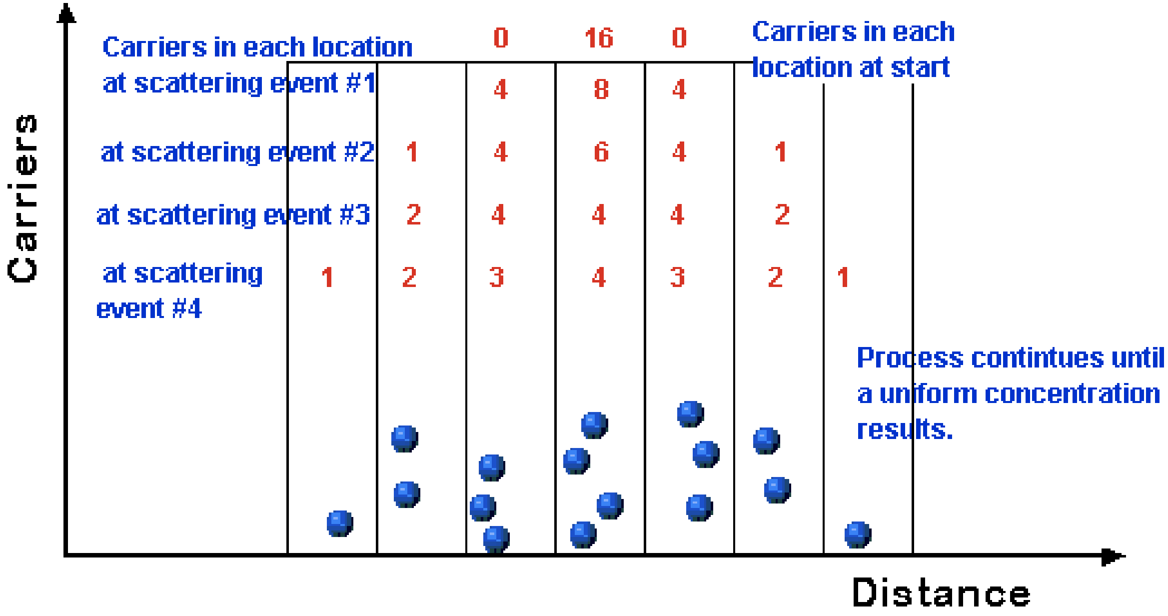
To achieve net charge flow (current), carriers must move via <u>diffusion</u> or <u>drift</u>.

Diffusion



In this animation, 1/4 of the carriers move to the right, 1/4 to the left and the remainder stay put (move up or down).

Courtesy Christiana Honsberg and Stuart Bowden. Used with permission.

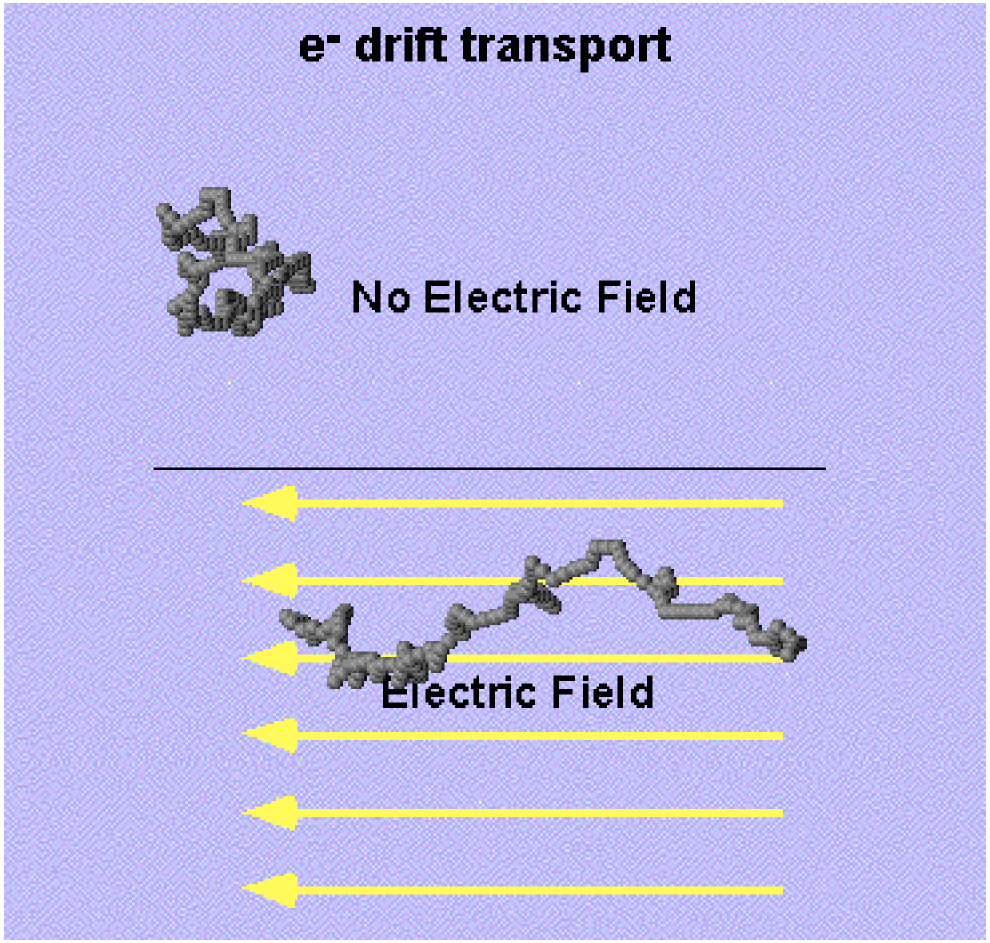


Carriers in each location at start			0	16	0		
Carriers in each location at scattering event #1			4	8	4		
at scattering event #2		1	4	6	4	1	
at scattering event #3		2	4	4	4	2	
at scattering event #4	1	2	3	4	3	2	1

Process contintues until a uniform concentration results.

From PVCDROM

Drift Current



From PVCDROM

Courtesy Christiana Honsberg and Stuart Bowden. Used with permission.

Advanced Concept: Thermalization

Energy Loss Due to Thermalization

Thermalization is an incredibly fast process, difficult to avoid…

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Please see http://www.tf.uni-kiel.de/matwis/amat/semi_en/kap_2/illustr/pair_generation.gif.

Energy Losses: First Approx.

Thermalization
Losses
(bandgap too small)

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Please see any diagram of thermalization loss, such as
https://engineering.purdue.edu/NANOENERGY/research/images/solar.gif, and any graph of non-absorption losses.

Non-Absorption
Losses
(bandgap too big!)

Energy Losses: First Approximation

Balance between Thermalization and Non-Absorption Losses

Image removed due to copyright restrictions. Please see any image of photovoltaic efficiency vs. bandgap energy, such as http://www.grc.nasa.gov/WWW/RT/RT1999/images/5410hepp-f3.jpg.