2.626 Fundamentals of Photovoltaics
Fall 2008

Charge Separation: How Voltage and Current Are Formed

Lecture 5 – 2.626

Tonio Buonassisi

General Announcements

- Concept Quiz (piece of cake!).
- Schedule: Quiz #1 in two weeks.

Outline

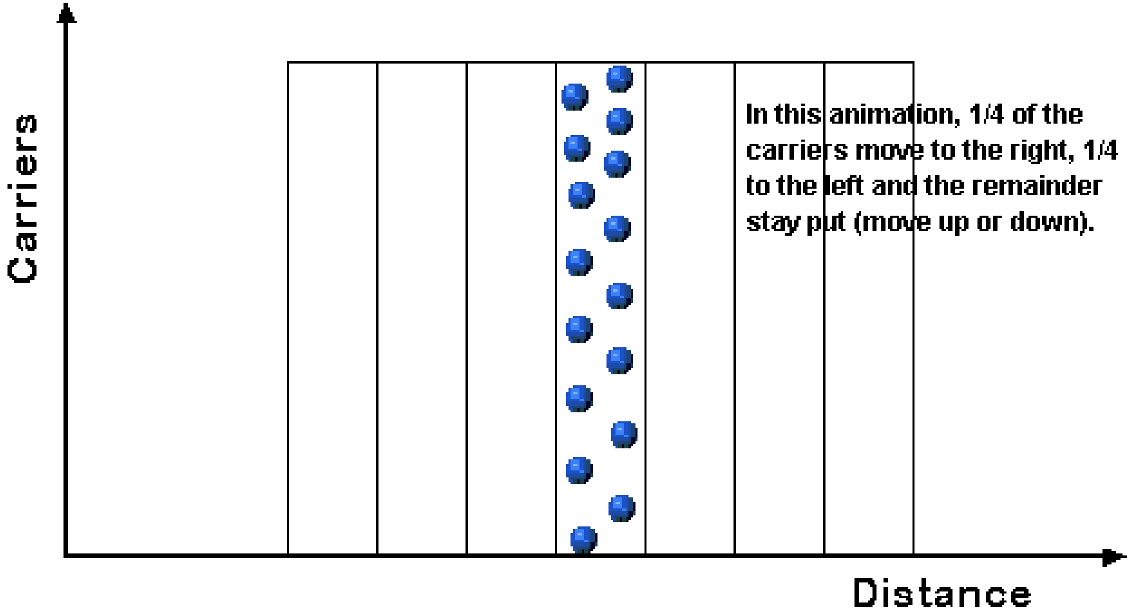
- Review: Carrier motion
- Excitons
- Drift and diffusion currents
- Charge separation mechanisms: pn-junctions and p-i-n junctions

Review: Carrier Motion

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

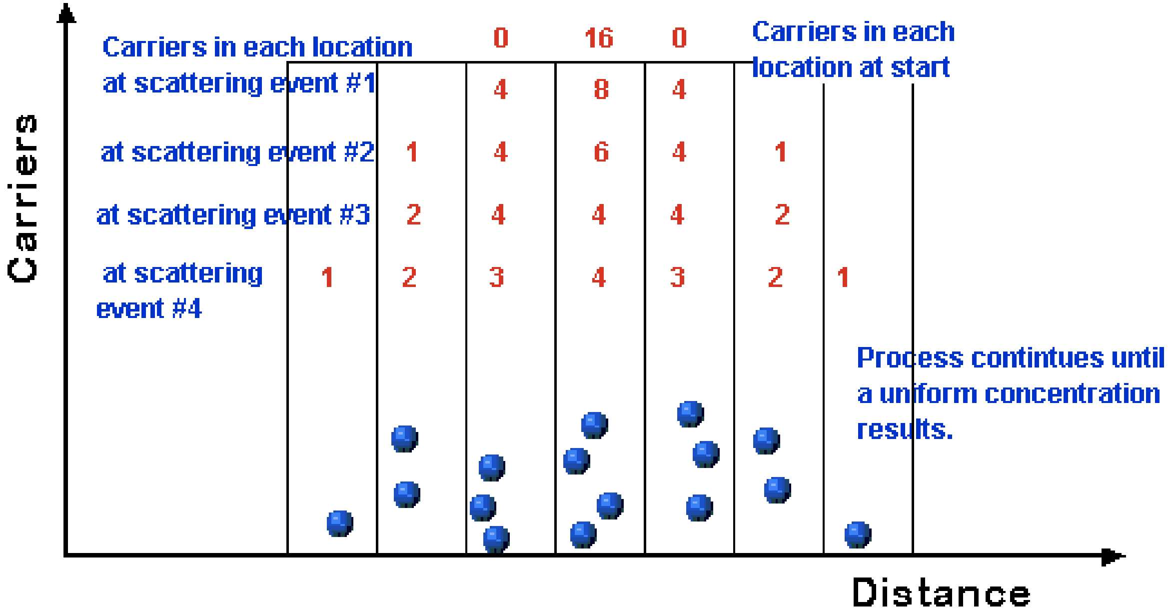
To achieve net charge flow (current), carriers must move via diffusion or drift.

Review: 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.

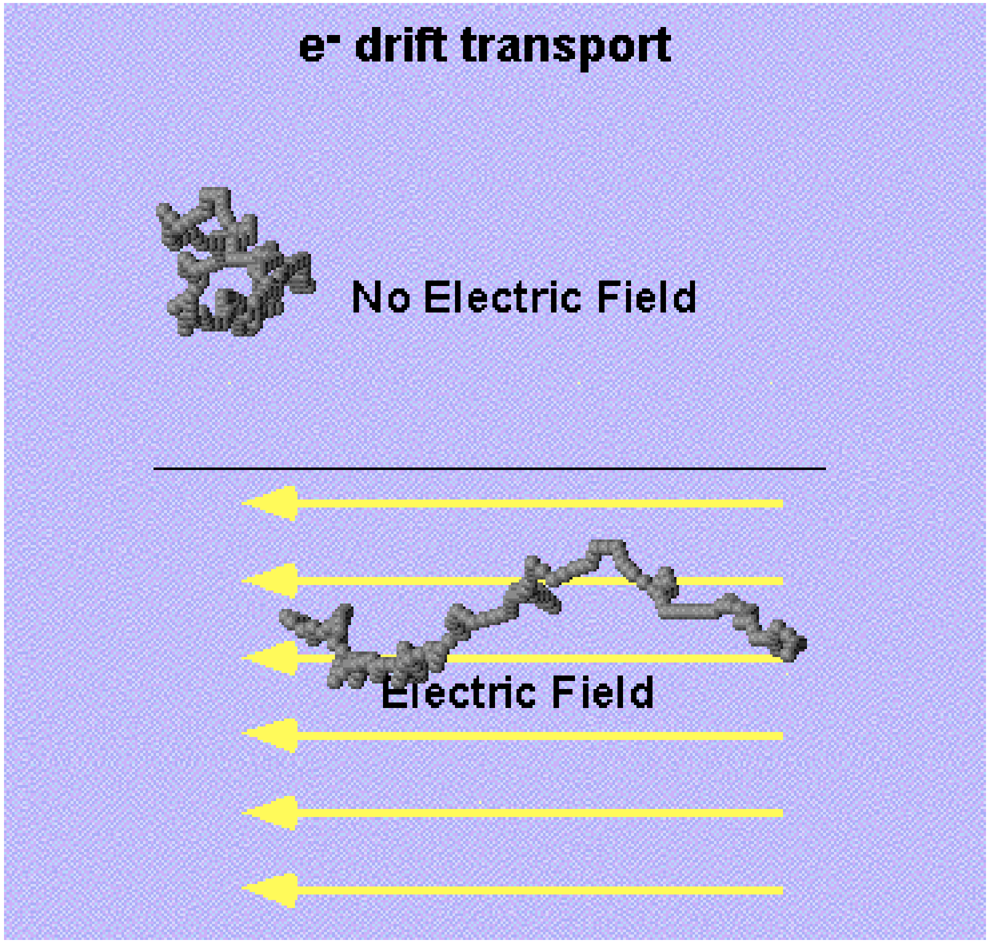


Carriers in each location at start			0	16	0		
Carriers in each location at scattering event #1			4	8	4		
at scattering event #2		1	4	6	4	1	
at scattering event #3		2	4	4	4	2	
at scattering event #4	1	2	3	4	3	2	1

Process contintues until a uniform concentration results.

From PVCDROM

Review: Drift Current



From PVCDROM

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Charge Separation: Microscopic Level

Exciton: Bound electron-hole pair

Cartoon Diagram

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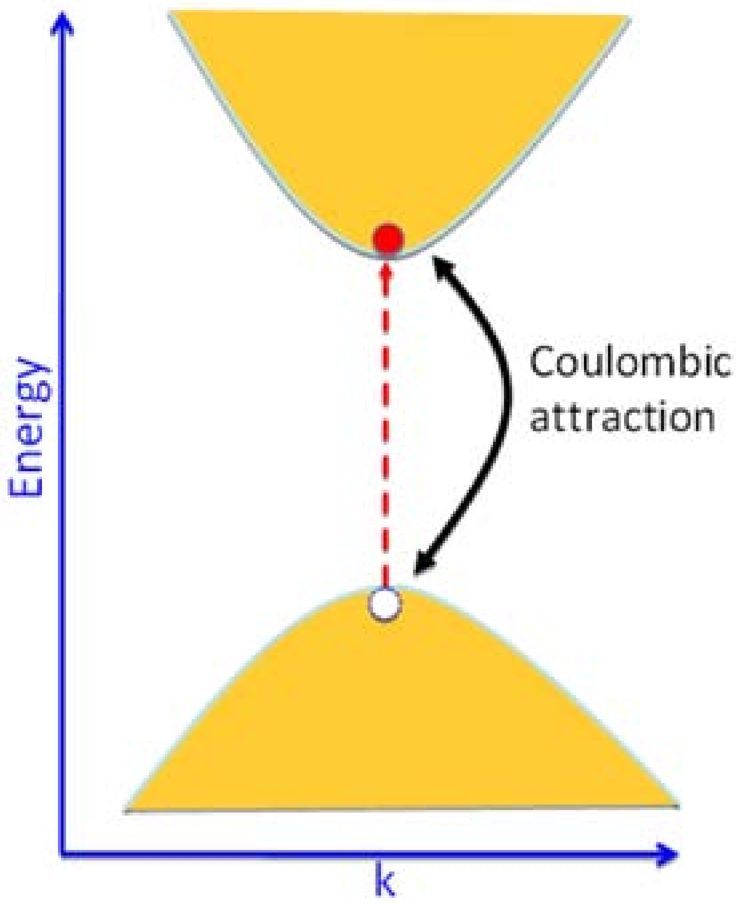
Band Diagram



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Charge Separation: Microscopic Level

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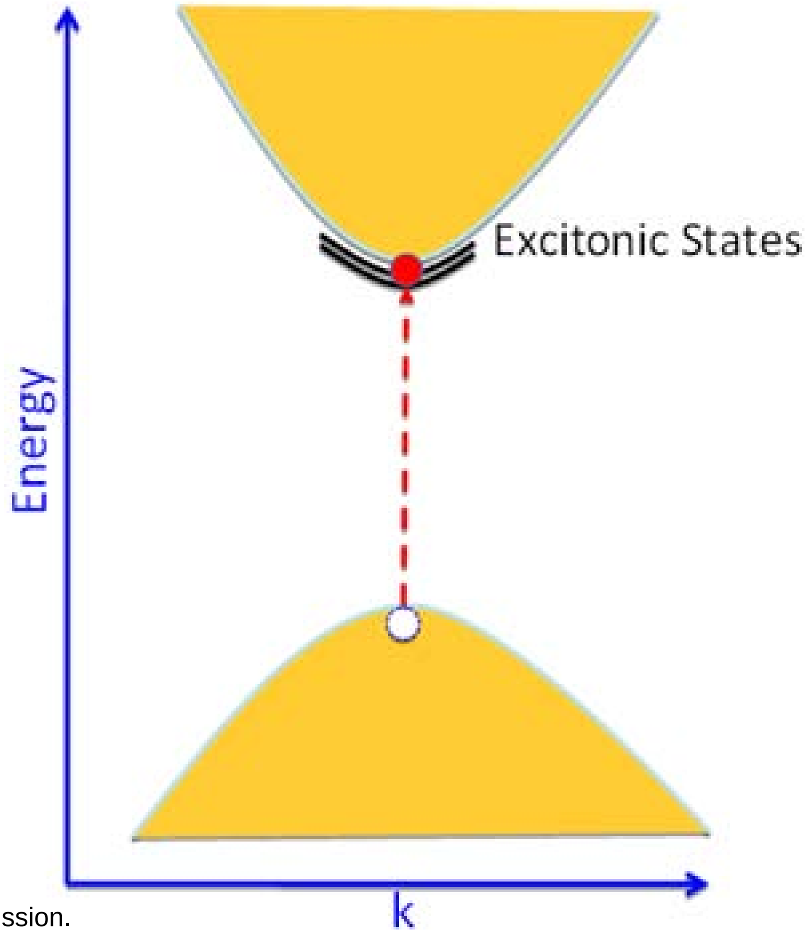
Band Diagram



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Charge Separation: Microscopic Level

Exciton: Bound electron-hole pair

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http://kottan-labs.bgsu.edu/teaching/workshop2001/chapter6_files/image067.jpg

http://kottan-labs.bgsu.edu/teaching/workshop2001/chapter6.htm

Mott-Wannier exciton

- Dielectric screening potential is large.
- Exciton radius is large.
- Exciton binding energy is small, typically a few meV (detectable only at low T).

  (27 meV for CdS, 15 meV for CdSe, 5.1 meV for InP, 4.9 meV for GaAs)
- Typical for bulk semiconductor materials.

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$$E_{\mathrm{n}} = E_{\infty} - \frac{R}{n^2}$$

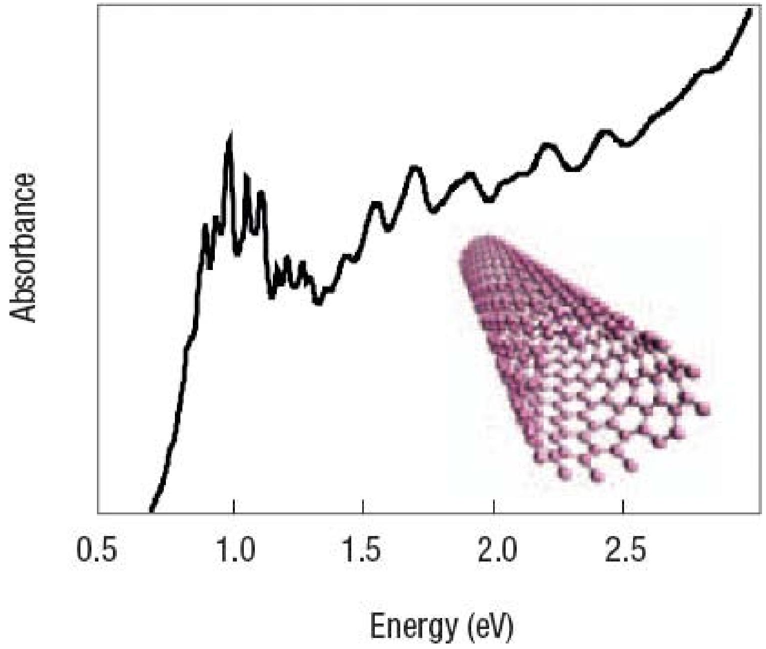
$$\text{where } R = \frac{m^* e^4}{2h^2\varepsilon^2}, \text{ and n} = 1, 2\ldots$$

Excitons. W Y Liang, *Phys. Educ.* **5** 226 (1970).

Frenkel exciton

- Dielectric screening potential is small.
- Exciton radius is small.
- Exciton binding energy is large, typically a few eV (detectable at RT).

  (~400 meV for CNT)
- Typical for molecules.



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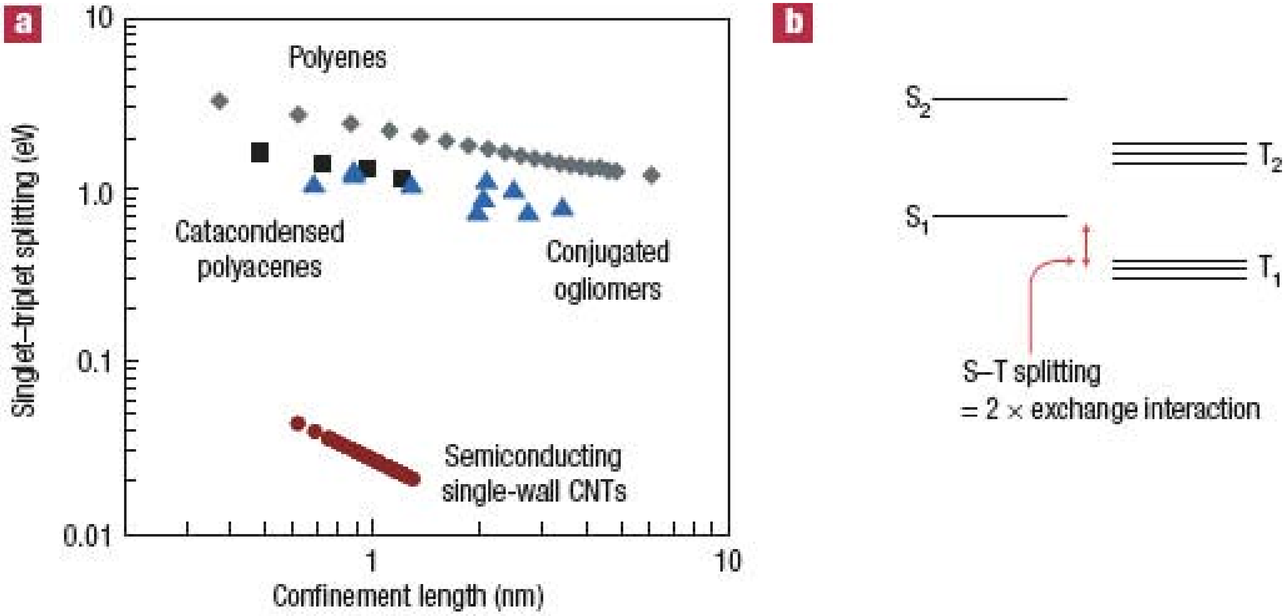
Size effects



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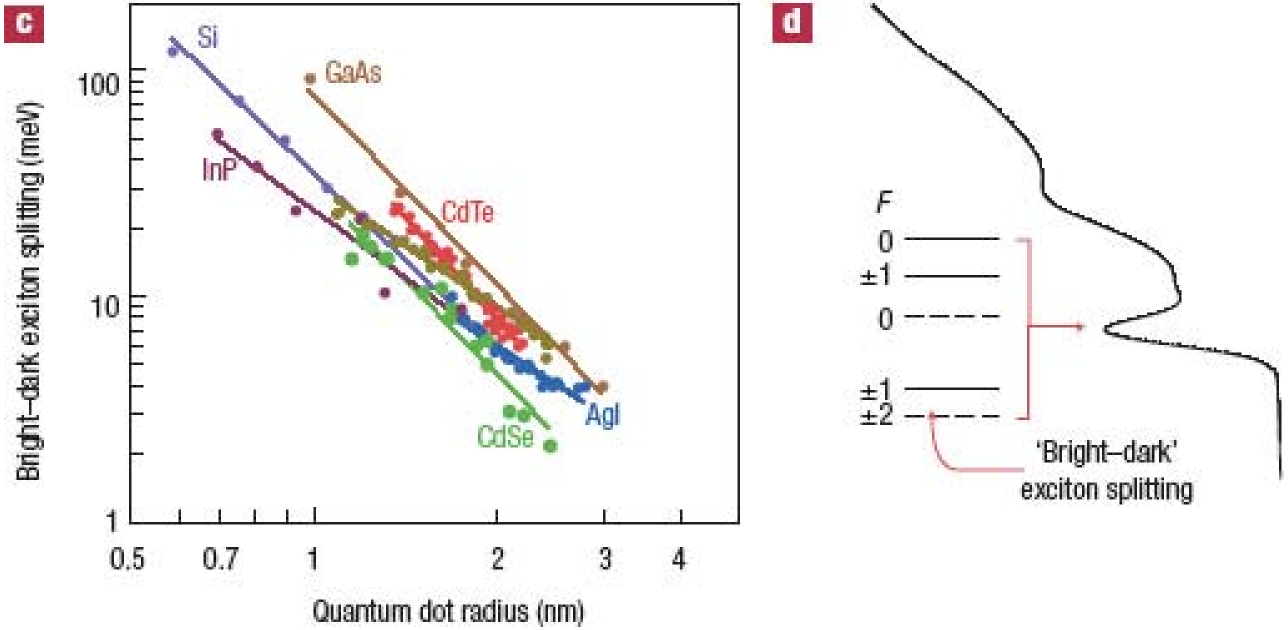

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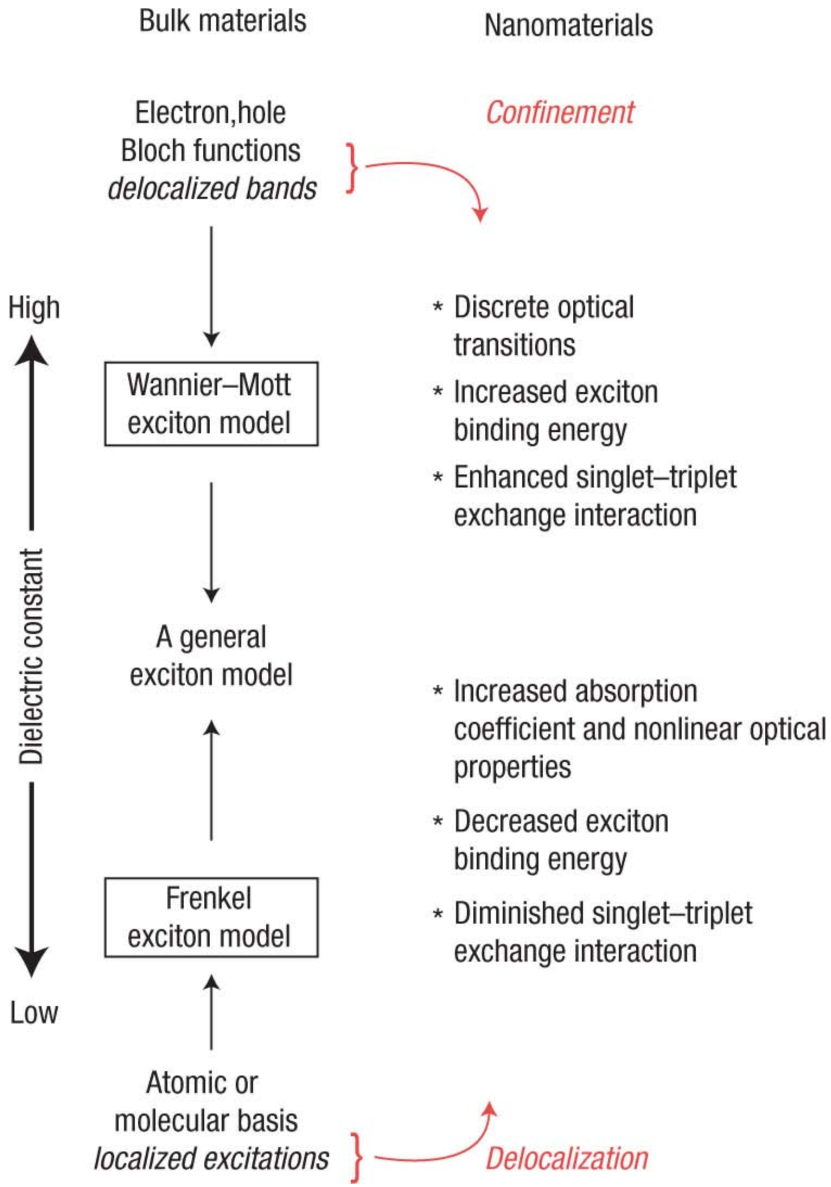

Bulk materials

Nanomaterials

Electron,hole
Bloch functions
delocalized bands

Confinement

High

Dielectric constant

Low

Wannier–Mott exciton model

A general exciton model

Frenkel exciton model

Atomic or
molecular basis
localized excitations

Delocalization

- Discrete optical transitions
- Increased exciton binding energy
- Enhanced singlet–triplet exchange interaction

- Increased absorption coefficient and nonlinear optical properties
- Decreased exciton binding energy
- Diminished singlet–triplet exchange interaction

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More considerations

The presence of a strong local electric field can help “split” excitons.

→ *either local (e.g., metal nanodots on a sc nanorod) or macroscopic (contacts).*

Exciton-phonon interactions (“Davydov” excitons / polarons / solitons)

→ *can be a factor in ringed molecules.*

Once excitons are split, then what happens?

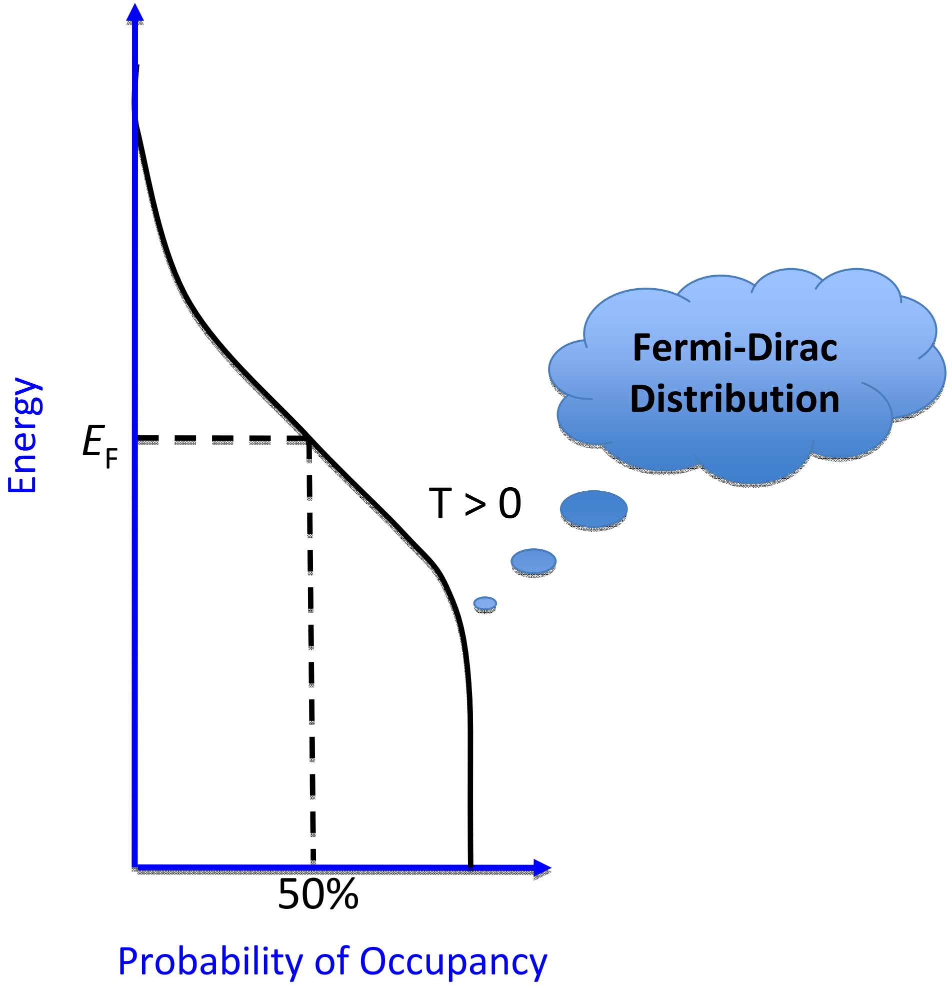
It all depends on the device architecture…

Let’s consider a simple pn-junction device

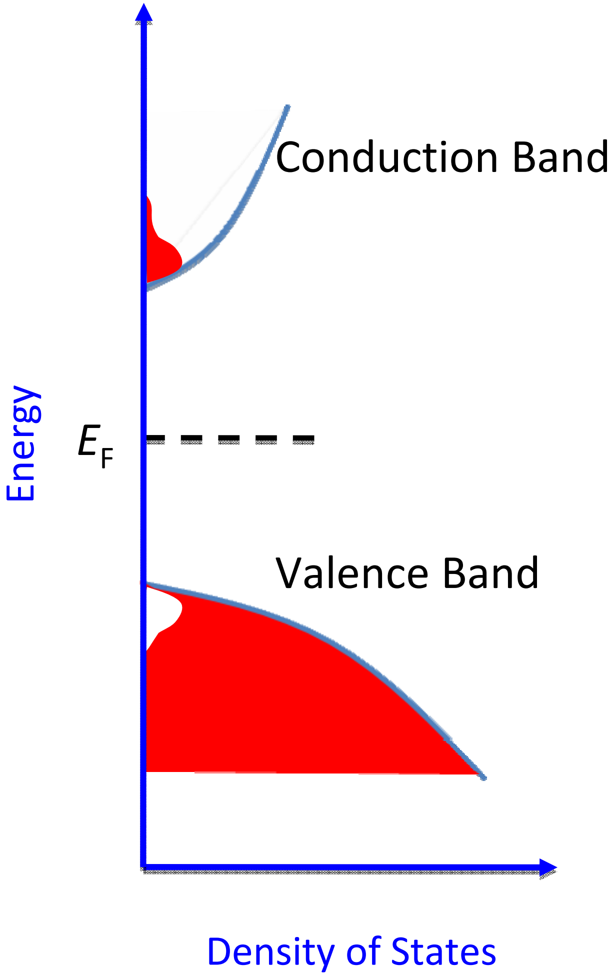
Also called a “minority carrier device.”

Defining the "Fermi Level"

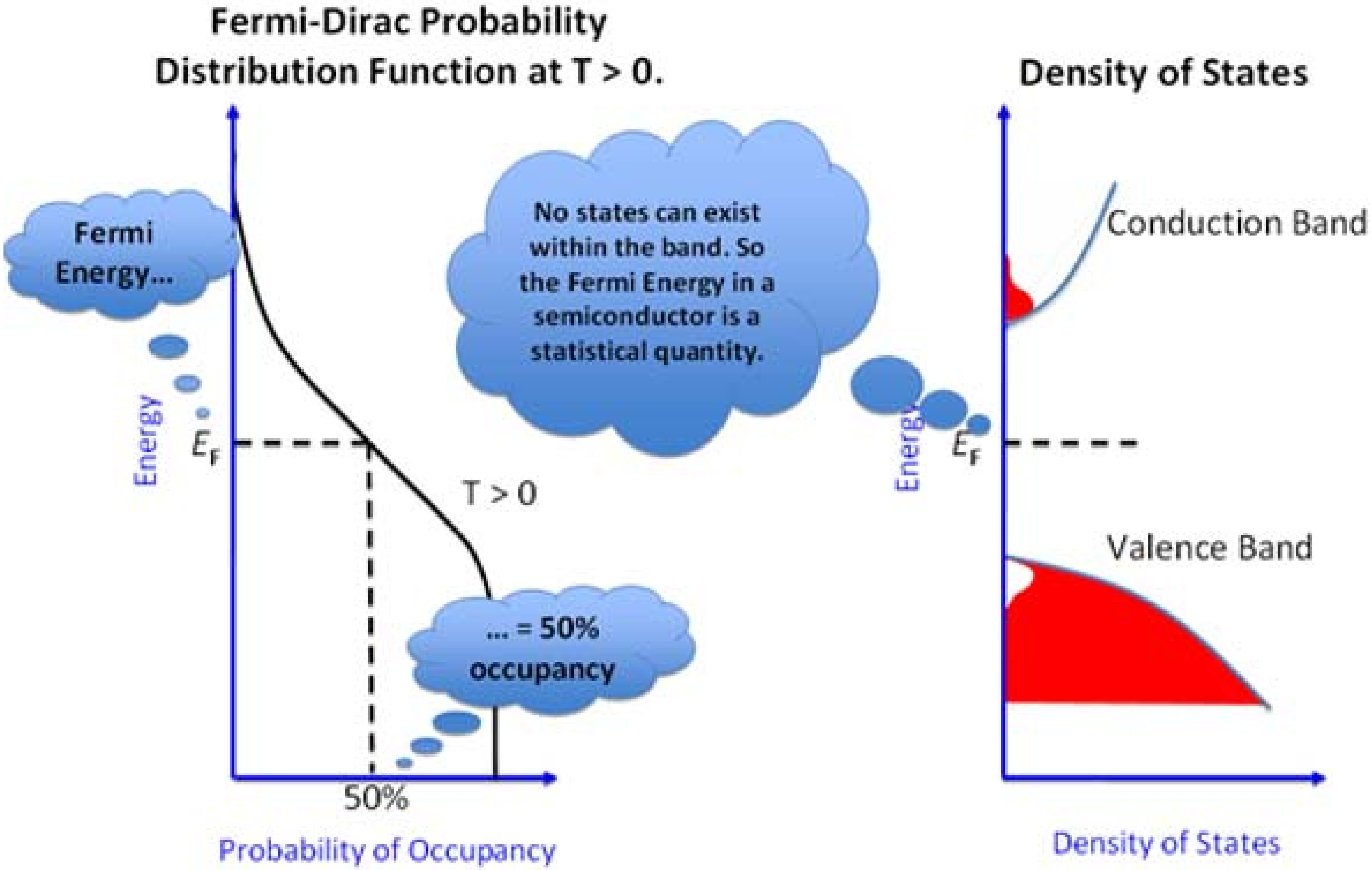
Fermi-Dirac Probability Distribution Function at T > 0.



Density of States



Defining the "Fermi Level"



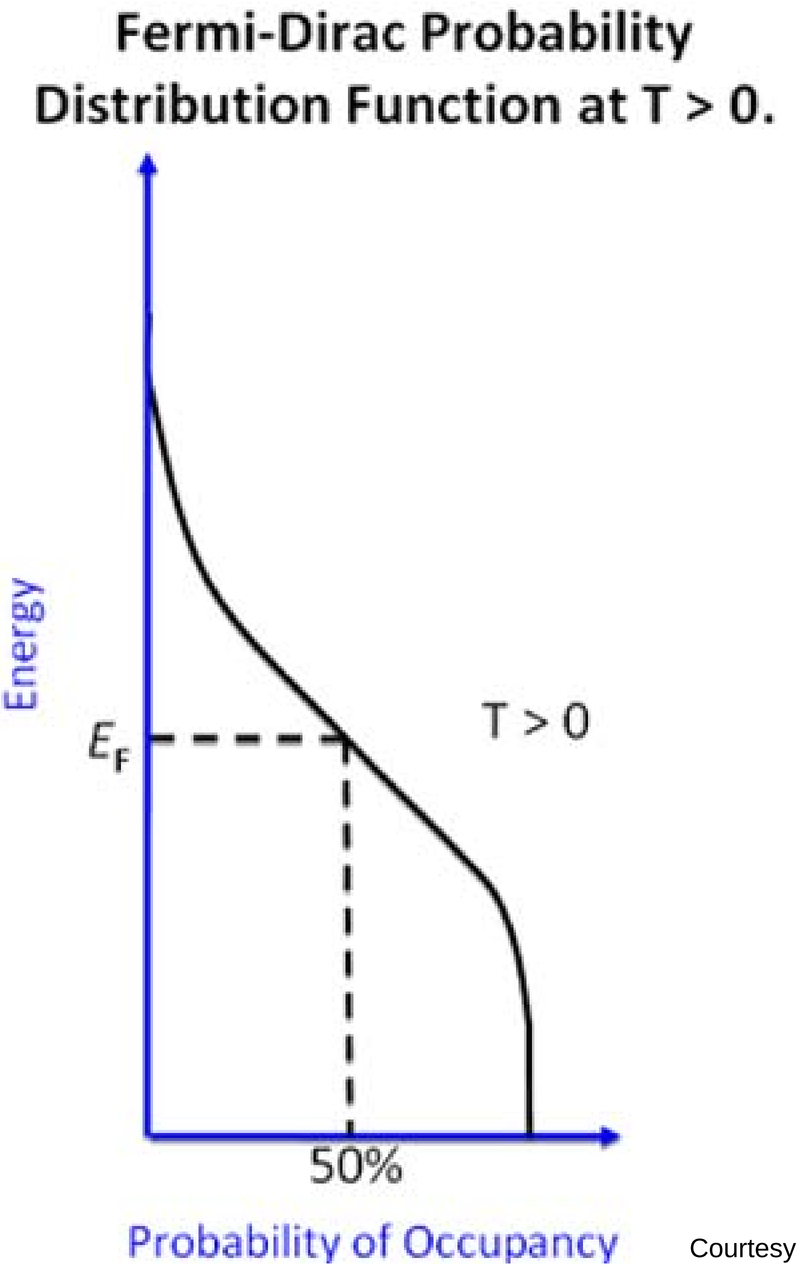
Fermi-Dirac Probability Distribution Function at T > 0.

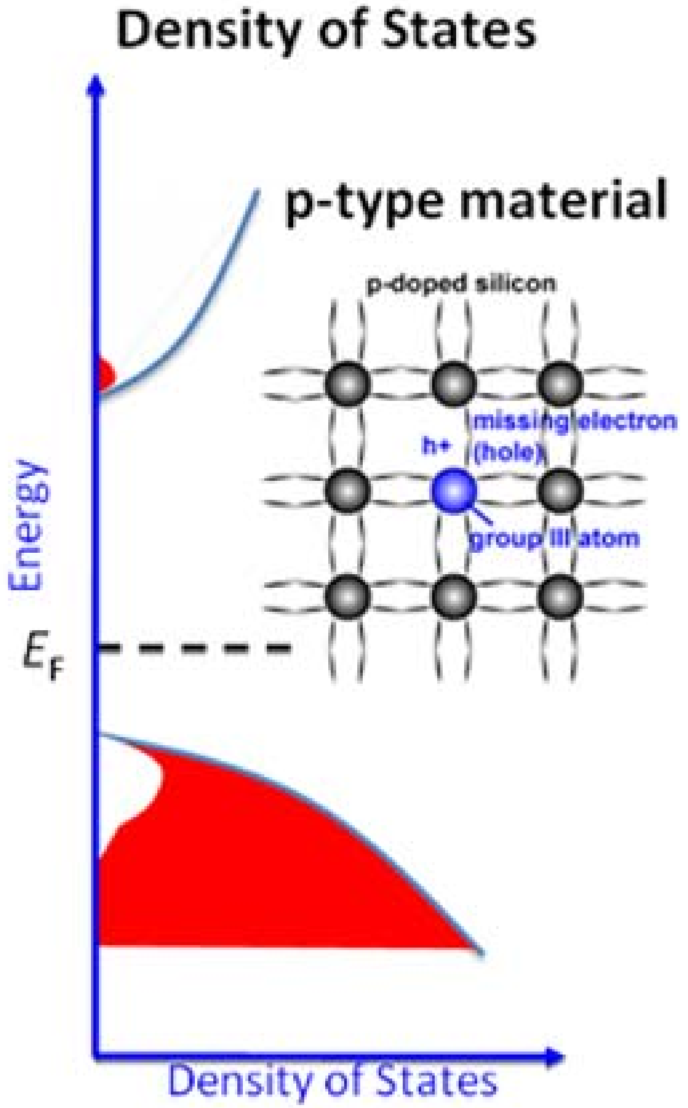
Density of States

Fermi Energy… … = 50% occupancy

No states can exist within the band. So the Fermi Energy in a semiconductor is a statistical quantity.

Fermi Level in p-type Material





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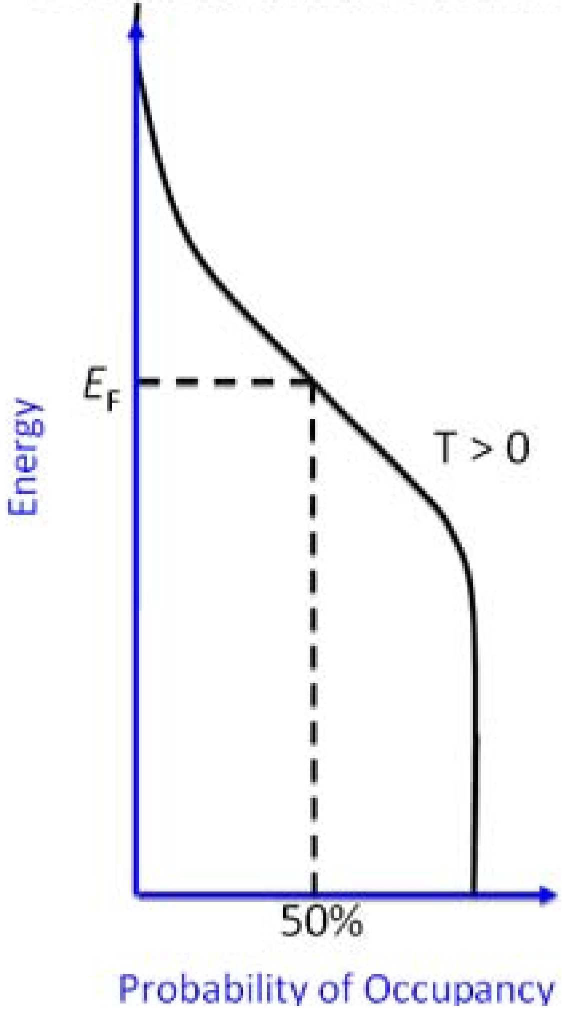
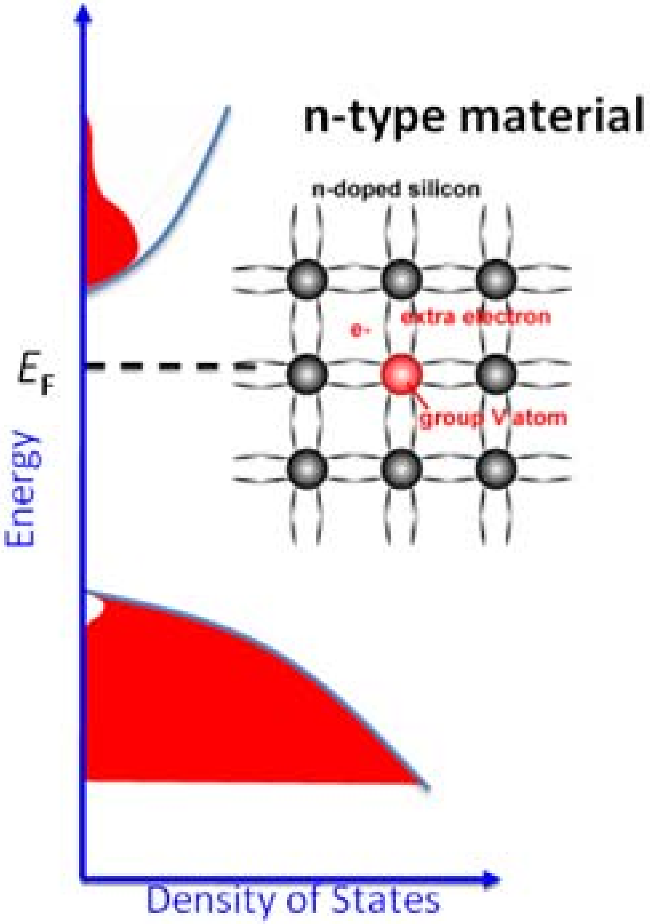
Fermi Level in n-type Material


Fermi-Dirac Probability Distribution Function at T > 0.


Density of States

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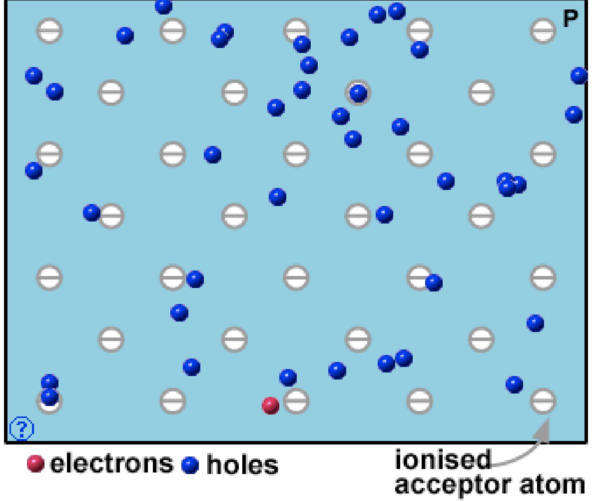

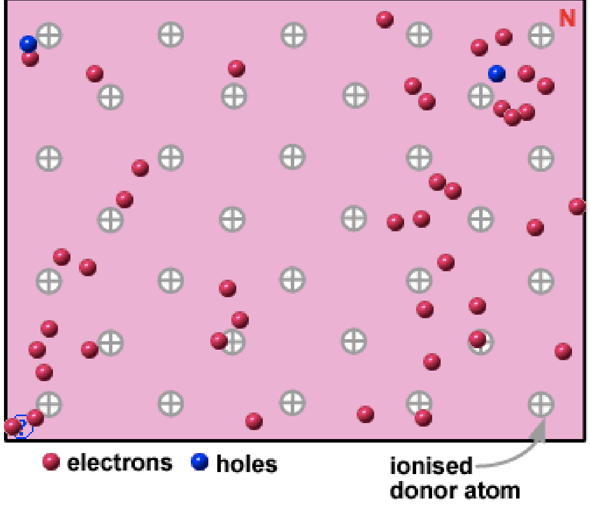

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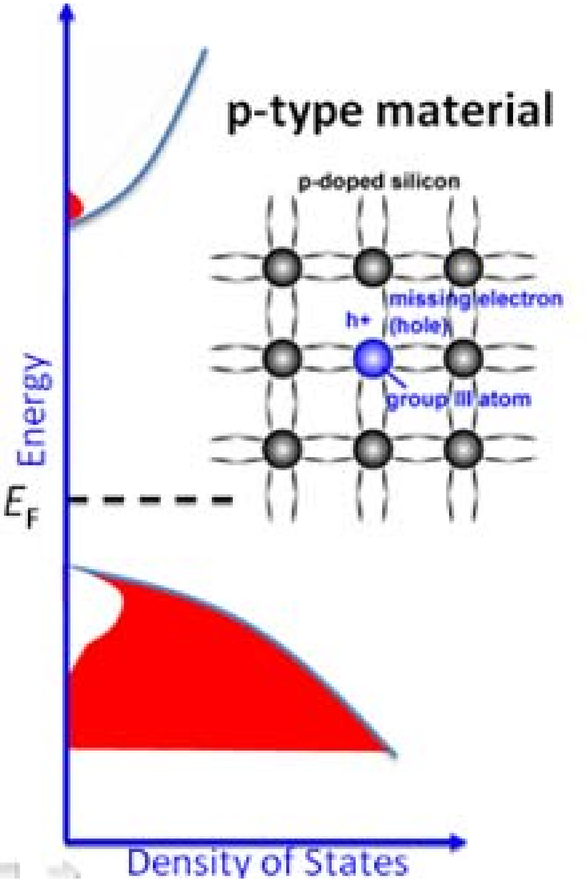

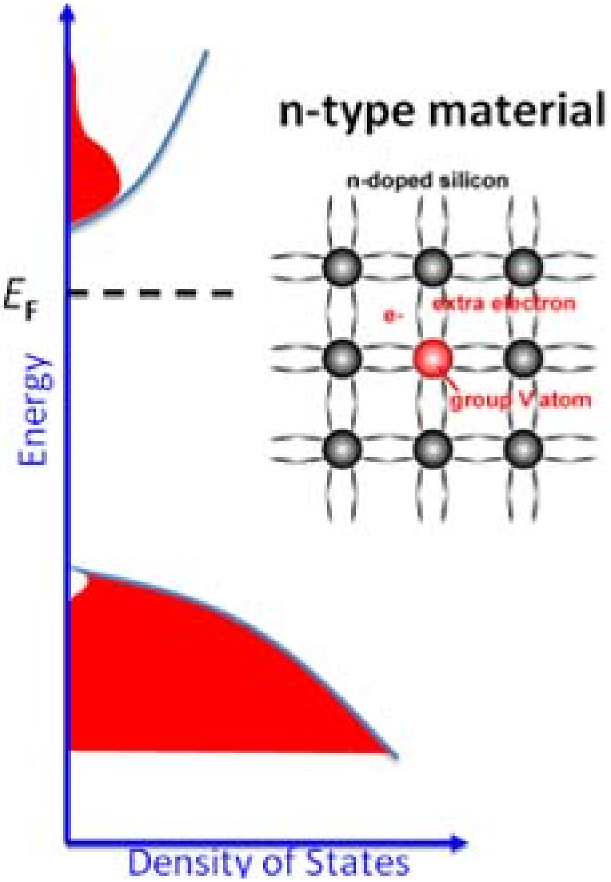

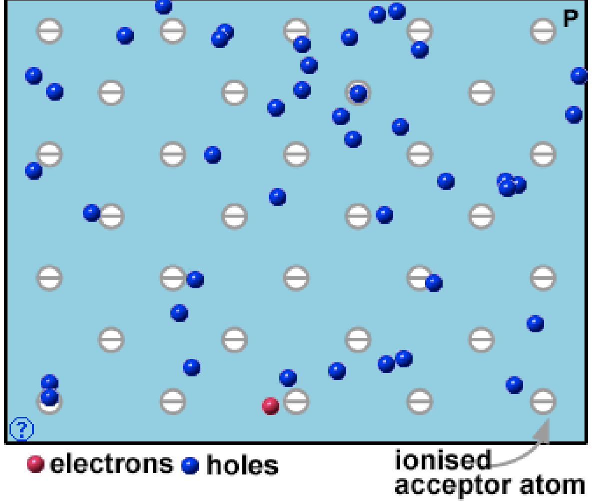

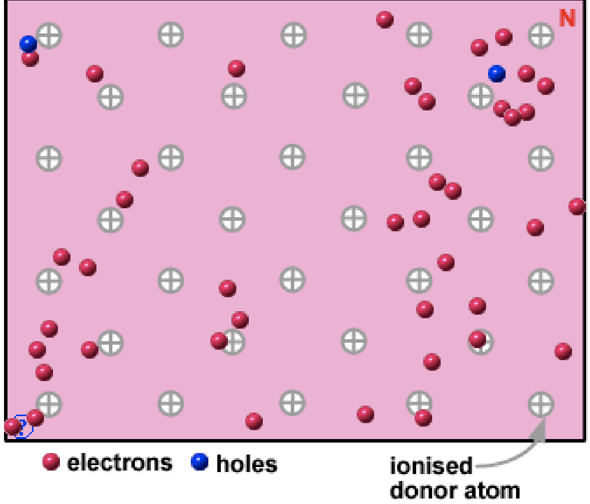

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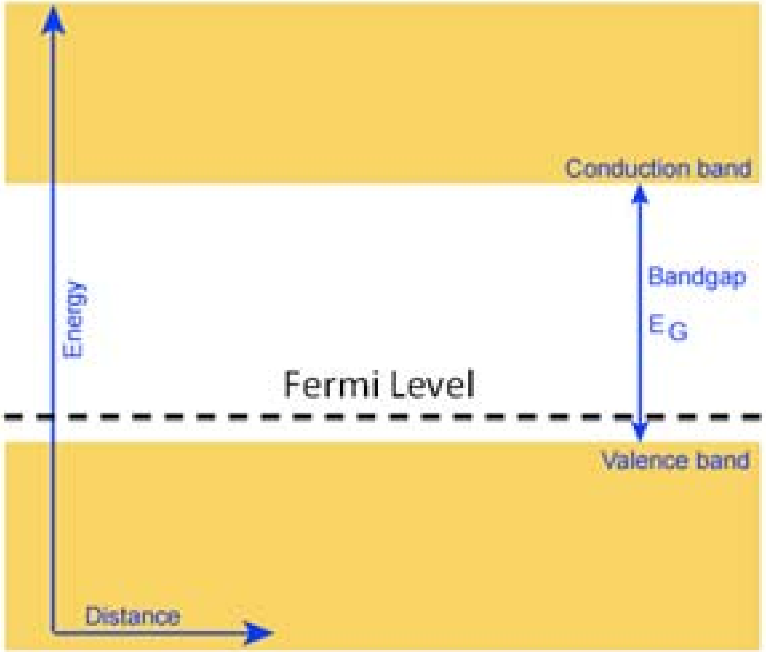
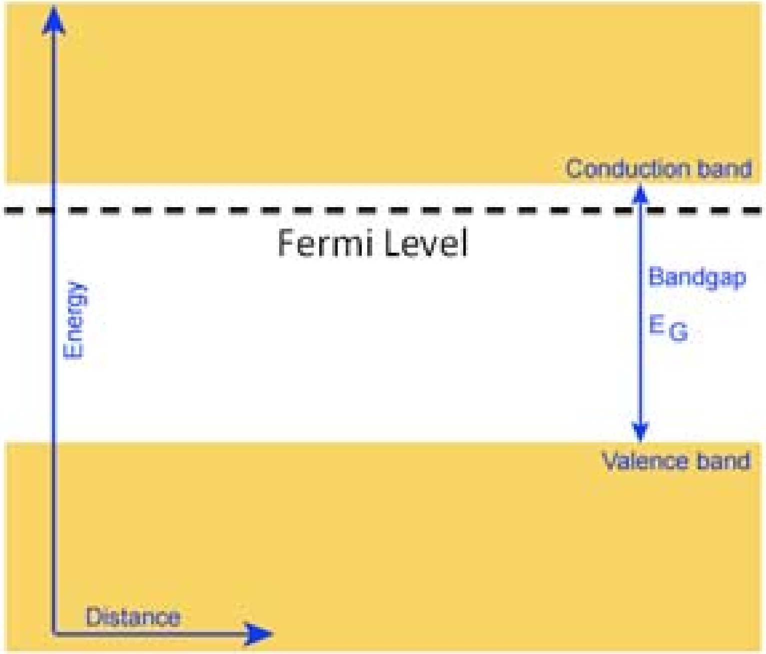
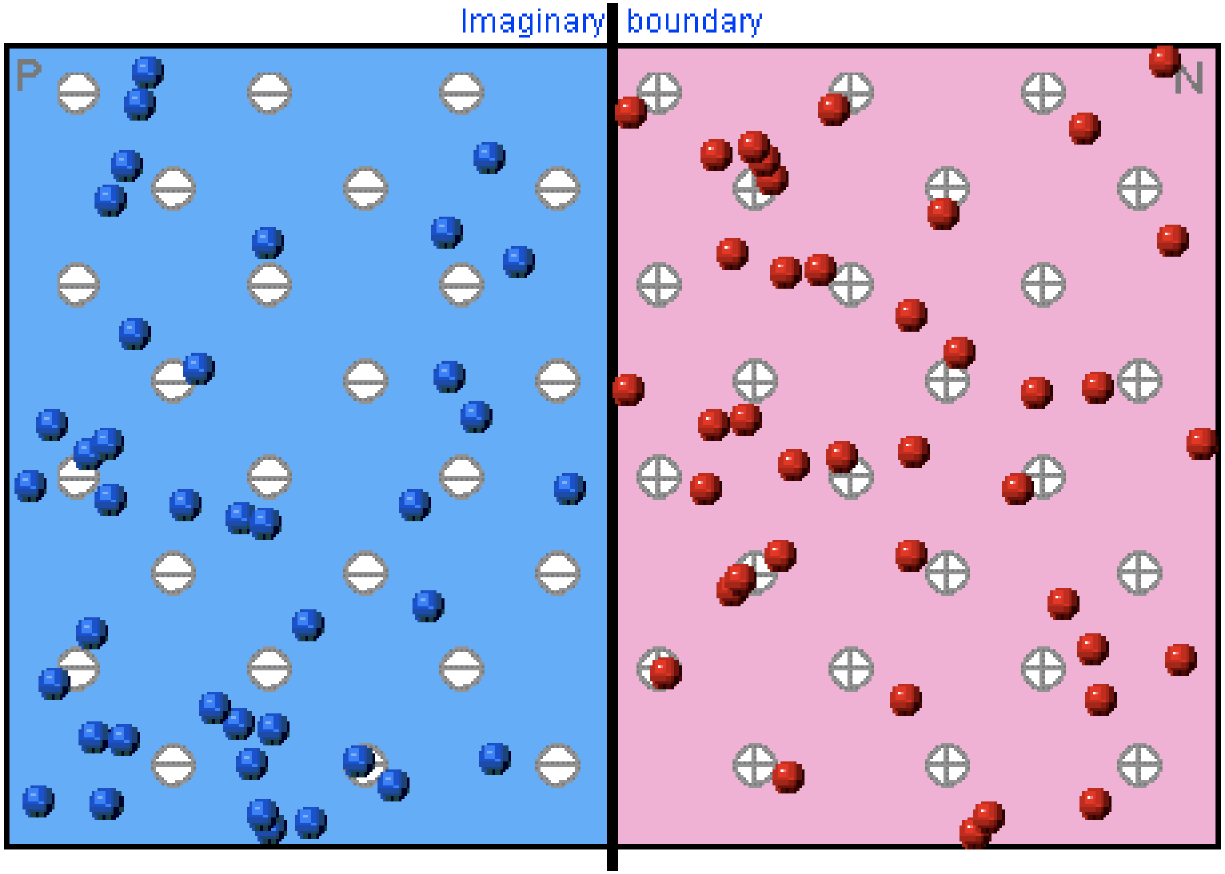




Let’s imagine the n- and p-type materials in contact, but with an imaginary barrier in between them.

How a pn-junction comes into being



With the P and N type materials separated the carriers diffuse around randomly.

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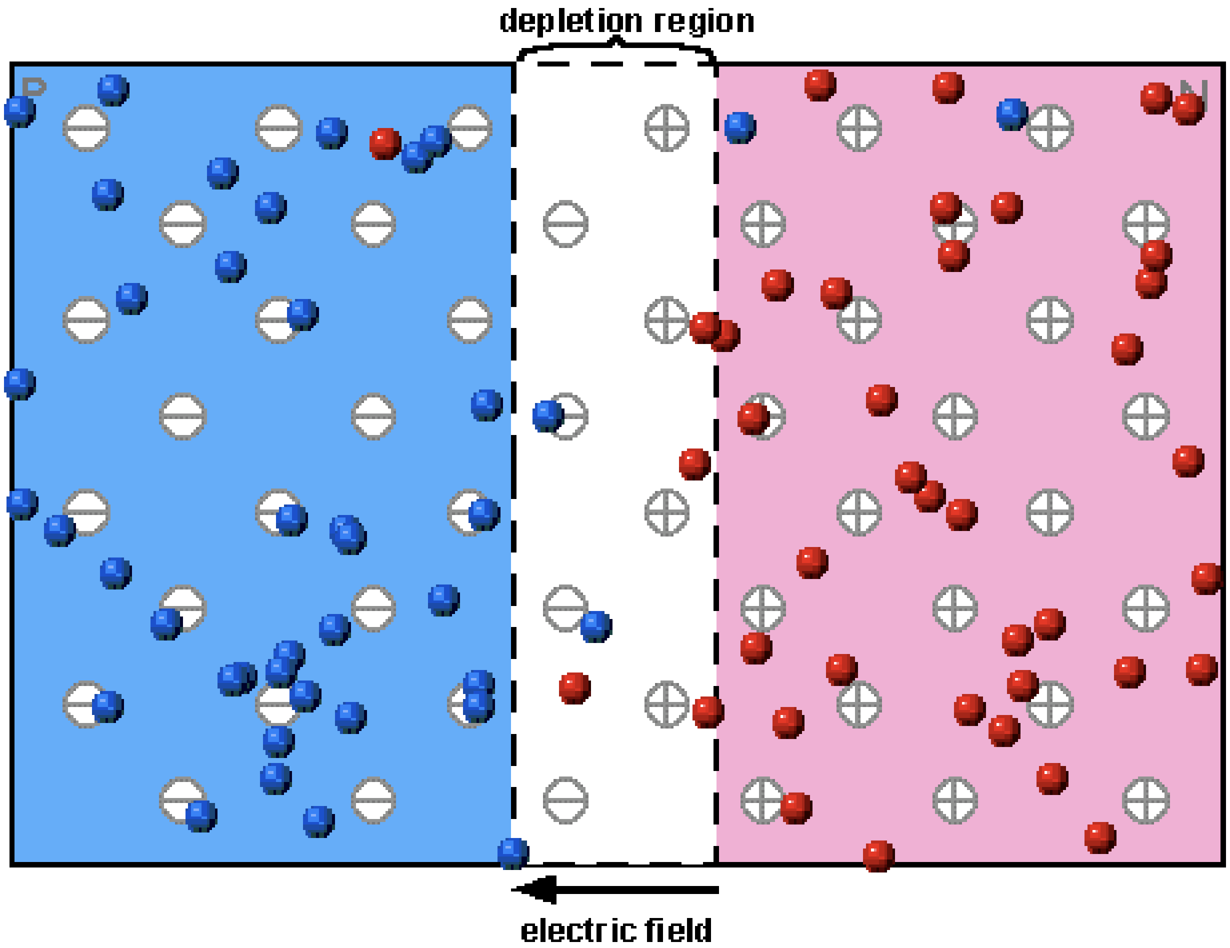
When that imaginary boundary is removed, electrons and holes diffuse into the other side.

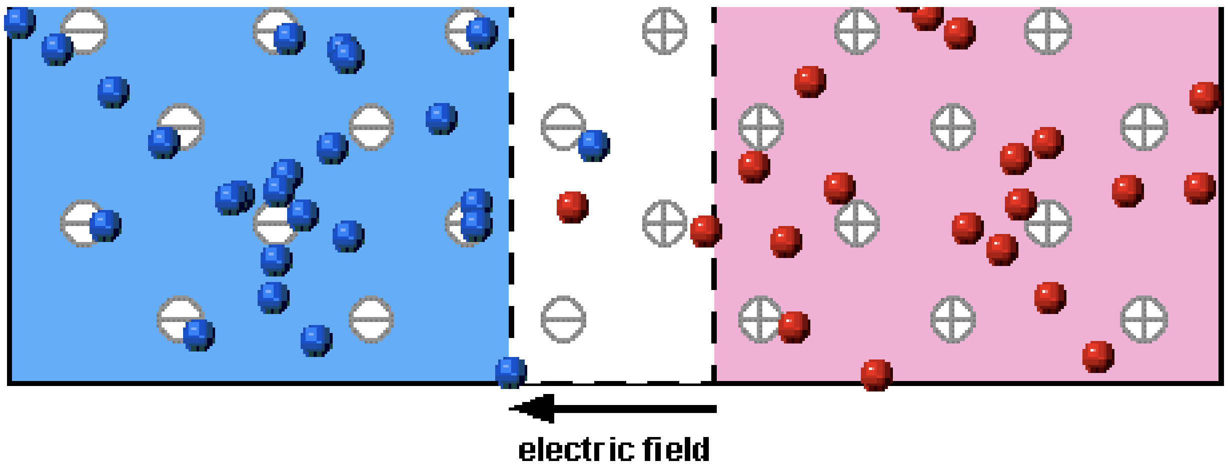
How a pn-junction comes into being



Courtesy Christiana Honsberg and Stuart Bowden. Used with permission.

Eventually, the accumulation of like charges [(h^+ + P^+) or (e^- + B^-)] balances out the diffusion, and steady state condition is reached.

How a pn-junction comes into being



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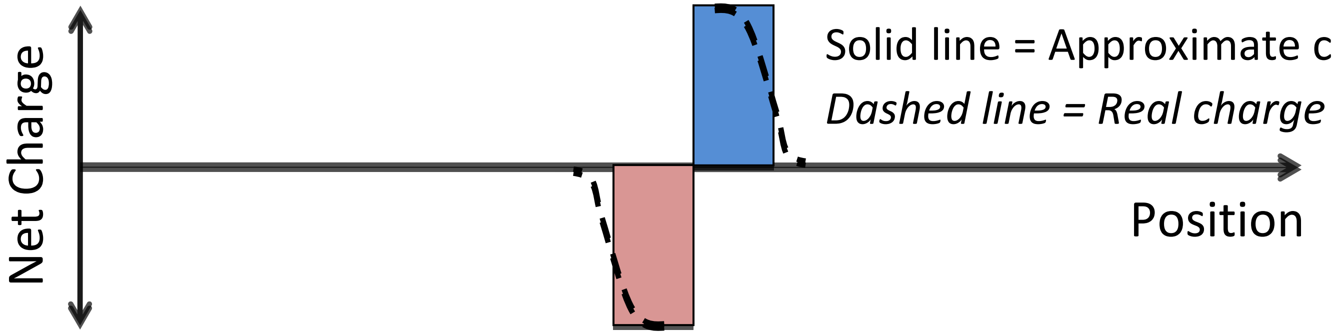
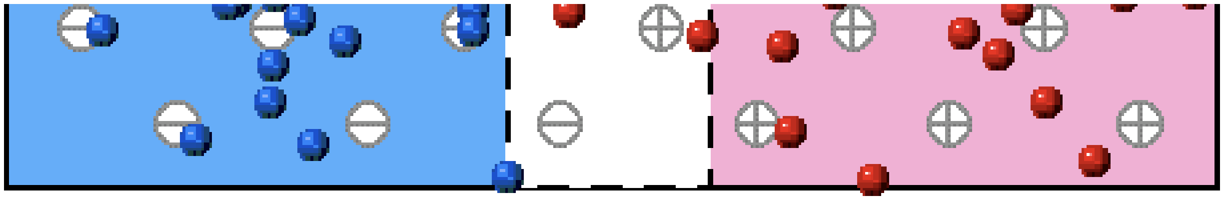


Solid line = Approximate charge distr.

Dashed line = Real charge distribution

The net charge can be approximated as shown above.

How a pn-junction comes into being



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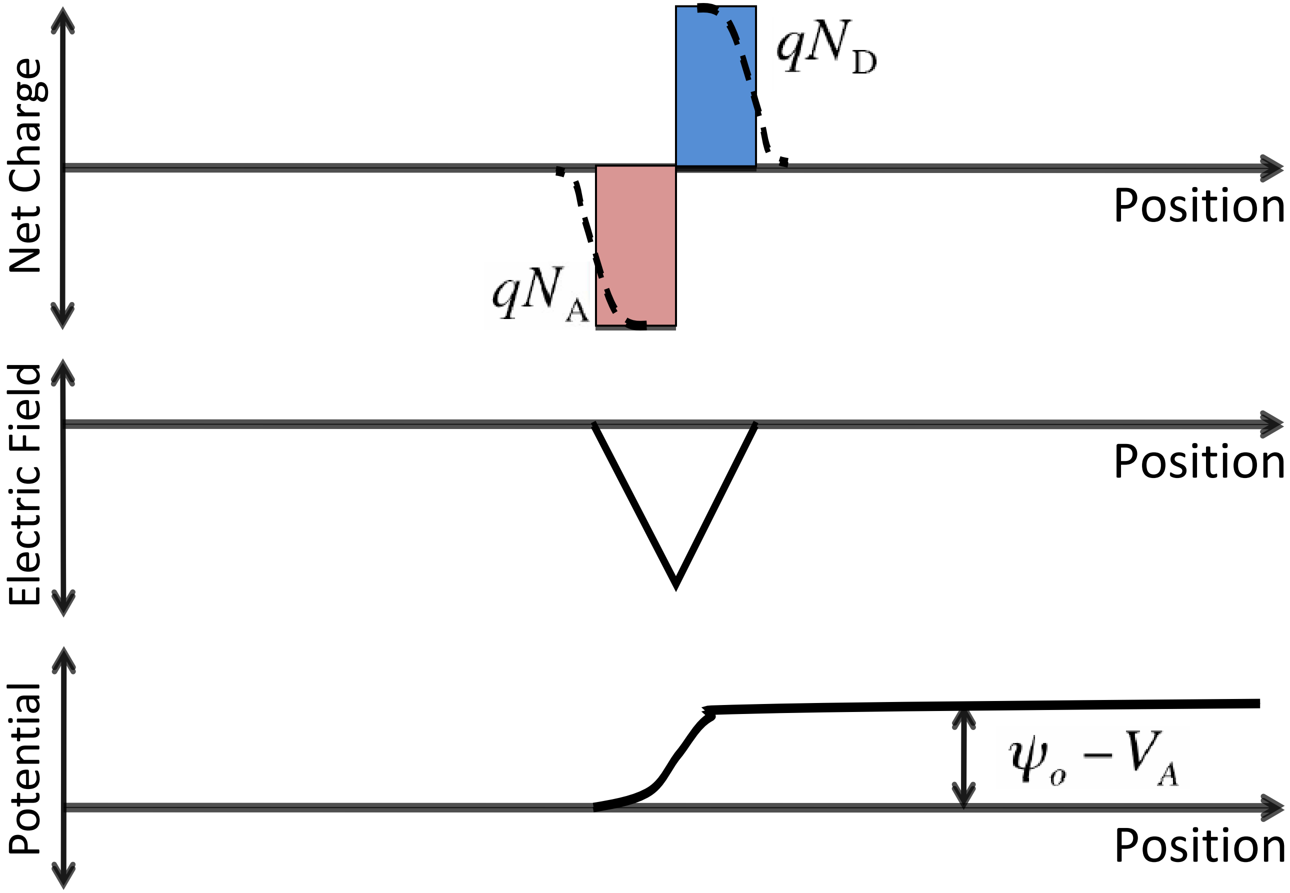
$$\frac{d\xi}{dx} = \frac{\rho}{\varepsilon}$$

$$\frac{d\psi}{dx} = -\xi$$



Nicer figure at Wikipedia!

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http://en.wikipedia.org/wiki/File:Pn-junction-equilibrium-graphs.png

http://en.wikipedia.org/wiki/P-n_junction

Let’s hop to PVCDROM for some interactive demos…

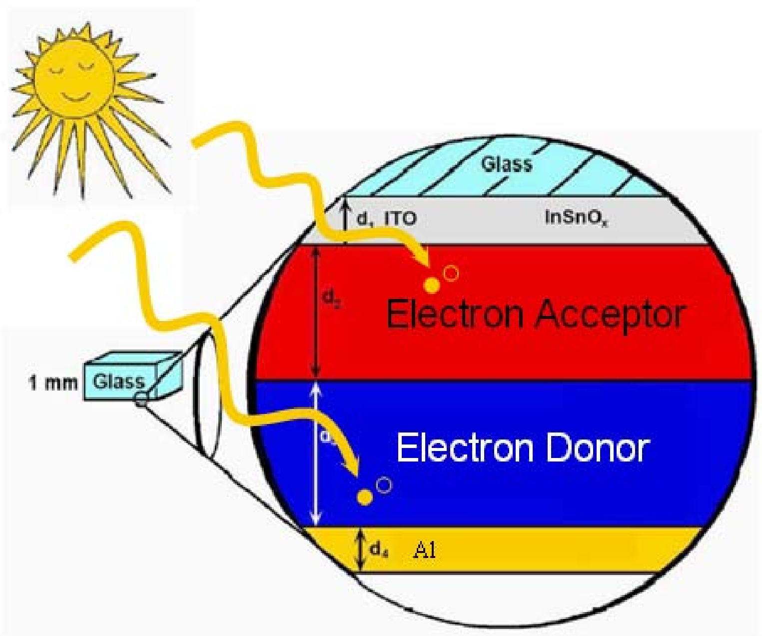
1)Forward bias of a pn-junction
2)Reverse bias of a pn-junction
3)Open circuit conditions
4)Closed circuit conditions

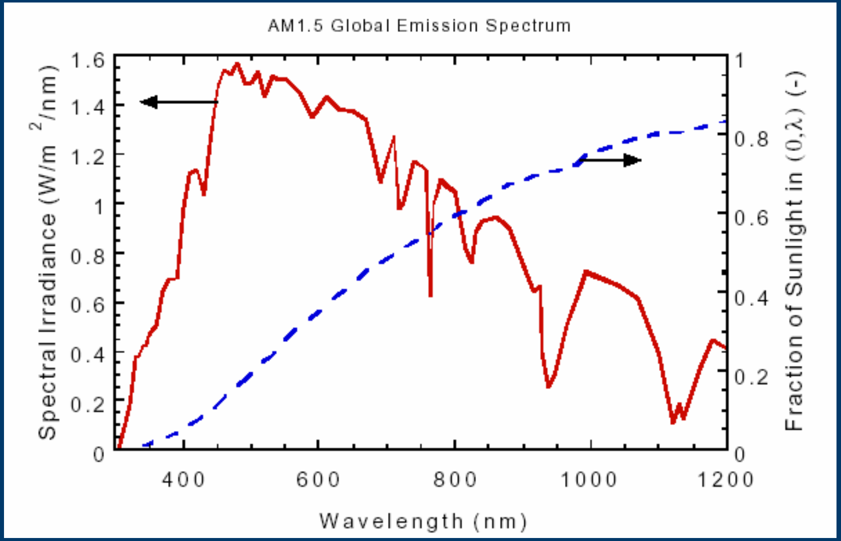
PVCDROM Chapter 3

Now, for the p-i-n structure (a.k.a “majority carrier device”)

Basics of Organic PVs

- **Absorption**
- Exciton diffusion
- Charge transfer at heterojunction
- Transport to electrodes





Organics exhibit extremely high absorptivity (extinction lengths **~100 nm** vs 1-100 μm in inorganics!

but... absorption limited to
- narrow band
- generally high energy

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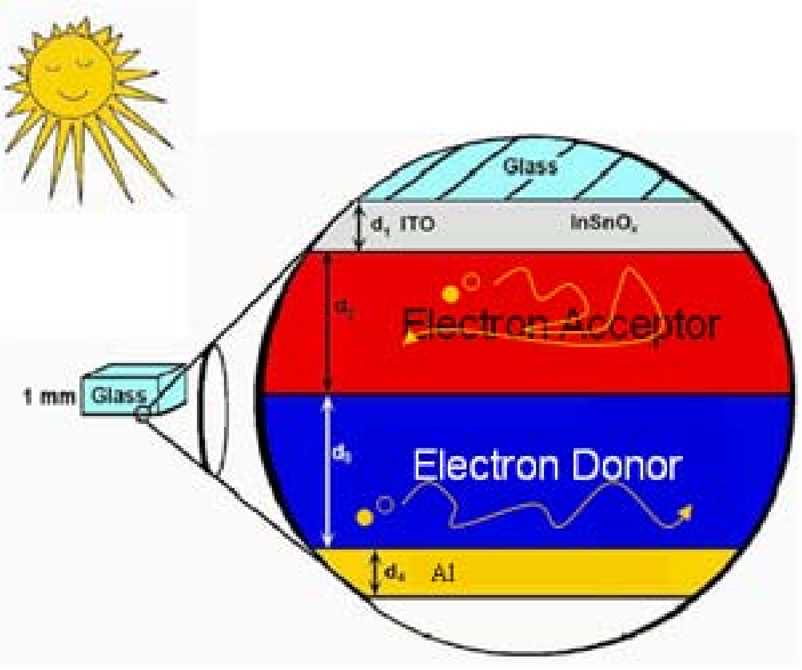
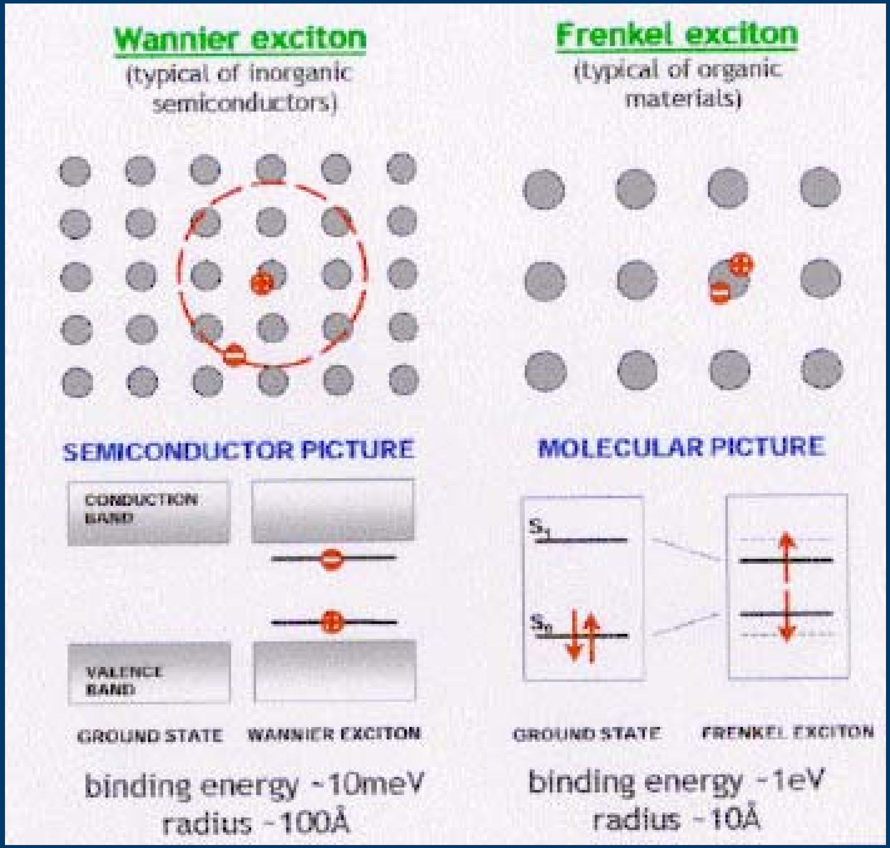
Basics of Organic PVs

- Absorption
- **Exciton diffusion**
- Charge transfer at heterojunction
- Transport to electrodes





Bound excitons undergo spontaneous recombination:

-Lifetimes dictate diffusion lengths of approximately 10 nm
- High binding energies: >0.2 eV

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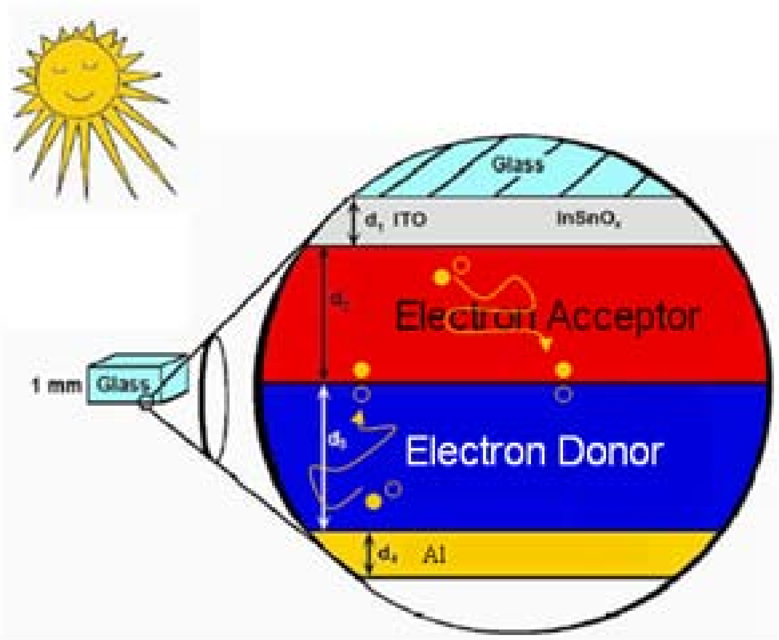
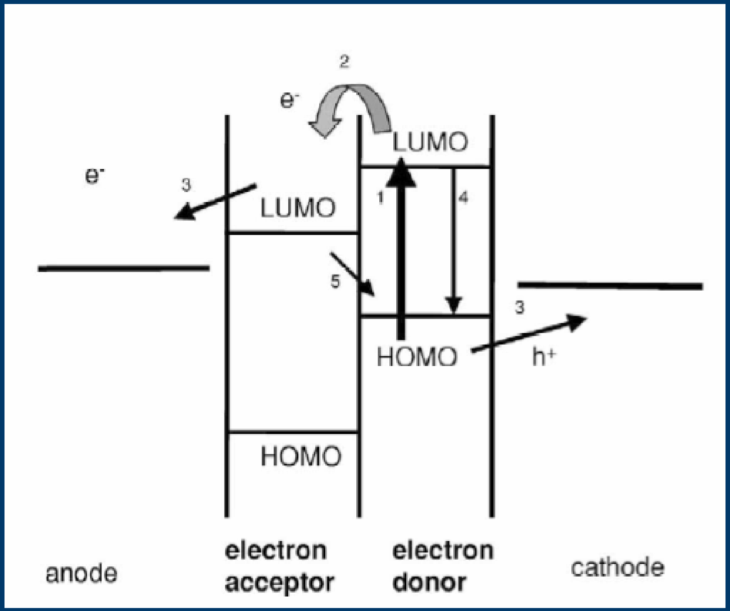
Basics of Organic PVs

- Absorption
- Exciton diffusion
- **Charge transfer at heterojunction**
- Transport to electrodes





- Charge transfer at interface due to energy minimization:

    - Edon-Eacc > Ebinding

- Only excitons created within a diffusion length make it to interface for dissociation

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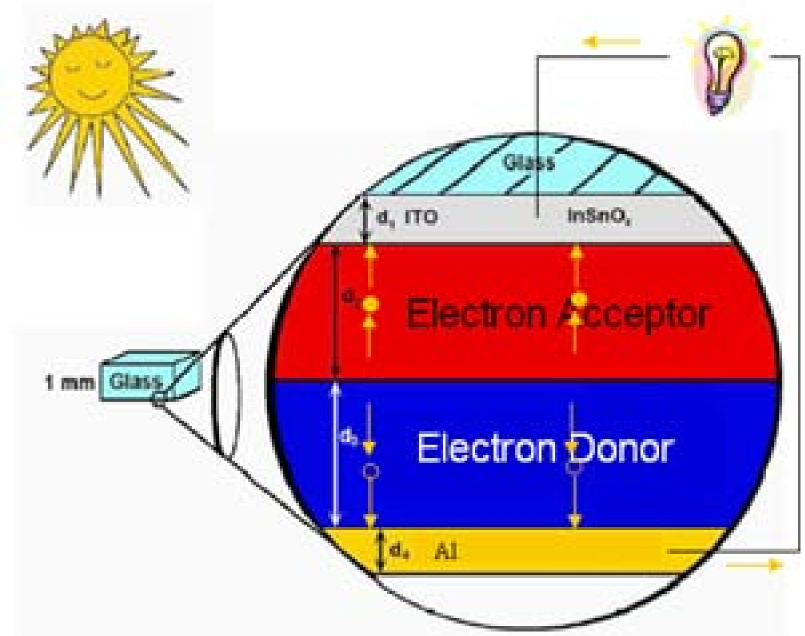
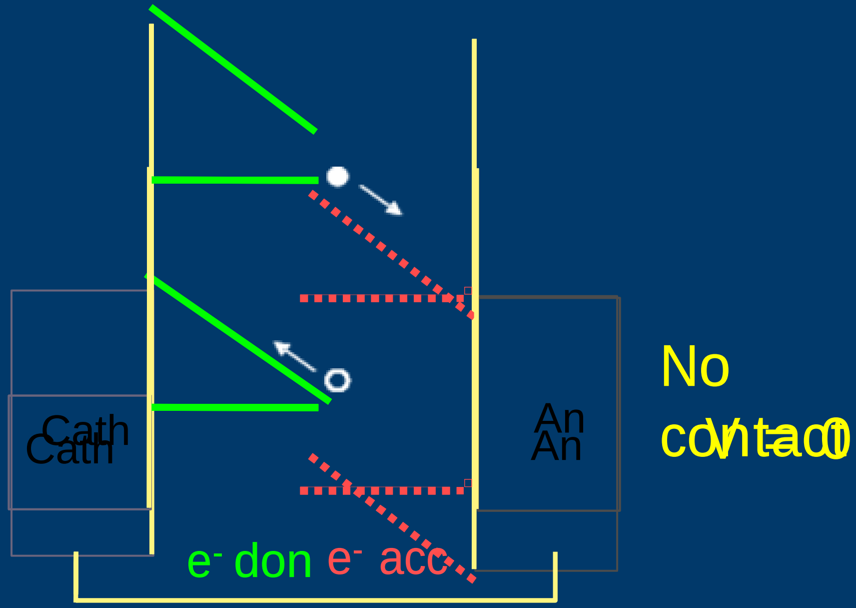
Basics of Organic PVs

- Absorption
- Exciton diffusion
- Charge transfer at heterojunction
- **Transport to electrodes**





- Built-in field results from the disparate work functions of the device electrodes
- Field overcomes exciton binding energy, and allows for transport and collection of charges
- Organics exhibit low mobilities

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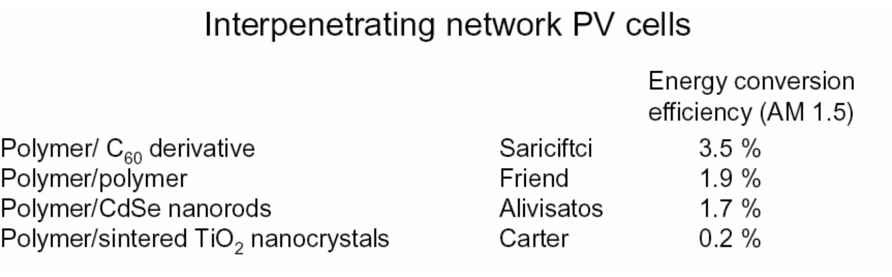
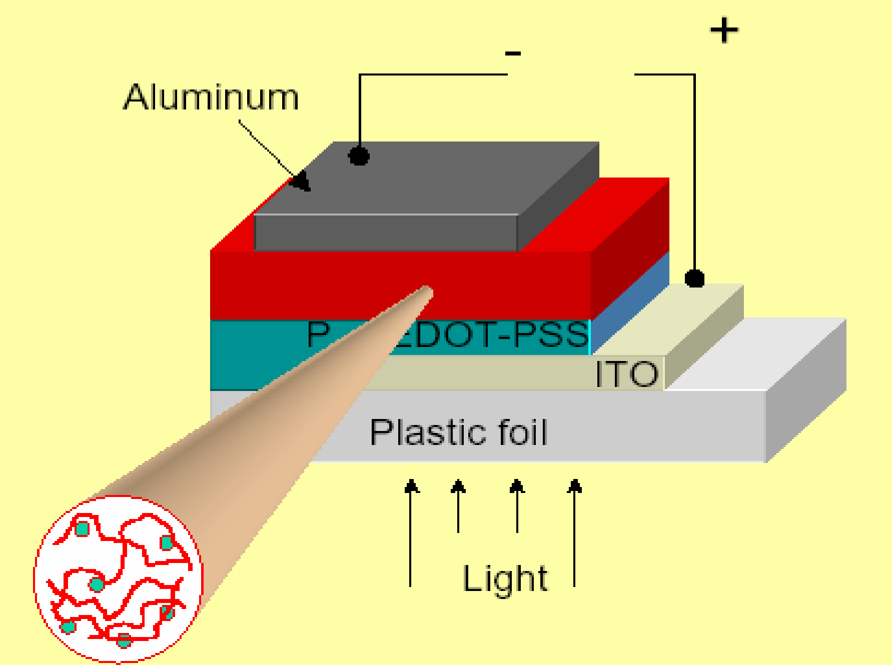
Distributed Heterojunctions



Interpenetrating network PV cells

		Energy conversion efficiency (AM 1.5)
Polymer/ C_{60} derivative	Sariciftci	3.5 %
Polymer/polymer	Friend	1.9 %
Polymer/CdSe nanorods	Alivisatos	1.7 %
Polymer/sintered TiO_2 nanocrystals	Carter	0.2 %



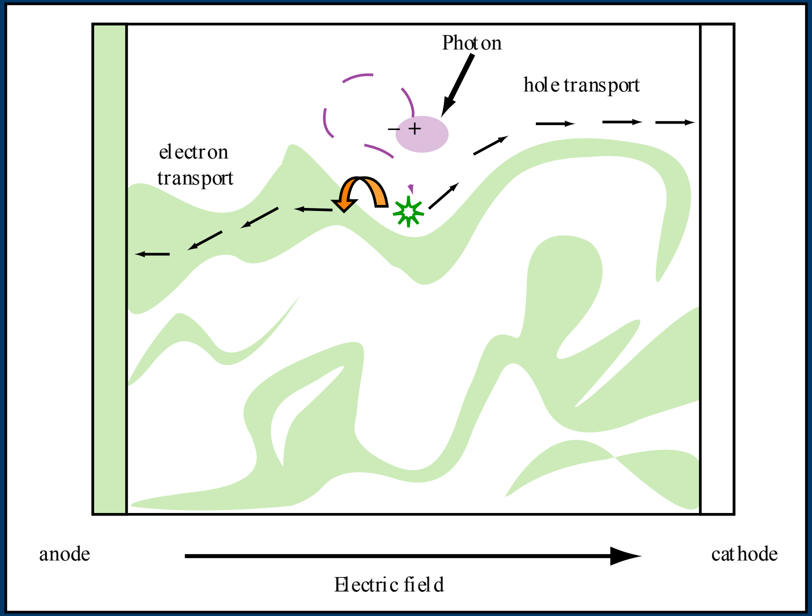


Figure by MIT OpenCourseWare.

Current Distributed Heterojunction Systems

- Polymer - Polymer
- Polymer - Fullerene
- Polymer - Nanocrystal

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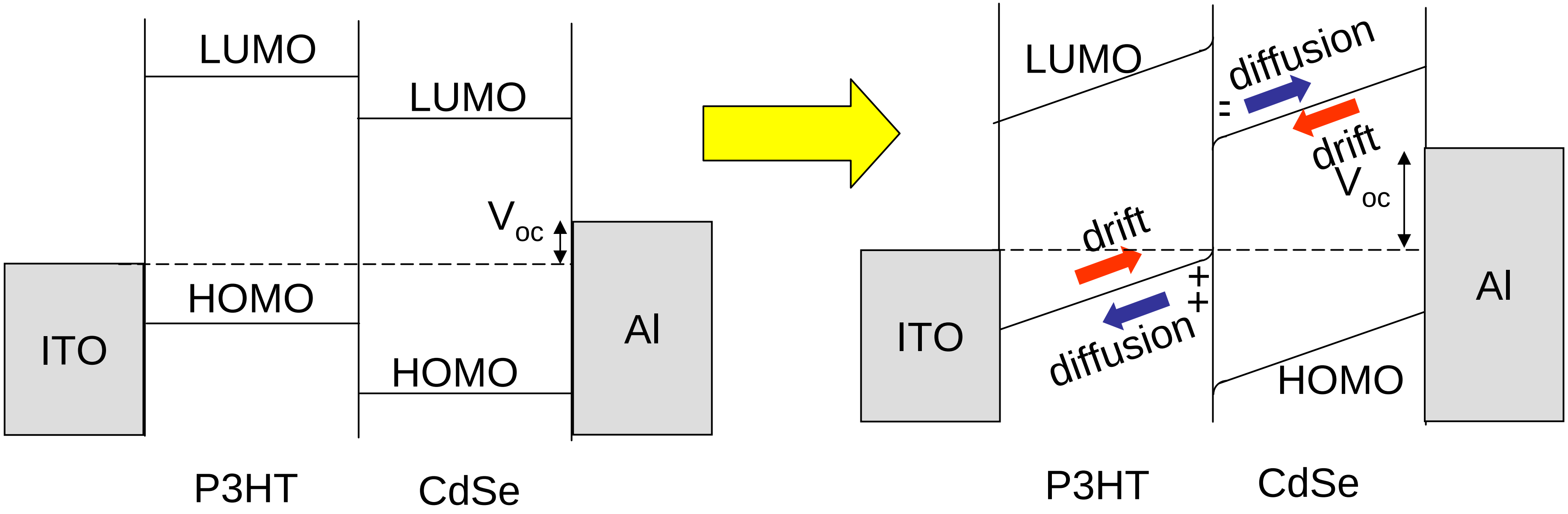
A more accurate model

- diffusion current away from the interface
- balancing drift current
- additional electric field
- additional contribution to V_{oc}



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Key Concepts

- First excitons, then free charge.
- Currents: Both drift and diffusion.
- Charge separation mechanisms: pn-junctions and p-i-n junctions.

- Schedule: Quiz #1 in two weeks.

Next Class

- *Solve the continuity equations for a pn-junction solar cell!*