

Solar Cell Materials and Device Characterization

March 22, 2011

The University of Toledo, Department of Physics and Astronomy
SSARE, PVIC

Principles and Varieties of Solar Energy (PHYS 4400)
and
Fundamentals of Solar Cells (PHYS 6980)



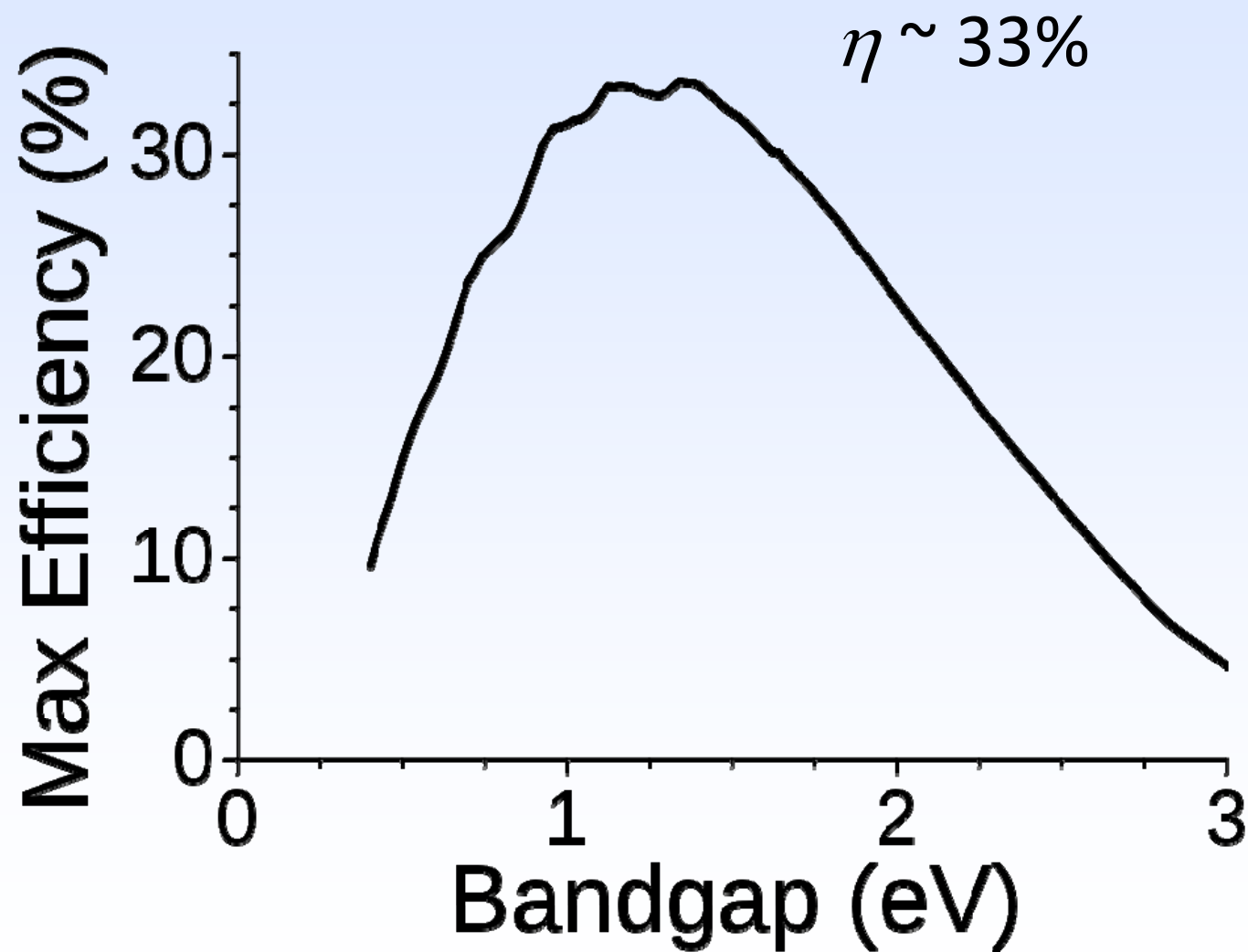
Requirements/conditions for constructing a valuable solar cell

A partial list...

- Absorb sunlight efficiently to optimize photogeneration of carriers
- Achieve charge separation, directing electron and holes to different contacts (e.g., use doped materials for p-n junction)
- Demonstrate strongly rectifying (diode) behavior
- Avoid excessive electron-hole recombination within the solar cell (maximize photocurrent)
- Maintain as much of the electric potential as possible (avoid resistive losses, and optimize energy band offsets)
- Resist/avoid degradation by air and water (sealing the modules is often essential) – i.e. achieve stability
- Do all of these things (a) with high yield, (b) inexpensively, and © at very large production levels
- What else?



Getting everything right...



So what's required? Is this easy?

If I do most of the things right, will I get an “A” on my solar cell (will my solar cell convert sunlight efficiently if I do 9 or 10 things right)? Probably not... Good solar cells are not easy to make, in principle – you must understand many subtleties of the materials, interfaces, and chemical evolution through oxidation, diffusion, or other reactions.

What can go wrong?

Back to the list...



Absorb sunlight efficiently

What matters for absorption of sunlight to make a good solar cell?

High extinction coefficient, short absorption length, large **absorption coefficient**.

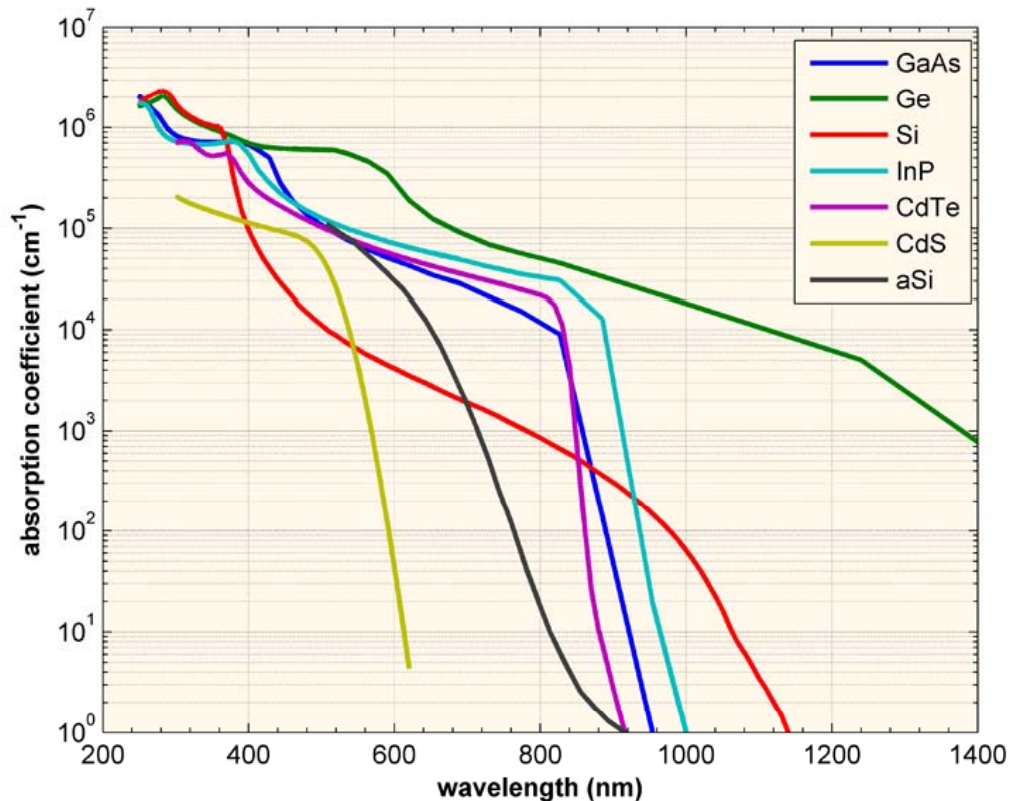
$$I = I_0 e^{-\alpha x}$$

$$I(\lambda) = I_0(\lambda) e^{-\alpha(\lambda)x}$$

Bandgap

Low **reflection** loss (can't convert reflected photons).

How do we measure the parameters in **bold**?



Measuring the bandgap energy (T-dependence of resistivity)

Solid State Physics: Experiment #5 Measuring the Band-Gap of a Semiconductor

According to the band theory of solids, insulators and semiconductors are materials which possess a band-gap (i.e., a range of forbidden energy values) at the Fermi level. Thus, these materials have a completely filled energy band below the gap and an empty band above the gap. The width of this band-gap is what distinguishes insulators from semiconductors. In semiconductors the band-gap is small enough (<2 eV) that at finite temperatures thermal excitation of electrons across the gap, into the empty "conduction" band, is possible leading to a small but measurable conductivity. The band-gap in insulators is simply too large to have any appreciable concentration of charge carriers excited into the conduction band. The temperature dependence of the resistivity of a pure (i.e., intrinsic) semiconductor is given by

$$\rho_i = B(T) \exp(E_g/2k_B T)$$

where E_g is the width of the gap and the function $B(T)$ is only very weakly dependent on temperature. To a good approximation we can take $B(T)=\text{constant}$. Thus, we can easily measure the gap energy of a semiconductor material by measuring the resistance of a sample over a range

$$I = I_0 e^{-\alpha x}$$

$$I(\lambda) = I_0(\lambda) e^{-\alpha(\lambda)x}$$



Measuring the bandgap energy (optical absorption)

$$I(\lambda) = I_0(\lambda)e^{-\alpha(\lambda)x} \longrightarrow I(E) = I_0(E)e^{-\alpha(E)x}$$

Direct-gap semiconductor

$$\alpha(E) = \alpha_0(E - E_g)^{\frac{1}{2}}$$

Indirect-gap semiconductor

$$\alpha(E) \propto (E - E_g)^2$$

Crystal	Gap	E_{gn} eV		Crystal	Gap	E_{gn} eV	
		0 K	300 K			0 K	300 K
Diamond	i	5.4		HgTe ^a	d	-0.30	
Si	i	1.17	1.14	PbS	d	0.286	0.34-0.37
Ge	i	0.744	0.67	PbSe	d	0.165	0.27
α Sn	d	0.00	0.00	PbTe	d	0.190	0.30
InSb	d	0.24	0.18	CdS	d	2.582	2.42
InAs	d	0.43	0.35	CdSe	d	1.840	1.74
InP	d	1.42	1.35	CdTe	d	1.607	1.45
GaP	i	2.32	2.26	ZnO		3.436	3.2
GaAs	d	1.52	1.43	ZnS		3.91	3.6
GaSb	d	0.81	0.78	SnTe	d	0.3	0.18
AlSb	i	1.65	1.52	AgCl		-	3.2
SiC(hex)		3.0	-	AgI		-	2.8
Te	d	0.33	-	Cu ₂ O		2.172	-
ZnSb		0.56	0.56	TiO ₂		3.03	-

^aHgTe is a semimetal; the bands overlap.

General references: D. Long, Energy bands in semiconductors. Interscience, 1968; also the A.I.P. Handbook, 3rd ed., Sec. 9.

Indirect gap: plotting α vs E shows an E^2 dependence, so plotting $\alpha^{1/2}$ shows a linear dependence.

Direct gap: Plotting α vs E shows an $E^{1/2}$ dependence, so plotting α^2 shows a linear dependence.

See, for example,
<http://engr.sjsu.edu/cme/MatELabs/MatE153/Ch7%20Optical%20Absorption.pdf>, or
<http://engphys.mcmaster.ca/undergraduate/outlines/3pn4/LAB3P>

N4-2%20Jan08.pdf

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Measuring the bandgap energy (optical absorption)

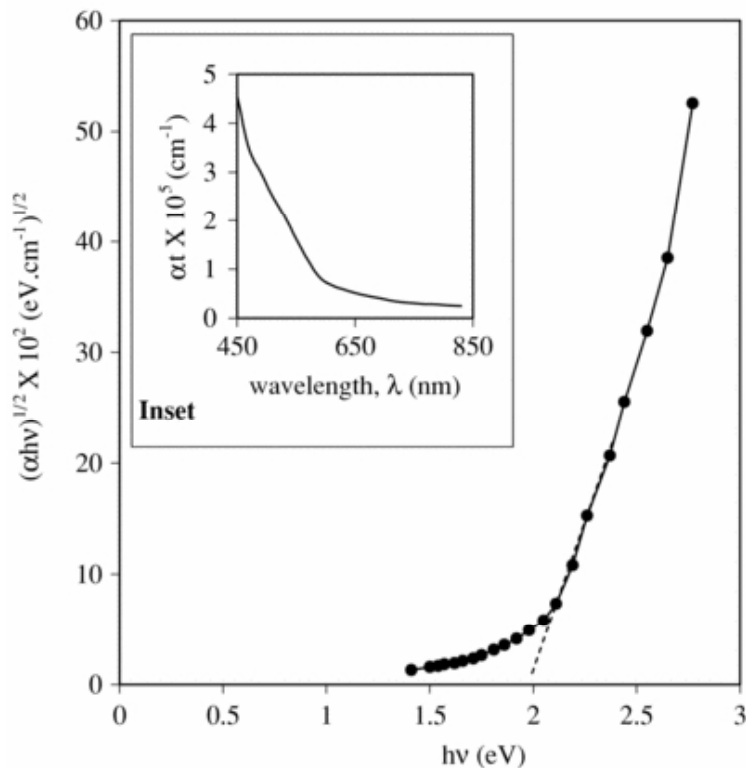
$$I(\lambda) = I_0(\lambda)e^{-\alpha(\lambda)x} \longrightarrow I(E) = I_0(E)e^{-\alpha(E)x}$$

Direct-gap semiconductor

$$\alpha(E) = \alpha_0(E - E_g)^{\frac{1}{2}}$$

Indirect-gap semiconductor

$$\alpha(E) \propto (E - E_g)^2$$



Fe_2O_3 , (haematite) –
direct or indirect gap?

Semicond. Sci. Technol. **20** No 8 (August 2005) 705-709

doi:10.1088/0268-1242/20/8/009

Nanocrystalline haematite thin films by chemical solution spray

J D Desai, H M Pathan, Sun-Ki Min, Kwang-Deog Jung
and Oh-Shim Joo



Measuring the bandgap of a thin film (optically)

<http://www.chalcogen.infim.ro/Patidar-CdSe-Final.pdf>

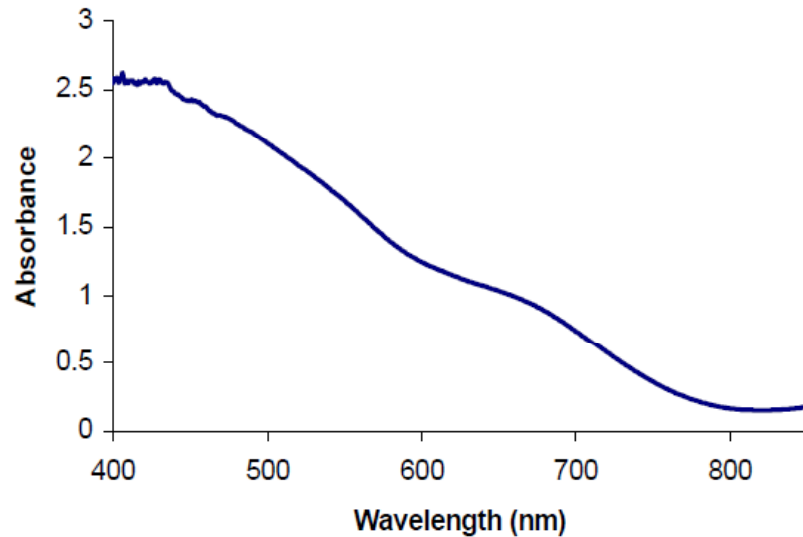


Fig 2. The absorption spectra of CdSe thin film.

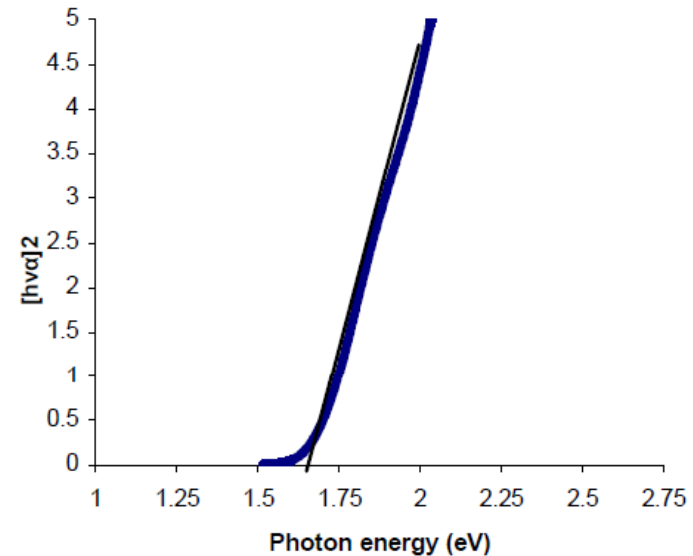


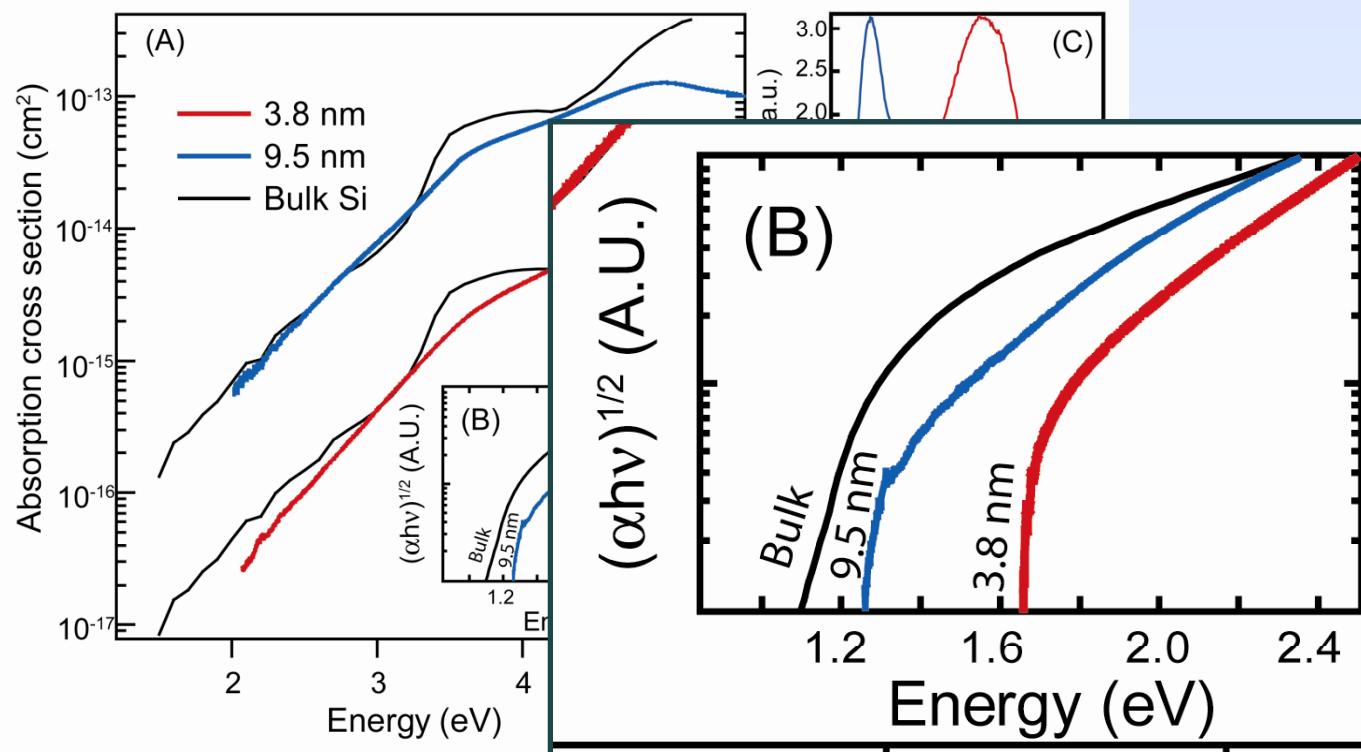
Fig.3. Energy band gap determination of CdSe thin film.

Therefore, if a plot of $h\nu$ versus α^2 forms a straight line, it can normally be inferred that there is a direct band gap, measurable by extrapolating the straight line to the $\alpha = 0$ axis. On the other hand, if a plot of $h\nu$ versus $\alpha^{1/2}$ forms a straight line, it can normally be inferred that there is an indirect band gap, measurable by extrapolating the straight line to the $\alpha = 0$ axis.

From http://en.wikipedia.org/wiki/Direct_and_indirect_band_gaps



Measuring the bandgap of Si NCs (optically)



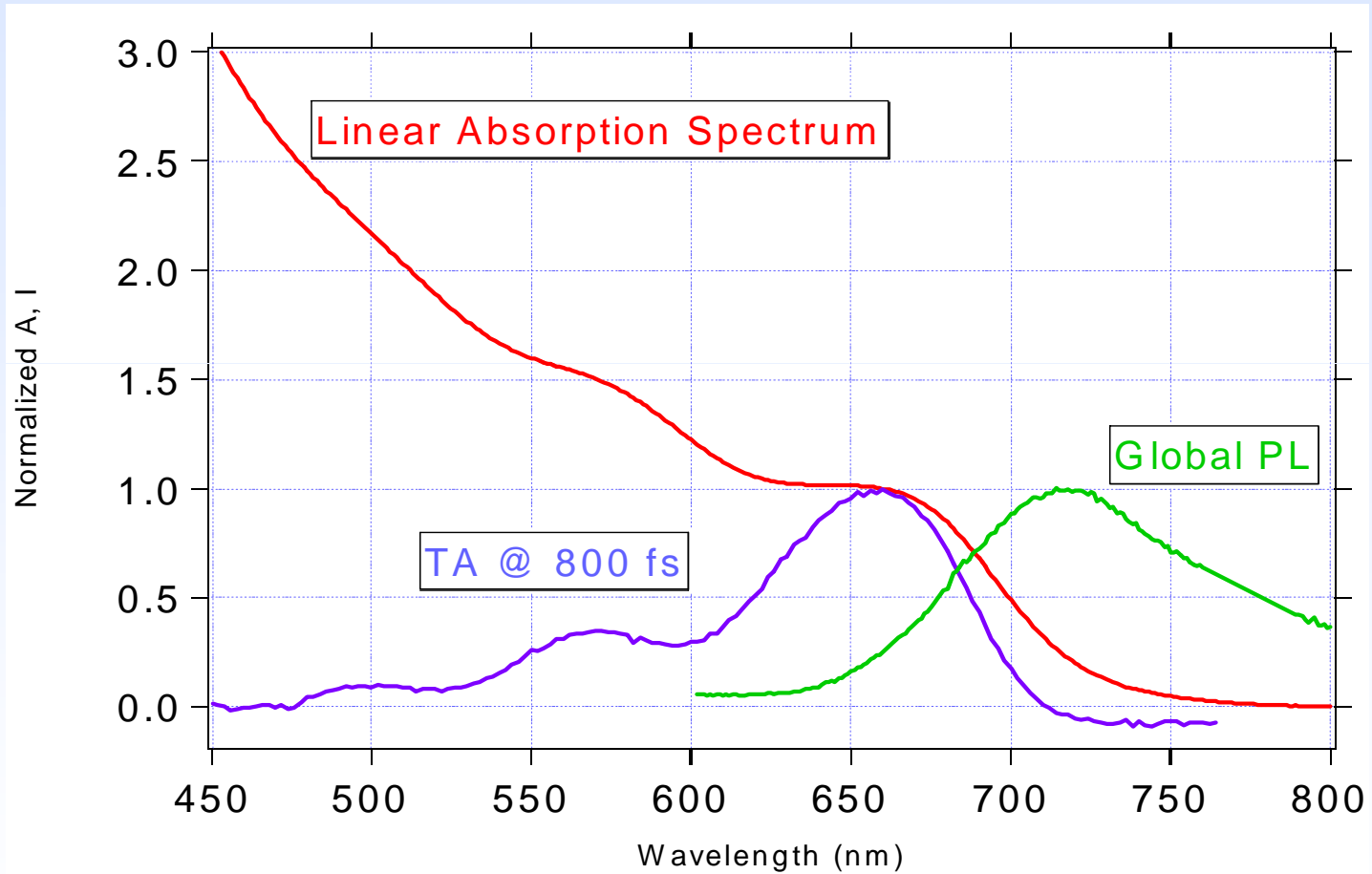
“Linear optical properties of colloidal Si NCs studied in this report. (A) The absorption cross section for the NCs dispersed in hexane. Black lines show the computed cross section of the NCs based on an equivalent bulk Si volume. Part (B) displays the onset of the absorption in a Tauc plot showing the blue-shifted absorption onset. (C) PL spectra. (D) PL lifetime data measured at the peak of the emission wavelength (red line 3.8 nm, blue line 9.5 nm). The peak of the emission spectrum is taken as the effective bandgap for each of the NC samples, yielding bandgaps of 1.68 eV for the 3.8 nm NCs and 1.20 eV for the 9.5 nm NCs.”

Multiple Exciton Generation in Colloidal Silicon Nanocrystals,
M. Beard et al., Nano Letters 2007, Vol. 7, No. 8, 2506-2512.



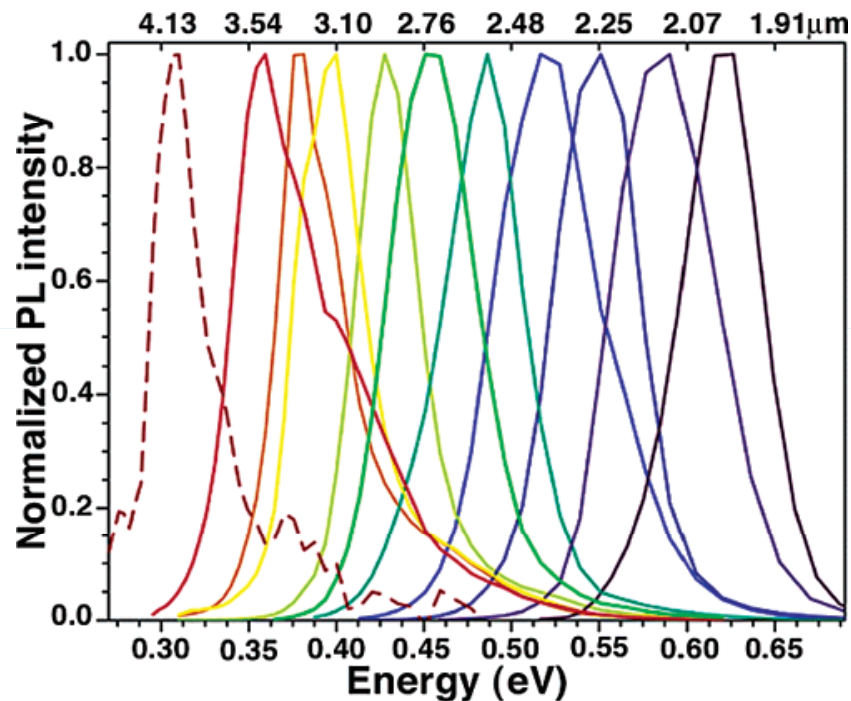
Measuring bandgap (PL)

Photoluminescence (occurs at the bandgap for direct gap semiconductors)



Measuring bandgap (PL)

Photoluminescence (occurs at the bandgap for direct gap semiconductors)



Pushing the Band Gap Envelope: Mid-Infrared Emitting Colloidal PbSe Quantum Dots, J. AM. CHEM. SOC. 2004, 126, 11752-11753, Hollingsworth et al.

Bandgap can also be measured with:

- SPS – surface photovoltage spectroscopy
- Spectroscopic ellipsometry (?)



Optical characterization (transient absorption)

- state filling

Electronic state occupation results in bleaching of interband transitions.

- carrier-induced Stark effect

Photogenerated carriers create local fields within nanoparticle which modify transition energies.

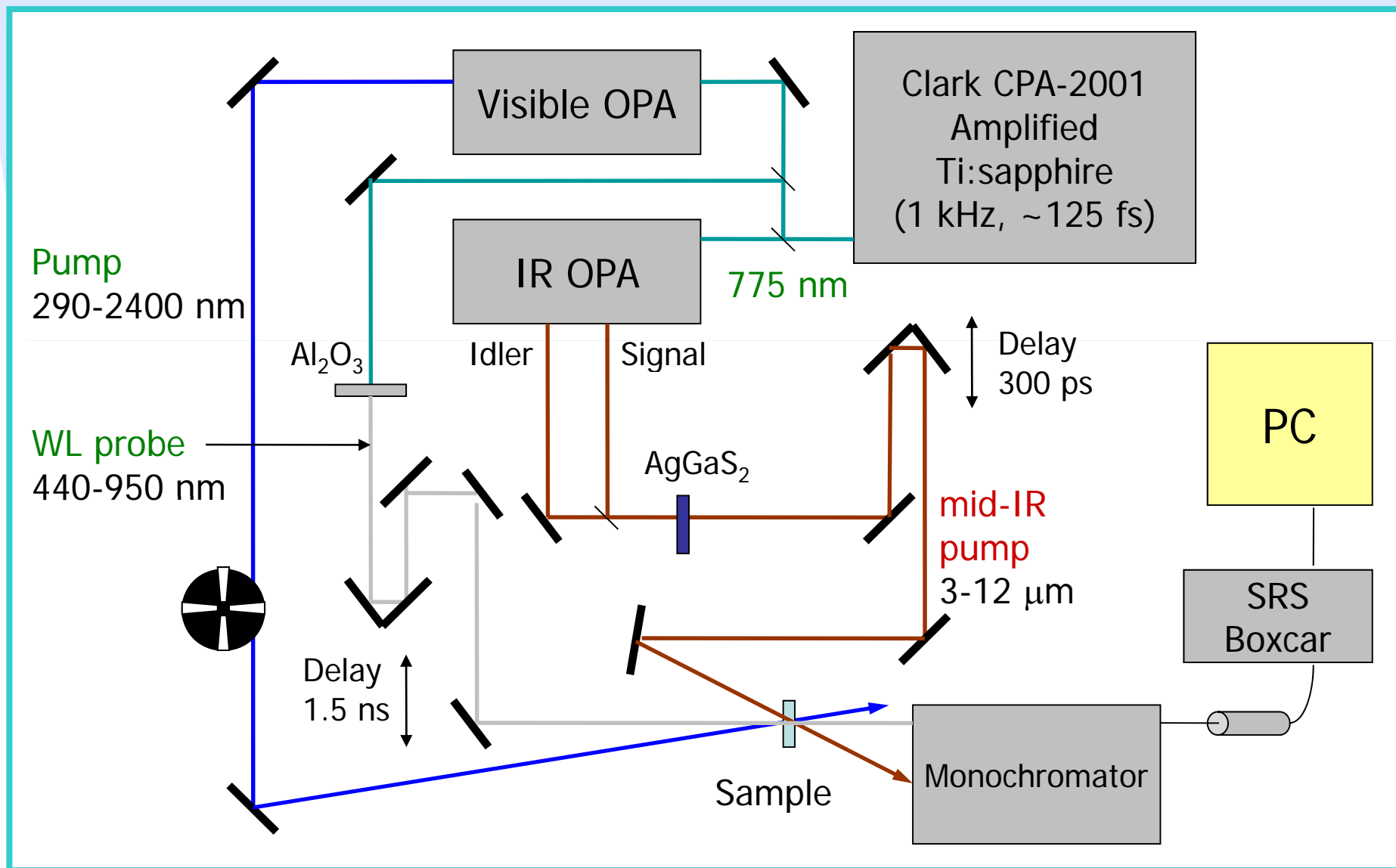
$$\frac{\Delta\alpha}{\alpha_0} = \frac{\ln T_0 - \ln T_{pumped}}{\ln T_0}$$

$$T_{pumped} = T_0 \left(1 + \frac{\Delta T}{T_0}\right)$$

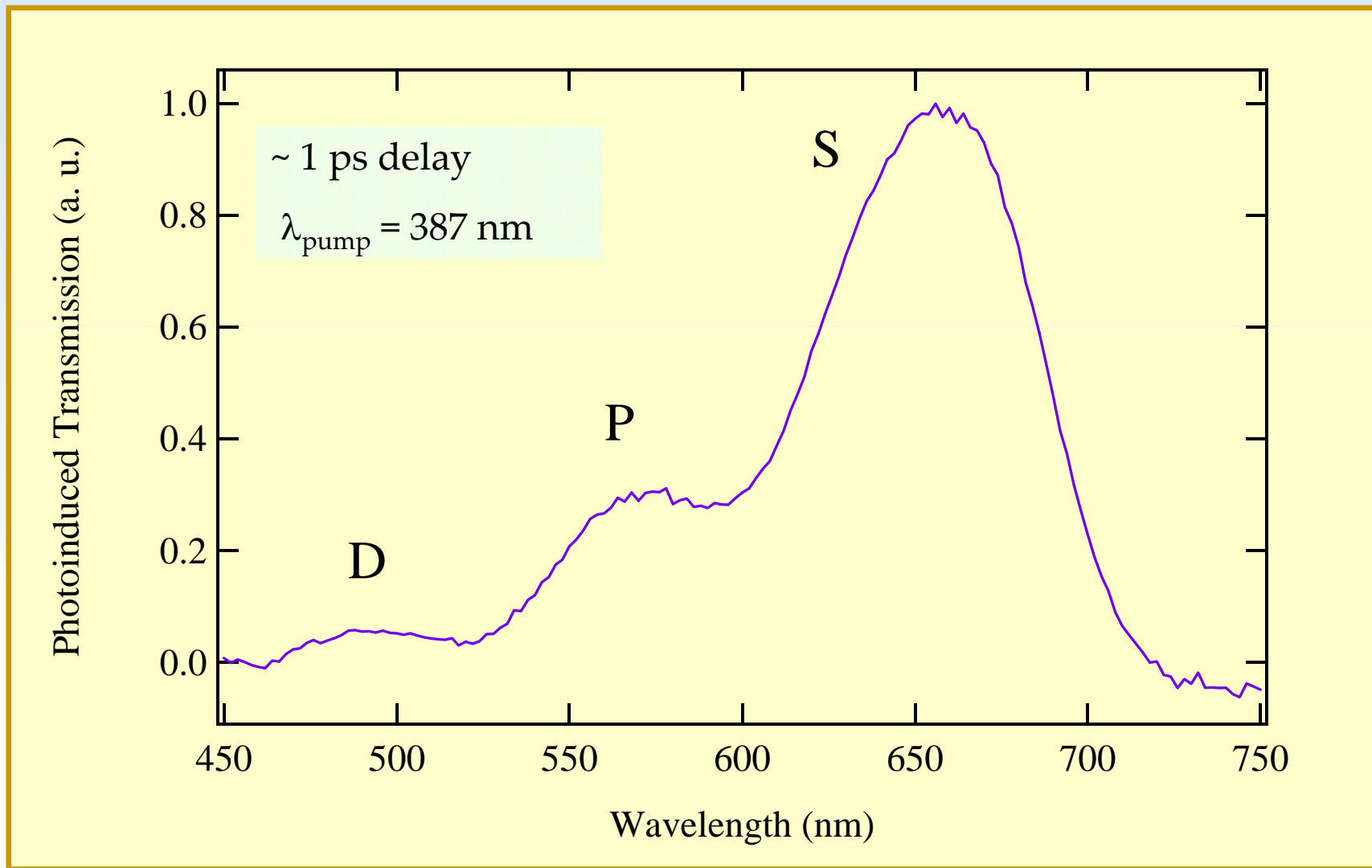
$$T = 10^{-O.D.} = e^{-\alpha_0 d}$$



Optical characterization (transient absorption setup)

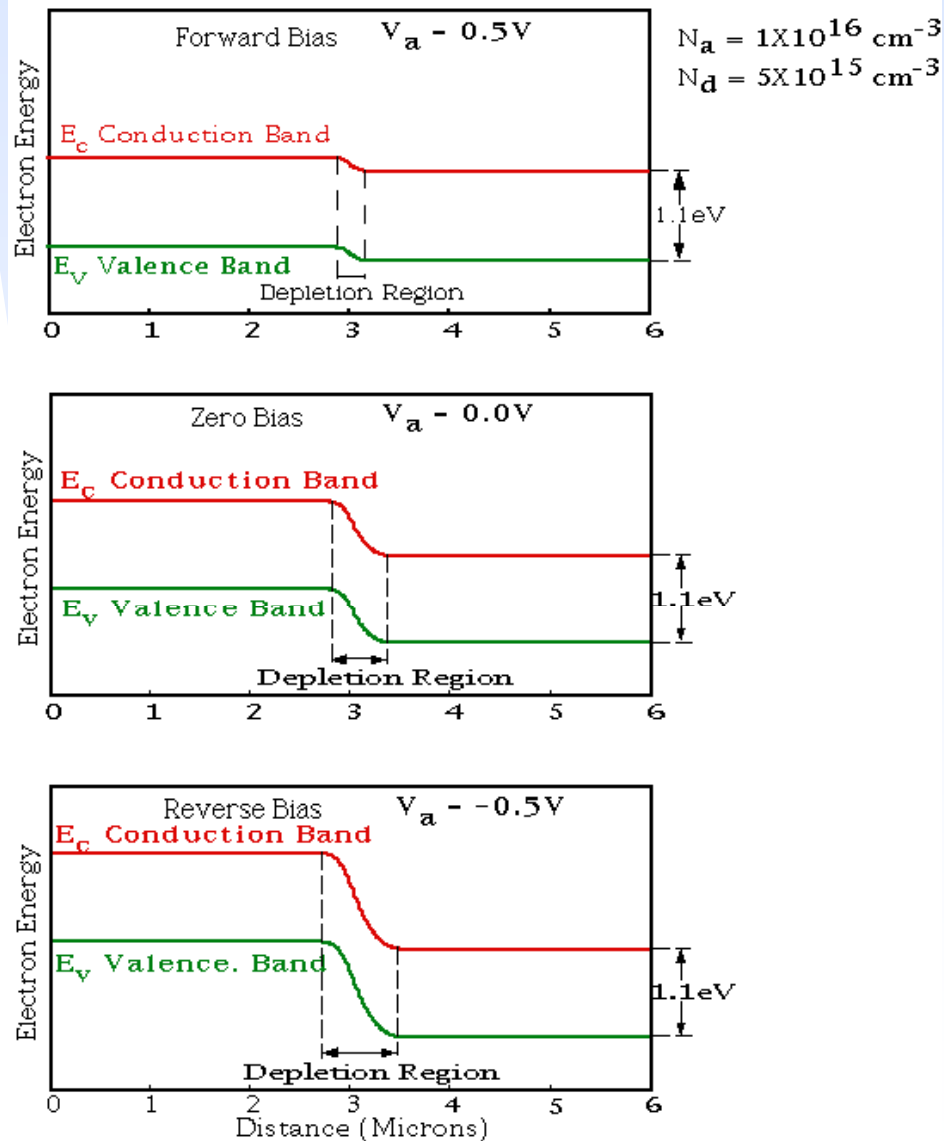


Optical characterization (transient absorption setup)



Achieve charge separation

Energy Band Diagram for p-n diode



Achieve charge separation, directing electron and holes to different contacts (e.g., use doped materials for p-n junction)...

Prepare your materials and junctions to establish a built-in electric field. How?

Homojunction: (junction between two layers of the same material, which can differ by doping, structure, etc. but show the same dominant elemental makeup) -- must vary the chemical potential of the material (Fermi function) across the interface between n-type and p-type.



Achieve charge separation

Achieve charge separation, directing electron and holes to different contacts (e.g., use doped materials for p-n junction)...

Prepare your materials and junctions to establish a built-in electric field.
How?

Heterojunction: (junction between two different semiconductor materials) -- must create an energy band structure that promotes charge separation – a combination of energy band offsets and doping.

How do we measure the **dopant type and density**?

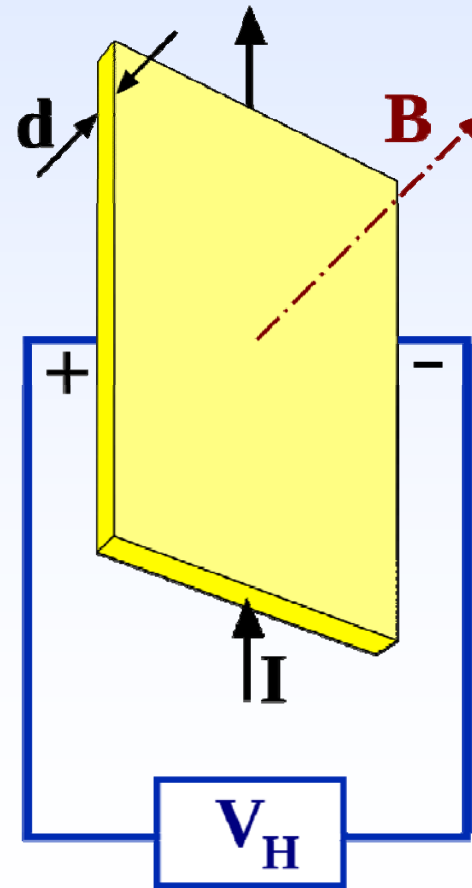


Measuring dopant type and density

Hall Effect: The Lorentz force, $F = -q\mathbf{v} \times \mathbf{B}$, deflects carriers to the left and right as they pass through a material under the influence of a magnetic field. The induced voltage lateral to the current flow direction provides information about the Hall coefficient, which can then be related to the carrier density and mobility:

$$R_H = \frac{E_y}{J_x B_z}$$

$$\mu = \frac{R_H}{\rho} \quad n = \frac{1}{eR_H}$$



Preston and Dietz, (Expt. 17; pp 303-315)



Measuring dopant type and density (Mott Schottky)

C_{sc} = capacitance of the space charge region

ϵ = dielectric constant of the semiconductor

ϵ_0 = permittivity of free space

N = donor density (electron donor concentration for an n -type semiconductor or hole acceptor concentration for a p -type semiconductor)

E = applied potential

E_{fb} = flatband potential

Mott-Schottky plots ($1/C^2$ vs. E)

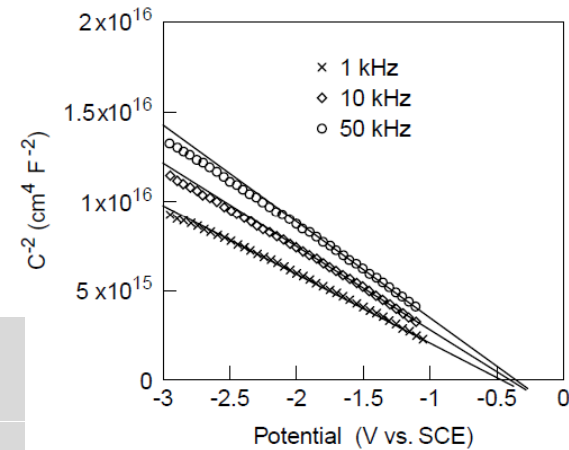
$$C = \frac{Q}{V} = \frac{\epsilon A}{W_d}$$

Mott-Schottky: measuring in depletion, not in accumulation. Changing the depletion width by applied voltage; when the capacitance reaches a maximum \rightarrow flat band potential.

$$W = \left[\frac{2K_s\epsilon_0}{q} \left(\frac{N_A + N_D}{N_A N_D} \right) (V_{bi} - V) \right]^{\frac{1}{2}}$$

F8

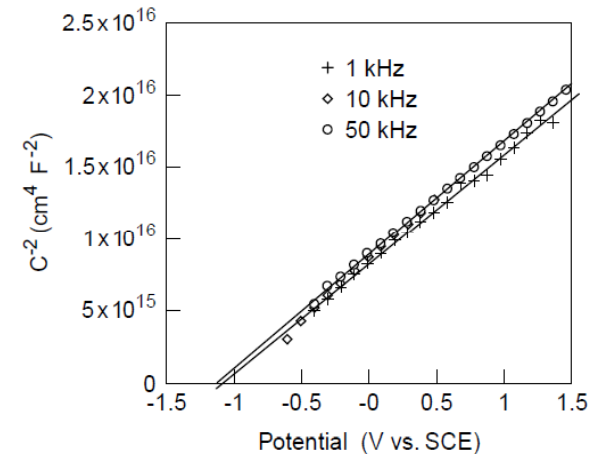
Mott-Schottky plot for a p -type semiconductor (figure adapted from ref. 2).



Sign of slope determined by free carrier type; slope related to free carrier density

F9

Mott-Schottky plot for an n -type semiconductor (figure adapted from ref. 2).



<http://www.currentseparations.com/issues/17-3/cs-17-3d.pdf>



Hot Probe Test to determine Carrier Type

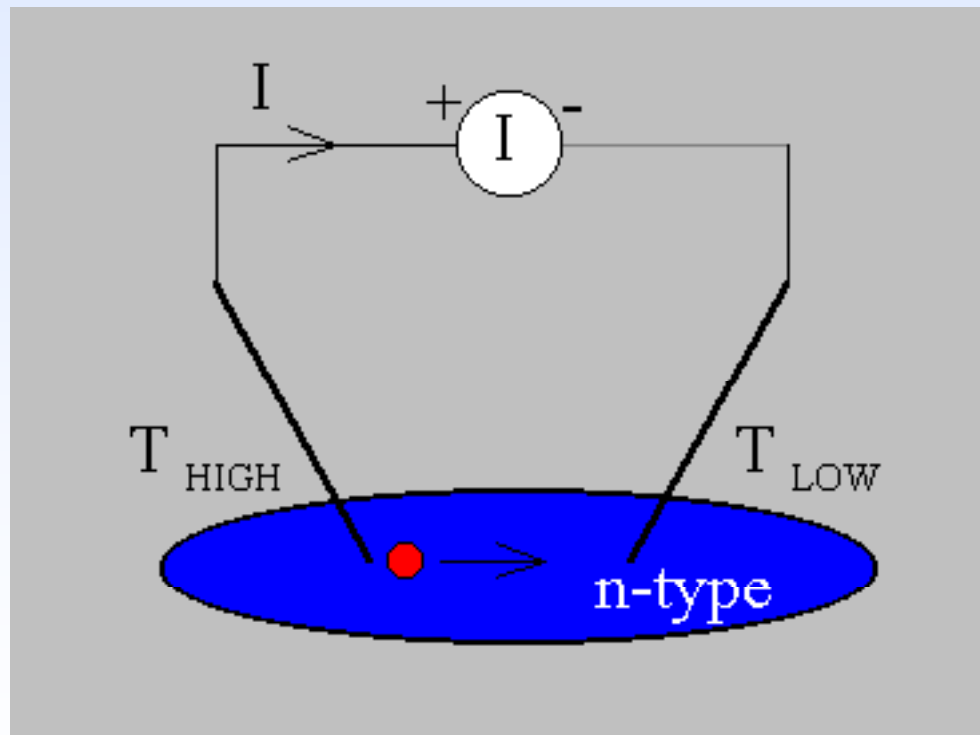
Seebeck Effect

- In 1821, Thomas Seebeck discovered that an electric current would flow continuously in a closed circuit made up of two dissimilar metals if the junctions of the metals were maintained at two different temperatures.
- When a metal wire is connected between two different temperatures, an additional number of electrons are excited at the hot end versus the cold end.
- Electrons drift from the hot end to the cold, and
- A thermal emf develops to oppose the drift
- If the material is uniform, the magnitude of the voltage developed depends only on the temperature difference.
- The Hot Probe is the trivial case.....i.e., no junctions.



Hot Probe Test to determine Carrier Type

All you need is a soldering iron, and an ammeter!

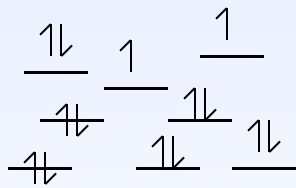
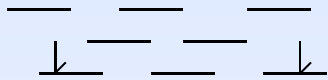


<http://ecee.colorado.edu/~bart/book/hotprobe.htm>



Hot Probe Test to determine Carrier Type

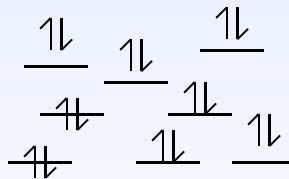
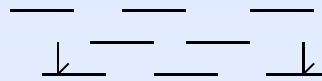
Intrinsic



$$p = n = n_i$$

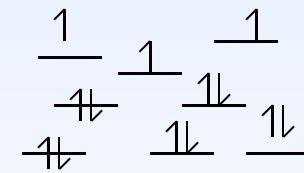
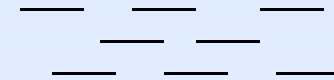
Number of thermally generated Holes equals number thermally generated free electrons

n-type



Number of free electrons equals number of positively charged donor ions

p-type



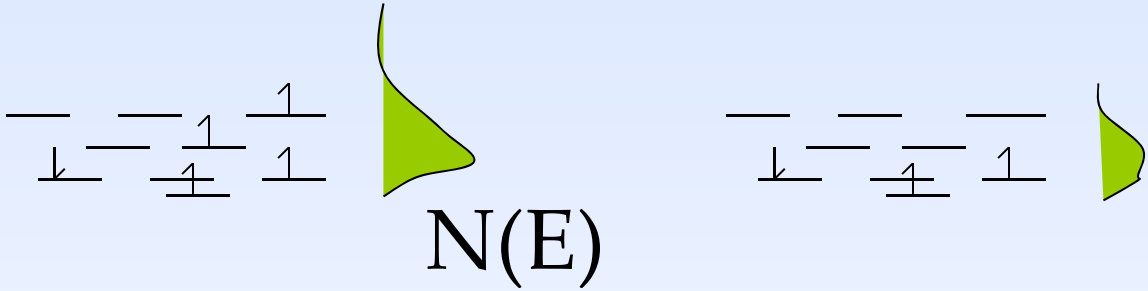
Number of free holes equals number of Negatively charged acceptor cores

After Hamers



Hot Probe Test to determine Carrier Type

Distribution of OCCUPIED
C.B. levels:



Hot

Cold

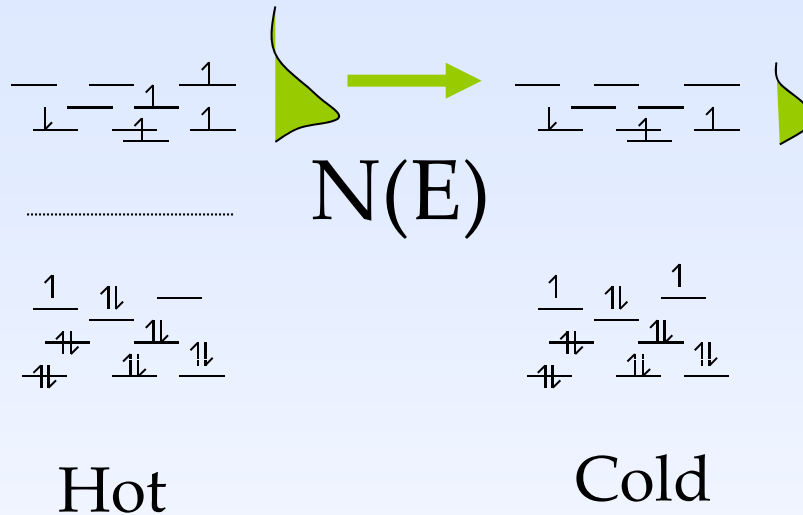
These are *not* in equilibrium!

After Hamers



Hot Probe Test to determine Carrier Type

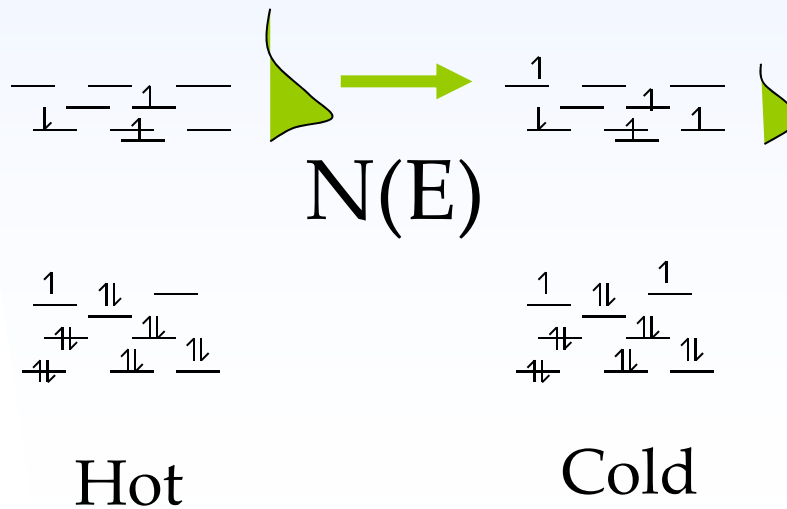
Seebeck effect, n-type semiconductor



Fick's Law of Diffusion:

$$J = -D \frac{\partial c}{\partial x}$$

Electrons diffuse from region of high Concentration to region of lower concentration



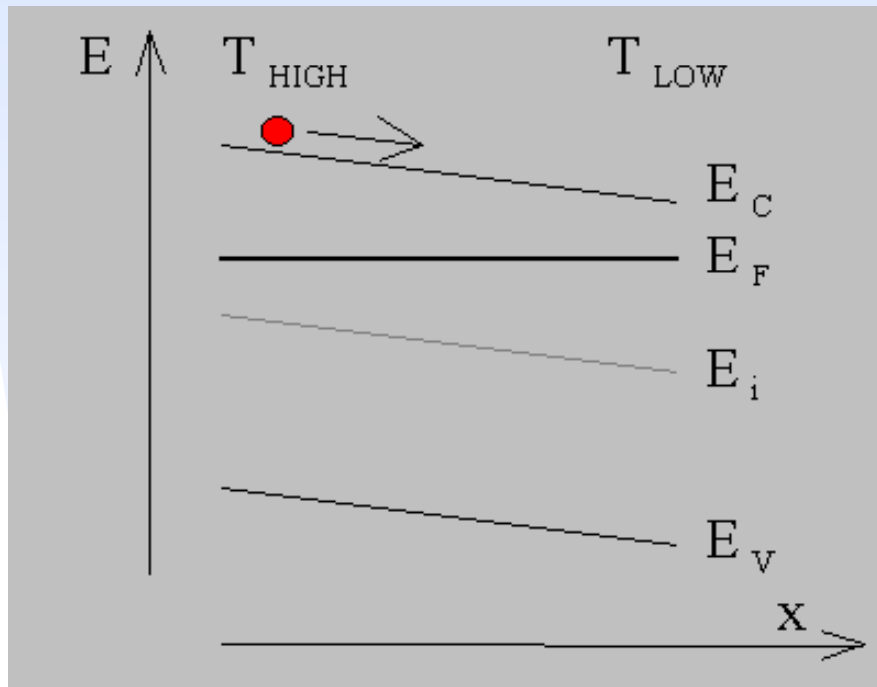
"Cold" side becomes slightly negatively charged
Hot side becomes positively charged

After Hamers



Hot Probe Test to determine Carrier Type

Another way to look at what is happening:



Fermi energy remains constant throughout the material. The variation in free carrier density then changes the positions of the CB and VB as a function of temperature (position).

“As the effective density of states decreases with decreasing temperature, one finds that the conduction band energy decreases with decreasing temperature yielding an electric field which causes the electrons to flow from the high to the low temperature. The same reasoning reveals that holes in a p-type semiconductor will also flow from the higher to the lower temperature.”

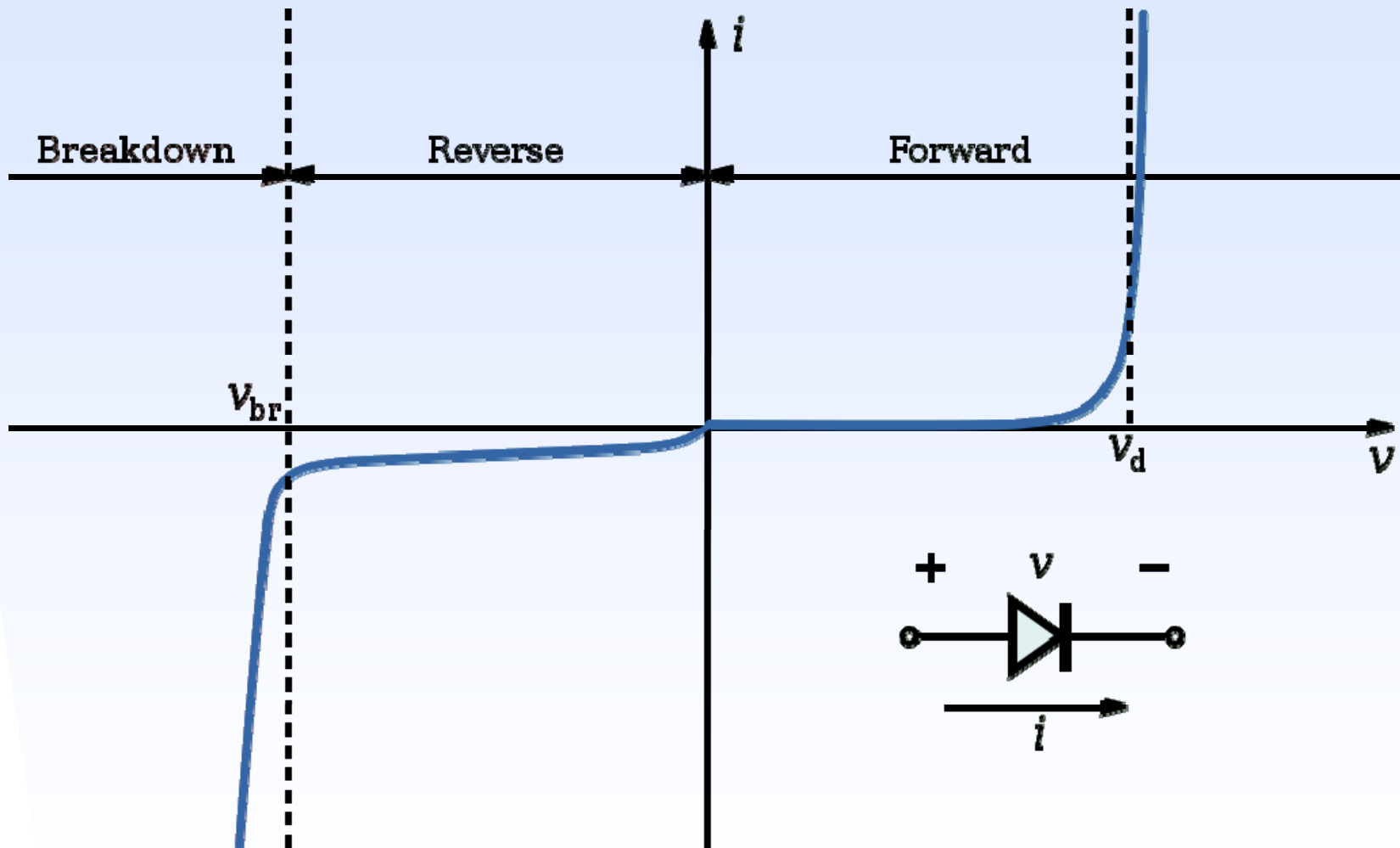
$$J = \mu_n n \left(\frac{\partial E_F}{\partial x} - q \mathcal{P} \frac{\partial T}{\partial x} \right)$$

$$q \mathcal{P} = -k \left(\frac{5}{2} - \frac{T}{\mu_n} \frac{\partial \mu_n}{\partial T} + \ln \frac{N_C}{n} \right)$$

<http://ecee.colorado.edu/~bart/book/hotprobe.htm>



Rectifying behavior



I-V characteristics of a P-N junction diode (not to scale). From <http://en.wikipedia.org/wiki/Diode>

