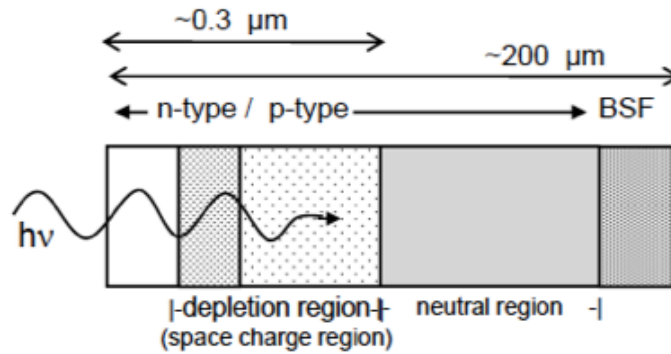


# Absorption coefficients of semiconductor thin films

October 8, 2013

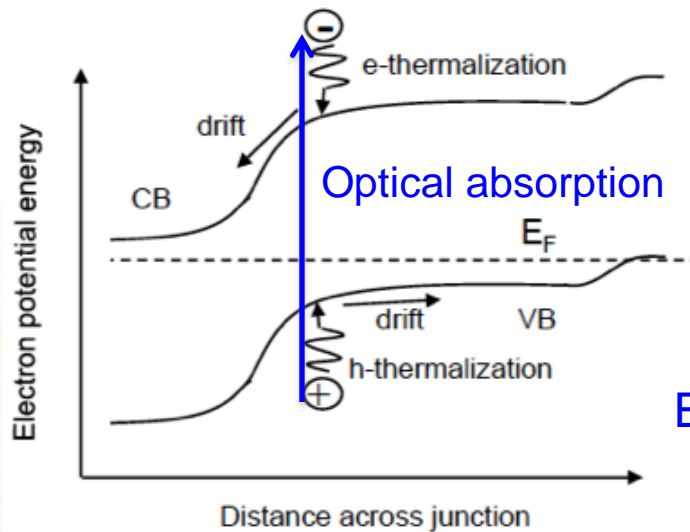
PHYS 4580, PHYS 6/7280  
The University of Toledo  
Profs. R. Ellingson and M. Heben

# Typical Si PV Cell Structure



Total Device Thickness:  
a few hundred microns

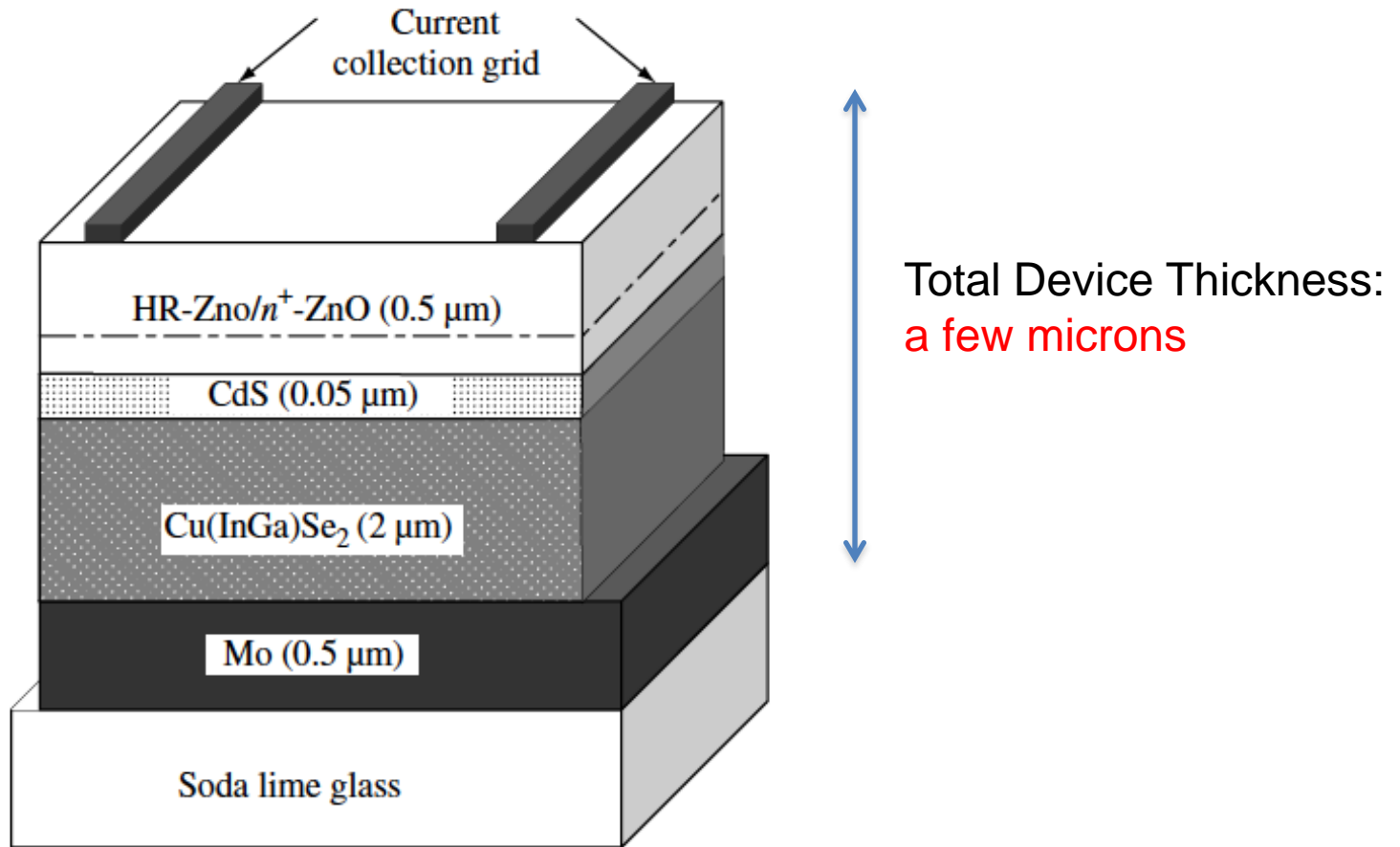
Real Space Schematic



Energy Band Diagram

Solar cell structure and energy band diagram showing valence (VB) and conduction bands (CB), Fermi level ( $E_F$ ), photoabsorption, electron-hole pair generation, thermalization, and drift.  
(from Compaan, APS News April, 2005)

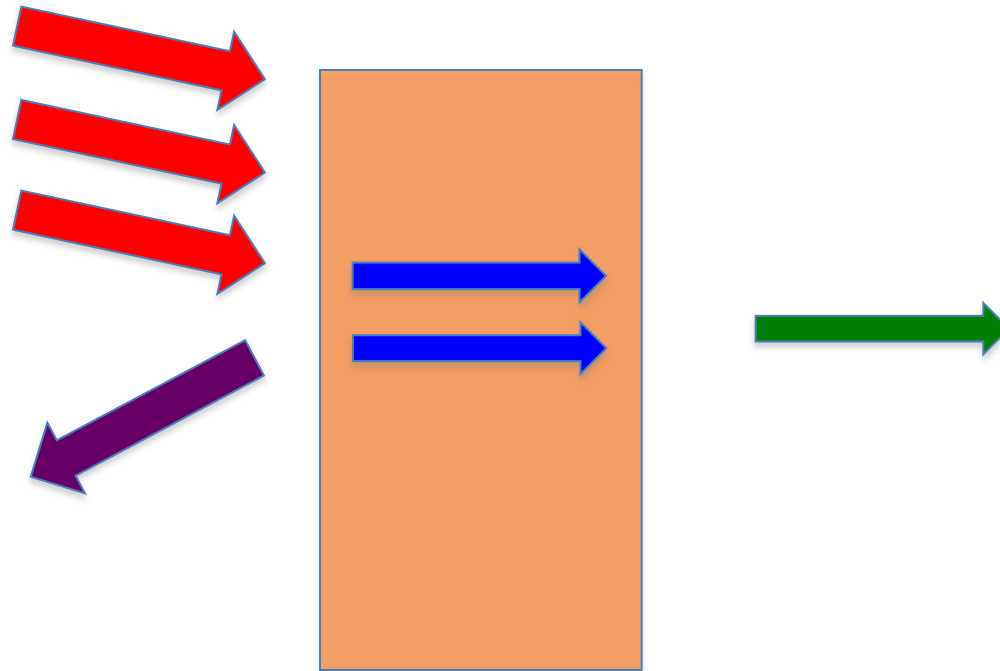
# Typical Thin Film (CIGS) Cell Structure



Schematic cross section of a typical Cu(InGa)Se<sub>2</sub> solar cell

# Conservation of Energy for each wavelength

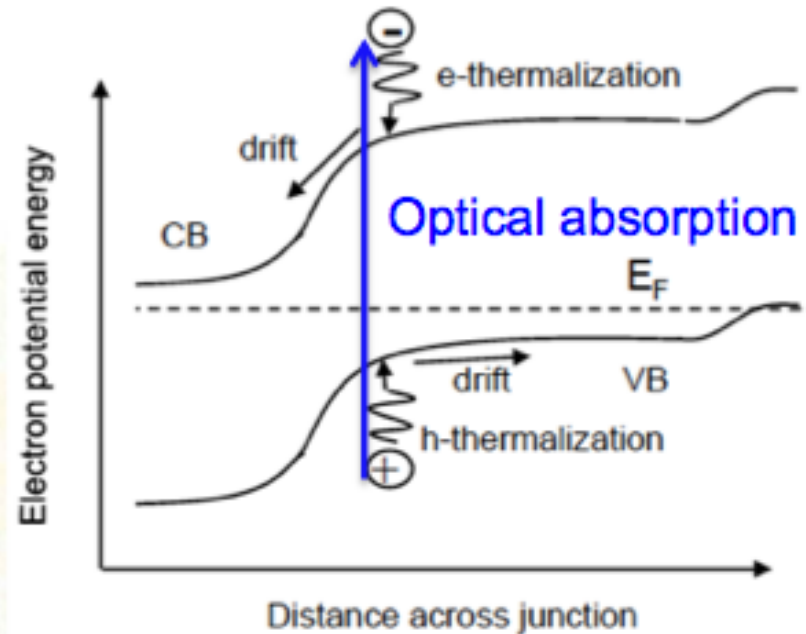
$$\text{Total Incident } (\lambda) = A(\lambda) + T(\lambda) + R(\lambda)$$



Why must some PV layers be so thick?  
(want to maximize absorption)

# Mechanisms of Optical Absorption

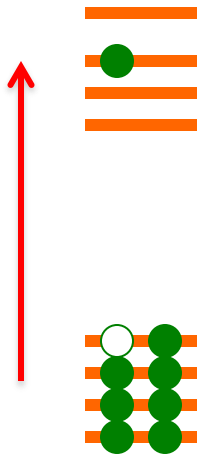
- Energy is absorbed by a “system”, potential energy of system is increased.
- For a system in which we are concerned with gravitational potential energy, consider the energy required to put a book on a shelf.
- For semiconductors, optical absorption occurs any time a “carrier” can be excited to a higher “state”.
- Typically, the carriers we are concerned with are electrons, and the excitation is across the band gap.



# Absorption coefficient

(a connection between the optical and electronic properties of materials)

$$\alpha(\lambda) \propto n_i(\lambda) P_{if}(\lambda) n_f(\lambda)$$



$\alpha(\lambda)$  - the absorption coefficient

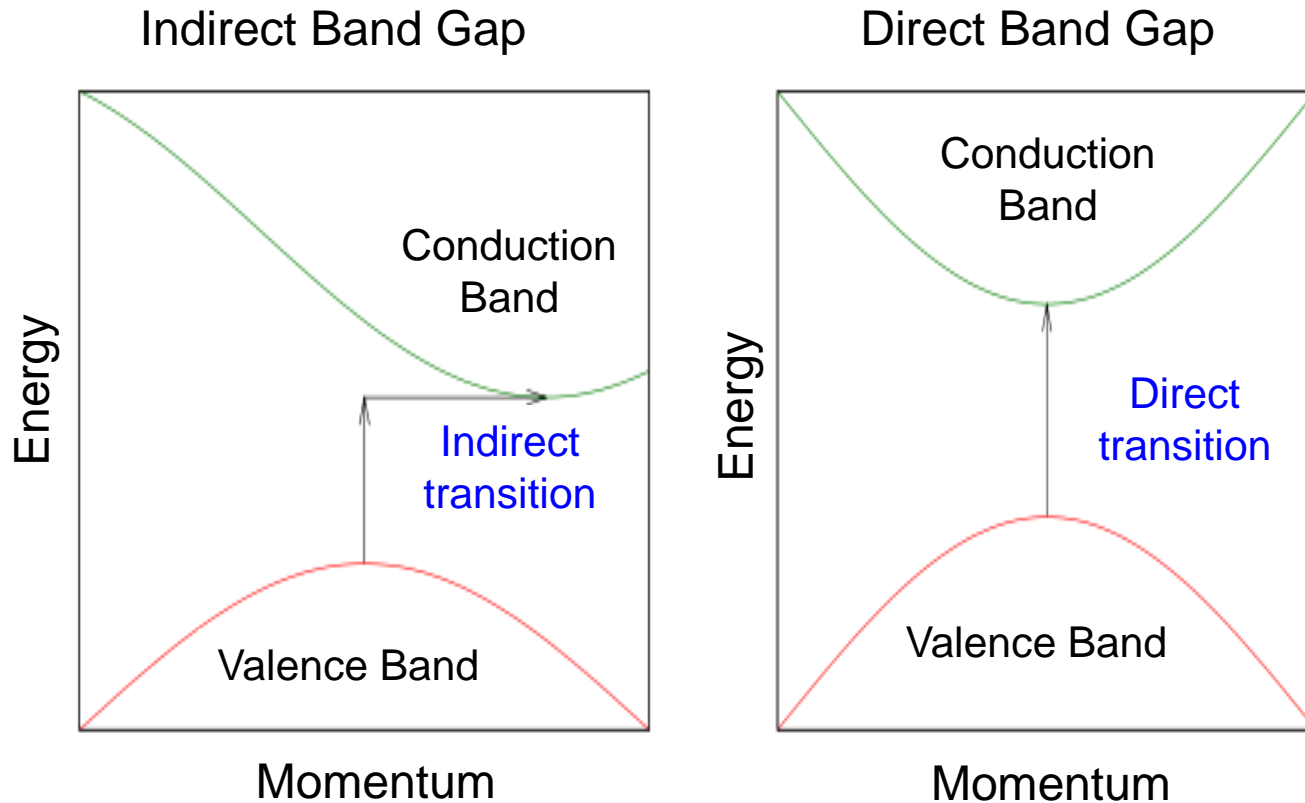
$n_i(\lambda)$  - density of carriers in an initial state

$n_f(\lambda)$  - density of unoccupied states

$P_{if}(\lambda)$  - probability that transition will take place

In addition to “band gap excitation”, another important absorption process is “free carrier absorption”, which is typically seen in metals and TCOs.

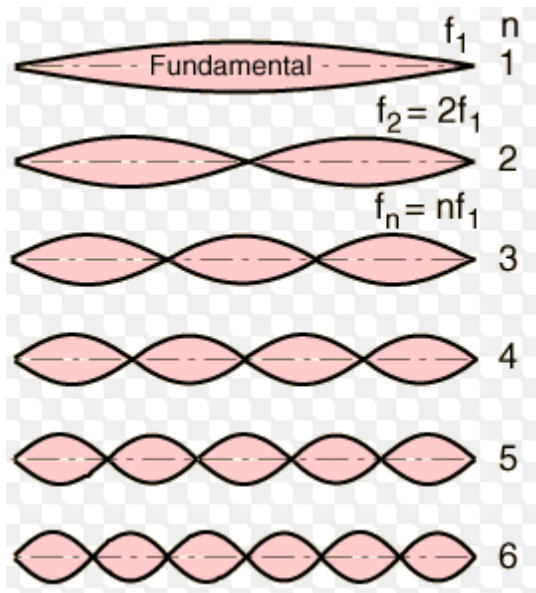
# Types of Semiconductor Band Gaps



- A direct transition requires just a photon of sufficient energy
- An indirect transition require both a photon *and* a phonon  
    “two body event” is lower probability.
- Energy *and* Momentum must be conserved.

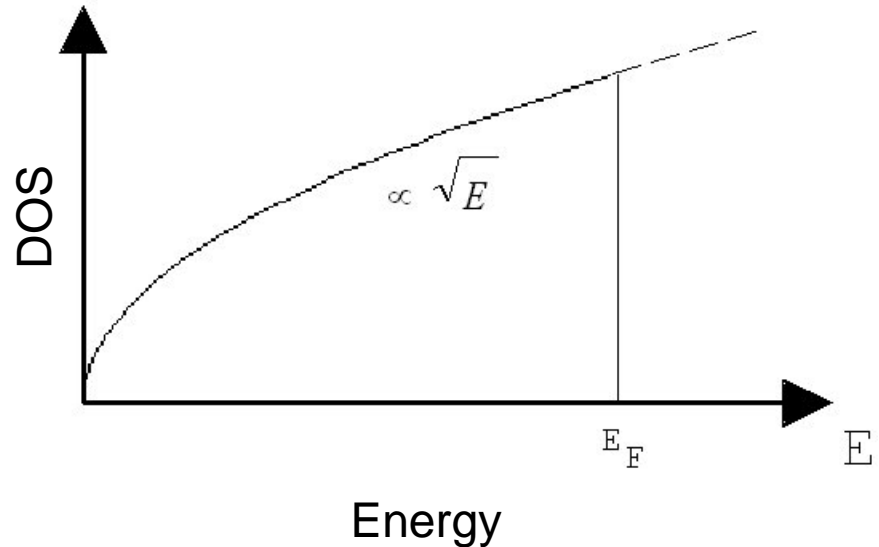
# Density of States in 3D Crystal

- “States” – allowed solutions to the Shrodinger Equation
- Analogy to waves on a string, but in 3 dimensions

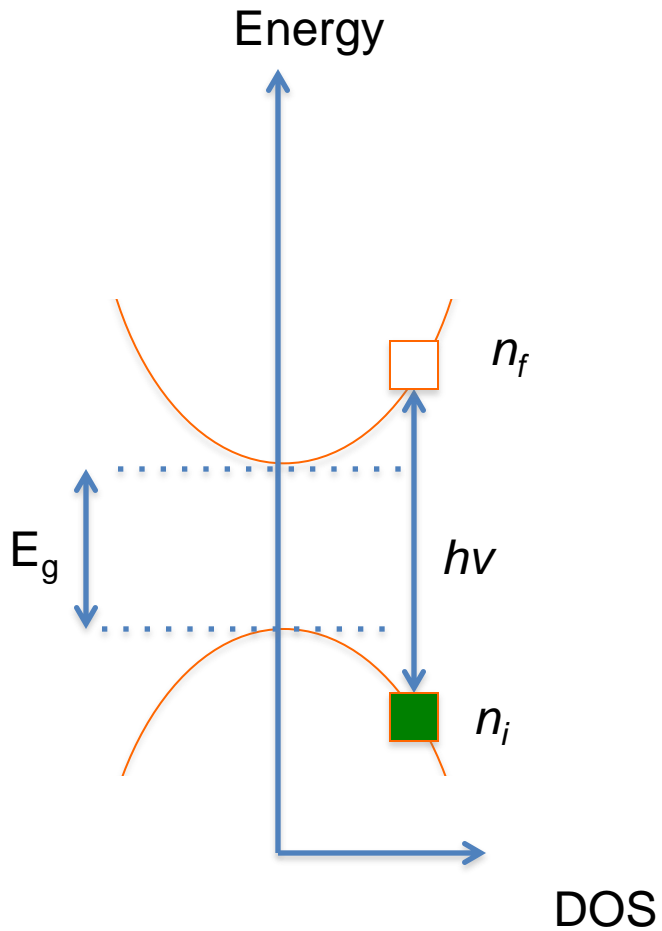


Density of States

Units of: # per energy-volume







$$\alpha(h\nu) \propto n_i(h\nu) P_{if}(h\nu) n_f(h\nu)$$

$$DOS \propto E^{1/2}$$

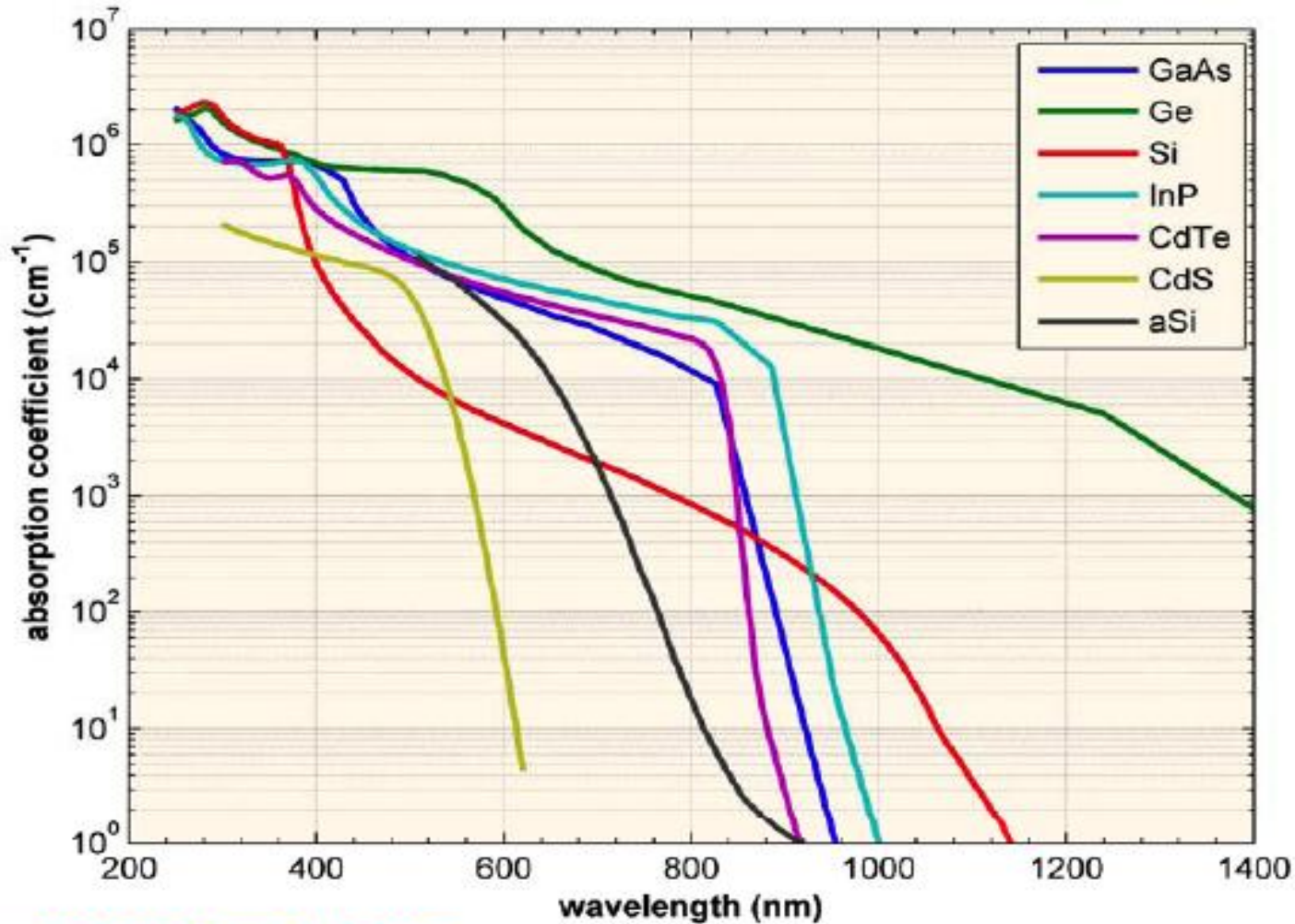
$$\alpha(h\nu) \propto E_i^{1/2} P_{if} E_f^{1/2}$$

$$\alpha(h\nu) \propto \Delta E^{1/2}$$

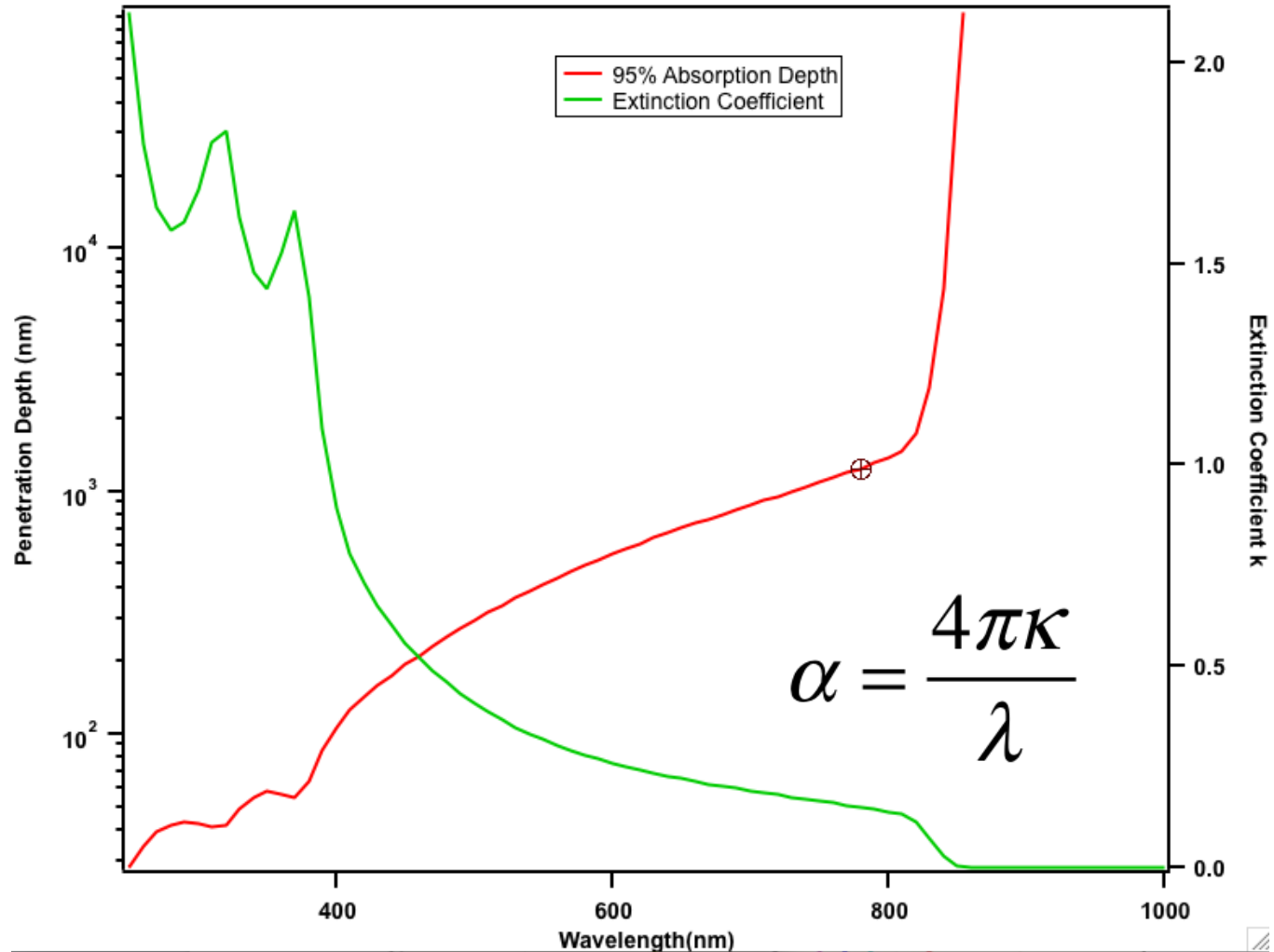
$$\Delta E = h\nu - E_g$$

$$\alpha(h\nu) \propto (h\nu - E_g)^{1/2}$$

# Absorption Coefficients for some Semiconductors

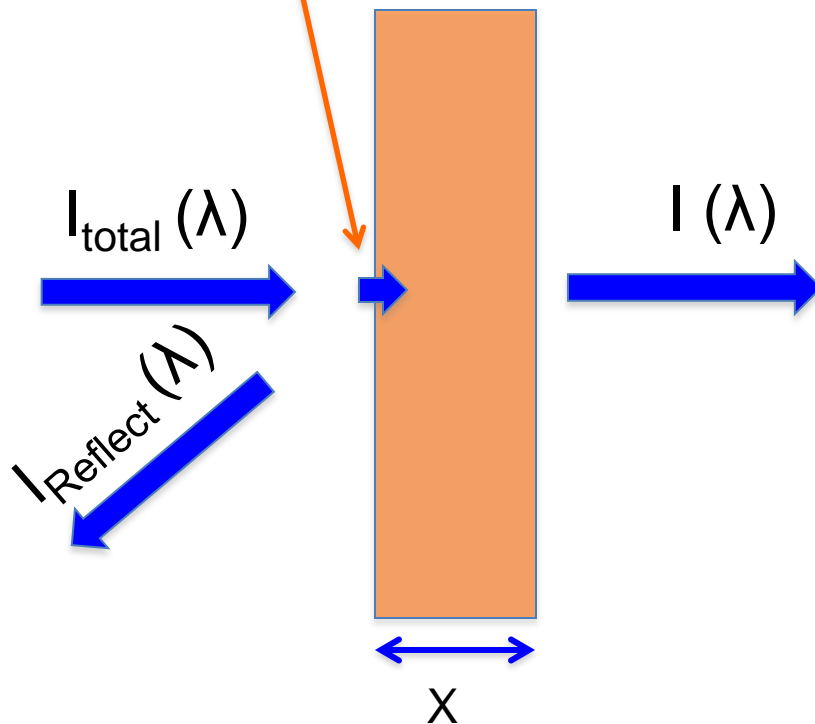


# 95% Absorption Depth (CdTe)



# Beer-Lambert Law

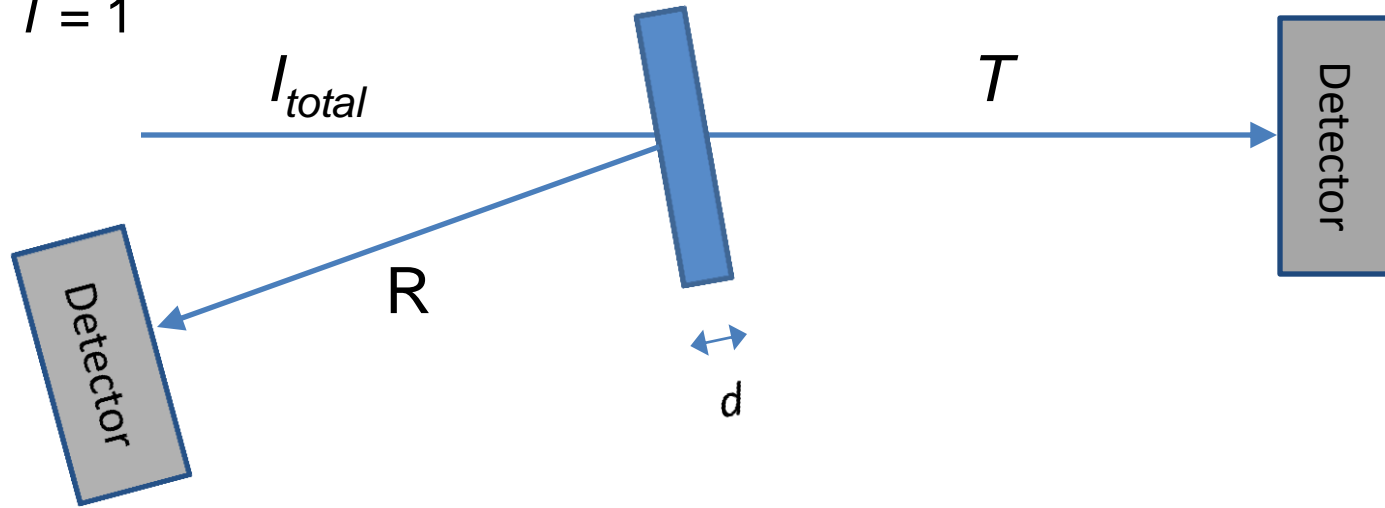
$$I(\lambda) = I_0(\lambda)e^{-\alpha(\lambda)x} \leftrightarrow I(E) = I_0(E)e^{-\alpha(E)x}$$



$$\alpha = -\frac{1}{x} \ln \left( \frac{I}{I_0} \right)$$

# Calculation of the absorption coefficient, $\alpha(\lambda)$ , for a thin film

$$A + R + T = 1$$



$$T = \frac{I_t}{I_{total}}$$

$$I_t = I_0 e^{-\alpha(\lambda)d}$$

$$I_0 = I_{total}(1 - R)$$

$$I_t = I_{total}(1 - R)e^{-\alpha(\lambda)d}$$

$$\text{Since } I_t = (T)(I_{total}) \rightarrow (T)(I_{total}) = (1 - R)(I_{total})e^{-\alpha(\lambda)d}$$

$$e^{-\alpha(\lambda)d} = \frac{T}{1 - R} \Rightarrow \alpha(\lambda)d = -\ln\left(\frac{T}{1 - R}\right)$$

$$\alpha(\lambda) = \frac{-\ln\left(\frac{T(\lambda)}{1 - R(\lambda)}\right)}{d}$$

## Measuring the bandgap energy (optical absorption)

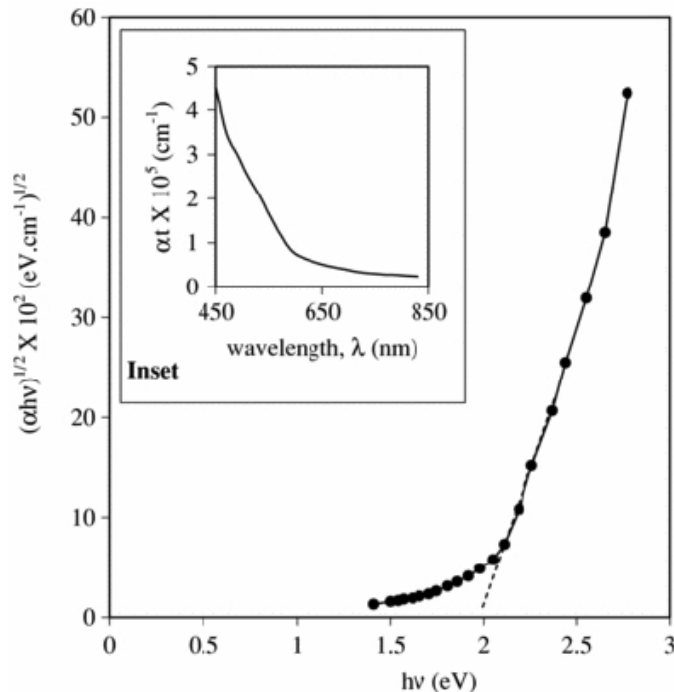
$$I(\lambda) = I_0(\lambda)e^{-\alpha(\lambda)x} \longrightarrow I(E) = I_0(E)e^{-\alpha(E)x}$$

Direct-gap semiconductor

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

Indirect-gap semiconductor

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



$\text{Fe}_2\text{O}_3$ , (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 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

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

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 <sup>a</sup>	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
$\alpha$ 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 <sub>2</sub> O		2.172	-
ZnSb		0.56	0.56	TiO <sub>2</sub>		3.03	-

<sup>a</sup>HgTe is a semimetal; the bands overlap.

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

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

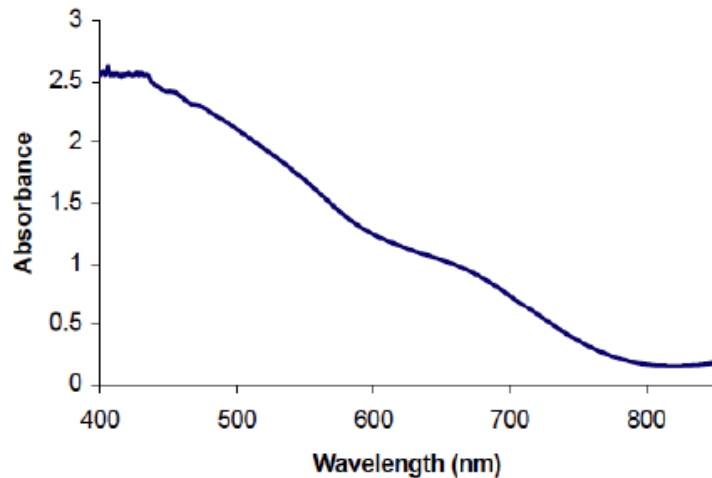
Direct gap: Plotting  $\alpha$  vs E shows an  $E^{1/2}$  dependence, so plotting  $\alpha^2$  shows a linear dependence.

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

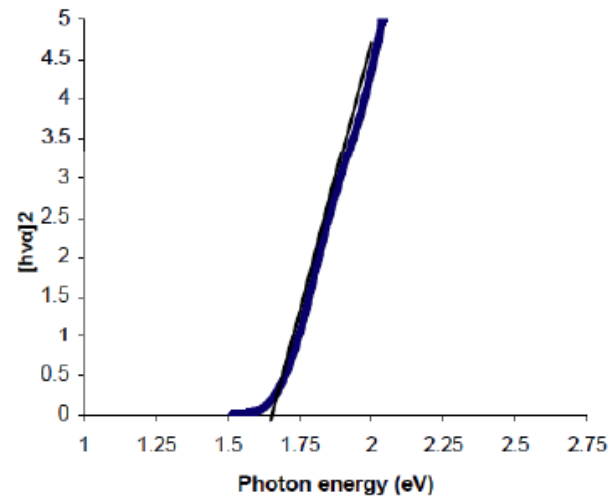


## Measuring the bandgap of a thin film (optically)

<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  $\alpha^2$  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](http://en.wikipedia.org/wiki/Direct_and_indirect_band_gaps)





	Energy gap		Lowest conduction-band minimum, direct or indirect	$\left(\frac{dE_g}{dT}\right) \times 10^4$ (300°K) eV/°K	$\left(\frac{dE_g}{dP}\right)_T \times 10^6$ eV/bar	Effective mass		Refractive index $n$	Static dielectric constant $\epsilon$	Lattice constant $a$ Å	Mobility				
	$E_g$ (0°K) eV	$E_g$ (300°K) eV				$m_l^*$	$m_h^*$				$\mu_e$ cm <sup>2</sup> / V·sec	$\mu_h$ cm <sup>2</sup> / V·sec			
IV	Si	1.166	1.11	ind 100	-2.3	-1.5	$m_l$ 0.98 $m_t$ 0.19	0.52	3.44	11.7	5.43	1,350	480		
	Ge	0.74	0.67	ind 111	-3.7	5.0	$m_l$ 1.58 $m_t$ 0.08	0.3	4.00	16.3	5.66	3,900	1,900		
IV-IV	SiC	-0.2†		dir 000		5.0					6.489	2,000	1,000		
		3.0 (6H)	2.8-3.2†	ind	-3.3				2.69 // $c$ 2.65 ⊥ $c$	10.2	$a$ 3.0817 $c$ 15.1123	400			
VI	Se	1.95	1.74	dir 0001	-14	-20		0.12	5.56 // $c$ 3.72 ⊥ $c$	8.5			1		
		Te	0.334	0.32	dir 0001	-0.3	-19		0.038 ⊥	0.26 // 0.10 ⊥	3.07 // $c$ 2.68 ⊥ $c$	5.0 // $c$ 2.2 ⊥ $c$		1,100	
III-V	BP		2	ind					2.6	6.9	4.538				
	AlP	2.5	2.43	ind 100	-3.5			0.13†		3.0	9.8	5.462	80		
	AlAs	2.24	2.16	ind				0.5	$m_l$ 1.06 $m_t$ 0.49		12	5.66	1,000	~100	
	AlSb	1.6	1.6	ind 100	-4	-1.6		0.11	0.39	3.4	11	6.135	50	400	
	GaN	3.5	3.4	dir 0000	-4.8	4.2		0.2	0.8	2.4	12	$a$ 3.18 $c$ 5.16	300		
	GaP	2.4	2.25	ind 100	-5.4	-1.7		0.13	0.678	3.37	10	5.450	120	120	
	GaAs	1.520	1.43	dir 000	-5.0	11		0.07	0.5	3.4	12	5.653	8,600	400	
	GaSb	0.81	0.69	dir 000	-4.1	12		0.045	0.39	3.9	15	6.095	4,000	650	
	InP	1.42	1.28	dir 000	-4.6	4.6		0.07	0.40	3.37	12.1	5.8687	4,000	650	
	InAs	0.43	0.36	dir 000	-3.3	5		0.028	0.33	3.42	12.5	6.058	30,000	240	
	InSb	0.235	0.17	dir 000	-2.9	15		0.0133	0.18	3.75	18	6.4787	76,000	5,000 (78°K)	
	ZnO		3.2	dir 0000	-9.5	0.6		0.32	0.27	2.02	7.9	$a$ 3.2496 $c$ 5.2065	180		
	ZnS			3.8	dir 0000	-3.8	9		0.28	>1 // 0.5 ⊥	2.4	8.3	$a$ 3.814 $c$ 6.257		
				3.6	dir 000	-5.3	5.7		0.39		2.4	8.3	5.406		
ZnSe	2.80	2.58	dir 000	-7.2	6		0.17		2.89	8.1	5.667	100			
ZnTe	2.39	2.28	dir 000	-5	6		0.15		3.56	9.7	6.101		7		
II-VI	CdS	2.58	2.53	dir 0000	-5	3.3		0.20	0.7 ⊥ $c$ 5 // $c$	2.5	8.9	$a$ 4.136 $c$ 6.713	210		
		1.85	1.74	dir 0000	-4.6			0.13	2.5 // † 0.4 ⊥		10.6	$a$ 4.299 $c$ 7.010	500		
CdTe	1.60	1.50	dir 000	-4.1	1.5		0.11	0.35	2.75	10.9	6.477	600			
HgS		2.5													
HgSe	-0.24	-0.15	dir 000				0.045			25	6.085	5,500			
HgTe	-0.28	-0.15 0.14	dir 000	+5.6			0.029	~0.3	3.7	20	6.42	22,000	100 (20°K)		
IV-VI	PbS	0.29	0.37	dir 111	+4	-7		0.1	0.1	3.7	170	5.936	550	600	
		PbSe	0.15	0.26	dir 111	+4	-8	$m_l$ 0.07 $m_t$ 0.039	$m_l$ 0.06 $m_t$ 0.03		250	6.124	1,020	930	
		PbTe	0.19	0.29	dir 111	+4	-9	$m_l$ 0.24 $m_t$ 0.02	$m_l$ 0.3 $m_t$ 0.02		3.8	412	6.460	1,620	750
		SnTe	0.3	0.18	dir 111								6.328		

... Relative to Semiconductors. Per-