Absorption coefficients of semiconductor thin films

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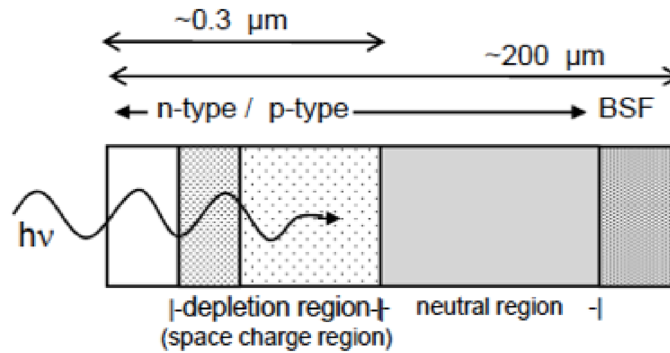
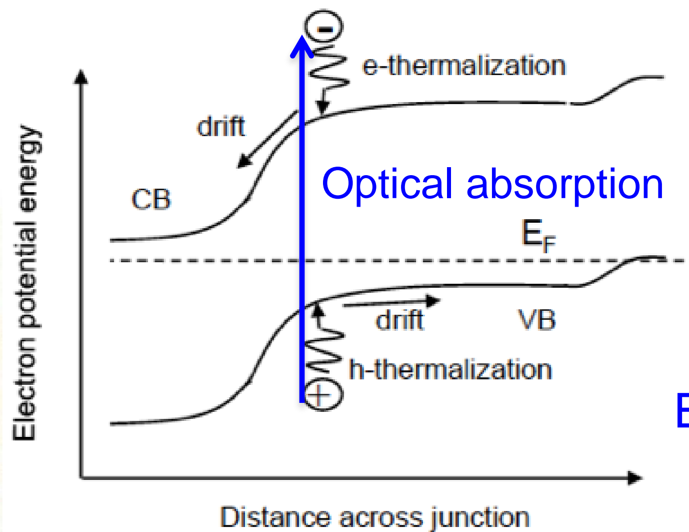
Typical Si PV Cell Structure



Total Device Thickness:
~200 μm

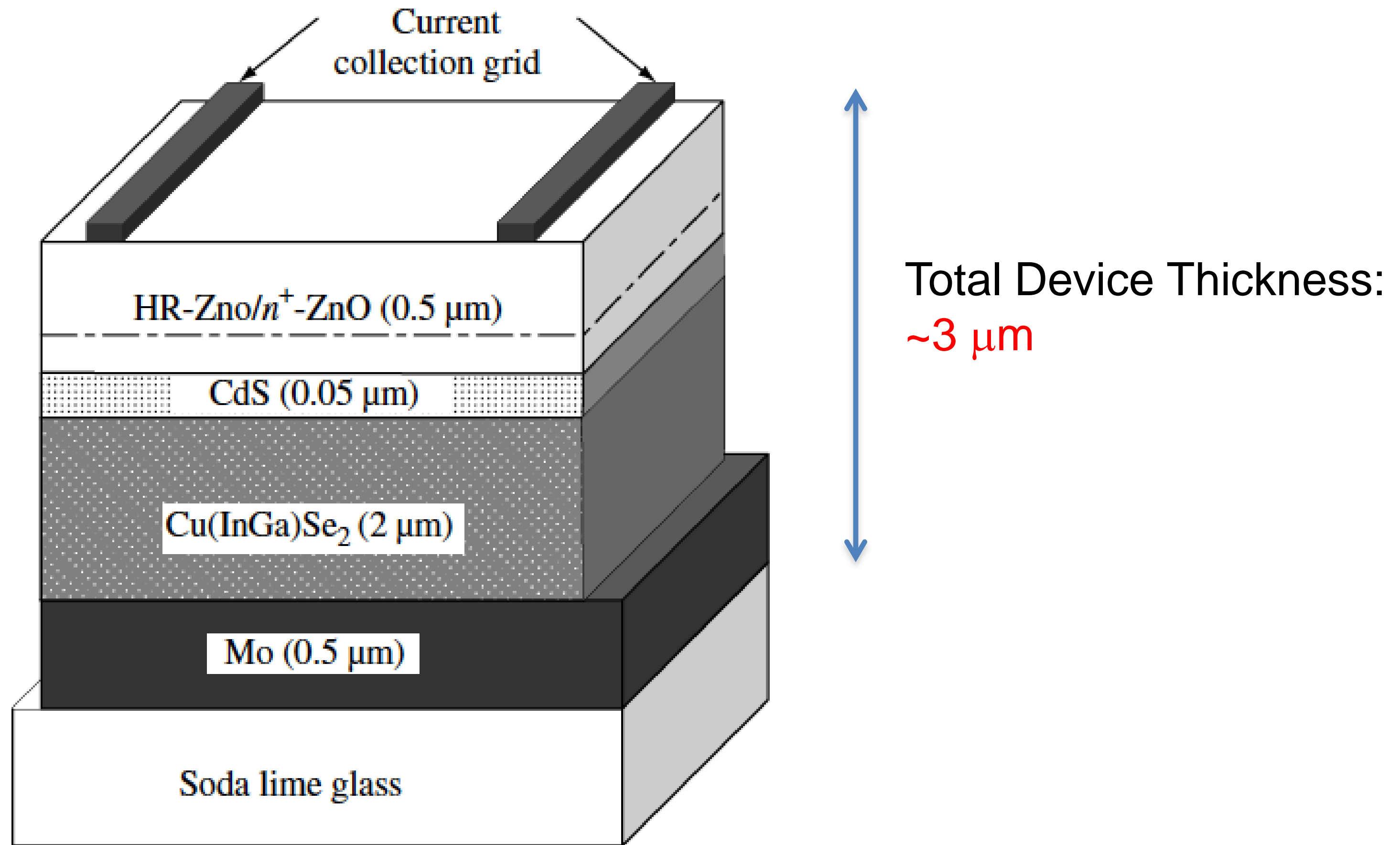
Real Space Schematic



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)

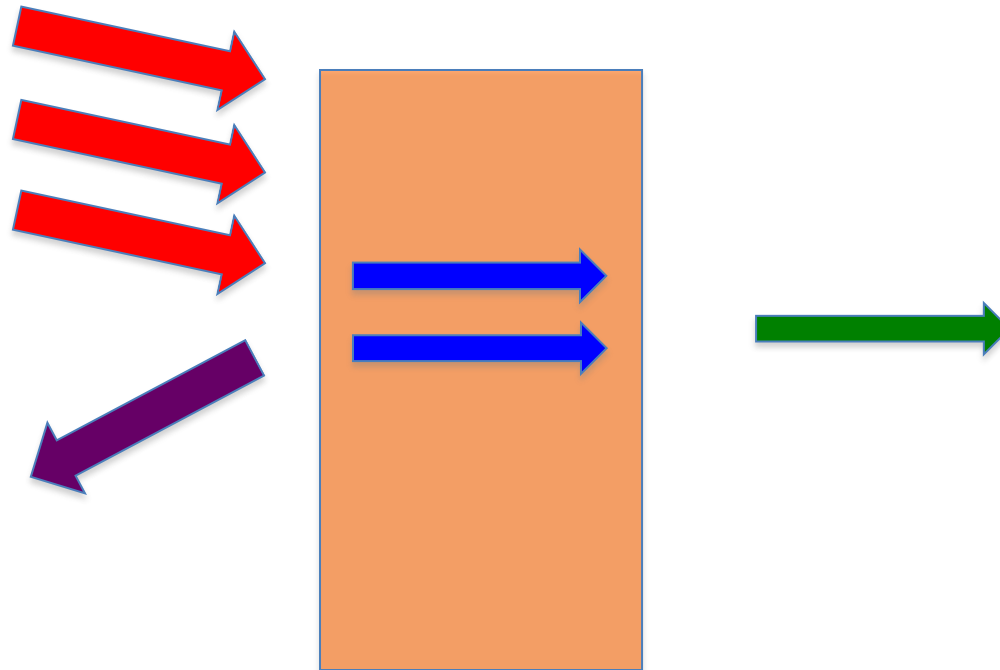
Typical Thin Film (CIGS) Cell Structure



Schematic cross section of a typical Cu(InGa)Se_2 solar cell

Conservation of Energy for each wavelength

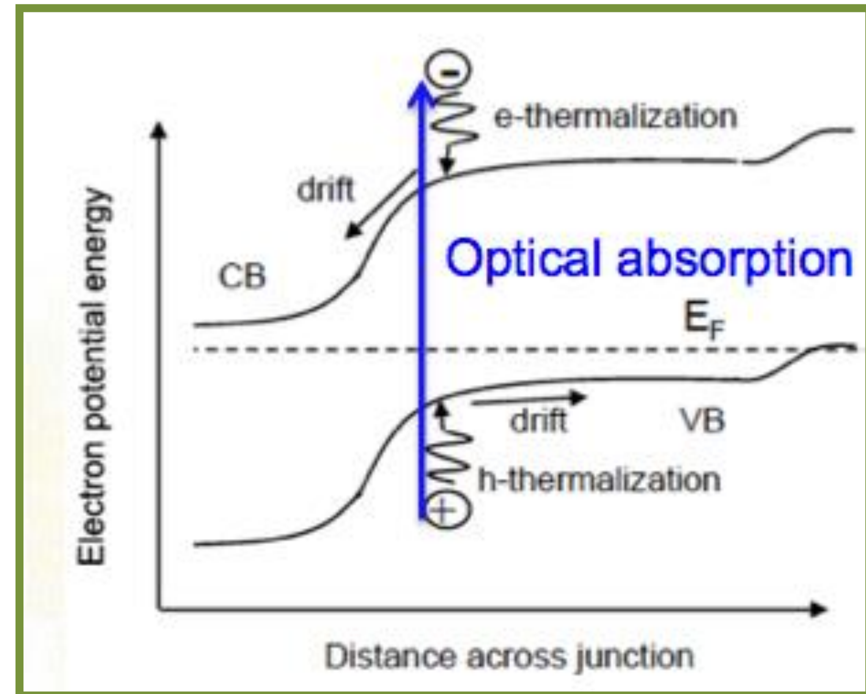
$$\text{Total Incident}(\lambda) = A(\lambda) + T(\lambda) + R(\lambda)$$



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

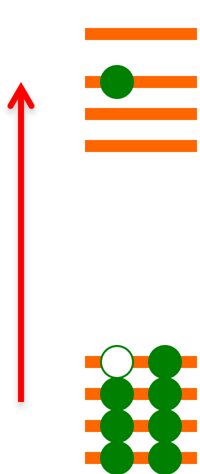
Mechanisms of Optical Absorption

- Energy is absorbed by a "system", potential energy of system is increased.
- Consider, e.g., gravitational potential energy →energy is required to lift a book onto a high 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

(connects the optical and electronic properties of materials)

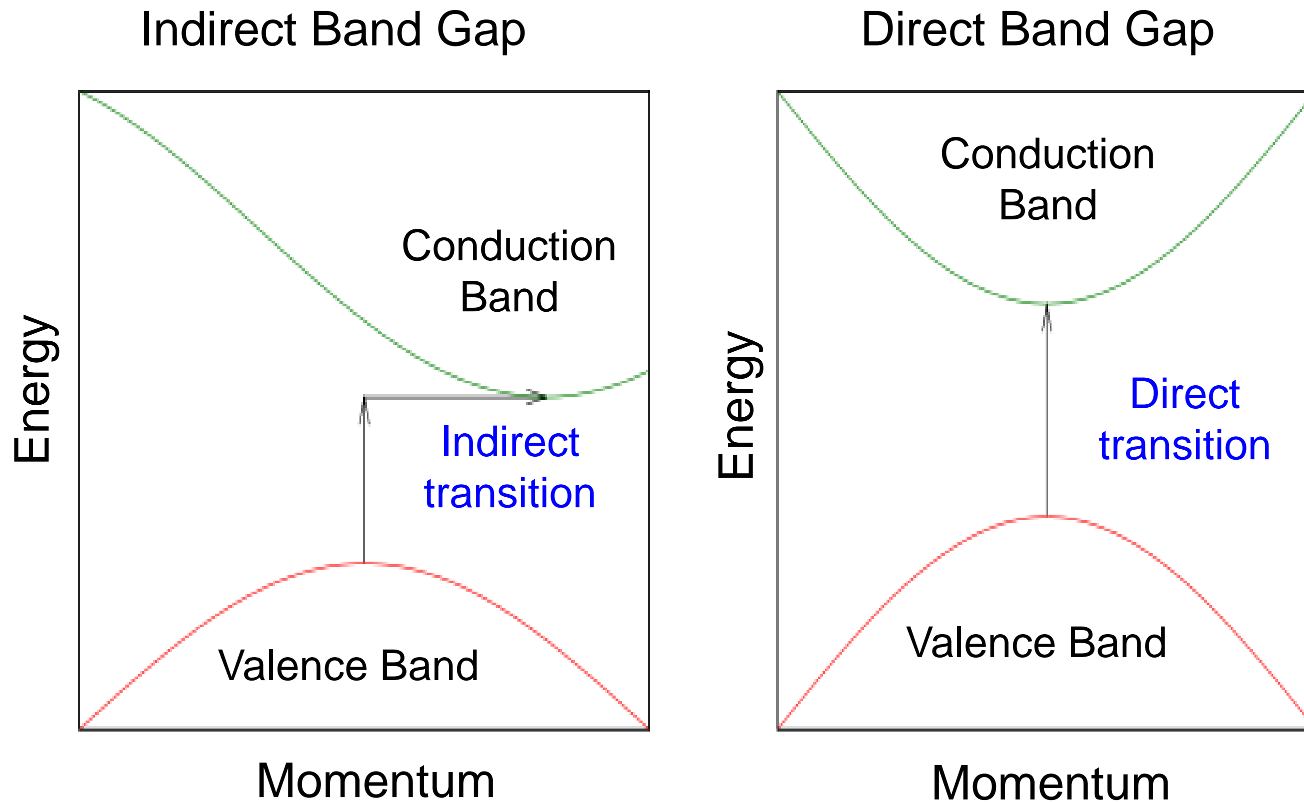


$$\alpha(\lambda) \propto n_i(\lambda) P_{if}(\lambda) n_f(\lambda)$$

$\alpha(\lambda)$ - 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. Free carrier absorption refers to an *intra*band absorption in which (e.g.) electrons absorb low energy photons and are promoted to a higher energy level within the conduction band.

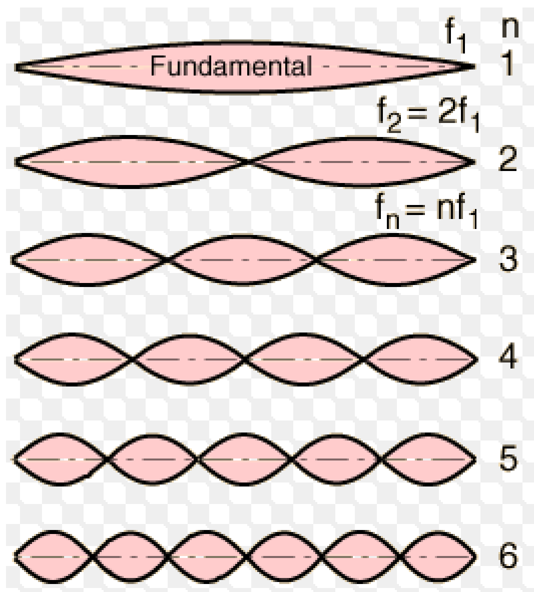
Types of Semiconductor Band Gaps



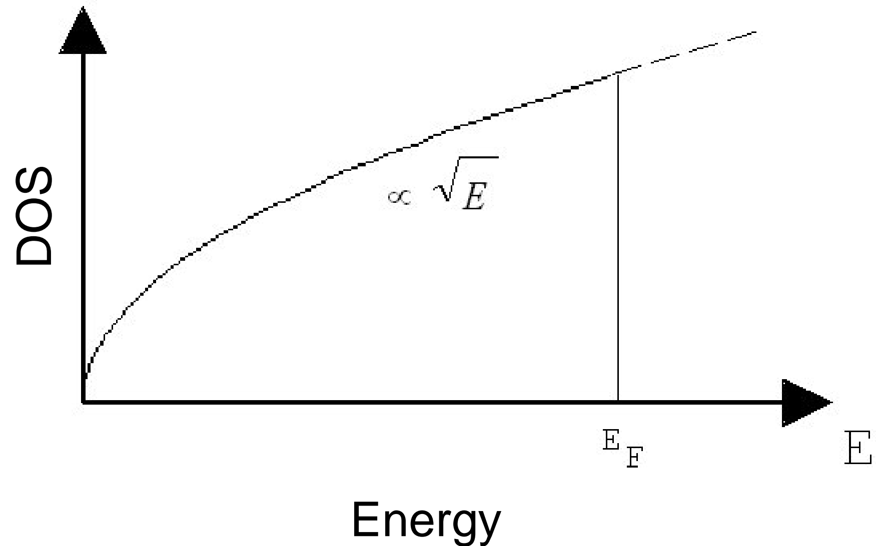
- A <u>direct</u> transition requires just a photon of sufficient energy
- An <u>indirect</u> transition require both a photon *and* a phonon --
  ("two body event" is lower probability!)
- Energy *and* Momentum must be conserved.

Density of States in 3D Crystal

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



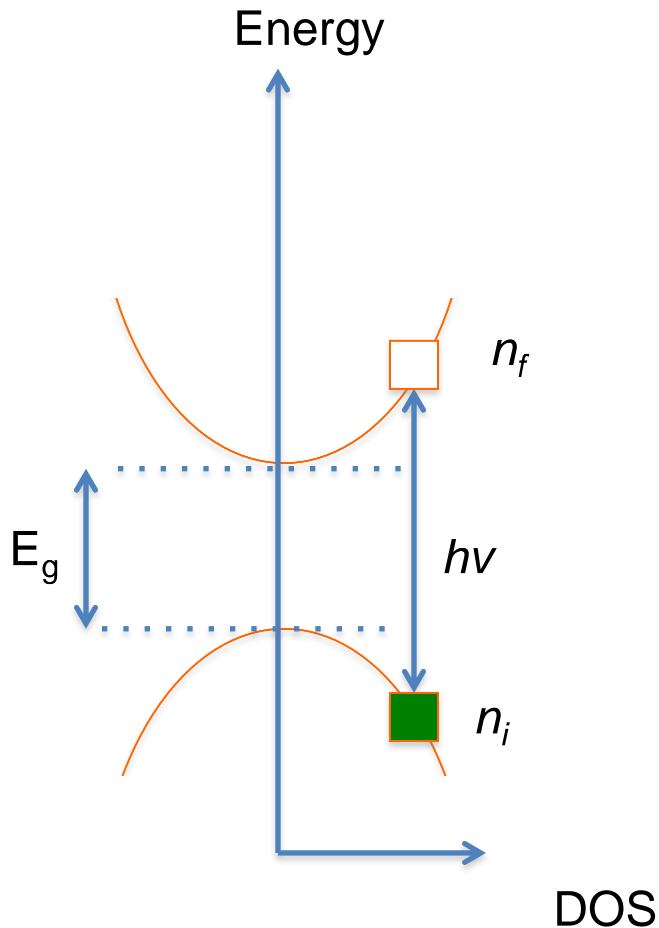
Density of States
Units of: # per energy-volume



Energy

http://hyperphysics.phy-astr.gsu.edu/hbase/waves/string.html

How does α depend on photon energy?



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

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

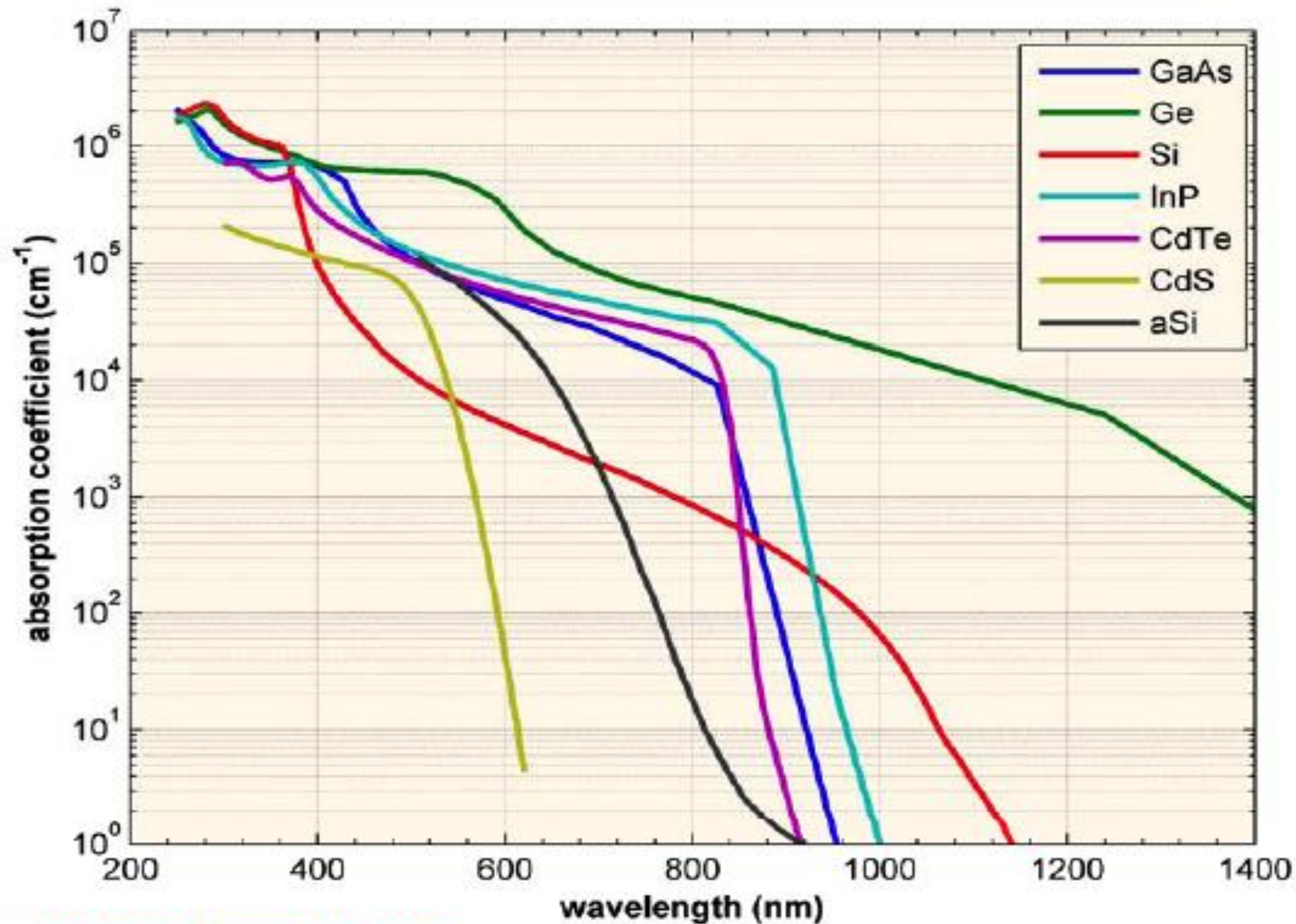
$$\alpha(h\nu) \propto E_i^{1/2}P_{if}E_f^{1/2}$$

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

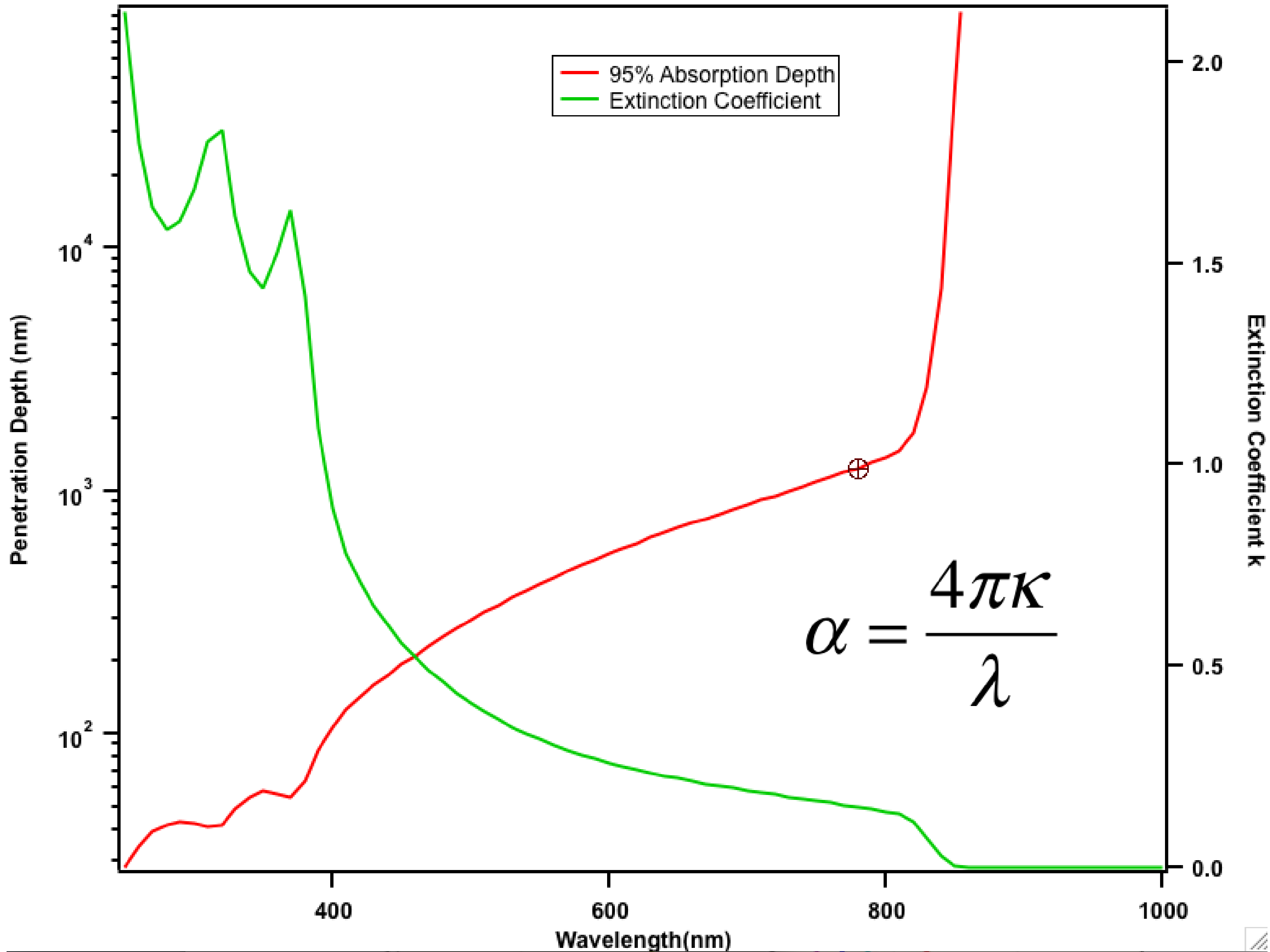
$$\Delta E = h\nu - E_g$$

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

Absorption Coefficients for some Semiconductors



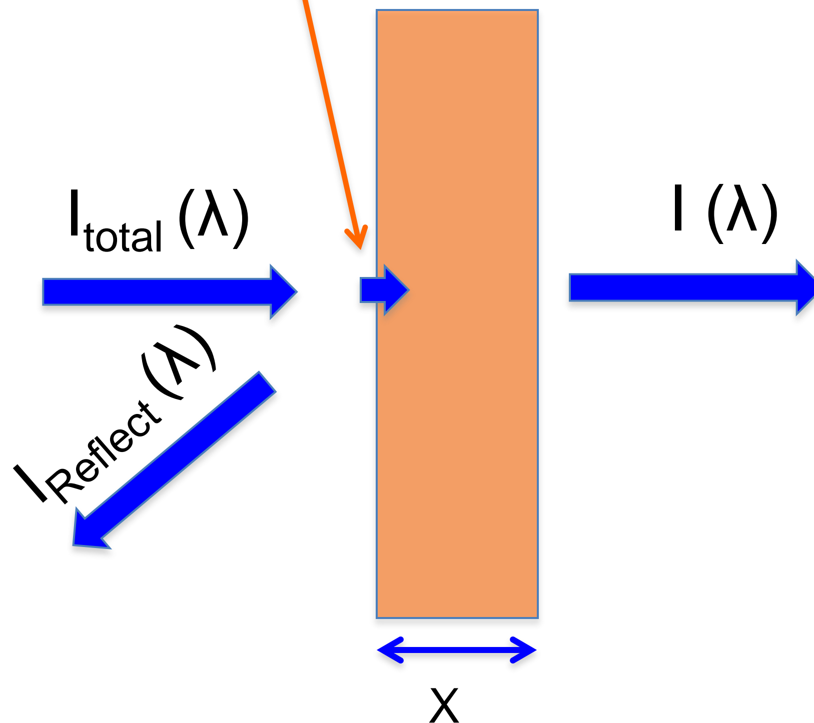
95% Absorption Depth (CdTe)



Beer-Lambert Law

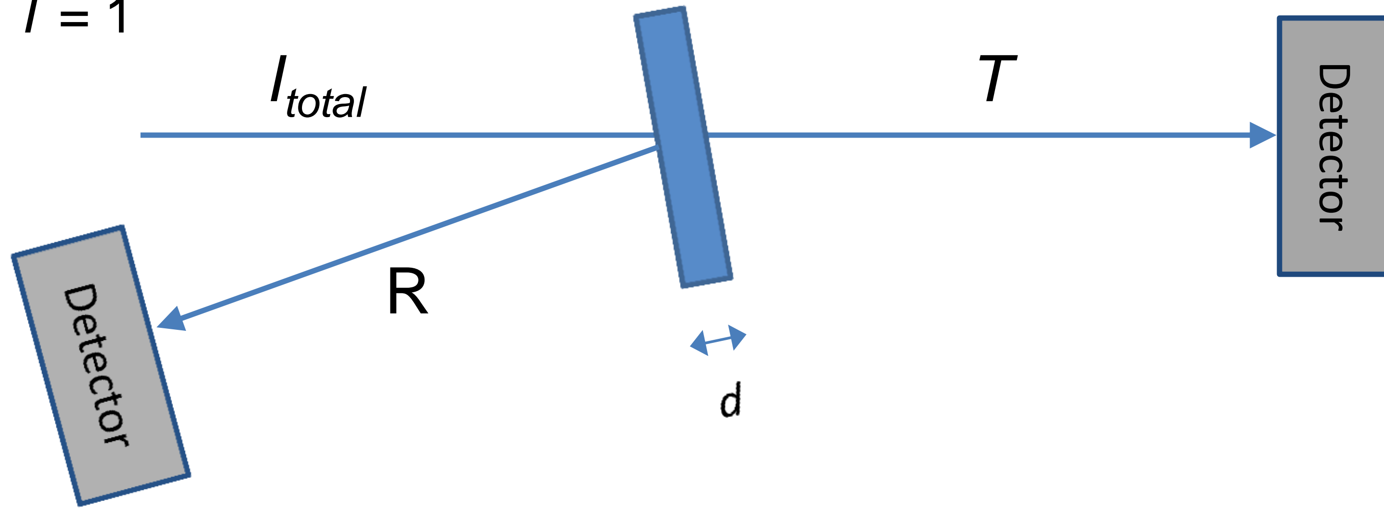
$$I(\lambda) = I_o(\lambda)e^{-\alpha(\lambda)x} \quad \Leftrightarrow \quad I(E) = I_o(E)e^{-\alpha(E)x}$$

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



Calculation of the absorption coefficient, α(λ), for a thin film

$A + R + T = 1$



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

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

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

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

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

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

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

Measuring the bandgap energy (optical absorption)

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

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 0 K	E_{gn} eV 300 K	Crystal	Gap	E_{gn} eV 0 K	E_{gn} eV 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
αSn	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	043	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_2O		2.172	-
ZnSb		0.56	0.56	TiO_2		3.03	-

[a]HgTe 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.

Measuring the bandgap energy (optical absorption)

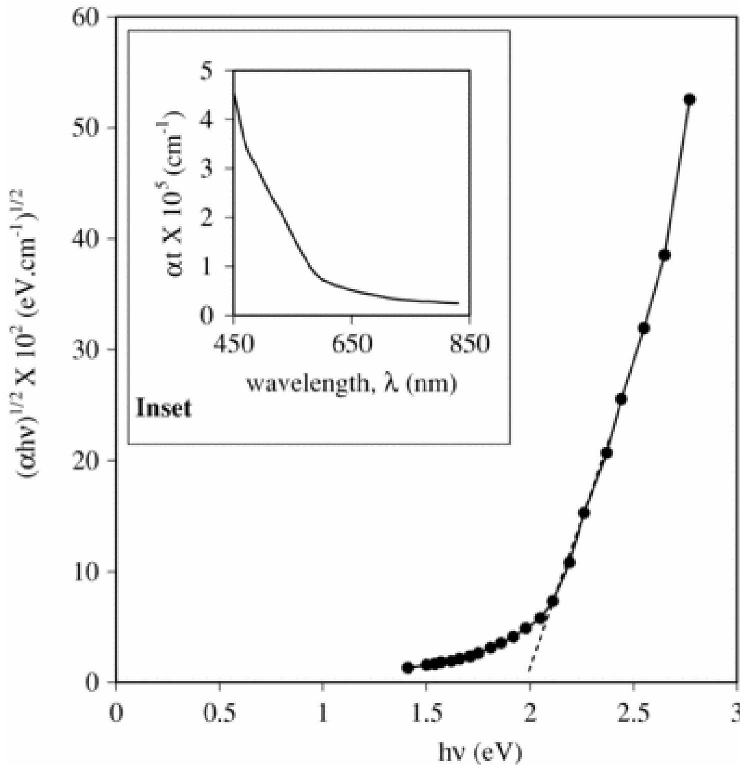
$$I(\lambda) = I_0(\lambda) e^{-\alpha(\lambda)x} \rightarrow I(E) = I_0(E) e^{-\alpha(E)x}$$

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?

if a plot of $h\nu$ versus $\alpha^{1/2}$ forms a straight line, → indirect gap material

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

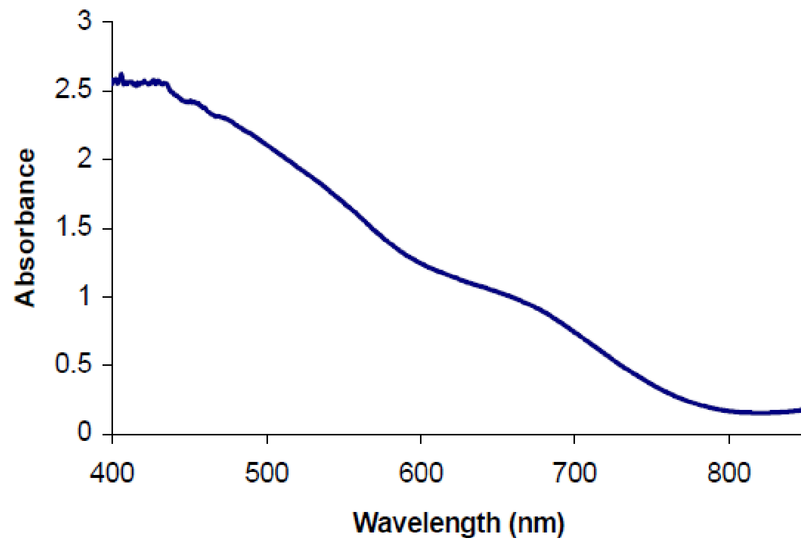


Fig 2. The absorption spectra of CdSe thin film.

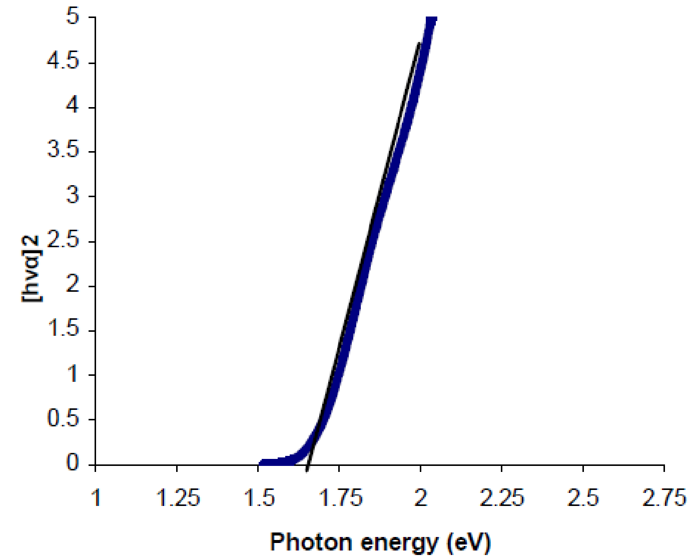


Fig.3. Energy band gap determination of CdSe thin film.

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

Group	Material	Energy gap E_g (0°K) eV	Energy gap E_g (300°K) eV	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 m_e^*	Effective mass m_h^*	Refractive index n	Static dielectric constant ϵ	Lattice constant a Å	Mobility μ_e cm²/V·sec	Mobility μ_h cm²/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
	α-Sn	−0.2‡		dir 000		5.0	0.02				6.489	2,000	1,000
IV–IV	SiC α	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	
	SiC β	2.68	2.2	ind							4.359		
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)
II–VI	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 α		3.8	dir 0000	−3.8	9	0.28	>1 ∥ 0.5 ⊥	2.4	8.3	a 3.814 c 6.257		
	ZnS β		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
	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	
	CdSe	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		

Reproduced From *"Optical Processes in Semiconductors", Pankove*