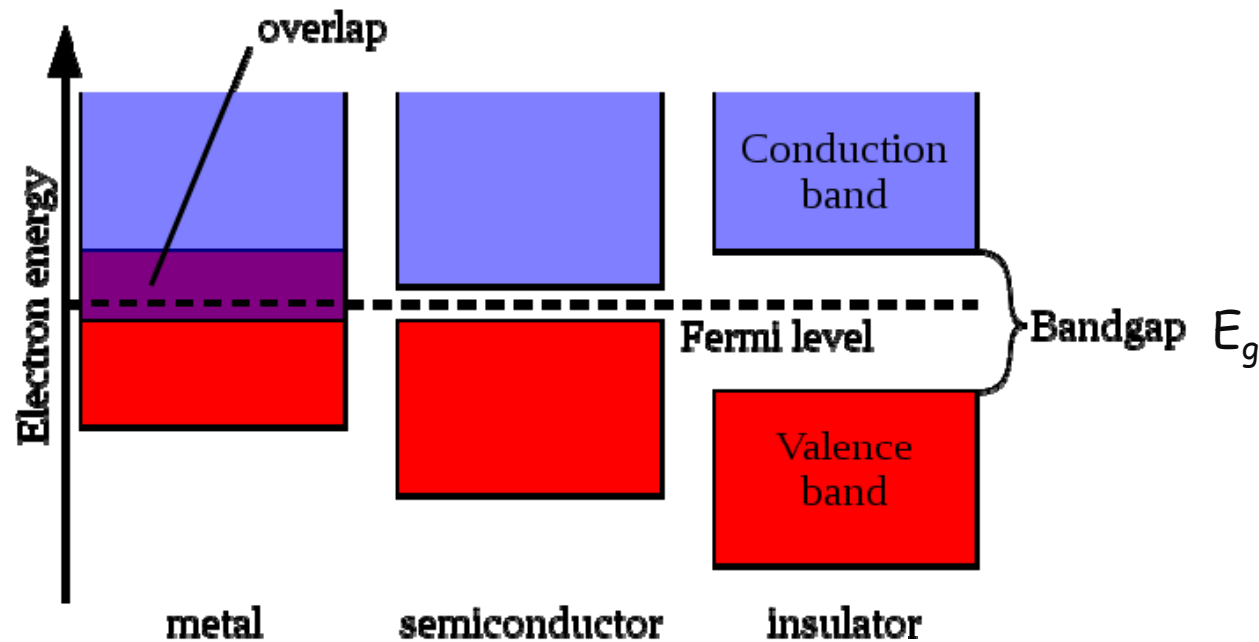


# SEMICONDUCTORS



characterized by:

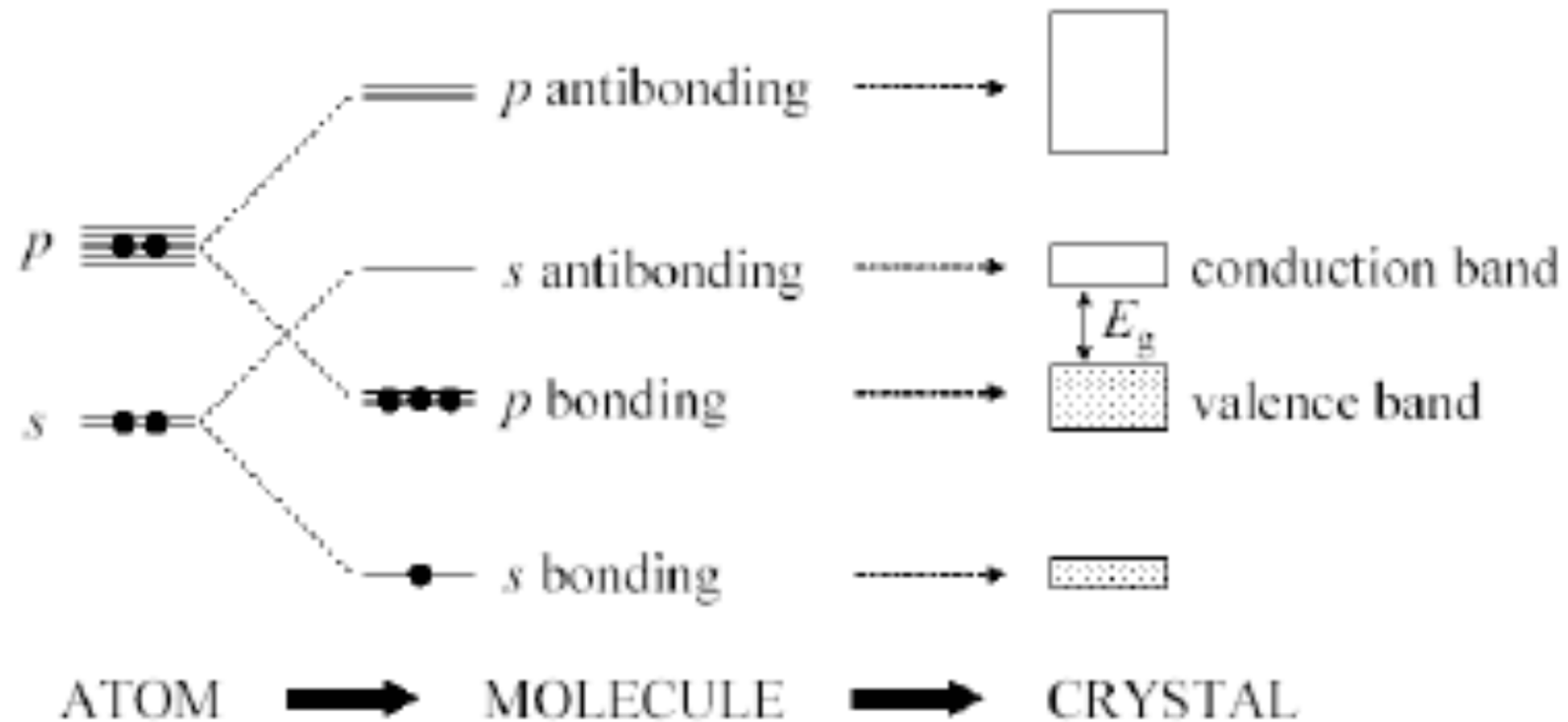
- 1) a band gap ( $E_g$ ) < 3.5 eV
- 2) increasing conductivity with increasing temperature

$$\sigma = \frac{ne^2\tau}{m}$$

metals:  $n$  is  $\sim$  constant;  $\tau$  decreases with increasing  $T$   
 SCs:  $\tau$  also decreases;  $n$  increases exponentially with  $T$

SCs: 
$$n \propto e^{-E_g/2k_B T}$$

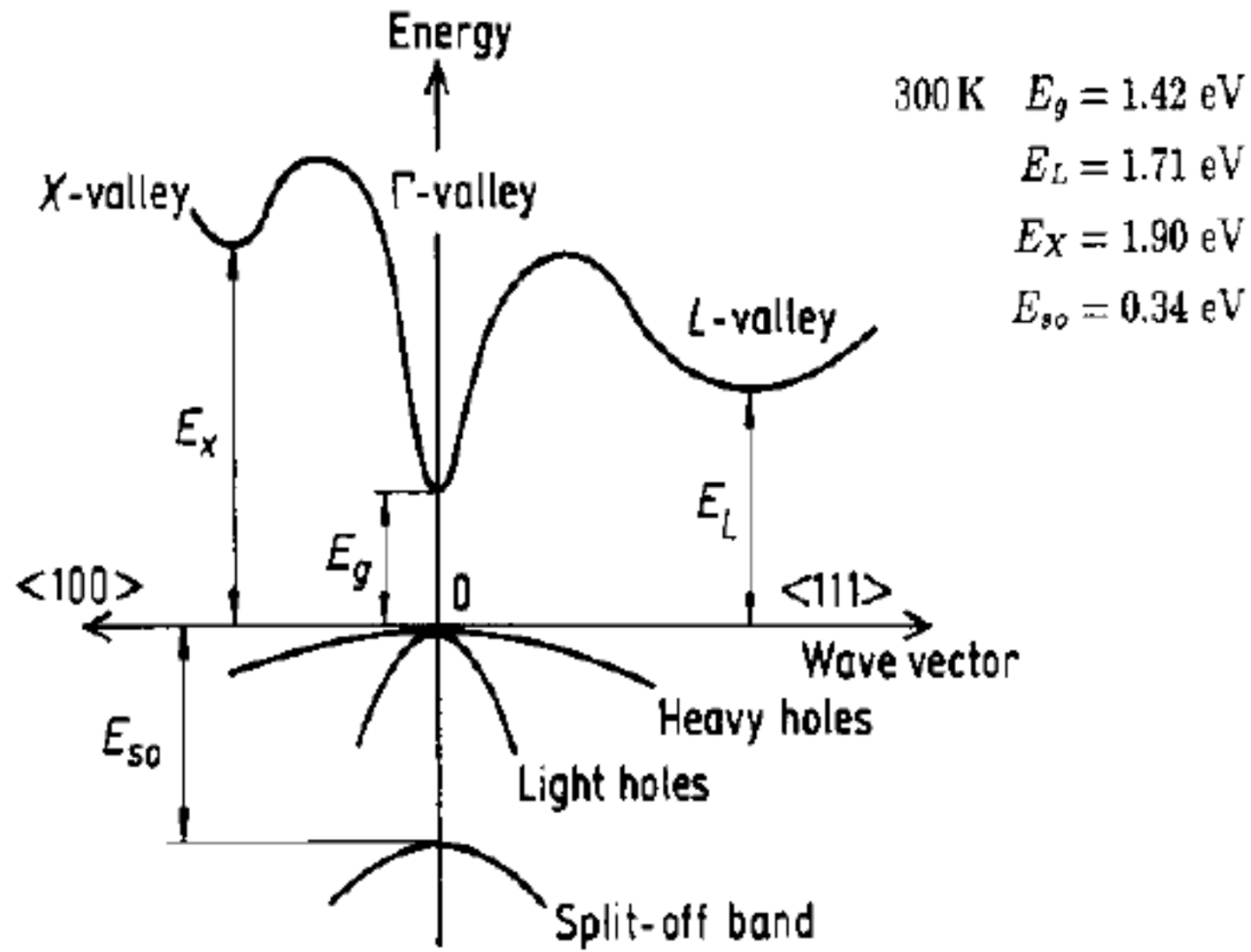
# $sp^3$ SEMICONDUCTORS



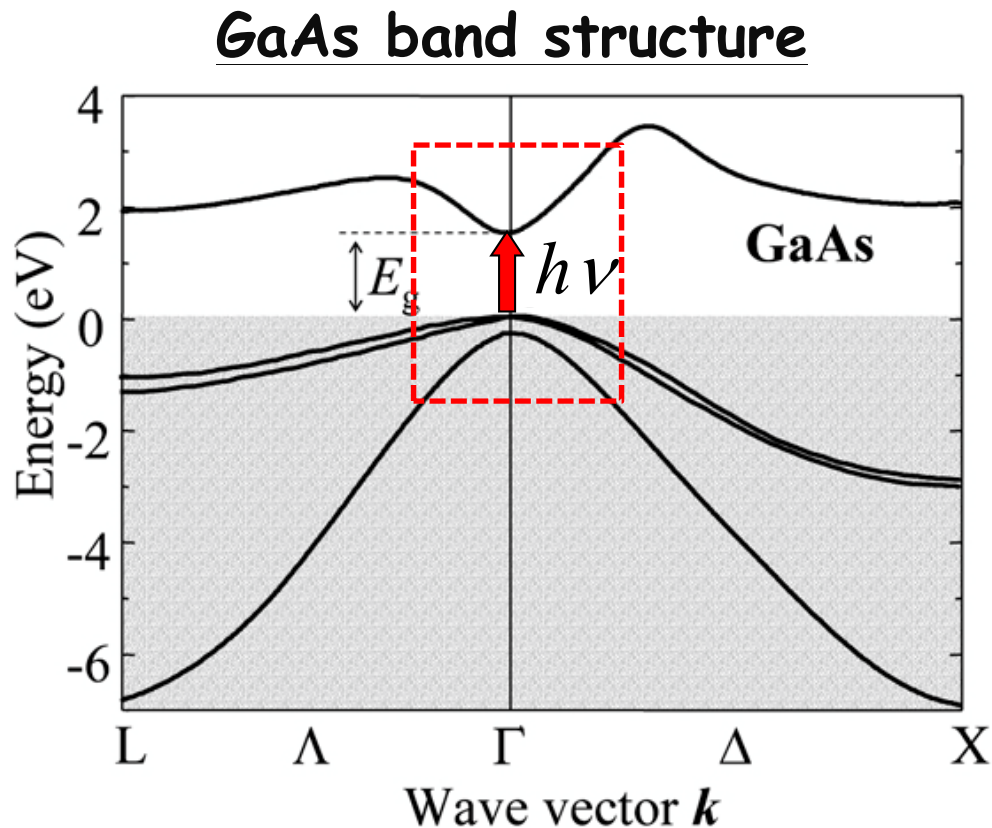
- Four valence electrons per atom: Group IV (C, Si, Ge)
- III-V compounds (GaAs, InAs, InSb, GaN ....)
- II-VI compounds (ZnS, ZnSe, CdSe, HgTe, ....)
- V.B.  $\rightarrow$  C.B. is  $p \rightarrow s$ , hence allowed dipole transition

# sp<sup>3</sup> SEMICONDUCTORS

## GaAs band structure



# PARABOLIC BAND PICTURE



near valleys, bands can always be approximated as parabolas:

## Parabolic Band Approximation

The diagram shows a blue arrow pointing from the GaAs band structure to a simplified parabolic approximation. The conduction band is represented by a parabola opening upwards, and the valence band is represented by a parabola opening downwards. The energy gap is labeled  $E_g$ .

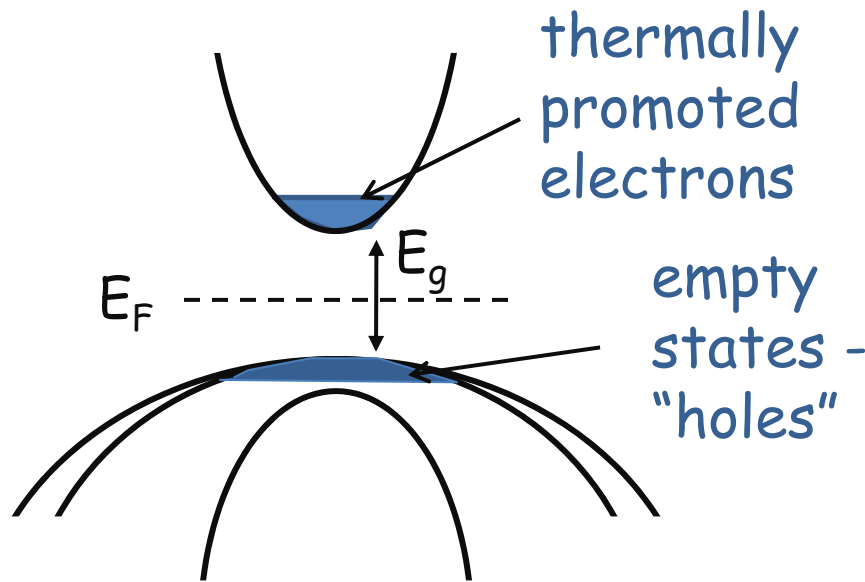
$$E = E_C + \frac{\hbar^2 k^2}{2m_e^*}$$
$$E = E_V - \frac{\hbar^2 k^2}{2m_h^*}$$

good approximation for SCs

- electrons near CBM
- holes near VBM

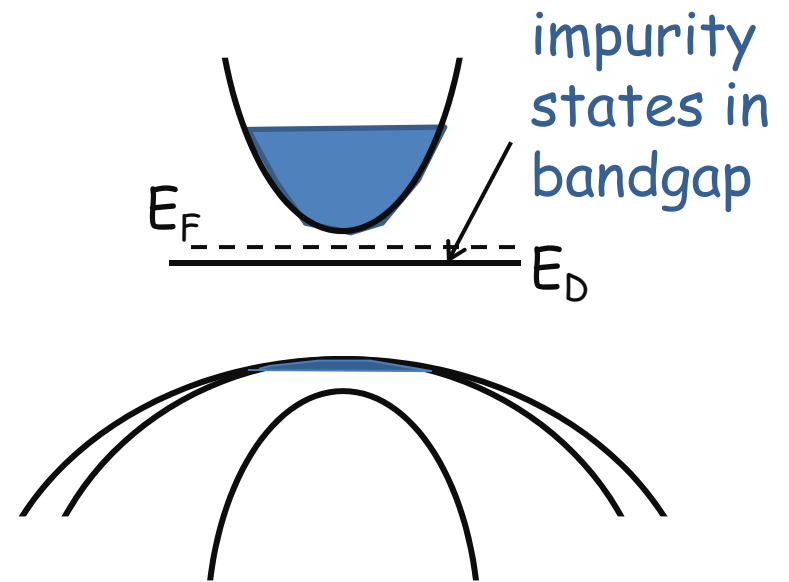
# INTRINSIC and EXTRINSIC SEMICONDUCTORS

## pure SC: intrinsic



- negligible impurities
- electrons thermally promoted across gap
- $n = p = n_i$

## doped SC: extrinsic

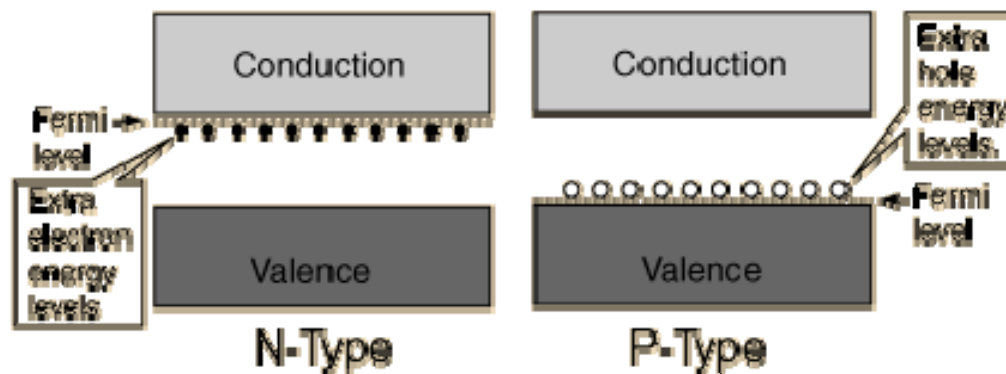
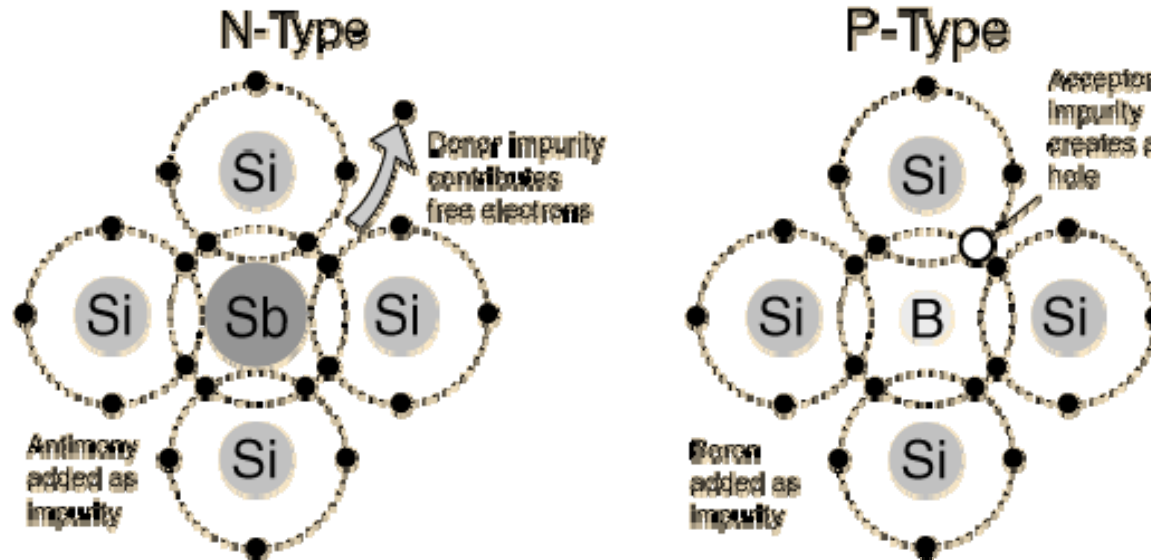


- impurities form states in gap ( $e^-$  donors or acceptors)
- electrons easily excited into conduction band from donor.
- $n > p \neq n_i$

# DOPING IN SEMICONDUCTORS

Adding foreign atoms (dopants) of Group V or Group III to a Group IV semiconductor produces *n*-type or *p*-type material.

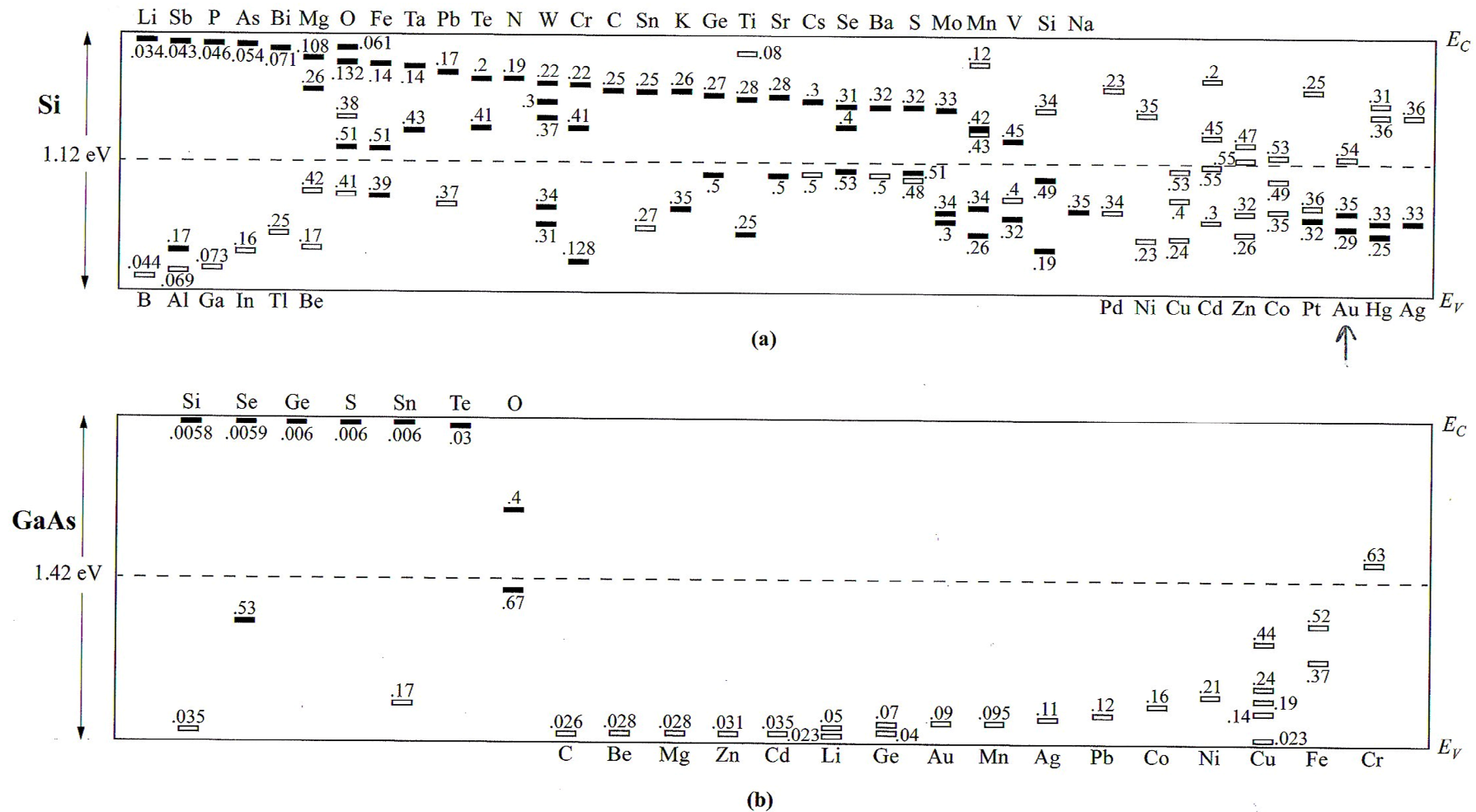
3	4	5
B	C	N
Al	Si	P
Ga	Ge	As
In	Sn	Sb
Tl	Pb	Bi



dopant type: donor  
majority carrier: electrons

dopant type: acceptor  
majority carrier: holes

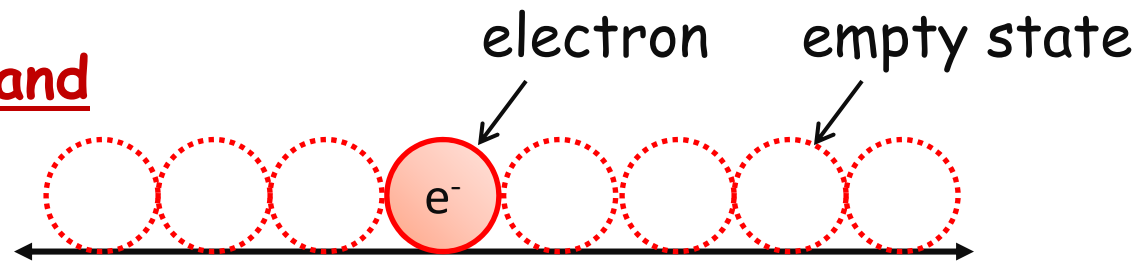
# DONOR and ACCEPTOR LEVELS



**Fig. 10** Measured ionization energies for various impurities in (a) Si and (b) GaAs. Levels below the gap center are measured from  $E_V$ . Levels above the gap center are measured from  $E_C$ . Solid bars represent donor levels and hollow boxes represent acceptor levels. (After Refs. 29, 31.)

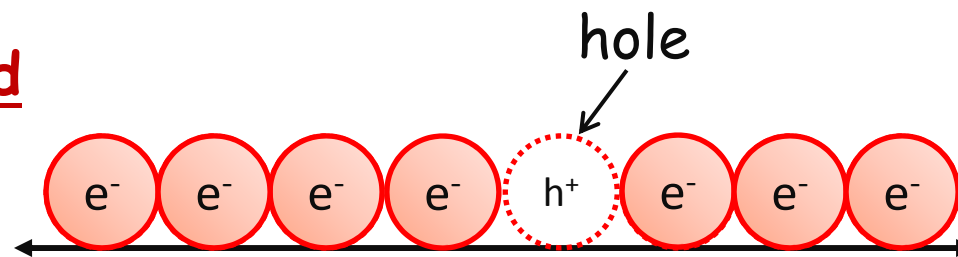
# ELECTRONIC CHARGE CARRIERS

## Conduction band



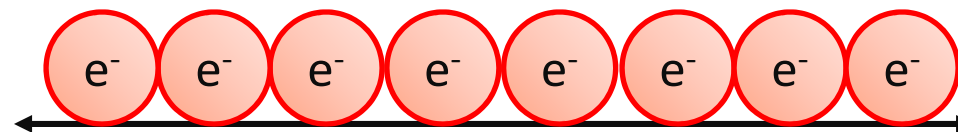
- Electrons move amid empty states
- Negative charges drift against field

## Valence band



- Electrons move by effective motion of positive holes
- Positive charges drift with field

## Filled band

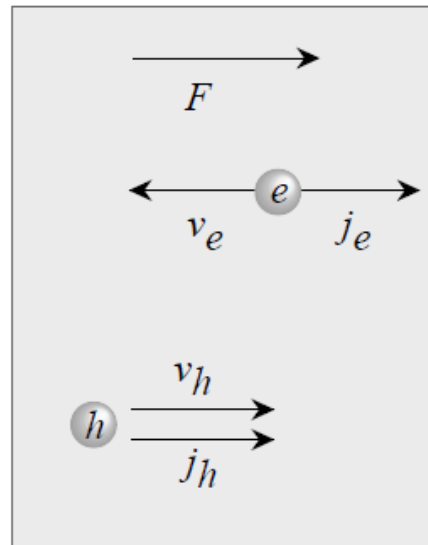


- All wavevectors fully occupied, no net motion
- Filled bands are **inert**



# HOLES

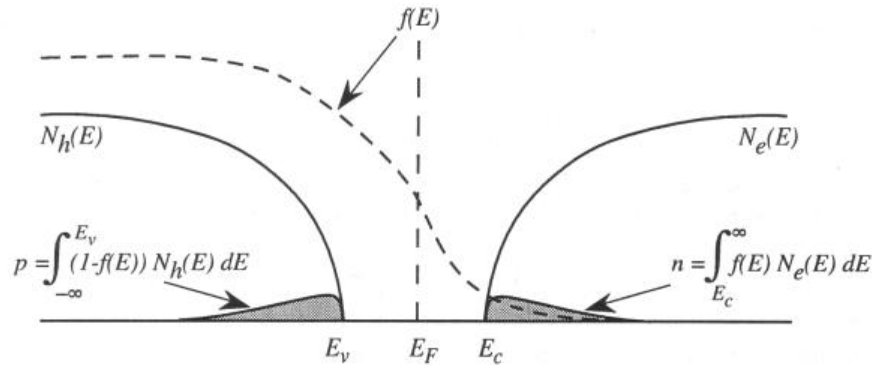
Electrons are the only charge carriers. However, we may, whenever it is convenient, consider the current to be carried entirely by fictitious particles of positive charge that fill all those levels in the band that are unoccupied by electrons. The fictitious particles are called *holes*.



Applied field causes electrons and holes to move in opposite directions, but the current is in the same direction (opposite charges moving in opposite dir.)

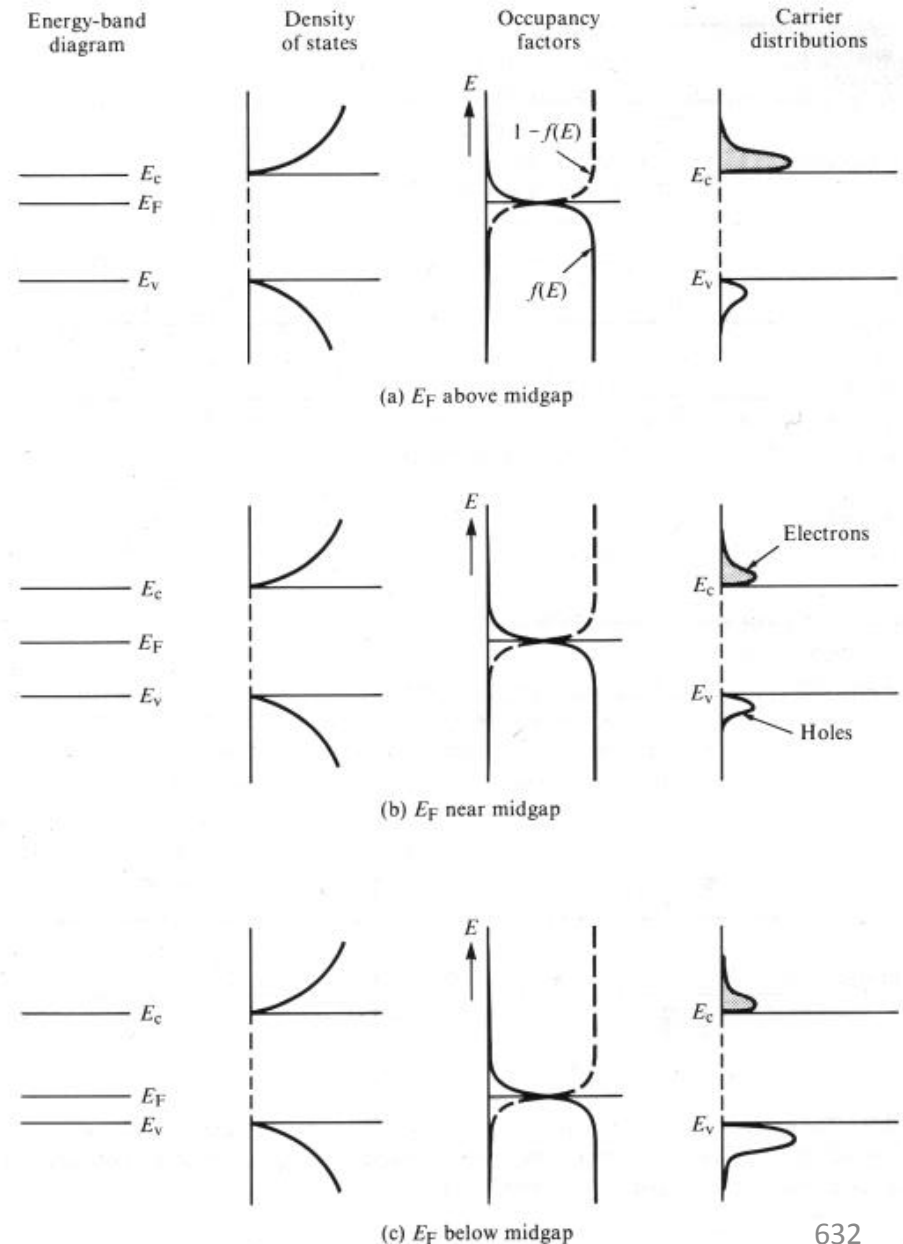
It is convention to consider CB currents to be carried by electrons and VB currents to be carried by holes. Be careful not to mix the two concepts in a single band!

# FERMI LEVEL SHIFTS WITH DOPING



The Fermi level moves up when electrons are added and down when electrons are removed, such that  $f(E_F) = 1/2$ .

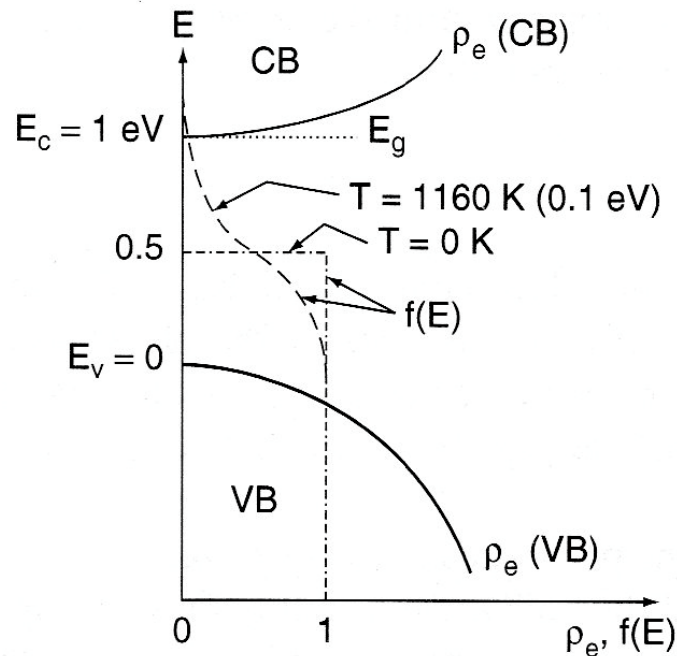
With sufficient doping, the Fermi level can move into a band, giving a **degenerate semiconductor** (metallic).



# EQUILIBRIUM CARRIER CONCENTRATION

**equilibrium**  $\equiv$  single temp, no applied fields (optical, electric, magnetic)

simplest case: direct gap, intrinsic semiconductor ( $n = p = n_i$ )



concentration of electrons in CB:

$$n(T) = \int_{E_c}^{\infty} g_e(E) f_e(E, T) dE$$

[electrons]      number of states at each  $dE$       occupancy

concentration of holes in VB:

$$p(T) = \int_{-\infty}^0 g_e(E) [1 - f_e(E, T)] dE$$

$$n(T) = \int_{E_c}^{\infty} g_e(E) f_e(E, T) dE$$

$$p(T) = \int_{-\infty}^0 g_e(E) [1 - f_e(E, T)] dE$$

in the parabolic approximation:

$$g_e(E) = \frac{1}{2\pi^2} \left( \frac{2m_{eds}^*}{\hbar^2} \right)^{3/2} (E - E_g)^{1/2}$$

for  $E > E_g$

$$g_e(E) = \frac{1}{2\pi^2} \left( \frac{2m_{hds}^*}{\hbar^2} \right)^{3/2} |E|^{1/2} \quad E < 0$$

$$f_e(E) = \frac{1}{\exp[(E - \mu) / k_B T] + 1}$$

for  $E_g > 0.15$  eV and  $|E - \mu| \gg k_B T$  the Fermi function reduces to the exponential Boltzmann distribution:

$$f_e(E) \approx \exp[(\mu - E) / k_B T] \ll 1$$

$$f_h(E) \approx \exp[(E - \mu) / k_B T] \ll 1$$

substituting these forms of  $g(E)$  and  $f(E)$  into the integrals gives:

$$n(T) = \frac{1}{2\pi^2} \left( \frac{2m_{eds}^*}{\hbar^2} \right)^{3/2} \int_{E_c}^{E_{\max}} e^{(\mu-E)/kT} (E - E_g)^{1/2} dE$$

and

$$p(T) = \frac{1}{2\pi^2} \left( \frac{2m_{hds}^*}{\hbar^2} \right)^{3/2} \int_{-E_{\min}}^0 e^{(E-\mu)/kT} |E|^{1/2} dE$$

the results are:

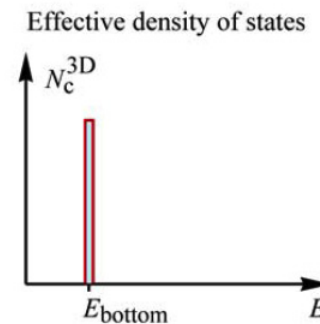
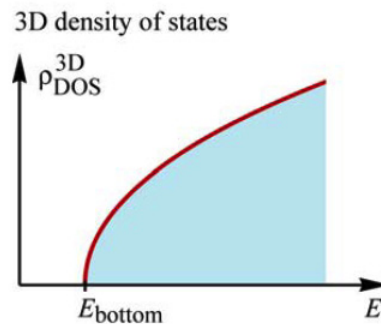
$$n(T) = 2 \left( \frac{m_{eds}^* k_B T}{2\pi\hbar^2} \right)^{3/2} e^{-(E_c-\mu)/kT} = N_C(T) e^{-(E_c-\mu)/kT}$$

$$p(T) = 2 \left( \frac{m_{hds}^* k_B T}{2\pi\hbar^2} \right)^{3/2} e^{-(\mu-E_v)/kT} = N_V(T) e^{-(\mu-E_v)/kT}$$

$$n(T) = N_C(T) e^{-(E_C - \mu)/kT}$$

$$p(T) = N_V(T) e^{-(\mu - E_V)/kT}$$

$N_C$  and  $N_V$  : *effective densities of states*  
at bottom of CB, top of VB



mathematical tool

$$E_g = E_C - E_V$$

$$\mu \approx E_g / 2$$

$$n(T) = N_C(T) e^{-[(E_C - \frac{E_C - E_V}{2})/kT]} = N_C(T) e^{-(E_g/2kT)} = N_C(T) e^{\left(-\frac{E_C - E_F}{kT}\right)}$$

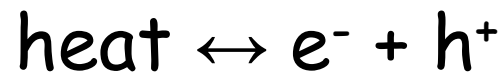
The concentrations of both electrons and holes increase exponentially with temperature with an activation energy of  $E_g/2$ .

\*The product  $n(T)p(T)$  is:

$$\begin{aligned}n(T)p(T) &= N_C(T)N_V(T)e^{-(E_C-\mu)/kT}e^{-(\mu-E_V)/kT} \\ &= N_C(T)N_V(T)e^{-E_g/kT} = n_i^2\end{aligned}$$

This product is independent of the position of the Fermi level. In other words, the product is a constant at a given temperature no matter the doping (n-type, intrinsic, or p-type).

it is an example of the LAW OF MASS ACTION



$$K_{eq} = [e][h] = np$$

For an intrinsic semiconductor:

$$n_i(T) = p_i(T) = \sqrt{n_i(T)p_i(T)} = 2 \left( \frac{k_B T}{2\pi\hbar^2} \right)^{3/2} \left( m_{eds}^* m_{hds}^* \right)^{3/4} e^{-E_g/2kT}$$

# FERMI LEVEL, INTRINSIC CASE

$$n = N_C e^{\left(\frac{E_C - E_F}{kT}\right)} \Rightarrow E_C - E_F = kT \ln\left(\frac{N_C}{n}\right)$$

$$p = N_V e^{\left(\frac{E_F - E_V}{kT}\right)} \Rightarrow E_F - E_V = kT \ln\left(\frac{N_V}{p}\right)$$

subtract the  
two equations

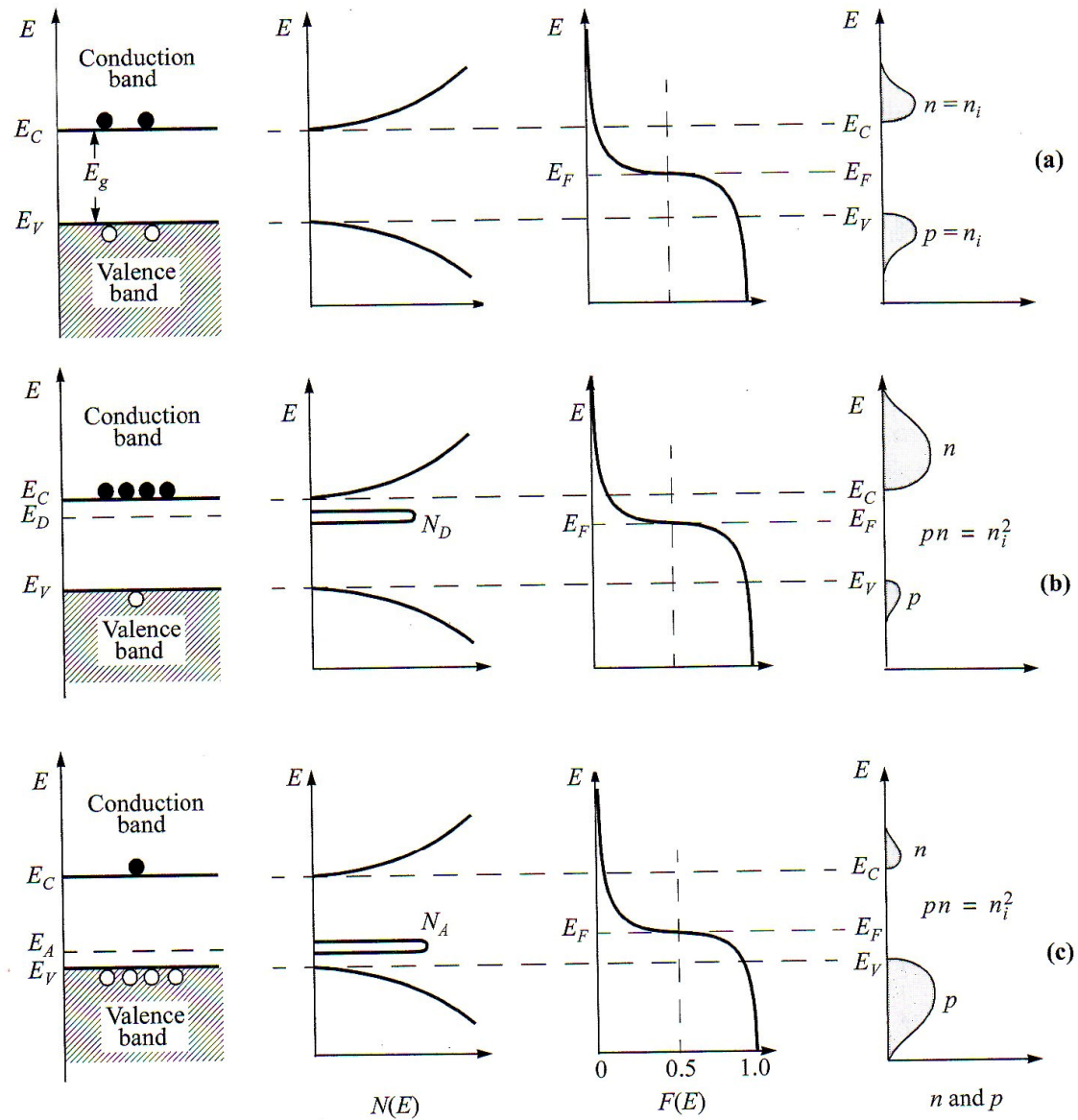
$$n = p$$

---

$$E_F = E_i = \frac{E_C + E_V}{2} + \frac{kT}{2} \ln\left(\frac{N_V}{N_C}\right)$$

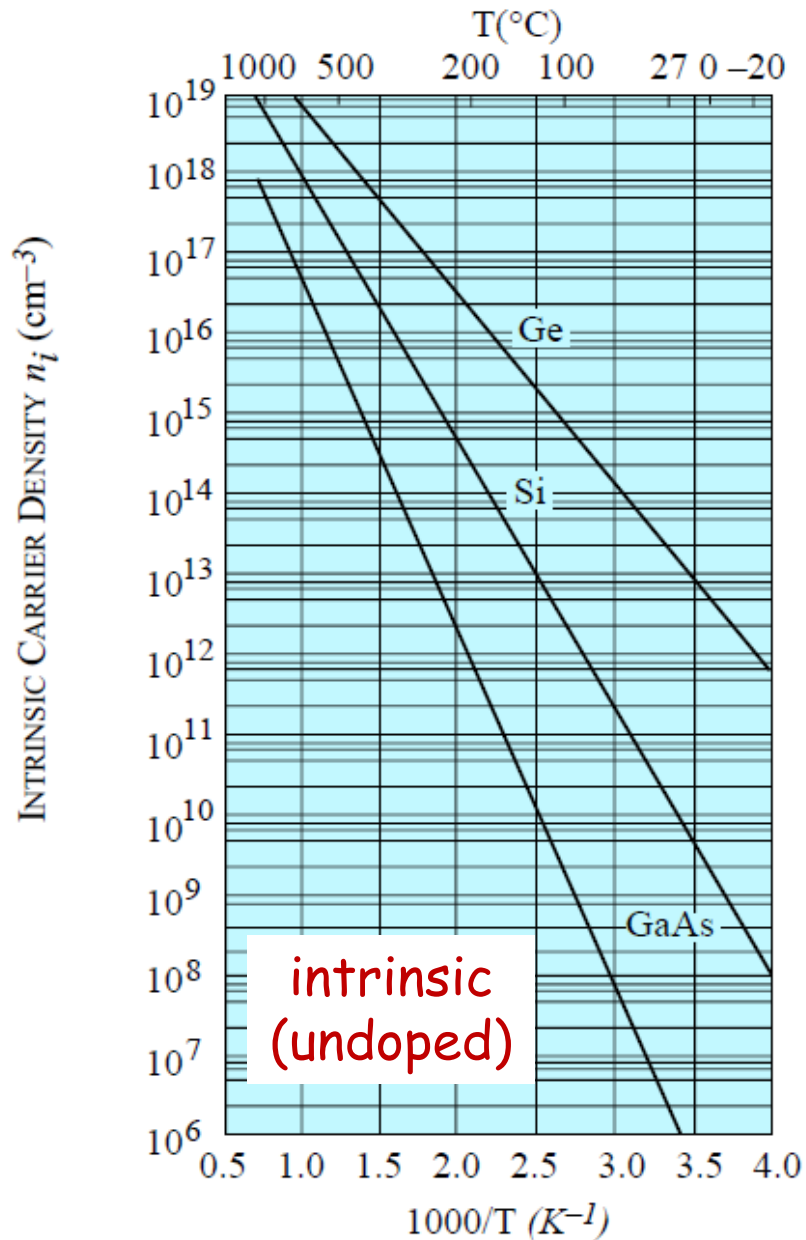
The Fermi level lies very close to the middle of the bandgap.





**Fig. 11** Schematic band diagram, density of states, Fermi-Dirac distribution, and carrier concentrations for (a) intrinsic, (b)  $n$ -type, and (c)  $p$ -type semiconductors at thermal equilibrium. Note that  $pn = n_i^2$  for all three cases.

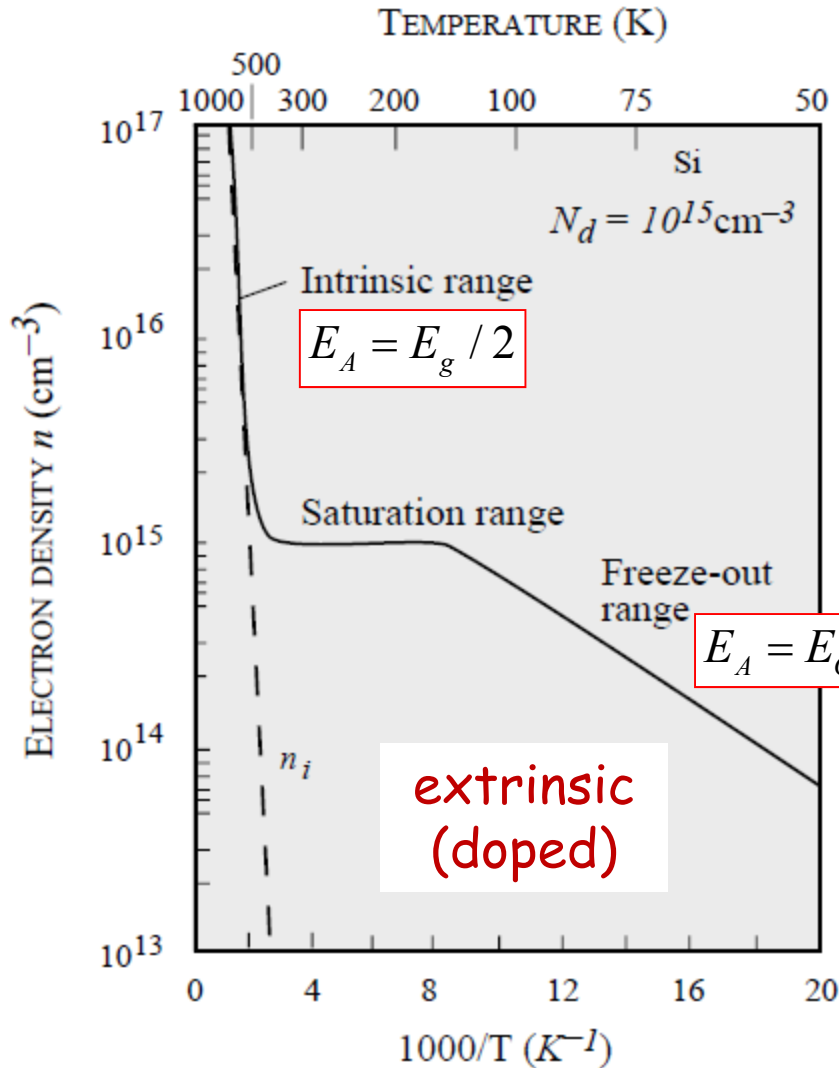
# TEMPERATURE DEPENDENCE, INTRINSIC



$$n_i = \sqrt{N_C N_V} e^{-E_g/2k_B T}$$

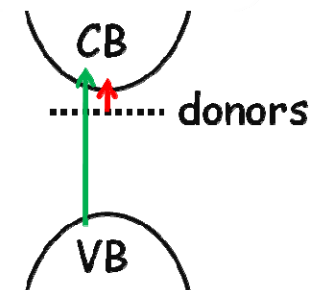
	$E_g$ (eV)
GaAs	1.42
Si	1.12
Ge	0.67

# TEMPERATURE DEPENDENCE, EXTRINSIC



Example: *n*-type silicon with donor concentration  $N_D \sim 10^{15}$

Promotion of electrons from donor to CB results in donor ionization (temp dependent)

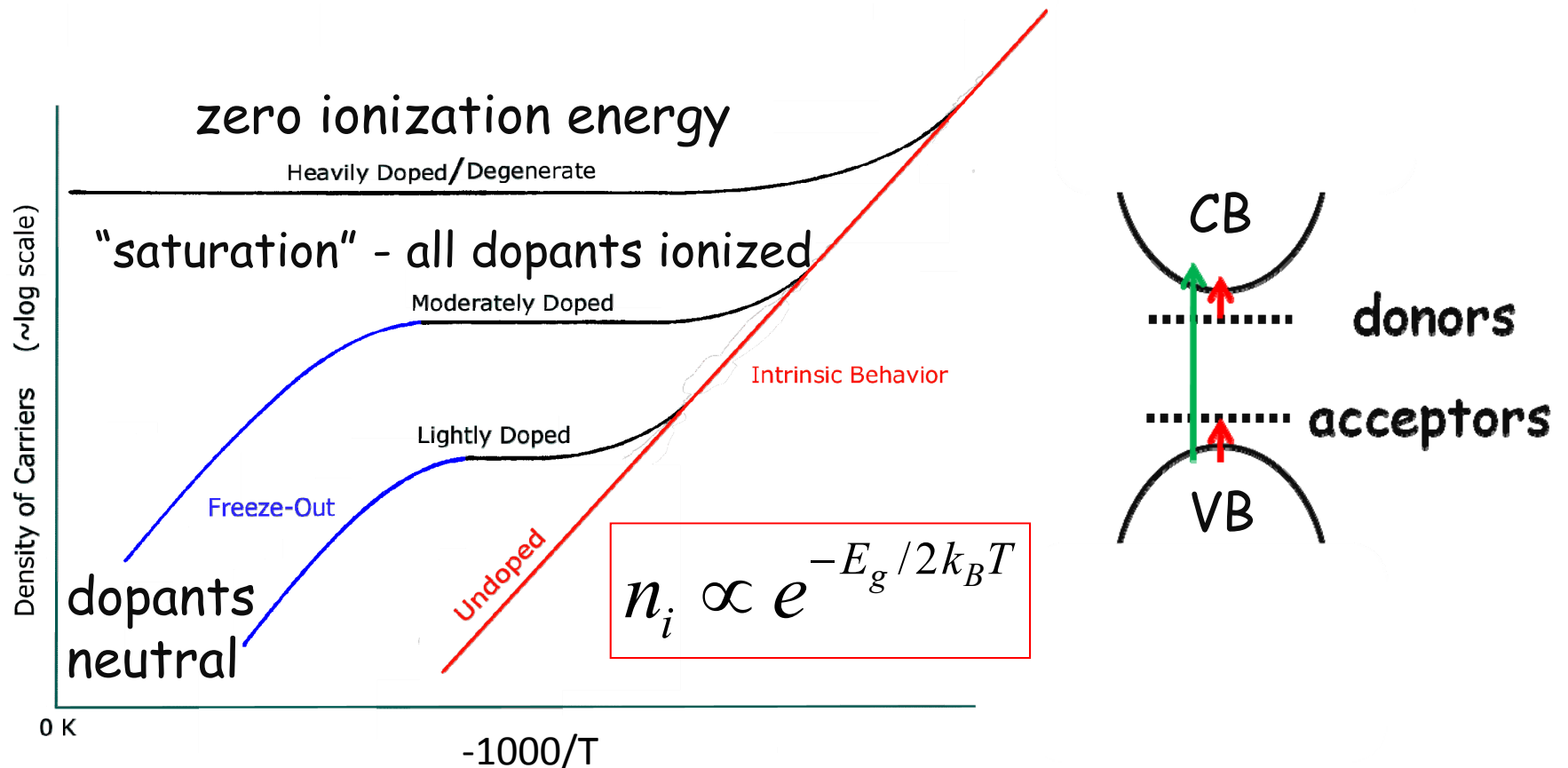


- Freezeout:** Temperature is too small to ionize the donors (acceptors), i.e.,  $k_B T < E_C - E_D$  ( $k_B T < E_D - E_V$ ).
- Saturation:** Most of the donors (acceptors) are ionized.
- Intrinsic:** Temperature is so high that  $n_i >$  doping density.

# TEMPERATURE DEPENDENCE of $n, p$

**Donor ionization** occurs when electrons are promoted to conduction band:  $D \rightarrow D^+ + e^-$

**Acceptor ionization** occurs when electrons are promoted from the valence band to the acceptor state:  $A + e^- \rightarrow A^-$

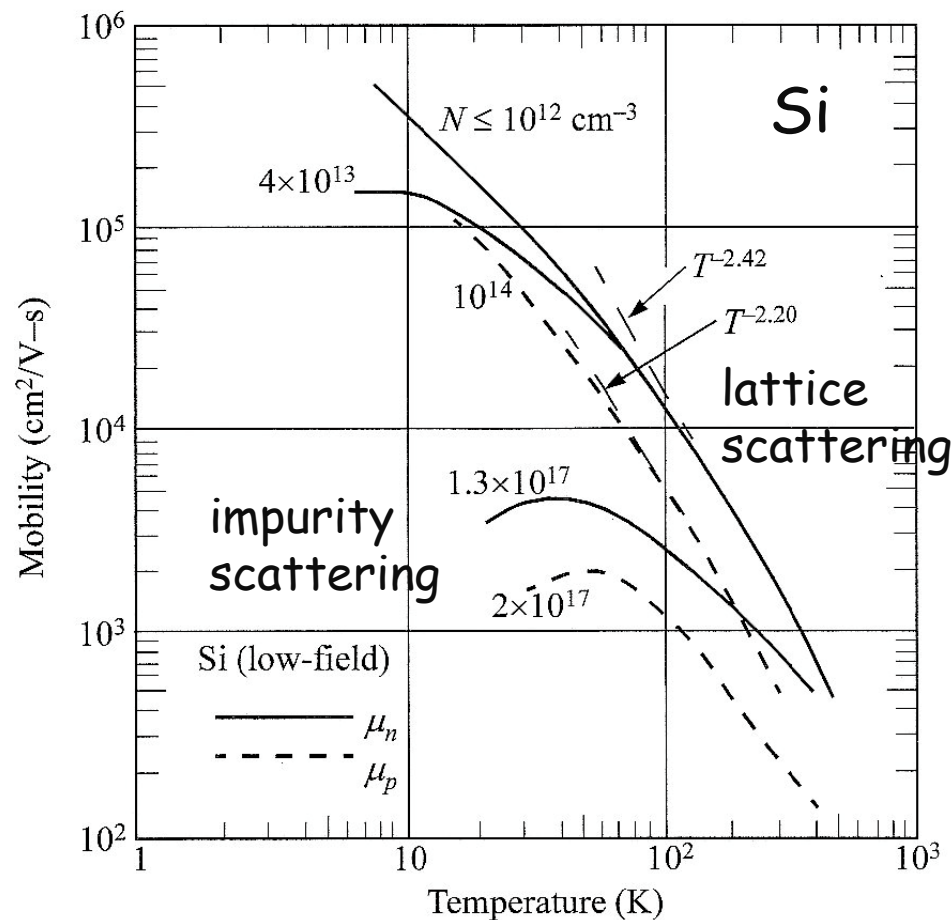


# TEMPERATURE DEPENDENCE of MOBILITY

$$\mathbf{v}_{\text{drift}} = \mu \mathbf{E} ; \mu = e\tau / m^*$$

mobility is the sum of scattering processes, often with one process dominant

$$\mu = \left( \frac{1}{\mu_{\text{lattice}}} + \frac{1}{\mu_{\text{impurities}}} + \dots \right)^{-1}$$



- ionized impurity scattering

$$\mu_i \propto T^{3/2}$$

- acoustic phonon scattering

$$\mu_l \propto T^{-3/2}$$

other scattering mechanisms are possible (surface, defects)

## RT MOBILITIES of SOME SEMICONDUCTORS

Compound	Structure	Bandgap (eV)	e <sup>-</sup> mobility (cm <sup>2</sup> /V-s)	h <sup>+</sup> mobility (cm <sup>2</sup> /V-s)
Si	Diamond	1.11 (I)	1,350	480
Ge	Diamond	0.67 (I)	3,900	1,900
AlP	Sphalerite	2.43 (I)	80	---
GaAs	Sphalerite	1.43 (D)	8,500	400
InSb	Sphalerite	0.18 (D)	100,000	1,700
AlAs	Sphalerite	2.16 (I)	1,000	180
GaN	Wurtzite	3.4 (D)	300	---

# TEMPERATURE DEPENDENCE of SIGMA

intrinsic case:

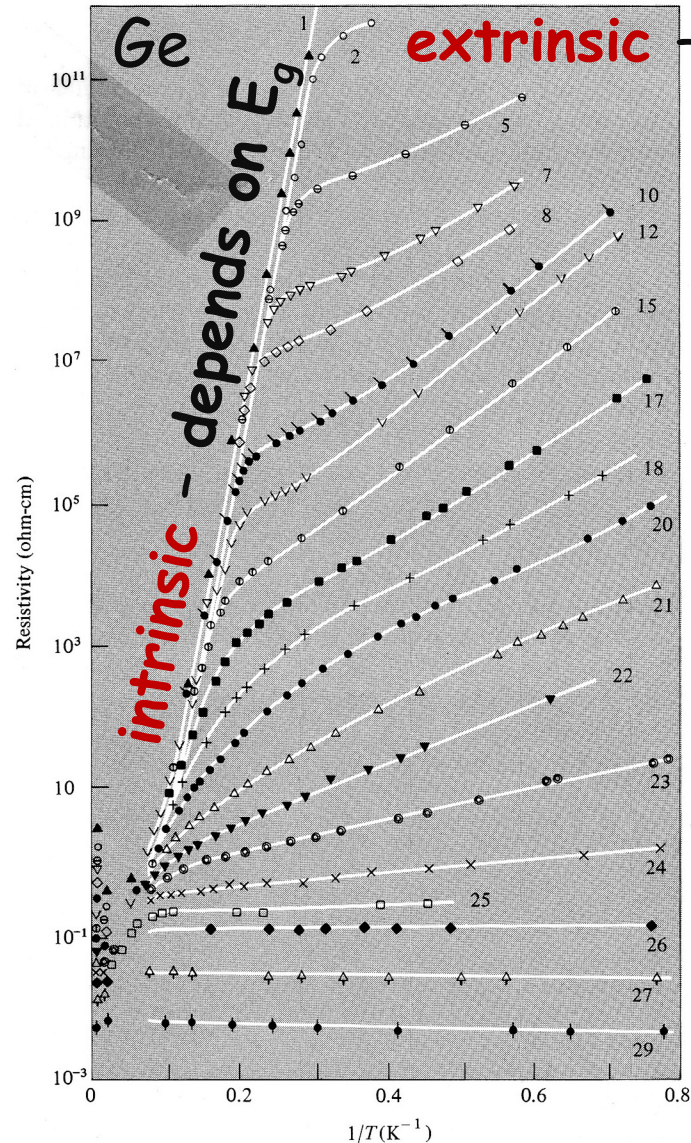
$$\sigma = e(n\mu_e + p\mu_h)$$

→  $\rho = \frac{1}{\sigma} \propto e^{E_g/2k_B T}$

extrinsic (n-type) case:

$$\sigma = ne\mu_e$$

→ complex variation of  $n$  with  $T$



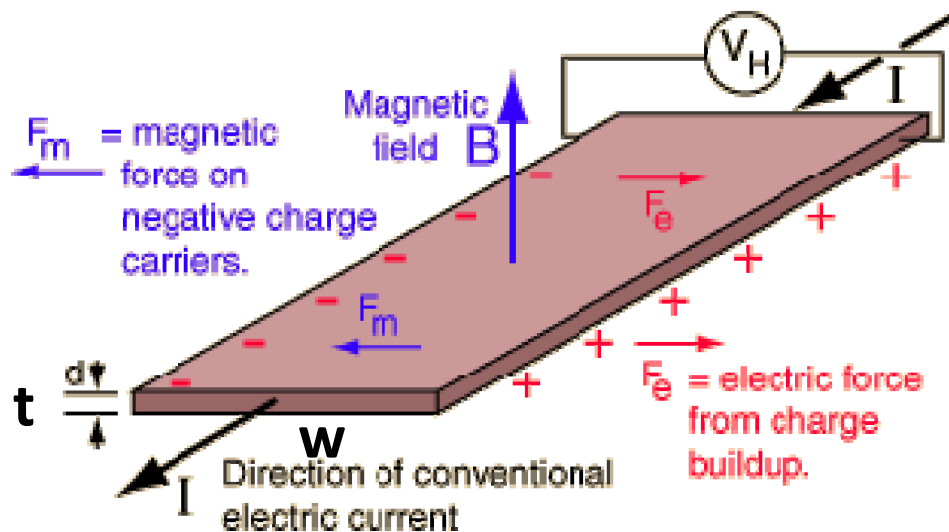
depends on doping

Specimen	Donor concentration (cm <sup>-3</sup> )
1	5.3 x 10 <sup>14</sup>
2	9.3 x 10 <sup>14</sup>
5	1.6 x 10 <sup>15</sup>
7	2.3 x 10 <sup>15</sup>
8	3.0 x 10 <sup>15</sup>
10	5.2 x 10 <sup>15</sup>
12	8.5 x 10 <sup>15</sup>
15	1.3 x 10 <sup>16</sup>
17	2.4 x 10 <sup>16</sup>
18	3.5 x 10 <sup>16</sup>
20	4.5 x 10 <sup>16</sup>
21	5.5 x 10 <sup>16</sup>
22	6.4 x 10 <sup>16</sup>
23	7.4 x 10 <sup>16</sup>
24	8.4 x 10 <sup>16</sup>
25	1.2 x 10 <sup>17</sup>
26	1.3 x 10 <sup>17</sup>
27	2.7 x 10 <sup>17</sup>
29	9.5 x 10 <sup>17</sup>

>10<sup>14</sup> fold variation at low temp

# HALL EFFECT to measure $n, p$

A conductor that carries a current in the presence of a transverse magnetic field develops a voltage across the sample normal to both.



simplest case (n-type):

$$F_m = qvB = \frac{JB}{n} = \frac{IB}{twn}$$

$$F_e = qE_{Hall} = \frac{qV_{Hall}}{w}$$

force balance gives:

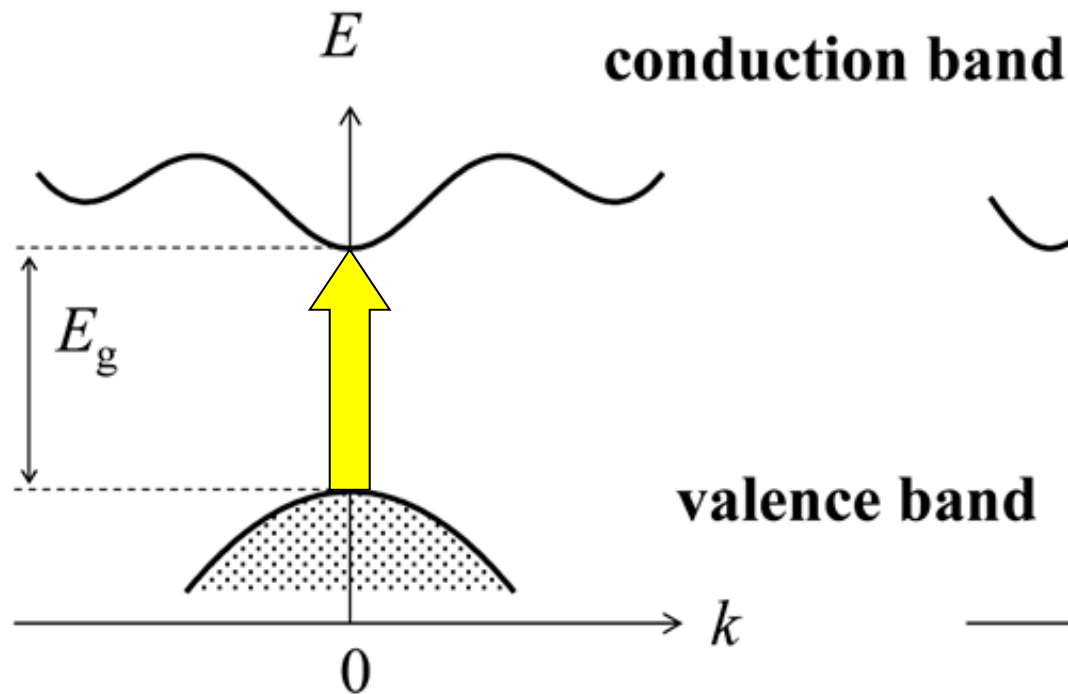
$$V_{Hall} = \frac{1}{qn} \frac{IB}{t}$$



# DIRECT / INDIRECT GAP SEMICONDUCTORS

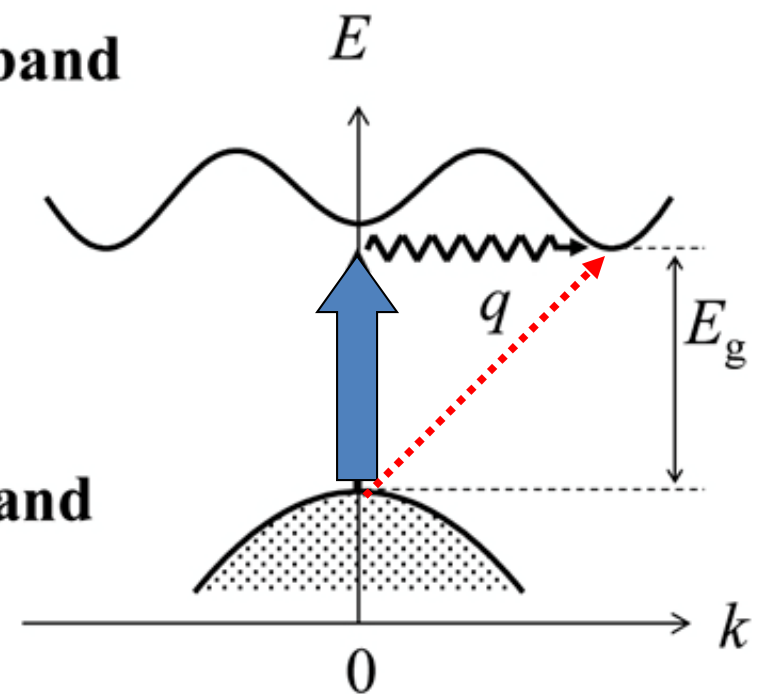
**(a) Direct band gap:**

C.B. minimum at  $k = 0$



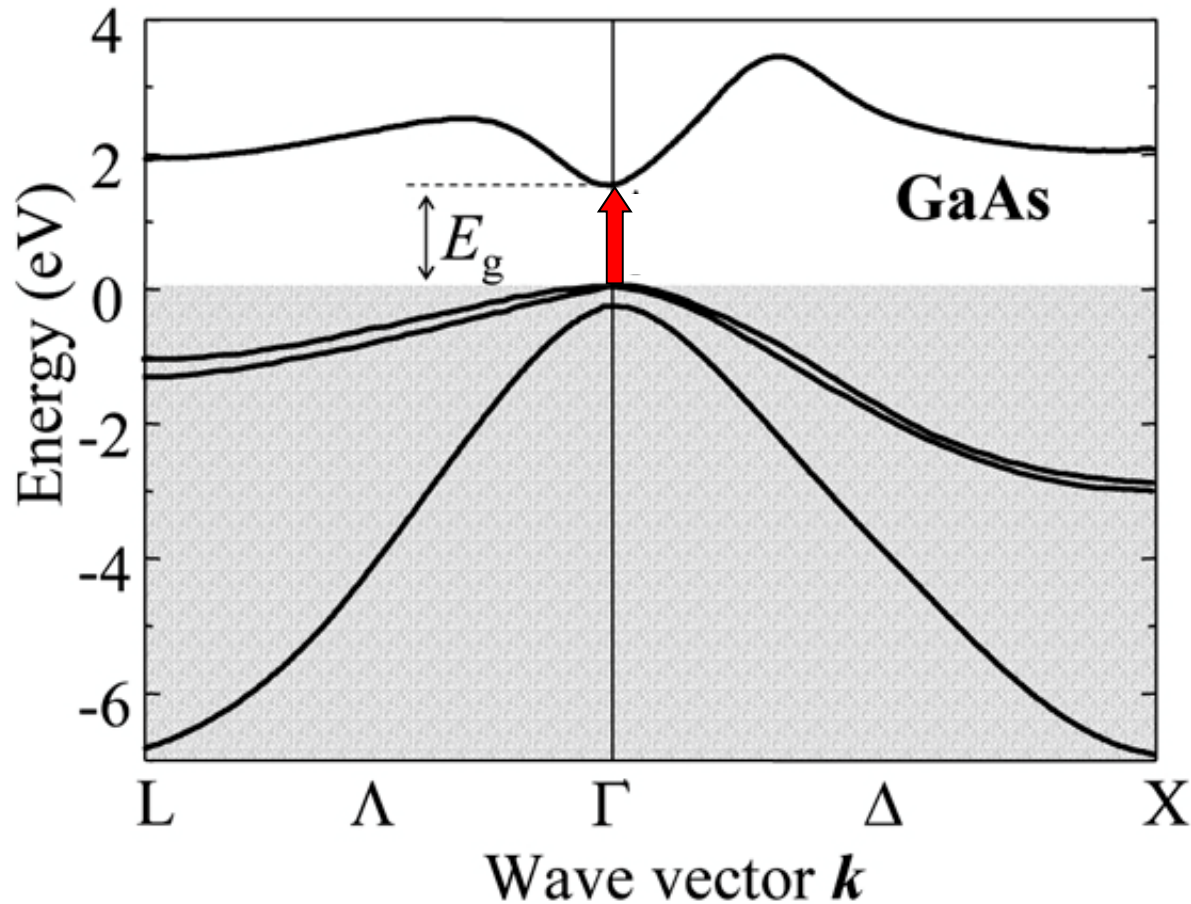
**(b) Indirect band gap**

C.B. minimum at  $k \neq 0$



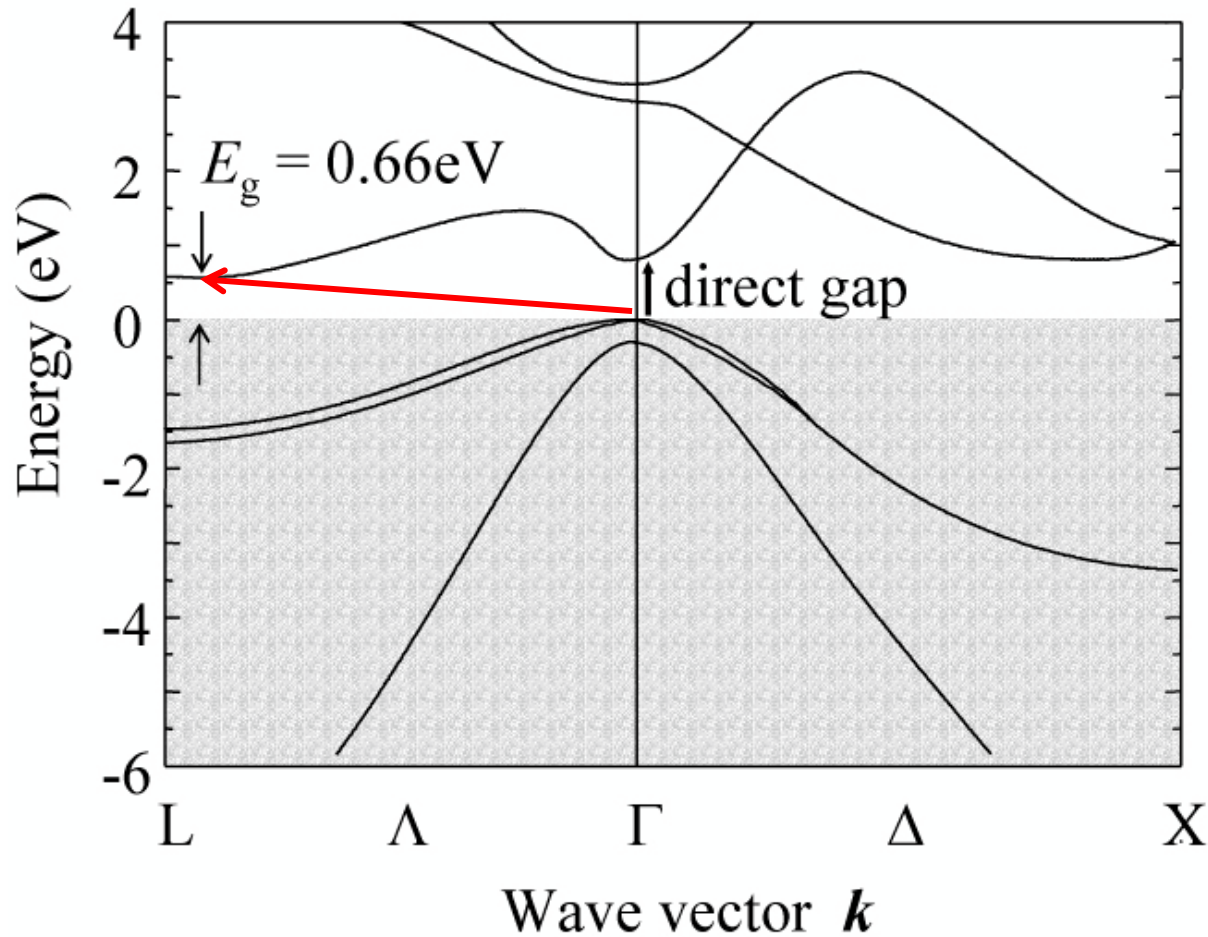
- $k_{\text{photon}} = 2\pi/\lambda \sim 10^7 \text{ m}^{-1}$  negligible compared to B.Z. size  $\pi/a \sim 10^{10} \text{ m}^{-1}$
- Transitions appear as vertical lines on  $E - k$  diagrams
- Phonon needed to conserve momentum for indirect gap materials
- Indirect absorption 2<sup>nd</sup> order process, therefore low probability

# GaAs band structure



- Direct gap at 1.5 eV
- Very important optoelectronic material
- Strong absorption for  $h\nu > E_g$

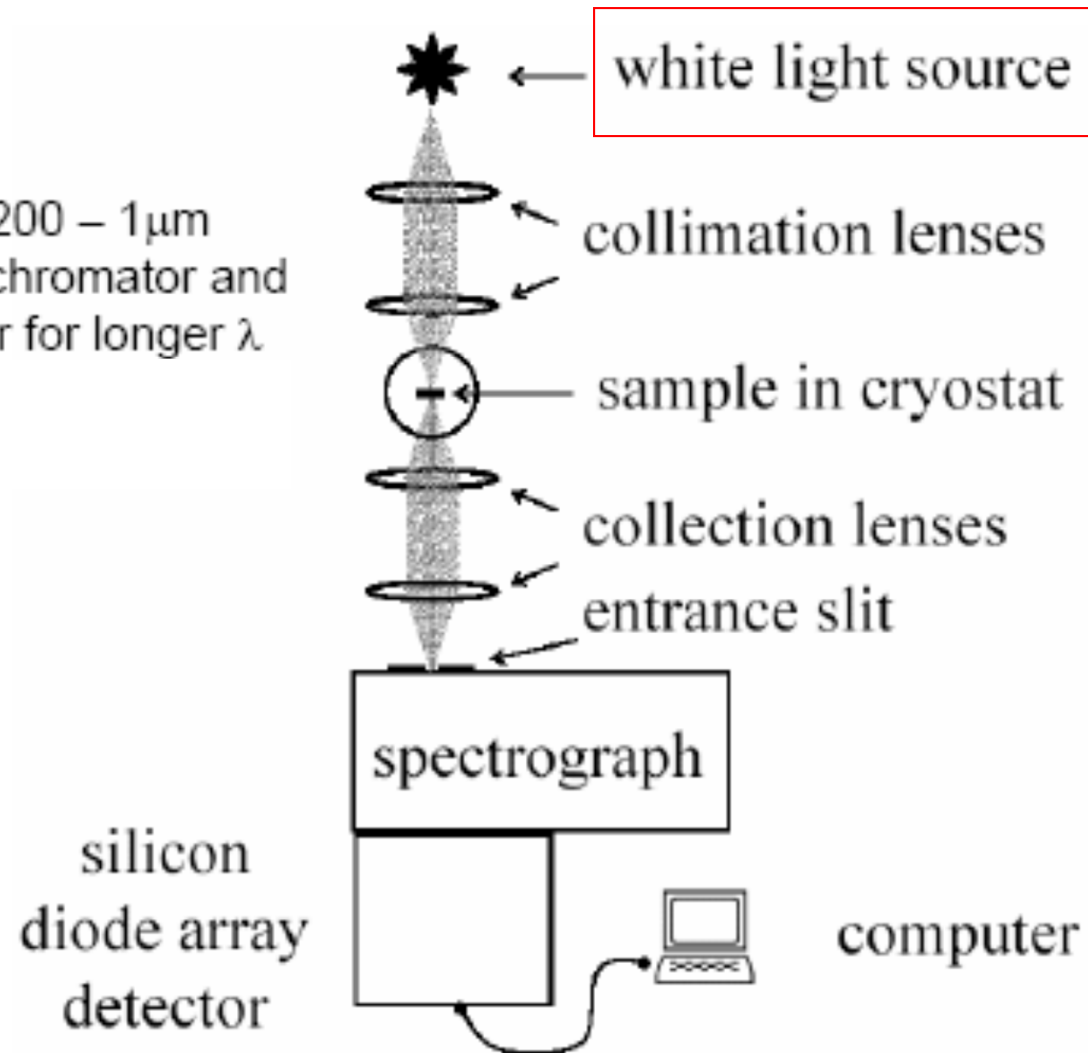
# Germanium band structure



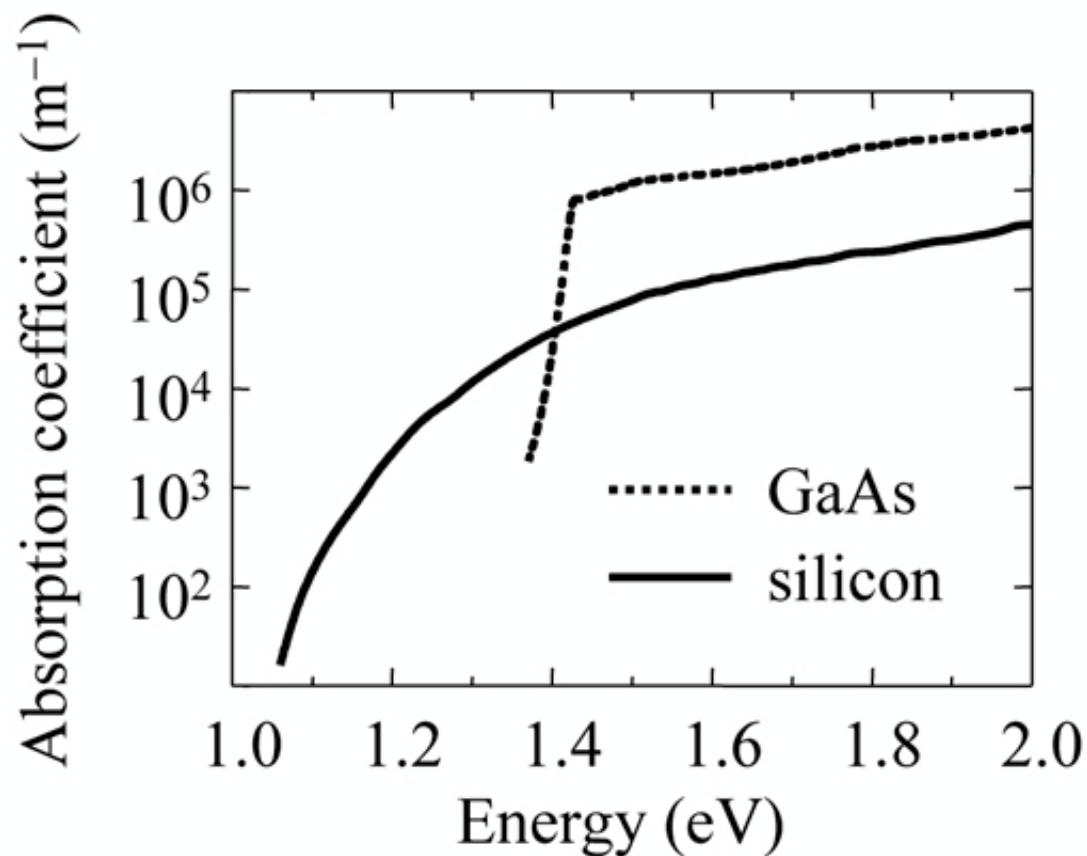
- Indirect gap at 0.66 eV
- Direct gap at 0.80 eV

# ABSORPTION SPECTROSCOPY

- working range: 200 – 1 $\mu$ m
- scanning monochromator and infrared detector for longer  $\lambda$



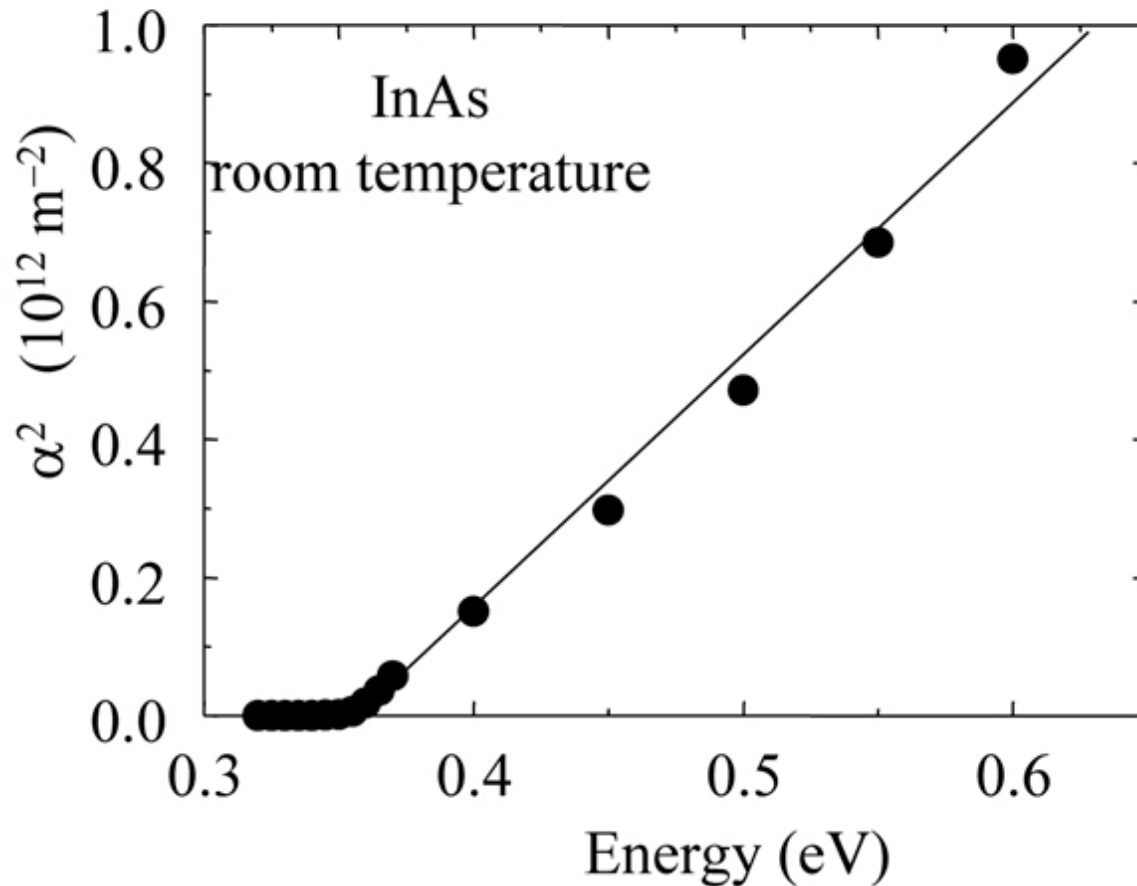
# Direct versus indirect absorption



- Direct absorption is much stronger than indirect absorption
- Silicon has **indirect** gap at 1.1 eV
- GaAs has **direct** gap at 1.4 eV

Implications for solar cells?

# BEHAVIOR NEAR ABSORPTION EDGE



InAs is a direct gap  
III-V semiconductor  
with  $E_g = 0.35 \text{ eV}$

$$h\nu < E_g : \alpha = 0$$

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

General expression:  $\alpha \propto (h\nu - E_g)^\gamma$

# FERMI'S GOLDEN RULE

The rate of an optical transition from a single initial state to a final state is given by:

## Transition Rate for Single State

$$\Gamma_{i \rightarrow f} = \frac{2\pi}{\hbar} E_0^2 \left| \langle f | H' | i \rangle \right|^2 \delta(E_f - E_i - h\nu)$$



square of matrix element  
(strength of coupling)



resonance condition  
(energy conservation)

- $E_0^2$  is light intensity
- $h\nu$  is the photon energy
- in the dipole approximation,  $H' = -e\mathbf{r} \cdot \mathbf{E}$
- derived w/ time-dependent perturbation theory

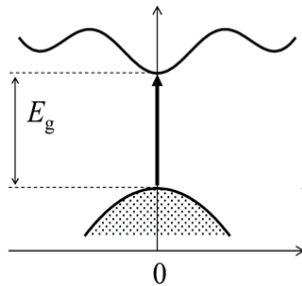
$$\langle f | H' | i \rangle = \int \psi_f^* H' \psi_i d\tau$$

## Transition Rate for Given Wavelength

$$\Gamma = \sum_{f,i} \Gamma_{i \rightarrow f} = \sum_{f,i} \frac{2\pi}{\hbar} E_0^2 \left| \langle f | H' | i \rangle \right|^2 \delta(E_f - E_i - h\nu)$$

$$\approx \frac{2\pi}{\hbar} E_0^2 \left| \langle f | H' | i \rangle \right|^2 \sum_{f,i} \delta(E_f - E_i - h\nu)$$

Let's assume the state  $f$  and  $i$  are conduction and valence band states. Then  $\langle f | H' | i \rangle \rightarrow \langle c | H' | v \rangle$ . We can define the **joint density of states** as

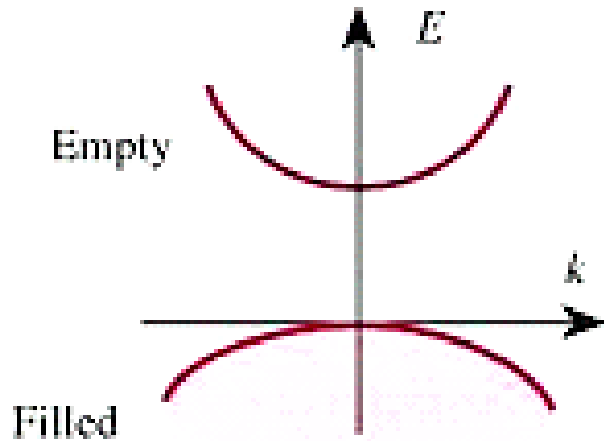


$$\rho_{CV}(h\nu) = \frac{2}{8\pi^3} \int \delta(E_C(k) - E_V(k) - h\nu) d^3k$$

- *vertical (direct) transitions only*

$$\Gamma = \frac{2\pi}{\hbar} E_0^2 \left| H'_{CV} \right|^2 \rho_{CV}(E_C(k) - E_V(k) - h\nu)$$

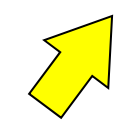




$$E_C(k) = E_C + \frac{\hbar^2 k^2}{2m_e^*}$$

$$E_V(k) = E_V - \frac{\hbar^2 k^2}{2m_h^*}$$

$$E_C(k) - E_V(k) = E_g + \frac{\hbar^2 k^2}{2m_r^*}$$



reduced mass of electron-hole pair (EHP)

$$\begin{aligned} \rho_{CV}(h\nu) &= \frac{2}{8\pi^3} \int \delta(E_C(k) - E_V(k) - h\nu) d^3k \\ &= \frac{2}{8\pi^3} \int \delta(E_g + \frac{\hbar^2 k^2}{2m_r^*} - h\nu) d^3k \end{aligned}$$

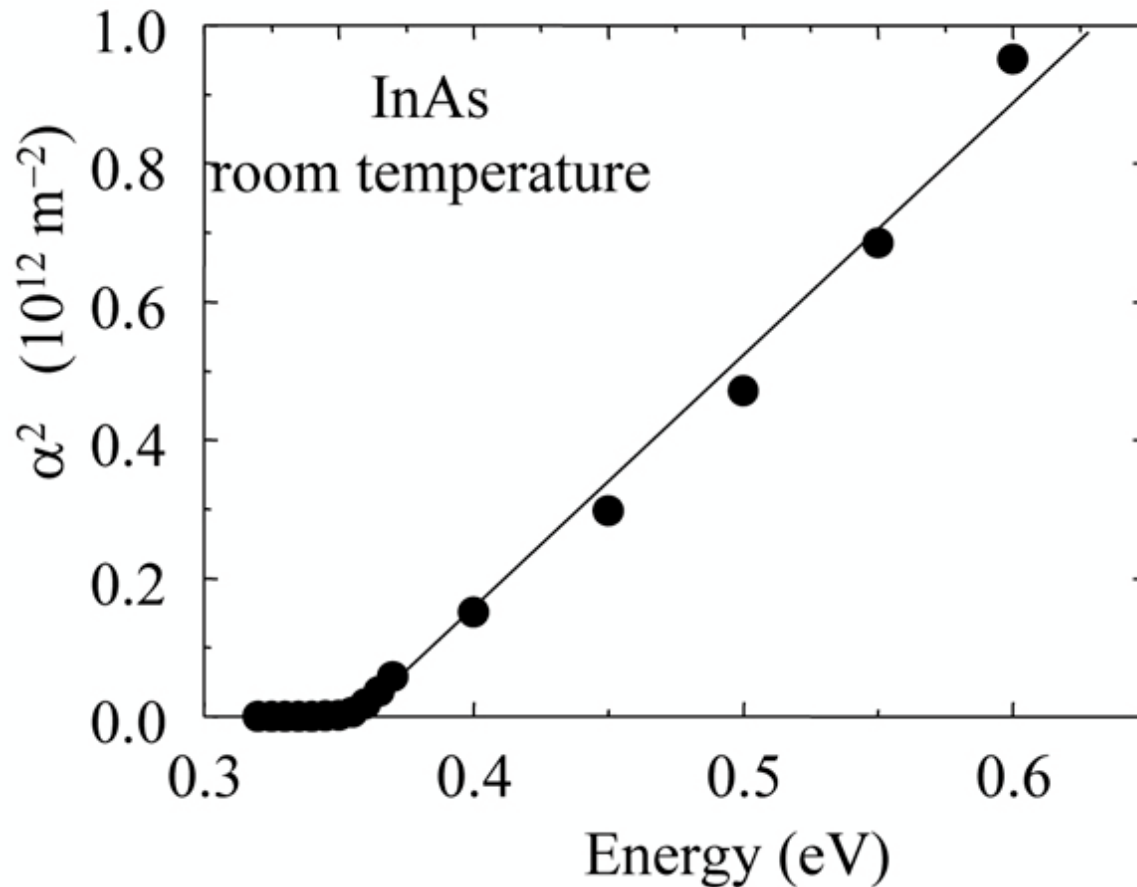
Let  $X = E_g + E - h\nu$      $E = \frac{\hbar^2 k^2}{2m_r^*}$

integral vanishes unless  $X = 0 \Rightarrow E = h\nu - E_g$

parabolic bands  
 free electron DOS:

$$\rho_{CV}(h\nu) = \frac{1}{2\pi^2} \left( \frac{2m_r^*}{\hbar^2} \right)^{3/2} (h\nu - E_g)^{1/2}$$

# InAs band edge absorption



InAs is a direct gap  
III–V semiconductor  
with  $E_g = 0.35 \text{ eV}$

$$h\nu < E_g : \quad \alpha = 0$$

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

# OPTICAL ABSORPTION EDGES

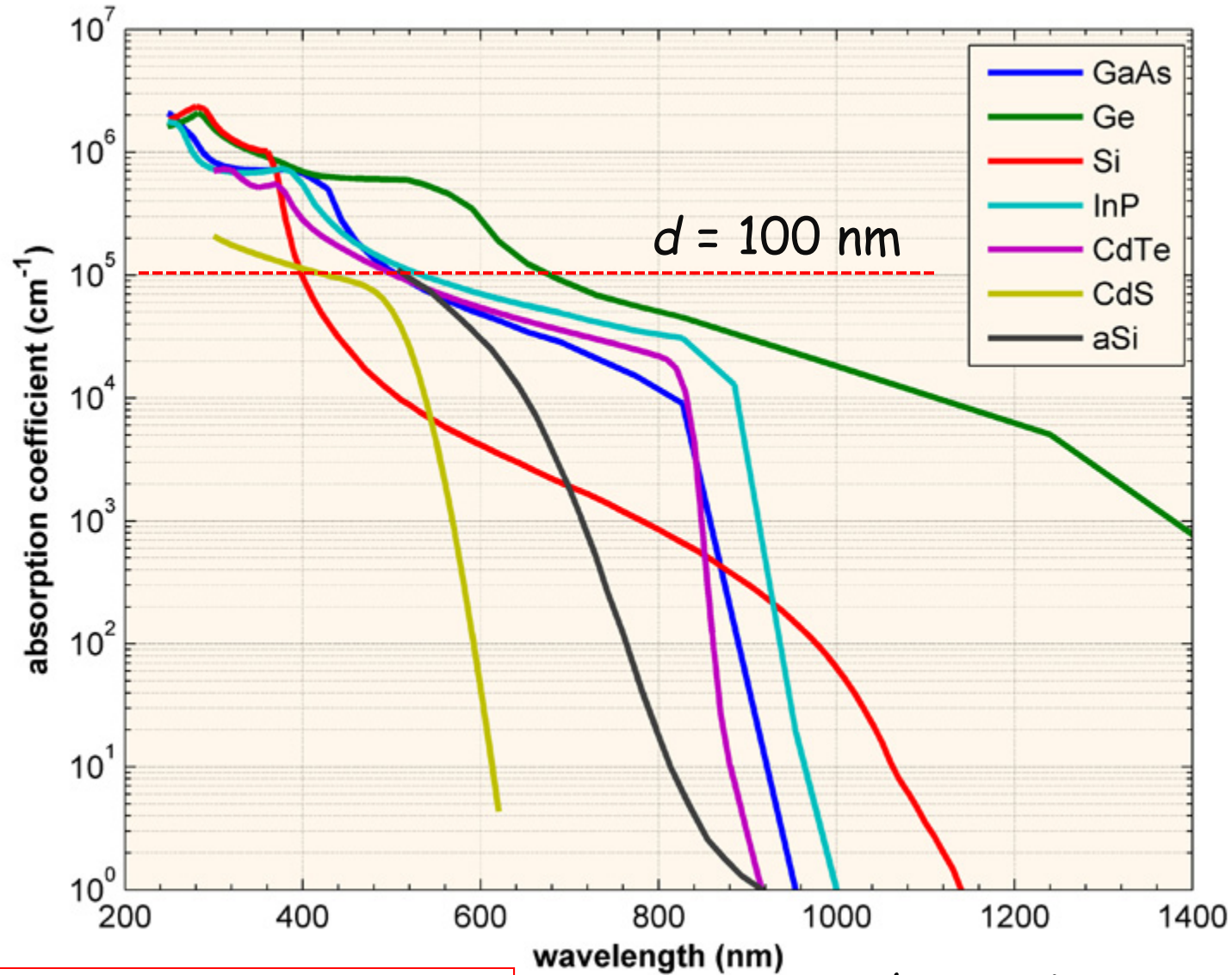
for allowed transitions in the parabolic approximation:

Direct gap:  $\alpha(\nu) = A_d (2m_r^*)^{3/2} (h\nu - E_g)^{1/2}$

Indirect gap:  $\alpha(\nu) = A_i (h\nu - E_g \pm E_{phonon})^2$

the prefactors  $A_d$  and  $A_i$  contain the matrix elements and fundamental constants

# OPTICAL SPECTRA



$$I = I_0 (1 - R) e^{-\alpha x}$$

absorption length:  $d = \frac{1}{\alpha}$

# SEMICONDUCTOR BANDGAPS

## Bandgaps (in eV) of some semiconductors

TETRAHEDRALLY BONDED MATERIALS				
V	C	Si	Ge	$\alpha$ -Sn
C	5.5i,D			
Si	2.6i,Z/W	1.1i,D	0.7-1.1i	
Ge		0.7-1.1	0.74i,D	
$\alpha$ -Sn				0.09,D
III-V	N	P	As	Sb
B	3.8,W	2.0i,Z	1.5i,Z	
Al	5.9,W	2.5,Z	2.2,Z	1.7,Z
Ga	3.5,W	2.4i,Z	1.5,Z	0.81,Z
In	<del>2.4,W</del>	1.4,Z	0.41,Z	0.24,Z
II-VI	O	S	Se	Te
Zn	3.4,W	3.6,Z/W	2.8,Z/W	2.4,Z
Cd	1.3i,R	2.5,Z/W	1.8,Z/W	1.6,Z
Hg	2.2,O/Rh	2.3,T	-0.6,Z	-0.3,Z
I-VII	F	Cl	Br	I
Cu		3.4,Z	3.1,Z	3.1,Z
Ag	2.8i,R	3.2i,R	2.7i,R	3.0,W

i: Indirect gap  
 D: Diamond  
 Z: Zinc Blende  
 W: Wurtzite  
 R: Rocksalt  
 O: Orthorhombic  
 Rh: Rhombohedral  
 T: Trigonal  
 OR: Orthorhombic distorted rocksalt  
 M: Monoclinic

## NON-TETRAHEDRAL BONDED MATERIALS

### IV-VI compounds

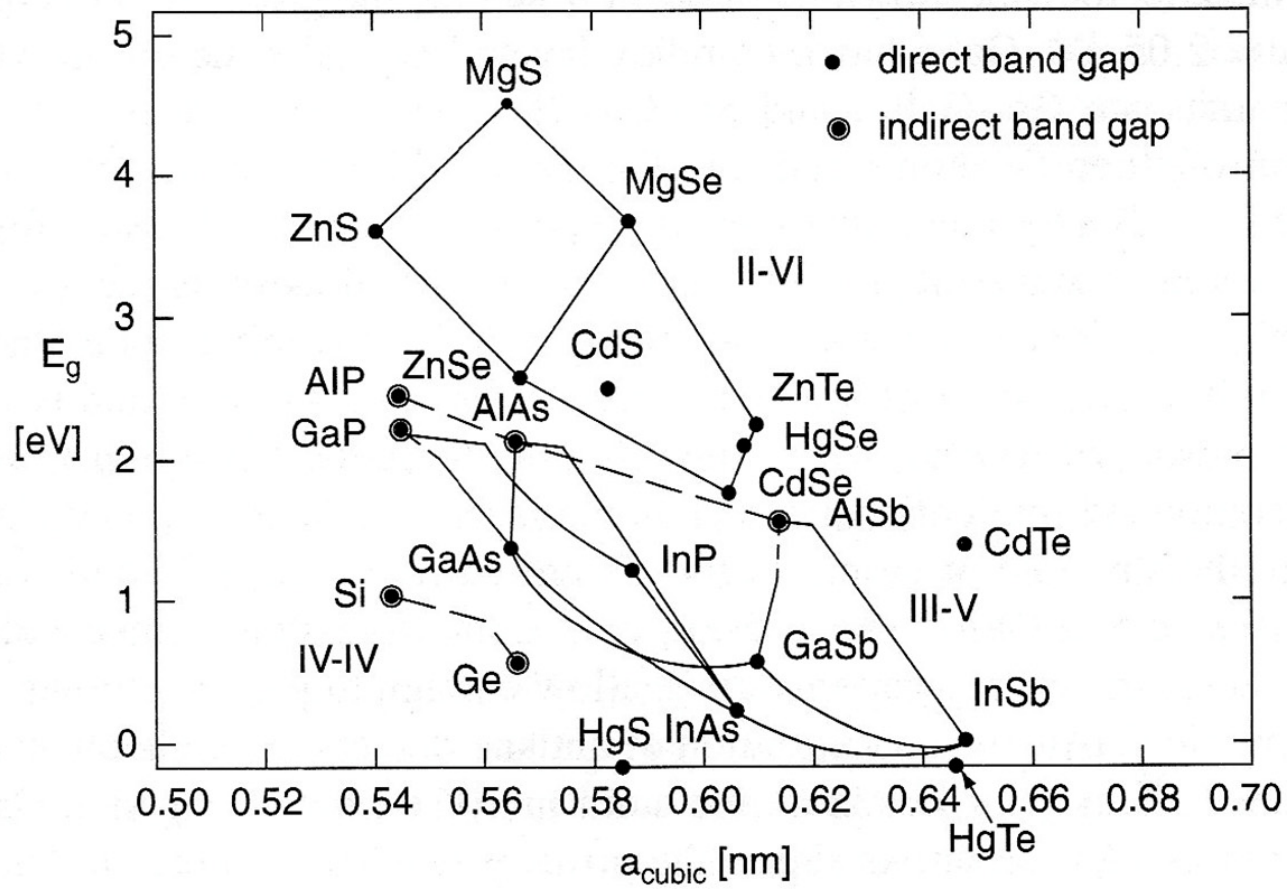
IV-VI	O	S	Se	Te
Ge		1.7,OR	1.1,OR	0.15,R
Sn		1.1,OR	0.9,OR	2.1,R
Pb	2.0,i	0.29,R	0.15,R	0.19,R

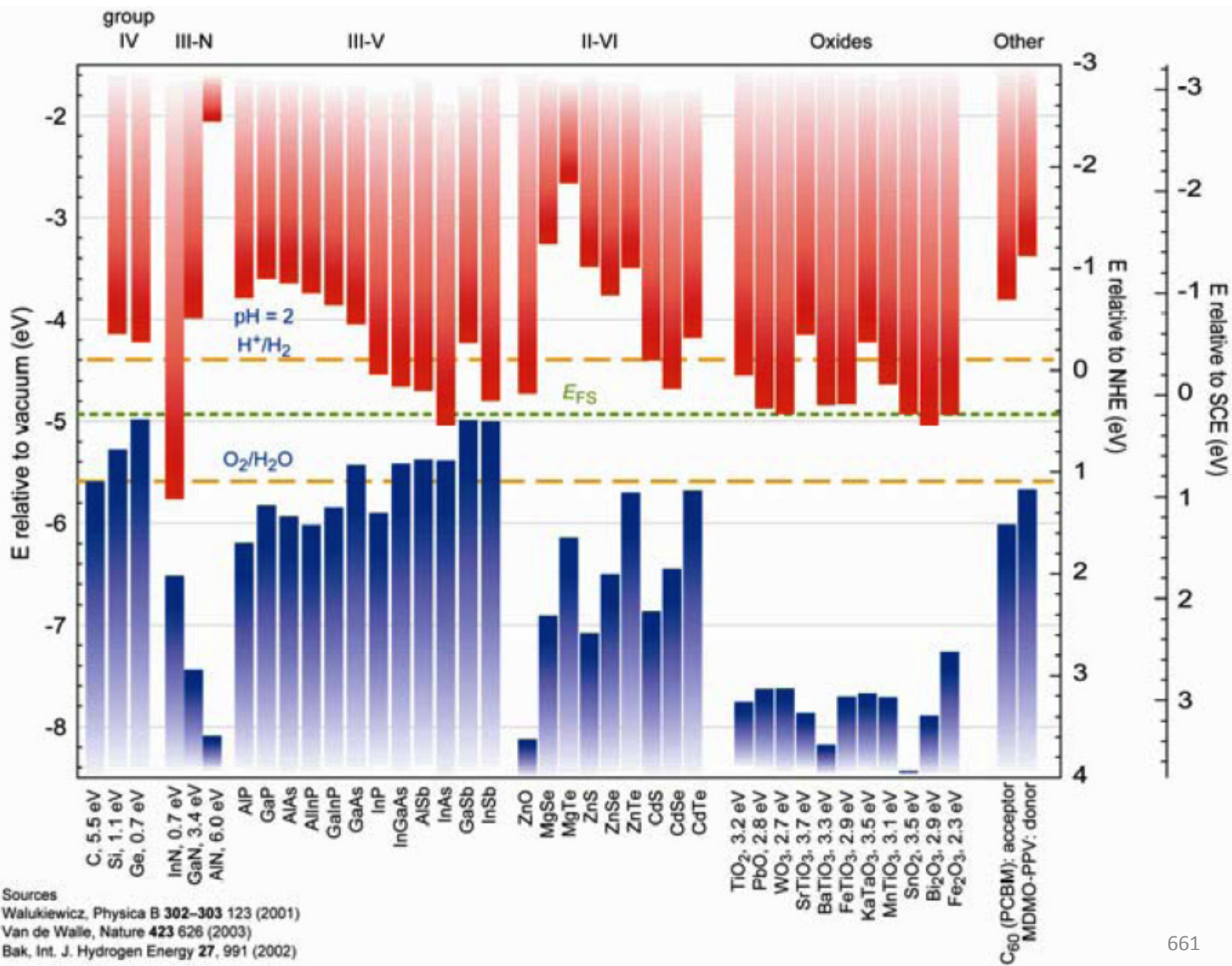
### Group VI elements

VI	S	Se	Te
	3.6,O	1.9i,T 2.5,M	0.33,T

### Group V elements

V	P	As	Sb	Bi
	.33,O	.17,Rh	.10	.015

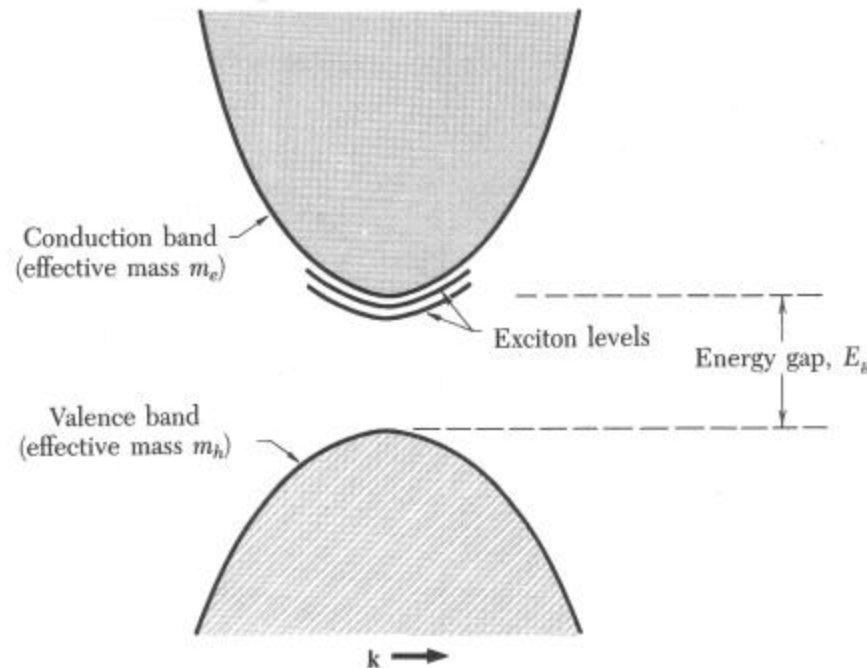




# EXCITONS

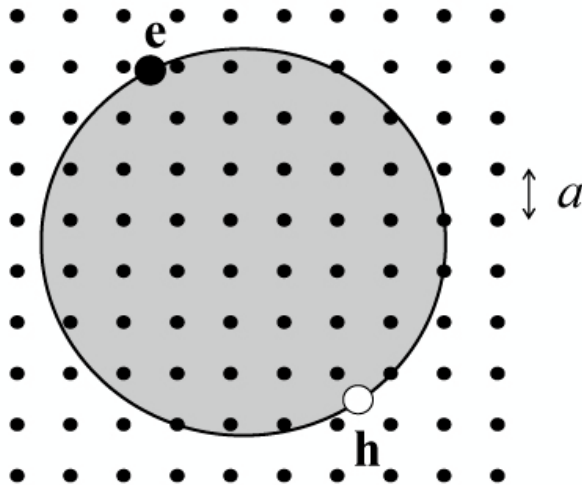
- The annihilation of a photon in exciting an electron from the valence band to the conduction band in a semiconductor can be written as an equation:  $h\nu \rightarrow e^- + h^+$
- Since there is a Coulomb attraction between the electron and hole, the photon energy required is lower than the band gap by this attraction (giving **bound states**).
- To correctly calculate the absorption coefficient we have to introduce a **two-particle state** consisting of an electron attracted to a hole, known as an **exciton** (a quasiparticle).

beyond the independent electron approximation (example of a correlation effect)





# WANNIER and FRENKEL EXCITONS



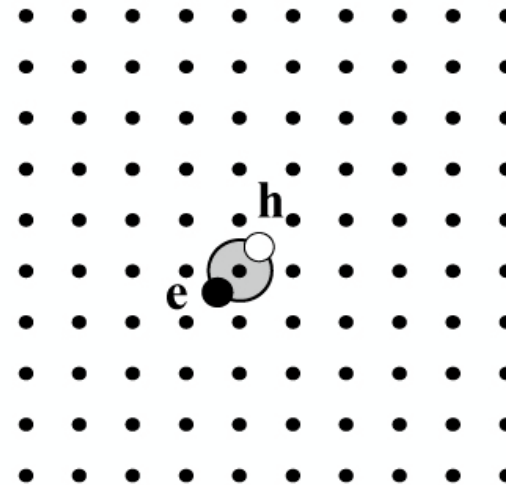
## Free (Wannier)

radius  $\gg a$

small binding energy

moves freely through crystal

**SCs of large dielectric constant**



## Tightly-bound (Frenkel)

radius  $\sim a$

large binding energy

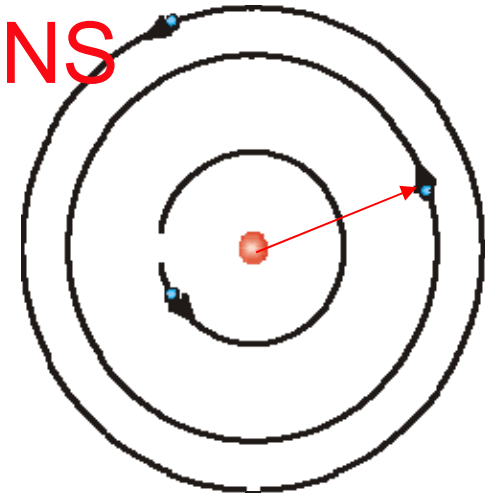
localized on one lattice site

**solids of small dielectric constant**

- Excitons represent *the elementary excitation* of a semiconductor. In the ground state the semiconductor has only filled or empty bands. The simplest excitation is to excite one electron from a filled band to an empty band, so creating an electron and a hole
- Excitons are *neutral* overall but carry an *electric dipole moment* and therefore can be excited by *either a photon or an electron*

# HYDROGENIC MODEL OF EXCITONS

Bohr atom picture, modified with effective mass and dielectric constant of crystal



## Hydrogen Atom:

Circular orbit: centripetal force = Coulombic force

$$\frac{m_e v^2}{r} = \frac{e^2}{4\pi\epsilon_0 r^2}$$

Angular momentum:  $m_e v r = n\hbar$

$$r_n = \frac{4\pi\epsilon_0 n^2 \hbar^2}{m_e e^2} = n^2 a_0$$

$r_1 = \text{Bohr radius} = a_0 = 0.529 \text{ \AA}$

$$\begin{aligned} E &= \frac{1}{2} m_e v^2 + \left( -\frac{e^2}{4\pi\epsilon_0 r} \right) \\ &= \frac{1}{2} \left( \frac{e^2}{4\pi\epsilon_0 r} \right) - \frac{e^2}{4\pi\epsilon_0 r} \\ &= -\frac{1}{2} \frac{e^2}{4\pi\epsilon_0 r} \end{aligned}$$

$$E_n = -\frac{m_e e^4}{2(16\pi^2 \epsilon_0^2) \hbar^2 n^2} = -\frac{R}{n^2}$$

$R (\text{Rydberg}) = 13.606 \text{ eV}$

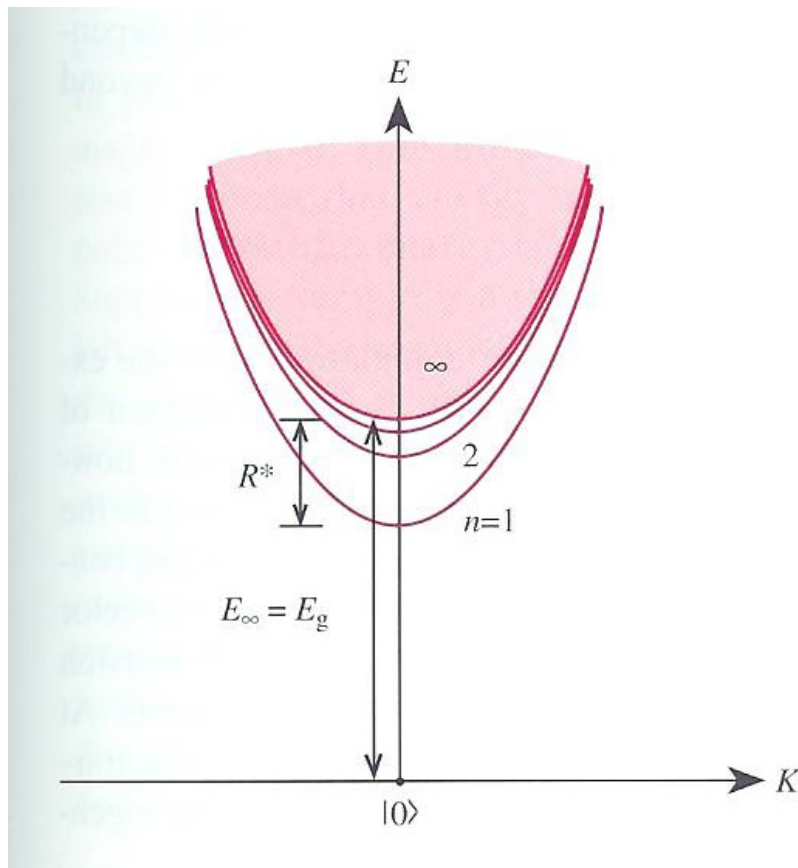
# HYDROGENIC MODEL OF EXCITONS

**Excitons:** 1. Use dielectric constant of crystal

$$U(r) = -\frac{e^2}{4\pi\epsilon\epsilon_0 r}$$

2. Use effective reduced mass

$$\frac{1}{m_r^*} = \frac{1}{m_e^*} + \frac{1}{m_h^*}$$



Exciton Bohr Radius:

$$r_n = \frac{4\pi\epsilon\epsilon_0 n^2 \hbar^2}{m_r^* e^2} = \frac{n^2 \epsilon m_e}{m_r^*} a_0$$

$$r_{ex} = \frac{\epsilon m_e}{m_r^*} 0.529 \text{ \AA}$$

Binding Energy:

$$E_n = -\left(\frac{m_r^*}{m_e \epsilon^2}\right) \frac{R}{n^2} = \frac{R_X}{n^2}$$

# TOTAL EXCITONIC ENERGY

if referenced to the top of the valence band:

$$E_{nlm}(K) = E_g + \frac{\hbar^2 K^2}{2M} - \left( \frac{m_r^*}{m_e \epsilon^2} \right) \frac{R}{n^2}$$



exciton kinetic energy  
(translational motion of  
neutral quasiparticle)



binding energy

## Exciton Parameters for Several SCs

Semiconductor	$E_g$ (eV)	$\epsilon(0)$	$m_r^* / m_e$ $(m_e^* / m_e ; m_h^* / m_e)$	$E_B$ (meV)	$r_{ex}$ (nm)
Si	1.11	11.8	0.190	18.6	3.28
Ge	0.67	16	0.132	7.01	6.41
GaAs	1.42	13.2	0.0616 (0.067, 0.76)	4.81	11.3
InSb	0.163	17.7	0.0135	0.586	69.4
CdSe	1.74		(0.13, 0.45)	15	5.2
Bi	0		0.001	small	> 50
ZnO	3.4		(0.27, ?)	59	3
GaN	3.4		(0.19, 0.60)	25	11

# FREE EXCITON ABSORPTION

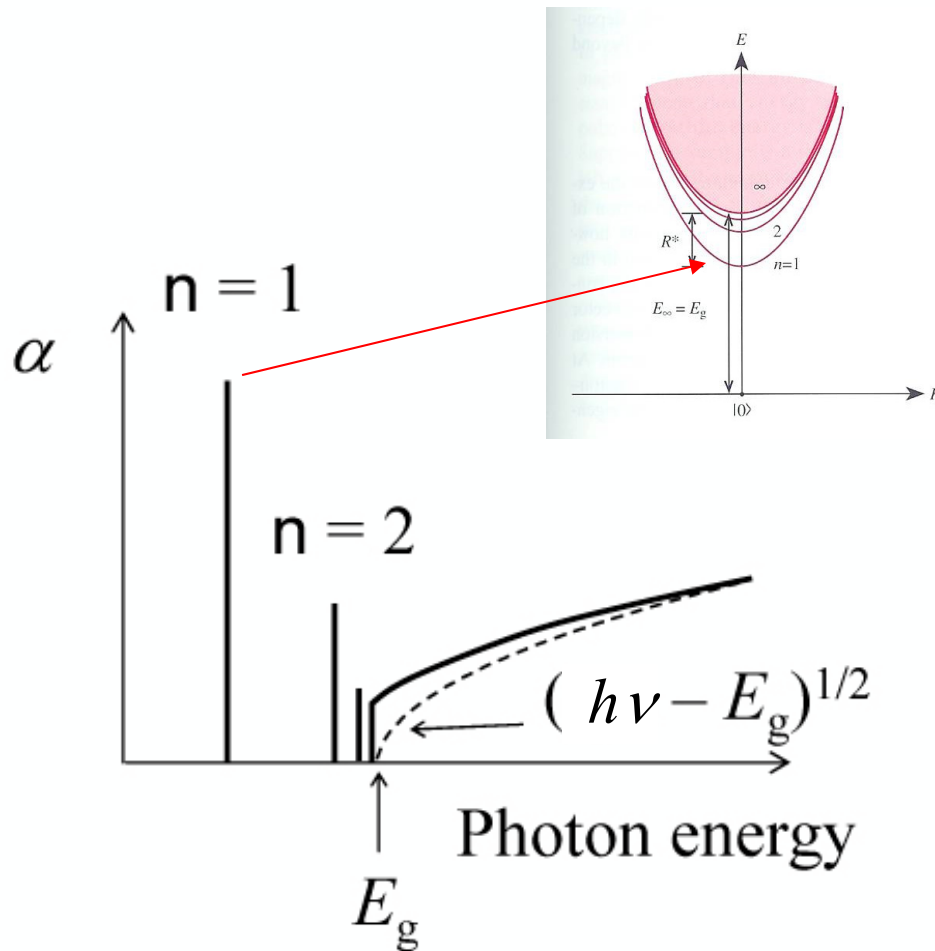
$R_X$  = exciton binding energy

- Hydrogenic series of lines satisfying :  

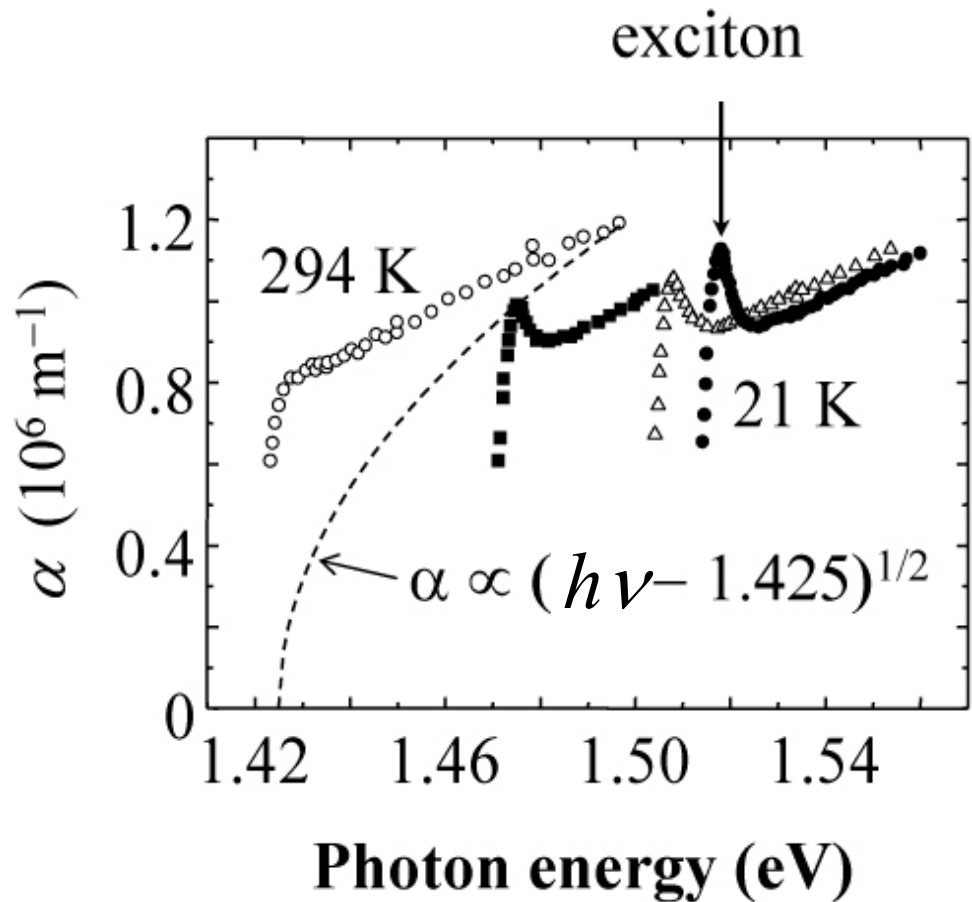
$$h\nu = E_g - R_X / n^2$$

- enhanced absorption for  
 $h\nu > E_g$

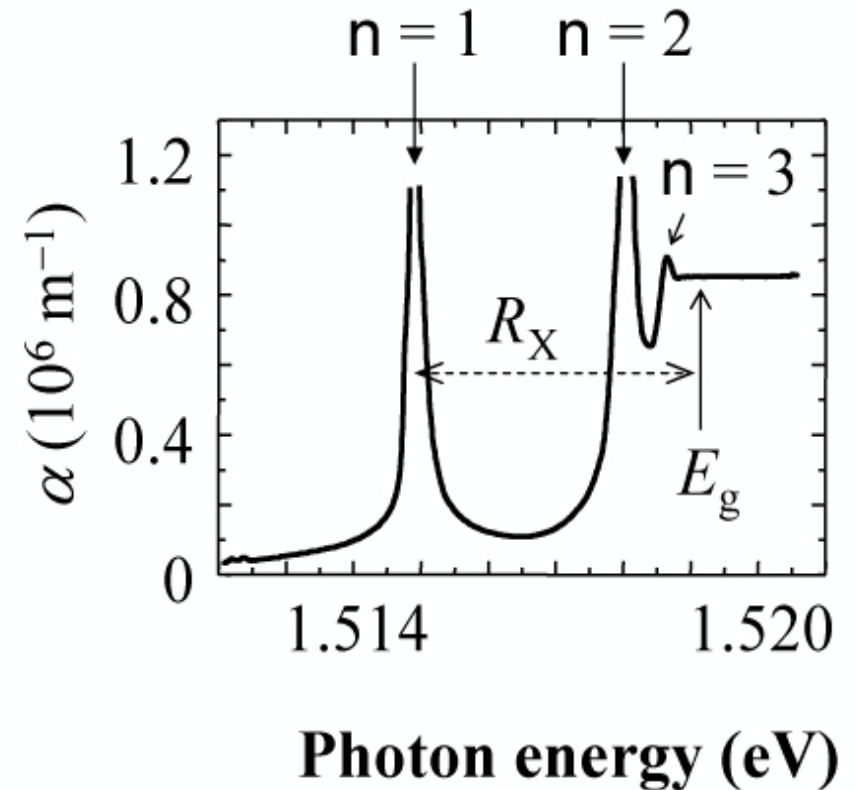
- only observed when  
 $T \leq (R_X / k_B)$



# EXCITONS in BULK GaAs



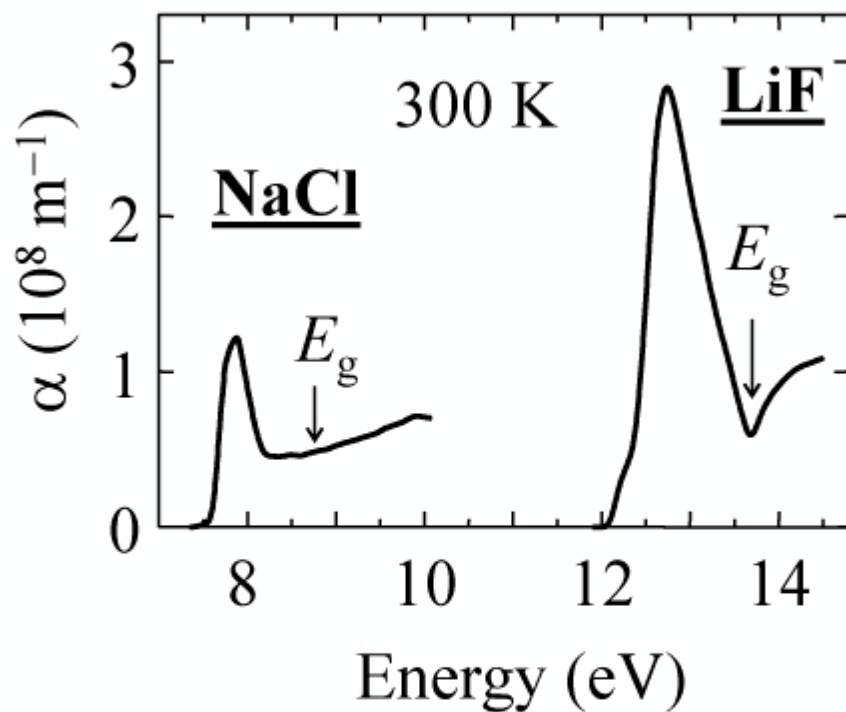
- standard purity sample
- $T = 21 \text{ K} - 294 \text{ K}$



- ultra pure sample
- $T = 1.2 \text{ K}$
- $R_X = 4.2 \text{ meV}$

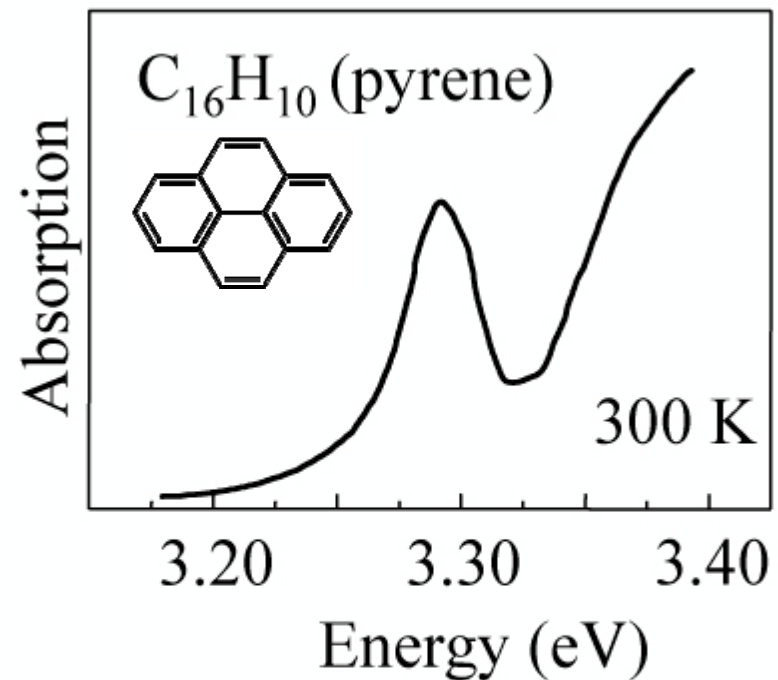
# FRENKEL EXCITONS

Alkali halides



	$E_g$ (eV)	$R_X$ (eV)
NaCl	8.8	0.9
LiF	13.7	1.9

Organic crystals

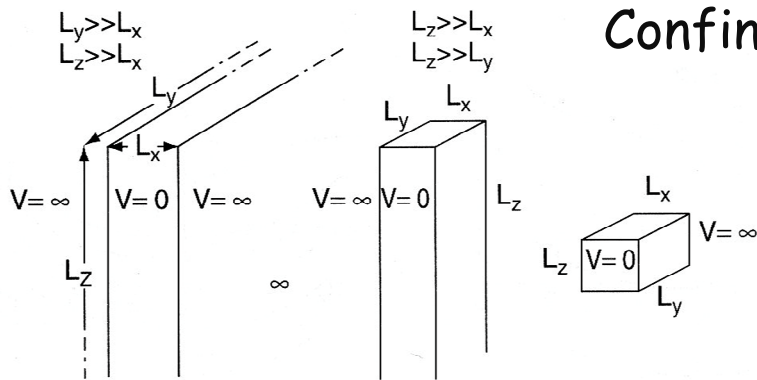


Also: Rare gas crystals  
(solid Ne, Ar, Kr, Xe)



# QUANTUM CONFINEMENT IN NANOSTRUCTURES

Materials with at least one dimension on the scale of the exciton diameter are said to be **quantum confined**. The electronic wavefunction, energy levels, and DOS will depend on the dimension(s).



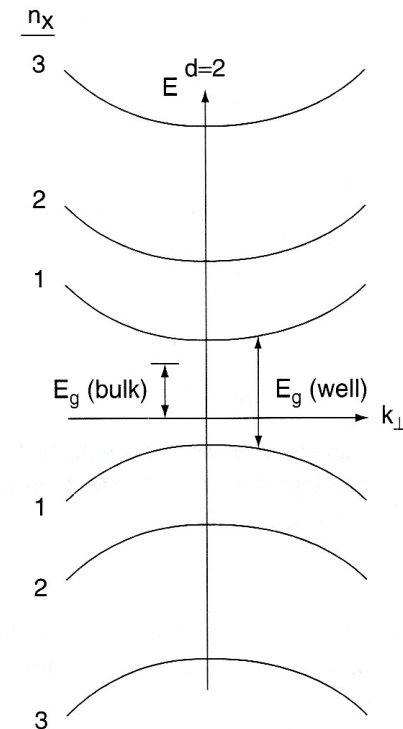
Confinement in 1 dimension = quantum well  
 2 dimensions = quantum wire  
 3 dimensions = quantum dot

**well wire dot**



“Particle in a box” model - energy level separation increases → discrete states

well: 
$$E_g(L_x) = E_{g0} + \frac{n_x^2 h^2}{8m_r^* L_x^2}$$

↑ bulk gap  
 ↑ 1D confinement



dot: 
$$E_g(L_x, L_y, L_z) = E_{g0} + \frac{\hbar^2}{8m_r^*} \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)$$


bulk gap

3D confinement

assumptions: parabolic bands, independent electrons, infinite barriers

TABLE 11.5 Properties of Electrons in Solids of Reduced Dimensionality

	Dimensionality			
	$d = 0$ (Quantum Dot)	$d = 1$ (Quantum Wire)	$d = 2$ (Quantum Well)	$d = 3$ (Bulk)
$\psi_{\mathbf{k}}(\mathbf{r})^a$	$A \sin k_x x (\sin k_y y) (\sin k_z z)$	$A \sin k_x x (\sin k_y y) e^{ik_z z}$	$A (\sin k_x x) e^{i(k_y y + k_z z)}$	$A e^{i(k_x x + k_y y + k_z z)}$
$E(\mathbf{k})^b = E(k_x) + E(k_y) + E(k_z); n_x, n_y, n_z = 1, 2, 3, \dots$	$\frac{\hbar^2}{8m_e^*} \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)$	$\frac{\hbar^2}{8m_e^*} \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} \right) + \frac{\hbar^2 k_z^2}{2m_e^*}$	$\frac{\hbar^2 n_x^2}{8m_e^* L_x^2} + \frac{\hbar^2 (k_y^2 + k_z^2)}{2m_e^*}$	$\frac{\hbar^2 (k_x^2 + k_y^2 + k_z^2)}{2m_e^*}$
$\rho_e(E)^{b,c}$	Discrete states	$\frac{\sqrt{2m_e^*}}{\pi \hbar L_x L_y} E^{-1/2}$	$\frac{m_e^*}{\pi \hbar^2 L_x}$	$\frac{1}{2\pi^2} \left( \frac{2m_e^*}{\hbar^2} \right)^{3/2} E^{1/2}$
$k_F^d$	— <sup>e</sup>	$\frac{\pi n L_x L_y}{2}$	$\sqrt{2\pi n L_x}$	$(3\pi^2 n)^{1/3}$

<sup>a</sup>The components of the wave vector  $\mathbf{k}$  of the electron are given by  $k_x = n_x \pi / L_x$ ,  $n_x = 1, 2, \dots$ .

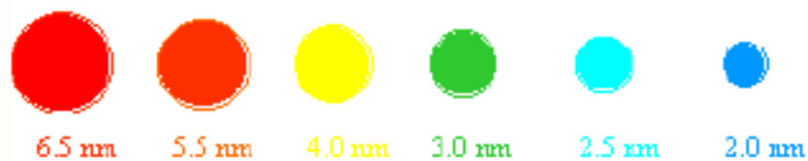
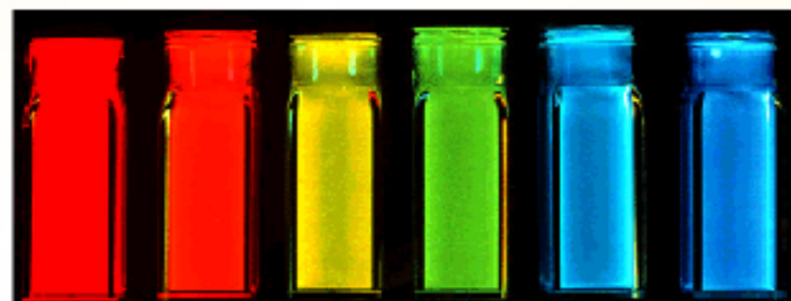
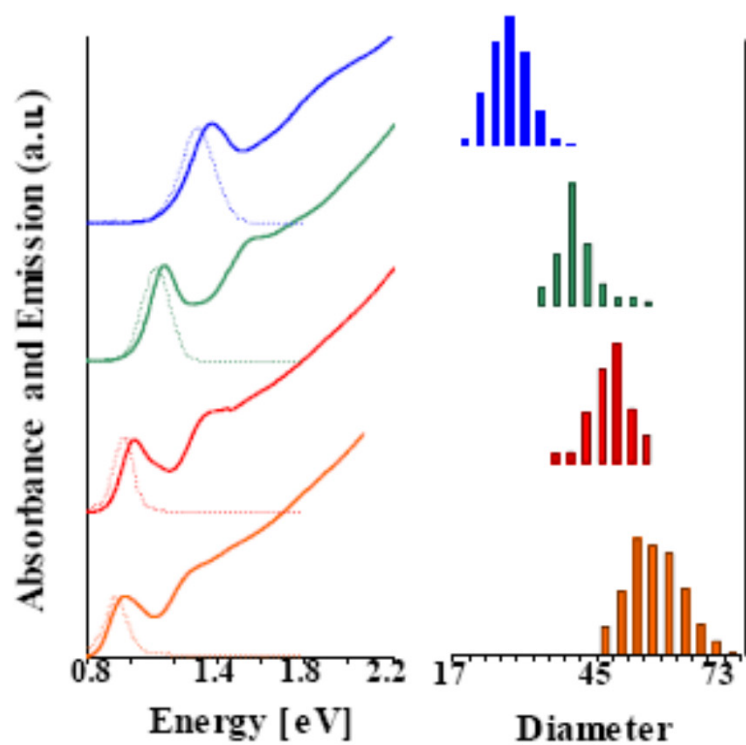
<sup>b</sup>The electron (or hole) effective mass or masses appropriate to the direction or the plane of motion should be used in  $E(\mathbf{k})$  and  $\rho_e(E)$ .

<sup>c</sup>Density of electron states per unit energy and unit volume.

<sup>d</sup> $n$  = electron concentration =  $N / L_x L_y L_z$ , where  $N$  is the number of electrons confined in the region. Note that  $n_{3d} = n$ ,  $n_{2d} = n L_x$ , and  $n_{1d} = n L_x L_y$ .

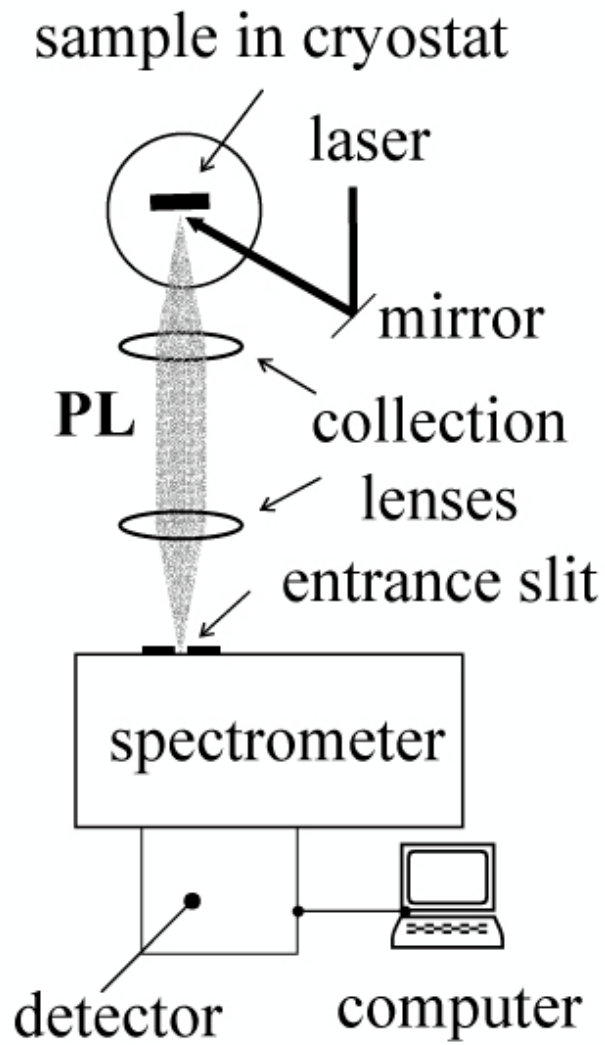
<sup>e</sup>For  $d = 0$ ,  $k_F = k_{\max}$ , where  $k_{\max}$  is the maximum value of  $k = \pi (n_x^2 / L_x^2 + n_y^2 / L_y^2 + n_z^2 / L_z^2)^{1/2}$  for any electron in the quantum dot.

## InAs nanocrystals (Banin group)



CdSe nanocrystals  
(Bawendi group)

# Photoluminescence spectroscopy



## **Photoluminescence (PL) spectroscopy**

- fixed frequency laser, measure spectrum by scanning spectrometer

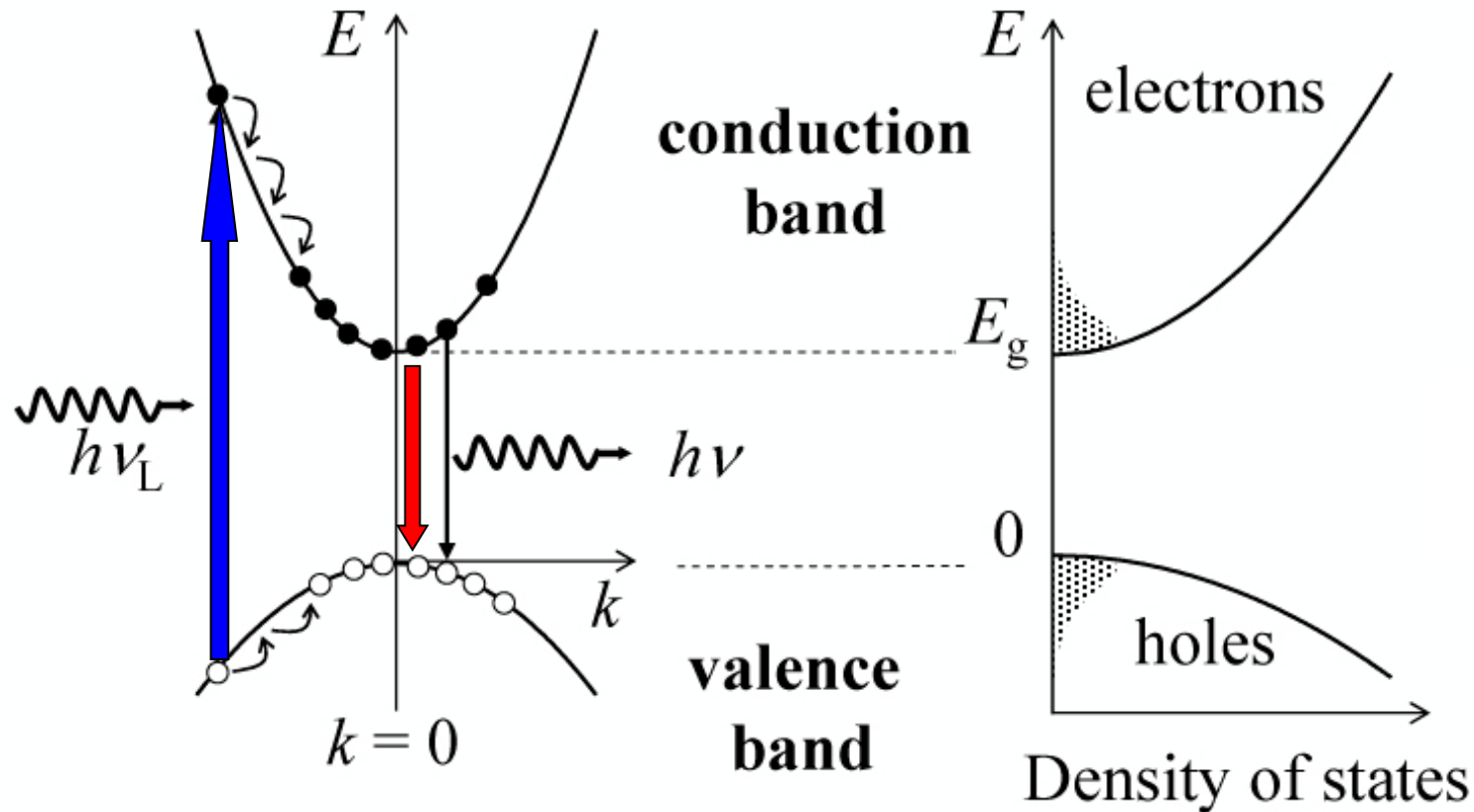
## **PL excitation spectroscopy (PLE)**

- detect at peak emission, vary laser frequency
- effectively measures absorption

## **Time-resolved PL spectroscopy**

- short pulse laser + fast detector
- measure lifetimes, relaxation processes

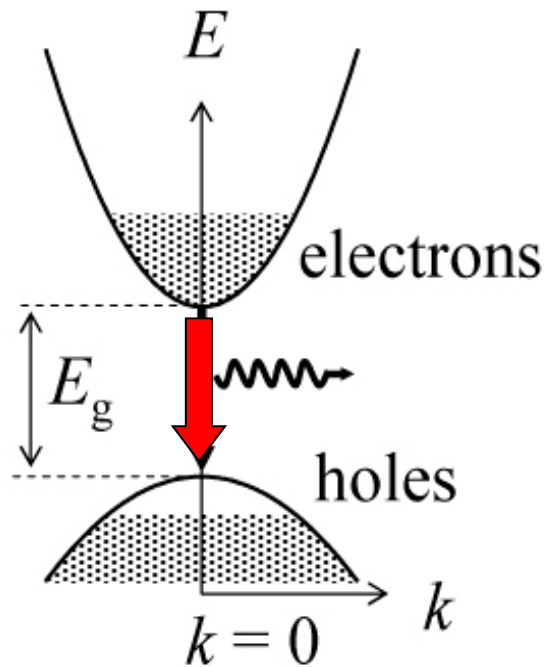
# Photoluminescence



- Excite using laser with photon energy  $> E_g$
- electrons and holes relax to the bottom of their bands
- thermal distributions formed according to **statistical mechanics**
- emission from  $E_g$  to top of carrier distributions

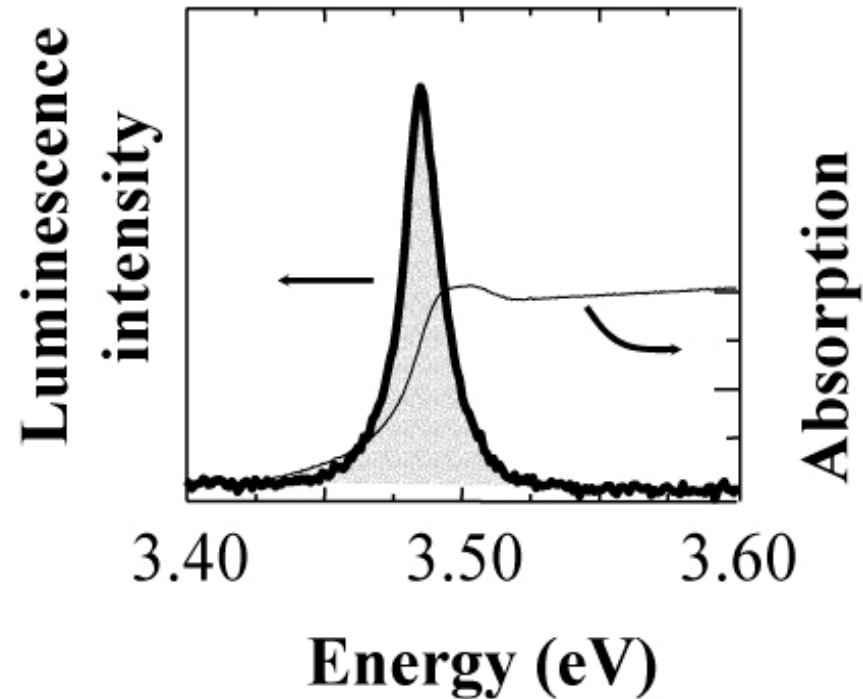
# Direct gap materials

**conduction band**



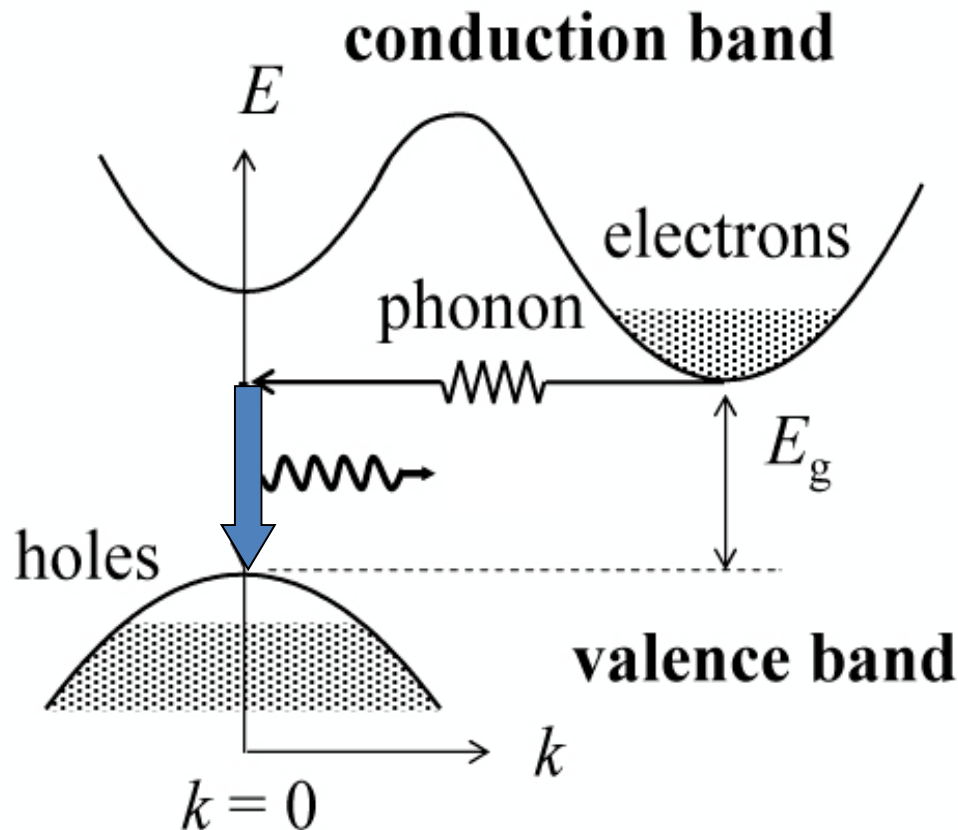
**valence band**

GaN  
 $T = 4 \text{ K}, E_g = 3.50 \text{ eV}$



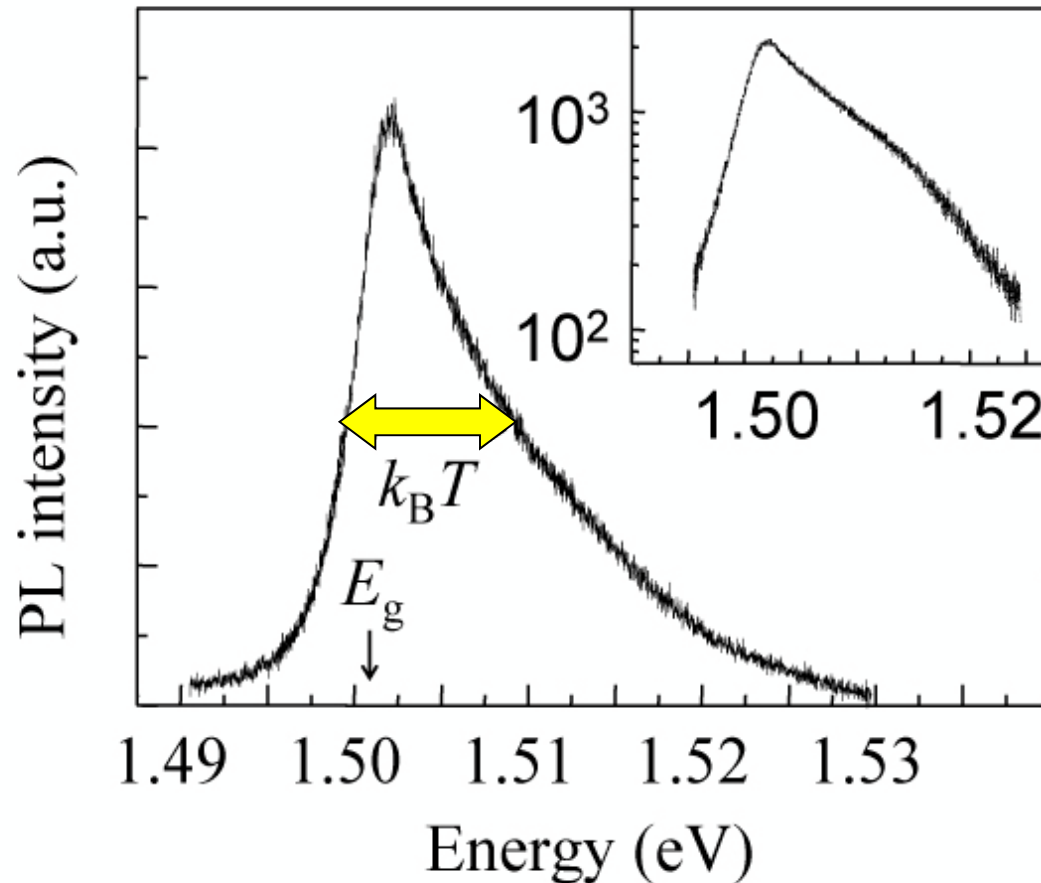
- Strong emission at the band gap
- most III-V and II-VI semiconductors
- linewidth  $\geq k_B T$

# Indirect gap materials



- Low emission probability (2nd order process)
- Long radiative lifetime  $\Rightarrow$  low radiative quantum efficiency
- diamond, silicon, germanium, AlAs

# Classical (Boltzmann) Statistics



GaAs

$T = 100 \text{ K}$

$k_B T = 8.6 \text{ meV}$

$E_g = 1.501 \text{ eV}$

Fermi's golden rule

$$\text{Rate} \propto |M|^2 \rho(h\nu)$$

- Boltzmann statistics:  $f(E) \propto \exp(-E/k_B T)$  (**occupancy factors**)
- $I(E) \propto \text{Density of states} \times f_e(E) f_h(E) \propto (h\nu - E_g)^{1/2} e^{-h\nu/k_B T}$
- PL rises sharply at  $E_g$ , then decays exponentially. Linewidth  $\sim k_B T$



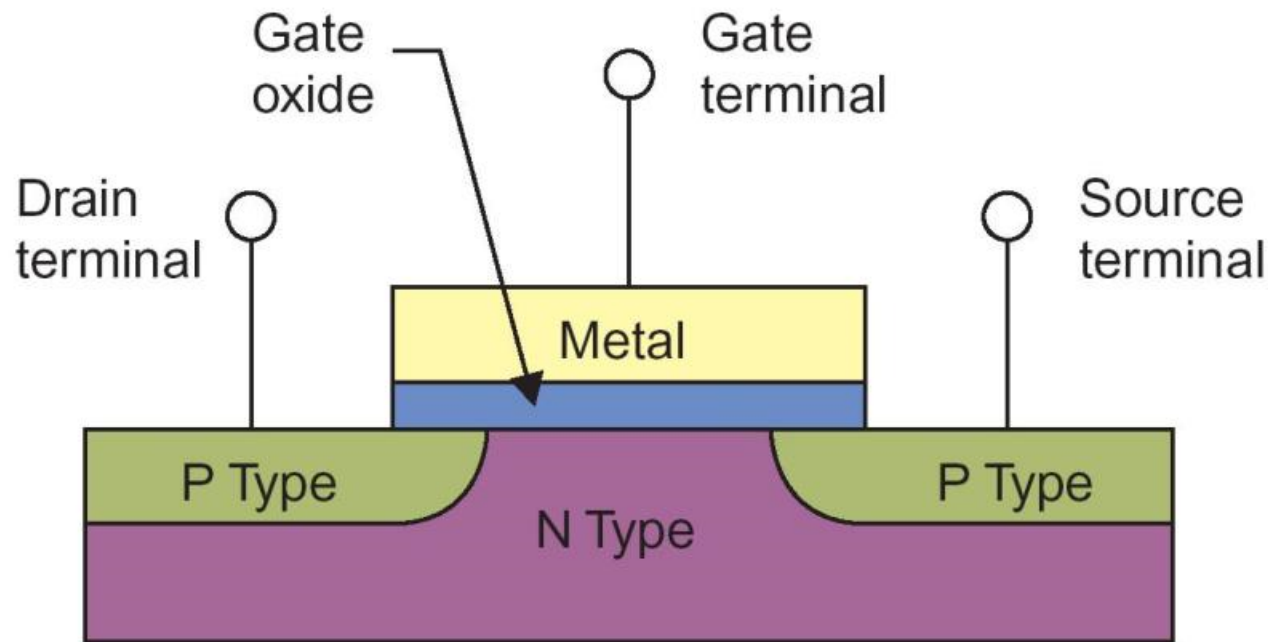
# BUILDING BLOCKS OF SEMICONDUCTOR DEVICES

- p-n junctions
- metal-semiconductor junctions
- metal-insulator-semiconductor (MIS) capacitors

Reading:  
AM Ch. 29

# THE MOSFET

(metal-oxide-semiconductor field-effect transistor)



amplification, switching, logic

# BASIC EQUATIONS FOR DEVICE PHYSICS

in 1D:

**Poisson's Equation:** 
$$-\frac{d^2\psi}{dx^2} = \frac{d\mathcal{E}}{dx} = \frac{\rho}{\epsilon_s} = \frac{q}{\epsilon_s} [p + N_D^+ - n - N_A^-]$$

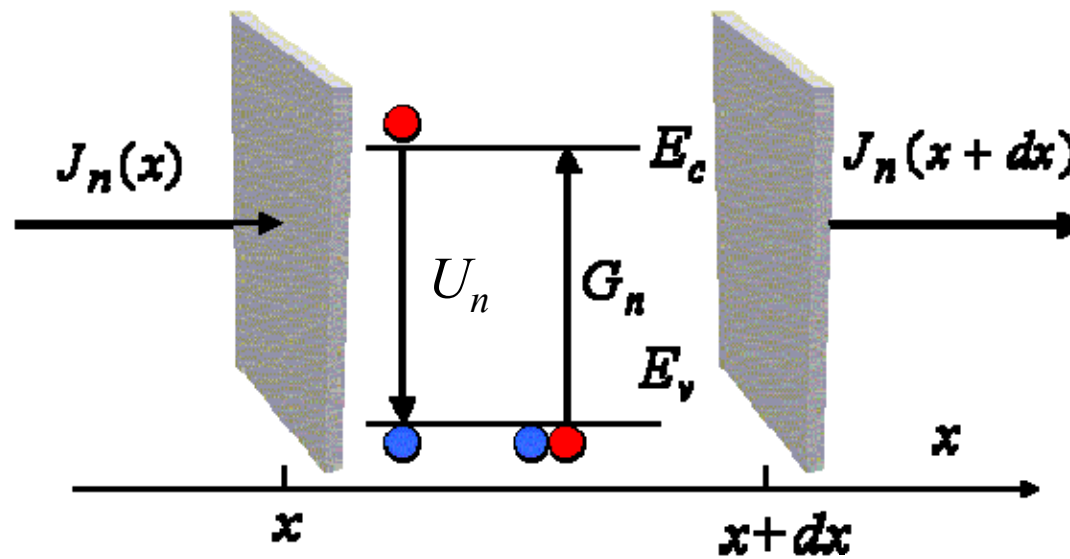
**Drift-Diffusion Equations:** 
$$J_n = q\mu_n n\mathcal{E} + qD_n \frac{dn}{dx}$$

$$J_p = q\mu_p p\mathcal{E} - qD_p \frac{dp}{dx}$$

**Continuity Equations:** 
$$\frac{\partial n}{\partial t} = G_n - U_n + \frac{\nabla J_n}{q} \qquad \frac{\partial p}{\partial t} = G_p - U_p - \frac{\nabla J_p}{q}$$

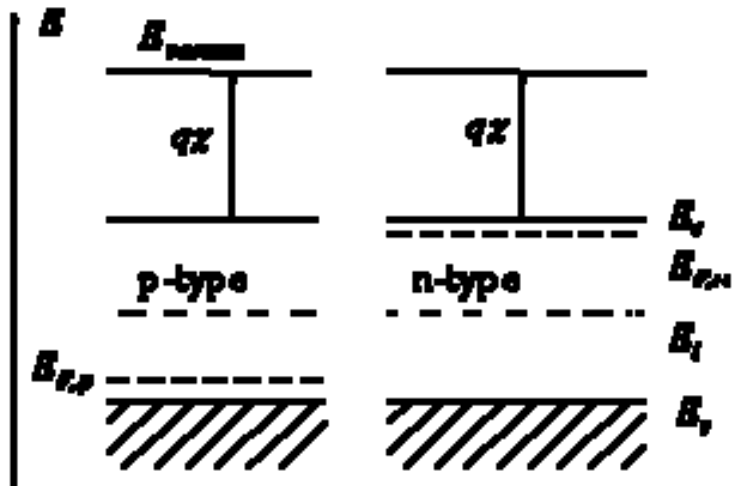
# CONTINUITY

$$\frac{\partial n}{\partial t} = G_n - U_n + \frac{\nabla J_n}{q}$$

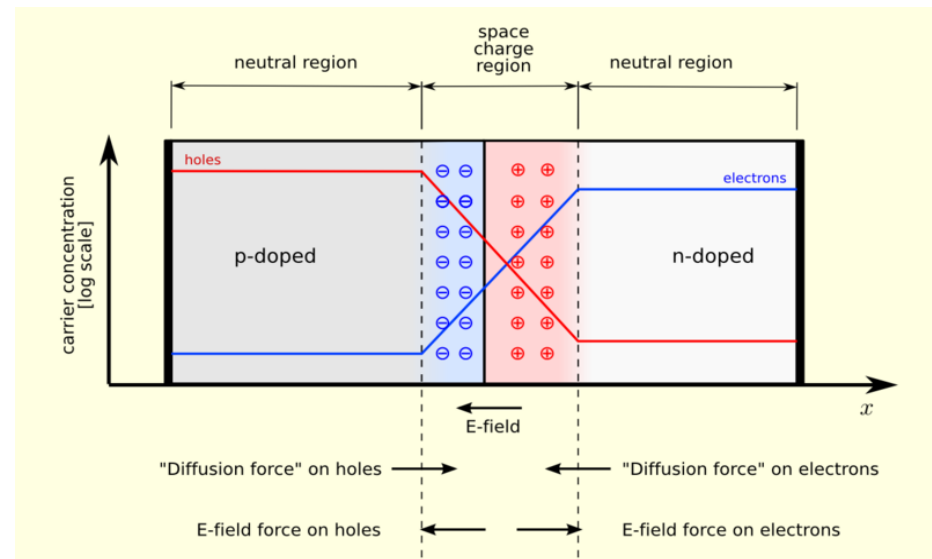
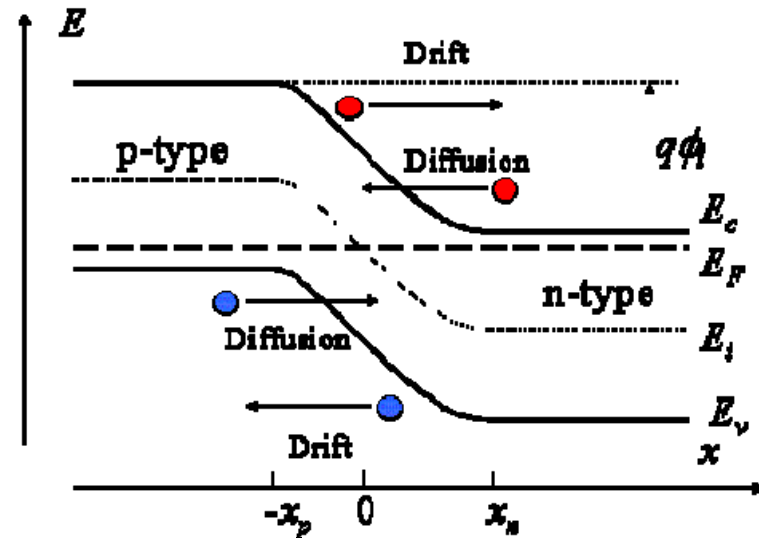


# THE PN (HOMO)JUNCTION

before contact

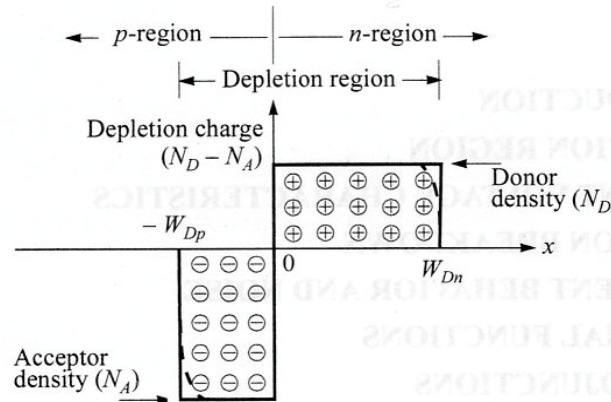


after contact, equilibrium

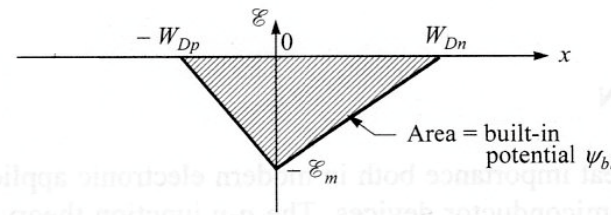


# ABRUPT PN JUNCTIONS

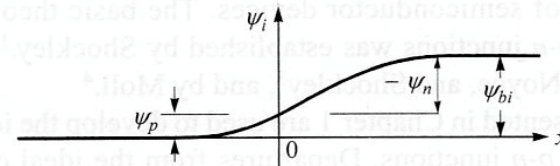
$$\frac{d^2\psi}{dx^2} = \frac{d\mathcal{E}}{dx} = \frac{\rho}{\epsilon_s}$$



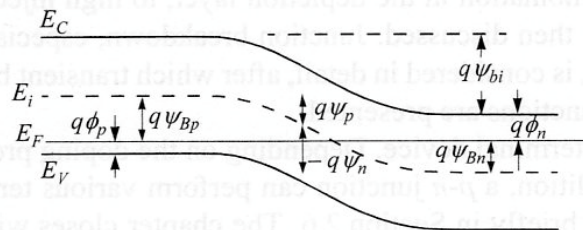
integrate



integrate, flip sign



flip sign



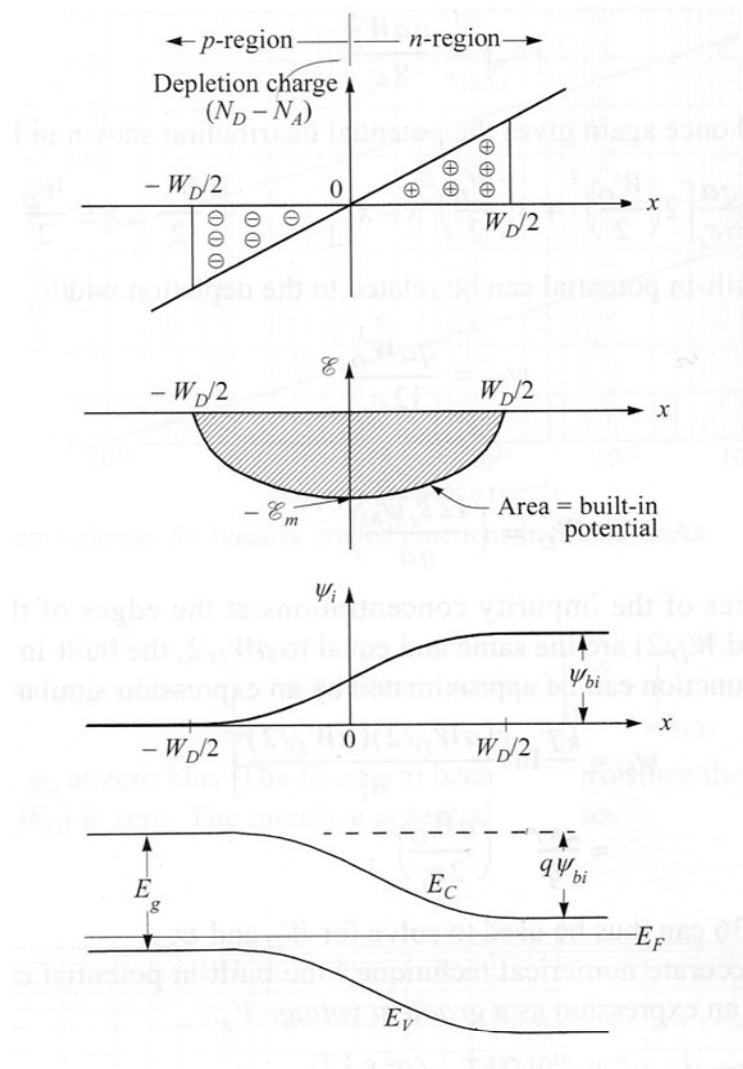
$$\mathcal{E}(x) = \epsilon_s \int_{-W_{Dp}}^{W_{Dn}} \rho(x) dx$$

$$\psi(x) = - \int_{-W_{Dp}}^{\infty} \mathcal{E}(x) dx$$

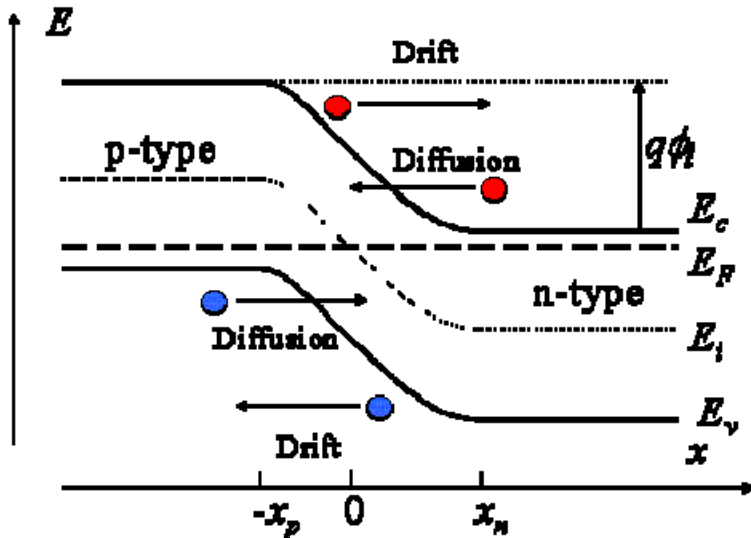
$$E(x) = -q\psi(x)$$

# LINEARLY-GRADED PN JUNCTIONS

more realistic  
doping profile,  
same basic result  
and device physics



# SIMPLE DERIVATION OF CURRENT-VOLTAGE CHARACTERISTICS



two electron currents:

- 1) generation current ( $J_{gen,e}$ )  
- electrons from p to n side
- 2) recombination current ( $J_{rec,e}$ )  
- electrons from n to p side

$$J_e^{rec} \propto e^{-q(\phi-V)/kT}$$

at equilibrium ( $V = 0$ ):  $J_e^{rec} = J_e^{gen} = e^{-q\phi/kT}$

so at any voltage  $V$ :  $J_e^{rec} = J_e^{gen} e^{qV/kT}$

total electron current:  $J_e = J_e^{rec} - J_e^{gen} = J_e^{gen} (e^{qV/kT} - 1)$

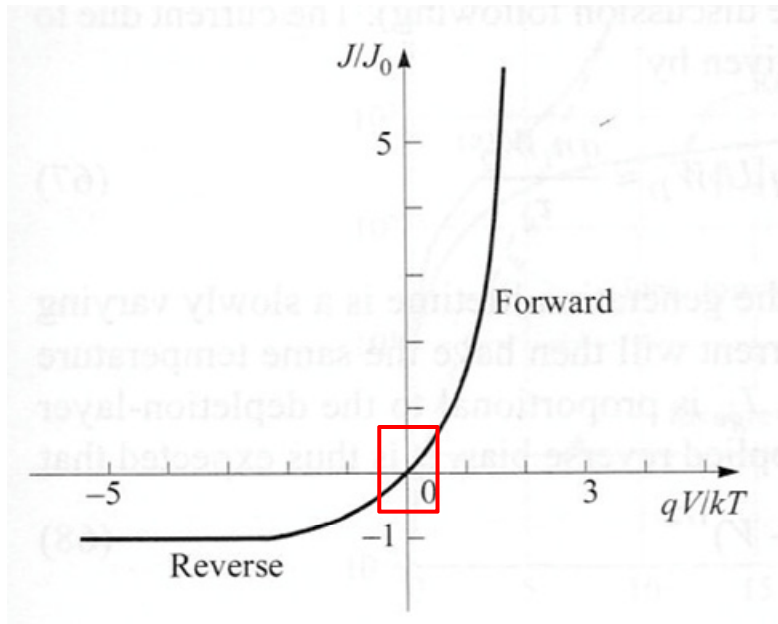
total current (e + h):  $J = J_e + J_h = (J_e^{gen} + J_h^{gen})(e^{qV/kT} - 1)$



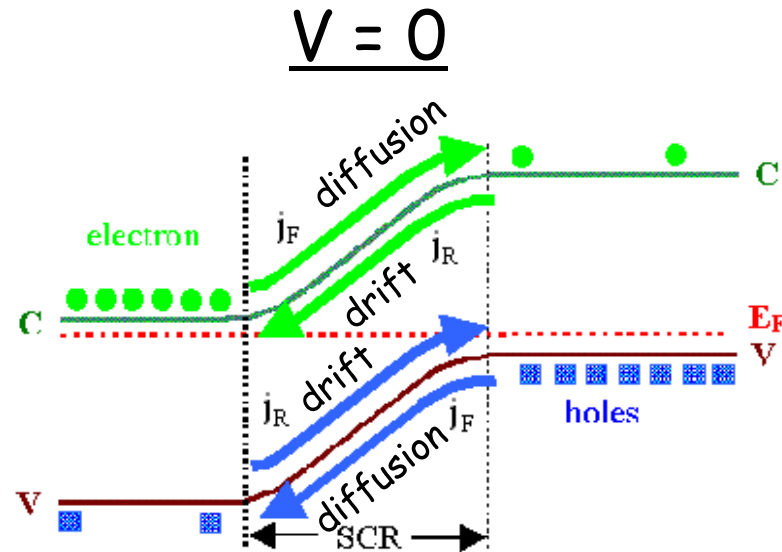
# DIODE AT EQUILIBRIUM

Shockley ideal diode equation (1949):

$$J = J_0 \left[ \exp\left(\frac{qV}{nkT}\right) - 1 \right]$$



rectification: current flows preferentially in one direction



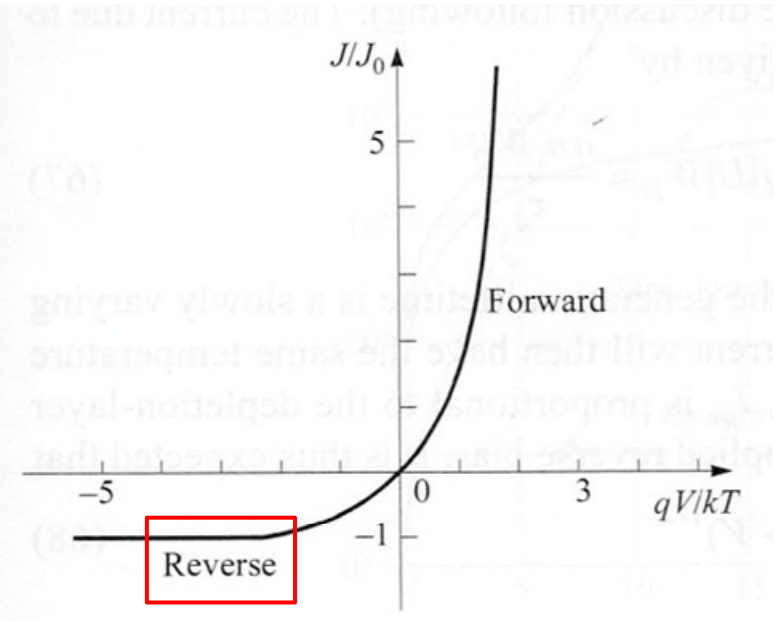
$$J_{diff,n} = J_{drift,n}$$

$$J_{diff,p} = J_{drift,p}$$

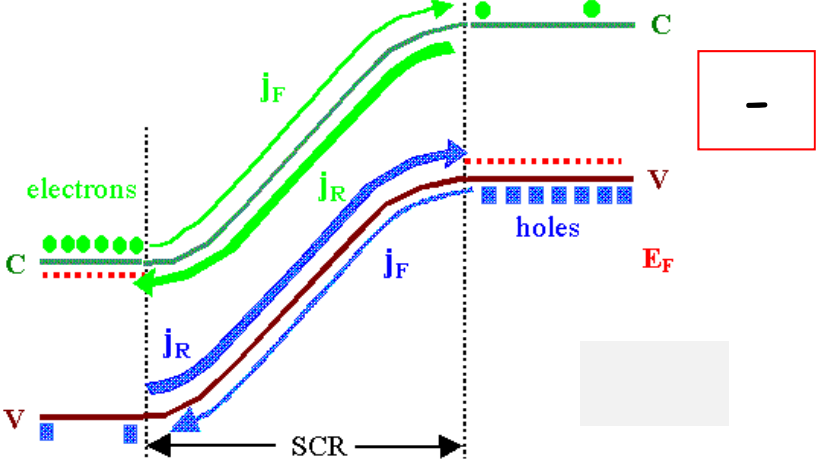
Zero net current

# REVERSE BIAS

$$J = J_0 \left[ \exp\left(\frac{qV}{nkT}\right) - 1 \right]$$



$V < 0$  (reverse bias)

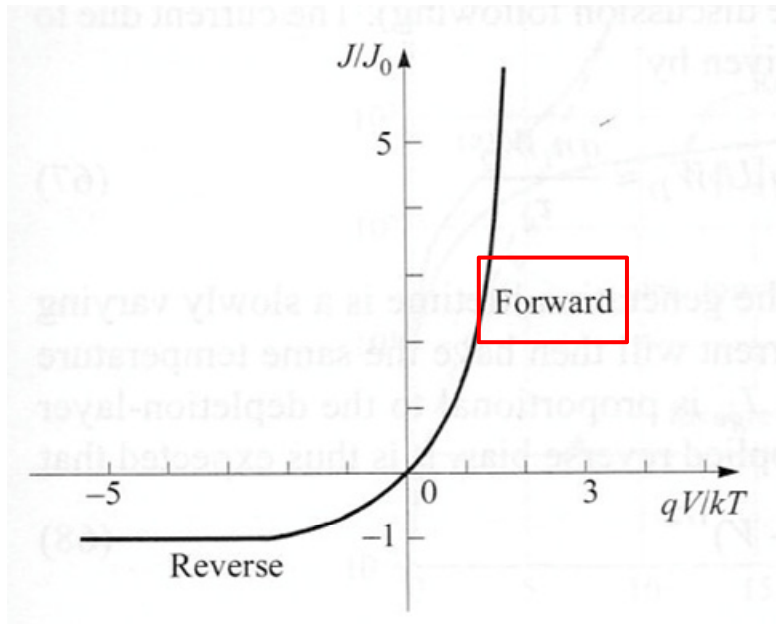


$$J_{diff,n} < J_{drift,n}$$

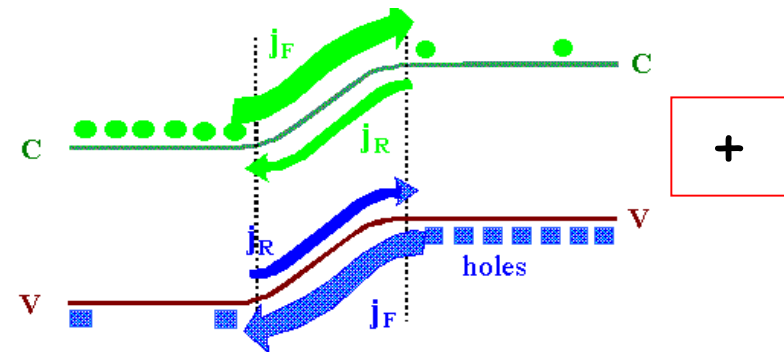
$$J_{diff,p} < J_{drift,p}$$

# FORWARD BIAS

$$J = J_0 \left[ \exp\left(\frac{qV}{nkT}\right) - 1 \right]$$



$V > 0$  (forward bias)



$$J_{\text{diff},n} > J_{\text{drift},n}$$

$$J_{\text{diff},p} > J_{\text{drift},p}$$

Only the diffusion current changes significantly with bias.  
Diffusion dominates in forward bias.

# DETAILED DERIVATION OF CURRENT-VOLTAGE CHARACTERISTICS

derivation of the Shockley ideal diode equation (1949):

at equilibrium:  $n = n_i \exp\left(\frac{E_F - E_i}{kT}\right)$        $p = n_i \exp\left(\frac{E_i - E_F}{kT}\right)$        $pn = n_i^2$

with bias V:  $n \equiv n_i \exp\left(\frac{E_{Fn} - E_i}{kT}\right)$        $p \equiv n_i \exp\left(\frac{E_i - E_{Fp}}{kT}\right)$        $qV = E_{Fn} - E_{Fp}$

$$pn = n_i^2 \exp\left(\frac{E_{Fn} - E_{Fp}}{kT}\right) \quad \begin{array}{l} pn > n_i^2 \text{ for } V > 0 \\ pn < n_i^2 \text{ for } V < 0 \end{array}$$

hole density at  $x = W_{Dn}$ :  $p_n(W_{Dn}) = p_{no} \exp\left(\frac{qV}{kT}\right)$

electron density at  $x = -W_{Dp}$ :  $n_p(W_{Dp}) = n_{po} \exp\left(\frac{qV}{kT}\right)$

} boundary conditions

# DETAILED DERIVATION CONTINUED

continuity on  $n$ -side: 
$$-U - \mu_p \mathcal{E} \frac{dp_n}{dx} - \mu_p p_n \frac{d\mathcal{E}}{dx} + D_p \frac{d^2 p_n}{dx^2} = 0 \quad \text{with, } U = \frac{p_n - p_{no}}{\tau_p}$$

in the neutral region (no field): 
$$-U + D_p \frac{d^2 p_n}{dx^2} = 0$$

solution ( $W_{Dn} \leq x < \infty$ ): 
$$p_n(x) - p_{no} = p_{no} \left[ \exp\left(\frac{qV}{kT}\right) - 1 \right] \exp\left(-\frac{x - W_{Dn}}{L_p}\right) \quad L_p = \sqrt{D_p \tau_p}$$

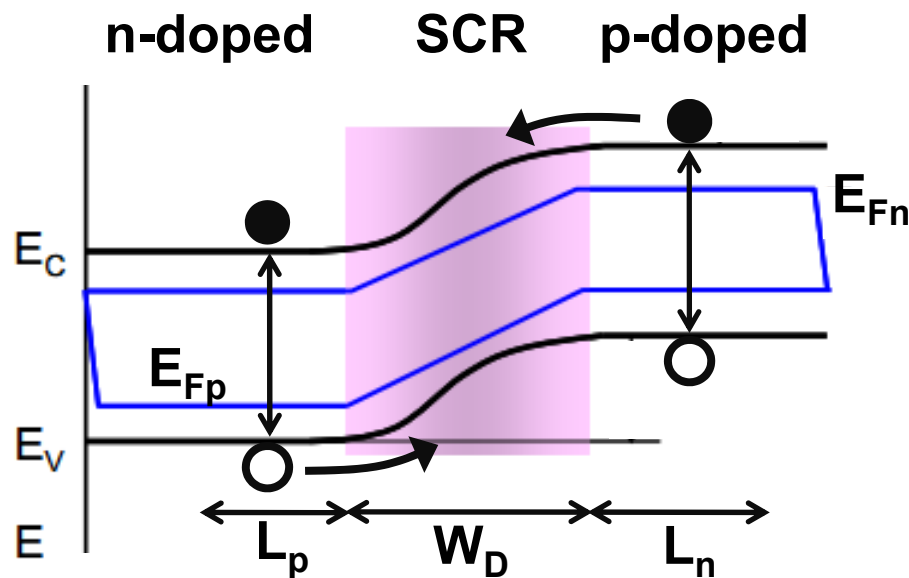
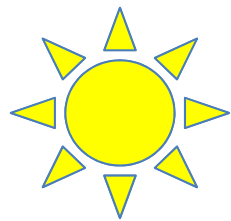
hole diffusion current at  $x = W_{Dn}$ : 
$$J_p = -qD_p \left. \frac{dp_n}{dx} \right|_{W_{Dn}} = \frac{qD_p p_{no}}{L_p} \left[ \exp\left(\frac{qV}{kT}\right) - 1 \right]$$

electron diffusion current at  $x = -W_{Dp}$ : 
$$J_n = \frac{qD_n n_{po}}{L_n} \left[ \exp\left(\frac{qV}{kT}\right) - 1 \right]$$

total current: 
$$J = J_p + J_n = J_0 \left[ \exp\left(\frac{qV}{kT}\right) - 1 \right] \quad \text{with, } J_0 \equiv \frac{qD_p p_{no}}{L_p} + \frac{qD_n n_{po}}{L_n}$$

# Illuminated pn junction

- Absorbed photons **generate** excess minority carriers
- Minority carriers within a diffusion length of the depletion region are swept across the junction by the electric field  
→ electrons and holes are **separated** and **collected**

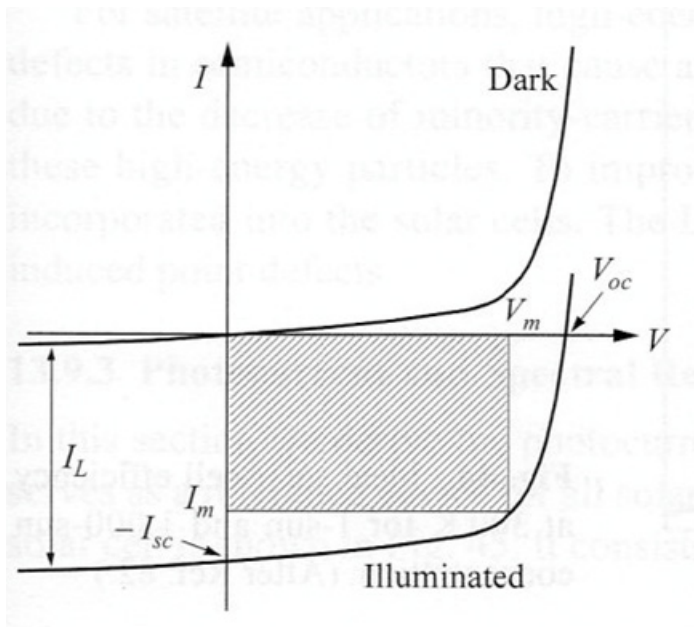


photocurrent  $J_L$  for uniform generation rate  $G$ :

$$J_L = qG(L_p + W_D + L_n)$$

# Current-voltage characteristics

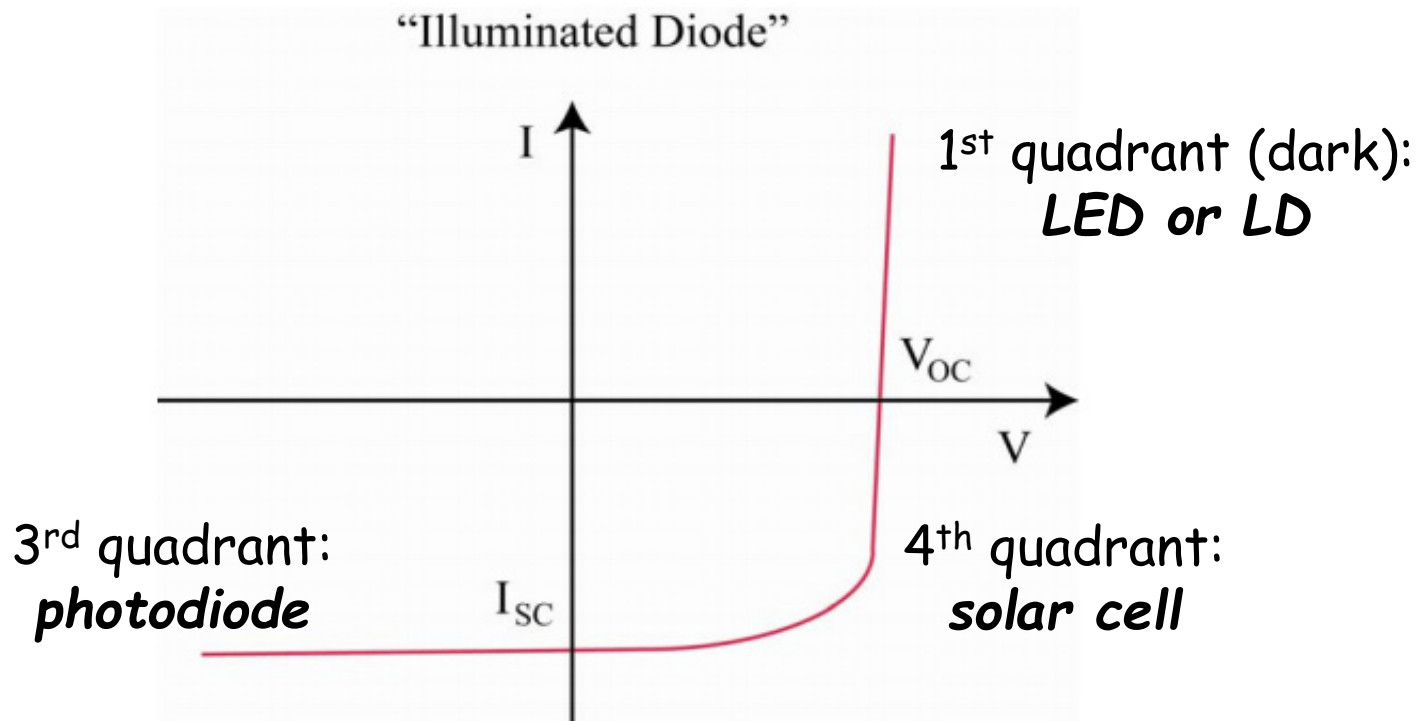
“Current superposition”:  $J_L$  causes downward shift of J-V curve



$$\text{dark: } J = J_0 \left[ \exp\left(\frac{qV}{nkT}\right) - 1 \right]$$

$$\text{light: } J = J_0 \left[ \exp\left(\frac{qV}{nkT}\right) - 1 \right] - J_L$$

# Operating modes





# Solar cell external parameters

$$\eta = \frac{P_{\max}}{P_{in}} = \frac{J_m V_m}{P_{in}} = FF \frac{J_{sc} V_{oc}}{P_{in}}$$

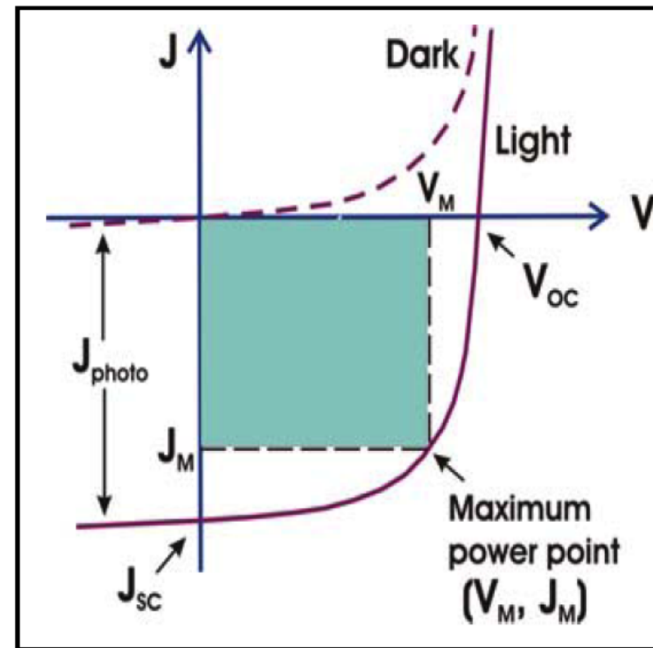
$P_{in}$  (normal sunlight):  $\sim 100 \text{ mW cm}^{-2}$

$$J_{sc} \approx J_L = qG(L_n + L_p + W_D)$$

- maximize light absorption ( $G$ )
- maximize  $W$  & diffusion lengths

$$V_{oc} = \frac{kT}{q} \ln \left( \frac{J_L}{J_0} + 1 \right)$$

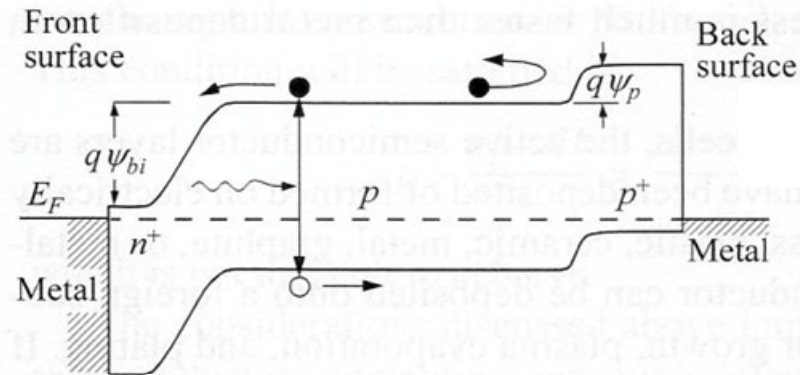
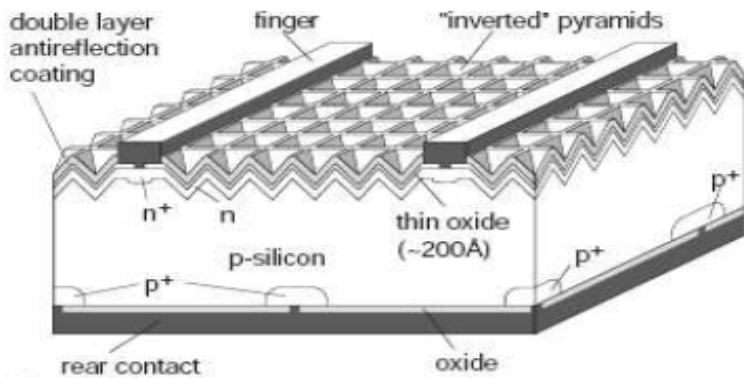
- minimize saturation current
- maximize photocurrent



$$FF = \frac{J_m V_m}{J_{sc} V_{oc}}$$

- reduce recombination
- reduce series resistance

# Silicon pn junction cells



$$\eta = FF \frac{J_{SC} V_{OC}}{P_{in}}$$

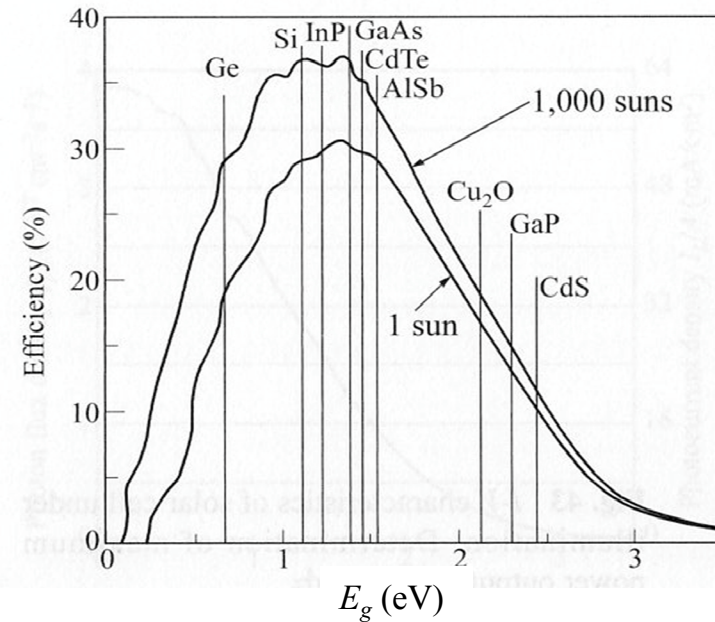
parameters of good lab cells

$$J_{SC} = 42 \text{ mA cm}^{-2}$$

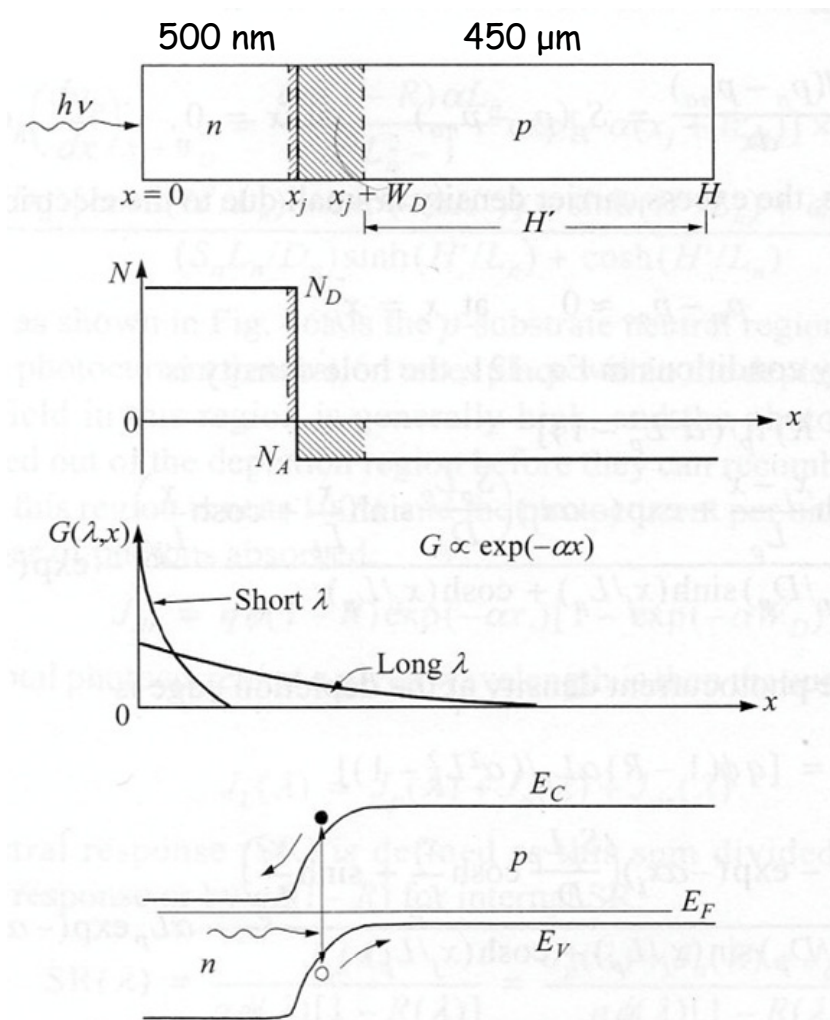
$$V_{OC} = 0.72 \text{ V}$$

$$FF = 0.80$$

$$\eta = 24\%$$



# Example of Si cell spectral response



## parameters

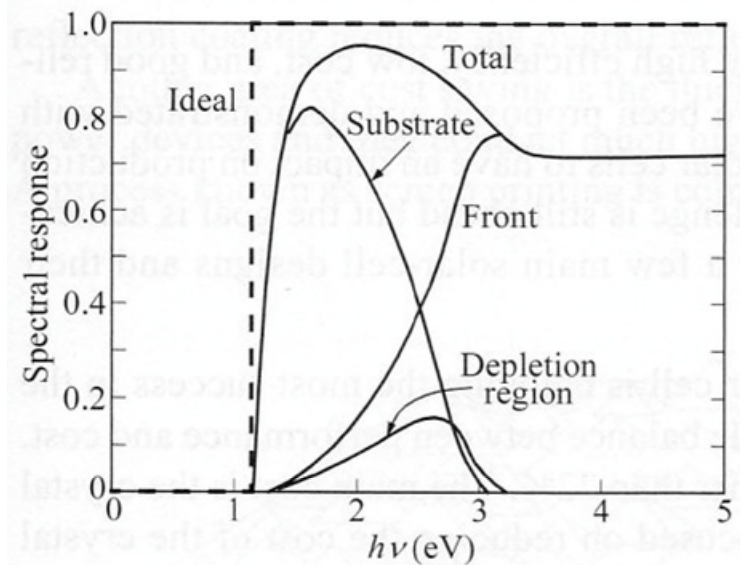
$$N_D = 5 \times 10^{19} \text{ cm}^{-3}$$

$$N_A = 1 \times 10^{16} \text{ cm}^{-3}$$

$$L_n = 51 \text{ } \mu\text{m}$$

$$L_p = 23 \text{ } \mu\text{m}$$

$$S_p = 10^4 \text{ cm/s}$$



$$J_L = q \int_0^{\lambda_m} \phi(\lambda) [1 - R(\lambda)] SR(\lambda) d\lambda$$

# Losses in ideal and real cells

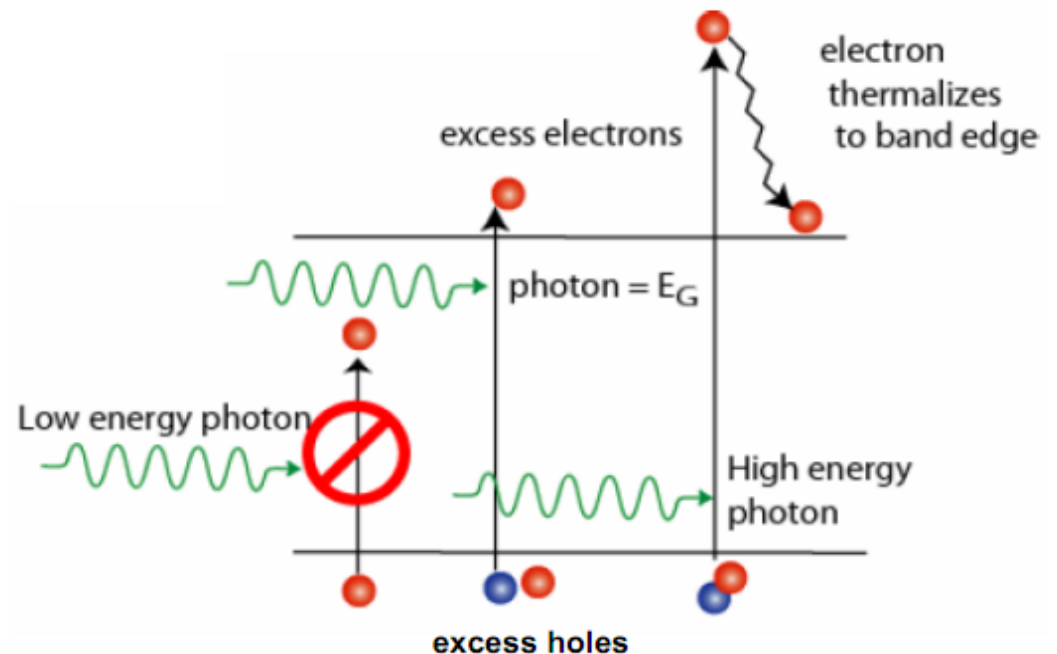
## Ideal cells (SR = 1)

- 1) transparency
- 2) relaxation (major loss)
- 3) thermodynamic loss

max  $\eta$ : ~33% at 1 sun

## Real cells

- 1) incomplete absorption (lowers  $J_{SC}$ )
- 2) parasitic dark currents (lowers  $V_{OC}$ , FF)
- 3) bulk, junction, and surface recombination ( $J_{SC}$ ,  $V_{OC}$ , FF)
- 4) series resistance and leakage currents (FF)

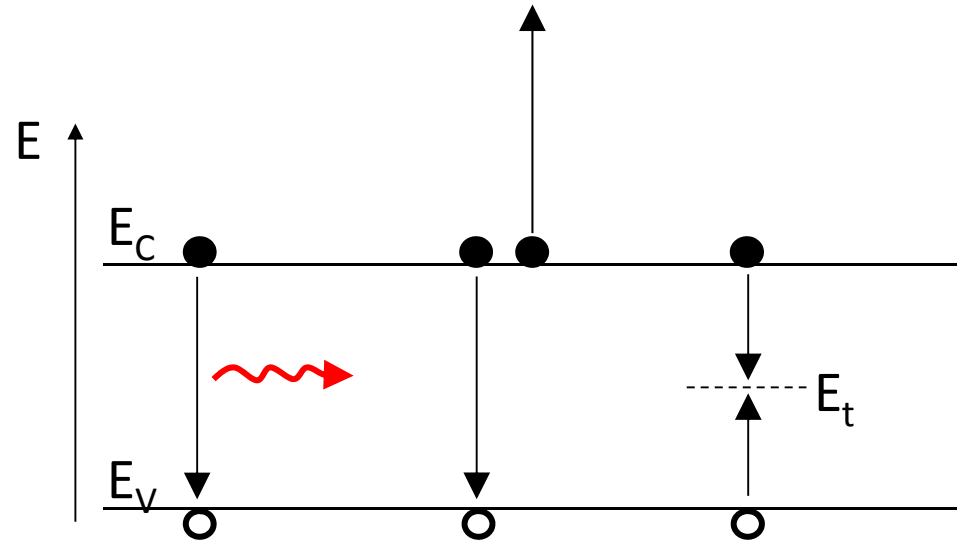


# Recombination processes

## 1) Band-to-band

- Radiative
- Auger

## 2) Trap assisted



Dominant mechanism(s) depend on semiconductor, cell design, and processing.

- Surface recombination
- Depletion region recombination
- Bulk recombination
- Recombination at metal semiconductor contacts

# Beyond silicon: PV design rules

Silicon is successful, deploying rapidly, but still expensive. (indirect gap semiconductor requires thick, high-purity, \$ layers).

Alternative (thin film) technologies must:

- 1) Be much more economical, at MW-TW scales
- 2) Absorb sunlight and collect charges with ~100% efficiency

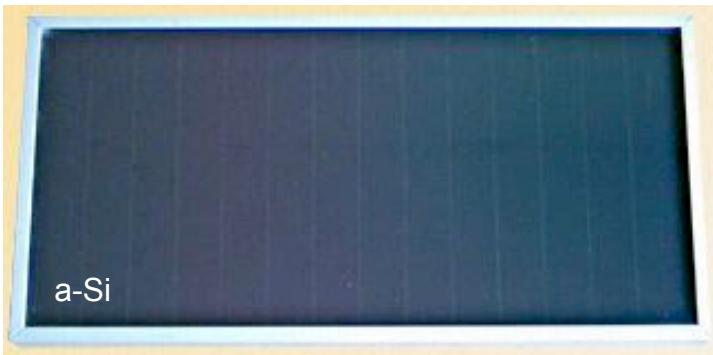
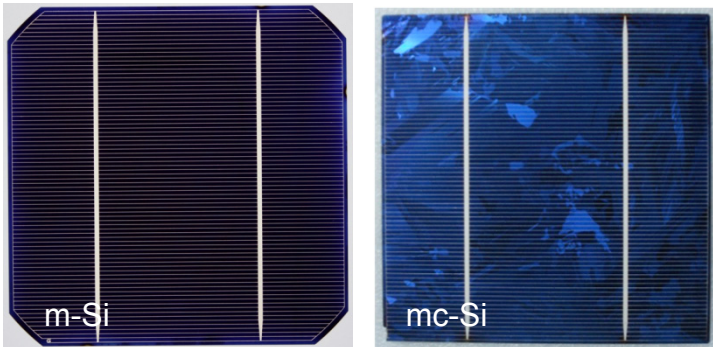
**carrier diffusion length > device thickness > absorption length**

$$(L_n + L_p) > d > \alpha^{-1}(\lambda)$$

- 3) Collect the carriers at a large voltage ( $V_{OC} > E_g/q - 0.5 \text{ V}$ )

$$E_g = 1-1.5 \text{ eV, large } \Delta \text{ in } E_F, \text{ low dark current}$$

# PV technologies



## Technologies

### 1. Crystalline Silicon

- \* Monocrystalline (m-Si)
- \* Poly- or multicrystalline (poly-Si or mc-Si)

### 2. Thin Film

- \* Cadmium Telluride (CdTe)
- \* Copper-Indium Gallium diSelenide (CIGS)
- \* Amorphous Silicon (a-Si)
- \* Thin-Film Silicon (TF-Si)

### 3. Multijunction Concentrators

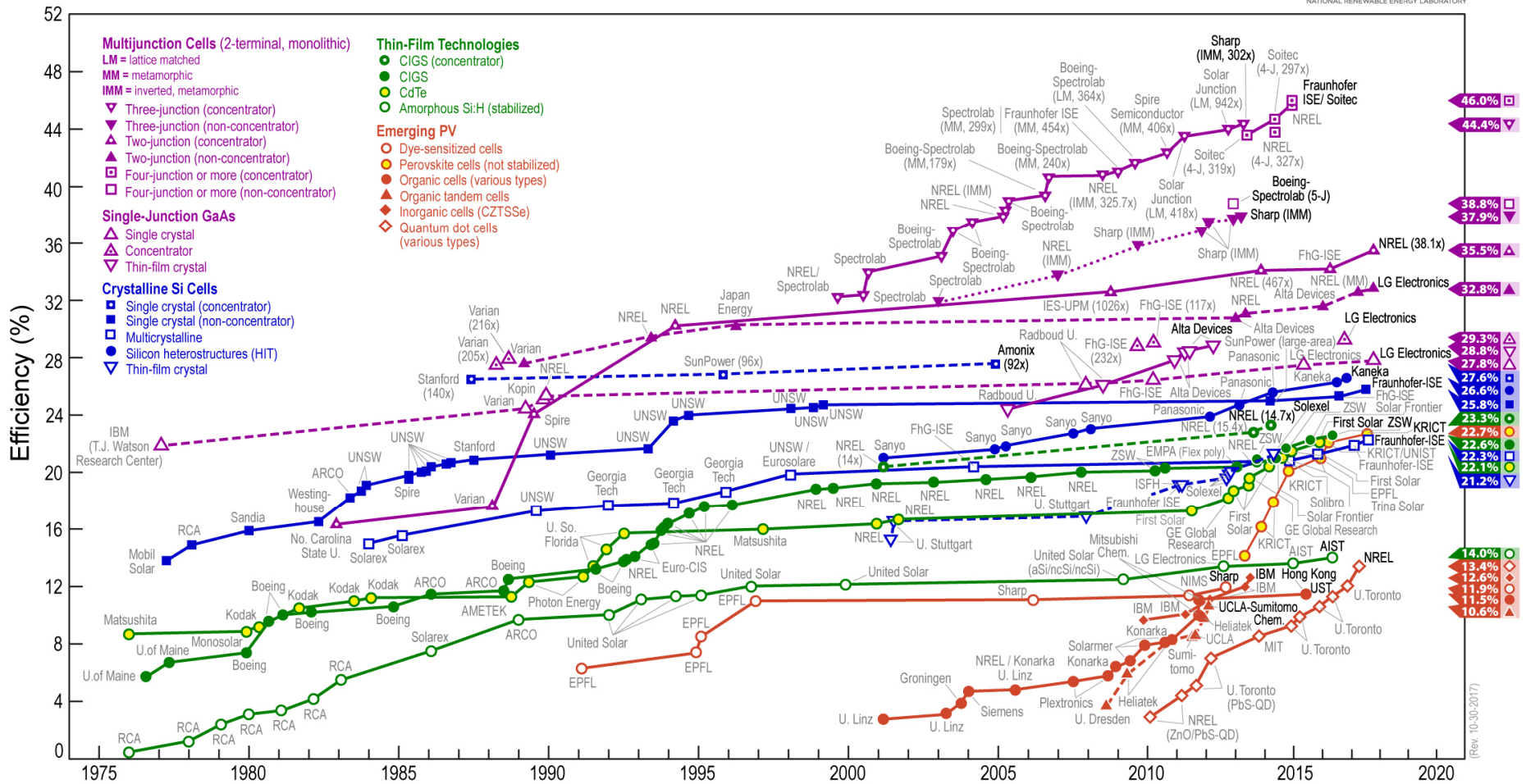
- \* Lattice-Matched (LM)
- \* Metamorphic (MM)
- \* Inverted Metamorphic (IMM)

### 4. Emerging Technologies

- \* Dye-Sensitized (DSC)
- \* Organic (OPV)
- \* Copper Zinc Tin Sulfide (CZTS)
- \* Other earth-abundant materials
- \* 3<sup>rd</sup> generation concepts (QDs, IB)

# PV CONVERSION EFFICIENCIES

## Best Research-Cell Efficiencies





FIN