The Atom and "Quantized Energy of Electrons"

- Recall the basic atomic structure:
- Positive charged nucleus of protons and neutrons
- Electrons in set orbitals around the core
- Outer electrons are the valence electrons, control conduction.
- Electrons can only exist in "quantized" energy unites,
- ie: electron may occupy only specific "quantum energy levels."
- Each orbital represents one of those "quantum energy levels"

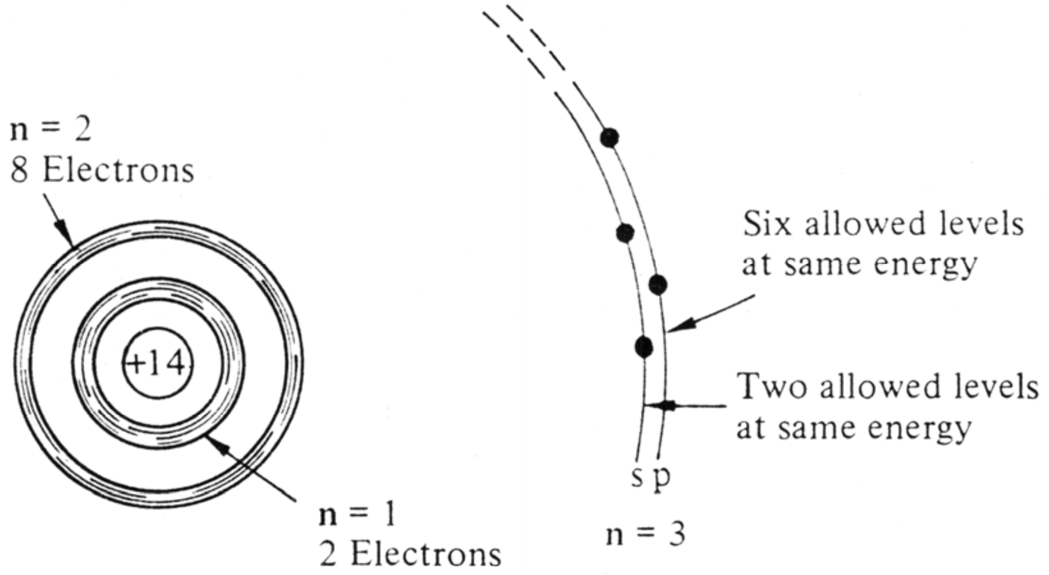


Fig. 2.2 Schematic representation of an isolated Si atom.

The Band Theory: the Basis of Semiconductors

- conductive behaviour of a material dependent
  electrons beign altered by presence of
  crystal structure of atoms through which e's move.

Simplified Case:

- Consider each atom to have given up an electron,
- get a "sea of electrons" with a periodic structure of atoms.
- Material confines the e's within a given volume:
  the crystal structure.
- confined volume creates "quantize energy levels"
  for the electrons within the "electron sea."
- three dimensional nature of the crystal structure of atoms
  creates certain number of "states"
- Each electron can exist at a given energy level
- Called "Density of states": D(E) per unite volume.

$$D(E) = \frac{dn}{dE}$$

where n is the number of electrons per cc.

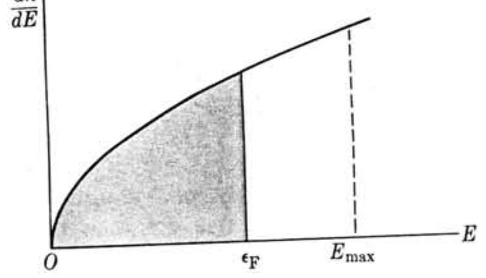
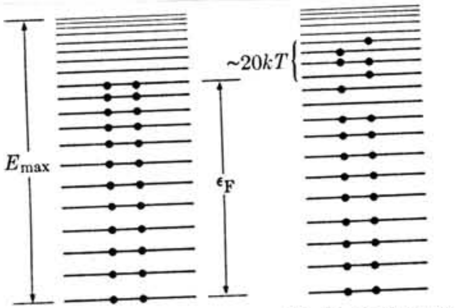


Fig. 6–20. Density of energy states of free electrons in a solid.



(a) Ground state (b) Excited state

Fig. 6–21. Distribution of free electrons among energy states in the conduction band.

Density and Fermi Distribution

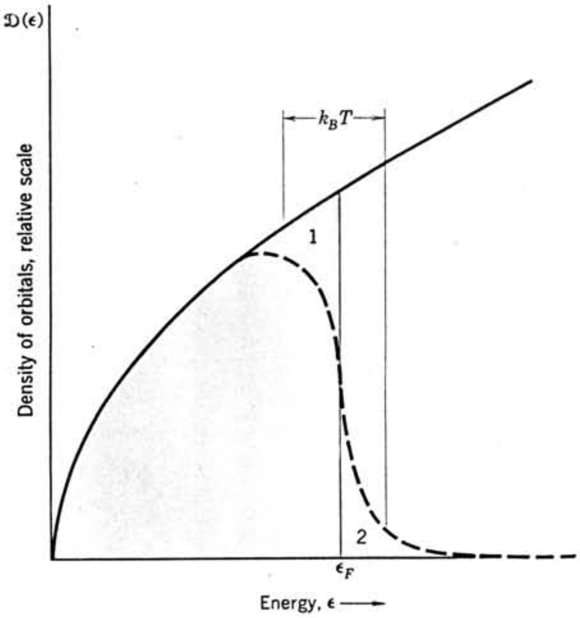
- number of states vary with the energy level,
- At absolute zero temperature (T = 0 Kelvin)
- the electrons fill up density of states
  level is number of states equal to number of electrons
- Point called the "Fermi Energy level" E_F.
- At higher temperatures some electrons above Fermi level

Fermi Distribution

- Above absolute zero the presence of heat adds energy
- some electrons occupy higher energy states.
- Changes the distribution D(E) by multiplying
  by the "Fermi Function", which depends on the Fermi level:

$$D(E)F(E_F) = D(E)\left[\frac{1}{1+\exp\left(\frac{E-E_F}{k_B T}\right)}\right]$$

Where k_B = Boltzmann's Constant = $1.3805\text{x}10^{-23}$ J/K
= $8.617\text{x}10^{-5}$ eV/K



The Creation of Energy Bands

Simplified Case:

- Again consider each atom giving up an electron, "sea of electrons" with a periodic structure of atoms.
- The atoms become positive ion cores
- produce a periodic electric field behaviour
- a periodic "potential energy distribution" (energy with potential for doing work on the charges near it).

Simple linear example

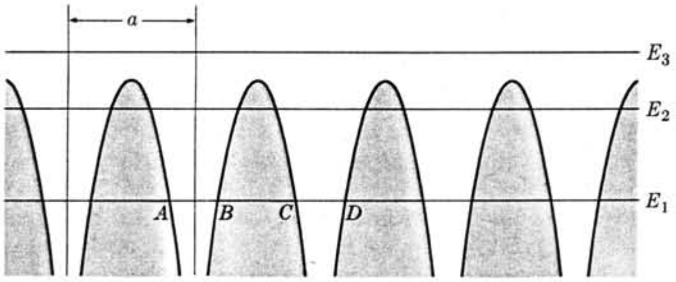


Fig. 6–16. Types of energy levels in a linear crystal lattice.

Energy Bands and the Band Gap

- periodic field change the "quantize energy levels" for the "electron sea."
- three dimensional position of the crystal structure of atoms creates first distorts the density of states, D(E).
- effect is to create "bands" of allowed energy states.
- For certain crystal structure/atom combinations some of those bands are separated by "energy band gaps";
- Band Gaps are forbidden energy levels: no electrons can exist.

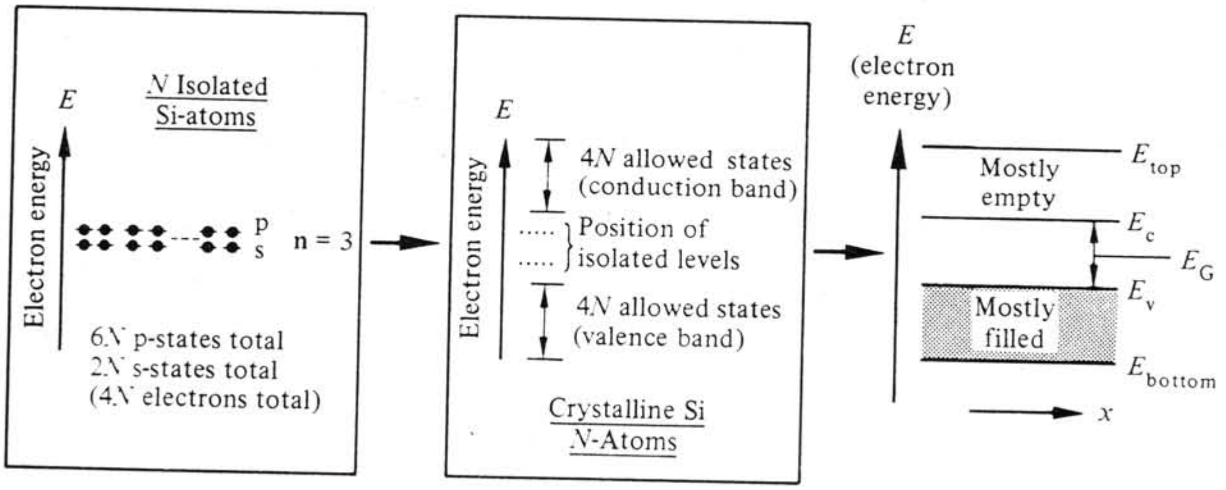


Fig. 2.5 Conceptual development of the energy band model starting with N isolated Si atoms on the left and concluding with a "dressed-up" version of the energy band model on the right.

Conductors, Insulators and Semiconductors

- What determines conductor, insulator and semiconductor?
- position of the "Fermi Energy" level within those bands and the size of the "band gap: E_g
- The lower band level is called the "Valance Band"
- The upper band level is called the "Conduction Band"
- NOTE: In electronics to draw the band structures as the straight lines.
- At T = 0 K here are some types of structures
- Good conductors: Copper, Sodium: many empty states below E_g
- Modest conductors: No bandgap (Conductance & valence overlap)
- Insulators: Full Valance band: large E_g
- Semiconductors: Valance filled but E_g small
  E_F within the band gap.
  small band gap: relatively easy to move electrons from the valance to the conduction band.
- conduction only occurs when there are empty states at adjacent energy levels.

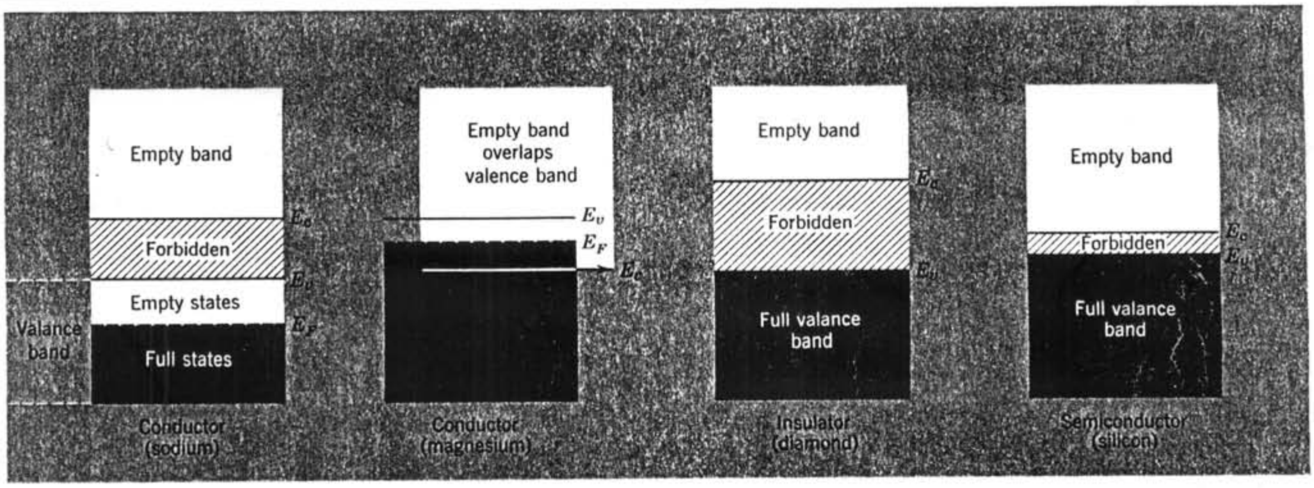


Figure 4.3 Simplified energy band diagrams for conductors, insulators, and semiconductors.

Conductor Copper   Conductor (Magnesium)   Insulator   Semiconductor

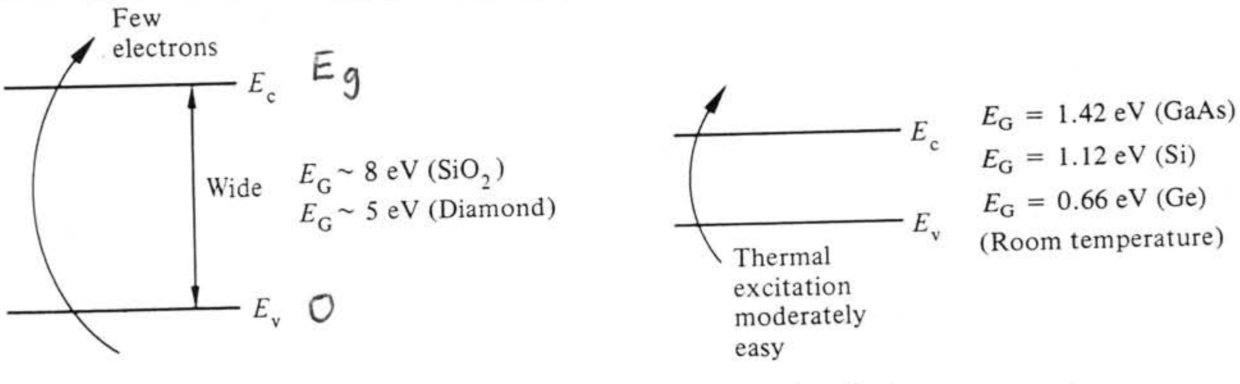
Semiconductors and the Band Gap

- Width of the Band Gap in terms of electron volts,
- energy an electron gains by being accelerated through a one volt electric field.

Typical Semiconductor band gaps

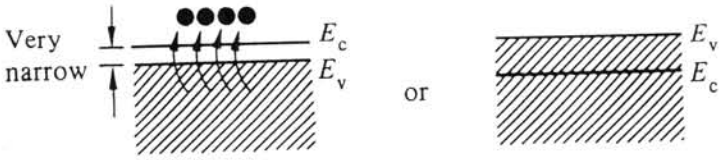
Germanium	0.67 eV
Silicon	1.11 eV
GaAs	1.40 eV
Diamond	5.60 eV

- NOTE: as the T increases, the band gap tends to change, usually becoming smaller in most materials.
- Usually use relative position in band diagrams, setting:
- The Valance Band Edge $E_V = 0$
- The Conduction Band Edge $E_C = E_g$
- measure the energies (eV) because most useful when doing the calculations on real devices.
- $1 \text{ eV} = 1.609 \times 10^{-19}$ Joules



(a) Insulator

(b) Semiconductor



(c) Metal

Fig. 2.8 Explanation of the distinction between (a) insulators, (b) semiconductors, and (c) metals using the energy band model.

Energy States and Absolute Zero

- Absolute Zero (T = 0 K):
  NOT the temperature where all motion ceases!
- electrons still circle the nucleus of an atom at absolute zero.
  Why?
- Energy only emitted from atom, when the electrons jump
  from a higher energy state to lower state.
- Energy absorbed from the environment by the atom
  e's jump from a lower state to a higher state (excited) state.
- Absolute Zero: point where all the electrons in
  lowest possible energy states.
- For an atom with "N" electrons, the "N" lowest energy orbitals
  are all filled.
- Thus no energy can be radiated from the atom
  because no lower states to make a transition ("jump") to.
- lowest energy that causes a change in the system causes
  transition from the "Nth" lowest states, to the "N+1th" state.

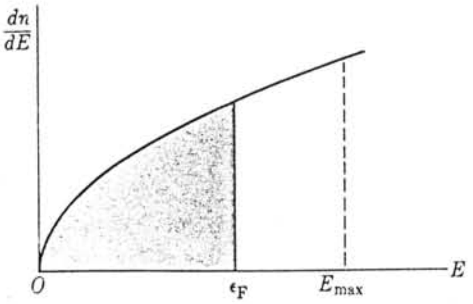
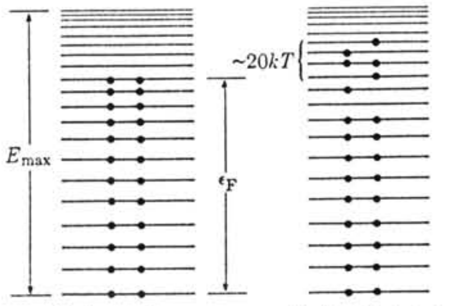


Fig. 6-20. Density of energy states of free electrons in a solid.



(a) Ground state (b) Excited state

Fig. 6-21. Distribution of free electrons among energy states in the conduction band.

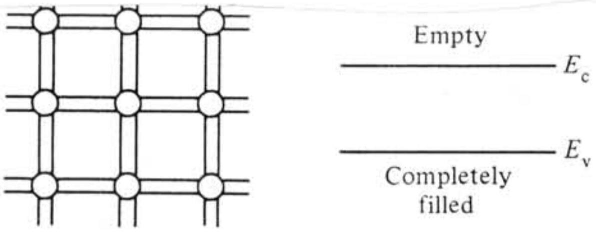
Creation of Current Carriers in Semiconductors.

- For current to flow must have adjacent energy states into which the electrons (carriers) can move.
- Voltage applied to semiconductor sets up an electric field
- E field causes the electrons to gain energy,
- moves them to a higher energy state.

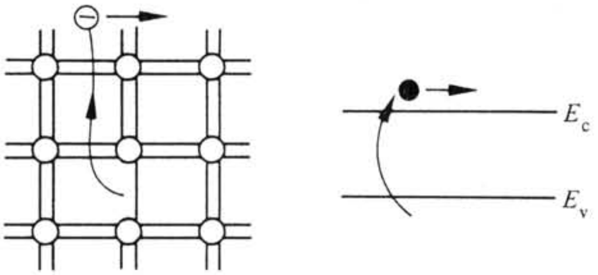
Two way conduction can occur:

- exciting electrons into energy states in the conduction band.
- lots of adjacent energy states for electrons to enter.

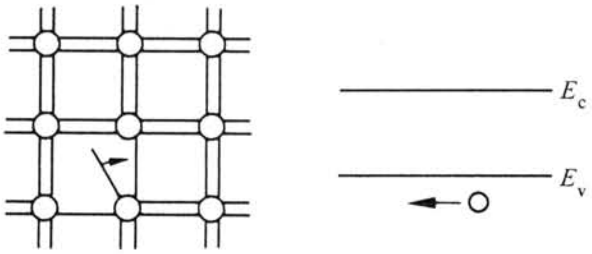
- removing electrons from energy states in the valance band,
- leaving a "hole" in the valance band.
- Adjacent states filled with electrons can then move their electrons into those "hole" states.



(a) No carriers



(b) The electron

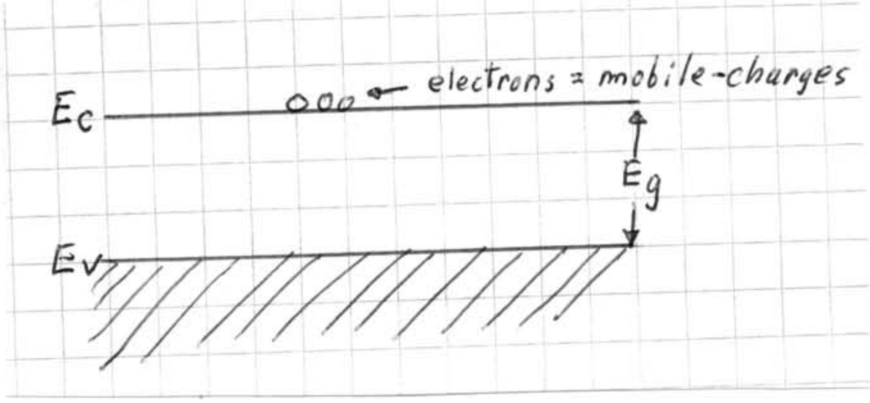


(c) The hole

Electrons as Negative Charge Carriers

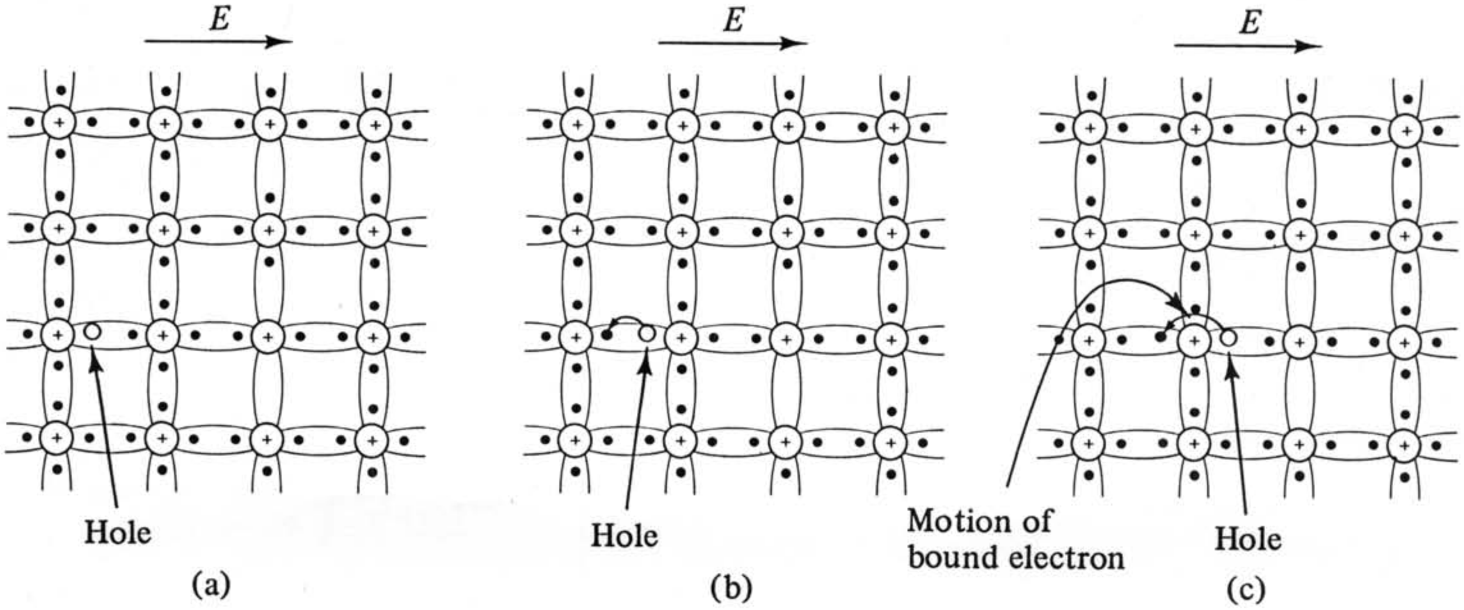
- electron elevated by energy conduction band
- no longer bound to its atom: floating "free"
  like the "sea of electrons" in metals.
- electrons bound to an atom do not act as carriers
- Free electrons act as mobile negative charges.
- application of an electric field (E)
  electron moves opposite direction to E "field vector"
  because the E field goes from + charge to - charge.

- density of free electrons (n) per unite volume
  n measured in cm^{-3}
- symbol "n" stands for "Negative"
- density of atoms in silicon 5.00×10^{22} per cm^{-3}
- Common values for n in Si 10^{10} to 10^{19} cm^{-3}



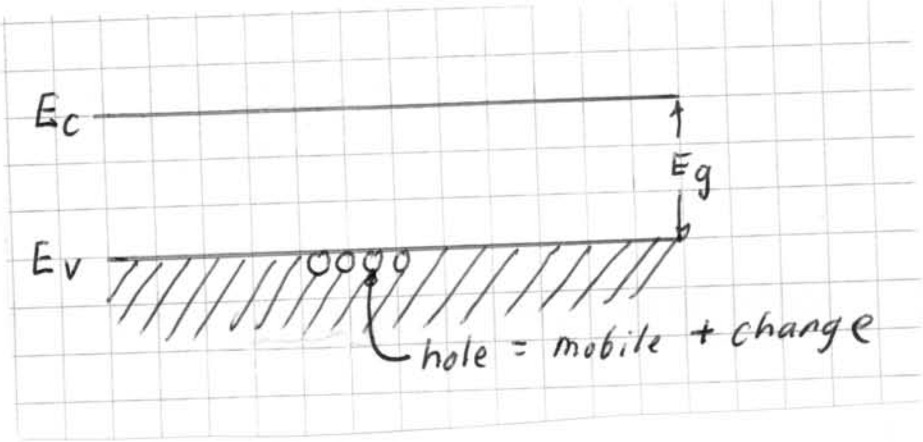
Hole's as Positive Carriers

- Hole is an absence of electron compared
  to crystal in the ground state.
- Hole an empty "bubble" in a sea of electrons.
- Each time an electron moves in to fill the bubble,
  it leaves behind a new hole
- E field applied e bound to an adjacent atom
  moves opposite to E direction, and fills hole.
- leaves a hole at that atom,
  effectively moving hole in field direction
- Bound e's filling holes, while bubble ripples on



Hole's as Positive Carriers

- Energy band diagram a "hole" an unfilled state below the Valance band edge E_V.
- Thus a hole acts as a mobile positive charge.
- density of mobile holes (p) per unite volume is: p measured in cm^{-3}
- symbol "p" stands for "Positive"
- Common values for p in Si are 10^{10} to 10^{19} cm^{-3}

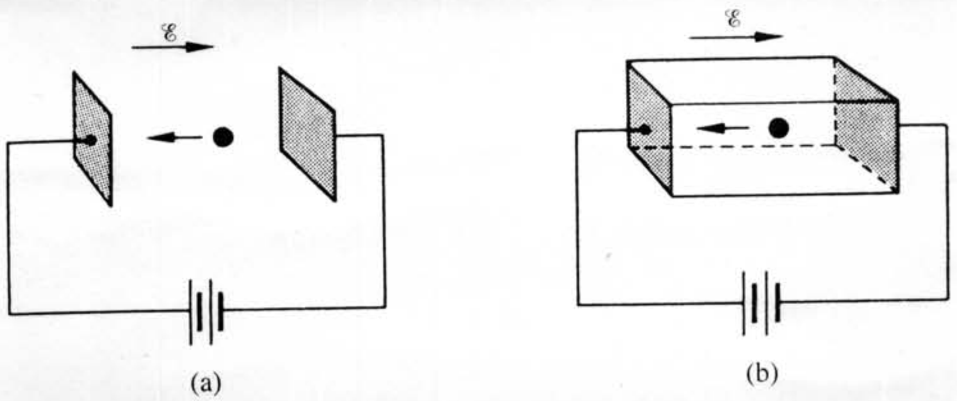


Effective mass

- Crystal fields changes the effective mass of charges
- When E field applied to charge then

$$F = -q\vec{E} = m_n^* \frac{dv}{dt}$$

- where m_n^* = effective mass of electron
- m_p^* = effective mass of hole
- where m_0 = rest mass of electron = 9.11×10^{-31} kg
- hole and electron effective mass are different
- Effective masses changes with materials
- Masses are different in different crystal directions



(a) (b)

Figure 2.9 An electron moving in response to an applied electric field (a) within a vacuum, and (b) within a semiconductor crystal.

Increase the temperature:

- By Fermi distribution, as T increases electrons in the conduction band must increase while spaces appear in the valance band.
- This is called the intrinsic carrier level.

$$n = \int_{E_c}^{\infty} D_c(E)\left[\frac{1}{1+\exp\left(\frac{E-E_F}{k_B T}\right)}\right] dE$$

$$p = \int_{-\infty}^{E_v} D_p(E)(1-F(E_F))dE = \int_{-\infty}^{E_v} D_v(E)\left[1-\frac{1}{1+\exp\left(\frac{E-E_F}{k_B T}\right)}\right] dE$$

- Why does a 1-F(E_F) factor appear for the hole?
- Fermi function calculates the number of electrons present.
- Want the empty places left by electrons not being there.
- An important number to remember:
  at room temperature (20 C) k_BT = 0.025 eV = 25 meV.
- This is the spread of the Fermi function at that temperature.

Density of States functions

- Real shape of bands is very complex
- Different for different materials
  and different directions
- Actually have "heavy holes & electrons" in some directions
- Note Si, GE are "indirect bandgap"
  minimum of Conduction is not opposite Valance band peak
- GaAs is direct bandgap

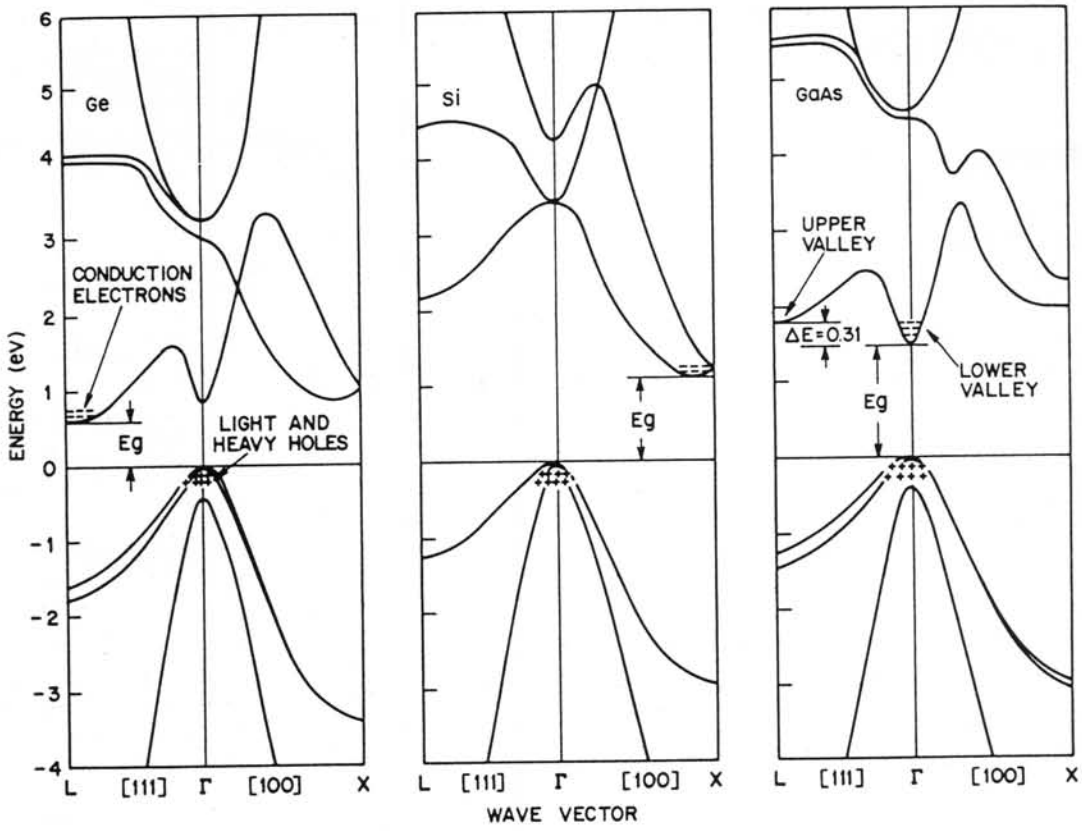


Fig. 5 Energy-band structures of Ge, Si, and GaAs, where E_g is the energy bandgap. Plus (+) signs indicate holes in the valence bands and minus (−) signs indicate electrons in the conduction bands. (After Chelikowsky and Cohen, Ref. 17.)

Density of States Approximation

- Near the band edges D(E) has parabolic shape
- Shape is function of effective masses
- Thus Conduction density of states (E E_C)is

$$D_c(E) = g_c(E) = \frac{m_n^*[2m_n^*(E - E_c)]^{1/2}}{\pi^2\hbar^3}$$

- Thus Valance density of states (E E_V)is

$$D_v(E) = g_v(E) = \frac{m_p^*[2m_p^*(E_v - E)]^{1/2}}{\pi^2\hbar^3}$$

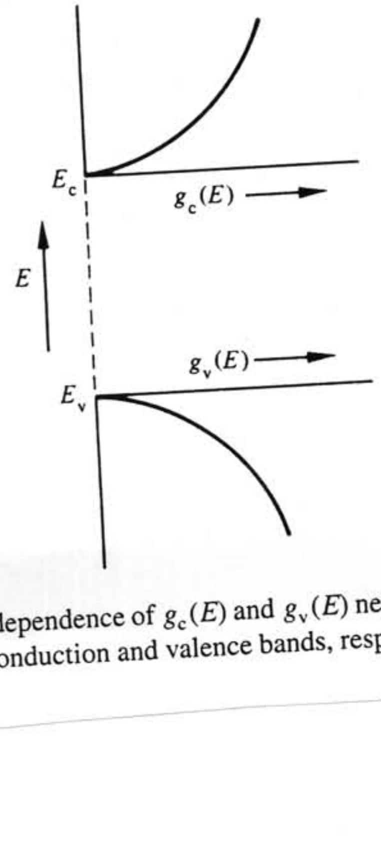
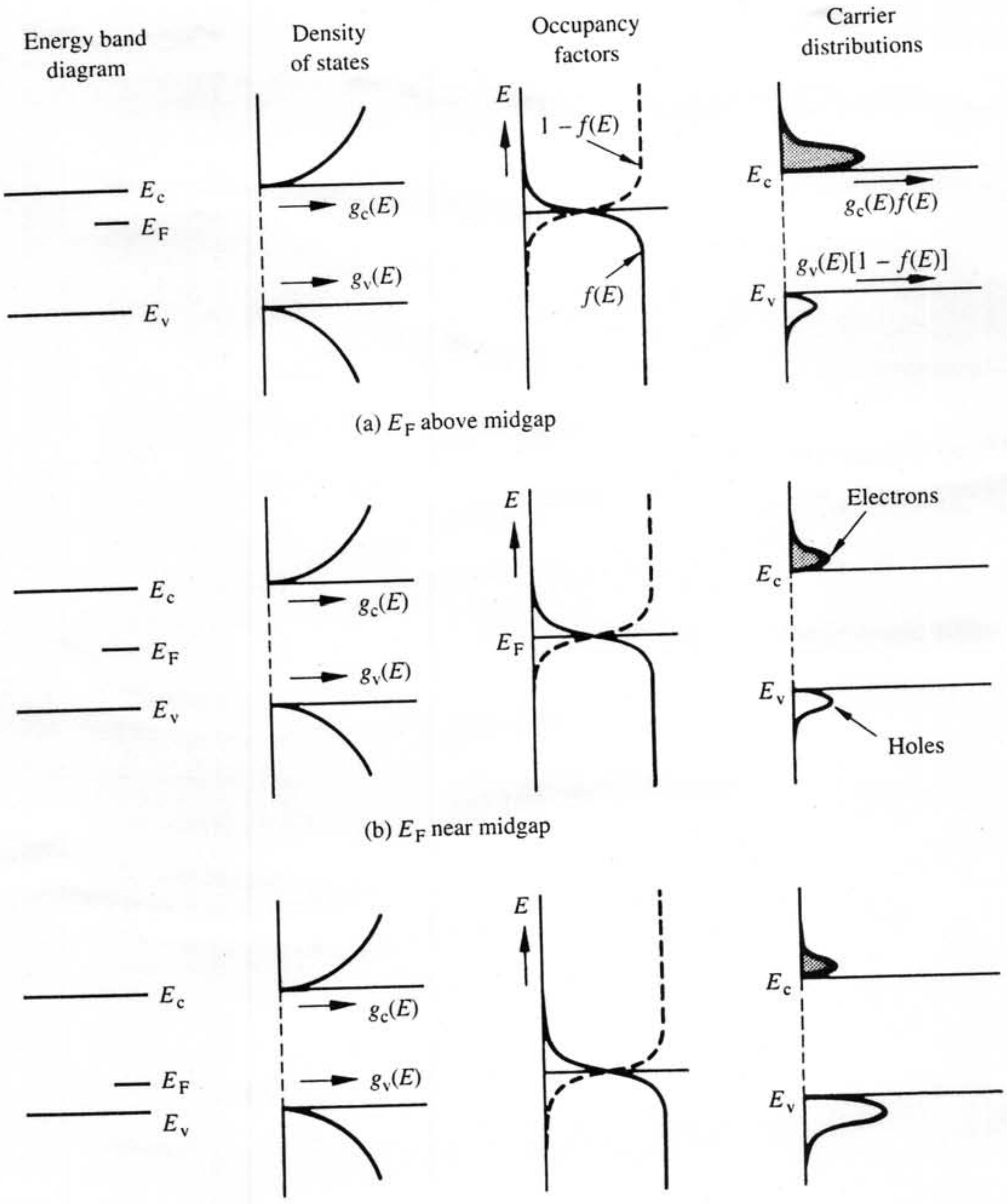


Figure 2.14 General energy dependence of $g_c(E)$ and $g_v(E)$ near the band edges. $g_c(E)$ and $g_v(E)$ are the density of states in the conduction and valence bands, respectively.

Fermi and Number of carriers

- As Fermi Energy moves in band ratio of n to p moves



(a) E_F above midgap

(b) E_F near midgap

(c) E_F below midgap

Figure 2.16 Carrier distributions (not drawn to scale) in the respective bands when the Fermi level is positioned (a) above midgap, (b) near midgap, and (c) below midgap. Also shown in each case are coordinated sketches of the energy band diagram, density of states, and the occupancy factors (the Fermi function and one minus the Fermi function).

Density of States

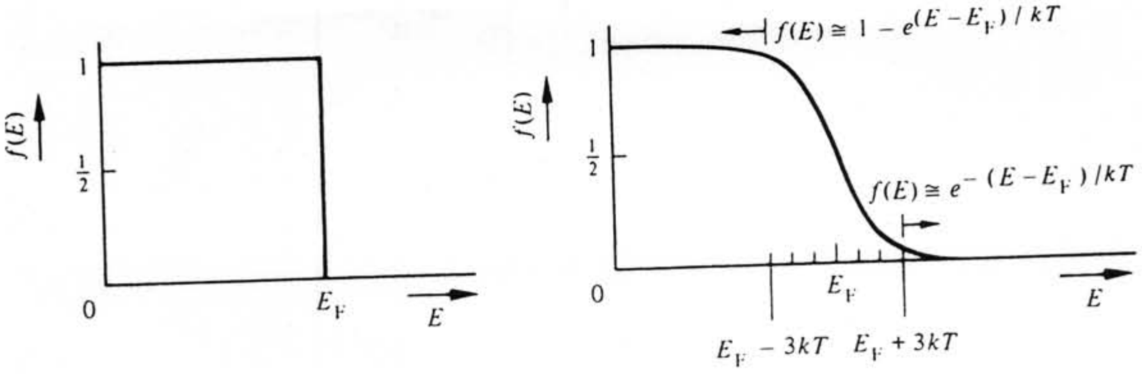
- From the equations the effective density of states:

$$N_c = 2\left[\frac{m_n^* k_B T}{2\pi\hbar^2}\right]^{3/2}$$

$$N_v = 2\left[\frac{m_p^* k_B T}{2\pi\hbar^2}\right]^{3/2}$$

- For Silicon at 300 K:

$N_c = 2.8\text{x}10^{19}\ \text{cm}^{-3}$
$N_v = 1.02\text{x}10^{19}\ \text{cm}^{-3}$



(a) $T \rightarrow 0$ K

(b) $T > 0$ K

Figure 2.15 Energy dependence of the Fermi function. (a) $T \rightarrow 0$ K; (b) generalized $T > 0$ K plot with the energy coordinate expressed in kT units.

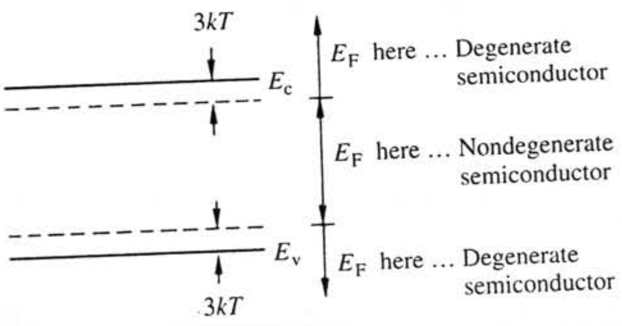


Figure 2.19 Definition of degenerate/nondegenerate semiconductors.

Intrinsic Semiconductor

- For an intrinsic semiconductor under steady state conditions:

$$n = p = n_i$$

- Where n_i is the intrinsic carrier density.
- For Silicon at T=300 K $n_i = 1.5 \times 10^{10}\ \text{cm}^{-3}$
- The Fermi Energy E_F lies near the band gap centre,
- point where number of electrons in conduction band equals the number of holes in the valance band.
- Free electrons are always falling into holes, thus filling states in the valance band (and removing electrons from the conduction),

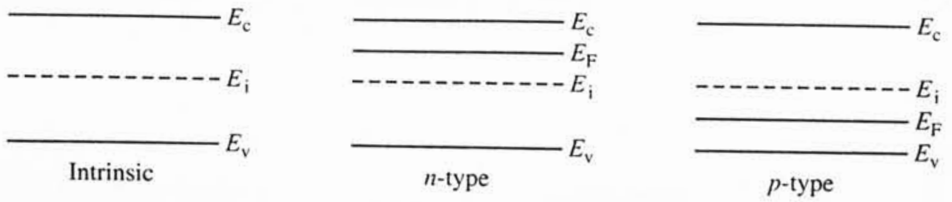


Figure 2.18 "At a glance" representation of intrinsic (left), *n*-type (middle), and *p*-type (right) semiconductor materials using the energy band diagram.

Laser Beam Interactions with Solids

- In absorbing materials photons deposit energy

$$E = h\nu = \frac{hc}{\lambda}$$

where h = Plank's constant = 6.63 x 10^{-34} J s

c = speed of light

- Also photons also transfer momentum p

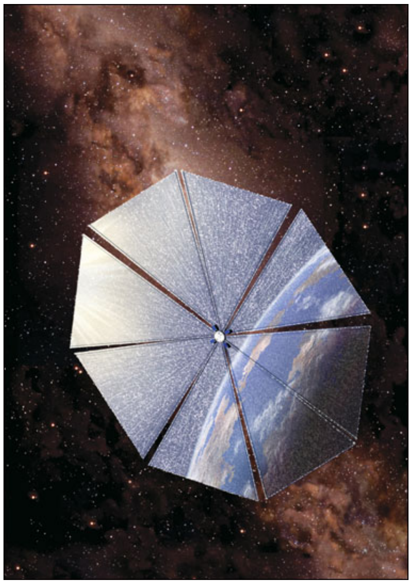
$$p = \frac{h}{\lambda}$$

- Note: when light reflects from a mirror momentum transfer is doubled
- eg momentum transferred from Nd:YAG laser photon hitting a mirror (λ= 1.06 microns)

$$p = \frac{h}{\lambda} = \frac{2\left(6.6x10^{-34}\right)}{1.06x10^{-6}} = 1.25x10^{-27}\, kg\ m/s$$

- Not very much but Sunlight 1 KW/m^2 for 1 sec has $5x10^{21}$ photons: force of $6.25x10^{-6}$ N/m^2
- Proposed for Solar Light Sails in space (get that force/sq m of sail) small acceleration but very large velocity over time.

- Russian Cosmos 1 solar sail
  Failed to reach 500 km orbit June 2005



Absorbing Solids

- Beam absorbed as it enters the material
- For uniform material follows Beer Lambert law

$$I(z) = I_0 \, exp(-\alpha z)$$

where $\alpha = \beta$ = absorption coefficient (cm^{-1})

z = depth into material

- Absorption coefficient dependent on wavelength, material & intensity
- High powers can get multiphoton effects
- Rayleigh scattering, Brillouin scattering, Raman scattering

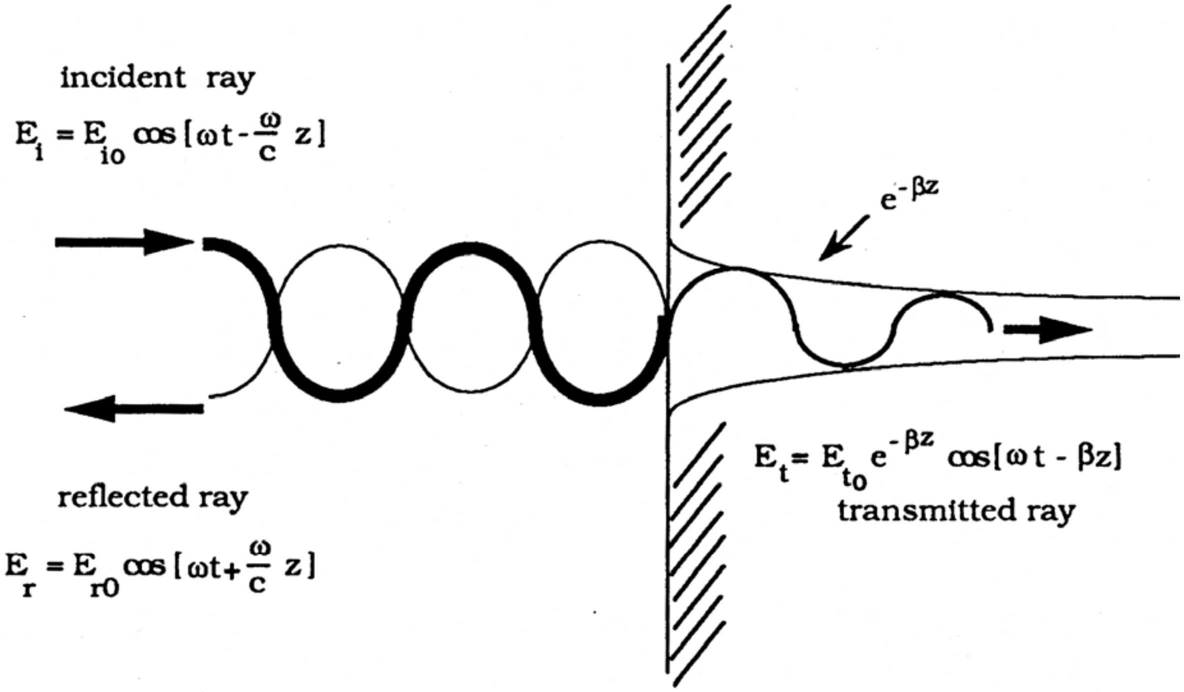


Fig. 2.1. The phase and amplitude of an electromagnetic ray striking an air/solid interface and undergoing reflection and transmission.

Single Crystal Silicon

- Absorption Coefficient very wavelength dependent
- Argon light 514 nm $\alpha = 11200/\mathrm{cm}$
- Nd:Yag light 1060 nm $\alpha = 280/\mathrm{cm}$
- Hence Green light absorbed within a micron
  1.06 micron penetrates many microns
- Very temperature dependent
- Note: polycrystalline silicon much higher absorption
  : at 1.06 microns $\alpha = 20{,}000/\mathrm{cm}$

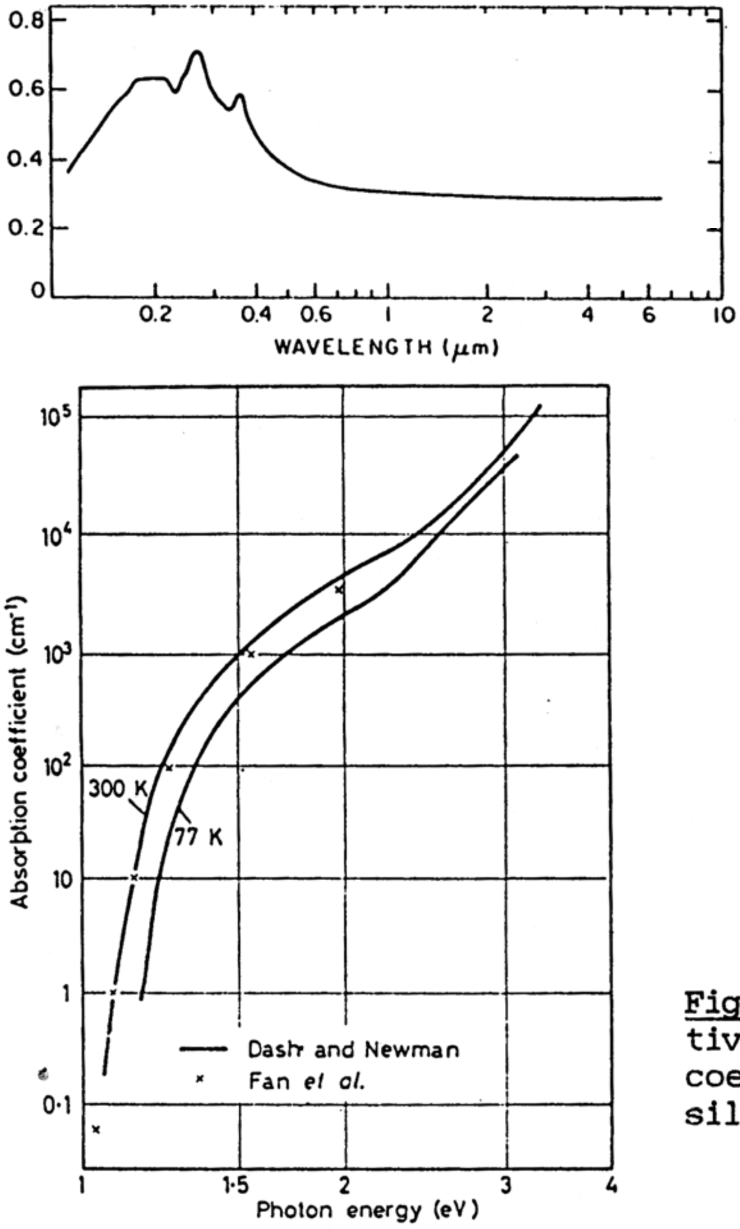


Fig.2.8. (a) Optical reflectivity, and (b) absorption coefficient of single crystal silicon [2.89,90],

Absorption Index

- Absorbing materials have a complex index of refraction

$$n_c = n - ik \qquad v = \frac{c}{n_c}$$

where n = real index of refraction
k = absorption index or extinction coefficient

- The Electric field then becomes

$$\vec{E}(t,z) = \hat{i}E_0 \exp\left[j\left(-\omega t + \frac{\omega n_c z}{c} \right) \right]$$

$$E(t,z) = E_0 \, exp\left(i\left[\omega t - \frac{\omega nz}{c} \right] \right) exp\left(-\frac{\omega kz}{\lambda} \right)$$

- The k can be related to the absorption coefficient by

$$\alpha = \frac{4\pi k}{\lambda}$$

where wavelength is the vacuum value

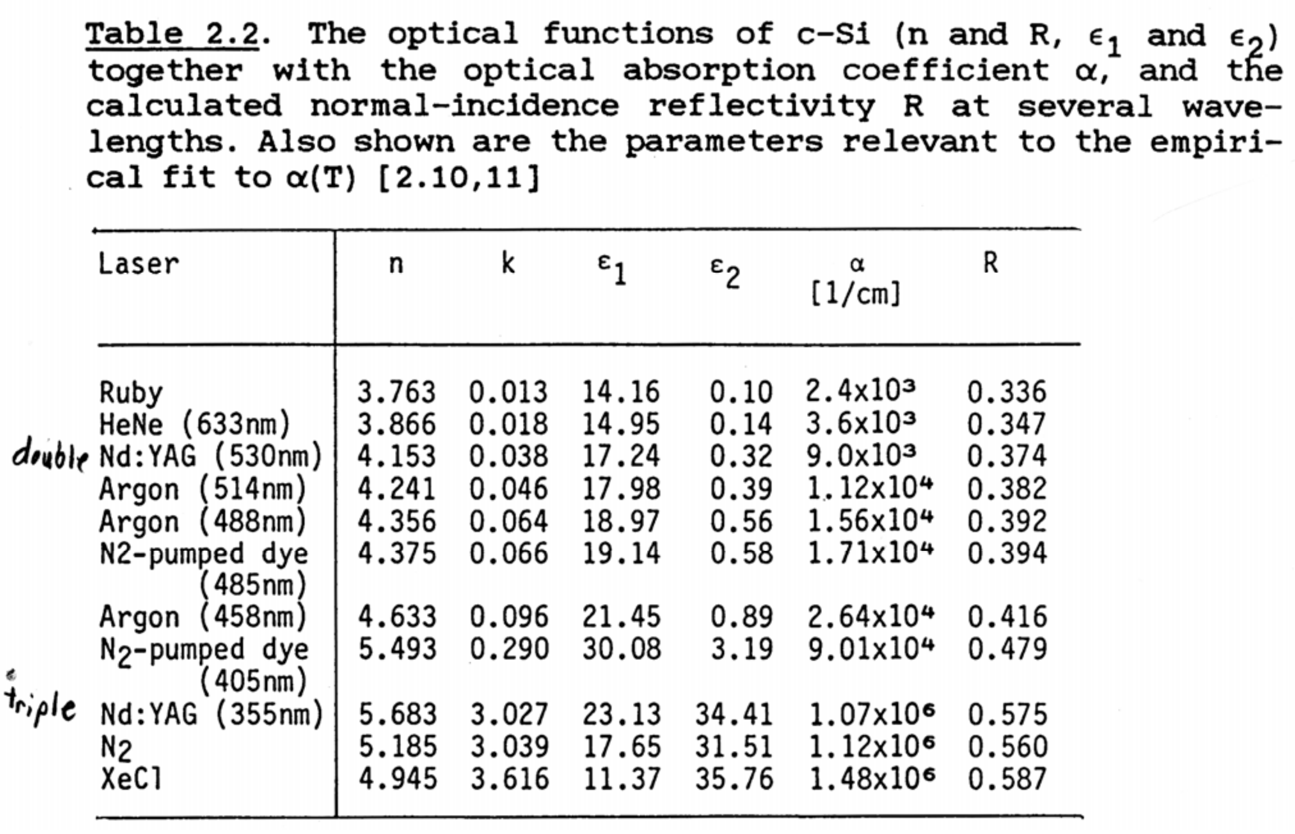


Table 2.2. The optical functions of c-Si (n and R, ϵ_1 and ϵ_2) together with the optical absorption coefficient α, and the calculated normal-incidence reflectivity R at several wavelengths. Also shown are the parameters relevant to the empirical fit to $\alpha(T)$ [2.10,11]

Laser	n	k	ε_1	ε_2	α [1/cm]	R
Ruby	3.763	0.013	14.16	0.10	2.4×10^3	0.336
HeNe (633nm)	3.866	0.018	14.95	0.14	3.6×10^3	0.347
double Nd:YAG (530nm)	4.153	0.038	17.24	0.32	9.0×10^3	0.374
Argon (514nm)	4.241	0.046	17.98	0.39	1.12×10^4	0.382
Argon (488nm)	4.356	0.064	18.97	0.56	1.56×10^4	0.392
N2-pumped dye (485nm)	4.375	0.066	19.14	0.58	1.71×10^4	0.394
Argon (458nm)	4.633	0.096	21.45	0.89	2.64×10^4	0.416
N_2-pumped dye (405nm)	5.493	0.290	30.08	3.19	9.01×10^4	0.479
triple Nd:YAG (355nm)	5.683	3.027	23.13	34.41	1.07×10^6	0.575
N_2	5.185	3.039	17.65	31.51	1.12×10^6	0.560
XeCl	4.945	3.616	11.37	35.76	1.48×10^6	0.587

Illuminating the semiconductor

- Absorption moves electrons into the conduction band
- If photon energy is greater than the band gap.
- Leaves a hole in the valance band.
- Called creating an "electron hole pair".
- Carriers in both bands are mobile, free to move
- Energy of the light in eV use the following: Photon energy

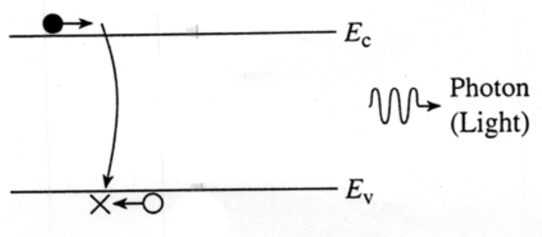
$$E = h\nu = \frac{hc}{\lambda} = \frac{1.240}{\lambda}\ eV$$

where h = Plank's constant = 6.63 x 10^{-34} J s
c = speed of light
where λ = light wavelength in microns

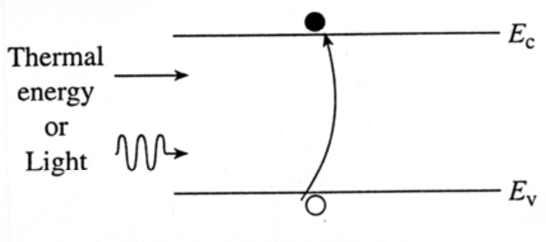
- Example: for silicon E_g = 1.12 eV
- Makes light of 1.1 microns the longest wavelength absorbed

Near infra red: red 0.75 microns, green light is 0.5 microns.
Example: for GaAs E_g = 1.45 eV,

- λ = 0.855 microns longest wavelength absorbed
- Almost visible red
- λ = creation of electron hole pairs from absorbed light
- The process by which solar cells operate.



(a) Band-to-band recombination



(d) Band-to-band generation

Optical Absorption and Crystal Momentum

Energy band density diagrams plot Energy vertical
Horizontal axis is "Crystal Momentum" k
This is the momentum carried by a phonon
Phonons are acoustic bundles with momentum
Both photons and phonons have momentum

$$p = \frac{hk}{2\pi} = \bar{h}k$$

For the phonon this is the momentum

$$k = \frac{\omega}{c}$$

where c = the velocity of light (sound) in the crystal
and ω = the angular frequency of the phonon

$$\omega = 2\pi f$$

For the phonon f is the sound frequency
C is the velocity of sound in the crystal
The two momentums add vector wise in an interaction

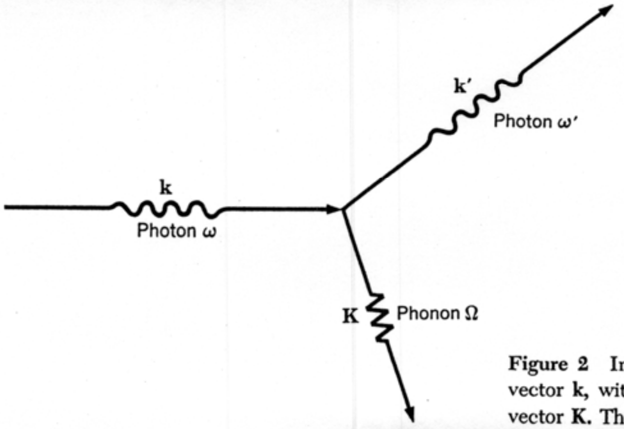


Figure 2 Inelastic scattering of a photon of wavevector **k**, with the production of a phonon of wavevector **K**. The scattered photon has wavevector **k′**.

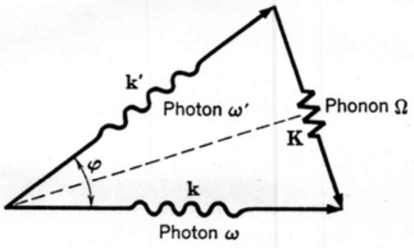


Figure 3 Selection rule diagram for the process of Fig. 2. If $k = k'$, the triangle is isosceles. The base of the triangle is $K = 2k \sin \frac{1}{2}\varphi$.

Optical Absorption and Band Structure

Direct band gap semiconductors

Adbsorb and emit photons directly

More efficient at light adsorption and emission

eg GaAs Silicon is "indirect band gap" semiconductor

Indirect bandgap Semiconductors

Requires a Crystal momentum k change before light absorption.

k = acoustical energy to be present in the crystal

Only "direct band gap" materials can become light emitting diodes,

Direct band gap make the most efficient solar cells

but indirect work as well

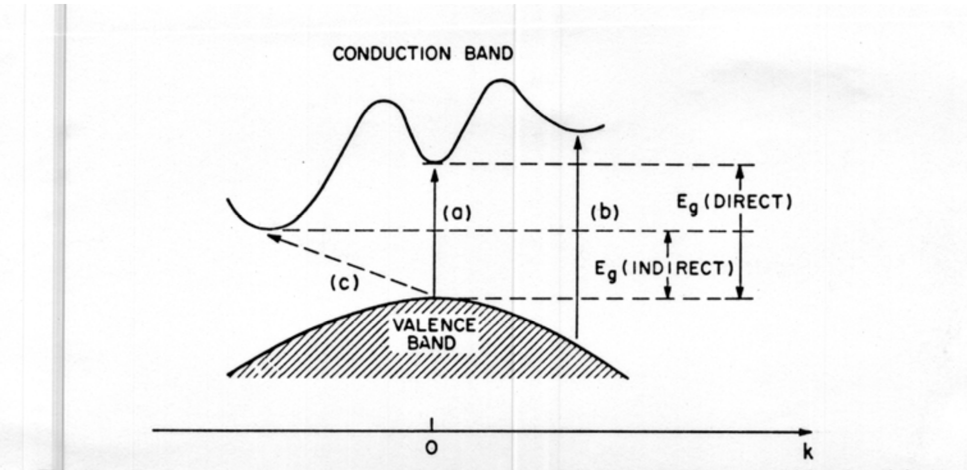


Fig. 26 Optical transitions: (*a*) and (*b*) direct transitions; (*c*) indirect transition involving phonons.

Illumination of a Semiconductor

- if a N type semiconductor is illuminated by light,
  create excess holes and electrons
- when the light is turned off the holes will decay as:

$$\frac{dp_n}{dt} = \frac{dp'_n}{dt} = -\frac{p'_n}{\tau_h}$$

- Solving this 1st order DE get the exponential solution
- boundry conditions: at t=0, p'_n added, at infinity, $p=p_{n0}$,

$$p_n = p_{n0} + p'_n \exp(-\frac{t}{\tau_h})$$

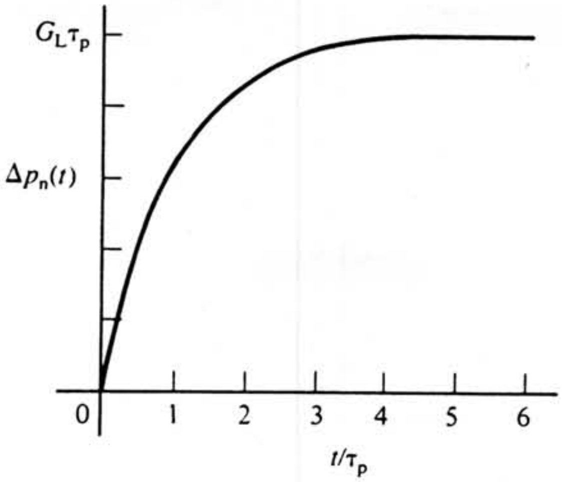


Figure 3.25 Solution to Sample Problem No. 1. Photogeneration-induced increase in the excess hole concentration as a function of time.

Quasi Fermi Levels

- With injection number of carrier changes from intrinsic
- Define a "Quasi Fermi level" to represent this
- Different for holes and electrons
- Using the Fermi level equations from before

$$E_F - E_i = k_B T \ln\left(\frac{n_n}{n_i}\right)$$

- Thus the n quasi Fermi is

$$F_N = E_i + k_B T \ln\left(\frac{n_n}{n_i}\right)$$

- Thus the p quasi Fermi is

$$F_p = E_i + k_B T \ln\left(\frac{p_n}{n_i}\right)$$

- This becomes important in devices
- Can see that quasi Fermi changes for the illumination case

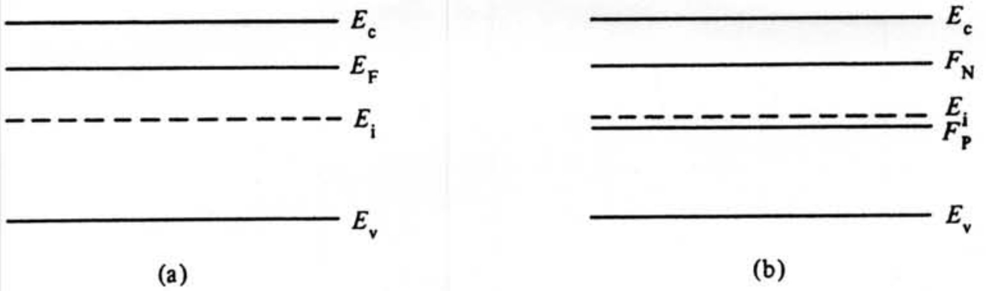


Figure 3.28 Sample use of quasi-Fermi levels. Energy band description of the situation inside the semiconductor of Sample Problem No. 1 under (a) equilibrium conditions and (b) nonequilibrium conditions ($t \gg \tau_p$).