CHEMISTRY 5570

Advanced Analytical Chemistry

Lecture 6

Semiconductors

Semiconductors

Silicon is a semiconductor.

A silicon atom has the electronic configuration of **[Ne]3s^{2}p^2**

The 3s and 3p however form 4 hybrid orbitals so that silicon can form four bonds.

For a silicon crystal lattice the resulting structure is a tetrahedron arrangement.

Semiconductors

Silicon is a semiconductor.

Electronic properties for solids can be described in terms of the band model.
For a crystalline solid, atoms assemble into a lattice forming molecular orbitals.

Semiconductors

The filled bonding orbitals form the valence band (VB) and the vacant antibonding orbitals form the conduction band (CB).

Since the CB is empty – an electron placed in the CB is free to move around.

These bands are separated by a band gap of energy, Eg (eV).

Semiconductors

The electrical and optical properties of the solid are strongly influenced by the size of the band gap.

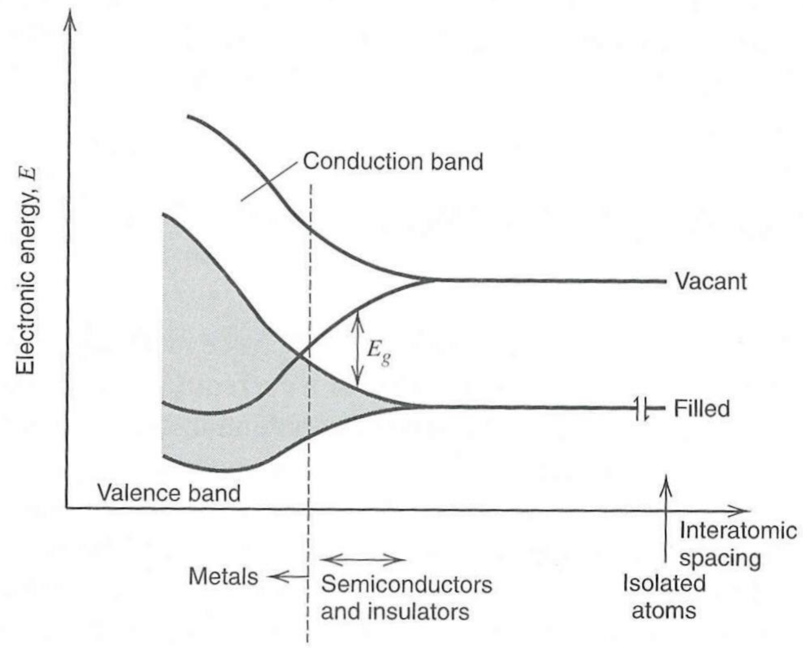


Figure 18.2.1 Formation of bands in solids (at left) by assembly of isolated atoms (characterized by orbitals at far right) into a lattice.

Semiconductors

When the gap is very small ($E_g << kT$) or the conduction and valence bands overlap, the material is a good conductor.

For larger values of E_g (i.e. Si, 1.1 eV), valence band is almost filled and conduction band is almost vacant.

Semiconductors

If Eg > 1.5 eV, RT thermal excitation does not produce enough carriers for conduction.

Example:	GaP	Eg = 2.2 eV
	TiO_2	Eg = 3.0 eV

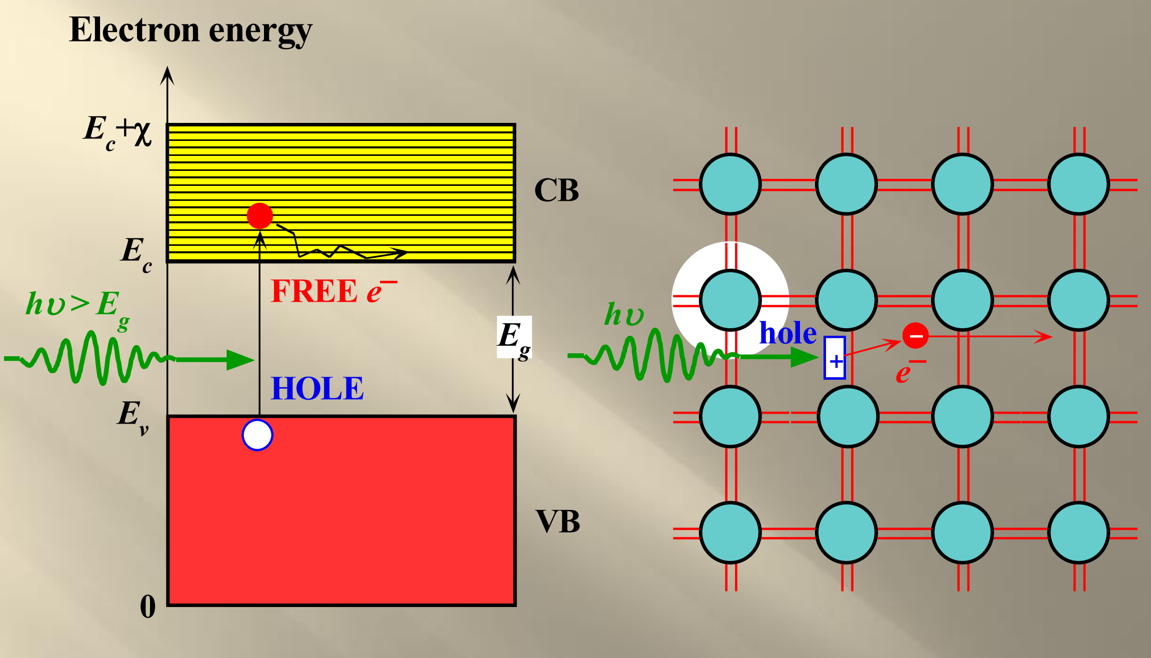
Semiconductors

Conduction occurs by thermal excitation of electrons from VB into the CB, producing electrons in CB and "holes" in VB.

The charge can then be carried by the electrons and holes.

This is called an intrinsic semiconductor.

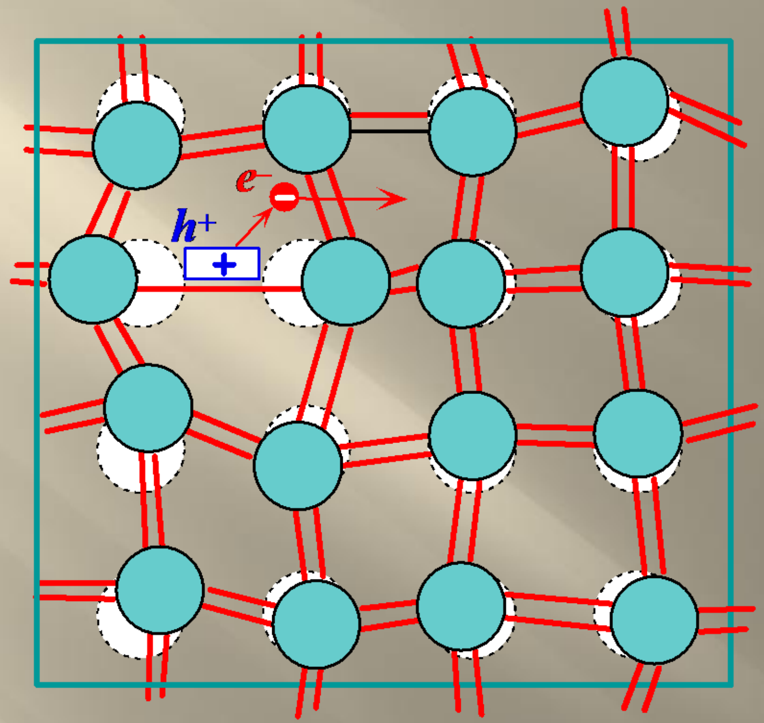
Semiconductors



(a) (b)

A photon with energy greater than Eg can excite an electron from VB to CB.
When a Si-Si bond is broken, a free electron and a hole in the Si-Si bond is created.

Semiconductors



Semiconductors

When the electron and hole recombine this process is called recombination.

In some semiconductors, i.e. GaAs and InP this process results in an emission of a photon.

In other semiconductors, the energy is simply lost as lattice vibrations (heat).

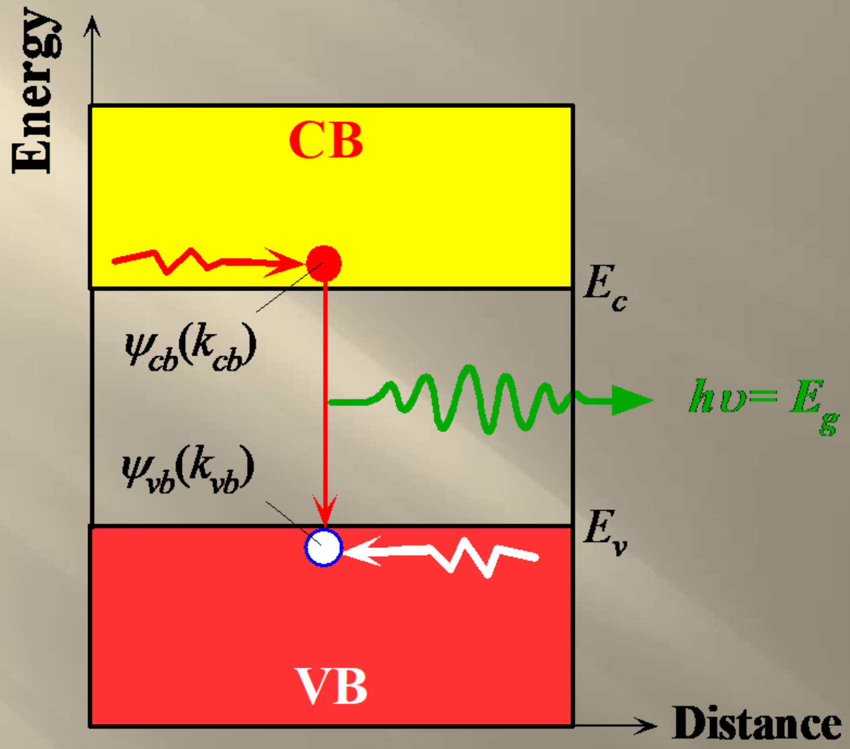
Semiconductors

Recombination corresponds to the free electron finding an incomplete bond with a missing electron. When the electron completes the bond, the free electron of the CB and hole of the VB are annihilated.

This is a direct recombination mechanism and the excess energy of the electron is lost as a photon $h\nu = E_g$.

Ex. Light emitting diodes (LEDs)

Semiconductors



Direct recombination that produces a photon.

Semiconductors

However, since there are no empty states in the VB of Si and Ge, direct recombination is not possible and recombination centers are used.

The recombination center may be an impurity atom or crystal defect which captures the electron and holds" it until a hole arrives.

For this process the energy of the electron is lost to lattice vibrations – these emitted lattice vibrations are called <u>phonons</u>.

Semiconductors

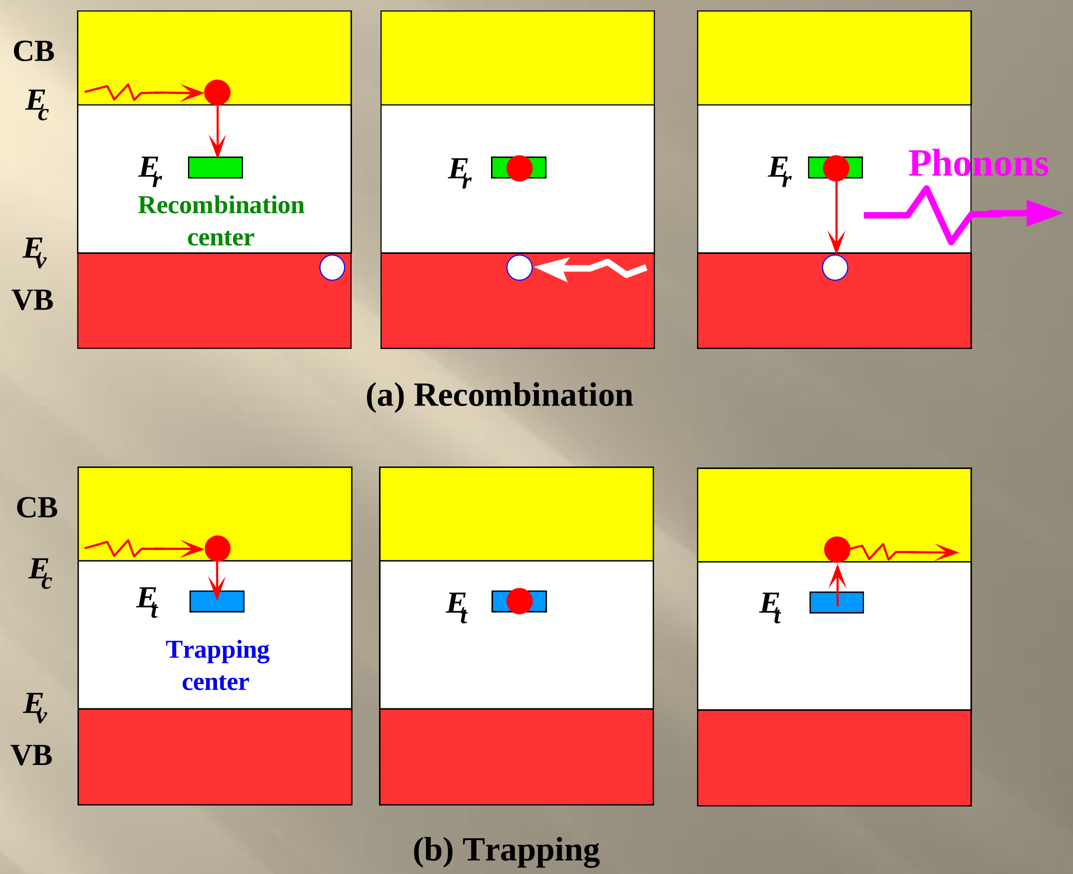


Fig. 5.23: Recombination and trapping. (a) Recombination in Si via a recombination center which has a localized energy level at E_r in the bandgap, usually near the middle. (b) Trapping and detrapping of electrons by trapping centers. A trapping center has a localized energy level in the band gap.

Semiconductors

The recombination difference occurs depending if the semiconductor has a <u>direct</u> or <u>indirect</u> bandgap.

Since the law of conservation of momentum must be followed in a wavefunction, Si is an indirect semiconductor.

Semiconductors

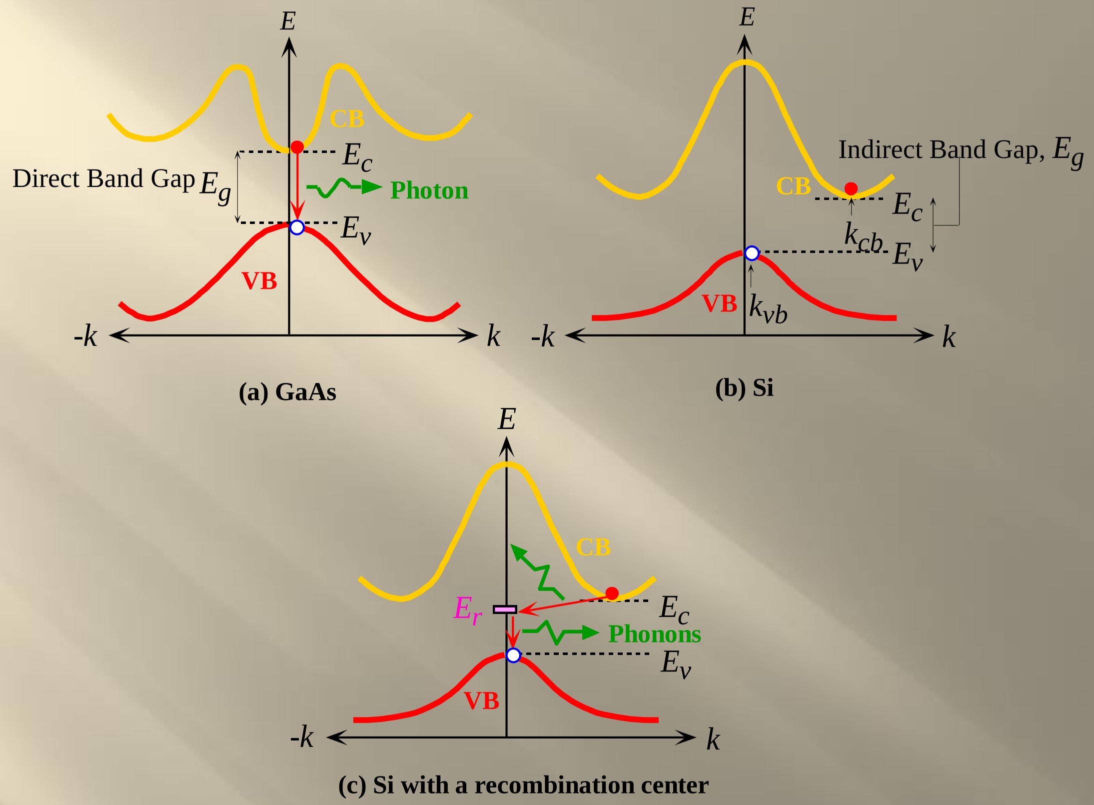


Fig. 5.50: (a) In GaAs the minimum of the CB is directly above the maximum of the VB. GaAs is therefore a direct band gap semiconductor. (b) In Si, the minimum of the CB is displaced from the maximum of the VB and Si is an indirect band gap semiconductor. (c) Recombination of an electron and a hole in Si involves a recombination center.

Semiconductors

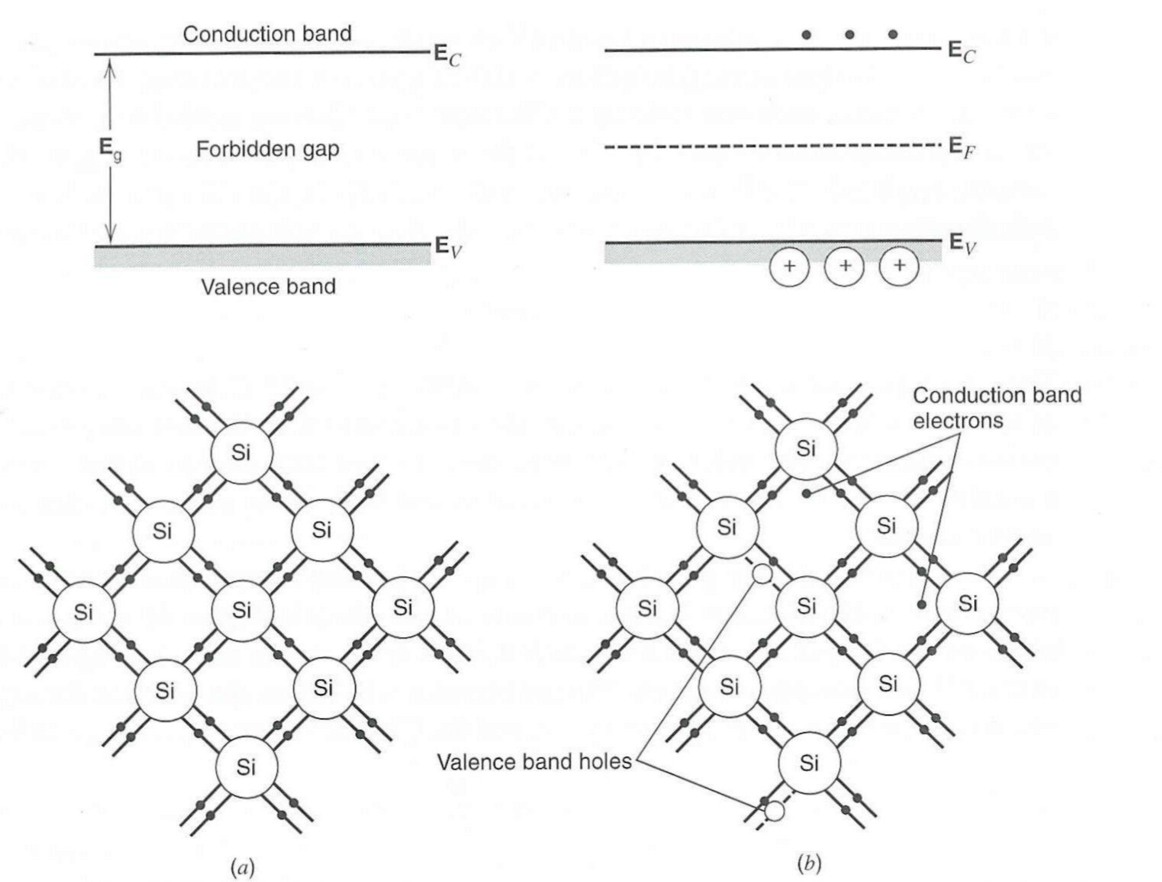


Figure 18.2.2 Energy bands and two-dimensional representation of an intrinsic semiconductor lattice. (*a*) At absolute zero (or $\mathbf{E}_g >> kT$), assuming a perfect lattice; no holes or electrons exist. (*b*) At a temperature where some lattice bonds are broken, yielding electrons in the conduction band and holes in the valence band. $\mathbf{E}_F$ represents the Fermi level in this intrinsic semiconductor.

Semiconductors

For an intrinsic semiconductor, the electrons and hole densities are equal.

n_i – density for CB electrons
p_i – density for VB holes
$n_i p_i$ = (constant)exp(-Eg/kT)

Semiconductors

$n_i = p_i = 2.5x10^{19}exp(-Eg/2kT)cm^{-3}$ (near 25^{o}C)

The mobile carriers move in the semiconductor and have mobilities of
$u_n = 1350\ cm^2V^{-1}s^{-1}$ and $u_p = 480\ cm^2V^{-1}s^{-1}$

An intrinsic semiconductor is a pure semiconductor crystal in which the electron and hole concentrations are equal.

Semiconductors

However , electrons in CB and holes in VB can be introduced by adding <u>dopants</u> (impurities) into the semiconductor lattice to produce an <u>extrinsic semiconductor</u>.

This causes the concentration of one of the carriers to be in excess of the other.

Semiconductors

Example: Add As atoms (Group V) which behave as electron donor for silicon (Group IV) and introduce an energy level, E_D just below the CB.

Thus at room temperature, the donor atoms are ionized and give a CB electron leaving a positive site.

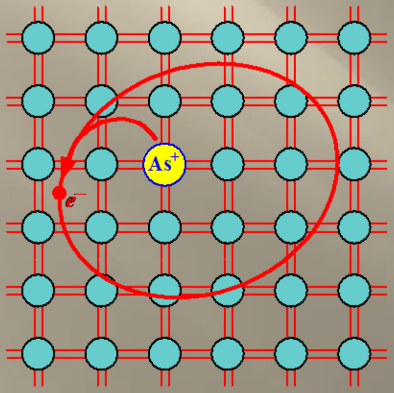


Fig. 5.9: Arsenic doped Si crystal. The four valence electrons of As allow it to bond just like Si but the fifth electron is left orbiting the As site. The energy required to release to free fifth-electron into the CB is very small.

Semiconductors

For 1 ppm of added dopant – the donor density is $N_D = 5 \times 10^{16}\ cm^{-3}$ – making up most of the CB electron density, n.

$$p = n_i^2/N_D$$

In this case, the electrical conductivity is attributed to the CB electrons and are called the majority carriers.

Thus a material doped with a donor atom is called a n-type semiconductor.

Semiconductors

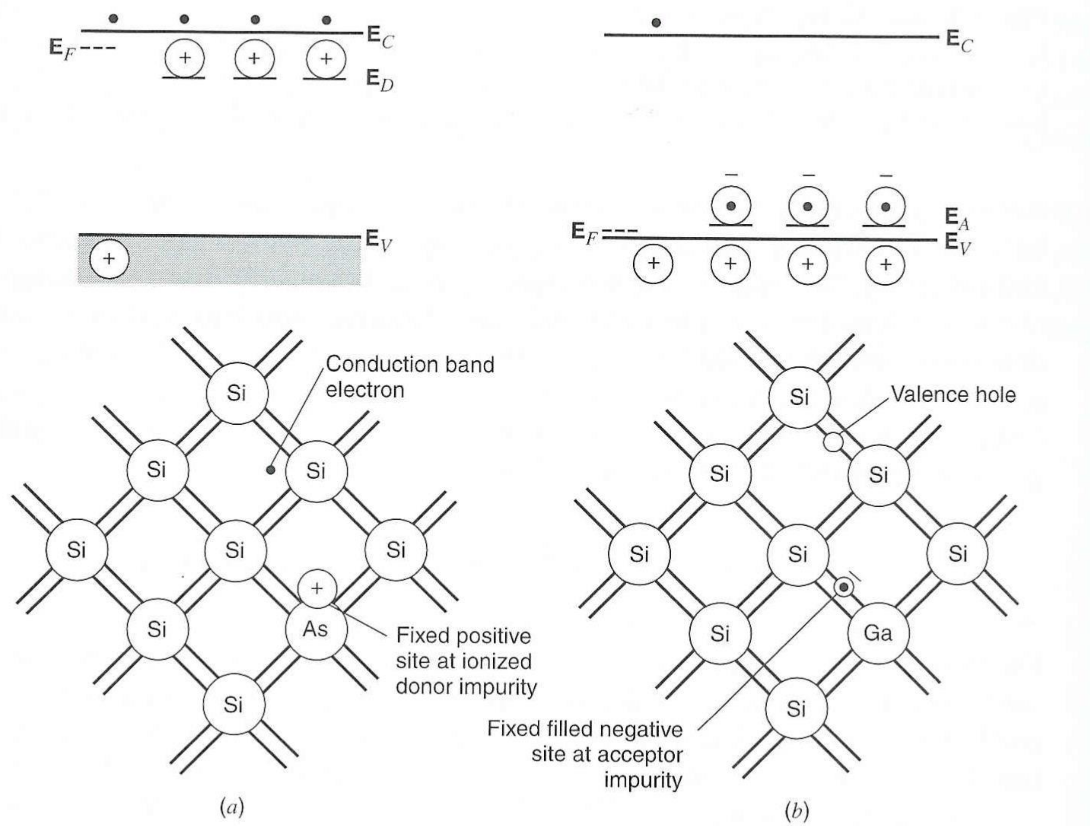


Figure 18.2.3 Energy bands and two-dimensional representation of extrinsic semiconductor lattices. (*a*) *n*-type. (*b*) *p*-type.

Semiconductors

Example: Add Ga atoms (Group III) which is an acceptor atom to silicon (Group IV) then introduce an energy level E_A just above VB.

Thus at room temperature, the electrons are thermally excited from the VB into the acceptor sites leaving mobile holes in the VB.

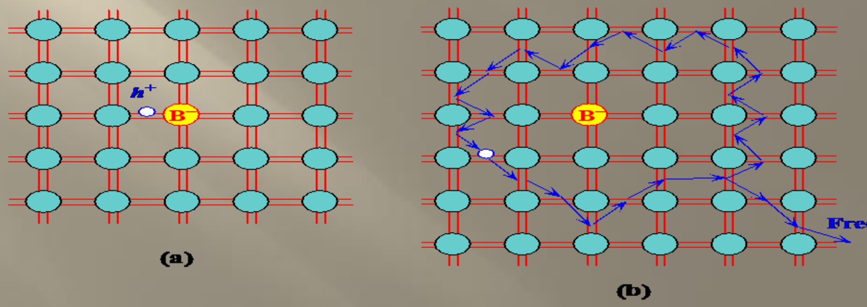


Fig. 5.11: Boron doped Si crystal. B has only three valence electrons. When it substitutes for a Si atom one of its bonds has an electron missing and therefore a hole as shown in (a). The hole orbits around the B– site by the tunneling of electrons from neighboring bonds as shown in (b). Eventually, thermally vibrating Si atoms provides enough energy to free the hole from the B– site into the VB as shown.

Semiconductors

Acceptor density, N_A makes up most of the hole density, p.

$$n = p_i^2/N_A$$

In this case, the electrical conductivity is attributed to the holes as the majority carriers and the material is called a p-type semiconductor.

Semiconductors

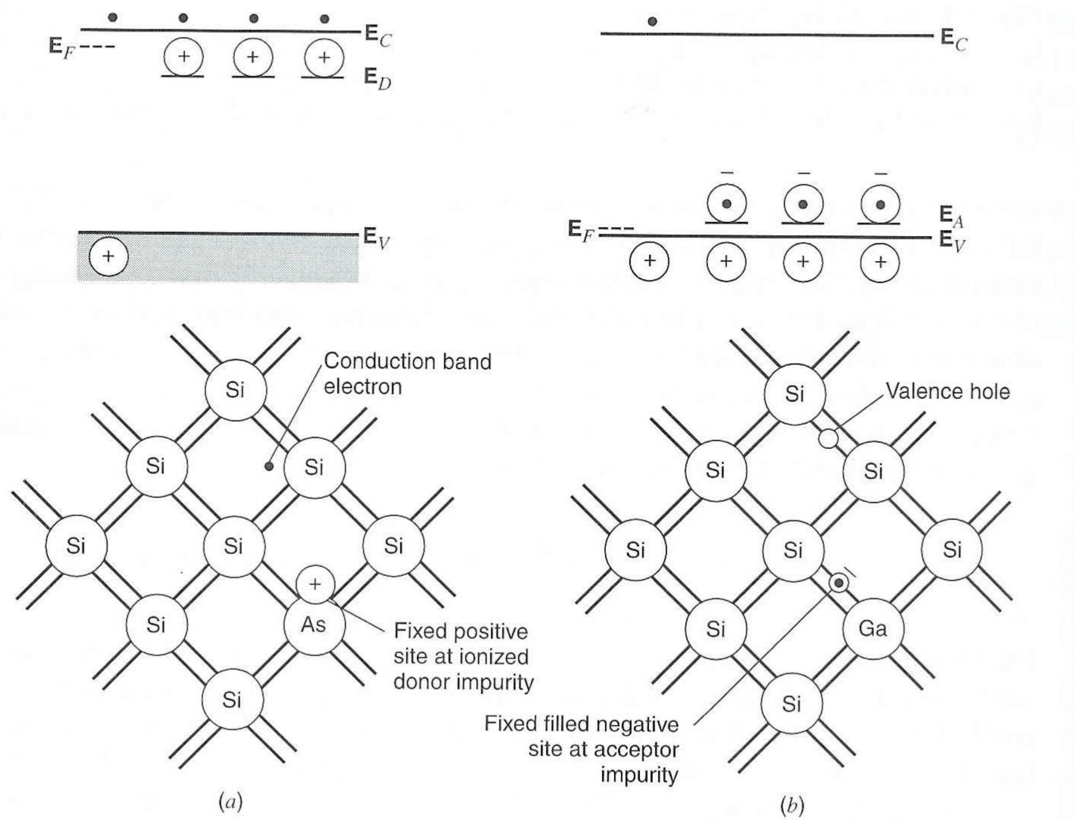


Figure 18.2.3 Energy bands and two-dimensional representation of extrinsic semiconductor lattices. (*a*) *n*-type. (*b*) *p*-type.

Semiconductors

For recombination in an n-type or p-type semiconductor, must consider the minority carrier concentration.

n-type – minority carriers are holes
p-type - minority carriers are electrons

Semiconductors

Example:

A n-type can be illuminated with a wavelength of light which will photogenerate electron-hole pairs.

For the n-type there are an excess of electrons (majority carriers) compare to holes (minority carriers).

When the light is turned off (dark), then the time for the electrons and holes to recombine is called the <u>minority carrier lifetime </u>(mean recombination time).

Semiconductors

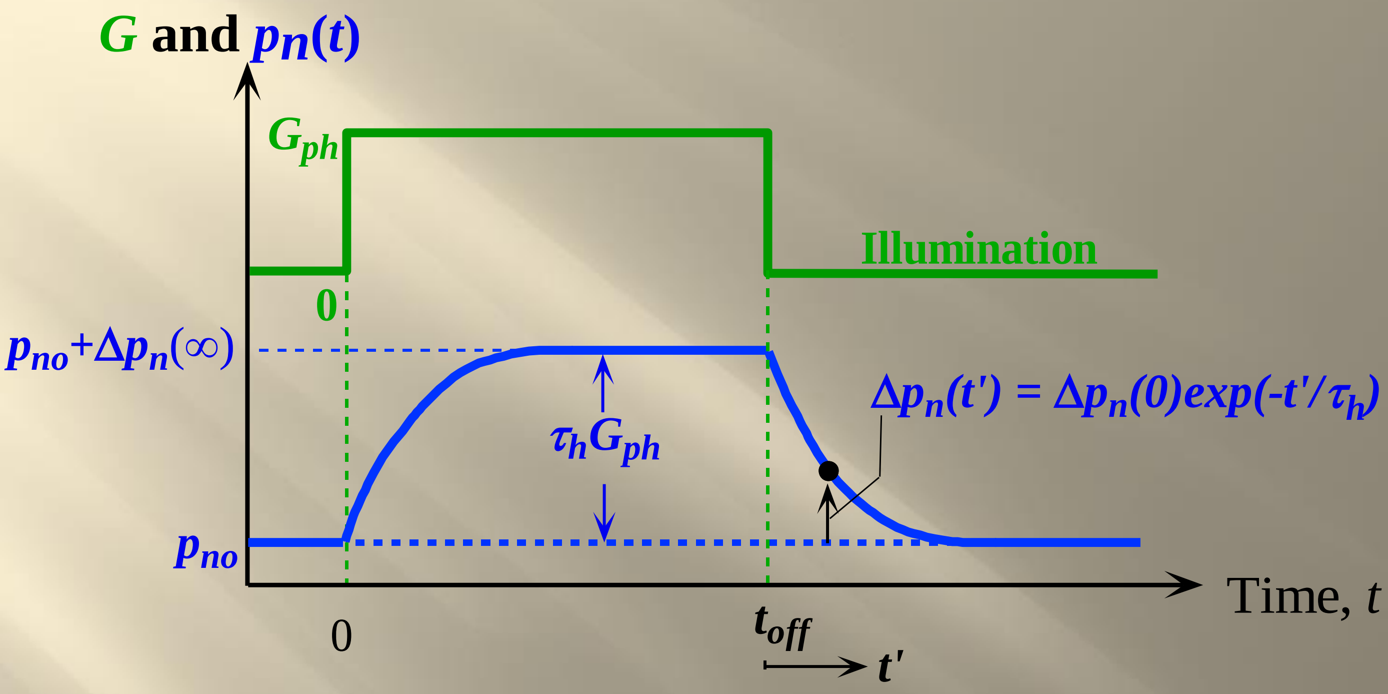


Fig. 5.27: Illumination is switched on at time $t = 0$ and then off at $t = t_{off}$. The excess minority carrier concentration, $\Delta p_n(t)$ rises exponentially to its steady state value with a time constant τ_h. From t_{off}, the excess minority carrier concentration decays exponentially to its equilibrium value.

Semiconductors

These lifetimes can be from nanoseconds to seconds.

Short lifetimes can be used in fast switching pn junctions.

Long lifetimes can be used for luminescence.

Semiconductors

Compensation Doping – when a semiconductor contains both donor and acceptors.

Electrons from donors recombine with holes from acceptors, since the mass action law $np=n_i^2$ is obeyed.

Semiconductors

Conductivity of semiconductors is dependent on temperature.

Two factors must be considered:
-temperature dependence of carrier concentration
-drift mobility

There are three temperature ranges to consider:
-$T<T_s$ (saturation temp)
-$T_s<T<T_i$ (ionization temp)
-$T>T_i$

Semiconductors

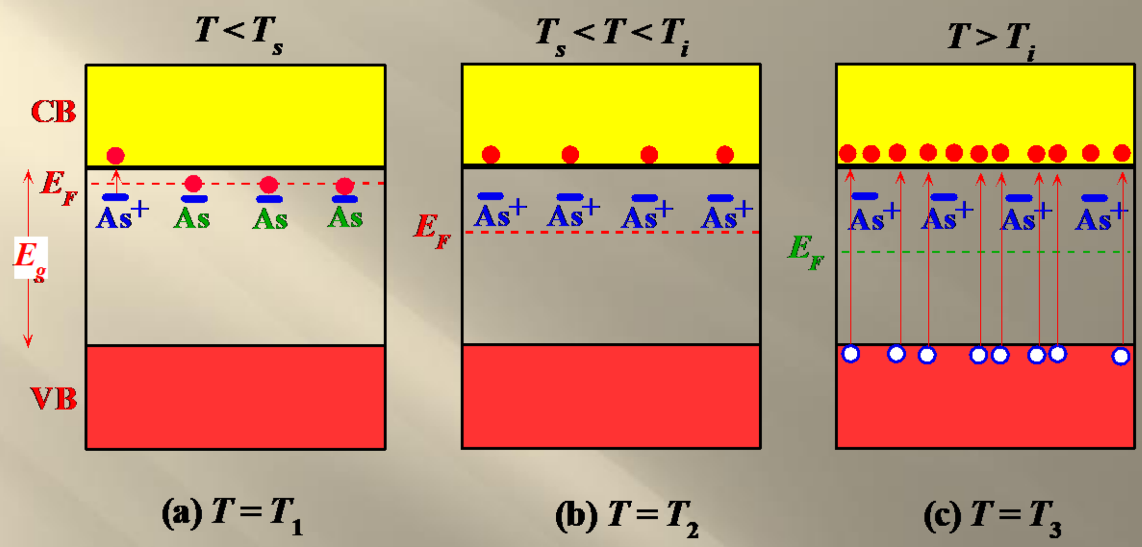


Fig. 5.14: (a) Below T_s, the electron concentration is controlled by the ionization of the donors. (b) Between T_s and T_i, the electron concentration is equal to the concentration of donors since they would all have ionized. (c) At high temperatures, thermally generated electrons from the VB exceed the number of electrons from ionized donors and the semiconductor behaves as if intrinsic.

Semiconductors

For $T<T_s$

At lower temperatures, there are few carriers in the conduction band. As the temperature increases, donor ionization continues until the saturation temperature is reached, T_s.

At T_s all the donors have been ionized, this temperature range is the <u>ionization range</u>.

Semiconductors

For $T_s<T<T_i$

In the mid temperature range, the donors are all ionized and remain unchanged, the semiconductor behaves according to its properties. This temperature range is referred to as the <u>extrinsic range</u>.

Semiconductors

For $T>T_i$

At high temperatures, excitation begins to occur across the bandgap, this range is referred to as the intrinsic range.

Semiconductors

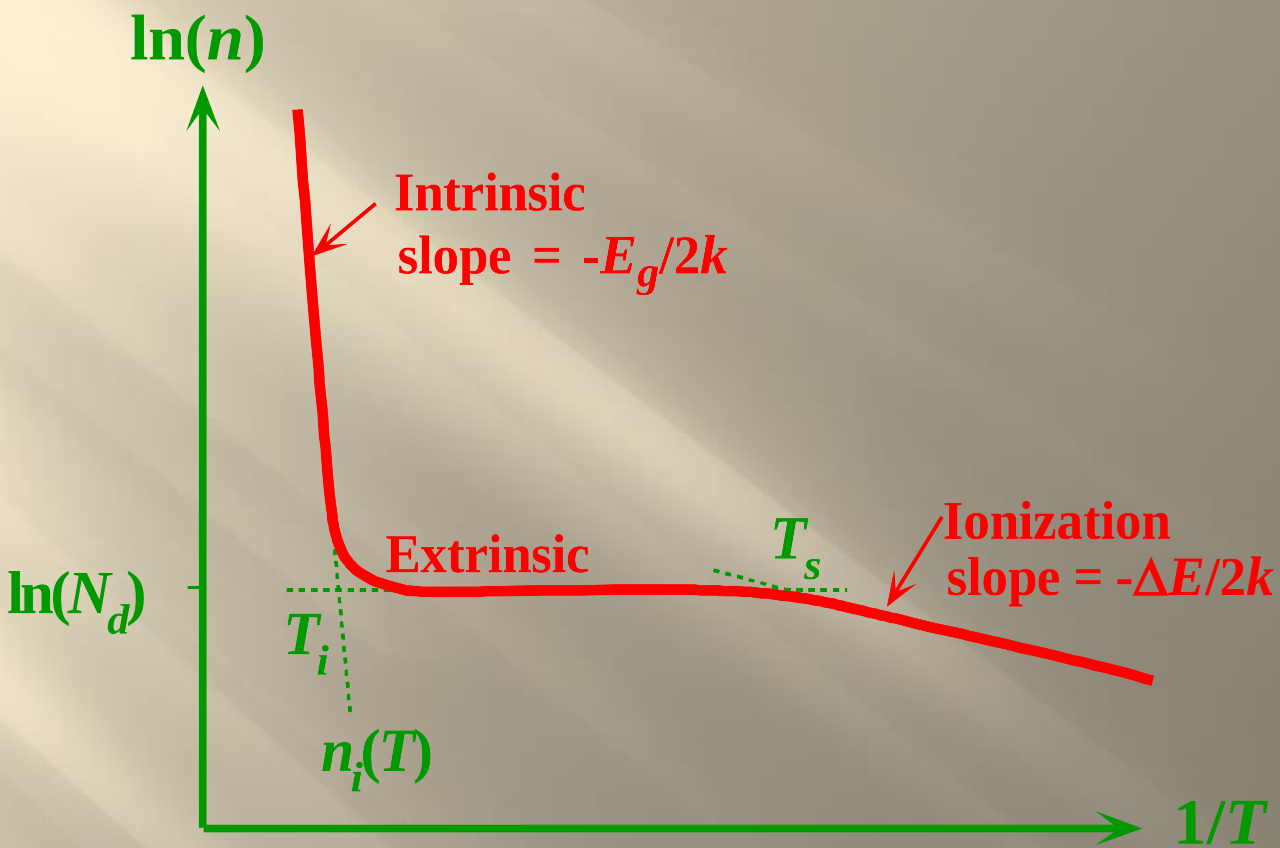


Fig. 5.15: The temperature dependence of the electron concentration in an n-type semiconductor.

Semiconductors

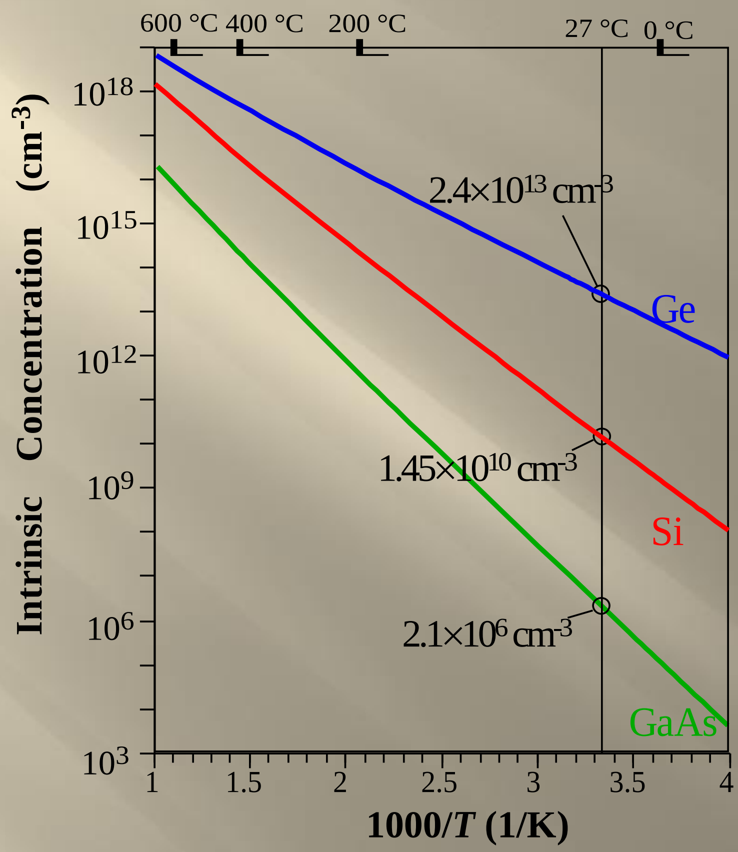


Fig. 5.16: The temperature dependence of the intrinsic concentration.

Semiconductors

Drift mobility is the drift velocity per unit applied field.

For $v_d = \mu_d E$

μ_d is the mobility

v_d is the drift velocity

E is the electric field

Semiconductors

The temperature dependence for drift mobility has two regions.

At high temperatures, mobility is limited by scattering from lattice vibrations. As atomic vibrations increase with temperature, mobility decreases,
μ is proportional to $T^{-3/2}$

Semiconductors

The temperature dependence for drift mobility has two regions.

At low temperatures, scattering of electrons by ionized impurities is the major mobility limiting mechanism and
μ is proportional to $T^{3/2}$

Semiconductors

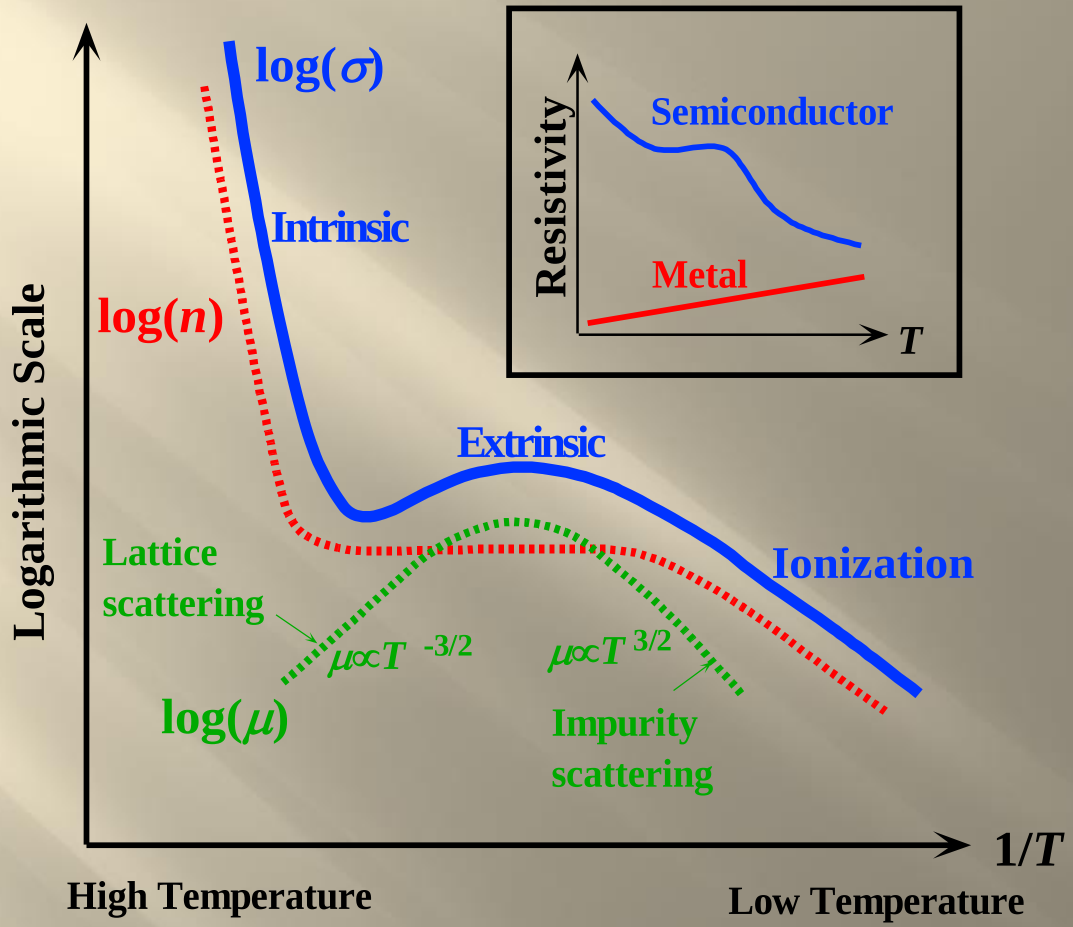


Fig. 5.20: Temperature dependence of electrical conductivity for a doped (*n*-type) semiconductor.

Semiconductors

For semiconductors, since the conduction band is above the Fermi level, it is assumed that the number of states in the CB far exceeds the number of electrons there, so two electrons both occupying the same state is nil.

Under these conditions, electron statistic can be described by Boltzmann statistics,
where $n \ll N_c$ and $p \ll N_v$

These semiconductors are called nondegenerate semiconductors.

Semiconductors

However, if a semiconductor is excessively doped then Boltzmann statistic do not hold and must use Fermi-Dirac statistics.

The semiconductor becomes metal-like and is called a degenerate semiconductor.

These semiconductors have uses in laser diodes, zener diodes, ohmic contacts in ICs, and metal gates in MOS devices.

Semiconductors

Optical Absorption

When a photon of energy higher than Eg strikes a semiconductor, electrons are excited from the VB to the CB.

Semiconductors

Optical Absorption

Beer-Lambert Law for the semiconductor:

$$I(x) = I_o \exp(-\alpha x)$$

where

$I(x)$ – transmitted intensity

I_o – intensity of photons incident on semiconductor

α – absorption coefficient of the semiconductor

x – thickness

The distance over which 67 percent of the photons are absorbed is called the <u>penetration depth</u>.

Semiconductors

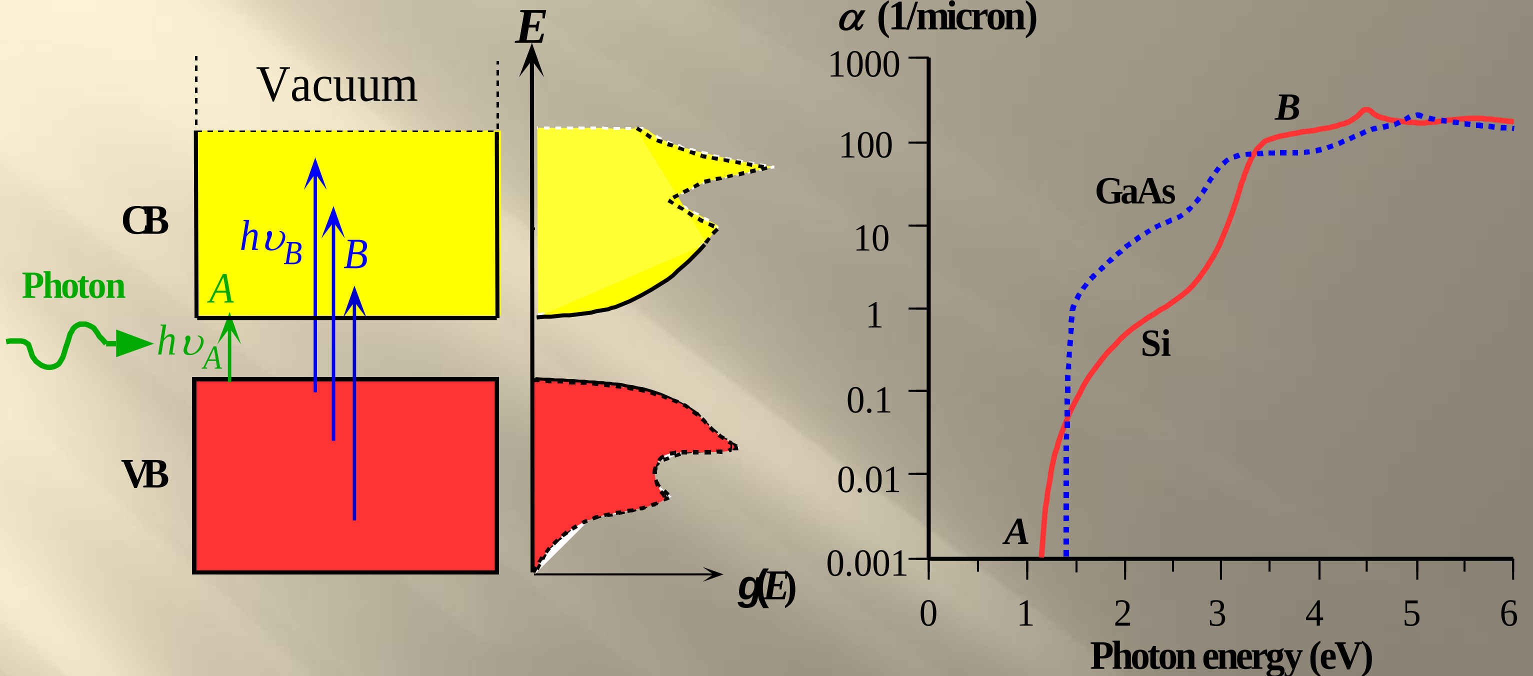


Fig. 5.37: The absorption coefficient α depends on the photon energy $h\upsilon$ and hence on the wavelength. Density of states increases from band edges and usually exhibits peaks and troughs. Generally α increases with the photon energy greater than E_g because more energetic photons can excite electrons from populated regions of the VB to numerous available states deep in the CB.

Semiconductors

Luminescence

During recombination a photon may be emitted. This emission is referred to as luminescence.

Luminescence may be fluorescence or phosphorescence.

The original electron excitation can occur by photons (photoluminescence), high-energy electron beam (cathodoluminescene), or an electric current (electroluminescence).

Semiconductors

Schottky Junctions

When a metal is evaporated onto the surface of a n-type semiconductor, the electrons in the CB tunnel into the metal to lower empty energy levels and accumulate near the surface of the metal.

A <u>depletion region</u> develops and is called a <u>space charge layer</u> (SCL).

Semiconductors

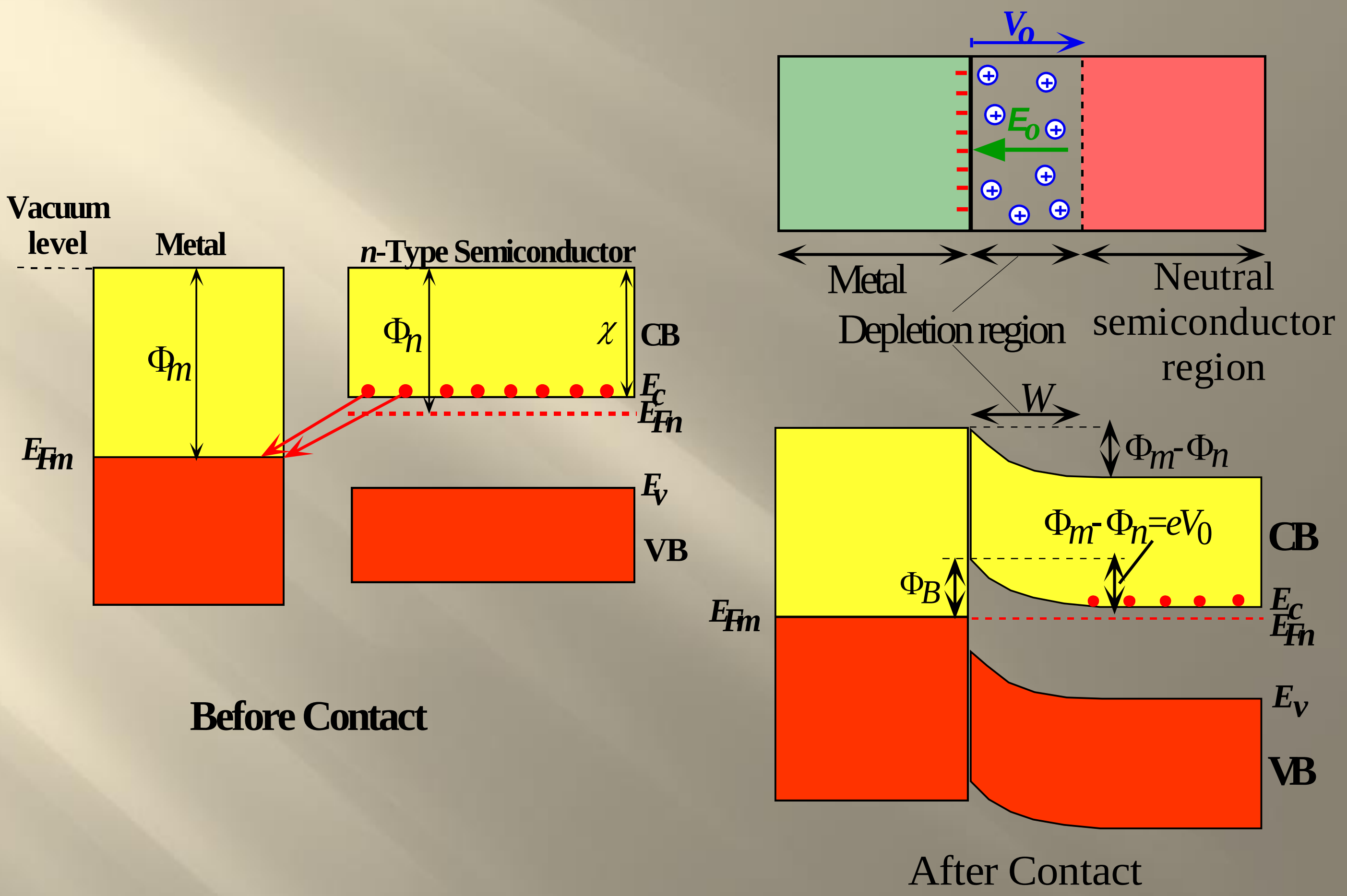


Fig. 5.39: Formation of a Schottky junction between a metal and an *n*-type semiconductor when $\Phi_m > \Phi_n$.

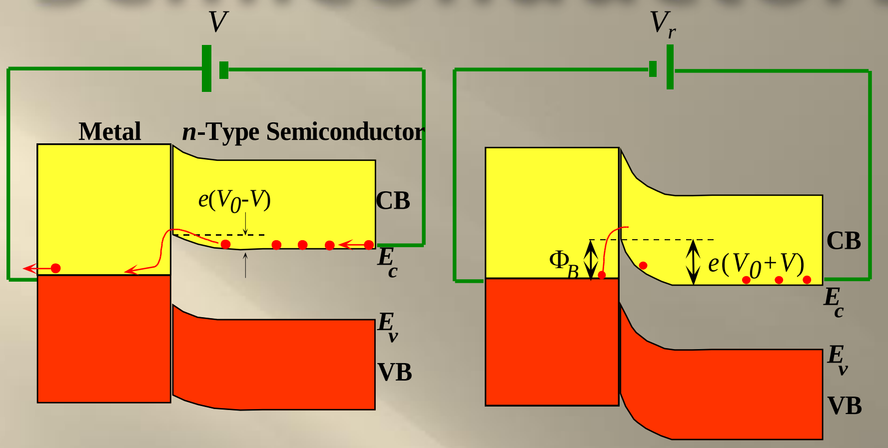
Semiconductors

The Schottky barrier height, ϕ_B is the potential energy barrier for electrons moving from the metal to the semiconductor.

At OCP, there is no current flowing except for some thermal emission both ways.

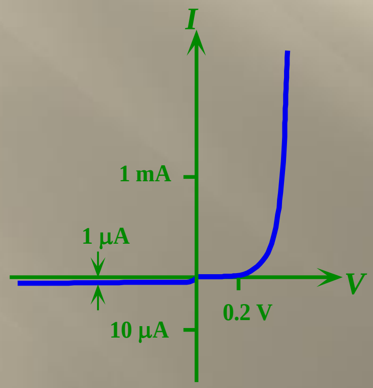
When under forward bias, the semiconductor is connected to the negative terminal.
When under negative bias, the semiconductor is connected to the positive terminal.

Semiconductors



(a) Forward biased Schottky junction. Electrons in the CB of the semiconductor can eadily overcome the small *PE* barrier to enter the metal.

(b) Reverse biased Schottky junction. Electrons in the metal can not easily overcome the *PE* barrier Φ_B to enter the semiconductor.



(c) *I-V* Characteristics of a Schottky junction exhibits rectifying properties (negative current axis is in microamps)

Fig. 5.40: The Schottky junction.

Semiconductors

The built-in field in the depletion region of the Schottky junction can be used as photovoltaic devices and photodetectors, creating electron-hole pairs when struck by a photon.

Example: 10 nm Au deposited on n-type semiconductor – electron will drift toward the semiconductor and holes towards the metal.

Photon energy is converted to electrical energy.

Advantage – the photon energy only has to be greater than ϕ_B not E_g.

Semiconductors

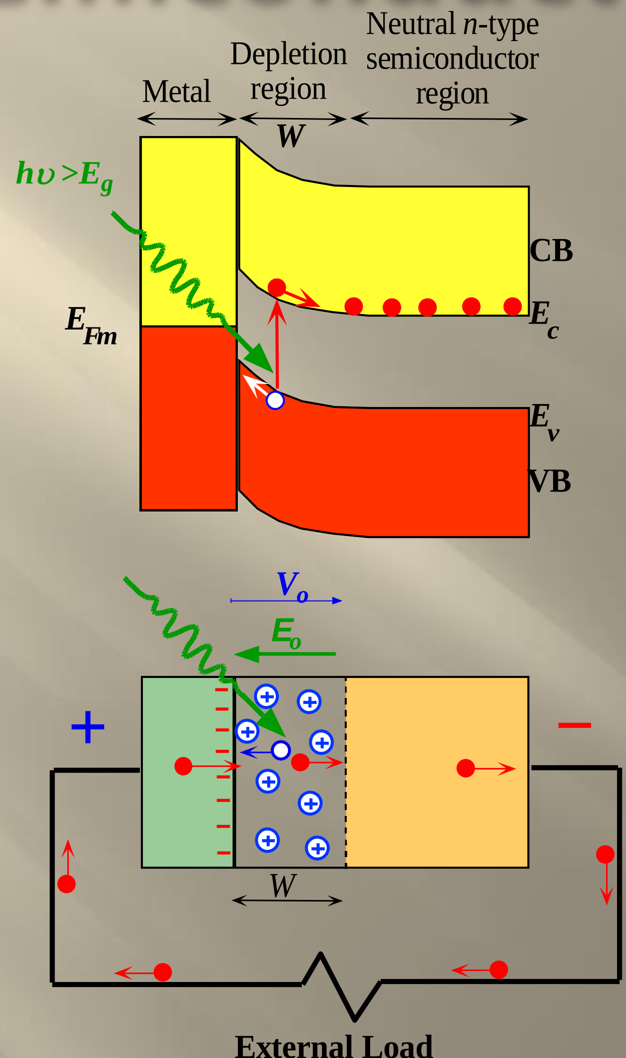


Fig. 5.41: The principle of the Schottky junction solar cell.

Semiconductors

Ohmic contact is when the junction between the metal and semiconductor does not limit current flow. Electrons easily tunnel into the semiconductor from the metal and accumulate until equilibrium is reached.

Ohmic contacts can be used for the Peltier effect (cooling at the junctions).

Semiconductors

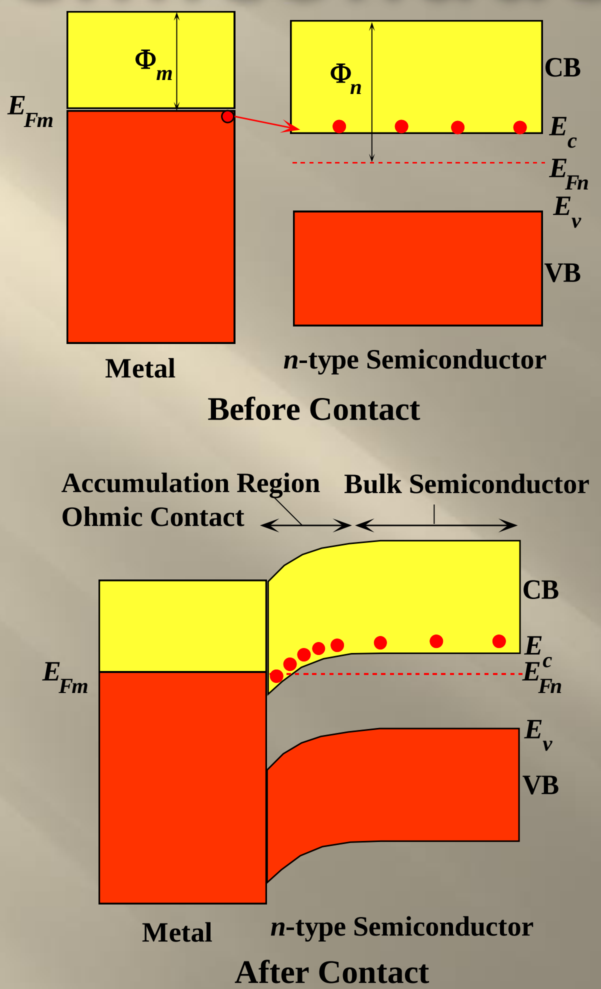


Fig. 5.43: When a metal with a smaller workfunction than an *n*-type semiconductor are put into contact, the resulting junction is an ohmic contact in the sense that it does not limit the current flow.

Semiconductors

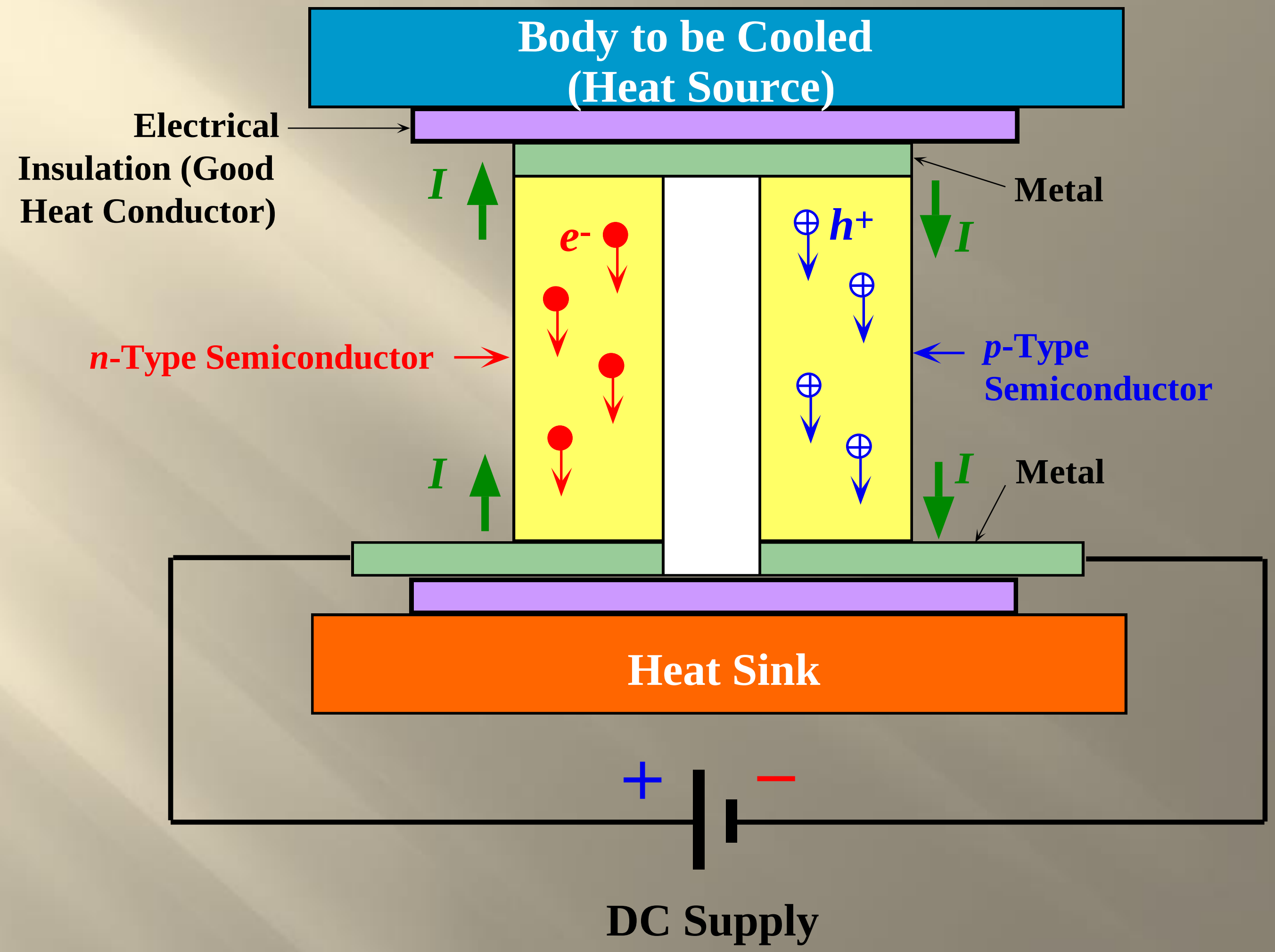


Fig. 5.46: Cross section of a typical thermoelectric cooler.

Semiconductors

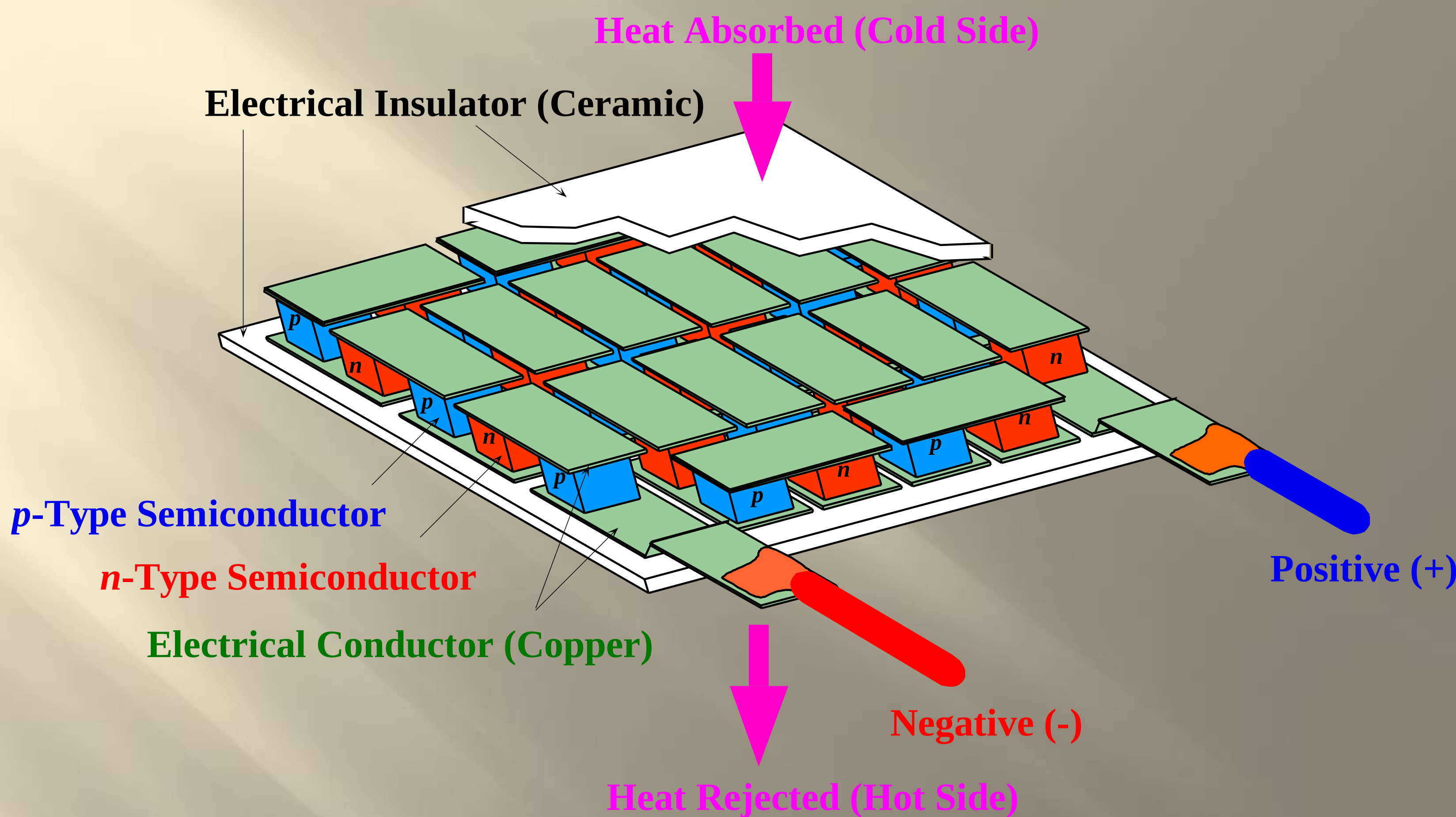


Fig. 5.47: Typical structure of a commercial thermoelectric cooler

Assignment

- Paper Abstract (Topic) due Today
- Take home Test due Today