Energy Bands and Charge Carriers in Semiconductors

Bonding Forces and Energy Bands in Solids

- Electrons are restricted to sets of discrete energy levels within atoms, with large gaps among them where no energy state is available for the electron to occupy.
- Electrons in solids also are restricted to certain energies and are not allowed at other energies.
- Difference → in the solid, the electron has a *range (or band)* of available energies.
- The discrete energy levels of the isolated atom spread into bands of energies in the solid because
  i) in the solid, the wave functions of electrons in neighboring atoms overlap, thus, it affects the potential energy term and the boundary conditions in the Schrödinger equation, and different energies are obtained in the solution, and
  ii) an electron is not necessarily localized at a particular atom.
- The influence of neighboring atoms on the energy levels of a particular atom can be treated as a small perturbation, giving rise to shifting and splitting of energy states into energy bands.

Bonding Forces in Solids

❖ Ionic Bonding

- Example: NaCl.
- Na (Z = 11) gives up its outermost shell electron to Cl (Z=17) atom, thus the crystal is made up of ions with the electronic structures of the inert atoms Ne and Ar.
- Note: the ions have net electric charges after the electron exchange → Na^+ ion has a net positive charge, having lost an electron, and Cl^- ion has a net negative charge, having acquired an electron.
- Thus, an electrostatic attractive force is established, and the balance is reached when this equals the net repulsive force.
- Note: all the electrons are tightly bound to the atom.
- Since there are no loosely bound electrons to participate in current flow → NaCl is a good insulator.

❖ Metallic Bonding

- In metals, the outer shell is filled by no more than three electrons (loosely bound and given up easily) => great chemical activity and high electrical conductivity.
- Outer electron(s) contributed to the crystal as a whole => solid made up of ions with closed shells immersed in a sea of free electrons, which are free to move about the crystal under the influence of an electric field.
- Coulomb attraction force between the ions and the electrons hold the lattice together.

Covalent Bonding

- Exhibited by the diamond lattice semiconductors.
- Each atom surrounded by four nearest neighbors, each having four electrons in the outermost orbit.
- Each atom shares its valence electrons with its four nearest neighbors.
- Bonding forces arise from a quantum mechanical interaction between the shared electrons.
- Both electrons belong to each bond, are indistinguishable, and have opposite spins.
- No free electrons available at 0 K, however, by thermal or optical excitation, electrons can be excited out of a covalent bond and can participate in current conduction => important feature of semiconductors.

Mixed Bonding

- Shown by III-V compounds bonding partly ionic and partly covalent.
- Ionic character of bonding becomes more prominent as the constituent atoms move further away in the periodic table, e.g., II-VI compounds.

Energy Bands

- As isolated atoms are brought together to form a solid, the electron wave functions begin to overlap.
- Various interactions occur, and, at the proper interatomic spacing for the crystal, the forces of attraction and repulsion find a balance.
- Due to Pauli exclusion principle, the discrete energy levels of individual atoms split into bands belonging to the pair instead of to individual atoms.
- In a solid, due to large number of atoms, the split energy levels for essentially *continuous bands of energy*.

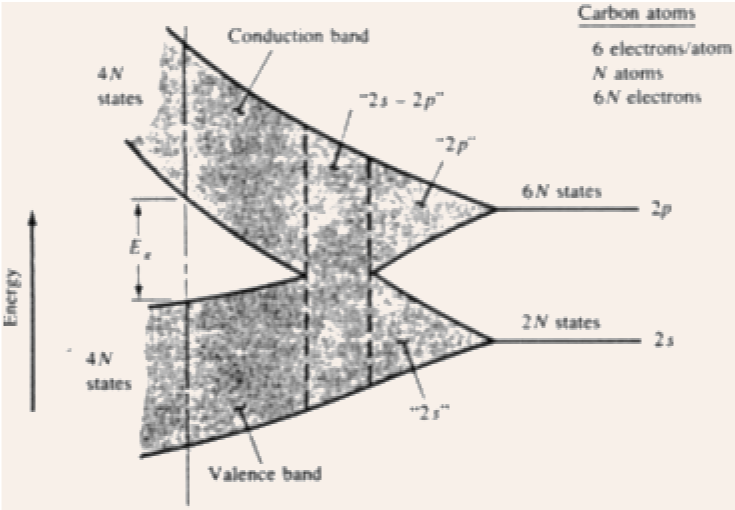


Fig.2.1 splitting of individual energy levels to energy bands as atoms is brought closer together.

- Imaginary formation of a diamond crystal from isolated carbon atoms .
- Each atom has two 1s states, two 2s states, six 2p states, and higher states.
- For N atoms, the numbers of states are 2N, 2N, and 6N of type 1s, 2s, and 2p respectively.
- With a reduction in the interatomic spacing, these energy levels split into bands, and the 2s and 2p bands merge into a single band having 8N available states.
- As the interatomic spacing approaches the equilibrium spacing of diamond crystal, this band splits into two bands separated by an energy gap E_g, where no allowed energy states for electrons exist => *forbidden gap*.
- The upper band (called the *conduction band*) and the lower band (called the *valence band*) contain 4N states each.
- The lower 1s band is filled with 2N electrons, however, the 4N electrons residing in the original n = 2 state will now occupy states either in the *valence band* or in the *conduction band*.
- At 0 K, the electrons will occupy the lowest energy states available to them => thus, the 4N states in the valence band will be completely filled, and the 4N states in the conduction band will be completely empty.

Metals, Semiconductors, and Insulators

- For electrons to move under an applied electric field, there must be states available to them.
- A completely filled band cannot contribute to current transport; neither can a completely empty band.
- Thus, semiconductors at 0 K are perfect insulators.
- With thermal or optical excitation, some of these electrons can be excited from the valence band to the conduction band, and then they can contribute to the current transport process.
- At temperatures other than 0 K, the magnitude of the band gap separates an insulator from a semiconductor, e.g., at 300 K, E_g(diamond) = 5 eV (insulator), and E_g (Silicon) = 1.12 eV (semiconductor).
- Number of electrons available for conduction can be increased greatly in semiconductors by reasonable amount of thermal or optical energy.
- In metals, the bands are either partially filled or they overlap =>thus, electrons and empty states coexist => great electrical conductivity.

Direct and Indirect Semiconductors

- In a typical quantitative calculation of band structures, the wave function of a single electron traveling through a perfectly periodic lattice is assumed to be in the form of a plane wave moving in the x-direction (say) with propagation constant k, also called a *wave vector*.
- In quantum mechanics, the electron momentum can be given by $p = \hbar k$.
- The space dependent wave function for the electron is

  $$\psi_k(x) = U(k_x, x)e^{-jk_x x} \quad (2.1)$$

where the function $U(k_x, x)$ modulates the wave function according to the periodicity of the lattice.

- Allowed values of energy, while plotted as a function of k, gives the E-k diagram.
- Since the periodicity of most lattices is different in various directions, the E-k diagram is a complex surface, which is to be visualized in three dimensions.

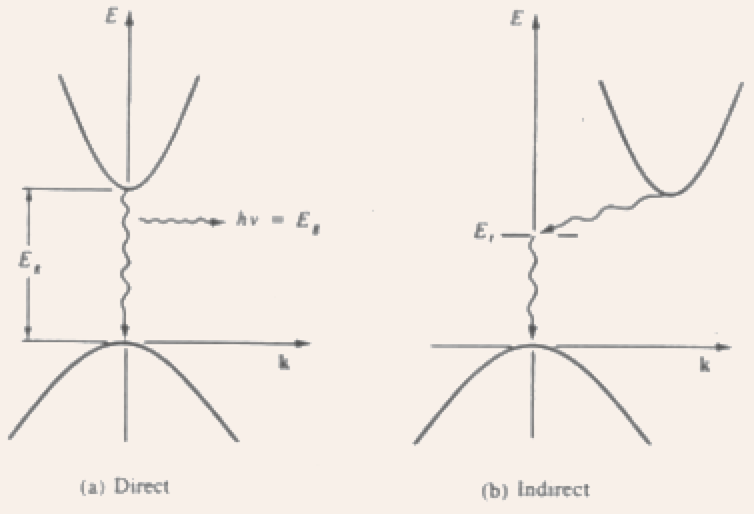


Fig.2.2 Direct and indirect transition of electrons from the conduction band to the valence band: (a) direct - with accompanying photon emission, (b) indirect via defect level.

- Direct band gap semiconductor: the minima of the conduction band and the maxima of the valence band occur at the same value of k $\Rightarrow$ an electron making the smallest energy transition from the conduction band to the valence band can do so without a change in k (and, the momentum).
- Indirect band gap semiconductor: the minima of the conduction band and the maxima of the valence band occur for different values of k, thus, the smallest energy transition for an electron requires a change in momentum.
- Electron falling from conduction band to an empty state in valence band $\Rightarrow$ recombination.
- Recombination probability for direct band gap semiconductors is much higher than that for indirect band gap semiconductors.
- Direct band gap semiconductors give up the energy released during this transition (= E_g) in the form of light $\Rightarrow$ used for optoelectronic applications (e.g., LEDs and LASERs).
- Recombination in indirect band gap semiconductors occurs through some defect states within the band gap, and the energy is released in the form of heat given to the lattice.

Variation of Energy Bands with Alloy Composition

- The band structures of III-V ternary and quaternary compounds change as their composition is varied.
- There are three valleys in the conduction band: Γ (at k = 0), L, and X.

- In GaAs, the Γ valley has the minimum energy (direct with E_g= 1.43 eV) with very few electrons residing in L and X valleys (except for high field excitations).
- In AlAs, the X valley has minimum energy (indirect with E_g= 2.16 eV).

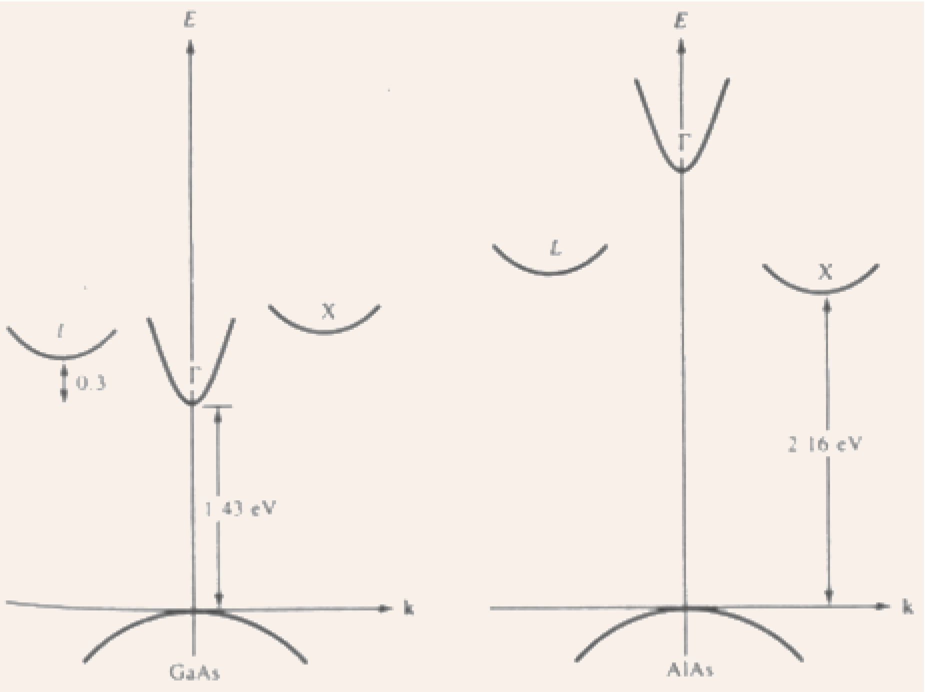


Fig.2.3 The E-k diagram of (a) GaAs and (b) AlAs, showing the three valleys (L, Γ, and X) in the conduction band.

Charge Carriers in Semiconductors

- In a metal, the atoms are imbedded in a "sea" of free electrons, and these electrons can move as a group under the influence of an applied electric field.
- In semiconductors at 0 K, all states in the valence band are full, and all states in the conduction band are empty.
- At $T > 0$ K, electrons get thermally excited from the valence band to the conduction band, and contribute to the conduction process in the conduction band.
- The empty states left in the valence band can also contribute to current conduction.
- Also, introduction of impurities has an important effect on the availability of the charge carriers.
- Considerable flexibility in controlling the electrical properties of semiconductors.

Electrons and Holes

- For $T> 0$ K, there would be some electrons in the otherwise empty conduction band, and some empty states in the otherwise filled valence band.
- The empty states in the valence band are referred to as holes.

- If the conduction band electron and the valence band hole are created by thermal excitation of a valence band electron to the conduction band, then they are called electron-hole pair (EHP).

- After excitation to the conduction band, an electron is surrounded by a large number of empty states, e.g., the equilibrium number of EHPs at 300 K in Si is $\sim 10^{10}/\mathrm{cm}^3$, whereas the Si atom density is $\sim 10^{22}/\mathrm{cm}^3$.
- Thus, the electrons in the conduction band are free to move about via the many available empty states.
- Corresponding problem of charge transport in the valence band is slightly more complex.
- Current transport in the valence band can be accounted for by keeping track of the holes themselves.
- In a filled band, all available energy states are occupied.
- For every electron moving with a given velocity, there is an equal and opposite electron motion somewhere else in the band.
- Under an applied electric field, the net current is zero, since for every electron j moving with a velocity v_j, there is a corresponding electron j' moving with a velocity -v_j.
- In a unit volume, the current density J can be given by

  $$J = (-q)\sum_{i}^{N} v_i = 0$$ (filled band) (2.2)

  where N is the number of $\mathrm{electrons/cm}^3$ in the band, and q is the electronic charge.

- Now, if the j^{th} electron is removed and a hole is created in the valence band, then the net current density

  $$\begin{aligned} J &= (-q)\sum_{i}^{N} v_i - (-q)v_j && (j^{th} \text{ electron missing}) \\ &= (+q)v_j && (\text{since the first term is zero}) \end{aligned}$$

- Thus, the current contribution of the empty state (hole), obtained by removing the jth electron, is equivalent to that of a positively charged particle with velocity v_j.
- Note that actually this transport is accounted for by the motion of the uncompensated electron j' having a charge of q and moving with a velocity v_j.
- Its current contribution (- q)(- v_j) is equivalent to that of a positively charged particle with velocity + v_j.
- For simplicity, therefore, the empty states in the valence band are called holes, and they are assigned positive charge and positive mass.
- The electron energy increases as one moves up the conduction band, and electrons gravitate downward towards the bottom of the conduction band.
- On the other hand, hole energy increases as one moves down the valence band (since holes have positive charges), and holes gravitate upwards towards the top of the valence band.

Effective Mass

- The "wave-particle" motion of electrons in a lattice is not the same as that for a free electron, because of the interaction with the periodic potential of the lattice.
- To still be able to treat these particles as "free", the rest mass has to be altered to take into account the influence of the lattice.
- The calculation of effective mass takes into account the shape of the energy bands in three-dimensional k-space, taking appropriate averages over the various energy bands.
- The effective mass of an electron in a band with a given (E,k) relation is given by
  $m^* = \frac{[h/(2\pi)]^2}{d^2E/dk^2}$ (2.4)

EXAMPLE 2.1: Find the dispersion relation for a free electron, and, thus, observe the relation between its rest mass and effective mass.

SOLUTION: For a free electron, the electron momentum is $\mathbf{p} = m_0 \mathbf{v} = \hbar \mathbf{k}$. Thus, $E = m_0 v^2/2 = \mathbf{p}^2/(2m_0) = \hbar^2 \mathbf{k}^2/(2m_0)$. Therefore, the dispersion relation, i.e., the E-k relation is parabolic. Hence, $m^* = \hbar^2/(\partial^2 E/\partial \mathbf{k}^2) = m_0$. This is a very interesting relation, which states that for a free electron, the rest mass and the effective mass are one and the same, which is due to the parabolic band structure. Most materials have non-parabolic E-k relation, and, thus, they have quite different rest mass and effective mass for electrons.

Note: for severely non-parabolic band structures, the effective mass may become a function of energy, however, near the minima of the conduction band and towards the maxima of the valence band, the band structure can be taken to be parabolic, and, thus, an effective mass, which is independent of energy, may be obtained.

- Thus, the effective mass is an inverse function of the curvature of the E-k diagram: weak curvature gives large mass, and strong curvature gives small mass.
- Note that in general, the effective mass is a tensor quantity, however, for parabolic bands, it is a constant.
- Another interesting feature is that the curvature $d^2E/d\mathbf{k}^2$ is positive at the conduction band minima, however, it is negative at the valence band maxima.
- Thus, the electrons near the top of the valence band have negative effective mass.
- Valence band electrons with negative charge and negative mass move in an electric field in the same direction as holes with positive charge and positive mass.
- Thus, the charge transport in the valence band can be fully accounted for by considering hole motion alone.
- The electron and hole effective masses are denoted by m_n^* and m_p^* respectively.

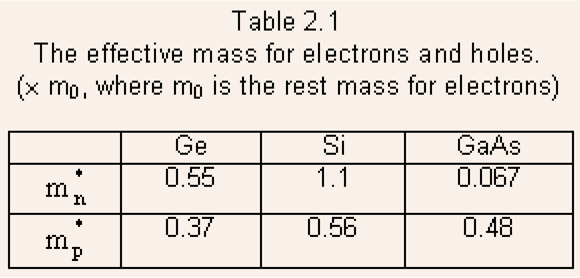


Table 2.1
The effective mass for electrons and holes.
($\times\ m_0$, where m_0 is the rest mass for electrons)

	Ge	Si	GaAs
m_n^*	0.55	1.1	0.067
m_p^*	0.37	0.56	0.48

Intrinsic Material

- A perfect semiconductor crystal with no impurities or lattice defects.
- No carriers at 0 K, since the valence band is completely full and the conduction band is completely empty.
- For T > 0 K, electrons are thermally excited from the valence band to the conduction band (EHP generation).
- EHP generation takes place due to breaking of covalent bonds $=>$required energy = E_g.
- The excited electron becomes free and leaves behind an empty state (hole).
- Since these carriers are created in pairs, the electron concentration (n/cm^3) is always equal to the hole concentration (p/cm^3), and each of these is commonly referred to as the *intrinsic carrier concentration* (n_i).
- Thus, for intrinsic material n = p = n_i.
- These carriers are not localized in the lattice; instead they spread out over several lattice spacings, and are given by quantum mechanical probability distributions.
- Note: ni = f(T).
- To maintain a steady-state carrier concentration, the carriers must also recombine at the same rate at which they are generated.
- Recombination occurs when an electron from the conduction band makes a transition (direct or indirect) to an empty state in the valence band, thus annihilating the pair.
- At equilibrium, $r_i = g_i$, where g_i and r_i are the generation and recombination rates respectively, and both of these are temperature dependent.
- g_i(T) increases with temperature, and a new carrier concentration ni is established, such that the higher recombination rate r_i(T) just balances generation.
- At any temperature, the rate of recombination is proportional to the equilibrium concentration of electrons and holes, and can be given by $r_i = \alpha_r n_0 p_0 = \alpha_r n_i^2 = g_i$ (2.5) where α_r is a constant of proportionality (depends on the mechanism by which recombination takes place).

Extrinsic Material

- In addition to thermally generated carriers, it is possible to create carriers in the semiconductor by purposely introducing impurities into the crystal $=>$*doping*.
- Most common technique for varying the conductivity of semiconductors.

- By doping, the crystal can be made to have predominantly electrons (n-type) or holes (p-type).
- When a crystal is doped such that the equilibrium concentrations of electrons (n0) and holes (p0) are different from the intrinsic carrier concentration (ni), the material is said to be *extrinsic*.
- Doping creates additional levels within the band gap.
- In Si, column V elements of the periodic table (e.g., P, As, Sb) introduce energy levels very near (typically 0.03-0.06 eV) the conduction band.
- At 0 K, these levels are filled with electrons, and very little thermal energy (50 K to 100 K) is required for these electrons to get excited to the conduction band.
- Since these levels donate electrons to the conduction band, they are referred to as the *donor* levels.
- Thus, Si doped with donor impurities can have a significant number of electrons in the conduction band even when the temperature is not sufficiently high enough for the intrinsic carriers to dominate, i.e., n_0>> n_i, p_0 $=>$n-type material, with electrons as *majority carriers* and holes as *minority carriers*.
- In Si, column III elements of the periodic table (e.g., B, Al, Ga, In) introduce energy levels very near (typically 0.03-0.06 eV) the valence band.
- At 0 K, these levels are empty, and very little thermal energy (50 K to 100 K) is required for electrons in the valence band to get excited to these levels, and leave behind holes in the valence band.
- Since these levels accept electrons from the valence band, they are referred to as the acceptor levels.
- Thus, Si doped with acceptor impurities can have a significant number of holes in the valence band even at a very low temperature, i.e., p_0 >> n_i , n_0 $=>$p-type material, with holes as majority carriers and electrons as minority carriers.
- The extra electron for column V elements is loosely bound and it can be liberated very easily $=>$ionization; thus, it is free to participate in current conduction.
- Similarly, column III elements create holes in the valence band, and they can also participate in current conduction.
- Rough calculation of the ionization energy can be made based on the Bohr's model for H_2 atoms, considering the loosely bound electron orbiting around the tightly bound core electrons. Thus,

  $E = \frac{m_n^* q^4}{2(4\pi\varepsilon_0\varepsilon_r)^2[h/(2\pi)]^2}$ (2.6)where ε_r is the relative permittivity of Si.

EXAMPLE 2.2: Calculate the approximate donor binding energy for Si (r = 11.7, m_n^* = 1.18 m_0).

SOLUTION: From Eq.(2.6), we have $E = \frac{m_n^* q^4}{8(\varepsilon_0\varepsilon_r)^2 h^2} = \frac{1.18 \times 9.11 \times 10^{-31} \times (1.6 \times 10^{-19})^4}{8 \times (8.854 \times 10^{-12} \times 11.7)^2 \times (6.63 \times 10^{-34})^2}$ = 1.867 x 10^{-20}J = 0.117 eV.

Note: The effective mass used here is an average of the effective mass in different crystallographic directions, and is called the "conductivity effective mass" with values of 1.28 m_0 (at 600 K), 1.18 m_0 (at 300 K), 1.08 m_0 (at 77 K), and 1.026 m_0 (at 4.2 K).

- In III-V compounds, column VI impurities (e.g., S, Se, Te) occupying column V sites act as donors. Similarly, column II impurities (e.g., Be, Zn, Cd) occupying column III sites act as acceptors.
- When a column IV material (e.g., Si, Ge) is used to dope III-V compounds, then they may substitute column III elements (and act as donors), or substitute column V elements (and act as acceptors) $\Rightarrow$ *amphoteric dopants*.
- Doping creates a large change in the electrical conductivity, e.g., with a doping of $10^{15}/cm^3$, the resistivity of Si changes from 2 x 10^5 Ω-cm to 5 Ω-cm.

Carrier Concentrations

- For the calculation of semiconductor electrical properties and analyzing device behavior, it is necessary to know the number of charge carriers/cm3 in the material.
- The majority carrier concentration in a heavily doped material is obvious, since for each impurity atom, one majority carrier is obtained.
- However, the minority carrier concentration and the dependence of carrier concentrations on temperature are not obvious.
- To obtain the carrier concentrations, their distribution over the available energy states is required.
- These distributions are calculated using statistical methods.

The Fermi Level

- Electrons in solids obey *Fermi-Dirac* (FD) statistics.
- This statistics accounts for the indistinguishability of the electrons, their wave nature, and the Pauli exclusion principle.
- The Fermi-Dirac distribution function f(E) of electrons over a range of allowed energy levels at thermal equilibrium can be given by

  $$f(E) = \frac{1}{1 + e^{(E-E_f)/kT}}$$ (2.7)where k is Boltzmann's constant (= 8.62 x 10^{-5}eV/K = 1.38 x 10^{-23}J/K).

- This gives the probability that an available energy state at E will be occupied by an electron at an absolute temperature T.

- E_F is called the Fermi level and is a measure of the average energy of the electrons in the lattice => an extremely important quantity for analysis of device behavior.
- Note: for (E - E_F) > 3kT (known as *Boltzmann approximation*), f(E) $\approx$ exp[- (E- E_F)/kT] => this is referred to as the Maxwell-Boltzmann (MB) distribution (followed by gas atoms).
- The probability that an energy state at E_F will be occupied by an electron is 1/2 at all temperatures.
- At 0 K, the distribution takes a simple rectangular form, with all states below E_F occupied, and all states above E_F empty.
- At T > 0 K, there is a finite probability of states above E_F to be occupied and states below E_F to be empty.
- The F-D distribution function is highly symmetric, i.e., the probability f(E_F + ΔE) that a state E above E_F is filled is the same as the probability [1- f(E_F - ΔE)] that a state E below E_F is empty.
- This symmetry about EF makes the Fermi level a natural reference point for the calculation of electron and hole concentrations in the semiconductor.
- Note: f(E) is the probability of occupancy of an available state at energy E, thus, if there is no available state at E (e.g., within the band gap of a semiconductor), there is no possibility of finding an electron there.
- For intrinsic materials, the Fermi level lies close to the middle of the band gap (the difference between the effective masses of electrons and holes accounts for this small deviation from the mid gap).
- In n-type material, the electrons in the conduction band outnumber the holes in the valence band, thus, the Fermi level lies closer to the conduction band.
- Similarly, in p-type material, the holes in the valence band outnumber the electrons in the conduction band, thus, the Fermi level lies closer to the valence band.
- The probability of occupation f(E) in the conduction band and the probability of vacancy [1- f(E)] in the valence band are quite small, however, the densities of available states in these bands are very large, thus a small change in f(E) can cause large changes in the carrier concentrations.

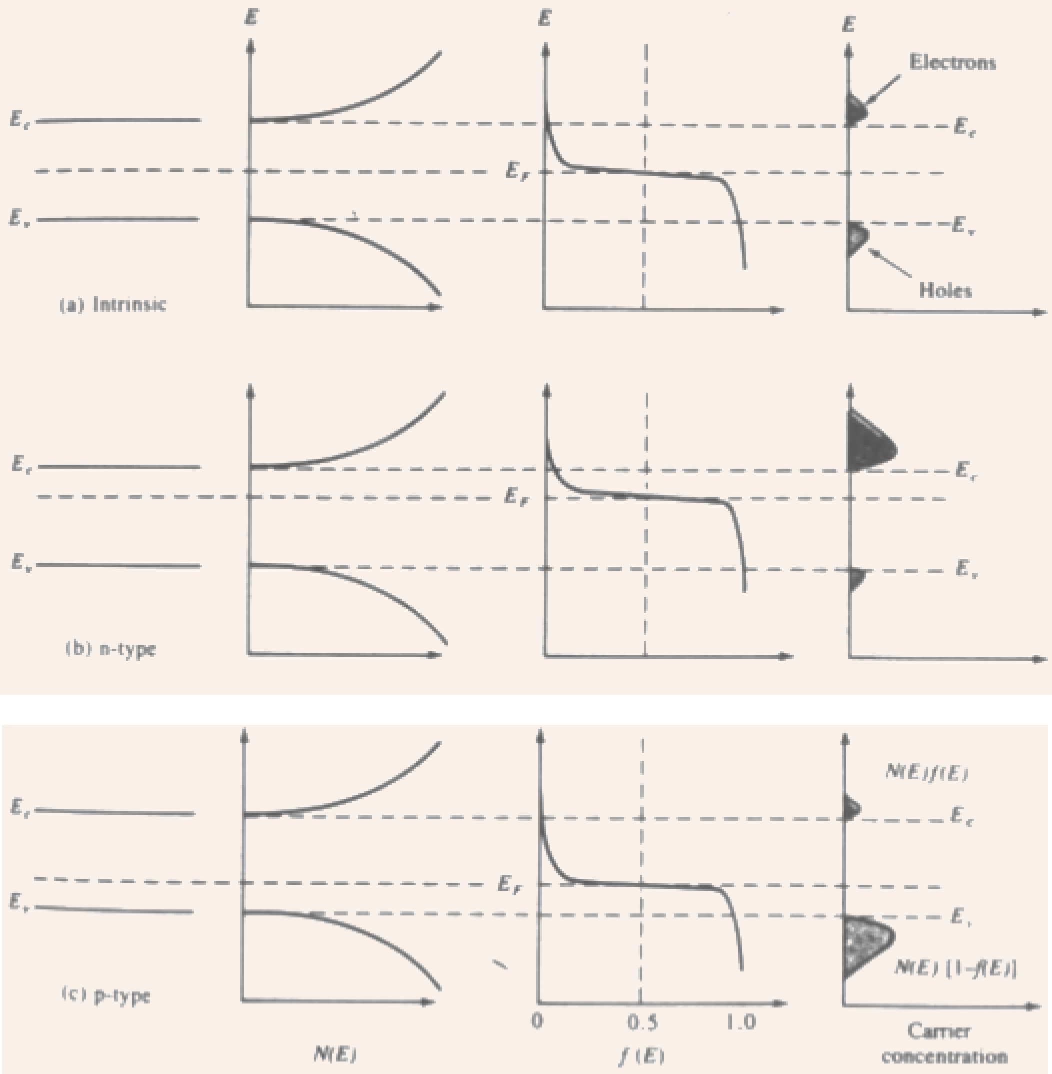


Fig.2.4 The density of states N(E), the Fermi-Dirac distribution function f(E), and the carrier concentration as functions of energy for (a) intrinsic, (b) n-type, and (c) p-type semiconductors at thermal equilibrium.

- Note: since the function f(E) is symmetrical about E_F, a large electron concentration implies a small hole concentration, and vice versa.
- In n-type material, the electron concentration in the conduction band increases as E_F moves closer to E_C ; thus, (E_C - E_F) gives a measure of n.
- Similarly, in p-type material, the hole concentration in the valence band increases as E_F moves closer to E_V; thus, (E_V - E_F) gives a measure of p.

Electron and Hole Concentrations at Equilibrium

- The F-D distribution function can be used to calculate the electron and hole concentrations in semiconductors, if the densities of available states in the conduction and valence bands are known.

- In equilibrium, the concentration of electrons in the conduction band can be given by

  $$n_0 = \int_{E_c}^{\infty} f(E)N(E)dE \quad (2.8)$$

  where N(E)dE is the density of available states/cm3 in the energy range dE.

- Note: the upper limit of is theoretically not proper, since the conduction band does not extend to infinite energies; however, since f(E) decreases rapidly with increasing E, the contribution to this integral for higher energies is negligible.
- Using the solution of Schrödinger's wave equation under periodic boundary conditions, it can be shown that

  $$N(E) = \frac{1}{2\pi^2}\left[\frac{2m^*}{(h/2\pi)^2}\right]^{3/2} E^{1/2} \quad (2.9)$$

- Thus, N(E) increases with E, however, f(E) decreases rapidly with E, thus, the product f(E)N(E) decreases rapidly with E, and very few electrons occupy states far above the conduction band edge, i.e., most electrons occupy a narrow energy band near the conduction band edge.
- Similarly, the probability of finding an empty state in the valence band [1 - f(E)] decreases rapidly below E_V, and most holes occupy states near the top of the valence band.
- Thus, a mathematical simplification can be made assuming that all available states in the conduction band can be represented by an effective density of states NC located at the conduction band edge E_C and using Boltzmann approximation.

  Thus, $n_0 = N_c f(E_c) = N_c e^{-(E_c - E_F)/kT}$ (2.10)

  where . $N_C = 2\left(\frac{2\pi m_n^* kT}{h^2}\right)^{3/2}$

- Note: as (E_C - E_F) decreases, i.e., the Fermi level moves closer to the conduction band, the electron concentration increases.
- By similar arguments,

  $$p_0 = N_V[1 - f(E_V)] = N_V e^{-(E_F - E_V)/kT} \quad (2.11)$$

  where N_V is the effective density of states located at the valence band edge E_V.

- Note: the only terms separating the expressions for N_C and N_V are the effective masses of electrons (m_n^*) and holes (m_p^*) respectively, and since , hence, N_C N_V.

- Thus, as (E_F - E_V) decreases, i.e., the Fermi level moves closer to the valence band edge, and the hole concentration increases.
- These equations for n_0 and p_0 are valid in equilibrium, irrespective of the material being intrinsic or doped.
- For intrinsic material E_F lies at an intrinsic level E_i (very near the middle of the band gap), and the intrinsic electron and hole concentrations are given by $n_i = N_C e^{-(E_c - E_i)/kT} \quad \text{and} \quad p_i = N_v e^{-(E_i - E_v)/kT}$ and (2.12)
- Note: At equilibrium, the product $n_0 p_0$ is a constant for a particular material and temperature, even though the doping is varied,

  i.e., $n_0 p_0 = n_i^2 = N_C N_v e^{-E_g/kT}$ (2.13)

- This equation gives an expression for the intrinsic carrier concentration ni as a function of N_C, N_V, and temperature:

  $n_i = \sqrt{N_C N_V}\, e^{-E_g/2kT}$ (2.14)

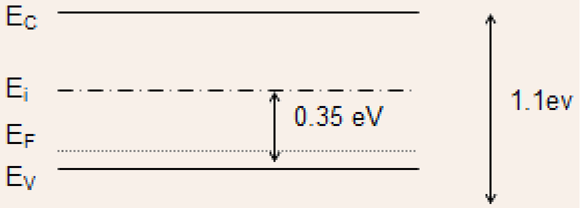
- These relations are extremely important, and are frequently used for calculations.
- Note: if N_C were to be equal to N_V, then E_i would have been exactly at mid gap (i.e., E_C- E_i = E_i - E_V = E_g/2).
- However, since N_C N_V, E_i is displaced slightly from mid gap (more for GaAs than that for Si).
- Alternate expressions for n_0 and p_0: $n_0 = n_i e^{(E_F - E_i)/kT} \quad \text{and} \quad p_0 = n_i e^{(E_i - E_F)/kT}$ and (2.15)

- Note: the electron concentration is equal to ni when E_F is at E_i, and n0 increases exponentially as E_F moves away from E_i towards the conduction band.
- Similarly, the hole concentration p_0 varies from n_i to larger values as E_F moves from E_i towards the valence band.

EXAMPLE 2.3: A Si sample is doped with 10^{16} B atoms/cm^3. What is the equilibrium electron concentration n0 at 300 K? Where is E_F relative to E_i? Assume n_i for Si at 300 K = 1.5 x 10^{10}/cm^3.

SOLUTION: Since B (trivalent) is a p-type dopant in Si, hence, the material will be predominantly p-type, and since N_A >> n_i, therefore, p_0 will be approximately equal to N_A, and $n_0 =$ $n_i^2/p_0 = 2.25 \times 10^{20}/10^{16} = 2.25 \times 10^4\ \text{cm}^{-3}$. Also,

$E_i - E_F = kT \ln(p_0/n_i) = 0.026 \ln[10^{16}/(1.5 \times 10^{10})] = 0.35$ eV. The resulting band diagram is:



Temperature Dependence of Carrier Concentrations

- The intrinsic carrier concentration has a strong temperature dependence, given by

$$n_i(T) = 2\left(\frac{2\pi kT}{h^2}\right)^{3/2}(m_n^* m_p^*)^{3/4} e^{-E_g/2kT} \quad (2.16)$$

- Thus, explicitly, ni is proportional to T3/2 and to e 1/T, however, Eg also has a temperature dependence (decreasing with increasing temperature, since the interatomic spacing changes with temperature).

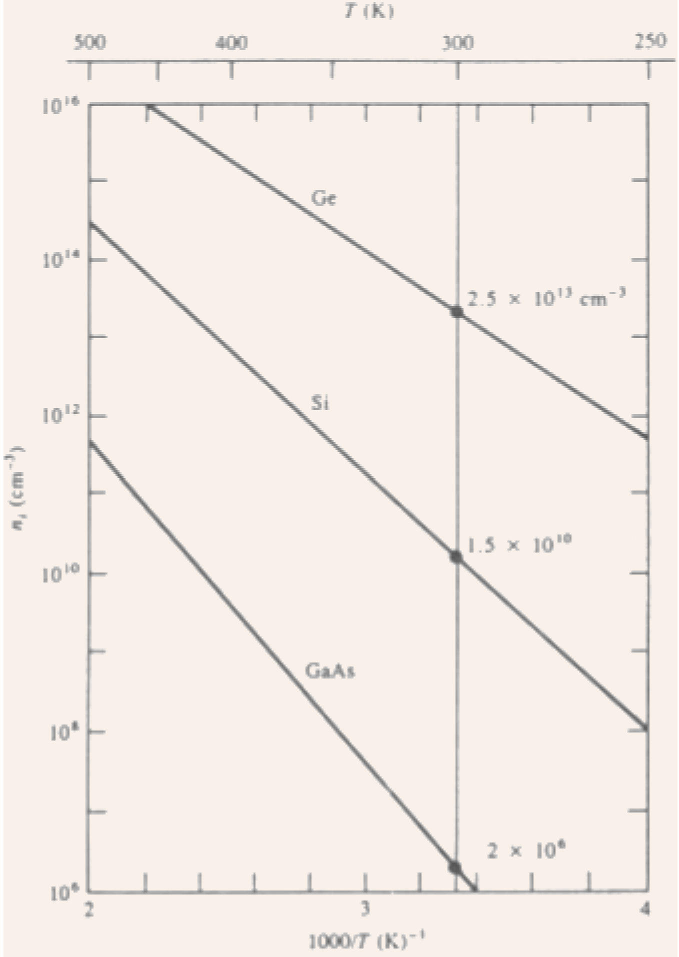


Fig.2.5 The intrinsic carrier concentration as a function of inverse temperature for Si, Ge, and GaAs.

- As n_i changes with temperature, so do n_0 and p_0.
- With n_i and T given, the unknowns are the carrier concentrations and the Fermi level position with respect to E_i one of these quantities must be given in order to calculate the other.
- Example: Si doped with $10^{15}/cm^3$ donors (N_d).
- At very low temperature, negligible intrinsic EHPs exist, and all the donor electrons are bound to the donor atoms.
- As temperature is raised, these electrons are gradually donated to the conduction band, and at about 100 K (1000/T = 10), almost all these electrons are donated => this temperature range is called the ionization region.

Once all the donor atoms are ionized, the electron concentration $n_0 \approx N_d$, since for each donor atom, one electron is obtained.

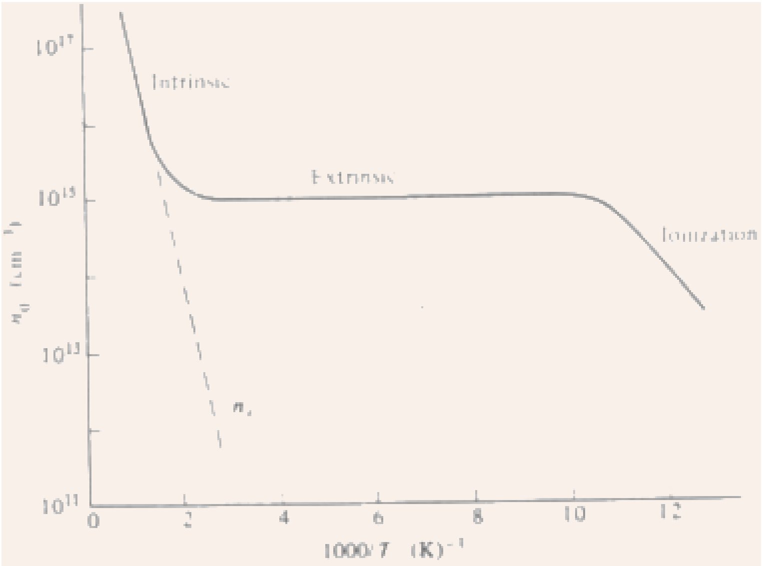


Fig.2.6 Variation of carrier concentration with inverse temperature clearly showing the three regions: ionization, extrinsic, and intrinsic.

- Thus, n_0 remains virtually constant with temperature for a wide range of temperature (called the extrinsic region), until the intrinsic carrier concentration ni starts to become comparable to N_d.
- For high temperatures, n_i >> N_d, and the material loses its extrinsic property (called the intrinsic region).
- Note: in the intrinsic region, the device loses its usefulness => determines the maximum operable temperature range.

Compensation and Space Charge Neutrality

- Semiconductors can be doped with both donors (N_d) and acceptors (N_A) simultaneously.

- Assume a material doped with $N_d > N_A$ => predominantly n-type => E_F lies above E_i => acceptor level Ea completely full, however, with E_F above E_i, the hole concentration cannot be equal to N_A.
- Mechanism:
  - Electrons are donated to the conduction band from the donor level E_d.
  - An acceptor state gets filled by a valence band electron, thus creating a hole in the valence band.
  - An electron from the conduction band recombines with this hole.
  - Extending this logic, it is expected that the resultant concentration of electrons in the conduction band would be N_d N_A instead of N_d.
  - This process is called compensation.
- By compensation, an n-type material can be made intrinsic (by making $N_A = N_d$) or even p-type (for $N_A > N_d$).

  Note: a semiconductor is neutral to start with, and, even after doping, it remains neutral (since for all donated electrons, there are positively charged ions (N_d^+); and for all accepted electrons (or holes in the valence band), there are negatively charged ions (N_a^-).
- Therefore, the sum of positive charges must equal the sum of negative charges, and this governing relation,

  given by $p_0 + N_d^+ = n_0 + N_a^-$ (2.17) is referred to as the equation for space charge neutrality.
- This equation, solved simultaneously with the law of mass action (given by $n_0 p_0 = n_i^2$) gives the information about the carrier concentrations.

  Note: for , $N_d^+ - N_a^- >> n_i^2 / n_0$, $n_0 \approx N_d^+ - N_a^-$, and, similarly, for $N_a^+ - N_d^- >> n_i^2 / p_0$, $p_0 \approx N_a^+ - N_d^-$.