

Lecture 4: Intrinsic semiconductors

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1 Introduction

Semiconductors can be divided into two categories.

1. Intrinsic semiconductors
2. Extrinsic semiconductors

This classification is related to the purity of the semiconductors. *Intrinsic or pure semiconductors* are those that are ideal, with no defects, and no external impurities. The conductivity of these semiconductors increases with temperature. As opposed to intrinsic semiconductors, *extrinsic semiconductors* have some impurities added to modify the concentration of charge carriers and hence the conductivity. Their conductivity has a more complex temperature dependence, given by the concentration of the impurities. Extrinsic semiconductors are used extensively due to the ability to precisely tailor their conductivity by adding the impurities. Intrinsic semiconductors (especially Si and Ge) are used as optical and x-ray detectors (at low T) where a low concentration of charge carriers is required.

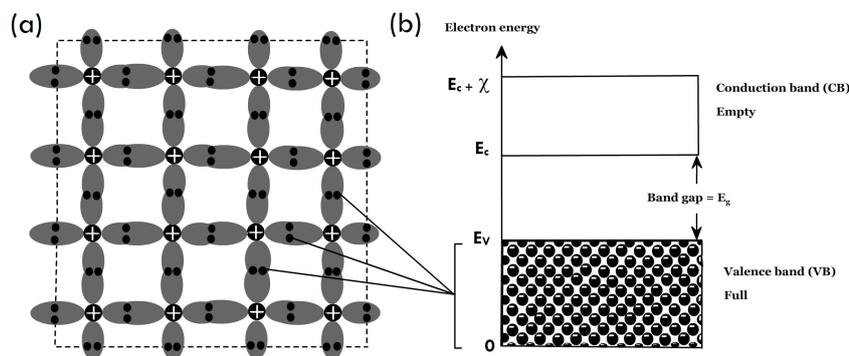


Figure 1: (a) Representation of the hybrid orbitals in Si. (b) These form a valence and conduction band with a band gap. At absolute zero the valence band is completely full and conduction band is completely empty. Adapted from *Principles of Electronic Materials - S.O. Kasap*.

2 Intrinsic Si

Si is a semiconductor material with 4 electrons in the outer shell. These 4 electrons occupy 4 sp^3 hybrid orbitals with a tetrahedral arrangement. This gives rise to a full valence band (VB) and an empty conduction band (CB). This energy gap is called the *band gap*. This information is summarized in figure 1.

The energy levels are referenced with respect to the bottom of the valence band. E_v and E_c represent the top of the valence band and the bottom of the conduction band. The energy difference between them is the band gap (E_g). The top of the conduction band is the vacuum level and is located at ($E_c + \chi$) above the conduction band where χ is the *electron affinity* of Si. For Si, the electron affinity value is 4.05 eV. The band gap at 0 K is 1.17 eV, while at room temperature the value is slightly lower, around 1.10 eV. At any temperature, thermal excitation causes electrons to move from the valence band to the conduction band. These electrons in the conduction band are delocalized and can move in the solid when an external electric field is applied. When electrons are ‘excited’ to the conduction band they leave behind holes in the valence band. These holes are also ‘delocalized’ and move in the direction opposite to the electrons. These electrons and holes are responsible for conduction. *Electron-hole pairs* in Si can also be generated by using electromagnetic radiation. The minimum energy of the radiation required is equal to the band gap. If the energy is less than E_g *electron excitation does not occur since there are no states in the band gap*. The relation between E_g and the maximum wavelength of excitation (λ) is

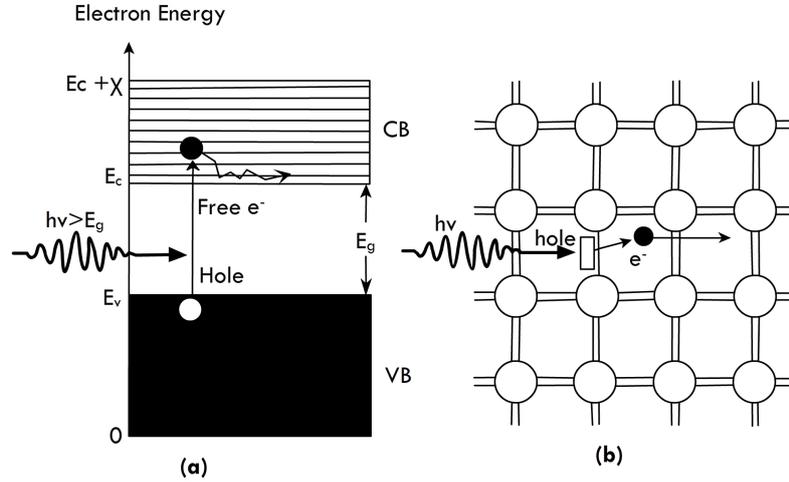


Figure 2: (a) Electron-hole formation in Si due to absorption of light. The minimum energy required is equal to the band gap. (b) The absorption of light by the Si lattice. An electron located at the bond is excited into the solid, leaving behind a hole. Adapted from *Principles of Electronic Materials* - S.O. Kasap.

given by

$$\lambda = \frac{hc}{E_g} \quad (1)$$

For Si, the wavelength is approximately 1060 nm and lies in the IR region. This is the reason why Si is opaque since visible radiation (400 - 700 nm) will be absorbed forming electron-hole pairs. Glass (SiO₂) on the other hand has a band gap of approximately 10 eV and hence the maximum wavelength is 100 nm (in the UV region) making it transparent. Absorption of light by Si is shown in figure 2.

3 Conductivity equation

Conductivity in a semiconductor is due to movement of electrons in the CB and holes in the VB in an applied electric field. This is shown schematically in figure 3. These move in opposite directions since hole motion in the VB is due to electron motion in the opposite direction. Figure 5 shows the hole motion in the VB due to electron tunneling from one bond to the next. Ultimately

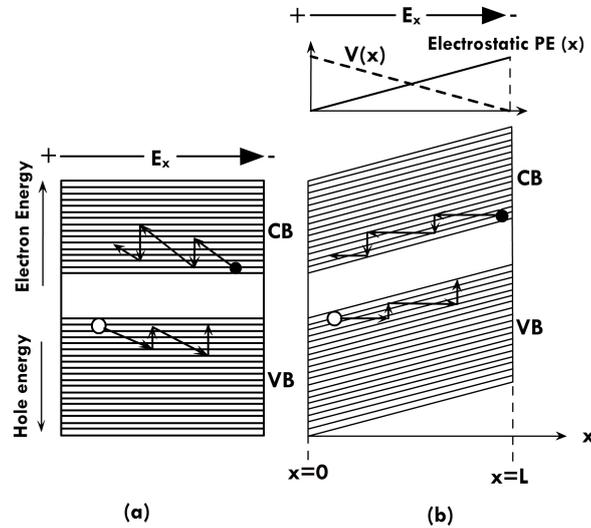


Figure 3: Conduction in a semiconductor. (a) Random motion of electron in the CB and holes in the VB. (b) When an electric field (external potential) is applied the energy levels are shifted. Electrons and holes move in opposite directions in the field, giving rise to a current. Adapted from *Principles of Electronic Materials* - S.O. Kasap.

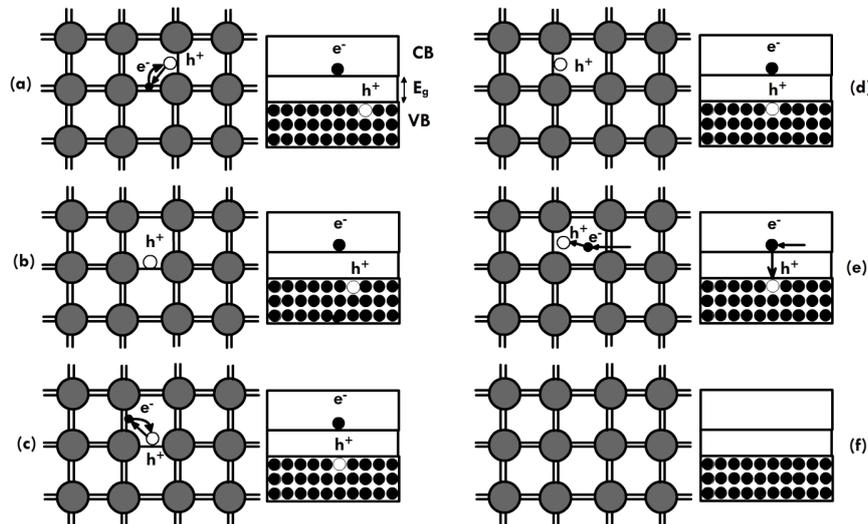


Figure 4: (a) - (f) Sequence of steps showing hole formation, motion, and finally annihilation in a semiconductor. Adapted from *Principles of Electronic Materials* - S.O. Kasap.

the hole recombines with the electron and gets annihilated. Thus, formation of electron and holes and their recombination is a *dynamic process*. This depends on the temperature of the sample (for an intrinsic semiconductor) so that there is an equilibrium concentration at any given temperature. Conductivity in a semiconductor depends on two factors

1. Concentration of electrons and holes. Denoted as n and p and is temperature dependent.
2. Ability of the electron and holes to travel in the lattice without scattering.

Electrons and holes are said to *drift* in the lattice. This is because they undergo multiple scatterings with the atoms. In typical semiconductors, concentration of electrons and holes are small, compared to the atomic concentration, so that electron-electron scattering can be ignored. But there is still the interaction between the electron and lattice. This is defined by a quantity called **mobility**, denoted by the symbol μ . Mobility refers to the ability of the charge carriers to move in the lattice. Mobility is related to the effective mass of the carrier (m_e^* and m_h^*) and the time between two scattering events (τ_e and τ_h). The relation is

$$\boxed{\begin{aligned} \mu_e &= \frac{e\tau_e}{m_e^*} \\ \mu_h &= \frac{e\tau_h}{m_h^*} \end{aligned}} \quad (2)$$

The effective mass term takes into account the effect of the lattice arrangement on the movement of the carriers. Using the carrier concentration and the concept of mobility it is possible to write a general equation for conductivity (σ) given by

$$\boxed{\sigma = ne\mu_e + pe\mu_h} \quad (3)$$

According to equation 3 higher the carrier concentration (n or p) higher the conductivity. Also, higher the mobility, higher the conductivity. Since mobility is related to the time between 2 scattering events, more the time between 2 scattering events greater is the conductivity.

3.1 Electron mobility in Si

Consider the case of Si, where the electron mobility (μ_e) is $1350 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and μ_h is $450 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. The effective masses are m_e^* is $0.26 m_e$ and m_h^*

is $0.38 m_e$. Using equation 2 it is possible to find the scattering time for electrons and holes. Consider electrons, τ_e is calculated to be 2×10^{-13} s or 0.2 ps (pico seconds). This time, between 2 scattering events, is extremely short. To calculate the distance traveled by the electron in this short time we can use an estimate of the velocity obtained from the thermal energy of electrons, which is given by $\frac{3}{2}k_B T$. For an electron in the CB the potential can be approximated to be zero and hence the thermal energy is equal to the kinetic energy ($\frac{1}{2}m_e v_{th}^2$). Equating the two, it is possible to find the thermal velocity of electrons at room temperature and the value is 1.16×10^5 $m s^{-1}$. From the thermal velocity and the scattering time it is possible to find the distance traveled between 2 scattering events. This distance is approximately 23 nm. In terms of number of unit cells this works out to be 43 unit cells (Si lattice constant is 0.53 nm). Thus, despite the short scattering time the electron can travel a substantial distance, in terms of unit cells, before scattering. This is because only the lattice can scatter and electron-electron scattering is limited due to the low concentration.

Mobility is temperature dependent. It also depends on the type of semiconductor and the presence of impurities. Mobility usually decreases with increasing impurity concentration since there are more scattering centers in the material. Ge has a higher mobility than Si. μ_e for Ge is 3900 $cm^2 V^{-1} s^{-1}$. μ_e for GaAs is even higher, 8500 $cm^2 V^{-1} s^{-1}$. Thus, based on mobility, GaAs would be the material with the highest conductivity. But conductivity also depends on the carrier concentration. The dominating term, in equation 3, would determine the conductivity.

4 Carrier concentration in semiconductors

The carrier concentration in an energy band is related to the density of available states, $g(E)$, and the probability of occupation, $f(E)$. This is given by

$$n = \int_{band} g(E) f(E) dE \quad (4)$$

where the integration is over the entire band. $f(E)$ represents the Fermi function and for energies much greater than $k_B T$ it can be approximated by the Boltzmann function.

$$f(E) = \frac{1}{1 + \exp\left(\frac{E - E_F}{k_B T}\right)} \simeq \exp\left(-\frac{E - E_F}{k_B T}\right) \quad (5)$$

To find the number of electrons in the conduction band (n) then equation 4 can be written as

$$n = \int_{E_c}^{E_c+\chi} g_{CB}(E)f(E)dE \quad (6)$$

where the simplified Fermi function is used. The actual density of states function in the CB depends on the semiconductor material but an approximation of a 3D solid with an uniform potential can be used. In this case $g_{CB}(E)$ turns out to be

$$g_{CB}(E) = \frac{8\pi\sqrt{2}}{h^3} (m_e^*)^{\frac{3}{2}} (E - E_c)^{\frac{1}{2}} \quad (7)$$

Since the density of states function is with respect to the bottom of the CB E is replaced by $(E - E_c)$. To further simplify the integral the limits can be changed from E_c to ∞ instead of $E_c + \chi$. This is because most of the electrons in the CB are close to the bottom and χ is usually much larger than $k_B T$. Hence, making the substitutions in equation 6 and doing the integration the electron concentration in the conduction band is given by

$$\boxed{\begin{aligned} n &= N_c \exp\left[-\frac{(E_c - E_F)}{k_B T}\right] \\ N_c &= 2 \left(\frac{2\pi m_e^* k_B T}{h^2}\right)^{\frac{3}{2}} \end{aligned}} \quad (8)$$

where N_c is a temperature dependent constant called the *effective density of states at the conduction band edge*. It gives the total number of available states per unit volume at the bottom of the conduction band for electrons to occupy. E_c is the bottom of the conduction band and E_F is the position of the Fermi level.

A similar equation can be written for holes

$$\boxed{\begin{aligned} p &= N_v \exp\left[-\frac{(E_F - E_v)}{k_B T}\right] \\ N_v &= 2 \left(\frac{2\pi m_h^* k_B T}{h^2}\right)^{\frac{3}{2}} \end{aligned}} \quad (9)$$

where N_v is the *effective density of states at the valence band edge*. Equations 8 and 9 give the electron and hole concentrations in semiconductors (intrinsic or extrinsic). The concentrations depend on the position of the Fermi level. The calculations are summarized in figure 5. This plots the DOS function in the CB and VB and the variation in the Fermi function in these bands.

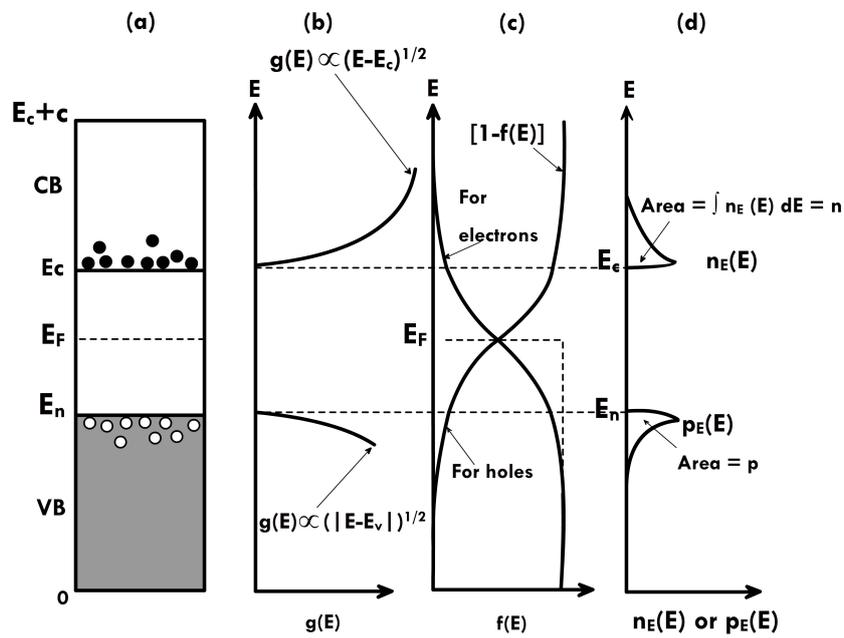


Figure 5: (a) Band picture of Si (b) DOS in CB and VB (c) Fermi function for electron and holes (d) Electron concentration in CB and hole concentration in VB, obtained by multiplying (b) and (c). Adapted from *Principles of Electronic Materials* - S.O. Kasap.

The Fermi level is usually far away from the band edges so that it can be approximated by the Boltzmann function. The electron and hole concentration is got by multiplying both and these are located close to the edge of the band. This also justifies the assumption that the upper integration limit can be changed to ∞ , since the carriers are located very close to the band edges.

5 Intrinsic carrier concentration

To eliminate E_F consider multiplying n and p in equations 8 and 9. This gives

$$np = N_c N_v \exp\left[-\frac{(E_c - E_v)}{k_B T}\right] \quad (10)$$

From figure 1 it can be seen that this is nothing but the band gap so that equation 10 becomes

$$np = N_c N_v \exp\left[-\frac{E_g}{k_B T}\right] \quad (11)$$

Thus, the product of electron and hole concentration is independent of the Fermi level position but only on the band gap and temperature, apart from N_c and N_v . In an intrinsic semiconductor $n = p$ since electron and holes are created in pairs (hole is the absence of electron). This is called n_i the **intrinsic carrier concentration**. Substituting in equation 11 the intrinsic carrier concentration can be calculated.

$$\boxed{n_i = \sqrt{N_c N_v} \exp\left(-\frac{E_g}{2k_B T}\right)} \quad (12)$$

Thus, the intrinsic carrier concentration in a semiconductor is dependent only on the band gap (E_g). n_i is a material property (at a given temperature). Equation 11 can now be rewritten as

$$\boxed{np = n_i^2} \quad (13)$$

This equation is called **law of mass action** and it is valid for any semiconductor at equilibrium. For an intrinsic semiconductor equation 13 is trivial since $n = p = n_i$ but even when n and p are not equal to product should still yield n_i^2 . This has important implications for extrinsic semiconductors. The conductivity equation 3 can now be rewritten for intrinsic semiconductors as

$$\sigma_i = n_i e (\mu_e + \mu_h) \quad (14)$$