Semiconductors

Insulators are characterized by a completely filled valence band and an empty conduction band. At T=0, they are insulating. But when T is not zero, there is a nonvanishing probability that some electrons will be thermally excited across the gap to the unoccupied levels in the conduction band. We will see later that this probability is \( \sim \exp(-E_g/2k_BT) \). At room temperature, \( k_BT = 0.025\text{eV} \). This factor is \( \exp(-80) \sim 10^{-35} \) when \( E_g = 4\text{eV} \); but it lowers to \( \exp(-5) \sim 10^{-2} \) when \( E_g = 0.25\text{eV} \). In the latter, conductivity is observable.

Semiconductors are insulators at T=0, but have an \( E_g \) is as such that at temperatures below the melting temperature, the thermal excitations can lead to observable conductivity. \( E_g \) is typically less than 2eV and the room temperature resistivity is usually \( 10^{-3} \) to \( 10^9 \) Ohm-cm (c.f. \( 10^{-6} \) and \( 10^{22} \) Ohm-cm for good conductors and insulators, respectively)

Since \( n(T) \sim \exp(-E_g/2k_BT) \) and \( \sigma \sim n \), the resistivity of semiconductors decreases with increasing T (i.e., a negative coefficient of resistance). Note that although the relaxation time increases with increasing T, the increase is described by a power law, which is readily dominated by the exponential dependence of n.

Impurities can have a significant effect on the conductivity. A concentration of 1 part in \( 10^8 \) can lead to observable effects. The resistivity varies at a given temperature by a factor of \( 10^{12} \) as the impurity concentration changes by only a factor of 1000. For a given concentration, the resistivity eventually falls onto a common (intrinsic resistivity) \( \rho(T) \) curve as the temperature increases.

The behavior at lower temperatures to this is referred to as extrinsic properties. A semiconductor is intrinsic if its properties are dominated by the electrons excited from the valence band to the conduction band, and extrinsic if the properties are dominated by the electrons excited to the conduction band from the impurities (or captured from the valence band by the impurities).
**Semiconductors**

**Different Kinds of Semiconductors**

The simplest kind are those made of the group IV elements. The most common are Si and Ge.

Another broad class is the III-V semiconductors (e.g. GaAs, InSb, AlSb, InP), consists of crystals of the zincblend structure, composed of elements in Groups III and V. The bonds are still covalent in character.

Semiconductors can also be made of elements in Groups II and VI (e.g. lead selenide PbSe, telluride PbTe, and sulfide PbS). They begin to have strong ionic as well as covalent characters. They are known as polar semiconductors. The common crystal structures include those of the zincblend and NaCl.

**Measurement of $E_g$**

Optical absorption provides an important means. When $\hbar \omega$ is bigger than the gap, strong absorption of the optical radiation by the semiconductor takes place. In the case where the band gap is not direct, the photon absorption must be assisted by the absorption of a phonon to preserve the crystal momentum. The energy conservation revises to $\hbar \omega + \hbar \omega_{phonon} = E_g$. So, a lower-energy photon is required to cause the threshold absorption. But typically, $\hbar \omega_{phonon}$ is $1/100$ times $E_g$. The revision is very small.

The $E_g$ can also be deduced from the intrinsic resistivity via $\rho \sim \exp[E_g/2k_BT]$. So, $E_g$ is related to the slope of a $\ln(\rho)$ vs. $1/T$ plot.

**Number of Carriers in Thermal Equilibrium**

For electrons:

$$n_e(T) = \int_{E_c}^{E} d\epsilon g_e(\epsilon) \frac{1}{\exp\left(\frac{\epsilon - \mu}{k_BT}\right) + 1} \quad (1)$$
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For holes:

\[ p_v(T) = \int_{-\infty}^{\infty} d\varepsilon g_v(\varepsilon) \left[ 1 - \frac{1}{\exp \left( \frac{\varepsilon - \mu}{k_B T} \right) + 1} \right] = \int_{-\infty}^{\infty} d\varepsilon g_v(\varepsilon) \frac{1}{\exp \left( \frac{\mu - \varepsilon}{k_B T} \right) + 1}. \]  

(2)

To proceed, we adopt the approximations:

\[ \varepsilon_c - \mu >> k_B T \text{ and } \mu - \varepsilon_v >> k_B T. \]  

(3)

Validity of this approximation depends on \( \mu \). They hold if \( E_g > \sim 0.1 \text{ eV} \) and the impurity concentration is sufficiently low. Semiconductors in which (3) is valid are called nongenerate semiconductors.

Assuming (3),

\[ n_v(T) = N_c(T)\exp\left[ -\frac{(\varepsilon_c - \mu)}{k_B T} \right] \]

\[ p_v(T) = P_v(T)\exp\left[ -\frac{(\mu - \varepsilon_v)}{k_B T} \right] \]  

(4)

where

\[ N_c(T) = \int_{-\infty}^{\infty} d\varepsilon g_c(\varepsilon) \exp\left[ -\frac{(\varepsilon - \varepsilon_c)}{k_B T} \right] \]

\[ P_v(T) = \int_{-\infty}^{\infty} d\varepsilon g_v(\varepsilon) \exp\left[ -\frac{(\varepsilon_v - \varepsilon)}{k_B T} \right] \]  

(5)

Equations (5) can be evaluated explicitly. Since the exponential becomes negligibly small except within \( k_B T \) from \( \varepsilon_c \) or \( \varepsilon_v \). Within this narrow range of the band edge, we can approximate \( \varepsilon \) by:

\[ \varepsilon = \varepsilon_c + \frac{\hbar^2 k^2}{2m_c} \text{ for electrons} \]

\[ \varepsilon = \varepsilon_v - \frac{\hbar^2 k^2}{2m_v} \text{ for holes.} \]  

(6)

This is the same dispersion relation we treated before for free electrons.
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(One may perceive that the same dispersion relation is valid for the holes by substituting \( \epsilon' = \epsilon_V - \epsilon = \hbar^2 k^2 / 2m^* \), with which \( P_{V}(T) = \int_{0}^{\infty} d\epsilon' g_{V}(\epsilon') \exp[-\epsilon' / k_{B}T]. \))

By the result we had before,

\[
N_{C}(T) = (1/4)(2m_{C}k_{B}T/\pi \hbar)^{3/2} \quad \text{(see below)}
\]

\[
P_{V}(T) = (1/4)(2m_{V}k_{B}T/\pi \hbar)^{3/2}
\]

\[
N_{C}(T) = (2.5)(m_{C}/m)^{3/2}(T/300 \text{ K})^{3/2} \times 10^{19} / \text{cm}^{3}
\]

\[
P_{V}(T) = (2.5)(m_{V}/m)^{3/2}(T/300 \text{ K})^{3/2} \times 10^{19} / \text{cm}^{3}
\]  

\( m_{C}/m \) and \( m_{V}/m \) are \( \sim 1 \) and the exponential factor in (4) is \( < \sim 0.1 \), the electron or hole density at room temperature is \( < 10^{18} - 10^{19} / \text{cm}^{3} \).

Note that in Drude model, \( r_{0} \approx 2a_{0} = 10^{-10} \text{m} \). So, \( n_{\text{metal}} = (10^{-2})^{3}(m^{3}/\text{cm}^{3}) \times (1/10^{-10})^{3} = 10^{24} \text{ m}^{-3} \)

______________________________

Proof of eqn. 7(a):

\[
N_{e}(T) = \int_{0}^{\infty} d\epsilon' g_{e}(\epsilon') e^{-\epsilon' / k_{B}T}
\]

\[
\epsilon' = \epsilon - \epsilon_{c} = \hbar^2 k^2 / 2m^* \quad \text{free electron}
\]

\[
N_{e}(T) = \int_{0}^{\infty} d\epsilon' g_{e}(\epsilon') e^{-\epsilon' / k_{B}T}
\]

\[
= \frac{1}{\pi^2} \int_{0}^{\infty} \frac{dk}{k^2} \frac{1}{\epsilon_{c}^2} e^{-\hbar^2 k^2 / 2m^* k_{B}T}
\]

\[
= \frac{1}{\pi^2} \int_{0}^{\infty} \frac{dk}{k^2} \frac{1}{\epsilon_{c}^2} e^{-\hbar^2 k^2 / 2m^* k_{B}T}
\]

\[
\left( \int_{0}^{\infty} e^{-\alpha x^2} dx = \frac{1}{2a} \sqrt{\pi / \alpha} \right)
\]

\[
N_{e}(T) = \frac{1}{\pi^2} \int_{0}^{\infty} \frac{dk}{k^2} \left( \frac{1}{\epsilon_{c}^2} \right) \frac{1}{2} \left( \frac{\hbar^2 k_{B}T}{2m^*} \right)^{3/2} = \frac{1}{4} \left( \frac{2m^* k_{B}T}{\eta \hbar^2} \right)^{3/2} \quad \text{\ldots \ E8 \ a. (7)}
\]
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We still cannot infer \( n_C(T) \) and \( p_V(T) \) until \( \mu \) is known. Consider the product:

\[
n_C(T) p_V(T) = N_C(T)P_V(T)\exp[-(\epsilon_C - \epsilon_V)/k_BT] = N_C(T)P_V(T)\exp[-E_g/k_BT].
\] (9)

Note that the RHS is a constant at a given temperature, determined entirely by the properties (i.e., \( m_C, m_C, E_g \)) of the semiconductor of question. This result, known as the law of mass action, suggests that at a given temperature it suffices to know the density of one carrier type to determine that of the other.

Intrinsic Case

If a semiconductor is so pure that impurities contribute negligibly to the carrier density, it is called an intrinsic semiconductor. In these cases, electrons in the conduction band can only come from formerly occupied valence band levels, leaving behind them the holes. So,

\[
n_C(T) = p_V(T) \equiv n_i(T)
\]

So, \( n_i(T) = [n_C(T)p_V(T)]^{1/2} = [N_C(T)P_V(T)]^{1/2}\exp(-E_g/2k_BT). \) (10)

By (7) and (8),

\[
n_i(T) = (1/4)(2k_BT/\pi\hbar^2)^{3/2}(m_cm_v)^{3/4}\exp(-E_g/2k_BT)
\]

\[
= (2.5) (m_c/m)^{3/4} (m_v/m)^{3/4}(T/300K)^{3/2} \exp(-E_g/2k_BT) \times 10^{19} / \text{cm}^3
\] (11)

We may now establish the condition for nondegenerate semiconductors to be valid in the intrinsic case. Dividing (4a) by (4b),

\[
\mu = \mu_i = \epsilon_V + E_g/2 + (k_BT/2)\ln(P_V/N_C),
\]

\[
= \epsilon_V + E_g/2 + (3/4)(k_BT)\ln(m_v/m_C).
\] (12)

This shows that as \( T \to 0, \mu_i \) lies precisely in the middle of the energy gap. Since \( m_v/m_C \) is \( \approx 1 \), the term linear in \( T \) is small so \( \mu_i \) doesn’t deviate much from \( E_g/2 \) even as \( T \) increases.
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For equation (3) to hold, namely, \( \varepsilon_C - \mu >> k_B T \) and \( \mu - \varepsilon_V >> k_B T \), we need \( E_g >> k_B T \), which is the precondition for semiconductors.

Extrinsic case

These are cases where impurities contribute a significant fraction of the conduction band electrons and/or valence band holes.

Because of the added sources of carriers, \( n_C - p_V = \Delta n \neq 0 \).

By the law of mass action, \( n_C(T)p_V(T) = n_i(T)^2 \)

\[
\left\{ n_C \right\} = \frac{1}{2} \left[ (\Delta n)^2 + 4n_i^2 \right]^{1/2} \pm \frac{1}{2} \Delta n. \tag{13}
\]

The quantity \( \Delta n/n_i \), which measures the importance of the impurities as a source of carriers, can be expressed by using the relations (eqns. 4a and 4b)

\[
n_C(T) = N_c(T) \exp\left[ - (\varepsilon_C - \mu)/k_B T \right] = \exp[\beta (\mu - \mu_i)]n_i, \tag{14a}
\]

\[
p_V(T) = \exp[\beta (\mu - \mu_i)]n_i \tag{14b}
\]

So, \( \Delta n/n_i = 2 \sinh[\beta (\mu - \mu_i)] \). \tag{15}

Eqn. (15) shows that if \( \mu \) is not \( \sim \mu_i \), \( \Delta n \) or \( (n \text{ or } p) \) \( \gg \) \( n_i \), i.e., in the extreme extrinsic case.

Eqn. (13) shows that if \( \Delta n \gg n_i \), the carrier concentrations are \( \sim \Delta n/2[1 + 2(n_i/\Delta n)^2] \pm \Delta n/2 \), i.e.,

\[
= \Delta n \quad \text{(upper sign)}
\]

\[
= \Delta n(n_i/\Delta n)^2 = n_i(n_i/\Delta n). \quad \text{(lower sign)} \tag{16}
\]

That means, one carrier type is \( \gg n_i \) and the other is \( \ll n_i \), whereby one of the two carrier types dominates. An extrinsic conductor is called \textit{n-type} or \textit{p-type} depending on whether the dominant carriers are electrons or holes. To fully determine \( n \) and \( p \), we must know \( \Delta n \) (eqn. 13) or \( \mu \) (14). So, we need to know the nature of the impurity levels and their statistics. Dividing (14a) by (14b), we obtain

\[
n_C(T)/p_V(T) = \exp[-2\beta(\mu - \mu_i)] \tag{17}
\]
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Subs. (16) in (17) and assume that electrons are the dominating carriers, we get:

\[(\Delta n/n_i)^2 = \exp[2\beta(\mu-\mu_i)] \Rightarrow \Delta n/n_i = \exp[\beta (\mu-\mu_i)].\]  

(18)

Impurity Levels

Impurities that contribute additional electrons to the conduction band when added to a host intrinsic semiconductor are donors. Those that supply additional holes to (i.e., capture electrons from) the V band are acceptors.

Given that the host semiconductor is Si or Ge (group IV elements), examples of donor impurities include P and As (group V) while examples of acceptor impurities include Al and Ga (group III).

Figure 28.11
(a) Schematic representation of a substitutional arsenic (valence 5) donor impurity in a germanium (valence 4) crystal. (b) The arsenic (As) can be represented as a germanium atom plus an additional unit of positive charge fixed at the site of the atom (circled dot). (c) In the semiclassical approximation, in which the pure semiconductor is treated as a homogeneous medium, the arsenic impurity is represented as a fixed point charge +e (dot).

The As site is perceived as one where there is an additional bound positive charge (=+e) plus an electron that can be iterant. In general, the donor/acceptor sites are distributed randomly, and each of the donor sites can bind an electron. If the impurities were not embedded in the semiconductor but in empty space, the binding energy of the electron would just be the first ionization potential of the impurity atom, which is 9.81 eV for As. But since the impurity is embedded in the host semiconductor, this binding energy is significantly reduced (to 0.013 eV for As in Ge) for the following two reasons:

The electrostatic forces responsible for the binding is reduced by the dielectric constant \(\varepsilon\) of the semiconductor (~16 in Ge), which is typically ~20 and can be 100 or more.

The effective mass of the charge carriers is typically < ~0.1 times the electron mass.
Because of the above two reasons, one may perceive that the radius of the bind electron orbit is
\[ r = \left( \frac{m}{m^*} \right) \varepsilon a_0, \]
which gives \( r \sim 100 \) to \( \sim 1000 \) \( a_0 \). The ground state binding energy becomes
\[ E = \left( \frac{m^*}{m} \right) \varepsilon^2 \times 13.6 \text{ eV} \sim 0.01 \text{ eV}. \]
Recall that \( E_g \sim 1 \) eV. So, the binding energy associated with an electron being bound to a donor impurity is small compared to \( E_g \). Since this binding energy is measured relative to the energy of the conduction-band levels (where the itertant electrons are), the donor impurities introduce energy levels (denoted \( \varepsilon_D \) in Fig. 28.12) below the conduction-band edge (denoted \( \varepsilon_C \) in Fig. 28.12). An electron is bound when a donor level is occupied. The binding energy of the electron is \( \varepsilon_C - \varepsilon_D \).

For acceptor impurities (e.g. P, Ga), one may perceive an acceptor site to be a fixed charge of \(-e\) situated in a fixed site along with one less electron in the host crystal. This acceptor site can bind a hole, where the binding energy is again small compared to \( E_g \). In terms of the electron picture, this bound hole will be manifested as an additional electronic level at an energy (\( \varepsilon_A \)) slightly above the valence band edge, \( \varepsilon_V \). A hole is bound to an acceptor site when the corresponding acceptor level is empty. The binding energy is \( \varepsilon_A - \varepsilon_V \), which is also the energy required to excite an electron from the valence band edge to the acceptor level. When an electron is excited from the valence band edge to an acceptor level, the hole in the vicinity of the acceptor is filled by that electron, while at the same time a free hole is created in the valence band.

Importantly, the donor (D) or acceptor (A) levels lie very close to the band edges making it very easy to thermally excite electrons from the valence (V) band to the acceptor (A) levels or from the D levels to the C band. This explains why the impurities, if present, constitute a far more important source of carriers than the intrinsic mechanism.