Semiconductors and its Properties

Anurag Srivastava
Basic characteristics of semiconductors

Key ideas

A semiconductor is neither a good insulator nor a very good conductor of electric current. The electrical resistivity of semiconductor generally decreases strongly with increasing temperature, whereas the resistivity of a metal generally increases weakly with increasing temperature.

A semiconductor can be an element, such as Si or Ge, or a compound, such as GaAs or InSb.

Solid semiconductors can exist in the crystalline or amorphous form.

A lattice is a periodic array of points in space.

A basis is a set of atoms associated with each lattice point.

Semiconductors can crystallize in the diamond, zincblende, wurtzite, or other structures.

The bonding between atoms in a semiconductor can be covalent, ionic, or mixed.

Layered semiconductors can intercalate foreign atoms or molecules.

Very pure semiconductors can be produced by the zone refining method.
Something about the history:

• 1833 M. Faraday:
  – For AgS decreasing $\rho$ with increasing $T$

• 1873 W. Smith:
  – Photoconductivity of Se

• 1874 F. Braun:
  – Rectifying properties of PbS

• 1948 Bardeen & Brattain:
  – Bipolar transistor
• The most usual semiconductors are the elemental ones, Si and Ge (and diamond C).
• They are tetrahedrally bonded, and thus, fourfold coordinated with sp³-hybridization.
• Semiconductors are typically:
  - stoichiometric: elemental, binary, tertiary, quaternary, ...
  - crystalline
  - small band gap materials ⇒ semiconducting
  - covalently bonded (mainly)

There are also semiconducting organic, magnetic and ferroelectric materials. Some high–Tc superconductors are semiconducting in N-state.
Semiconductors

• Semiconductors constitute a large class of substances which have resistivities lying between those of insulators and conductors.

• The resistivity of semiconductors varies in wide limits, i.e., $10^{-4}$ to $10^4 \, \Omega \cdot m$ and is reduced to a very great extent with an increase in temperature.

Fig. 1.1 The temperature dependence of the resistance in semiconductors.
Semiconductors

• The most typical and extensively employed semiconductors whose electrical properties have been well investigated, are Germanium (Ge), Silicon (Si) and Tellurium (Te). The study of their electrical properties reveals that
  – Semiconductors have **negative temperature Coefficient of resistance**, i.e., the resistance of semiconductor decreases with increase in temperature and vice versa
  – The resistivity of semiconductors lies between that of a good insulator and of a metal conductor, i.e., lying in the range $10^{-4}$ to $10^4$ Ω-m.
  – The electrical conductivity of a semiconductor is very much affected when a suitable impurity, e.g., Arsenic, Gallium, Indium etc. is added to it. This property of semiconductors is most important.
Semiconductors

As compared to electronic valves, semiconductor devices offer the following advantages:

(i) low weight and small size
(ii) no power for the filament
(iii) Long service life (thousands of hours)
(iv) mechanical ruggedness
(v) low power losses and
(vi) Low supply voltages.
Semiconductors

At the same time semiconductor devices suffer from a number of disadvantages:

- deterioration in performance with time (ageing); higher noise level than in electronic valves
- Unsuitability of most transistors for use at frequencies over tens of megahertz;
- low input resistance as compared with vacuum triodes;
- inability to handle large power
- deterioration in performance after exposure to radioactive emissions.
R & D has reduced the demerits

• There are semiconductor rectifiers for currents of thousands of amperes.
• Replacement of Germanium with Silicon makes crystal diodes and transistors suitable for operation at temperatures upto 125°C.
• There are transistors for operation at hundreds of megahertz and more, and also microwave devices such as gunn diode, tunnel diode.
How semiconductor works?

• To understand how semiconductors work, one must have a good knowledge of atomic structure.
• The smallest particle that an element can be reduced to and still retain its properties is called an atom.
• There are a number of different subatomic particles, but only three of these are of interest in basic electronics—the proton, the neutron and the electron.
• An, atom has the same number of electrons and protons, and so it is electrically neutral. If an atom does have more electrons, it is called a negative ion. If it has more protons, it is called a positive ion.
quantum numbers

To understand the location and energy of each electron in an atom, one must have the knowledge of four quantum numbers:

(i) Principal Quantum Number (n).

- This characterises the average distance of an electron from the nucleus and corresponds to the principal energy level in which electron resides.
- $n$ can have positive integer values starting from 1, i.e. $n = 1, 2, 3, \ldots$.
- The principal energy levels or shells having different values of $n$ are designated by the letters K, L, M, N and so on.
- The maximum numbers of the electrons that can be accommodated in a shell corresponding to $n$ is equal to $2n^2$. 
(ii) **Azimuthal Quantum Number** \((l)\).

– This is also called as **orbital angular momentum quantum number** and gives a **measure of the angular momentum** of an electron in the orbit.

– Physically, \(l\) indicates the **shape of the classical orbit**.

– For a given value of \(n\), \(l\) can take all positive integer values from \(0\) to \((n – l)\).

– The particular \(l\) value defines the subshell, and the sub shells with \(l = 0, 1, 2, 3, \ldots\) are designated as \(s, p, d, f, g, \ldots\) respectively.
(iii) Magnetic Quantum Number ($m_l$).

- This is also called as **orbital magnetic number** and this determines the preferred orientation of the orbitals in space with respect to an applied magnetic field.

- We know that the magnetic moment of an electron due to its orbital motion gives rise to a magnetic field which can interact with an external magnetic field. The electrons orient themselves in certain preferred region of space around the nucleus under the influence of the external field.

- For a given value of $l$, $m_l$ can take integer values between –1 to +1 including 0, *i.e.* total allowed values of $m_l$ are $(2l + 1)$.
• (iv) **Spin Quantum Number** \((m_s)\).
  – Electron is spinning about its own axis in the atom.
  – The spin of the electron produces a spin magnetic moment which can either parallel or antiparallel to the surrounding magnetic field.
  – For an electron there are two spin states.
  – Spin quantum number is concerned with the spinning of the electron about its own axis.
  – Thus \(m\) can take only two possible states, \(+\frac{1}{2}\) or \(-\frac{1}{2}\).
Pauli Exclusion Principle.

– This states that in an atom no two electrons can exist in the same quantum state, i.e. in an atom there cannot be two electrons with the same value of all the four quantum numbers.

– With the help of this principle, one can write the configuration of electrons.

– All the electrons with the same value of \( n \) constitute a shell and a shell can have a maximum of \( 2n^2 \) electrons.
Table 1.1. Electron distribution in subshells

<table>
<thead>
<tr>
<th>Shell</th>
<th>K</th>
<th>L</th>
<th>M</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>n</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>l</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Subshell</td>
<td>s</td>
<td>s</td>
<td>p</td>
<td>s</td>
</tr>
<tr>
<td>No. of electrons</td>
<td>2</td>
<td>2</td>
<td>6</td>
<td>2</td>
</tr>
</tbody>
</table>
Table 1.2. Electronic configuration of some elements of group IV A

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic number</th>
<th>Electronic configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>6</td>
<td>(1s^22s^22p^2)</td>
</tr>
<tr>
<td>Si</td>
<td>14</td>
<td>(1s^22s^22p^63s^23p^2)</td>
</tr>
<tr>
<td>Ge</td>
<td>32</td>
<td>(1s^22s^22p^63s^23p^63d^{10}4s^24p^2)</td>
</tr>
<tr>
<td>Sn</td>
<td>50</td>
<td>(1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^2)</td>
</tr>
<tr>
<td>Pb</td>
<td>82</td>
<td>(1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}4f^{14}5s^25p^65d^{10}6s^26p^2)</td>
</tr>
</tbody>
</table>
Atomic structures of H, B, Si, P and Ge atoms.

(a) Hydrogen atom (\(1^1\)\(^H\))

(b) Boron atom (\(5^5\)\(^B\))

(c) Silicon atom (\(14^{14}\)\(^Si\))

(d) Phosphorus atom (\(15^{15}\)\(^P\))

(e) Germanium atom (\(32^{32}\)\(^Ge\))

Fig. 1.3 Atomic structure of a few atoms.
- The electrons in the inner shells of an atom do not normally leave the atom. But the electrons which are in the outermost shell, so called *valence shell* do not always remain confined to the same atom.
- Some of these valence electrons move in a random manner and may travel from one atom to another in a crystal lattice. These electrons are called as free electrons.
- It is due to the presence of these free electrons in a material, that electrical conduction is possible.
- The electrons in the inner orbits of the atom remain bound to the nucleus and are, therefore, called *bound electrons*. 
chemical stability

– The tendency of an atom to give up its valence electrons depends on chemical stability.

– When an atom is stable, it resists giving up electrons, and when it is unstable, it tends to give up electrons.

– The level of stability is determined by the number of valence electrons, because the atom strives to have its outermost or valence shell completely filled.
Fig. 1.6 Energy band in a crystal as a function of interatomic spacing.
Classification of solids

**Fig. 1.6** Energy band diagram exhibiting energy band gap in (a) Insulators, (b) and (c) Conductors, and (d) Semiconductors.
Figure 1.1 Energy level diagram of (a) direct and (b) indirect band gap semiconductors.
Exciton:

When an electron is excited from the valence band to conduction band, an electron-hole pair is created. This bound state electron-hole pair is called exciton and it requires a minimum energy to excite it. Changes in the band gap due to particles size, leads to the corresponding changes in the properties of the material.

The increase in exciton energy with respect to bulk semiconductor band gap is given by,

$$\Delta E = \frac{\hbar^2}{2\mu} \left[ \frac{\pi}{R} \right]^2$$

(1.2)

where, \( R \) is the radius of spherical quantum dots, \( \mu \) is the reduced mass of electron-hole pair and it is given as,

$$\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_h}$$

(1.3)

where, \( m_e \) and \( m_h \) are effective mass of electron and hole respectively. The reduced mass is generally smaller than the electron rest mass \( m_0 \). The exciton Rydberg energy is given as,
The exciton Rydberg energy is given as,

$$E_R = \frac{\hbar^2}{2\mu a_B^2}$$  \hspace{1cm} (1.4)

and exciton Bohr radius ($a_B$) is given as,

$$a_B = \frac{\varepsilon \hbar^2}{\mu e^2}$$  \hspace{1cm} (1.5)

where, $e$-electronic charge, $\varepsilon$-dielectric constant.

Therefore, the energy shift is written as

$$\Delta E = E_R \left[ \frac{\pi a_B}{R} \right]^2$$  \hspace{1cm} (1.6)
quantum confinement effect

– The tuning of fundamental properties such as optical and vibrational properties of nanostructured semiconductor material is possible when the size of the nanostructured semiconductor material approaches the exciton Bohr radius.

– Though significant variation in the fundamental properties is observed when the size is less than the exciton Bohr radius. This is due to the confinement of charge carriers and phonons within the nanoparticles. This is called quantum confinement effect.

– Efros and Efros (1982) introduced three regimes of quantum confinement, depending on the ratio of the nanocrystallite radius \( R \) to the Bohr radius of the electrons, holes and electron-hole pair.
quantum confinement effect
Quantum Confinement Effect

Quantum Confinement

Surface to volume ratio

Nanoparticles vs Bulk Material

Energy Level

Quantum Confinement

Radiation shift between the two edges of visible spectra

ΔE\text{nano} < ΔE\text{bulk}

Band Gap (eV)

Surface area to Volume Ratio (1/nm)
Semiconducting Materials

Besides Elemental, Compound and Diluted Magnetic Semiconductors.

**Organic semiconductors:**
- Semiconductor like properties are also found in "organic compounds" like polydiacetylene \((CH_2)_n\) with conjugate carbon chains, fullerenes, nanotubes, BN nanotubes, etc.
- Organic molecules can easily be tailored at the molecular level and "tuned" for applications.
- However, these are not used too much, yet, but they seem promising materials for nonlinear optics (NLO), for example.

**Magnetic Semiconductors**
- Strong magnetooptical effect allows the material to be used in optical modulators. Their Faraday rotation can be up to six orders of magnitude higher than that of nonmagnetic semiconductors.
- Magnetic field can also be used to cause the metal to semiconductor transition, a phenomenon also called colossal magnetoresistance.

Other ...
- Ferroelectric and complex inorganic materials ... for NLO
Types of Semiconductor Materials

• The silicon doped with **extra electrons** is called an “**N type**” semiconductor.
  – “**N**” is for negative, which is the charge of an electron.

• Silicon doped with material **missing electrons** that produce locations called **holes** is called “**P type**” semiconductor.
  – “**P**” is for positive, which is the charge of a hole.
Current Flow in N-type Semiconductors

• The DC voltage source has a positive terminal that attracts the free electrons in the semiconductor and pulls them away from their atoms leaving the atoms charged positively.

• Electrons from the negative terminal of the supply enter the semiconductor material and are attracted by the positive charge of the atoms missing one of their electrons.

• Current (electrons) flows from the positive terminal to the negative terminal.
Current Flow in P-type Semiconductors

- Electrons from the negative supply terminal are attracted to the positive holes and fill them.
- The positive terminal of the supply pulls the electrons from the holes leaving the holes to attract more electrons.
- Current (electrons) flows from the negative terminal to the positive terminal.
- Inside the semiconductor current flow is actually by the movement of the holes from positive to negative.
Diamond

- In the diamond structure, the carbon atoms are arranged on an fcc-type lattice with a total of 16 electrons per primitive cell.

- The valence band and 7 lower bands are full, leaving no electrons in the conduction band.

The valence band and 7 lower bands are full, leaving no electrons in the conduction band.
Diamond

Electrons may be thermally activated to jump a gap. At room temperature, $k_B T$ is only 0.026 eV. To jump the energy gap, the electron requires very high temperatures. So, diamond is an excellent insulator.

\[ \rho = 10^{18} \, \Omega \cdot \text{m} \]
Graphite/Graphene

\[ \rho = 9 \ \mu\Omega \cdot \text{m} \]
• Silicon has the diamond structure.
• There are 14 electrons per primitive cell.
• Gap is only 1.12 eV, however.

Now there is a small (but finite) chance for a few electrons to be thermally excited from valence band to conduction band.
Silicon

\[ 1.12 \text{ eV} \]
Effective Mass \( (m_e) \) Revisited

• An electron moving in the solid under the influence of the crystal potential is subjected to an electric field.
• We expect an external field to accelerate the electron, increasing \( E \) and \( k \) and change the electron’s state.
• If this external field is much weaker than the internal field, the effect the latter is to modify the mass of carriers in such a way that the carriers respond to the applied field with this modified mass obeying classical mechanics. This modified mass is termed as effective mass of carriers and is usually different from electron mass \( (m_0) \) in vacuum.
Effective Mass Revisited

\[ m_e = \left( \frac{1}{\hbar^2} \frac{d^2 \varepsilon}{dk^2} \right)^{-1} \]

- This relates the curvature of the band to the “effective mass.”
- One can show that a free electron “band” gives an effective mass equal to the rest mass of an electron.
- Electrons in a crystal are accelerated in response to an external force just as though they were free electrons with effective mass \( m_e \).
- Usually, \( m_e < m_0 \).
Effective Mass Revisited

Consider the following $E-k$ curve:

Suppose there are electrons in these states.
Effective Mass Revisited

<table>
<thead>
<tr>
<th>Material</th>
<th>Electron Effective Mass</th>
<th>Hole Effective Mass</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Group IV</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si (4.2 K)</td>
<td>1.08</td>
<td>0.56</td>
</tr>
<tr>
<td>Ge</td>
<td>0.555</td>
<td>0.37</td>
</tr>
<tr>
<td><strong>Groups III-IV</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GaAs</td>
<td>0.067</td>
<td>0.45</td>
</tr>
<tr>
<td>InSb</td>
<td>0.013</td>
<td>0.60</td>
</tr>
<tr>
<td><strong>Groups II-VI</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnO</td>
<td>0.19</td>
<td>1.21</td>
</tr>
<tr>
<td>ZnSe</td>
<td>0.17</td>
<td>1.44</td>
</tr>
</tbody>
</table>

in multiples of the free electron mass

\[ m_0 = 9.11 \times 10^{-31} \text{ kg} \]
Experimental Measurement

• Traditionally effective masses were measured using cyclotron resonance, a method in which microwave absorption of a semiconductor immersed in a magnetic field goes through a sharp peak when the microwave frequency equals the cyclotron frequency.

\[ \omega_c = \frac{eB}{m^*c} \]

• In recent years effective masses have more commonly been determined through measurement of band structures using techniques such as angle-resolved photoemission or, most directly, the de Haas-van Alphen effect.

• Effective masses can also be estimated using the coefficient \( \gamma \) of the linear term in the low-temperature electronic specific heat at constant volume \( C_v \).

• The specific heat depends on the effective mass through the density of states at the Fermi level and as such is a measure of degeneracy as well as band curvature.
Electrons & Holes

\[ E_{G} = 0.5 \text{ to } 1.5 \text{ eV} \]

conduction-band

valence-band
In a semiconductor, there are two charge carriers:

- **Electrons** (conduction band)
  - negative mass
  - negative charge
- **Holes** (valence band)
  - positive mass,
  - positive charge

For the electrons occupying the vacant states,

\[ \frac{1}{h^2} \frac{d^2 \varepsilon}{dk^2} < 0 \]

(Negative!) and the electrons will move in the same direction as the electric field (wrong way!)

In a semiconductor, there are two charge carriers:
To calculate the carrier concentrations in energy bands we need to know the following parameters:

- The *distribution of energy states* or levels as a function of energy within the energy band, $D(\varepsilon)$.
- The *probability* of each of these states being occupied by an electron, $f(\varepsilon)$.

**Electron Density**

$$\begin{align*} n &= \int_{\varepsilon_c}^{\infty} f(\varepsilon) \ D(\varepsilon) \ d\varepsilon \\
\text{Hole Density} &= \int_{-\infty}^{\varepsilon_v} [1 - f(\varepsilon)] \ D(\varepsilon) \ d\varepsilon \end{align*}$$
A band is shown for a one-dimensional crystal. The square represents an initially empty state in an otherwise filled band. When an electric field is applied, the states represented by arrows successsively become empty as electrons make transitions.
The band is completely filled except for a state marked by a square. Except for the electron represented as a circle, each electron can be paired with another, so the sum of their crystal momentum vanishes. The total crystal momentum for the band and the crystal momentum of the hole are both $\hbar k$. 
The empty state and the unpaired electron for two times are shown when an electric field is applied. The change in momentum is in the direction of the field.
Conduction Band Carrier Concentration

\[ n = \int_{\varepsilon=0}^{\infty} f(\varepsilon) \, D(\varepsilon) \, d\varepsilon \]

\[ D(\varepsilon) = \frac{dN(\varepsilon)}{dE} = \frac{1}{2\pi^2} \left( \frac{2m_e}{\hbar^3} \right)^{3/2} \sqrt{\varepsilon} \]

For \( \varepsilon >> \varepsilon_p \), the Boltzmann distribution approximates the F-D distribution:

\[ f(\varepsilon) = \frac{1}{1 + e^{(\varepsilon-\varepsilon_F)/k_BT}} \approx e^{-(\varepsilon-\varepsilon_F)/k_BT} \]

\[ = e^{-(\varepsilon-\varepsilon_c)/k_BT} e^{-(\varepsilon_c-\varepsilon_F)/k_BT} \]

which is valid for the tail end of the distribution.
Conduction Band Carrier Concentration

\[ n = e^{-\frac{(\varepsilon_c - \varepsilon_F)}{k_BT}} \int_{\varepsilon=0}^{\infty} D(\varepsilon) e^{\frac{\varepsilon - \varepsilon_c}{k_BT}} \, d\varepsilon \]

\[ N_C = 2 \left( \frac{m_e k_B T}{2\pi \hbar^2} \right)^{3/2} \]

Effective Density of States for the Conduction Band

\[ n = N_C e^{\frac{\varepsilon_F - \varepsilon_c}{k_BT}} \]
Conduction Band
Carrier Concentration

Intrinsic Carriers vs T
Valence Band Carrier Concentration

- The hole distribution is related to the electron distribution, since a hole is the absence of an electron.

\[
f_h = 1 - f_e = 1 - \frac{1}{e^{(\varepsilon - \varepsilon_F)/k_BT} + 1} = \frac{1}{e^{(\varepsilon_F - \varepsilon)/k_BT} + 1} \approx e^{(\varepsilon - \varepsilon_F)/k_BT} \quad \text{(as long as } \varepsilon_F - \varepsilon >> k_BT)\text{)}
\]

- The holes near the top of the valence band behave like particles with effective mass \(m_h\); and the density of states is

\[
D(\varepsilon) = \frac{1}{2\pi^2} \left( \frac{2m_h}{\hbar^2} \right)^{3/2} \sqrt{\varepsilon - \varepsilon_v}
\]

\[
p = \int_{-\infty}^{\varepsilon_v} \left[1 - f(\varepsilon)\right] D(\varepsilon) \, d\varepsilon = 2 \left( \frac{m_h k_B T}{2\pi\hbar^2} \right)^{3/2} e^{(\varepsilon_v - \varepsilon_F)/k_BT}
\]
Equilibrium Relation

• Multiply $n$ and $p$ together:

$$np = 4 \left( \frac{k_B T}{2 \pi \hbar^2} \right)^3 (m_h m_e)^{3/2} e \left( \frac{-\varepsilon_g}{k_B T} \right)$$

• The product is constant at a given temperature.

• It is also independent of any impurity concentration at a given temperature. This is because any impurity that adds electrons, necessarily fills holes.

• This is important in practice, since we could reduce the total carrier concentration $n + p$ in an impure crystal via the controlled introduction of suitable impurities – such reduction is called compensation.
A perfect semiconductor crystal containing no impurities or lattice defects is called an intrinsic semiconductor. As the carriers are generated in pairs, the concentration \( n \) of electrons in the conduction band equals the concentration \( p \) of holes in the valence band,

\[
n = p = n_i
\]

\[
N_c e^{(\varepsilon_F - \varepsilon_c)/k_B T} = N_v e^{(\varepsilon_v - \varepsilon_F)/k_B T}
\]

\[
\Rightarrow k_B T \ln \left( \frac{N_c}{N_v} \right) = \varepsilon_c - \varepsilon_F - \varepsilon_F + \varepsilon_v
\]

\[
\varepsilon_F = \frac{\varepsilon_c + \varepsilon_v}{2} - \frac{1}{2} k_B T \ln \left( \frac{N_c}{N_v} \right)
\]
Extrinsic Semiconductors

- Extrinsic semiconductors: we can add impurities to make a material semiconducting (or to change the properties of the gap).
- There are 2 types of extrinsic semiconductors: p-type and n-type.
- These are materials which have mostly hole carriers (p) or electron carriers (n).
- These give you ways of modifying the band gap energies (important for electronics, detectors, etc).
Extrinsic Semiconductors: \( n \) type

- Add a small amount of phosphorus (P: \( 3s^23p^3 \)) to Silicon (Si: \( 3s^23p^2 \)) (generally, a group V element to a group IV host) \( P \) replaces a Si atom and it donates an electron to the conduction band (P is called the donor atom). The periodic potential is disrupted and we get a localized energy level, \( \varepsilon_D \).

- This is an \( n \)-type semiconductor – more electrons around that can be mobile; and the Fermi energy is closer to the conduction band.
Extrinsic Semiconductors: $n$ type

Phosphorus provides an extra electron.

$\varepsilon_c - \varepsilon_D = 45 \text{ meV}$

So, its easy for the donor electrons to enter the conduction band at room temperature. This means that at room temperature $n \approx N_D$.

This is called complete ionization (only true if $n_i << N_D$). Therefore, by doping Si crystal with phosphorus, we increase the free electron concentration.

At low temperature, these extra electrons get trapped at the donor sites (no longer very mobile) - the dopant is frozen out.
Extrinsic Semiconductors: \( p \) type

- Next suppose Si atom is replaced with Boron (B: 2s\(^2\)2p) to Silicon (Si: 3s\(^2\)3p\(^2\)). Again, we have a perturbed lattice and a localized E-level created.
- Boron is missing an electron and accepts an electron from valence band, creating a hole.
- Therefore doping with B increases hole concentration. We call this \( p \)-type doping, the electron concentration \( n \) is reduced.
- \( \varepsilon_F \) moves closer to \( \varepsilon_V \).
Extrinsic Semiconductors

The graph shows the electron density, $n$, as a function of temperature (K). The extrinsic range is characterized by a constant electron density, $N_d$, until a specific temperature, $T$, where the electron density starts to increase sharply. The intrinsic range follows, where the electron density is determined by the intrinsic carrier concentration, $n_i$. The graph also indicates the freeze-out region, where the electron density remains constant before the onset of the extrinsic range.
Extrinsic Semiconductors

Boron in Silicon

Resistivity ($\Omega \text{ cm}$) vs. Temperature (K)

- $p=9.67 \times 10^{14} \text{ cm}^{-3}$
- $p=5.74 \times 10^{15} \text{ cm}^{-3}$
- $p=1.08 \times 10^{16} \text{ cm}^{-3}$
- $p=2.36 \times 10^{16} \text{ cm}^{-3}$
- $p=2.83 \times 10^{16} \text{ cm}^{-3}$
- $p=4.85 \times 10^{16} \text{ cm}^{-3}$
Mass Action Law \[ np = n_i^2 \]

- Valid for both intrinsic and extrinsic semiconductors.
- It is important in devices to control \( n \) and \( p \) concentrations and to suppress the influence of the intrinsic concentration.
- These equations are important in establishing upper limits in semiconductor operating temperature.
- We generally require \( n_i << \) (minimum doping density) and, practically, this means we need doping concentrations above \( 10^{14} \) cm\(^{-3}\).
Semiconductors
The Hall Effects
Discovery

- Observed in 1879
- Edwin Herbert Hall
- Discovered 18 years before the electron

- The Hall effect was discovered in 1879 by Edwin Hall while he was working on his doctoral degree at Johns Hopkins University in Baltimore, Maryland.

- His measurements of the tiny effect produced in the apparatus he used were an experimental tour de force, accomplished 18 years before the electron was discovered and published under the name "On a New Action of the Magnet on Electric Currents".
Hall effect in Metals

For a simple metal where there is only one type of charge carrier (electrons) the Hall voltage $V_H$ can be derived by using the Lorentz force and seeing that in the steady-state condition charges are not moving in the y-axis direction because the magnetic force on each electron in the y-axis direction is cancelled by a y-axis electrical force due to the buildup of charges.
\[ \mathbf{F} = q \left[ \mathbf{E} + (\mathbf{v} \times \mathbf{B}) \right] \]

0 = E_y - v_x B_z where \( E_y \) is assigned in direction of y-axis, not with the arrow as in the image.

In wires, electrons instead of holes are flowing, so \( v_x \rightarrow -v_x \) and \( q \rightarrow -q \). Also \( E_y = \frac{-V_H}{w} \). Substituting these changes gives

\[ V_H = v_x B_z w \]

The conventional "hole" current is in the negative direction of the electron current and the negative of the electrical charge which gives \( I_x = ntw(-v_x)(-e) \) where \( n \) is charge carrier density, \( tw \) is the cross-sectional area, and \(-e\) is the charge of each electron. Solving for \( w \) and plugging into the above gives the Hall voltage:

\[ V_H = \frac{I_x B_z}{nte} \]

If the charge build up had been positive (as it appears in some semiconductors), then the \( V_H \) assigned in the image would have been negative (positive charge would have built up on the left side).

The Hall coefficient is defined as

\[ R_H = \frac{E_y}{j_x B_z} \]

where \( j \) is the current density of the carrier electrons, and \( E_y \) is the induced electric field. In SI units, this becomes

\[ R_H = \frac{E_y}{j_x B} = \frac{V_H t}{IB} = -\frac{1}{ne}. \]

(The units of \( R_H \) are usually expressed as \( m^2/C \), or \( \Omega \cdot \text{cm/G} \), or other variants.) As a result, the Hall effect is very useful as a means to measure either the carrier density or the magnetic field.
Principles

• Mobile charges pressed to one side from Lorentz force, immobile charges unaltered
• Creates internal electric potential, known as Hall voltage.
• For simple metals, \( V_H = \frac{I \times B}{n \times e \times t} \)

Note: \( t \) refers to the thickness of the metal along the direction of the B-field
Concept:

• The Hall effect is due to the nature of the current in a conductor.
• Current consists of the movement of many small charge carriers, typically electrons, holes, ions (see Electromigration) or all three.
• When a magnetic field is present, these charges experience a force, called the Lorentz force.
• When such a magnetic field is absent, the charges follow approximately straight, 'line of sight' paths between collisions with impurities, phonons, etc.
• However, when a magnetic field with a perpendicular component is applied, their paths between collisions are curved so that moving charges accumulate on one face of the material. This leaves equal and opposite charges exposed on the other face, where there is a scarcity of mobile charges. The result is an asymmetric distribution of charge density across the Hall element, arising from a force that is perpendicular to both the 'line of sight' path and the applied magnetic field.
• The separation of charge establishes an electric field that opposes the migration of further charge, so a steady electrical potential is established for as long as the charge is flowing.
A Visual Representation

- Hall Effect measurement setup for electrons.
- Initially, the electrons follow the curved arrow, due to the magnetic force.
- At some distance from the current-introducing contacts, electrons pile up on the left side and deplete from the right side, which creates an electric field $\xi_y$ in the direction of the assigned $V_H$.
- $V_H$ is negative for some semi-conductors where "holes" appear to flow.
- In steady-state, $\xi_y$ will be strong enough to exactly cancel out the magnetic force, so that the electrons follow the straight arrow (dashed).
Hall effect in semiconductors

• When a current-carrying semiconductor is kept in a magnetic field, the charge carriers of the semiconductor experience a force in a direction perpendicular to both the magnetic field and the current. At equilibrium, a voltage appears at the semiconductor edges.

• The simple formula for the Hall coefficient given above becomes more complex in semiconductors where the carriers are generally both electrons and holes which may be present in different concentrations and have different mobilities. For moderate magnetic fields the Hall coefficient is

\[
R_H = \frac{p \mu_h^2 - n \mu_e^2}{e(p \mu_h + n \mu_e)^2}
\]

or equivalently

\[
R_H = \frac{(p - nb^2)}{e(p + nb)^2}
\]

with

\[
b = \frac{\mu_e}{\mu_h}.
\]
Hall Coefficient

- Magnitude parameter: \( R_H \)

- In metals:
  \[
  R_H = \frac{E_y}{j_x \times B_z}
  \]

- In semiconductors:
  \[
  R_H = \frac{p \times \mu_p^2 - n \times \mu_n^2}{e \times (p \times \mu_p + n \times \mu_n)^2}
  \]
achievement

• Classical Picture: only electrons moving in same average direction in both hole (p-type) and electron (n-type) conductivity

• Opposite sign indicates that electrons in valence bands move in opposite direction than previously thought
Applications

• Measurement can tell about charge carrier mobility and concentration.

• Conversely, knowing the above allows for sensitive measurement of an external B-field.

• Resistant to outside contaminants unlike optical, electromechanical testing.
Hall Probes

Via LessEMF.com

Via the NDT Resource Center
Rotation Sensing

• Hall Effect sensors capable of switching very fast, does not distort like capacitative or inductive sensors

• Contactless sensing
In Cars

• Used expansively in rotating systems

• Anti-lock brakes, motor feedback, ignition

Via Power Systems Design, Ltd.

Via Draper, 2005
In Space

- Hall Effect thruster
- Trap electrons in a magnetic field, electrons ionize propellant, creates thrust
New Discoveries

• Quantum Hall Effect

• Spin Hall Effect

• Anomalous Hall Effect
Quantum Hall Effect

• For a two-dimensional electron system which can be produced in a MOSFET, in the presence of large magnetic field strength and low temperature, one can observe the quantum Hall effect, in which the Hall conductance $\sigma$ undergoes quantum Hall transitions to take on the quantized values.

• Quantization of normal Hall Effect

\[ \sigma = \nu \frac{e^2}{h} \]

• Seen at low temperature, high magnetic field

• Very precise, magnitude determined by Landau levels and electron interaction
Spin Hall Effect

• Separation of electron spins in current-carrying object, no magnetic field needed.

• Predicted in 1971, observed in 2004 via emission of circularly polarized light.

• Universal, present in metals and semiconductors at high and low temperature.
Anamolous (extraordinary) Hall Effect

• Ferromagnetic materials have internal magnetic field
• Much larger than normal Hall Effect, but not well understood.

Via Toyosaki et al. 2004
Personal Experiments

• Aluminum-doped Germanium 1 sq cm chip

• Van Der Pauw configuration
Hall Coefficients
Extrapolated Carrier Mobility

Clear temperature dependence! Has to do with electron energy
<table>
<thead>
<tr>
<th>Symbols</th>
<th>Definitions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>acceleration (m s^{-2})</td>
</tr>
<tr>
<td>$b$</td>
<td>ratio of electron to hole drift mobility ($b = \frac{\mu_e}{\mu_h}$)</td>
</tr>
<tr>
<td>$B_z$</td>
<td>applied magnetic field along the $z$ direction, transverse to $J_x$ (T)</td>
</tr>
<tr>
<td>$e$</td>
<td>electronic charge (1.602 x 10^{-19} C)</td>
</tr>
<tr>
<td>$E_x$</td>
<td>applied electric field along the $x$-direction, along the direction of current flow, $J_x$ (V m^{-1})</td>
</tr>
<tr>
<td>$E_y$</td>
<td>electric field along the $y$-direction (or the Hall field), transverse to $J_x$ and $B_z$ (V m^{-1})</td>
</tr>
<tr>
<td>$F_{ey}$</td>
<td>external applied force acting on an electron in the conduction band along $y$ (N)</td>
</tr>
<tr>
<td>$F_{hy}$</td>
<td>external applied force acting on a hole in the valence band along $y$ (N)</td>
</tr>
<tr>
<td>$F_{net}$</td>
<td>net force (N)</td>
</tr>
<tr>
<td>$J_x$</td>
<td>current density along $x$ (A m^{-2})</td>
</tr>
<tr>
<td>$J_y$</td>
<td>current density along $y$ (A m^{-2})</td>
</tr>
<tr>
<td>$KE$</td>
<td>kinetic energy</td>
</tr>
<tr>
<td>$m_e$</td>
<td>mass of electron in free space (9.10939 x 10^{-31} kg)</td>
</tr>
<tr>
<td>$n$</td>
<td>concentration of electrons (number of electrons per unit volume) in the conduction band (m^{-3})</td>
</tr>
<tr>
<td>$n_i$</td>
<td>intrinsic concentration (m^{-3})</td>
</tr>
<tr>
<td>$p$</td>
<td>concentration of holes in the valence band (m^{-3})</td>
</tr>
<tr>
<td>$R_H$</td>
<td>Hall coefficient (m^{3} C^{-1})</td>
</tr>
<tr>
<td>$v_{ex}$</td>
<td>drift velocity of an electron in the $x$-direction due to an applied external force along $x$ (m s^{-1})</td>
</tr>
<tr>
<td>$v_{ey}$</td>
<td>drift velocity of an electron in the $y$-direction due to an applied external force along $y$ (m s^{-1})</td>
</tr>
<tr>
<td>$v_{hx}$</td>
<td>drift velocity of a hole in the $x$-direction due to an applied external force along $x$ (m s^{-1})</td>
</tr>
<tr>
<td>$v_{hy}$</td>
<td>drift velocity of a hole in the $y$-direction due to an applied external force along $y$ (m s^{-1})</td>
</tr>
<tr>
<td>$\mu_e$</td>
<td>drift mobility of electrons in the conduction band (m^{2} V^{-1} s^{-1})</td>
</tr>
<tr>
<td>$\mu_h$</td>
<td>drift mobility of holes in the valence band (m^{2} V^{-1} s^{-1})</td>
</tr>
</tbody>
</table>
USEFUL DEFINITIONS

Hall coefficient \((R_H)\) is a parameter that gauges the magnitude of the Hall effect. If \(E_y\) is the electric field set up in the \(y\)-direction due to a current density, \(J_x\), along \(x\) and a magnetic field, \(B_z\), along \(z\), then \(R_H = E_y / J_x B_z\).

Hall effect is a phenomenon that occurs in a conductor carrying a current when it is placed in a magnetic field perpendicular to the current. The charge carriers in the conductor become deflected by the magnetic field and give rise to an electric field (Hall field) that is perpendicular to both the current and magnetic field. If the current density, \(J_x\), is along \(x\) and the magnetic field, \(B_z\), is along \(z\), then the Hall field is either along \(+y\) or \(-y\) depending on the polarity of the charge carriers in the material.

Drift mobility is the drift velocity per unit applied field. If \(\mu_d\) is the mobility then the defining equation is \(v_d = \mu_d E\) where \(v_d\) is the drift velocity and \(E\) is the electric field.

Drift velocity is the average velocity, over all the conduction electrons in the conductor, in the direction of an applied electrical force \((F = -eE\) for electrons). In the absence of an applied field, all the electrons are moving around randomly and the average velocity, over all the electrons, in any direction is zero. With an applied field, \(E_x\), there is a net velocity per electron, \(v_{dx}\), in the opposite direction to the field where \(v_{dx}\) depends on \(E_x\) via \(v_{dx} = \mu_d E_x\) where \(\mu_d\) is the drift mobility.

Lorentz force is the force experienced by a moving charge in a magnetic field. When a charge \(q\) is moving with a velocity \(v\) in a magnetic field \(B\), then it experiences a force, \(F\), that is proportional to the magnitude of its charge, \(q\), its velocity, \(v\) and the field \(B\) such that \(F = qv \times B\).

Mass action law in semiconductor science refers to the law \(n_p = n_i^2\) which is valid under thermal equilibrium conditions and in the absence of external biases and illumination.