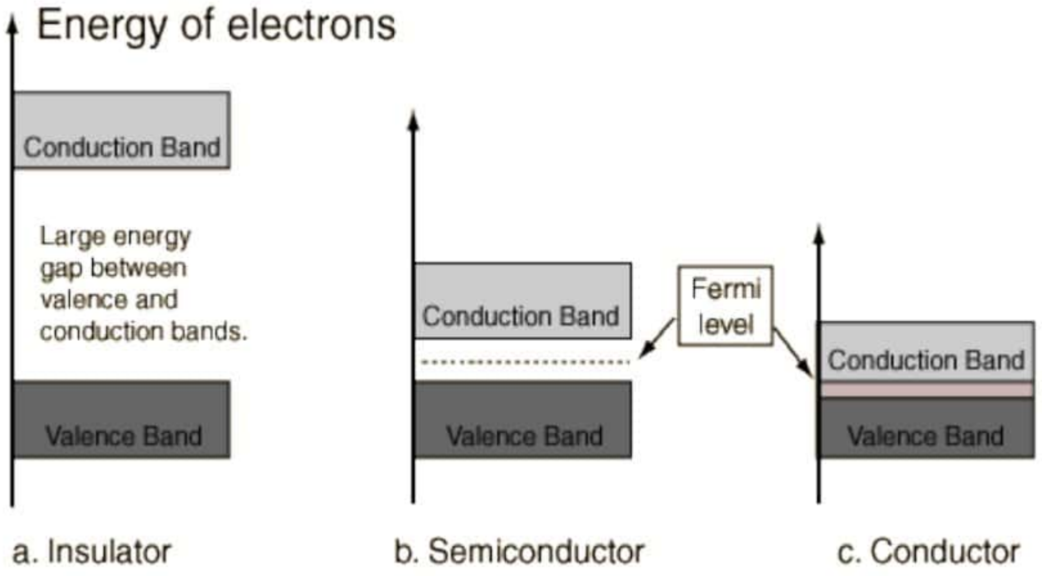
Band Theory of Solids

A useful way to visualize the difference between conductors, insulators and semiconductors is to plot the available energies for electrons in the materials. Instead of having discrete energies as in the case of free atoms, the available energy states form bands. Crucial to the conduction process is whether or not there are electrons in the conduction band. In insulators the electrons in the valence band are separated by a large gap from the conduction band, in conductors like metals the valence band overlaps the conduction band, and in semiconductors there is a small enough gap between the valence and conduction bands that thermal or other excitations can bridge the gap. With such a small gap, the presence of a small percentage of a doping material can increase conductivity dramatically.

An important parameter in the band theory is the Fermi level, the top of the available electron energy levels at low temperatures. The position of the Fermi level with the relation to the conduction band is a crucial factor in determining electrical properties.



Valence Band

The band of energy where all of the valence electrons reside and are involved in the highest energy molecular orbital.

Conduction Band

The band energy where positive or negative *mobile charge carriers* exist. Negative mobile charge carriers are simply electrons that had enough energy to escape the valence band and jump to the conduction band. Here, they move freely throughout the crystal lattice and are directly involved in the conductivity of semiconductors. Positive mobile charge carriers are also referred to as *holes*. *Holes* refer to the lack of an electron in the conduction band. In other words, a *hole* refers to the fact that within the band there is a place where an electron *can* exist (ie. negative mobile charge carrier), and yet the electron ceases to exist at that particular location. Because the electron has the *potential* to be there and yet *isn't* there, it is referred to as positive mobile charge carrier.

Fermi Level

This level refers to the highest occupied molecular orbital at absolute zero. It is usually found at the center between the valence and conduction bands. The particles in this state each have their own quantum states and generally do not interact with each other. When the temperature begins to rise above absolute zero, these particles will begin to occupy states above the Fermi level and states below the Fermi level become unoccupied.

Semiconductors

Semiconductors are defined to have conductivity in between an insulator and a conductor. Due to this property, semiconductors are very common in every day electronics since they likely will not short circuit like a conductor. They get their characteristic conductivity from their small band gap. Having a band gap prevents short circuits since the electrons aren't continuously in the conduction band. A small band gap allows for the solid to have a strong enough flow of electrons from the valence to conduction bands in order to have some conductivity.

Electrons in the conduction band become free from the nuclear charge of the atom and thus can move freely around the band. Thus, this free-moving electron is known as a *negative charge carrier* since having the electron in this band causes electrical conductivity of the solid. When the electron leaves the valence band, the state then becomes a *positive charge carrie*r, or a *hole*.

Intrinsic Semiconductors

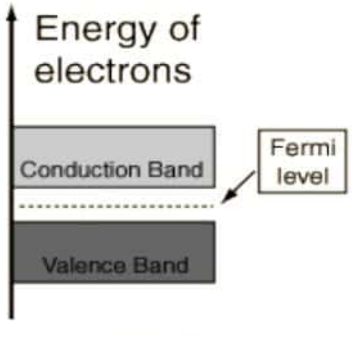
Pure semiconductors in which its properties are solely based off of the material itself. Here, the number of electrons in the conduction band equal the number of holes in the valence band. Theses semiconductors are also known as *i-types*.

Extrinsic Semiconductors

Impure semiconductors that have been "doped" in order to enhance its conductivity. There are two types of extrinsic semiconductors: *p-type* and *n-type*. A "dopant" atom is added to the lattice in order to draw electrons from the valence band. This atom is referred to as an *acceptor*. As more acceptors are added to the lattice, the number of holes will begin to exceed the number of negative charge carriers, eventually leading to a p-type (positive type) semiconductor. N-type semiconductors have a large number of *donors,* "dopant" atoms that donate electrons to the conduction band.

Semiconductor Energy Bands

For intrinsic semiconductors like silicon and germanium, the Fermi level is essentially halfway between the valence and conduction bands. Although no conduction occurs at 0 K, at higher temperatures a finite number of electrons can reach the conduction band and provide some current. In doped semiconductors, extra energy levels are added.



b. Semiconductor

The increase in conductivity with temperature can be modeled in terms of the Fermi function, which allows one to calculate the population of the conduction band.

Doping

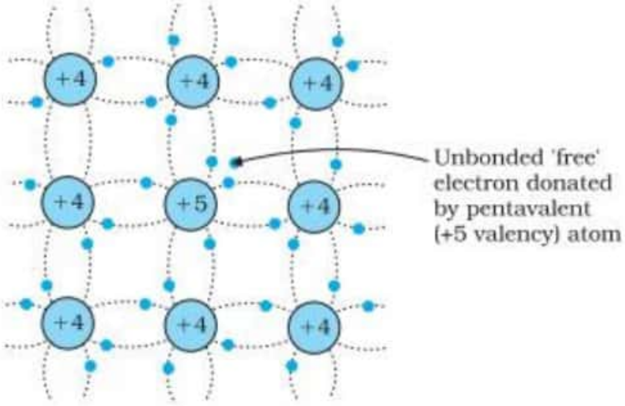
Pure Silicon or Germanium are rarely used as semiconductors. Practically usable semiconductors must have controlled quantity of impurities added to them. Addition of impurity will change the conductor ability and it acts as a semiconductor. The process of adding an impurity to an intrinsic or pure material is called **doping**

Doping means the introduction of impurities into a semiconductor crystal to the defined modification of conductivity. Two of the most important materials silicon can be doped with, are boron (3 valence electrons = 3-valent) and phosphorus (5 valence electrons = 5-valent). Other materials are aluminum, indium (3-valent) and arsenic, antimony (5-valent).

The dopant is integrated into the lattice structure of the semiconductor crystal, the number of outer electrons define the type of doping. Elements with 3 valence electrons are used for p-type doping, 5-valued elements for n-doping. The conductivity of a deliberately contaminated silicon crystal can be increased by a factor of 10^6.

n-type semiconductor

An n-type semiconductor is created when pure semiconductors, like Si and Ge, are doped with pentavalent elements.



As can be seen in the image, when a pentavalent atom takes the place of a Si atom, four of its electrons bond with four neighbouring Si atoms. However, the fifth electron remains loosely bound to the parent atom. Hence, the ionization energy required to set this electron free is very small. Thereby, this electron can move in the lattice even at room temperature.

The ionization energy required for silicon at room temperature is around 1.1 eV. On the other hand, by adding a pentavalent impurity, this energy drops to around 0.05 eV.

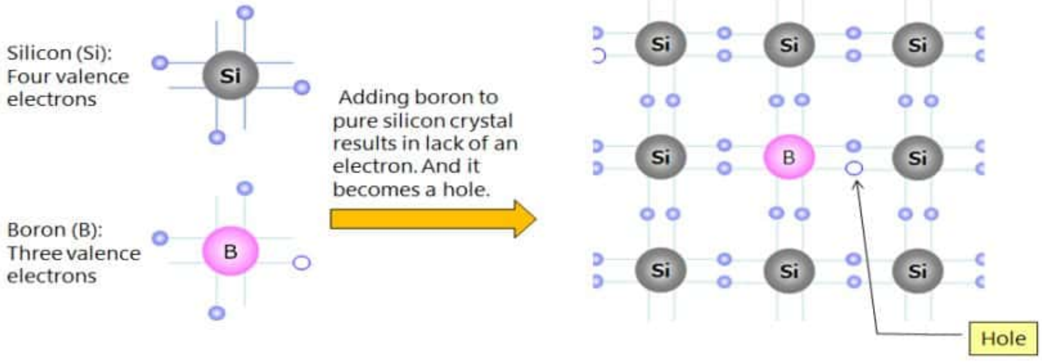
It is important to remember that the number of electrons made available by the dopant atoms is independent of the ambient temperature and primarily depends on the doping level. Also, as the temperature rises, the Si atoms free some electrons and generate some holes. But, the number of these holes is very small. Hence, at any given point in time, the number of free electrons is much higher than the number of holes. Also, due to recombination, the number of holes reduce further.

n a nutshell, when a semiconductor is doped with a pentavalent atom, electrons are the majority charge carriers. On the other hand, the holes are the minority charge carriers. Therefore, such extrinsic semiconductors are called n-type semiconductors. In an n-type semiconductor,

Number of free electrons (n_e) >> Number of holes (n_h)

p-type semiconductor

A p-type semiconductor is created when trivalent elements are used to dope pure semiconductors, like Si and Ge. As can be seen in the image, when a trivalent atom takes the place of a Si atom, three of its electrons bond with three neighboring Si atoms. However, there is no electron to bond with the fourth Si atom.



Adding boron to pure silicon crystal results in lack of an electron. And it becomes a hole.

This leads to a hole or a vacancy between the trivalent and the fourth silicon atom. This hole initiates a jump of an electron from the outer orbit of the atom in the neighborhood to fill the vacancy. This creates a hole at the site from where the electron jumps. In simple words, a hole is now available for conduction.

It is important to remember that the number of holes made available by the dopant atoms is independent of the ambient temperature and primarily depends on the doping level. Also, as the temperature rises, the Si atoms free some electrons and generate some holes. But, the number of these electrons is very small. Hence, at any given point in time, the number of holes is much higher than the number of free electrons. Also, due to recombination, the number of free electrons reduces further.

In a nutshell, when a semiconductor is doped with a trivalent atom, holes are the majority charge carriers. On the other hand, the free electrons are the minority charge carriers. Therefore, such extrinsic semiconductors are called p-type semiconductors. In a p-type semiconductor,

Number of holes (n_h) >> Number of free electrons (n_e)

Important note: The crystal maintains an overall charge neutrality. The charge of additional charge carries is equal and opposite to that of the ionized cores in the lattice.