When atoms are brought together, they can form molecules. There are two important types of bond between atoms: ionic bond and valence or covalent bond. In an ionic bond one or more electrons of one of the atoms go over to the other atom or atoms; the binding force is here electrostatic in origin and can be described by classical physics.

In a valence bond the atoms share each other’s electrons; a particularly strong bond occurs if neighboring atoms share one or more electron pairs. The binding force here is also of electrostatic origin but, since it depends on the motion of the electrons, it can be described adequately only by wave mechanics. True ionic bonds are very rare; in most cases the binding force is a mixture of an ionic bond and a valence bond.

The fundamental characteristics that determine the use of materials in electron devices are molecular structure and the form of the energy used to effect the matter-energy interaction that permits the generation of mobile charges within the physical system. While the devices employed are characterized by their macroscopic behavior, it is the microscopic structure of matter that determines this behavior. We can describe all matter by systems of atoms, each atom consisting of a positive nucleus and the appropriate number of orbiting electrons. The state in which each electron exists is defined by the energy, momentum and spin about its axis that it possesses. No two electrons in the atom may exist in the same state, a concept embodied by the Pauli exclusion principle.

Since the energies possessed by the electrons can vary only in discrete steps, the states associated with a given energy level are grouped and called “shells”. The farther an electron is from the nucleus, the higher the energy that is possesses. The outermost shell, which is composed of the valence electrons, is most important since these electrons have the greatest effect on the electrical, thermal and chemical properties of the material. Most elements having the same number of valence electrons have similar properties. In fact, the periodic table used in chemistry is a grouping of similar elements, the group number corresponding to the number of valence electrons.

The atoms in solids are physically close to and interact with each other. The structure of the material is determined by the manner in which the atoms are
bound. It is not possible to determine exactly the momentum and position of the electrons, a fact known as the Heisenberg uncertainty principle. The electrons must be associated with a group of atoms rather than with single atoms. As no two electrons may exist in the same state, the interaction of the atoms alters the energy that the electrons may possess. The states associated with these energies also differ. The groupings of energy levels are called energy bands, each band related to the corresponding energy level in a single atom.

In metals, the outer electrons of an atom are shared by all the other atoms of a crystal. If an electron field is applied, the electric current has the same direction as the applied field. Thus, a metal will conduct electricity at all temperatures of practical interest, and because of the large number of current carriers (electrons) involved, it is a good conductor.

In insulators, the outer electrons of an atom are shared by its neighbors. It takes an energy of several electron volts to remove an electron from one of the covalent bonds and as a consequence each electron is firmly bond to its particular atom pair. When an electric field is applied, the electrons cannot move freely through the crystal, but remain bound to the atoms. As a result no current will flow and the material is a nonconductor over a wide temperature range.

Solids whose resistivities have values between those of conductors and insulators are called semiconductors. They are elements primarily in group IV of the periodic table, germanium (Ge) and silicon (Si) being the most common. Ge and Si each have four valence electrons. Semiconductors are called “intrinsic” when they are chemically pure and have no imperfections in the crystal structure. The electrical properties exhibited by intrinsic semiconductors are those attributed to the electronic structure of the pure material and not to the presence of any foreign atoms or to the crystal structure faults.

A two dimensional representation of the intrinsic semiconductor crystal is shown in Figure 1. The positive charges represent the ions formed by the nuclei and all the inner electronic “shells”. The valence electrons are presented by the negative charges. Electrons from two adjacent atoms are shared mutually by the two atoms in an arrangement called covalent bonding. Each atom is in covalent bond with each of four adjacent atoms; this forms the crystal structure. The effect is that each atom appears to have a completed outer shell and is highly stable as a result of the large bonding energy. A consequence of the strong atomic bonding is that no mobile charges are available without the expenditure of a good deal of energy.
The energy band diagram shown in Figure 2 describes the number of available states in which electrons can exist at given energy levels. The valence band represents the energy levels associated with the valence electrons. The conduction band describes the states in which the electrons are relatively free of atomic bonding and are capable of being mobile current carriers. As shown, the greatest energy an electron can possess in the valence band is $E_v$, and $E_c$ is the lowest energy level of an electron in the conduction band. The gap, or what is called the Forbidden Band, between $E_v$ and $E_c$ arises because of the interaction of the atoms. No electrons can exist in the forbidden band. In intrinsic semiconductors at zero Kelvin, all valence band states are filled. As all covalent bonds are intact, no electrons are in the conduction band and no mobile current carriers are available. Thus the semiconductor will act like an insulator. If current conduction is desired in intrinsic semiconductors, sufficient energy must be given to the valence band electrons to raise them into the conduction band.

In intrinsic semiconductors at temperatures greater than 0 K, the material has been given thermal energy, which causes the ions and electrons to vibrate. This thermal agitation may be sufficient to break some covalent bonds, producing two kinds of mobile charges. These are electrons and holes, and when generated by breaking of covalent bonds, they are called electron-hole pairs. If the thermal energy is high enough some electrons may be able to “jump” the forbidden band and pass to
occupy conduction band energy states. The hole is really the absence of a valence electron, this absence behaving as if it were a positive charge.

The generation of electron-hole pairs in an intrinsic semiconductor is shown in Figure 3. An electron is missing from a covalent bond structure. This means that a vacant valence band space exists, which is represented by a hole. Electrons and holes are created in equal numbers, maintaining the overall electronic neutrality. Both are mobile and may be influenced by forces and contribute to the current flow. Holes move by an ionization transfer process which can occur with zero-energy exchange. This may be accomplished by other valence electrons in the vicinity moving to the existing hole, thereby producing a hole at the site that the valence electron vacated with the apparent effect being the movement of a hole. This thermal generation of electron-hole pairs at normal device operating temperatures is insufficient to produce the current flow necessary for the operation of electronic devices. To produce more current flow, other forms of energy must be utilized.

A very common expedient used to produce large numbers of charge carriers is to introduce a carefully controlled impurity into the intrinsic semiconductor. Then the semiconductor is said to have been “doped” and we have an extrinsic semiconductor.

The impurities most commonly used are atoms from group III or group V of the periodic table. Arsenic (As) and antimony (Sb) are typically group V and gallium (Ga) and boron (B) are typically group III elements. Each type of impurity will establish a semiconductor that has a predominance of one kind of carrier.

In extrinsic semiconductors, carriers are generated through replacement of some atoms of the intrinsic semiconductor by impurity atoms at various points in the crystal. The impurity concentrations, or doping level, generally used are in the
range of 1 atom impurity to at least 1 million or more atoms of the intrinsic semiconductor. Thus, most physical and chemical properties are essentially those of the base or intrinsic semiconductor. Only its electrical properties are affected.

Arsenic has five valence electrons. Thus, when added to the intrinsic semiconductor only four of them are needed to fill the covalent bonds, as shown in Figure 4 and one arsenic electron remains free to move, when energy is supplied to the crystal. In addition, if the energy is high enough an electron-hole pair, or many electron-hole pairs may be created.

![Loosely bound excess electron in crystal structure](image)

Figure 4: Loosely bound excess electron in crystal structure

Group V impurities, such as As are referred to as donors, for they make additional valence electrons available for the conduction of current. Extrinsic semiconductors with group V impurities are called n-type semiconductors because the negatively charged electrons are the predominant current carriers, referred to as the majority carriers.

When atoms from group III are added, as shown in the diagram in Figure 5, only three electrons are provided for covalent bonding. One valence-band state will remain vacant, the vacancy being a hole which may move about by the process of ionization transfer. As positively charged holes are the mobile charges provided, the resulting extrinsic semiconductor is said to be p-type. Group III elements are called acceptors because an additional electron is needed to complete the covalent bonds.
At normal operating temperatures and applied voltages, both electrons and holes will be present in extrinsic semiconductors. The dominant carrier is called the majority carrier and the lesser charge is called the minority carrier.

TRANSPORT PHENOMENA

Transport phenomena is the study of the connection between observed fluxes and the forces that produce those fluxes. Transport theory studies the microscopic mechanisms that explain the observed effects and the calculation of such quantities as electrical conductivity and the Seebeck coefficient.

Transport theory is based on the Boltzmann transport equation, whose solution is extremely difficult. We will discuss transport phenomena from a more elementary point of view.

**Ohm's Law:** \[ V = IR \text{ (for d-c) or } V = I\rho L/A \]

Electric field intensity \( E = V/L = I\rho/A = J\rho = J/\sigma \)

or \( \sigma = J/E \), where \( \sigma \) is the conductivity and \( J \) is the current density.

Normally we define current density in terms of charge carriers, i.e.: electrons in a unit volume times speed of travel times their charge, or,

\[ J = neu \]
The mobility of the charge carriers is by definition,
\[ \mu = \frac{u}{E} \]
Therefore \( J/E = \sigma = ne\mu \) (for one type of carrier only)

If we would consider both types of carriers, holes and electrons, we would find the average drift velocity as the electrons move in a random manner, while the hole appears to move in discrete jumps.

When both type of carriers are present, the electrical conductivity is given by,
\[ \sigma = e(n\mu_n + p\mu_p) \]
\( n = \) electrons/unit volume in conduction band
\( p = \) holes/unit volume in valence band

Thermal conductivity is an index of how well a solid will conduct thermal energy. Thermal conduction on a microscopic scale is essentially a diffusion process. In semiconductors used for energy converters, thermal conductivity is mostly due to free electrons and lattice vibrations (phonons) conduction.